LUBRICITY ADDITIVE-HYDROGENATED DI-CARBOXYLIC ACID AND A GLYCOL

Michael J. Furey, Berkeley Heights, and John K. Appel- doorn, Bernardsville, N.J., and Albin F. Turbak, Dan- ville, Ill., assignors to Eso Research and Engineering Company, a corporation of Delaware

No Drawing. Filed Sept. 9, 1965, Ser. No. 486,221
15 Claims. (Cl. 222—56)

This application is a continuation-in-part of application Serial Number 284,857, filed June 3, 1963 (now abandoned).

The present invention is broadly concerned with a novel class of lubricity additives, additive concentrates, and oleopholic liquid compositions containing the same. It is preferred that the oleopholic liquid compositions be substantially anhydrous. The invention is more specifi- cally concerned with improving the lubricity of hydrocarbon liquids such as gasolines, aviation turbine fuel, kerosene, diesel fuel, lubricating oil and mineral lubricating oils. Other base fluids include liquid carbohydrates and esters such as diocetyl sebacate and didecyl adipate. The present invention also contemplates the use of the lubricity additives in solid products such as paraffin wax, lubricating grease and Carbowax. The invention in one specific aspect relates to improving the lubricity of middle distillates, particularly jet fuels.

The lubricity additives of the present invention comprise a reaction product between a dicarboxylic acid and an oil insoluble glycol, wherein the dicarboxylic acid is preferably characterized by having at least 9 carbon atoms between the respective carboxylic groups. It is preferred that the number of carbon atoms between the respective carboxylic groups of the dicarboxylic acid be in the range from about 12 to 42. The additives also have molecular weights below about 1700, preferably below about 1300 as determined by the "Osmometer Method," Anal. Chem., vol. 33, No. 1, pp. 135—137, January 1961, Wilson.

In one preferred embodiment of the present invention the lubricity additives preferably comprise predominantly partial esters of an oil insoluble glycol and dicarboxylic acids that are obtained by the polymerization of dienoic or trienoic monocarboxylic acids. In a second embodiment of the present invention, the lubricity additives preferably comprise esters of an oil insoluble glycol and the dicarboxylic acids previously described. In still another embodiment of the present invention, the lubricity additives comprise esters of an oil insoluble glycol and hydrogenated dicarboxylic acids obtained as hereinafter described.

In general, the compositions of the present invention improve the lubricity of distillate fuels boiling in the range from about 50° to 750° F. Such fuels include aviation turbo-jet fuels, rocket fuel (MIL-R—25576B), kerosenes, diesel fuels, and heating oils. Aviation turbo-jet fuels in which the dimer acid or hydrogenated dimer acid/glycol esters may be used normally boil between about 50° and about 550° F. and are used in both military and civilian aircraft. Such fuels are more fully defined by U.S. Military Specifications MIL-F—5624F, MIL-F—25565A, MIL-F—2554A, MIL-F—25545B, and amendments thereto, and in ASTM D—1655—62T. Kerosenes and heating oils will normally have boiling ranges between about 300° and about 750° F. and are more fully described in ASTM Specification D—396—48T and supple- ments thereto, where they are referred to as No. 1 and No. 2 fuel oils. Diesel fuels in which the dimer acid or hydrogenated dimer acid/glycol esters may be employed are described in detail in ASTM Specification W—975— 35T and later version of the same specification.

The additives of the present invention may be em- ployed in conjunction with a variety of other additives commonly used in fuels such as those set forth above. Typical of such additives are oxidation inhibitors such as phenothiazine or phenyl alpha-naphthylamine; rust inhibi- tors such as heptalin or petroleum sulfonates; sorbitan monooileate; detergents such as the barium salt of isononyl phenol sulfide; pour point depressants such as copolymers of vinyl acetate with fumaric acid esters of coconut oil alcohols; viscosity index improvers such as polymeth- acrylates; dispersants, dyes, dye stabilizers, haze inhibitors, antiaitic agents, and the like.

Many oil compositions are designed for lubricating under boundary conditions (e.g., crankcase oils, aviation oils and gear oils) where the prevention of wear of the metal surfaces is a serious problem that occurs under heavy loading. One common example of such heavy loading occurs in the operation of the valve lifter mecha- nism of gasoline engines. Here, pressures of 50,000 to 100,000 p.s.i. can occur between the valve lifter and its actuating cam and metal wear is accordingly high. It has now been found that metal wear can be significantly re- duced by adding to an oleopholic liquid such as a mineral oil lubricant, a reaction product between a dicarboxylic acid and an oil insoluble glycol wherein the dicarboxylic acid is preferably characterized by having at least 9 carbon atoms between the respective carboxylic groups. Preferred oil insoluble glycols include the alkane diols having relatively short carbon chains as, for example, from about 2 to 8, e.g. 2 to 5, carbon atoms. A very suitable glycol for the purposes of the present invention is ethylene glycol.

As pointed out heretofore, the preferred dicarboxylic acids utilized are those which contain at least 9 carbon atoms between the respective groups. It is greatly preferred that the number of carbon atoms between the car- boxylic groups be in the range from about 12 to 42. Spec- ific examples of these acids are the dimers of linoleic acid, oleic acid, the mixed dimer of linoleic and oleic acids and the dimer of dodecadienoic acid. It is also possible to employ the dimer of dicyclopentadiene diolic acid. While the foregoing acids are preferred, similar dicar- boxylic acids such as "VR—1," described in U.S. 2,833,713, and "D—50," described in U.S. 2,470,849, may be used. The dienoic or trienoic monocarboxylic acid, that is po- lymerized to give the dicarboxylic polymer, can have from 12 to 30 carbon atoms. Extremely suitable dimer acids for use in the present invention are commercially avail- able from Emery Industries Inc., under the trade name of Empol dimer acids. These dimer acids are available in various grades of dimer acid purity relative to trimer and monobasic acid content. For example, Empol 1014 dimer acid consists of 95% dimer acid, a trace of mono- basic acids and the remainder essentially consists of tri- mer acid. Also available are Empol 1018 dimer acid (containing 17% trimer and a trace of monobasic acid),
Empol 1022 dimer acid (19 to 22% trimer and 2 to 5% monobasic acids) and Empol 1024 dimer acid (containing the same trimer acid content as Empol 1022 but containing only a trace amount of monobasic acid). The specifications and typical compositions of the Empol dimer acids discussed above are given in Table I:

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>Empol 1014</th>
<th>Empol 1018</th>
<th>Empol 1022</th>
<th>Empol 1024</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutralization Equivalent</td>
<td>288-294</td>
<td>287-299</td>
<td>288-301</td>
<td>289-301</td>
</tr>
<tr>
<td>Acid Value</td>
<td>191-195</td>
<td>198-196</td>
<td>198-196</td>
<td>198-196</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>0.926</td>
<td>0.923</td>
<td>0.923</td>
<td>0.923</td>
</tr>
<tr>
<td>Color, Gardner 10F8, Max</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Monobasic Acids, Percent</td>
<td>Max</td>
<td>1.5</td>
<td>1</td>
<td>2-5</td>
</tr>
<tr>
<td>Dimer Acid</td>
<td>83</td>
<td>83</td>
<td>77</td>
<td>77</td>
</tr>
<tr>
<td>Trimer Acid</td>
<td>4</td>
<td>17</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>Monotertiary Acids</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
</tr>
<tr>
<td>Dimer:Trimer Molar Ratio</td>
<td>2:1</td>
<td>7:1</td>
<td>6:1</td>
<td>6:1</td>
</tr>
</tbody>
</table>

The commercial dimer acids discussed above are generally produced by polymerization of unsaturated C18 fatty acids to form C26 dibasic dimer acids. Depending on the raw materials used in the commercial process, the C18 monomeric acid may be linoleic acid or oleic acid or mixtures thereof. The resulting dimer acids may therefore be the dimers of linoleic acid, oleic acid or a mixed dimer of linoleic and oleic acid. Representative formulas of the foregoing monomeric and dimer acids may be illustrated as follows. (It should be noted that the structure generally given for linoleic acid is that of 9,12-octadecadienoic acid but it is believed that prior to dimerization this acid isomerizes to the 9,11 structure, see in this regard the article "Dimer Acids," the Journal of the American Oil Chemists Society, vol. 39, December 1962, p. 535, J. C. Cowan.)

(a) \[
\begin{align*}
\text{CH}_2(\text{CH}_2)_2\text{CH}=\text{CHCHCH=CHCH=CH(C_2\text{H}_5)}\text{COOH} & \xrightarrow{\Delta} \text{9,12 linoleic acid} \\
2 \text{molecules} & \xrightarrow{\text{Diels-Alder}} \\
\text{CH}_2(\text{CH}_2)_3\text{CH}=\text{CHCH=CHCH=CH(C_2\text{H}_5)}\text{COOH} & \xrightarrow{\Delta} \text{9,11 linoleic acid}
\end{align*}
\]

(b) \[
\begin{align*}
\text{CH}_2(\text{CH}_2)_2\text{CH}=\text{CHCH=CH(C_2\text{H}_5)}\text{COOH} & \xrightarrow{\Delta} \text{Oleic acid} \\
2 \text{molecules} & \xrightarrow{\text{Diels-Alder}} \\
\text{HOOC(\text{CH}_2)_2\text{CH}=\text{CHCH=CH(C_2\text{H}_5)}\text{COOH} & \xrightarrow{\Delta} \text{Linoleic acid dimer (dihilene acid)}
\end{align*}
\]

(c) \[
\begin{align*}
\text{CH}_2(\text{CH}_2)_2\text{COOH} & \xrightarrow{\Delta} \text{Diels-Alder} \\
\text{CH}_2(\text{CH}_2)_2\text{CH}=\text{CHCH=CH(C_2\text{H}_5)}\text{COOH} & \xrightarrow{\Delta} \text{Linoleic acid dimer (dioleic acid)}
\end{align*}
\]

(d) \[
\begin{align*}
\text{HOOC(\text{CH}_2)_2\text{CH}=\text{CHCH=CH(C_2\text{H}_5)}\text{COOH} & \xrightarrow{\Delta} \text{Diels-Alder} \\
\text{CH}_2(\text{CH}_2)_2\text{CH}=\text{CHCH=CH(C_2\text{H}_5)}\text{COOH} & \xrightarrow{\Delta} \text{Linoleic acid dimer (dioleic acid)}
\end{align*}
\]

It should be noted that the above structural formulae only indicate one of the several possible structural isomers. It is believed that the commercial dimer acids would contain mixtures of such structural isomers.

The dimer acid of linoleic acid with which one embodiment of the present invention is concerned is a C26 dimer acid and is described in U.S. Patent 2,424,588, issued July 75.

Thus, it is essential that the amount of dimer acid present in the acid composition be at least 50% and preferably above 75%, such as 95% by weight. It is to be understood that, under certain circumstances, these dicarboxylic acids can be substituted acids such as with bromine, fluorine or a hydroxy group.

The lubricity additives of the present invention comprising a reaction product between a dimerized dicarboxylic acid and an oil insoluble glycol, such as the aliphatic glycol, may be produced by various techniques. The oil insoluble glycol reacted with the dicarboxylic acid may be an alkyl alkane diol or an oxa-alkane diol, straight chain or branched. The alkane diol has from about 2 to 8 carbon atoms, preferably 2 to 5 carbon atoms in the molecule.

The oxa-alkane diol can have 4 to 100 carbon atoms with periodically repeating groups of

\[\text{O} \quad \text{C} \quad \text{O} \quad \text{H} \quad \text{H}\]

wherein R is H or CH₃.

The preferred alkane diol is ethylene glycol and the preferred oxa-alkane diol is 1,2-ethylene glycol-diol-2,6. As pointed out, the preferred dimeric dicarboxylic acids are the dimers of linoleic acid, oleic acid or the mixed dimer of linoleic and oleic acids, which may also contain some monomer as well as trimer. Other specific satisfactory glycols are, for example, propylene glycol, polypropylene glycol, polyethylene glycol and the like.

The molar quantities of the dicarboxylic acid and glycol reactants may be adjusted so as to secure either a complete diester or a partial ester.

Turning now to the embodiment wherein a diester of a dimeric dicarboxylic acid is used, as previously indicated, the molar quantities of reactants are adjusted in this embodiment so as to secure a complete diester. For example, one process is to reflux an excess of the diol with the selected dioic acid at 80° C. In the presence of benzene as diluent and toluene sulfonic acid as catalyst until the theoretical amount of water has been produced in a water-trap in the reflux condenser. The diluent is then stripped off under vacuum at 40° C. The general reaction equation is as follows:

\[
\text{HOOC--R--COOH} + \text{XHO--R'--OH} \rightarrow \text{HO--R'OOC--R--COOR'}--\text{OH} + \text{XH}_2\text{O}
\]
wherein R is the hydrocarbon skeleton of the dicarboxylic acid having more than 9 carbon atoms between the acid groups. R' is either the hydrocarbon skeleton of a C<sub>6</sub> to C<sub>8</sub> glycol or the oxa-alkane diol and X is 2 or greater.

Particularly desirable base fuels wherein the additives of the present embodiment are most effective are those base fuels wherein the viscosity is below about 3 centistokes and which fuels are substantially free of polar compounds, sulfur compounds, and nitrogen compounds. In essence, the concentration of these compounds is less than about 0.01% by weight, which is secured when the jet fuel is highly refined, such as by hydrofining.

If the diester additives of the present embodiment are used as an additive concentrate, the concentrate may consist essentially of from about 25 to 75% of the additives, the remainder being a satisfactory solvent such as kerosene, a Varsol, a naphtha and the like. The preferred concentrate contains about 50 to 60% of the additive in the solvent.

When the diester additive is used in conjunction with oleophilic liquid, the concentration may vary appreciably. For example, when the additive is used in a fuel, the concentration is in the range of from about 0.001 to 0.4% by weight, preferably in the range of from about 0.01 to 0.05% by weight. On the other hand, if the additive is used with a hydrocarbon lubricating oil, the concentration may vary in the range from about 0.001 to 4.9% by weight, preferably in the range from about 0.1 to 2.0% by weight.

The embodiment relating to the glycol diesters of dimer acids may be more easily understood by reference to the following examples.

EXAMPLE 1

In order to further illustrate the invention, a number of tests were carried out using the additives of the present invention in base jet fuels and the load carrying capacity of the fuels determined.

One mole of C<sub>2</sub>-C<sub>4</sub> dimer acid (Empol 1014—previously identified) was reacted with 2 moles each of either of two glycols (ethylene and neopentyl) by refluxing in benzene in the presence of p-toluene sulfonic acid monohydrate as a catalyst. The water evolved was measured and the benzene solutions were water washed. On evaporation of the benzene under vacuum at 35° to 40° C, the resultant products were found to be dark amber, clear, viscous fluids quite soluble in hydrocarbons.

Effect on Scuffing

As shown by the data below, the addition of 0.1% of the C<sub>2</sub>-C<sub>4</sub> dimer acid/ethylene glycol diester to a jet fuel greatly increased the load-carrying capacity as measured by the Ryder gear test. The dimer acid alone has little effect.

<table>
<thead>
<tr>
<th>Fluid:</th>
<th>Ryder rating (#/in.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base jet fuel</td>
<td>400</td>
</tr>
<tr>
<td>Base+0.1% diester of C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt; dimer acid and ethylene glycol</td>
<td>7,110</td>
</tr>
<tr>
<td>Base+0.1% C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt; dimer acid</td>
<td>480</td>
</tr>
</tbody>
</table>

Highly isoparaffinic fuel of 87° to 89° F, boiling range, high thermal stability, low freezing point and low sulfur content.

2 Run under more severe condition of 52 F load steps rather than 25 F. Under this condition (25 F step), the base fails on the first step.

As shown by the above data, the addition of 0.1% of the diester increases the anticutting properties of jet fuel as measured by the Ryder gear test (E. A. Ryder, ASTM Bulletin 184, 41 (1952)). The ratings represent the load in pounds/inch of tooth width to produce a given amount (22/2%) of gear scuffing. It can also be seen that the C<sub>2</sub>-C<sub>4</sub> dimer acid itself has substantially no effect.

EXAMPLE 2

Another test was carried out with the following results:

<table>
<thead>
<tr>
<th>Additive wt percent</th>
<th>Ryder Scuff Test #/in.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral Mineral Oil, Viscosity 45 SUS at 20° F</td>
<td>0</td>
</tr>
<tr>
<td>Mineral Oil with Diester of Ethylene Glycol and Dimer of Linoleic Acid</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Thus, it is apparent that the diester is very effective.

EXAMPLE 3

The preparation and tests of Example 1 are repeated except that the C<sub>4</sub>-C<sub>6</sub> dimer acid is obtained from oleic acid. The ethylene glycol diester of the dioleic acid is observed to have the effect of improving the anticutting properties of jet fuel as measured by the Ryder gear test.

EXAMPLE 4

The preparations and tests of Example 1 are repeated except that the C<sub>6</sub>-C<sub>8</sub> dimer acid is obtained from the mixed dimer of oleic and linoleic acids. The ethylene glycol diester of the dioleic acid is observed to have the effect of improving the anticutting properties of jet fuel as measured by the Ryder gear test.

Turning now to the embodiment of the present invention relating to the use of partial esters of dicarboxylic acids having at least 9 carbon atoms between the carboxylic acid groups in the molecule, the partial esters of the aforementioned acids generally consist of a mixture containing a major portion of the monoester with minor proportions of the diester and unreacted acid. The preparation of these partial esters can best be illustrated by reference to the following equation:

\[ \text{HOOC-R}\vdash\text{COOH+YHO-R'}\vdash\text{OH}\rightarrow\text{HO-R'OOC-R}\vdash\text{COOH+H}_2\text{O} \]

wherein R is the hydrocarbon skeleton of the dicarboxylic acid having more than 9 carbon atoms between the acid groups, R' is either the hydrocarbon skeleton of a C<sub>2</sub> to C<sub>8</sub> glycol or the oxa-alkyl skeleton of an oxa-alkane diol and Y is less than 2.

The procedure used in preparing the partial ester consisted of weighing out the dimer acid and glycol in equimolar quantities and carrying out the esterification in benzene under reflux conditions (80° C) with a small amount of paratoluene sulfonic acid as a catalyst. A condenser and trap were used—the refluxing being stopped when the theoretical amount of water was collected. (The water azeotropes off with the benzene.) Then the benzene solution was cooled and water washed to remove the catalyst. The benzene was then stripped off under vacuum at 35° to 40° C, leaving the product usually a clear, dark amber viscous fluid.

EXAMPLE 5

The procedure outlined immediately above was used to make 6 different monoesters. In each case, 0.1 mole of C<sub>2</sub>-C<sub>4</sub> dimer acid (Empol 1014—essentially linoleic dimer acid), 0.1 mole of glycol and 1.5 grams paratoluene sulfonic acid were mixed with 1 pint of benzene and then the reaction was carried out. Monoesteric esters of the following glycols were made:

- Ethylene
- Triethylene
- Neopentyl (2,2-dimethyl,1,3 propane dial)
- 1,4 butane dial
- 1,6 hexane dial
- 1,12 dihydroxy octadecane

Each of the above monoesters was quite soluble in hydrocarbons.
Effect of monomeric esters on load-carrying capacity of jet fuels

As shown by the data below, the addition of 0.1% of several of the monoesters increases the anti-scuffing properties of jet fuel as measured by the Ryder Gear Test (E. A. Ryder, ASTM Bulletin 184, 41 (1952)). The ratings represent the load in pounds/inch of tooth width to produce a given amount (22 1/2%) of gear scuffing. It can be seen that the ethylene glycol derivative is by far the most effective, while the neopentyl compound is the least effective. It can also be seen that the C₈ dimer acid itself has substantially no effect.

Effect of monomeric esters of C₂₈ dimer acid and glycols on load-carrying capacity of jet fuels

<table>
<thead>
<tr>
<th>Run</th>
<th>Additive in Base Jet Fuel</th>
<th>Ryder Rating (lbs/in.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>None</td>
<td>400</td>
</tr>
<tr>
<td>B</td>
<td>0.1% C₈Ethylene Glycol Monoester</td>
<td>1,380</td>
</tr>
<tr>
<td>C</td>
<td>0.1% C₈Glyceryl Monoester</td>
<td>1,380</td>
</tr>
<tr>
<td>D</td>
<td>0.1% C₈Neopentyl Glycol Monoester</td>
<td>770</td>
</tr>
<tr>
<td>E</td>
<td>0.1% C₈Ethylene Glycol Dimer Acid</td>
<td>1,380</td>
</tr>
<tr>
<td>F</td>
<td>0.1% C₈Dimer Acid</td>
<td>1,380</td>
</tr>
<tr>
<td>G</td>
<td>Rahn B except Dimer Acid Hydogenated</td>
<td>2,260</td>
</tr>
</tbody>
</table>

1 Highly isoparaffinic fuel of 375° to 60°F boiling range, high thermal stability, low freezing point and low sulfur content.

Furthermore, it has also been found that the ethylene glycol monoester blend (at 0.1% concentration) passes a critical thermal stability test for jet fuels. This is a 5 hour test in which the fuel, held at 300°F in bulk, is pumped through a heat exchanger to reach 500°F and then through a filter. The requirements are that no deposits should form on the metal heat exchanger tube and that there should be no (or little) pressure drop across the filter. Many conventional load-carrying additives fail to test.

EXAMPLE 6

The procedures and tests of Example 5 are repeated with the exception that the dimer of oleic acid is utilized as the dicarboxylic acid. The addition of 0.1% of the resulting monoesters is found to increase the anti-scuffing properties of jet fuel.

EXAMPLE 7

The procedures and tests of Example 5 are repeated with the exception that the mixed dimer of linoleic and oleic acids is utilized as the dicarboxylic acid. The addition of 0.1% of the resulting monoesters is found to increase the anti-scuffing properties of jet fuel.

EXAMPLE 8

A number of compositions were prepared using several percentages of the lubricity additives of the present invention and were tested by means of the "Ryder Scuff Test." The particular lubricity agent used was an ester of a linoleic dimer reacted with ethylene glycol under refluxing conditions as described hereinbefore. The results of these tests are illustrated in the following table:

<table>
<thead>
<tr>
<th>Run</th>
<th>Additive, Wt. Percent</th>
<th>Ryder Scuff Test Load Inch</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>D(2-ethylhexyl) sebacate</td>
<td>0.1  1,900</td>
</tr>
<tr>
<td>B</td>
<td>C₈-Ox acid adipate</td>
<td>0.5  2,830</td>
</tr>
<tr>
<td>C</td>
<td>Blend of 60% No. A with 32.5% C₈ adipate and 5.0% C₈ sebacate</td>
<td>0.1  2,000</td>
</tr>
<tr>
<td>D</td>
<td>Blend of 50% trimethyloxane triester of polyglyceric acid and 49% complex ester of neopentyl glycol, trimethyloxane and dicarboxylic acid.</td>
<td>0.5  2,500</td>
</tr>
<tr>
<td>E</td>
<td>Aviation grade mineral oil, viscosity 100 SUS at 20°F.</td>
<td>0.5  3,010</td>
</tr>
<tr>
<td>F</td>
<td>Neutral mineral oil, viscosity 43 SUS at 20°F.</td>
<td>0.5  1,170</td>
</tr>
<tr>
<td>G</td>
<td>No. F with additive made using 2 moles of diol for 1 mole of dicarboxylic acid.</td>
<td>0.5  1,170</td>
</tr>
</tbody>
</table>

From the above, it is readily apparent that the additive of the present invention materially reduced scuffing in every case.

It has now further been found that especially effective lubricity additives can be prepared from the reaction product of an oil insoluble glycol and a hydrogenated dicarboxylic acid having at least 9 carbon atoms and two dicarboxylic acid groups. While either the dicarboxylic acid or the ester product may be hydrogenated, it is preferred that the dicarboxylic acid be hydrogenated prior to esterification. This hydrogenation may be accomplished by any suitable process known to the art. For example, the acid may be reduced with hydrogen over platinum catalyst at a temperature in the range from 20° to 100°C in a steel bomb. The hydrogen pressure in the system may range from about 10 to 300 pounds. Another method by which hydrogenation may be accomplished is by the use of lithium hydride using conventional techniques at ambient temperatures. As before, the preferred dicarboxylic acids for use in this embodiment consist of the dimer of linoleic acid, the dimer of oleic acid and the mixed dimer of linoleic and oleic acids. Additionally, the preferred oil insoluble glycols include alkane diols or oxa-alkane diols having straight or branched chains. The alkane diol may have from about 2 to 8 carbon atoms, preferably 2 to 5 carbon atoms in the molecule. A preferred alkane diol is ethylene glycol and a preferred oxa-alkane diol is 4-oxa-heptane diol-2,6. Other specific satisfactory glycols are, for example, propylene glycol, polypropylene glycol, polyethylene glycol and the like. Diesters and partial esters of the hydrogenated dicarboxylic acids may be prepared by any of the methods previously disclosed in prior embodiments of the present invention.

In order to further illustrate the advantages obtained by utilizing a hydrogenated dicarboxylic acid to form an ester product for use as a lubricity additive, a number of tests were carried out on several additives including a monoester prepared from a hydrogenated C₂₈ dimer acid (Empol 1014).

EXAMPLE 9

A number of additives were added to base jet fuels and the load carrying capacity of the fuels determined. As shown by the data below, the addition of 0.1% of each of the monoesters of C₂₈ dimer acid increases the anti-scuffing properties of jet fuel as measured by the Ryder Gear Test. The ratings represent the load in pounds/inch of tooth width to produce a given amount (22 1/2%) of gear scuffing. It can be seen that the hydrogenated dimer acid derivative shows greatly superior results.
Effect of monomeric esters of C₅₆ dimer acid and glycols on load-carrying capacity of jet fuels

<table>
<thead>
<tr>
<th>Run</th>
<th>Additive in Base Jet Fuel</th>
<th>Relative Valve Lifter Wear</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>None</td>
<td>400</td>
</tr>
<tr>
<td>B</td>
<td>0.5% C₅₆ Dimer Acid/Ethylene Glycol Monoster</td>
<td>1,200</td>
</tr>
<tr>
<td>C</td>
<td>0.1% C₅₆ Dimer Acid</td>
<td>1,264 (1,200)</td>
</tr>
<tr>
<td>D</td>
<td>Run B except Dimer Acid Hydrogenated</td>
<td>2,250</td>
</tr>
</tbody>
</table>

1 Highly isoparaffinic fuel of 25°C to 50°C boiling range, high thermal stability, low freezing point and low sulfur content.

The importance of maintaining control over the molecular weight of the reaction products of the present invention was investigated. It should be noted that the diesters and partial esters heretofore described have contained hydroxy groups arising either from the carboxylic acid groups that have not been esterified or from the unreacted portion of the glycol. It is possible that under the conditions of esterification that these groups react further causing condensation of 2 or more ester molecules forming condensation polymers of relatively high molecular weight. Such polymers are described in U.S. Patent 2,424,588, previously cited. In this patent, the condensation reaction between molecules is allowed to proceed until polymers having molecular weight as high as 20,000–25,000 are obtained. It is possible to control the amount of condensation by following the amount of water produced in the reaction mixture and stopping the reaction when the theoretical amount of water for the desired polymer state has been obtained. The effect of increasing the polymeric state of the reaction product between a C₅₆ dimer acid (Empol 1014—dillinoic acid) was determined as per the following Example 10.

EXAMPLE 10

The comparative lubricity of additive compositions containing various degrees of polymerization between the ethylene glycol ester of a C₅₆ dimer acid was determined. Reaction products of varying degrees of polymerization were obtained by stopping the esterification reaction at various points based on the amount of water collected. Compounds having essentially one ester molecule, 2 ester molecules and 4 ester molecules were prepared. The respective physical characteristics of these compounds are given in the following table:

<table>
<thead>
<tr>
<th>Reaction product of ethylene glycol and C₅₆ dimer acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number Molecules Ester Condensed</td>
</tr>
<tr>
<td>Product A</td>
</tr>
<tr>
<td>Product B</td>
</tr>
<tr>
<td>Product C</td>
</tr>
</tbody>
</table>

1 Based on water removed from the reaction mixture.

It is seen from the above table that Product A consisted essentially of a monomeric monoester of ethylene glycol and the C₅₆ dimer acid. Product B, on the other hand, consisted of a dimer of the monoester wherein 2 molecules of the monoester have condensed. The slightly lower acid number than theoretical and the slightly higher molecular weight than theoretical can be attributed to small amounts of higher polymer condensation products. Similarly, Product C is seen to be a tetramer of the monoester and also is observed to contain small amounts of more highly condensed material.

The above materials were tested in order to determine the effect on the lubricity properties of a fluid to which they have been added. The test results are given below:

Additive in solvent 100 neutral:

<table>
<thead>
<tr>
<th>Relative Valve Lifter Wear</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
</tr>
<tr>
<td>1% of Product A</td>
</tr>
<tr>
<td>1% of Product B</td>
</tr>
<tr>
<td>1% of Product C</td>
</tr>
</tbody>
</table>

As indicated, for the purposes of the present invention, it is necessary that n have a value no greater than about 2 in order to prepare operative esters for use as lubricity additives.

It is similarly possible to form polyesters of the diesters of the dicarboxylic acids of the present invention.

What is claimed is:

1. A new composition of matter, suitable for addition to a composition selected from the group consisting of hydrocarbon liquids and synthetic ester lubricants, which comprises an ester, formed by reacting an oil-insoluble glycol having between about 2 and about 8 carbon atoms per molecule with a hydrogenated dimer of a C₁₂ to C₁₅ unsaturated monocarboxylic acid, said ester being selected from the group consisting of monomeric esters having the formule:

\[ \text{HOOC—R—COOH} + \text{HO—R'—OH} \rightarrow \text{HOOC—R—COO—R'—OH} + \text{H₂O} \]

2. As indicated, for the purposes of the present invention, it is necessary that n have a value no greater than about 2 in order to prepare operative esters for use as lubricity additives.

3. It is similarly possible to form polyesters of the diesters of the dicarboxylic acids of the present invention.

4. A new composition of matter, suitable for addition to a composition selected from the group consisting of hydrocarbon liquids and synthetic ester lubricants, which comprises an ester, formed by reacting an oil-insoluble glycol having between about 2 and about 8 carbon atoms per molecule with a hydrogenated dimer of a C₁₂ to C₁₅ unsaturated monocarboxylic acid, said ester being selected from the group consisting of monomeric esters having the formule:

\[ \text{HOOC—R—COOH} + \text{HO—R'—OH} \rightarrow \text{HOOC—R—COO—R'—OH} + \text{H₂O} \]

and esters formed by reacting a hydrogenated dimer of said carboxylic acid with said glycol in the mole ratio of 2 to 1 respectively, wherein R is the hydrocarbon radical of the said dimer acid and R' is the hydrocarbon radical of said glycol.

5. A composition of matter as in claim 1 wherein the acid is the hydrogenated mixed dimer of linoleic and oleic acids.

6. A composition of matter as in claim 1 wherein the acid is the hydrogenated dimer of oleic acid.

7. A composition of matter as in claim 1 wherein the glycol is ethylene glycol. 

8. A composition of matter as in claim 1 wherein the glycol is ethylene glycol and the acid is the hydrogenated mixed dimer of linoleic and oleic acids.

9. A composition of matter as in claim 7 wherein the liquid is a light jet fuel and the ester is present in an amount ranging between about 0.01% and about 0.4 wt. percent.

10. A composition of matter as in claim 7 wherein the liquid is a mineral lubricating oil and the ester is present...
in an amount ranging between about 0.001 and about 4.9 wt. percent.

10. A composition of matter as in claim 8 wherein the ester is a partial ester.

11. A composition of matter as in claim 9 wherein the ester is a partial ester.

12. A composition of matter as in claim 8 wherein the acid is the hydrogenated dimer of linoleic acid.

13. A composition of matter as in claim 8 wherein the acid is a hydrogenated dimer of oleic acid.

14. A composition of matter as in claim 8 wherein the acid is a hydrogenated mixed dimer of linoleic and oleic acids.

15. A composition of matter as in claim 8 wherein the glycol is ethylene glycol.