This invention relates to synthetic lubricating compositions and particularly to new and improved synthetic lubricants having outstanding properties of viscosity at low and high temperatures. More particularly the invention relates to new and improved synthetic lubricants which are formed by esterifying the reaction product of an alkylene oxide and phosphoric acid with a long chain aliphatic carboxylic acid.

In recent efforts to obtain superior lubricating compositions which have unusual and specific properties, there have been developed entirely new synthetic materials with lubricating properties. In general these new synthetic lubricants are characterized by viscosity properties that are outstanding at both low and high temperatures, especially when compared to mineral oils. These outstanding low and high temperature properties are especially desirable for use in equipment designed to operate over a great temperature differential, such as jet engines or turbines for aircraft use, internal combustion reciprocating engines for aircraft and the like. It has been found that mineral lubricating oils have generally undesirable limitations for the lubrication of these engines particularly in respect to their high and low temperature viscosity characteristics.

It has also been found that synthetic lubricants may be desirable for the lubrication of standard automotive engines. In addition to the versatility of their viscosity-temperature relationships, some types of synthetic lubricants investigated have another advantage in that their use has been found to result in very low rates of combustion chamber deposit formation, particularly when they are used for long periods of time. Low rates of formation of combustion chamber deposits result in a more efficient utilization of fuel, less increase in the octane requirement of an engine, less pre-ignition tendency, and an overall improvement in engine operation. These lubricants may also serve to reduce or remove combustion chamber deposits from an engine already containing such deposits.

The present invention relates to a new type of synthetic lubricating composition which comprises the esters of hydroxyphosphoric acid having the following general formula:

$$\left[\begin{array}{c}
\text{O} \\
\text{R} \cdot \text{O} \cdot \text{O} \cdot (\text{R'})_n \cdot \text{O} \\
\text{P} = \text{O}
\end{array}\right]$$

wherein R is a monovalent hydrocarbon radical, R' is a divalent hydrocarbon radical, and n is a number from 1 to 10.

The esters of this invention are prepared by reacting a monooxyalcoholic hydroxycarbonate acid having from 6 to 20 carbon atoms per molecule with the reaction product of an alkylene oxide and phosphoric acid.

The invention will be more clearly explained by reference to the following examples, which are to be considered as being illustrative only, and are not restrictive in scope.

**Example 1.**—In a 2 liter 4 necked flask fitted with a thermometer, stirrer, gas inlet bubbler, and condenser, were placed 260 g. (1.73 m.) of 85% \(\text{H}_2\text{PO}_4\) and 65 g. (0.46 m.) of \(\text{P}_4\text{O}_{10}\). Ethylene oxide was bubbled into the mixture with stirring, at such a rate that the temperature was maintained at 50°-60° C., until a gain in weight of 1100 g. was observed. A diluent, such as dioxane, may be added if desired. After stripping to constant weight on a steam bath, 1315 g. of product was obtained. Acid, 0.000 centiequivalent/g., alcohol, 0.608 centiequivalent/g.

**Example 2.**—In a 1 liter flask fitted with an esterification water trap and condenser were placed 100 g. (0.63 m.) \(\text{C}_8\text{Oxo acid}, 98 g. (0.6\text{ equiv.})\) of the hydroxyphosphate, 100 ml. toluene, and 0.5 g. of p-toluene sulfonic acid mono-hydrate. The mixture was refluxed until no more \(\text{H}_2\text{O}\) was entrained. After washing with \(\text{Na}_2\text{CO}_3\) solution until neutral and drying, it was stripped to 202°/2 mm.

**Example 3.**—In a 1 liter flask filled with a reflux condenser connected to a drying tube were placed 143 g. (0.64 m.) of a \(\text{C}_{12}\) Oxo acid chloride and 98 g. (0.6\text{ equiv.}) of hydroxyphosphate. The mixture was refluxed until no more HCl evolved, washed with \(\text{Na}_2\text{CO}_3\) solution until neutral, dried, and stripped at 198°/2 mm.

The materials prepared according to the inventive concept were submitted to the standard ASTM determinations for flash point, pour point, and viscosity at both 100° F. and 210° F. Their ASTM slopes were calculated as were their viscosity indices. Data are presented in Table I below.

<table>
<thead>
<tr>
<th>Component</th>
<th>Kin. Vis. ASTM 100°F</th>
<th>ASTM Slope</th>
<th>ASTM V. I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_8\text{Oxo acid})</td>
<td>44.59</td>
<td>13.65</td>
<td>0.578</td>
</tr>
<tr>
<td>(\text{C}_{12}\text{Oxo acid chloride})</td>
<td>42.3</td>
<td>13.65</td>
<td>0.578</td>
</tr>
</tbody>
</table>

The above values indicate that the new synthetic lubricants of invention have outstanding properties of low pour point and high flash point. Their ASTM slopes and viscosity indices show that they have excellent viscosity-temperature properties and therefore have outstanding utility as lubricants for both low and high temperature uses.

To form the hydroxy compounds used as a starting material for the preparation of the esters of this invention, phosphoric acid may be reacted with a number of alkylene oxides. The number of units reacted with one molecule of the acid may be varied within wide ranges. For instance, instead of the ethylene oxide units utilized above, one may use propylene, butylene oxides, or mixtures of epoxides. The number of moles added will vary depending upon the desired molecular weight of the product as well as the acid to be used to form the esters. It is preferred to use either ethylene oxide or propylene oxide, however, and to add from about 3 to about 12 units to each molecule of phosphoric acid.

As was pointed out above, the hydroxy-phosphate resulting from the reaction of alkylene oxide to phosphoric acid will have the formula:

$$\text{HO} \cdot (\text{R'})_n \cdot \text{O} \cdot (\text{R'}')_m \cdot \text{OH}$$

where \(x, y\), and \(z\) may be the same or different integers.

It may be desirable to react three, two or one moles of acid with this hydroxy-phosphoric acid, and any number up to and including three moles of acid may be used,
depending again upon the properties desired in the finished ester. It may also be desired to add different acids, or use a mixture of acids which may also be done. The acid used will ordinarily be a monocarboxylic acid having from about 6 to 20 carbon atoms per molecule and may be of either branched or straight chain configuration.

Especially preferred, and contemplated in the preferred embodiment of this invention are the highly branched chain acids that are derived from aldehydes or alcohols obtained by subjecting an olefin to the action of carbon monoxide and hydrogen in the Oxo process. This process, described in detail in U. S. Patent No. 2,367,066, issued to Koelen in 1943, involves the use of temperatures in the order of 150° C. to 350° C. and pressures of about 3000 pounds per square inch, or higher. A cobalt catalyst is used. When hydrogen is used in conjunction with the carbon monoxide an alkylate results which may be converted to the acid by oxidation. Further hydrogenation of the alkylate results in the alcohol which may be converted to the acid by caustic fusion, or other of the well known processes. If water is used instead of hydrogen, the acid results directly from the Oxo process. Preferred olefins are the polymers or copolymers of C2 and/or C4 olefins, the resulting polymer or copolymer having from about 7 to about 16 carbon atoms.

By using as a starting material the reaction product of the alkylene oxide and the phosphoric acid, that is, the hydroxylphosphates and other materials such as dibasic acids and alcohols, one may build complex molecules which have varying properties. One complex ester so prepared has the following schematic formula:

\[ \text{Alcohol-dibasic acid-hydroxyphosphate-dibasic acid-alcohol} \]

Dibasic acid-alcohol

Other possibilities will be apparent to those skilled in the art. For example, substituting a glycol reactant for the alcohol depicted above and esterifying the remaining hydroxyl group with another acid will form a different type ester. Chains of varying sizes and molecules of varying molecular weight may thus be built around a nucleus of the hydroxy-phosphate.

The new synthetic lubricants of invention may be thickened to grease compositions by using any of the common grease forming soaps. The alkali or alkaline earth metal soaps of high molecular weight substantially saturated fatty acids may be used and the grease compositions prepared by any of the methods with which the art is familiar. For instance, such soaps as the oleates, stearates, hydroxy stearates, or ricinoleates of sodium, potassium, lithium, calcium, barium, strontium, aluminium, and the like may be used, as well as the soaps formed by heating animal, fish, or vegetable oils with soda, lime, baria hydrate or lithia hydrate.

If it is desired to enhance particular properties of the synthetic lubricants of invention, they may be blended with additive agents, such as viscosity index improvers, pour point depressants, detergent inhibitors, oxidation inhibitors, and the like. Such materials as ester polymers and copolymers with other polymerizable materials, such as copolymers of fumarate or maleate esters with vinyl acetate, acrylate or methacrylate polymers or copolymers, phenyl alpha naphthylamine, phenothiazine, 2,6-di-tert-butyl-para-cresol and many other additive materials may be blended with the synthetic lubricants of this invention.

The esters of invention may also find wide application in a great variety of industrial uses outside the lubricant field. For instance, these new esters may have utility as plasticizers, solubilizers, heat transfer agents, insecticides, weed killers, rust preventatives, solvents, dewaxing aids, detergents, oiliness agents as in penetrating oils, and as raw materials for many other industrial applications. They may be blended with mineral oils, with other synthetic lubricants such as formals, dibasic acid esters, complex esters, polymerized hydrocarbons, and the like.

To reiterate briefly, the instant invention relates to new and improved synthetic lubricants which comprise a material of the formula

\[ R-C-O-(N'O)\_n-O-(O'R')_m-O-R \]

wherein R is an alkyl group containing from 5 to 19 carbon atoms, wherein R' represents a divalent hydrocarbon radical containing from 2 to 4 carbon atoms, and wherein x, y, and z are integers of from 1 to 10. R may be alike or different and is preferably branched chain in configuration.

What is claimed is:

1. A process for preparing an ester of the formula

\[ \text{Dibasic acid-alcohol} \]

wherein R is a monovalent hydrocarbon radical, R' is a divalent hydrocarbon radical of from 2 to 4 carbon atoms and n is an integer of from 1 to 10, which comprises passing an alkylene oxide through phosphoric acid at a temperature of 50° to 60° C., recovering a hydroxyphosphate from the reaction mixture, and further esterifying said hydroxyphosphate with an aliphatic hydrocarbon monocarboxylic acid having about 6 to 20 carbon atoms per molecule.

2. A process according to claim 1 wherein said alkylene oxide is ethylene oxide and said acid is a C4 Oxo acid.

3. A process according to claim 1 wherein said alkylene oxide is ethylene oxide and said acid is a C12 Oxo acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,224,360 Rozenbrock et al. December 3, 1940
2,365,291 Prutton et al. December 14, 1944
2,643,261 Matuszak June 23, 1953

FOREIGN PATENTS

452,508 Great Britain August 24, 1936