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SYNTHETIC ESTER LUBRICANTS

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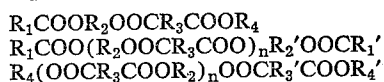
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5 Claims. (Cl. 252—57)

This invention relates to improved synthetic lubricants and particularly improved synthetic lubricants based on esters e.g. diesters and complex esters. It has previously been suggested to use complex esters and blends of complex esters with diesters as lubricants. These materials have better viscosity temperature characteristics than mineral lubricating oils and they can be made to have a wide range of characteristics by suitable choice of components.

A disadvantage that has been found with complex esters is that they exhibit a form of thixotropy at low temperatures. That is to say, that if the complex ester is maintained at a low temperature it gets increasingly thick. This is a substantial disadvantage for lubricants where mobility at low temperatures is vital. This low temperature thixotropy is particularly observed in aliphatic complex esters, which are the preferred products from the point of view of low variation of viscosity with temperature. It has now been discovered, and is the subject of the present invention, that the introduction of a small proportion of aromatic groupings into aliphatic complex esters results in a lubricant that exhibits very little variation of viscosity with time after extended storage at very low temperatures.

A complex ester, according to this invention, is obtained by reacting dicarboxylic acids, glycols, acids and alcohols to produce compounds having the formulae—



where R_1 and R_1' are the residues of monocarboxylic acids, R_2 and R_2' are the residues of diols, R_3 and R_3' are the residues of dicarboxylic acids and R_4 and R_4' are the residues of monohydric alcohols.

These complex esters may be prepared by reacting appropriate proportions of the materials providing the residues, under esterification conditions in one or more stages. It is essential that all the components are substantially saturated. That is to say that they contain no polymerisable double bonds. The glycol radical may consist of a saturated aliphatic hydrocarbon group, straight chain, or branched, containing 2 to 18 carbon atoms, or it may be a series of saturated aliphatic hydrocarbon radicals linked by oxygen or sulphur atoms, or by both oxygen and sulphur atoms provided there are at least two carbon atoms between each carboxyl group, and the nearest oxygen and sulphur atoms and at least two carbon atoms between each oxygen or sulphur atom in the chain and provided, further, that the total number of carbon, oxygen and sulphur atoms in the entire radical is from 5 to 80 and the number of sulphur atoms is not greater than 2. The monohydric alcohol residue may be a saturated aliphatic hydrocarbon radical either straight chain or branched containing 1 to 20 carbon atoms, or it may be a series of saturated aliphatic hydrocarbon radicals, straight chain or branched, interlinked by oxygen or sulphur atoms, or both oxygen and sulfur

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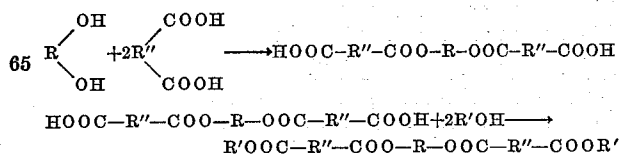
atoms, the total number of carbon, oxygen and sulfur atoms being from 4 to 20. The maximum number of oxygen or sulfur atoms or both in the radical is not greater than 5, the number of sulfur atoms does not exceed 2 and there is a chain of at least two carbon atoms between the acid radical and the first oxygen or sulfur atoms and a similar chain of at least two carbon atoms between each pair of oxygen or sulfur atoms in the radical. The residue of the mono carboxylic acid may be a saturated aliphatic hydrocarbon radical, straight chain or branched, containing 1 to 22 carbon atoms, or it may represent a series of aliphatic hydrocarbon radicals interlinked by 1 to 5 oxygen atoms, there being at least two carbon atoms between each pair of oxygen atoms and at least one carbon atom between the carboxyl group and the nearest oxygen atom, the total number of carbon and oxygen atoms in the radical being from 3 to 22, or it may represent an organic radical consisting of an aliphatic hydrocarbon chain containing a single interlinked sulfur atom which is separated from the carboxyl group by at least one carbon atom, the total number of carbon and sulfur atoms in the radical being 3 to 22, or it may represent an organic radical consisting of an aliphatic hydrocarbon chain containing a single interlinked sulfur atom which is separated from the carboxyl group by at least one carbon atom, the total number of carbon and sulfur atoms in the radical being 3 to 22.

The residue of the dicarboxylic acid may be a saturated aliphatic hydrocarbon radical straight chain or branched, containing up to 26 carbon atoms or it may be organic radical consisting of a series of saturated aliphatic hydrocarbon radicals linked by one or more atoms of oxygen or sulfur provided that there are at least two carbon atoms between each pair of oxygen or sulfur atoms, and provided further, that the total number of carbon, oxygen and sulfur atoms is from 3 to 80 and the total number of sulfur atoms is not greater than 2. The molecular weight of entire ester should be at least 300, it is preferably saturated and the viscosity at 210° F. should not be greater than 150 seconds (Saybolt) to provide a product having lubricating properties.

Among the various components of the complex esters of the present invention certain preferences may be pointed out as giving the optimum of desired properties from the standpoint of service as a lubricant. The preferred monohydric alcohols are the aliphatic primary alcohols, whether straight chain or branched, containing no oxygen or sulfur atoms and having from 6 to 10 carbon atoms per molecule. The preferred monocarboxylic acids are the fatty acids containing 2 to 10 carbon atoms per molecule.

The preferred dibasic acids are the straight or branched chain dibasic acids of the paraffinic group, having from 6 to 10 carbon atoms per molecule e.g. adipic acid, azelaic acid, sebacic acid, suberic acid, pimelic acid and the corresponding iso-acids.

These complex esters may be prepared either by the monohydric alcohol half ester method or by refluxing all the components together in the presence of an esterification catalyst and water entrainer. The preferred method, however, is to carry out the esterification in two stages through the glycol half ester as shown below.

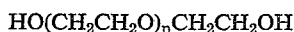


The esterification is conveniently carried out under reflux at elevated temperatures in the region of 150–200° C. (although the exact temperature is not critical), using

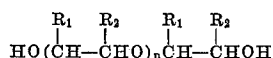
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an esterification catalyst such as sulphuric acid, sodium bisulphate, or an aryl sulphonic acid and a water entrainer such as an aromatic hydrocarbon. In order that the finished product should be fully effective as a lubricant, residual reactants should be removed and this is most effectively done by vacuum stripping, the complex ester being left as bottoms.

The glycols employed in preparing the esters of the present invention include ethylene glycol and any of the paraffinic homologues of the same containing up to 18 carbon atoms. These may include for example, ethylene glycol, propylene glycol, butylene glycols, pinacone, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, and the like. Since the glycols may also contain oxygen or sulfur atoms compounds such as diethylene glycol, triethylene glycol, the polyethylene glycols of the formula



where n is 1 to 26, and the polypropylene glycols of the general formula



where either R_1 or R_2 is a methyl group and the other is hydrogen, and where n is 1 to 20, may likewise be employed. Glycols containing sulfur atoms in thio-ether linkages may also be employed, and these include such compounds as thiodiglycol and 1,2-bis(2-hydroxyethylmercapto)ethane. There also may be used glycols containing both oxygen and sulfur in similar linkages; such a compound is bis-[2-(2-hydroxyethoxy)ethyl]sulfide.

The monohydric alcohols employed are typified by the following:

Methyl alcohol
Ethyl alcohol
n-Butyl alcohol
n-Hexyl alcohol
n-Octyl alcohol
2-ethylhexyl alcohol
Cetyl alcohol
Oleyl alcohol
Ethylene glycol mono-n-butyl ether
Ethylene glycol mono-2-ethylbutyl ether
Ethylene glycol mono-2-ethylhexyl ether
Ethylene glycol mono-tert.-octyl ether
 β -n-Butylmercaptoethanol
 β -Tert.-octylmercaptoethanol
 β -n-Dodecylmercaptoethanol
Diethylene glycol mono-n-butyl ether
Diethylene glycol mono-2-ethylbutyl ether
Diethylene glycol mono-2-ethylhexyl ether
Propylene glycol mono-butyl thioether
Propylene glycol mono-tert.-octyl thio-ether
Propylene glycol mono-n-dodecyl thio-ether
n-Butylmercaptoethoxyethanol
Tert.-octylmercaptoethoxyethanol
n-Dodecylmercaptoethoxyethanol
n-Butylmercaptopropoxypropanol
Tert.-octylmercaptopropoxypropanol
n-Dodecylmercaptopropoxypropanol
Propylene glycol mono-n-butyl ether
Dipropylene glycol monomethyl ether
 C_8 - C_{10} oxo alcohols
Dipropylene glycol monoethyl ether
Dipropylene glycol mono-n-butyl ether
Tripropylene glycol monomethyl ether
Tripropylene glycol monoethyl ether
Tripropylene glycol mono-n-butyl ether
Propylene glycol monoisopropyl ether
Dipropylene glycol monoisopropyl ether
Tripropylene glycol monoisopropyl ether

Many of the above listed ether alcohols, formed by the reaction of ethylene oxide or propylene oxide with aliphatic alcohols, are known in the industry as "Dowanols,"

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"Carbitols," or "Cellosolves." ("Cellosolve" is a registered trademark.)

A group of alcohols especially adapted for use in connection with the present invention are the so-called "Oxo" alcohols, prepared by the reaction of carbon monoxide and hydrogen upon the olefins obtainable from petroleum products. Materials such as diisobutylene and C_7 olefins are suitable for this purpose; also higher molecular weight olefinic materials are sometimes employed. The alcohols obtained in this manner normally have a branched chain structure.

Among the monocarboxylic acids which may be employed in the preparation of the esters of the present invention, the following may be listed as illustrative:

Acetic acid
Propionic acid
Butyric acid
Valeric acid
Caproic acid
Capyric acid
2-ethylcaproic acid
Lauric acid
Palmitic acid
Stearic acid
Oleic acid
 β -Methoxypropionic acid
 β -Ethoxypropionic acid
 β -Tert.-octoxypropionic acid
 β -Ethylmercaptopropionic acid
 β -Tert.-octylmercaptopropionic acid
 β -Tert.-dodecylmercaptopropionic acid

If desired, various addition agents may be incorporated in the esters of the present invention for the purpose of improving their properties with respect to their usefulness as lubricants. For example, antioxidants, viscosity index improvers, thickeners, pour depressants, dyes, etc., may be added.

The introduction of aromatic groupings to the ester chain according to this invention may be achieved by including a small proportion of an aromatic dicarboxylic acid in the dicarboxylic acid reacted to form the ester or by including a small proportion of aromatic diol in the dihydric alcohol or of an aromatic alcohol in the alcohol or of an aromatic acid in the acid. The proportion of aromatic material is normally less than 20%. Higher proportions are, of course, effective but they result in deterioration of the viscosity temperature characteristics of the complex ester. It is preferred to use less than 10% aromatic materials in the finished product about 5% being usually ideal. Of course, it is not necessary that the aromatic groupings be solely present in one component of the complex ester. Correspondingly similar proportion of aromatic materials may be present in two or more components. It should be noticed that generally speaking, the viscosity temperature characteristics of the ester are adversely affected by the aromatic groupings and so it will be obvious that only enough aromatics will be introduced to produce the desired stability at low temperatures. Generally, this desired stability can be achieved without serious deterioration of the viscosity temperature characteristics. Examples of suitable aromatic dicarboxylic acids for the practice of this invention are phthalic acid, isophthalic acid, terephthalic acid, homophthalic acid, o-, m-, or p-phenylenediacetic acid and the corresponding higher acids such as higher phenylene alkanic acids e.g. phenylene acetic- β -propionic acid, together with the various alkyl substituted dicarboxylic acids. The phthalic acids, phenylene diacetic acids and phenylene acetic- β -propionic acids are phenylene dicarboxylic acids having 1 to 3 carbon atoms per carboxylic acid group. Suitable aromatic diols include phenyl glycol, diphenyl glycol, dimethylol benzene, benzo pinacol dimethylol naphthalene compounds. Suitable aromatic alcohols include benzyl alcohol, phenyl ethyl alcohol and

their substituted homologues. Similar suitable aromatic carboxylic acids include acids such as benzoic acid. The invention will be better understood by contemplation of the following example.

A blend of a complex ester and a diester was made by reacting 1 mol tetraethylene glycol (polyglycol 200) with more than 2 mols of sebacic acid and twice the molecular excess of 2-ethylhexanol. This results on esterification of a blend of a complex ester and di-2-ethylhexyl sebacate. The greater the proportion of di-2-ethylhexyl sebacate in the blend the thinner the lubricant. Using carefully controlled conditions wherein the local glycol concentration is kept low it is possible to produce blends which, if sufficiently thin, do not exhibit low temperature thixotropy. However, as will be seen from perusal of Table I, the thicker the blend (that is to say the higher the proportion of complex ester) the greater is the low temperature thixotropy, and in fact with these particular reactants it is not possible by direct reaction to produce a blend of complex ester and diester having a viscosity at 210° F. of more than 6.5 cs. without encountering substantial low temperature thixotropy. Table I, however, also includes preparations in which 5 molecular percent of the sebacic acid was replaced with phthalic anhydride. It will be seen that these latter blends exhibit little, if any, thixotropy.

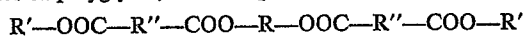
Table I

K.V. cs. at:	Properties of Complex Ester-Diester Blends by Reaction Prepared from 2-ethyl Hexanol: Polyglycol 200 and Sebacic Acid			Preparation with 5 mol. percent sebacic acid replaced by phthalic anhydride	
210° F.-----	6.09	6.64	7.34	6.10	7.08
100° F.-----	27.9	30.81	34.14	28.07	33.72
-40° F.-----	7,350	8,240	9,990	7,320	10,400
-40° F. after -65° F. soak-----	7,300	8,920	14,170	7,160	10,410
K.V. increase at -40° F., cs.-----	-50	+680	+4,180	-160	+10
A.S.T.M. Slope:					
210-100° F.-----	0.625	0.613	0.594	0.627	0.608
100--40° F.-----	0.668	0.660	0.653	0.666	0.659
210--40° F.-----	0.646	0.640	0.630	0.650	0.640

To sum up, this invention comprises an ester lubricant comprising a complex ester or a mixture of a complex ester and a diester in which a proportion of the reactants of said diester or complex ester or both comprises aromatic material.

What we claim is:

1. An improved synthetic ester lubricant, having a kinematic viscosity at 210° F. of more than 6.5 cs. and less than 150 SSU at 210° F., and consisting essentially of a mixture of a complex ester and diester prepared by combining more than two moles each of a dicarboxylic acid and an aliphatic monohydric alcohol per mol of polyglycol, said complex ester having the formula



wherein R', R'' and R are hydrocarbon radicals of C₆ to C₁₀ saturated aliphatic monohydric alcohols, C₆ to

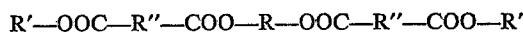
C₁₀ dicarboxylic acids and C₂ to C₁₈ polyglycols respectively, and said diester comprises the reaction product of said C₆ to C₁₀ dicarboxylic acids and said C₆ to C₁₀ monohydric alcohols in a ratio of two moles of said alcohol per mole of said acid; and wherein about 2 to 10 mole percent, based on the total number of moles of said dicarboxylic acid, is an aromatic dicarboxylic acid which is added to said mixture prior to esterification and the remainder of said dicarboxylic acid is a saturated aliphatic dicarboxylic acid.

2. The improved synthetic ester lubricant according to claim 1 wherein the aromatic dicarboxylic acid radical is derived from a phenylene dicarboxylic acid having 1 to 3 carbon atoms per carboxylic acid group.

3. The improved synthetic ester lubricant according to claim 1 wherein said aromatic dicarboxylic acid is derived from phthalic anhydride.

4. The improved synthetic ester lubricant according to claim 1 wherein said saturated aliphatic dicarboxylic acid is sebacic acid, said aliphatic monohydric alcohol is 2-ethylhexanol, said polyglycol is tetraethylene glycol and said aromatic dicarboxylic acid is phthalic acid.

5. In the method of preparing a synthetic ester lubricant, having a kinematic viscosity at 210° F. of more than 6.5 cs. and less than 150 SSU at 210° F., which consists essentially of a mixture of a complex ester and diester said complex ester having the formula



wherein R', R'' and R are hydrocarbon radicals of a C₆ to C₁₀ saturated aliphatic monohydric alcohol, a C₆ to C₁₀ dicarboxylic acid and a C₂ to C₁₈ polyglycol respectively, and said diester comprises the reaction product of said C₆ to C₁₀ dicarboxylic acid and said C₆ to C₁₀ monohydric alcohol in a ratio of two moles of said alcohol per mole of said acid; the improvement, which comprises reducing the low temperature thixotropy of said mixture by adding 2 to 10 mole percent based on the total number of moles of said dicarboxylic acid of an aromatic dicarboxylic acid the remainder being a saturated aliphatic dicarboxylic acid and preparing said mixture of complex ester and diester by reacting one mole of said polyglycol with more than two moles each of said dicarboxylic acid and said monohydric alcohol.

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