This invention relates to novel synthetic lubricating compositions and particularly to synthetic lubricating compositions which have outstanding lubricating characteristics at both high temperatures and low temperatures.

This application is a continuation-in-part of our co-pending application Serial No. 713,801, which was filed on February 7, 1958.

With the development of aircraft engines that operate at peak efficiency at extremely high altitudes there has arisen the need to provide lubricants suitable for use in these engines. These lubricants must have a combination of properties not possessed by conventional lubricants: they must remain effective over a wide range of temperatures, they must have good oxidation and thermal stability in order that they may retain their useful properties after operation for long periods of time at high temperatures, they must have low pour points so that they may function at low temperatures and they must have high flash points to avoid risk of fire during high temperature operation.

The conventional mineral oil lubricants have been found to be unsatisfactory for use in modern aircraft engines. Those mineral oils that have satisfactory low temperature viscosities generally have flash points that are dangerously low and high temperature viscosities that are insufficient to provide the required lubricity, whereas those mineral oils that have satisfactory properties at elevated temperatures are too viscous for use at low temperatures. The incorporation of the usual lubricant additives does not overcome the deficiencies of the mineral oils as lubricants for jet aircraft engines.

Esters prepared from a wide variety of monohydric or dihydric alcohols and monocarboxylic or dicarboxylic acids have been suggested as lubricants. While they provide an improvement over the mineral oil lubricants, these esters do not, in general, have the combination of high temperature and low temperature properties that are essential in lubricants for jet aircraft engines.

We have discovered a new class of compounds that are useful as lubricating compositions and which possess properties which are superior to those of lubricating compositions of the art. The present compounds exhibit surprising stability and other desirable properties at elevated temperatures and also excellent properties at low temperatures. This combination of properties makes them valuable as lubricants for jet aircraft engines.

The compounds of the present invention are diesters of dicarboxylic acids which are fully esterified with a neopentyl glycol, the hydroxyl group in the alcohol not esterified with the dicarboxylic acid being esterified with a monocarboxylic acid. These compounds may also be considered to be esters of a dicarboxylic acid esterified with two moles per mole of acid of a mono ester of a neopentyl alcohol and a monocarboxylic acid. These esters have the structural formula

\[ R_1\text{OCO} \cdot R_{\text{C}} \text{OOC} \cdot R_2 \]

wherein \( \text{OCO} \cdot R_{\text{C}} \text{OOC} \cdot \) represents a dicarboxylic acid radical, \( R_1 \) represents a neopentyl glycol radical in which the hydroxyl group has been replaced by an acid radical, and \( R_2 \) represents a neopentyl glycol radical, a neopentyl trihydric alcohol radical, or a neopentyl tetrahydric alcohol radical in which all of the hydroxyl groups have been replaced by acid radicals or by acid and alkoxy radicals.

The neopentyl alcohols used in the preparation of the novel esters of this invention are those compounds which contain a neopentyl nucleus and which contain two or more hydroxyl groups. These alcohols have the structural formula

\[ \text{CH}_2\text{A}_1\text{H} \equiv \text{CH}_{\text{CH}}\text{CH}_2\text{OH} \equiv \text{CH}_{\text{CH}}\text{CH}_2\text{OH} \equiv \text{CH}_2\text{A}_1\text{H} \]

When the alcohol is a neopentyl glycol, \( A_1 \) and \( A_2 \) each represents \( \text{H}, \text{Cl}, \text{Br}, \text{an alkyi group containing 1 to 4 carbon atoms}, \) or an alkoxy radical containing 1 to 5 carbon atoms. In each case \( A_1 \) and \( A_2 \) may have the same value, or they may have different values. Illustrative of these neopentyl glycols are 2,2-dimethyl-1,3-propanediol, which is also known as neopentyl glycol; 2-ethyl-2-butyl-1,3-propanediol; 2,2-bis(chloromethyl)-1,3-propanediol; 2-methyl-2-chloromethyl-1,3-propanediol; and 2,2-bis(ethoxymethyl)-1,3-propanediol.

When a trihydric neopentyl alcohol is used, \( A_1 \) in the foregoing formula represents a hydroxyl group; when a tetrahydric neopentyl alcohol is used, both \( A_1 \) and \( A_2 \) represent hydroxyl groups. Illustrative of these polyhydric neopentyl alcohols are pentamethylenetriol, pentaerythritol monomethyl ether, pentaerythritol monochloride, trimethylolether, trimethylolpropane, and trimethylolbutane.

In order to obtain the novel esters of this invention it is necessary that at least one mole and not more than about two moles of a neopentyl glycol be used for each mole of dicarboxylic acid. When less than two moles of the neopentyl glycol is used for each mole of dicarboxylic acid, a trihydric or tetrahydric alcohol in an amount that is the difference between the amount of the neopentyl glycol used and two moles is used to complete the esterification of the dibasic acid.

The dibasic acids which may be used are saturated aliphatic dicarboxylic acids and aromatic dicarboxylic acids. Included among these aliphatic acids are acids having a straight chain, branched chain, or cyclic chain and containing from 2 to 36 carbon atoms. Illustrative of these acids are oxalic acid, adipic acid, suberic acid, sebacic acid, dodecanedioic acid and eicosanedioic acid. Either acids, such as dicyclic acid, and dimerized fatty acids may also be used. Among the aromatic dicarboxylic acids that may be used are the following: phthalic acid, terephthalic acid, isophthalic acid, naphthalene 1,5-dicarboxylic acid, and methylene bis benzoic acid.

If desired, a mixture of two or more of the dicarboxylic acids may be used. It is to be understood that the term "dicarboxylic acids" as used herein includes the anhydrides of these acids.

The monocarboxylic acids which are used in the esterification are generally saturated aliphatic monocarboxylic acids containing from 2 to 22 carbon atoms, preferably from 4 to 18 carbon atoms. These acids may have straight chains or branched chains and may contain an alicyclic group or an aryl substituent. Among these acids are butyric acid, caproic acid, caprylic acid, 2-ethylhexanoic acid, pelargonic acid, lauric acid, palmitic acid, stearic acid, arachidic acid, behenic acid, and phenylacetic acid. Mononuclear aromatic acids, such as benzoic acid, toluic acid, and p-tolybenzoic acid, may also be used. A single monocarboxylic acid or a mixture of two or more of these acids may be used in the preparation of the esters.
The novel esters may be represented by the structural formula

\[ \text{CH}_2\text{At} \quad \text{CH}_2\text{At} \]

\[ \text{Zi} \text{H}_2\text{C} - \text{C} - \text{CH}_2\text{OOC-CH}_2\text{O} - \text{C} - \text{CH}_2\text{H}_2 \quad \text{CH}_2\text{H}_2 \]

\[ \text{CH}_2\text{A}^+ \quad \text{CH}_2\text{A}^+ \]

In this formula, \( A_1 \) and \( A_2 \) may be the same or different and each represents \( H, \) an alkyl group containing from 1 to 4 carbon atoms, \( Cl, Br, \) or an alkyl radical containing 1 to 5 carbon atoms; \( A_3 \) and \( A_4 \) may be the same or different and each represents \( H, \) an alkyl group containing from 1 to 4 carbon atoms, \( Cl, Br, \) an alkyl group containing 1 to 5 carbon atoms, a saturated aliphatic acid radical containing 2 to 22 carbon atoms, or a mononuclear aromatic acid radical. \( Z_1 \) and \( Z_2 \) may be the same or different and each represents a saturated aliphatic acid radical containing 2 to 22 carbon atoms or a mononuclear aromatic acid radical. \( R \) represents the residue of a saturated aliphatic dicarboxylic acid containing from 2 to 36 carbon atoms or the residue of an aromatic dicarboxylic acid. Illustrative of these novel esters are the following:

1. **Di(neopentyl glycol monopelargonate) azelate**

\[ \text{CH}_2\text{H}_4\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{H}_4 \]

2. **Di(neopentyl glycol monocaproate) adipate**

\[ \text{CH}_2\text{H}_4\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{H}_4 \]

3. **(Trimethylolpropane divalerate) (neopentyl glycol monovalerate) azelate**

\[ \text{CH}_2\text{H}_4\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{H}_4 \]

4. **(Pentacrythritol trivalerate) (neopentyl glycol monopelargonate) phthalate**

\[ \text{CH}_2\text{H}_4\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{H}_4 \]

5. **(Trimethylolhexane diurate) (2-methyl-2-butyl-1,3-propanediol monobuturate) sebacate**

\[ \text{CH}_2\text{H}_4\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{H}_4 \]

6. **Di(neopentyl glycol monocaproate) diglycolate**

\[ \text{CH}_2\text{H}_4\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{H}_4 \]

7. **(Pentaerythritol monomethyl ether dipelargonate) (neopentyl glycol monovalerate) succinate**

\[ \text{CH}_2\text{H}_4\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{OOCCH}_2\text{O} - \text{C} - \text{CH}_2\text{H}_4 \]

The novel esters of this invention may be prepared by any of several possible methods. For example, the neopentyl alcohol or alcohols may be esterified first with the dicarboxylic acid and then with the monocarboxylic acid; all of the reactants may be mixed together and then heated to form the ester; or the neopentyl alcohol component may be esterified with one or more monocarboxylic acids so as to form a partially esterified product which contains an average of one hydroxyl group per molecule, the partially esterified product subsequently being esterified with dicarboxylic acid. The conditions under which the esterification is carried out are not critical. Conventional esterification procedures are generally employed; for example, the esterification may be carried out at a temperature between 130° and 180° C. in the presence of an inert solvent and in the presence or absence of an esterification catalyst. The crude product of the esterification may be purified by conventional procedures; for example, unreacted acid may be removed by washing with alkaline and volatile impurities by distillation.

The following examples illustrate this invention:

**EXAMPLE I**

**Di(NEopENTYL GlyCOL MonoPellARGOnATE) Azelate**

A mixture of 333.3 grams (2 moles) of neopentyl glycol, 503.3 grams (2 moles) of pelargonic acid, 4.19 grams of phosphoric acid, 22.9 grams of activated carbon, and 114 grams of xylene was placed in a flask equipped with a thermometer, an agitator, and a Dean-Stark water trap surmounted by a reflux condenser. The mixture was heated with agitation at 160°-176° C. for 5 hours and then cooled to room temperature. Azelatic acid (301.2 grams) was added, and the reaction mixture was heated at 170°-178° C. for about 5 hours. At the end of this time the ester had an acid number of 18.4. An additional 50.3 grams of pelargonic acid was added and the esterification was continued at 176°-181° C. for 6.5 hours. The crude product was washed with carbon dioxide to drive off the xylene and then filtered to remove the carbon. After dilution with an equal weight of petroleum ether, the ester was washed with sufficient methanolic sodium hydroxide solution to neutralize the unreacted acid and then with methanolic sodium chloride solution. About 2% by weight of activated carbon was added to the washed ester. The ester was then heated at about 40° C. at about 20 mm. absolute pressure and then at about 150° C. at 2 mm. absolute pressure to remove the petroleum ether, water, and any other low boiling materials that were present. The residue was cooled to 100° C. and filtered. The ester prepared by this procedure had the following properties:

- **Acid number** = 0.06
- **Hydroxyl content** = 0.12 percent
- **Saponification value** = 340.3
- **Viscosity (cs.):**
  - At 32°F. = 315.4
  - At 100°F. = 41.3
  - At 210°F. = 7.9
- **Flash point** = 140° F.
- **Pour point** = -73° F.

**EXAMPLE II**

**Di(NEopENTyl GlyCOL MonoVAle RATE) Azelate**

A mixture of 333.3 grams (2 moles) of neopentyl glycol, 301.2 grams (1 mole) of azelitic acid, 100 grams of xylene, 4 grams of phosphoric acid, and 22.9 grams of activated carbon was heated at reflux temperature for about 5 hours. Then 204.3 grams (2 moles) of valeric acid and 9 grams of phosphoric acid were added and the heating was continued until the calculated amount of water of esterification had been collected. The crude ester so formed was purified by the procedure described in Example I. The purified ester had the following properties:

- **Acid number** = 0.04
- **Hydroxyl content** = 0.13 percent
- **Saponification value** = 424.8
- **Pour point** = -40° F.
- **Flash point** = 423° F.
- **Fire point** = 486° F.
EXAMPLE III
Di(Neopenylyl Glycol Monocaproate) Diglycolate

This ester was prepared by the reaction of 2 moles of neopenylyl glycol, 2 moles of capric acid, and 1 mole of diglycolic acid according to the procedure described in Example I. After purification, this ester had the following properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid number</td>
<td>0.02</td>
</tr>
<tr>
<td>Hydroxyl content</td>
<td>0.95</td>
</tr>
<tr>
<td>Saponification value</td>
<td>411.2</td>
</tr>
<tr>
<td>Pour point</td>
<td>60° F</td>
</tr>
<tr>
<td>Flash point</td>
<td>361° F</td>
</tr>
<tr>
<td>Fire point</td>
<td>370° F</td>
</tr>
</tbody>
</table>

EXAMPLE IV
Di(Neopenylyl Glycol Monocaproate) Adipate

This ester was prepared by the reaction of 2 moles of neopenylyl glycol, 2 moles of capric acid, and 1 mole of adipic acid according to the procedure described in Example I. After purification, this ester had the following properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid number</td>
<td>0.15</td>
</tr>
<tr>
<td>Hydroxyl content</td>
<td>0.08</td>
</tr>
<tr>
<td>Saponification value</td>
<td>434.5</td>
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<tr>
<td>Pour point</td>
<td>52° F</td>
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<tr>
<td>Flash point</td>
<td>392° F</td>
</tr>
<tr>
<td>Fire point</td>
<td>423° F</td>
</tr>
</tbody>
</table>

EXAMPLE V
(Neopenylyl Glycol Monovalerate)(Trimethylolpropane Diallylate) Adipate

This ester was prepared by the reaction of 1 mole of neopenylyl glycol, 1 mole of trimethylolpropane, 3 moles of valeric acid, and 1 mole of adipic acid according to the procedure described in Example I. After purification, this had the following properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid number</td>
<td>0.01</td>
</tr>
<tr>
<td>Hydroxyl content</td>
<td>0.08</td>
</tr>
<tr>
<td>Saponification value</td>
<td>467.5</td>
</tr>
<tr>
<td>Pour point</td>
<td>42° F</td>
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</table>

The novel esters of this invention are characterized by high viscosity indices; that is, their viscosities undergo relatively little change over a wide temperature range. In addition these esters have excellent low temperature properties. These properties combine to make the esters useful as lubricants for modern aircraft engines. Each of the esters herein described or combinations of these esters may be used directly as lubricants, or they may be blended with other materials, such as mineral oil, to obtain many combinations having special characteristics. It may also be desirable to add to these esters certain of the well-known lubricant adjuvants. For example, antioxidants, such as phenyl a-naphthylamine, 2,2'-dipyridylamine, or phenothiazine, may be present in the lubricating compositions. The amount of antioxidant used in each case is dependent upon the specific ester used and upon the choice of antioxidant. Generally about 0.5% to about 5% by weight of antioxidant is used. Viscosity index improvers, pour point depressants, detergents, and corrosion inhibitors may also be incorporated into these compositions to improve their properties. It is to be understood, however, that the lubricating compositions of the present invention contain a major amount of aforesaid novel esters and a minor amount of one or more of the lubricant adjuvants.

While the present lubricating compositions are particularly useful as lubricants for jet aircraft engines, it is to be understood that they can also be employed as high temperature or extreme pressure lubricants for other equipment such as valves, gear boxes, pumps, and transmission bellings where the lubricant is interposed between relatively moving metal surfaces.

We claim:
1. An ester represented by the structural formula
   \[
   \text{CH}_3
   \begin{array}{c}
   \text{CH}_3 \\
   \text{ZnH}_2\text{C-\text{CH}2OHOC-R-\text{COOCH}_2\text{H-CH}_3} \\
   \text{CH}_3
   \end{array}
   \]
   wherein \( Z_1 \) and \( Z_2 \) each represents a member selected from the group consisting of a saturated aliphatic monocarboxylic acid radical containing from 2 to 22 carbon atoms and a mononuclear aromatic monocarboxylic acid radical; and \( R \) represents a member selected from the group consisting of the residue of a saturated aliphatic dicarboxylic acid containing from 2 to 36 carbon atoms and the residue of an aromatic dicarboxylic acid.
2. Di(neopenylyl glycol monovalerate) azelate.
3. Di(neopenylyl glycol monovalerate) azelate.
4. (Neopenylyl glycol monovalerate) (trimethylolpropane divallylate) adipate.

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