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LINEAR MIXED ESTER LUBRICANTS

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The present invention is directed to lubricants, more particularly to synthetic liquid compounds which are linear complex esters.

In recent years there have been developed engines particularly for use in aviation which operate at high temperatures and high pressures. Accordingly the lubricants used therein must be capable of withstanding the extreme conditions occurring in such engines as jet and rocket engines. Previously lubricants produced from petroleum had been sufficient in their characteristics for use in the conventional engines of the past. However, they are completely inadequate to fulfill the demands of jet and rocket engines.

In view of this, there have been developed lubricants of a synthetic nature in the form of esters, silicone compounds and silicate esters. Whereas lubricants made from petroleum were adequate for use at temperatures between about 200° to 350° F., such synthetic ester lubricants were capable of use under temperature conditions from 250° to 350° F. and in the case of silicones, up to temperatures of 400° to 450° F. However, the target specifications for lubricants for use in the most modern engines require that they must withstand temperatures of about 500° to 700° F. without losing their lubricity.

The silicones have the viscosity characteristics and the thermal stability for some of the target specifications but they are not good lubricants. The linear complex esters of this application, however, are excellent lubricants and fall in the same target specification range in their flash and fire point characteristics.

The present invention is intended and adapted to overcome the disadvantages of prior lubricants and to provide a synthetic ester type lubricant which is suitable for use at temperatures over about 500° F. and maintains its fluidity at temperatures under about 0° F.

It is also among the objects of the present invention to provide a lubricant which consists of mixed linear esters having excellent lubricating value at extremely high temperatures.

It is further among the objects of the present invention to provide a lubricant of the class described, which may be made by a simple chemical procedure and wherein the lubricating values may be reproduced in batch after batch in commercial scale operation.

In practicing the present invention there is formed complex esters of polyhydric alcohols having two or more functional alcohol groups, preferably compounds which possess the alpha hydroxy groups rather than beta hydroxy groups. Alcohols in which the beta carbon does not have any available hydrogen appear to give derivatives which are somewhat more stable than products derived from polyols in which such hydrogen on the beta carbon is available. Similar esters from polyols having labile hydrogen on the beta carbon show unusually good stability contrary to expectations. Diols, triols and polyols are suitable raw materials for the linear mixed esters of the present application.

As examples of the broad class of polyhydric alcohols may be mentioned pentaerythritols, hexanetriol, trimethylolethane and glycerol, etc. The alcohol is reacted with a dibasic acid of organic nature in order to form a linear polymer. The amount of the dibasic acid is insufficient to combine with all of the hydroxy groups present in the alcohol. Typical acids usable in the invention are sebacic, adipic, maleic, isophthalic and terephthalic. In general, dibasic acids can all be adapted to the reaction but certain combinations of dibasic acids and monobasic acids give the best results.

To the initial ester so formed there is introduced a monobasic acid of organic nature, sufficient in amount to combine with the remaining free hydroxy groups of the alcohol to form a mixed linear ester. The relative amounts of the several constituents may be varied within certain limits so as to yield esters having fluidity below 0° F. and maintain flash and fire points ranging between about 500° and 700° F.

While usually the monobasic acid has a short chain, long chain acids both saturated and unsaturated may be used in whole or in part and the number of carbon atoms may be odd or even.

The following are specific examples of the operation of the present invention:

Example 1

A mixture is made of 2 mols. of pentaerythritol and 1 mol. of adipic acid. The mixture is heated in a closed vessel with a blanket of nitrogen at atmospheric pressure at a temperature ranging from about 150° C. to 225° C. for about 4 hours, whereby esterification of substantially all of the acid has taken place. Then there is added thereto a mixture of acids consisting of 65% capric and 35% caprylic in the amount of 6 mols. The reaction is continued over substantially the same range of temperatures, namely from about 150° to 225° C. for 6 to 6½ hours, thereby completing the esterification.

The resulting complex ester is refined and bleached as is common in the art. The product has a solidification point of about —30° F., a flash point of about 535° F. and a fire point of about 590° F.

Example 2

A mixture is made of 2 mols. of dipentaerythritol and 1 mol. of adipic acid. It is reacted under the same conditions as set forth in Example 1 until the free fatty acid value is lowered to not over 1. Then there is added thereto 4 mols. of a mixture of butyric, caproic, capric and caprylic acids and the reaction continued in accordance with the procedure of Example 1 until the esterification is complete. After refining, the lubricant so produced has a solidification point of about —35° F., a flash point of about 557° F. and a fire point of about 615° F.

Example 3

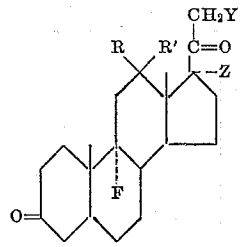
4 mols. of pentaerythritol and 2 mols. of adipic acid are reacted in a closed vessel at atmospheric pressure with a blanket of nitrogen at temperatures of about 147° to 230° C. over a period of about 4 hours. When the reaction is completed to the extent that the acid value has dropped to about 1, there is introduced 14.4 mols. of a mixture consisting of about 80% caprylic acid, 15% capric acid and 5% of a mixture of caproic and lauric acids.

The reaction is continued at temperatures ranging from about 155° to 225° C. for 6½ hours to complete the reaction. The product is refined and bleached as usual. It has a solidification point of about —30° F., a flash point of about 540° F. and a fire point of about 595° F.

Example 4

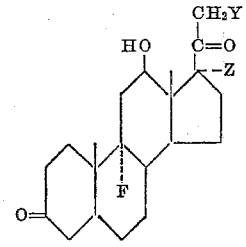
A mixture is made of 1 mol. of polypentaerythritol and 1 mol. of adipic acid, the mixture being reacted as set forth in the above examples. There is then added thereto 4 mols. of a mixture consisting of about 85% caprylic

9. A steroid of the general formula

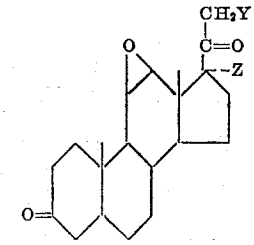


wherein individually R is hydrogen, R' is selected from the group consisting of β-hydroxy and β-acyloxy, and together R and R' is keto, Y is selected from the group consisting of hydrogen, hydroxy and acyloxy, and Z is selected from the group consisting of hydrogen and α-hydroxy.

10. A process for preparing a steroid of the general formula



wherein Y is selected from the group consisting of hydrogen, hydroxy and acyloxy, and Z is selected from the group consisting of hydrogen and α-hydroxy, which comprises interacting a steroid of the general formula



wherein Y and Z are as above defined, with hydrogen fluoride and recovering the 9α-fluoro-12β-hydroxy steroid formed.

11. A process for preparing 9α-fluoropregnane-12β-ol-3,20-dione, which comprises interacting 11β,12β-epoxypregnane-3,20-dione with hydrogen fluoride and recovering the 9α-fluoro-12β-hydroxy steroid formed.

12. A process for preparing 9α-fluoro-12β-hydroxyprogesterone, which comprises interacting 11β,12β-epoxyprogesterone with hydrogen fluoride and recovering the 9α-fluoro-12β-hydroxy steroid formed.

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bining with one of the OH groups of a different polyhydric alcohol so that two alcohol molecules are linked by the acid molecule. Then, in the second stage, the monobasic acid esterifies all of the remaining free OH groups. Thereby, there are formed compounds of definite structures, so that they have the same properties in batch after batch.

The present products have high lubricity contrary to the silicone oils. They also cause swelling of rubber whereas silicone oils do not. In these important properties the present products are superior. They may be blended with certain of the silicone oils in certain proportions whereby the desirable properties of both are obtained. The blend combines the high temperature stability of the silicones with the high lubricity of the present invention.

Dibasic acid esters as well as monobasic acid esters of mono- and polyhydric alcohols which have been made heretofore have too low a molecular weight and suffer from too high a volatility at the higher temperatures and too low a flash and fire point. The esters of the present application in contrast have high molecular weight and high flash and fire points.

There are a number of advantages in the present invention over ester lubricants of the prior art. The process used in the production thereof is simple and is of a character well known so that operators in the plant would have no difficulties in reproducing results. The products have substantial fluidity at extremely low temperatures and are stable at the high temperatures produced in the engines in full operation. The products have a high flash point and a high fire point so as to enable the use thereof effectively at the high temperatures.

Although the invention has been described setting forth several specific embodiments thereof, various changes in the details may be made without departing from the principles herein set forth. In the production of the lubricants, variations in temperatures, pressures and other conditions may be made as is well known in the art of esterification. The relative proportions of the polyhydric alcohols, dibasic acids and monobasic acids may be varied within the limits set forth and such variations will alter the physical characteristics of the products in accordance with the applications thereof. In all cases the proportions of the constituents are such that the final product should be fluid at 0° F. and lower and should have flash and fire points above 500° F. The invention also contemplates the use of polyhydric alcohols having one or more substituent groups, such as amino groups, which add the property of preventing corrosion in the engine or better stability of the product, for example, amino-trimethylolmethane.

What is claimed is:

1. A synthetic lubricant which is the product of reacting an acyclic polyhydric alcohol having at least 3 OH groups with a dibasic carboxylic acid having 4 to 10 carbon atoms, in the molar ratio of about 1–2 of said alcohol to 1 of said acid, and then reacting the product with 1–6 mols. of monobasic acid per mole of alcohol having 6 to 10 carbon atoms to form fully esterified mixed linear esters having a flash point of above 500° F. and being liquid below 0° F.

2. A synthetic lubricant according to claim 1 wherein said monobasic acid consists of a mixture of capric and caprylic acids.

3. A synthetic lubricant according to claim 2 wherein the ratio of capric to caprylic acids is 65 to 35.

4. A synthetic lubricant according to claim 1 wherein said alcohol is taken from the class consisting of a pentaerythritol, trimethylolethane, and hexanetriol.

5. A synthetic lubricant according to claim 1 wherein said dibasic acid is taken from the class consisting of adipic, maleic, terephthalic, isophthalic, azelaic and sebacic.

6. A synthetic lubricant according to claim 1 wherein said monobasic acid is saturated.

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