HIGH TEMPERATURE SYNTHETIC ESTER BASE LUBRICANT COMPOSITION BLENDS WITH LIQUID DIESTERS OF DIHYDROXY BIPHENYLS

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ABSTRACT OF THE DISCLOSURE

Esters of certain branched chain fatty acids containing a quaternary carbon atom and dihydroxy biphenyls are employed as base fluids or blending stock in lubricants. Lubricants containing these esters possess suitable viscosity characteristics and greater thermal and oxidative stability and are of special value in lubricating engines which are subject to high temperatures.

This invention is concerned with liquid synthetic esters which are superior, for instance, for use as base fluids in lubricants. Lubricants composed in whole or in part of synthetic components have been developed in an effort to obtain superior lubricating compositions. In general, these lubricating compositions are characterized by higher viscosity index, lower pour point and greater heat stability than mineral oils of corresponding viscosity. Such properties are of special value in lubricating engines which are subjected to high temperatures, such as combustion turbine engines. Mineral oil lubricants, even those containing added VI improvers, pour point depressors, or other additives are undesirable for use in such engines because of the relatively high volatility, low flash point and poor thermal and oxidative stability of the mineral oils, which also have a tendency to leave deposits which accumulate and interfere with the operation of the engine. Particularly, in high performance jet engines, such as those designed for supersonic transport and other advanced aircraft, and in industrial gas turbines which operate continuously at full power settings, lubricants are required to have high thermal and oxidative stability.

Certain neoalkyloxy polyl esters of straight chain fatty acids, e.g., pentaerythritol tetracarboxylate, which are known as high VI improvers, have been utilized as base fluids or blending stock in jet engines but do not possess the thermal and oxidative stability required of the more advanced engine models. On the other hand, esters derived from neoalkyloxy polyls and branched chain fatty acids, e.g., pentaerythritol tetrapivalate, although having good oxidative stability, are solids at room temperature and thus have poor handling, starting and low temperature properties. Polyethylene ethers, e.g., m,m',m'-bisphenoxyphenoxybenzene, have pour points above 35—40° F. and do not flow and pour at subzero temperatures, as required to achieve their functions, especially during the critical start up time for jet engines.

It has now been found that the esters formed by reacting certain branched chain fatty acids or acid chlorides containing a quaternary carbon atom with dihydroxy biphenyls possess superior properties of thermal and oxidative stability along with suitable viscosity, volatility and low temperature properties and therefore may be employed as either base fluids or blending stocks in lubricants for high performance supersonic aircraft and other gas turbine engines. In addition these esters can be used as base fluids or thickeners for high temperature hydraulic fluids, base fluids for high temperature greases and as components for other lubricants which require high thermal and oxidative stability. They can also be used as advanced plasticizers for high temperature polymers such as polyvinyl chloride, polyethylene, polyesters, polyamides, polyimides, polycarbonates, synthetic rubber, etc.

Aromatic dihydroxy biphenyls suitable for forming the esters of this invention may be described by the general formula:

\[
\begin{align*}
\text{O} - \text{R}_1 - \text{O} - \text{R}_2 - \text{O} - \text{R}_3 - \text{O} \\
\text{CH}_2 \text{CH}_2 \text{OH}
\end{align*}
\]

wherein \( x \) equals 0—2, \( y \) equals 0—2, and \( x+y \) equal 2—4. The aromatic rings of these dihydroxy biphenyls may be further substituted with non-deleterious organic groups, especially those of up to about four carbon atoms, such as the lower alkyls and lower alkoxy.

Suitable dihydroxy-biphenyls include 2,2'-dihydroxy biphenyl, 4,4'-dihydroxy biphenyl, 2,4'-dihydroxy biphenyl, 3,3'-dihydroxy biphenyl, 2,2'-dihydroxy-4,4'-dimethyl - biphenyl, 2,2'-dihydroxy-4,4'-dimethoxy biphenyl, 4,4'-dihydroxy-3,3',5,5'-tetramethyl biphenyl, etc. These compounds are readily prepared by the oxidative coupling of the corresponding monohydric phenols. For example, 2,2'-dihydroxy-4,4'-dimethyl biphenyl is obtained when p- cresol is oxidized in the presence of FeCl_3 (Bowden & Reece, J. Chem. Soc. 1950, 2249).

The fatty acid chlorides are prepared by reacting appropriate fatty acids with compounds such as PCl_3, POCl_3, SOCl_2. These fatty acids have the general structure:

\[
\begin{align*}
\text{R}_1 - \text{CH}_2 \text{CH}_2 \text{OH} \\
\text{R}_2 \\
\text{R}_3
\end{align*}
\]

wherein \( m \) is 0 to 3 and \( R_1, R_2 \) and \( R_3 \) are alkyl groups having 1 to 4 carbons. Exemplary of these acids are the following acids which can be used separately or as mixtures thereof to produce the esters of this invention: 2,2'-dimethylpentanoic acid, 3,3'-dimethylpentanoic acid, 4,4'-dimethylpentanoic acid, 4,4'-dimethylexanoic acid, 3,3'-trimethylpentanoic acid, 4,4,5-trimethylhexanoic acid, 3,3'-dimethylbutyric acid, 2-methyl-2-ethyl pentanoic acid, 3-methyl - 3-ethyl pentanoic acid, 3-methyl-3-ethyl butanoic acid, neo-octanoic acid (mixture of C_8 acids having neo acid structures), and neoodecanic acid.

The esterification reaction with the dihydroxy biphenyl can be carried out using either the fatty acid directly or using the acid chloride. In the event the fatty acid is reacted directly with the aromatic hydroxy compound a suitable reagent such as trifluoroacetic anhydride or polyphosphoric acid can also be employed to combine with the water of reaction. If the acid chloride is employed rather than the acid, the reaction is facilitated by the presence of a compound which will react with the HCl as it is formed. Such HCl acceptors include certain amines which have no hydrogen on the nitrogen atom, such as pyridine, dimethyl aniline, and triethylamine, and also inorganic bases such as Na_2CO_3 and CaCO_3. The HCl may also be removed from the reacting mixture by applying sufficient heat and bubbling nitrogen through it. Suitable solvents such as benzene, toluene, xylene, chloroform and ether may be employed to facilitate the reaction and to make stirring easier. The rate of the reaction is increased by the use of a catalyst such as dimethyl formamide.

An illustration of the esterification is given in the example.

**EXAMPLE**

2,2'-bis(2,2, - dimethylpentanoyloxy)biphenyl was prepared in the following manner:

A mixture of 186 g. (1.0 mole) of 2,2'-dihydroxy bi-
phenyl (also called O,O'-biphenol) and 400 g. of toluene was refluxed in a 3 liter, 4-neck flask equipped with a Dean-Stark trap to remove a trace of water. The solution was heated to about 80°C when 145 ml. of dimethylformamide was added. With constant stirring and keeping the mixture in the flask at 76°-82°C, 328 g. (2.2 moles) of neodecanoyl chloride was added during a period of about 4.5 hours. Vivid evolution of HCl gas was observed. The mixture was stirred at 80-100°C for 6 hours. After the addition of 30 ml. of pyridine, the mixture was further stirred (at 90-100°C) for 6 hours. Upon cooling, it was washed twice with dilute HCl, twice with 10% NaOH and twice with water. The solution was then topped to 180°/111 mm., yielding 400 g. of light colored liquid. The light colored liquid was distilled at 187-192° pot temperature and 0.15 to 0.20 mm. Hg to give an almost colorless liquid having a kinematic viscosity at 210° F. of 6.164 cs. and pour point of -20° F.

Using the general procedure described in the example, any of the dihydroxybiphenyls named herein can be reacylated with any of the fatty acids named herein or their corresponding acid chlorides to give the esters of this invention. Thus 4.4'-bis(2,2'-dimethylpentanoyloxy)biphenyl is prepared by reacting 4,4'-dihydroxbiphenyl with 2,2-dimethylpentanoyl chloride or 2,2-dimethylpentanoic acid. In the same manner, 2,2'-bis(3,3-dimethylpentanoyloxy)biphenyl is obtained by reacting 2,2'-dihydroxybiphenyl with 3,3-dimethylpentanoyl chloride or 3,3-dimethylpentanoic acid. Using 2,4-dihydroxybiphenyl and 2,2-dimethylpentanoic acid, there is obtained 2,4-bis(2,2-dimethylpentanoyloxy)biphenyl. 2,2'-dihydroxy-4,4'-dimethoxybiphenyl with 3,3-dimethylpentanoic acid gives 2,2'-bis(3,3-dimethylpentanoyloxy) - 4,4'-dimethoxybiphenyl. 4,4'-dihydroxy-3,3',5,5'-tetramethylbiphenyl with 4,4'-dimethoxybiphenyl produces 4,4'-bis(4,4'-dimethoxybiphenyl) - 3,3',5,5'-tetramethylenxylbiphenyl.

The esters produced by the process of this invention are dialkoxybiphenyl compounds having the following structure:

\[
\begin{align*}
\text{R}_1 & \quad \text{O} \quad \text{R}_2 \\
\text{R}_3 & \quad \text{O} \quad \text{R}_4 \\
\text{R}_5 & \quad \text{O} \quad \text{R}_6
\end{align*}
\]

where R1, R2, R3, x and y are the same as defined hereinbefore, w and n are 0-3, and each of the aromatic rings may be substituted with non-deleterious organic groups, especially those of up to about four carbon atoms such as lower alkyls and lower alkoxyis.

It has also been found that the esters of this invention may be blended with other suitable esters to produce lubricating compositions having improved thermal and oxidative stability. Typical of the esters which may advantageously be blended with the esters of this invention are normal, neo, and gem alkanoic fatty esters of branched chain alcohols having 4 to 12 carbons and 2-6 OH's, e.g., esters of branched chain aliphatic alcohols, pentaerythritol, dipentaerythritol, alkylene glycols, and fatty acids or mixtures thereof having 4-10 carbons, dibasic acid esters of monohydric aliphatic alcohols having 6 to 12 carbons and aliphatic acids of 6 to 12 carbons, and esters of dihydric phenols and fatty acids. These esters may be blended with the esters of the invention in amounts of from about 10° to 90° based on the weight of the lubricant. Examples of these blends of esters are found in Table III. Base fluids containing the esters of this invention have been found to possess improved oxidation resistance compared with conventional base fluids used as high temperature lubricants.

Oxidation resistance of the esters can be determined by the Oxygen Absorption Test which measures the rate of oxygen absorption in the presence of an inhibitor such as 1% N-phenyl-alpha-naphthylamine. The Oxygen Absorption Test is carried out in the following manner: a 75 gm. sample of the ester containing a standard anti-

oxidant is oxidized at 450° F. with 1 ft. of oxygen in a tube of about 9" long and 1 1/4" in I.D. The exit gases pass through a reflux condenser, an entrainment trap and two absorption tubes. The first tube is filled with active charcoal, Drierite and Ascarite to remove organic vapor, water and CO2. The gases come out from the first tube then pass through a catalytic oxidation tube filled with CuO, in which CO and hydrocarbons are converted to CO2. The exit gas from the oxidation tube then passes through a second absorption tube filled with Drierite and Ascarite and is circulated with a tubing pump back into the sample tube. Thus oxygen is continuously circulated through the system until it is used up by the sample. The decrease in the volume of oxygen in the system which represents the volume of O2 absorbed is continuously measured by a Statham gauge and recorded on a Brown recorder. The recorder is so calibrated that the slope of the curve represents the rate of oxygen absorption. During the earlier part of the test the oil is effectively inhibited by the antioxidant and the rate of O2 absorption is usually small. The rate usually stays constant until a time is reached at which the inhibitor is either exhausted or is no longer effective in inhibiting the oxidation. At this point there is generally a fast increase in the rate of oxidation. The time in minutes required for this change of rate to take place is called induction time (T1). The volume of O2 absorbed during this period of time is represented by V1. The test is continued until a total of 2500 ml. of O2 has been absorbed. The time in minutes for this to take place is called total time (T2). The total volume of O2 absorbed (V2) is usually 2500 ml., unless some other volume of O2 was used for special reasons.

Two conventional base fluids, pentaerythritol tetraacetate and trimethylolpropane tribenzoate, were subjected to the Oxygen Absorption Test along with esters of this invention. The results are summarized in Table I.

### Table I

<table>
<thead>
<tr>
<th>Base fluid</th>
<th>T1</th>
<th>T2</th>
<th>V1</th>
<th>V2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylolpropane tribenzoate</td>
<td>238</td>
<td>304</td>
<td>264</td>
<td>453</td>
</tr>
<tr>
<td>Pentaerythritol tetraacetate</td>
<td>298</td>
<td>598</td>
<td>474</td>
<td>742</td>
</tr>
<tr>
<td>2,2'-bis(3,3'-dimethylpentanoyloxy)</td>
<td>906</td>
<td>906</td>
<td>2,000</td>
<td>2,000</td>
</tr>
<tr>
<td>2,2'-bis(3,3'-dimethylpentanoyloxy)</td>
<td>1,928</td>
<td>1,928</td>
<td>2,000</td>
<td>2,000</td>
</tr>
<tr>
<td>2,2'-bis(3,3'-dimethylpentanoyloxy)</td>
<td>1,493</td>
<td>1,493</td>
<td>2,000</td>
<td>2,000</td>
</tr>
</tbody>
</table>

As may be seen in Table I, the esters containing the biphenyl groups have induction times (T1) and total times (T2) 3 to 6 times greater than the two conventional base fluids tested which are often present in Type II synthetic lubricants. This much greater period of time required for the esters of this invention to absorb 2500 ml. of O2 is indicative of the improved resistance to oxidation which will result. Lubricants containing these esters as base fluids will therefore last longer in gas turbine engines, and form less troublesome oxidation products such as sludge, coke and acids. It is further seen in Table II that there is no sacrifice in desirable properties of viscosity, pour, flash, and fire points found in the compounds.

### Table II

<table>
<thead>
<tr>
<th>Kinematic viscosity:</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>20°F</td>
<td>6,164</td>
<td>14,6</td>
<td>4,7</td>
<td>311</td>
</tr>
<tr>
<td>100°F</td>
<td>83,29</td>
<td>222,9</td>
<td>174,1</td>
<td>658</td>
</tr>
<tr>
<td>Pour point,°F</td>
<td>-20</td>
<td>998</td>
<td>-15</td>
<td></td>
</tr>
<tr>
<td>Flash point,°C</td>
<td>405</td>
<td>445</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fire point,°C</td>
<td>470</td>
<td>513</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE III

<table>
<thead>
<tr>
<th>70 wt. percent</th>
<th>50 wt. percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2'-bis(2,2-dimethylpentanoyloxy) biphenyl, 50 wt. percent</td>
<td>2,2'-bis(2,2-dimethylpentanoyloxy) biphenyl, 50 wt. percent</td>
</tr>
<tr>
<td>dibasic acid ester of valeric and neodecanoic acids</td>
<td>ester of valeric and neodecanoic acids</td>
</tr>
<tr>
<td>Kinematic viscosity, centistokes</td>
<td>7.04</td>
</tr>
<tr>
<td>210° F</td>
<td>105</td>
</tr>
<tr>
<td>90° F</td>
<td>60.71</td>
</tr>
<tr>
<td>Pour point, °F</td>
<td>below -30</td>
</tr>
<tr>
<td>Cloud point, °F</td>
<td>below -30</td>
</tr>
<tr>
<td>Flash point, °F</td>
<td>440</td>
</tr>
<tr>
<td>Fire point, °F</td>
<td>505</td>
</tr>
</tbody>
</table>

It is claimed:

1. A high temperature synthetic ester base lubricant composition consisting essentially of a blend of:
   (A) from about 10 to 90 weight percent of a liquid diester of (a) a dihydroxy biphenyl of the formula
   \[
   \text{(OH)}_x \longleftrightarrow \text{(OH)}_y
   \]
   wherein \(x\) and \(y\) is 0-2 but \(x+y=2\) and (b) a branched chain acid having a quaternionary carbon atom selected from the group consisting of: 2,2-dimethylpentanoic acid, 3,3-dimethylpentanoic acid, 4,4-dimethylpentanoic acid, 4,4-dimethylhexanoic acid, 5,5,4-trimethylpentanoic acid, 4,4,5-trimethylhexanoic acid, 3,3-dimethylbutanoic acid, 2-methyl-2-ethyl pentanoic acid, 3-methyl-2-ethyl pentanoic acid, and 3-methyl-3-ethyl butanoic acid, and
   (B) from about 90 to 10 weight percent of an ester selected from the group consisting of (a) the normal, neo and gem alkanoic fatty acid esters of branched chain aliphatic alcohols having 4 to 12 carbons and 2 to 6 hydroxy groups and alkanoic fatty acids having 4 to 10 carbons and mixtures thereof, (b) dibasic acid esters of monohydric aliphatic alcohols having 6 to 13 carbons and aliphatic acids of 6 to 12 carbons, and (c) esters of dihydric phenols and fatty acids.

2. A high temperature synthetic ester base lubricant composition consisting essentially of a blend of (a) dihydroxy diphenyl (A) is 2,2'-bis(2,2-dimethylpentanoyloxy) dibenzylic acid ester (B) is resorcinol dineooctanoate.

3. A high temperature synthetic ester base lubricant composition consisting essentially of a blend of (a) dihydroxy diphenyl (A) is 2,2'-bis(2,2-dimethylpentanoyloxy) dibenzylic acid ester (B) is pentacyclohexyl ester of a mixture of valeric and neodecanoic acids.

4. A high temperature synthetic ester base lubricant composition consisting essentially of a blend of (a) dihydroxy diphenyl (A) is 2,2'-bis(2,2-dimethylpentanoyloxy) dibenzylic acid ester (B) is resorcinol dineooctanoate.

5. A high temperature synthetic ester base lubricant composition consisting essentially of a blend of (a) dihydroxy diphenyl (A) is 2,2'-bis(2,2-dimethylpentanoyloxy) dibenzylic acid ester (B) is pentacyclohexyl ester of a mixture of valeric and neodecanoic acids.

6. A high temperature synthetic ester base lubricant composition consisting essentially of a blend of (a) dihydroxy diphenyl (A) is 2,2'-bis(2,2-dimethylpentanoyloxy) dibenzylic acid ester (B) is pentacyclohexyl ester of a mixture of valeric and neodecanoic acids.

7. A high temperature synthetic ester base lubricant composition consisting essentially of a blend as set forth in claim 1 wherein said liquid diester of a dihydroxy diphenyl (A) is 2,2'-bis(3,3-dimethylpentanoyloxy) dibenzylic acid ester (B) is the pentacyclohexyl ester of a mixture of valeric and neodecanoic acids.

8. A high temperature synthetic ester base lubricant composition consisting essentially of a blend as set forth in claim 6 wherein said 2,2'-bis(3,3-dimethylpentanoyloxy) dibenzylic acid ester (B) is 50 weight percent and said pentaerythritol ester of a mixture of valeric and neodecanoic acids is 50 weight percent.

9. A high temperature synthetic ester base lubricant composition consisting essentially of a blend as set forth in claim 8 wherein said dihydroxy diphenyl is 2,2'-dihydroxy diphenyl or 2,4'-dihydroxy diphenyl.

References Cited

UNITED STATES PATENTS

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3,347,884 10/1967 Vories

FOREIGN PATENTS

855,242 11/1960 Great Britain

OTHER REFERENCES


DANIEL E. WYMAN, Primary Examiner
J. M. HICKEY, Assistant Examiner
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION


Inventor(s) Tai S. Chao and Manley Kjonaas

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the formula which appears in Column 2, Line 32,

\[ \text{---C---} \] should be \[ \text{---C---} \].

In Column 4, Table I, "T1" should read \[ \text{Tt} \].

In Column 4, Table II, "940" should read \[ 0\]

In Column 5, Table III, the right hand column of Table III, "Valerie" should read \[ \text{valeric} \].

In Column 5, Table III, the next to the right hand column "84.99" should read \[ 84.89\].

SIGNED AND SEALER

OCT 1, 1970

(SEAL)

Attest:

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