SPERM OIL SUBSTITUTE FROM BLEND OF CARBOXYLIC ACID ESTERS OF GLYCOLS

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Int. Cl. ..................... C10m 3/20, C10m 1/26
Field of Search ............. 252/56 S, 56 R, 49.5

References Cited
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ABSTRACT
A liquid lubricant comprising a blend of mono- and di-esters of an organic glycol having from 2 to 6 carbon atoms and a molecular weight of up to 200, and a monocarboxylic acid having from 10 to 24 carbon atoms. The blend includes a sufficient amount of mono-esters to serve as a nonionic emulsifier and to impart water-miscibility to the blend. Preferably a sufficient amount of carbon-to-carbon unsaturation is present in the esters to provide to the blend an iodine number up to about 190. The lubricant blend has a balance of properties adapting it to be used as a substitute for sperm oil. The blend may be used as such or chemically combined with sulfur, chlorine or other halogens, phosphorous, and the like.

2 Claims, No Drawings
SPERM OIL SUBSTITUTE FROM BLEND OF CARBOXYLIC ACID ESTERS OF GLYCOLS

BACKGROUND OF THE INVENTION

Sperm oil has long been used as an industrial lubricant, both in a refined natural state and in a sulfurized, sulfonated, or phosphated form. Sperm oil comprises a mixture of fatty alcohol-fatty acid esters and glycerides and is a good lubricant by itself, such as for oiling light machinery, or for blending with other lubricants, such as mineral oil, to form compounded lubricants. Similarly, when chemically combined with sulfur, chlorine, phosphorous, and the like, sperm oil is popularly used either by itself as a lubricant or as an additive to other lubricants, particularly in cutting oils and for lubricating metal surfaces.

The Congress of the United States recently enacted the "Endangered Species Act of 1969" which prohibits importation of sperm oil and derivatives thereof after 1971. Consequently, not only is the supply of this valuable commodity presently diminishing, but after 1971 crude sperm oil will no longer be available for purchase. The cost of presently available oil is also correspondingly increasing.

Although sperm oil does have many valuable properties, the presence of glycerides in the oil, which may vary in amount from about 5 percent to as much as 35 percent by weight, has been a detriment. Derivatives of glycerin tend to revert to glycerin which is easily polymerized or oxidized. The presence of glycerin, therefore, can cause deleterious gumming and sludging where relatively high temperatures and pressures attend the use of the lubricant. When the sperm oil with its glycerin content is sulfurized, the glycerides tend to form long chains with other reactants and form oil insoluble polymers. This causes emulsion problems and also increased sludge formation. Sulfurized glycerides are also an irritant on the skin of users.

Due to the Endangered Species Act, the industry faces an increasing demand for a replacement for sperm oil. Preferably, the replacement should be one that is free of glycerides and one that is at least equal to or surpasses sperm oil in its adaptability for an industrial lubricant when used either alone or in combination with sulfur, chlorine, phosphorous, and the like.

SUMMARY OF THE INVENTION

A general object of the present invention is to provide a liquid lubricant which can be used in lieu of sperm oil. Another object is the provision of such a lubricant that can be used alone or in admixture with other lubricants. A further object is the provision of a lubricant which can be chemically combined with sulfur, halogens, phosphorous, and the like and either be employed by itself or as an additive to other lubricants, and in which amounts of these elemental additions of sulfur and the like can exceed that possible with commercial sperm oil.

The lubricant of the present invention contains no glycerides and can be varied in its make-up so as to tailor it to meet certain demands of water-solubility and/or carbon-to-carbon unsaturation, both of these factors being highly contributory as well to subsequent sulfation, sulfonation, and sulfurizing when the sperm oil substitute is to be so treated.

In one form, the present lubricant comprises a blend of both mono-esters and di-esters of an organic glycol having from 2 to 6 carbon atoms and a molecular weight up to 200, such as ethylene glycol, and a monocarboxylic organic acid having from 10 to 24 carbon atoms, such as a fatty acid. The blend comprises a sufficient amount of the mono-esters (having a free hydroxyl group) to serve as a nonionic emulsifier and impart water-miscibility to the blend. For this purpose, the blend may have a hydroxyl number in the range of about 15 to about 70. The monocarboxylic organic acids may be saturated or unsaturated, or a blend of the two types of acids may be used to provide in the blend an iodine number from about 0 to about 190. Preferably, some unsaturation is present if the blend is to be chemically combined with sulfur or the like. In this event, the blend should have an iodine number within the range of about 50 to about 90.

The blend should have a pour point below 30°F. and an S.U.S. viscosity at 100°F. within the range of about 90 to about 120 to provide other desired physical attributes. A small amount of free monocarboxylic organic acid may be present, for example, to impart to the blend an acid number less than 15. This has been found to reduce the coefficient of friction of the lubricant.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Considering initially the materials from which the blends are prepared, an organic glycol of from 2 to 6 carbon atoms is selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, trimethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, tetraethylene glycol, trimethylene glycol, pentahexylol glycol, neopentyl glycol, hexaethylene glycol, polymers thereof having a molecular weight up to 200, and mixtures thereof. Glysols or polyglycols having a molecular weight in excess of 200 tend to introduce smoking when the blend is heated and are harder to esterify under conditions favoring the desired formation of both mono- and di-esters. As a result, usually only the dimers or trimers of the lower molecular weight glycols indicated are used. The preferred glycol is monomeric ethylene glycol.

Oxo-acids, such as 2-ethyl hexaoac acid and neo-decanoic acid, may be used, but the preferred monocarboxylic organic acids are the fatty acids. When carbon-to-carbon unsaturation in the blend is not necessary, saturated fatty acids can be used such as capric, undecylic, lauric, tridecic, myristic, pentadecanoic, palmitic, margaric, stearic, nonadecic, arachidic, behenic, and carnaubic acids. However, normally some unsaturation is preferred to accommodate sulfurization at the unsaturated sites. Useful unsaturated fatty acids include hypogic, oleic, ricinoleic, erucic, linoleic, palmitolic, stearolic, behenic, and linolenic acids. Mixtures of different acids may be used, and the hydrocarbon chain of the acids may be straight, branched, or cyclic. Substituents can be present on the hydrocarbon chains of the acids as long as they do not alter the physical characteristics of the acids or the blends outside of those values stated. For example, hydroxylated acids may be used. A preferred source of the fatty acids, both saturated and unsaturated, is tallow oil. Saturated fatty acids may be obtained from petroleum fractions.

The blend may be prepared by reacting the glycol and acid reactants, or mixtures of each principal reac-
tant, under standard esterification conditions, which are well known, but in such a molar ratio as to provide a desired amount of the mono-esters. Mono-esters form even though the acid is present in excess, some free acid remaining after the esterification. For example, by reacting 0.6 to 0.7 mole of a glycol with 1 mole of a monocarboxylic acid, sufficient hydroxyls are present in the mono-esters to provide the desired properties in the blend. Satisfactory results are obtained by reacting 0.64 mole of a glycol with 1 mole of a monocarboxylic acid, although more or less can be reacted without free glycol being present in the end product. However, molar ratios outside of the range indicated can be used, depending on the properties desired in the final blend.

The reaction may be carried out in a standard esterification kettle. Approximately one percent by weight of water is used based on the weight of the carboxylic acid. The presence of water reduces the initial esterification temperature. No catalyst is needed. The kettle is heated up to about 500°F., for example. Provision may be made for reflux of the glycol. A steam heated reflux may be used to permit water formed by the esterification process to be vented. Any excess unreacted glycol present at the end of the esterification can be stripped from the blend by vacuum.

Esterification is continued until the acid number is reduced to a desired figure. In the present blend, the presence of some free carboxylic acid has been found desirable. Free fatty acids, for example, decrease the coefficient of friction of the blend as compared to a neutral lubricant. However, the acid number should not exceed about 15, or the blend becomes too acidic. Also, an insufficient amount of the mono-esters are formed at an acid value above about 15.

The blend should have a hydroxyl value of about 15 to 70, as determined by standard test procedures established by the American Oil Chemists' Society. A hydroxyl value of about 15 to 30 corresponds to about 10 to about 30 percent mono-esters by weight of the blend. The presence of the hydroxyl groups provides several advantages. Because of their affinity for water, the hydroxyl groups impart a water-miscibility to the blend and make it suitable for use with rust preventative. The hydroxyl groups can also serve as nonionic emulsifiers which is significant when the lubricant blend is to be used with other materials in an aqueous medium. This attribute of the blend eliminates the need for adding other emulsifiers. Further, when it is desired to sulfonate the blend, the hydroxyl groups provide responsive sites for the chemical addition of the sulfur-containing groups.

When the blend contains little or no unsaturation such that the iodine number is approximately zero, the blend still has an oily or fatty feel and may be used in drawing compounds, textile lubricants, emulsifiers, metal working compounds, and in high temperature metal forming operations. Normally, some unsaturation is desired to provide sites for chemical combination with other materials, such as free sulfur, although an unsaturated blend without sulfuration still has lubricity and can be used in metal working compounds.

When unsaturation is desired, the blend may have an iodine number up to about 190. Upon sulfuration, such unsaturation enables relatively large amounts of sulfur or the like to be chemically added to the esters.

In the preferred embodiment, the iodine number should not fall below 50 when subsequent addition of other elements is to be made. Below this iodine number, the pour point of the blend becomes undesirably high, and there are not sufficient unsaturated sites for sulfuration and the like.

The pour point of the blend must be below about 30°F., so that it remains in the liquid state under general conditions of use. The blend itself can serve as a pour point depressant. Similarly, the blend has a viscosity befitting it for general application when it has a S.U.S. viscosity at 100°F. within the range of about 90 to about 120.

Although preparation of the esters has been described as by standard esterification between a glycol and an acid, it is to be understood that it is immaterial how the esters are, in fact, formed. For example, the methyl esters of the described monocarboxylic acids can be used to react with the glycols. In this case, the described mono- and di-esters of the glycols are still obtained but methyl alcohol is released instead of water otherwise formed by esterification. Also, an alkylene oxide such as ethylene oxide may be reacted in lieu of the corresponding alkylene glycol in some reactions to provide the esters of the alkylene glycol. Still further, the esters may be prepared by transesterification.

It has long been known that sulfur, the halogens notably chlorine, and phosphorous can be added to lubricating oils to enhance their lubricating properties. The exact manner in which these elements or radicals containing them act to produce the improved results is not clearly understood. The techniques for adding such elements as sulfur, chlorine, and phosphorous to lubricants are well known in the art. However, to illustrate the adaptability and flexibility of the present blend, the addition of sulfur is described in detail.

In general, the more sulfur that can be chemically attached to the molecules comprising the lubricant, the better for lubricating purposes, especially the cutting of metals. There are three different types of sulfur additions to a lubricant which may be defined as follows:

Sulfurizing (or sulfuretting)

The addition of elemental sulfur to an unsaturated or saturated organic hydrocarbon chain. In the case of an unsaturated site, an atom of sulfur adds to the double bond, thereby satisfying the bond without the release of any by-product but with a reduction in the iodine value since the unsaturated site becomes saturated. With a saturated hydrocarbon chain, two hydrogen atoms are removed and escape with an atom of sulfur as hydrogen sulfide, while another atom of sulfur satisfies the bonds previously satisfied by the two hydrogen atoms. Sulfation

The reaction of such sulfur-containing materials as sulfur trioxide, chlorosulfuric acid, and sulfuric acid to hydroxyl groups. The product is called a sulfate. Sulfination

The reaction of such sulfur-containing materials as sulfur trioxide, chlorosulfuric acid, or sulfuric acid with carbon-to-carbon unsaturated sites in hydrocarbon chains and with carboxyl groups. The product is called a sulfinate.

Each type of addition has its advantages. Sulfurizing is employed with the lubricant to be subjected to extreme pressures such as, for example, a lubricant for hypoid gears. Sulfation is used when a surface-active,
wetting lubricant is desired, since sulfates reduce the surface tension of a lubricant. Sulfonation similarly imparts surface-active properties to lubricants which are not obtainable with either sulfurizing or sulfation.

The wider adaptability of the present blend resides in the fact that any and all of these three techniques to add sulfur can be used. When a hydrocarbon chain of the ester is saturated or unsaturated, it can be sulfurized. The hydroxyl groups of the mono-esters can be sulfated. And an unsaturated hydrocarbon chain can be sulfonated.

To add sulfur, the blend is mixed with the requisite amount of a sulfur-containing compound and heated in a closed vessel with agitation. Uniform heating by means of a surrounding heat-transferring medium is desirable to avoid scorching as the viscosity of the mass increases. Alternatively, the sulfur can be added periodically or continuously as the reaction proceeds but in a manner to increase the temperature gradually. Up to about 20 parts of the sulfur-containing compound are used per 100 parts of the blend, although these relative amounts are not critical.

In addition to those materials previously noted, such sulfur-containing compounds may be used as sulfur monochloride, sulfur dichloride, phosphorous trisulfide, and phosphorous pentasulfide. The reaction temperature may vary from as low as 150°F to as high as 500°F or higher, depending principally on the sulfur-containing compound used. For example, sulfur monochloride is used at the lower temperatures of the range indicated, while flowers of sulfur is used at temperatures at the higher end of the range. The reaction is continued until a sufficient amount or a maximum amount of sulfur possible has been chemically combined. The course of the reaction may be followed by withdrawing test samples and determining the change in viscosity. The end viscosity of the sulfurized blend should preferably be within the range of about 200 to about 300, S.U.S. viscosity at 210°F. The present blend can contain as little as one percent by weight of sulfur to as much as 18 percent. After the reaction has been completed, the blend is cooled to room temperature when it can be stored in suitable containers.

To add chlorine, free chlorine can be bubbled through the blend at room temperature for a time sufficient to add chlorine chemically to a desired extent up to the maximum possible. Phosphorous trichloride or phosphorous pentachloride can be used similarly admixed with the blend, usually at room temperature, to add phosphorous or phosphorous-containing groups. These techniques are well known in the art. Reference is also made to U.S. Pat. No. 3,068,218 to Beretvas et al. which discloses sulfochlorination of hydrocarbons, such patent being hereby incorporated by reference.

The following examples are intended to illustrate the invention and should not be construed as limiting the claims. Percentages are by weight.

**EXAMPLE 1**

Tall oil purchased from Arizona Chemical Company under the trademark acintol had this analysis:

<table>
<thead>
<tr>
<th>Component or Property</th>
<th>Percentage or Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color, Gardner</td>
<td>1</td>
</tr>
<tr>
<td>Acid Number</td>
<td>198</td>
</tr>
<tr>
<td>Saponification Value</td>
<td>200</td>
</tr>
</tbody>
</table>

**EXAMPLE 2**

A procedure was carried out like the procedure of Example 1 except that 282 grams of the fatty acid material, acintol, and 116 grams of diethylene glycol were used. The reactants were heated to raise their temperature gradually from room temperature to about 480°F in about 12 hours. A reflux condenser was used to prevent excessive loss of the ethylene glycol. At the end of the cook, the kettle was allowed to cool. The resulting blend of esters in the kettle had the analysis noted in Table A for this example.

**EXAMPLE 3**

A procedure was carried out like the procedure of Example 1 except that 282 grams of the acintol fatty acid tall oil, 141 grams of dipropylene glycol, and 0.9 gram of 85 percent of an aqueous solution of phosphoric acid were used. The phosphoric acid was included to lighten the dark color of the fatty acid tall oil reactant. The contents of the kettle were heated to raise its temperature gradually from room temperature to 430°F in about 8 hours. An analysis of the resultant, cooled blend of esters had the analysis shown in Table A.

**EXAMPLE 4**

A procedure was carried out like the procedure of Example 1 except that the fatty acid tall oil was purchased from Union Bag Company under the trademark Unitol LFA. It had this analysis:

<table>
<thead>
<tr>
<th>Component or Property</th>
<th>Percentage or Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acids</td>
<td>90.5</td>
</tr>
<tr>
<td>Rosin Acids</td>
<td>7.0</td>
</tr>
<tr>
<td>Unsaponifiables</td>
<td>2.5</td>
</tr>
<tr>
<td>Acid Number</td>
<td>193</td>
</tr>
<tr>
<td>Saponification Number</td>
<td>194</td>
</tr>
<tr>
<td>Color — Gardner Scale</td>
<td>94</td>
</tr>
<tr>
<td>Viscosity — Gardner Secs.</td>
<td>1</td>
</tr>
</tbody>
</table>
A cook was prepared comprising 11,440 grams of the Unitol fatty acid material, 1241 grams of ethylene glycol, 12 grams of an aqueous solution of phosphoric acid of 85 percent strength, and 114 grams of water. This formulation represented a mole ratio of ethylene glycol to fatty acid of 1:2, or zero percent excess of fatty acid. The cook was gradually heated from room temperature to 470°F. in 8.25 hours and then allowed to cool. There was a yield of esters of about 94 percent. The resulting blend of esters had the analysis shown in Table A.

EXAMPLE 5

A procedure was carried out like the procedure of Example 4 except that the mole ratio of ethylene glycol to fatty acid was 0.65 to 1.0. After cooling, the cook comprised a blend of esters of diethylene glycol having the analysis shown in Table A.

EXAMPLE 6

A procedure was carried out like the procedure of Example 4 except that the mole ratio of ethylene glycol to fatty acid was 0.636 to 1.0. After cooling the cook, the blend of esters had the analysis shown in Table A.

EXAMPLE 7

A procedure was carried out like the procedure of Example 4 except that the cook comprised 11,440 grams of the Unitol fatty acid material, 1862 grams of ethylene glycol, 12 grams of an aqueous solution of phosphoric acid of 85 percent strength, and 114 grams of water. This formulation represented a mole ratio of ethylene glycol to fatty acid of 3:4. After cooling the cook, the blend of esters had an analysis shown in Table A.

In place of the tall oils, separate pure or relatively pure fatty acids may be used having from 10 to 24 carbon atoms. Mixtures of the pure acids can also be fabricated to meet diverse requirements, especially as to the amount of carbon-to-carbon unsaturation.

The blends may be used as such or with additions of such elements as sulfur, the halogens, or phosphorus, or groups containing these elements. The blends may be sulfurized, sulfonated, and/or sulfated. In any case, the blends may be used as a lubricant by themselves or incorporated with still other lubricants such as mineral oil.

The blend of the present invention has physical characteristics between those of fatty alcohol esters, such as are found in sperm oil, and triglycerides, such as are found in animal, vegetable, and fish fats or oils. The hydroxyl groups of the mono-esters serve as nonionic emulsifiers and render the lubricant water-attractive and therefore suitable for use with rust preventatives, metal working compounds, textile lubricants, emulsification of the blends, and the like. Also, because of the presence of the greater amounts of hydroxyl groups, the present blends are better suited for sulfonation, sulfation, or acetylation than sperm oil or glycerides. The present blends can chemically acquire as much or more sulfur than sperm oil.

Since the present blends are entirely free of triglycerides, they not only are more stable than other fats, such as lard oil, but there are no objectionable glycerides to break down and form oil insoluble polymers, sludge, or to impart rancidity to the lubricant.

Anti-foaming agents, surfactants, etc., can be used if desired in the preparation of the present blends.

Although the foregoing describes several embodiments of the present invention, it is to be understood that the invention may be practiced in still other forms within the scope of the following claims.

I claim:

1. A lubricant comprising a blend consisting essentially of fatty acids each having from 10 to 24 carbon atoms and mono-esters and di-esters of said fatty acids with glycols selected from the class consisting of simple

<table>
<thead>
<tr>
<th>TABLE A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Ex. 1</td>
</tr>
<tr>
<td>Cloud Point °F.</td>
</tr>
<tr>
<td>Pour Point °F.</td>
</tr>
<tr>
<td>Acid Number</td>
</tr>
<tr>
<td>Saponifiables</td>
</tr>
<tr>
<td>Unsaponifiables</td>
</tr>
<tr>
<td>Iodine Number</td>
</tr>
<tr>
<td>Color — Gardner Scale</td>
</tr>
<tr>
<td>Flash °F.</td>
</tr>
<tr>
<td>Fire °F.</td>
</tr>
<tr>
<td>SUS — 100°F.</td>
</tr>
<tr>
<td>SUS — 140°F.</td>
</tr>
<tr>
<td>SUS — 210°F.</td>
</tr>
<tr>
<td>Hydroxyl Number</td>
</tr>
</tbody>
</table>
glycols, each having from 2 to 6 carbon atoms, polymers thereof having molecular weights up to 282, and mixtures thereof, at least 10 percent by weight of said total mono-esters and di-esters being mono-esters, said blend having a hydroxyl number in the range of about 15 to about 70, an acid number less than 15, a pour point below 30°F., an S.U.S. viscosity at 100°F. in the range of about 90 to about 120 and an iodine number from 0 to 190.

2. A lubricant in accordance with claim 1 wherein all of said fatty acids are employed in the form of tall oil.