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SYNTHETIC LUBRICANTS

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11 Claims. (Cl. 260—404.8)

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This invention relates to a new class of compounds which have been found to be particularly suitable for use as synthetic lubricants because of their low pour points and high viscosity indices.

In the lubricant art, considerable progress has been realized in recent years in the production of lubricants characterized by one or more specific properties and adapted for particular uses. In the main, this progress can be attributed to two developments: the first, new refining procedures, and the second, addition agents capable of imparting particular properties to available lubricants. Thus, viscosity index improves and pour depressants are added to automotive lubricants to render the lubricants more adaptable to wide changes in temperature conditions, while other agents are added to improve the load carrying properties of a lubricant which is to be employed, for example, under extreme pressure conditions.

Recently, in an effort to obtain superior lubricants endowed with specific and superior characteristics, a new field has been explored, namely the synthesis of lubricants from various materials. Esters represent one class of materials which have attracted unusual interest as synthetic lubricants. In general, they are characterized by higher viscosity indices and lower pour points than mineral oils of corresponding viscosity. The esters described in the present specification have been found to exhibit very low pour points and high viscosity indices. Lubricants possessing such properties are of special value in the lubrication of engines which are subjected to high temperatures such as combustion turbine engines, particularly those of the "propjet" type. Mineral oil lubricants containing added viscosity index improvers, thickeners or other highly non-volatile additives are undesirable for use in such engines because of the tendency to leave a residue which accumulates and interferes with the operation of the engine. A synthetic lubricant of the type described in the present specification is especially adapted to use under such conditions, since the lubricant contains no additives and thus tends to leave no residue upon volatilization.

The new compounds of the present invention which have been found to be particularly suitable for use as lubricating oils are complex esters prepared by fully esterifying a dicarboxylic acid with an ester of a hydroxyaliphatic acid containing at least one ether group. The hydroxy esters are conveniently prepared by first esterifying a hydroxyaliphatic acid with an alcohol or glycol and then reacting the ester that is formed with an alkylene oxide, whereby the hydroxyl group of the ester is converted into a hydroxyalkoxy

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group. The resulting hydroxylated ester may then be employed to esterify a dibasic acid to form the desired products of the present invention.

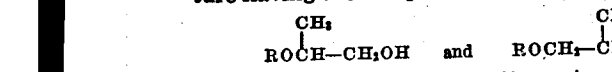
If two mols of the hydroxyaliphatic acid are esterified with one mol of a glycol to form an ester of the glycol, the reaction product with at least two mols of the alkylene oxide will then contain two hydroxyl groups. Such a product may then be employed to esterify a dibasic acid. Such esters are also to be considered as within the scope of the present invention.

The hydroxyaliphatic acids which may be employed as starting materials in the preparation of the new compounds of the present invention may be any open chain aliphatic carboxylic acids containing an aliphatic hydrocarbon chain, which may be a straight or branched chain, saturated or unsaturated, containing 1 to 22 carbon atoms, and having one hydroxyl group attached to any carbon atom in the chain; or acids may be used having two aliphatic hydrocarbon chains interlinked by a single oxygen or sulfur atom, the total number of carbon atoms in such acid exclusive of the carboxyl group being from 2 to 22, and having one substituent hydroxyl group.

The alcohols or glycols which may be employed to esterfy the hydroxyaliphatic acids described above may contain a single hydrocarbon chain, saturated or unsaturated, straight or branched, containing 1 to 20 carbon atoms, or, in place of the unbroken hydrocarbon chain, there may be a series of short saturated aliphatic hydrocarbon radicals, straight chain or branched, interlinked by oxygen or sulfur atoms, or both oxygen and sulfur atoms, the total number of carbon, oxygen and sulfur atoms, exclusive of the hydroxyl group, being from 4 to 20. The maximum number of oxygen or sulfur atoms or both in such alcohol or glycol should not be greater than five, and there should be a chain of at least two carbon atoms between the hydroxyl group and the first oxygen or sulfur atom and a similar chain of at least two carbon atoms between each pair of oxygen and/or sulfur atoms in the radical. Thus, the acid may be esterified with a monohydric aliphatic alcohol, glycol, polyglycol, or thioglycol.

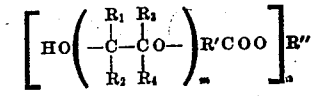
The hydroxyaliphatic acid ester prepared from the materials described above is then reacted with an alkylene oxide, which may contain from 2 to 4 carbon atoms, and such alkylene oxide may be reacted in proportions ranging from 1 to 20 mols per mol of the hydroxyaliphatic ester. When an alkylene oxide containing more than two carbon atoms is employed, the product of the reaction with the hydroxy ester will consist of a mixture of compounds. Thus, when one mol of the hydroxy ester is reacted with one mol of

propylene oxide, the resulting product is a mixture having the compositions

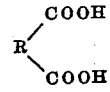


where R represents the entire ester radical to which the hydroxyl group is attached. When this product is reacted with a dicarboxylic acid in accordance with the present invention, the resulting product will likewise consist of a mixture, but such mixtures are useful as synthetic lubricating oils as well as esters having a single molecular composition.

Thus, the products after reaction with an alkylene oxide may be represented by the formula



where R' and R'' represent hydrocarbon, ether, or thioether groups in accordance with the above descriptions of the acids, alcohols, glycols, and thioglycols which may be employed to form the hydroxy ester; R_1, R_2, R_3 and R_4 each represent hydrogen or an alkyl group of one to two carbon atoms; m is an integer from 1 to 20; and n is 1 or 2. To form the products useful as synthetic lubricating oils in accordance with the present invention, a hydroxy ester of this type is reacted with a dicarboxylic acid in proportions to completely esterify the acid. The dicarboxylic acid may be an aliphatic, cycloaliphatic, aromatic, or aromatic-aliphatic acid, and in such acid the two carboxyl groups are attached to a hydrocarbon radical or to a series of hydrocarbon radicals interconnected by oxygen and/or sulfur atoms. More precisely, the dibasic acids employed are those having the formula



where R is a hydrocarbon radical, straight chain or branched, open chain or cyclic, saturated or unsaturated, containing 0 to 26 carbon atoms, or it may be an organic radical consisting of a series of saturated aliphatic hydrocarbon radicals linked by one or more atoms of oxygen or sulfur, or both oxygen and sulfur, provided there are at least two carbon atoms between each pair of oxygen and/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 two.

The molecular weight of the entire ester prepared in accordance with the above descriptions should be at least 300 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 dibasic acids are the straight chain dibasic acids of the paraffinic group having from 2 to 10 carbon atoms per molecule. The preferred monohydric alcohols employed to esterify the hydroxyaliphatic acids are the aliphatic primary alcohols, whether straight chain or branched, containing no oxygen or sulfur atoms and having from 4 to 10 carbon atoms per molecule.

Illustrative examples of the dibasic acids which

may be employed in the synthesis of the complex esters of the present invention are the following:

Oxalic acid
Malonic acid
Succinic acid
Glutaric acid
Adipic acid
Pimelic acid
Suberic acid
Azelaic acid
Sebacic acid
Brassylic acid
Pentadecanedicarboxylic acid
Tetracosanedicarboxylic acid
C_4–C_{24} alkenylsuccinic acids
Diglycolic acid
Thiodiglycolic acid
Thiodipropionic acid

The C_4–C_{24} alkenylsuccinic acids listed above are prepared by condensing olefins or mixtures of olefins with maleic anhydride.

Examples of the hydroxyaliphatic acids which may be employed include the following: glycolic acid, lactic acid, γ-hydroxybutyric acid, α-hydroxy-isobutyric acid, 12-hydroxystearic acid, and ricinoleic acid.

The monohydric alcohols which may be employed in esterifying the hydroxyaliphatic acids 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-ethylhexyl ether
β-n-Butylmercaptoethanol
Diethylene glycol mono-n-butyl ether
Propylene glycol mono-tert.-octyl thioether
n-Butylmercaptoethoxyethanol
Tert.-octylmercaptopropoxypropanol
Propylene glycol mono-n-butyl ether
Dipropylene glycol monomethyl ether
Tripropylene glycol n.onomethyl 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," "Carbitols," or "Cellosolves."

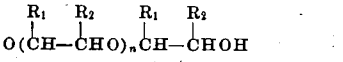
A group of alcohols especially adapted for use in connection with the present invention are the so-called "Oxo" alcohols, prepared by the reaction of carbon monoxide and hydrogen upon the olefins obtainable from petroleum products and hydrogenation of the resulting aldehydes. Materials such as diisobutylene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

As indicated previously, glycols may be employed instead of alcohols in the esterification of the hydroxyaliphatic acids. These glycols are reacted with the acids in a 2 to 1 ratio to form a diester of the glycol. Typical glycols useful for this purpose include ethylene glycol, propylene glycol, butylene glycol, 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

$$HO(CH_2CH_2O)_nCH_2CH_2OH$$

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



where 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. Compounds corresponding to glycols and containing sulfur atoms in thioether 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 esterifications required to produce the compounds of the present invention are carried out by the usual esterification methods, preferably employing an esterification catalyst such as p-toluene sulfonic acid. The reaction of the hydroxy ester with an alkylene oxide may be carried out by contacting the oxide with the ester by gradual addition of the former to the latter at a slightly elevated temperature, preferably in the presence of a catalyst such as stannic chloride or boron trifluoride, or a basic catalyst such as sodium ethoxide.

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.

Data will be given below showing the properties of several examples of complex esters within the scope of the present invention, indicating the adaptability of these esters to lubricating service. All of these esters were prepared by a general method which was carried out in detail as follows: One mol of the hydroxyaliphatic acid was first placed in a reaction flask fitted with reflux condenser and water trap, and to this was added two mols of an alcohol or 0.5 mol glycol, and 0.5% by weight, based on the total acid and alcohol present, of p-toluene sulfonic acid monohydrate, and 100 ml. of a water entraining agent such as naphtha, benzene, toluene, or the like. The mixture was refluxed until no more water was collected in the water trap. The product was washed until neutral with a saturated aqueous Na_2CO_3 solution and then in water. After drying over a desiccant, such as anhydrous $CaSO_4$, the material was stripped at a pressure of 5 mm. to a bath temperature sufficient to remove unreacted starting materials.

One mol of the hydroxy ester prepared as described above and 1.8 ml. of anhydrous $SnCl_4$ were placed in a reaction flask and heated to 60° C. The olefin oxide was then added dropwise with stirring at such a rate that the temperature was maintained at 60° C. The product was then esterified with the dibasic acid in the ratio of two mols of the hydroxy ester-olefin oxide reaction product to one mol of dibasic acid, using the esterification method described above for the monobasic acid esterification and stripping at a pressure of 5 mm. to a bath temperature of 200–250° C.

The results of tests of various properties of esters prepared by the above general method are shown in the table.

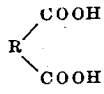
Table

Components of Ester	Mols Oxide Per Mol Hydroxy Ester	Flash Point, °F.	ASTM Pour Point, °F.	Kinematic Viscosity		ASTM Slope	Viscosity Index
				100° F.	210° F.		
12-Hydroxystearic acid n-Butyl alcohol Ethylene oxide Oxalic acid	1	445	+30	38.490	8.223	0.574	158
Lactic acid n-Butyl alcohol Ethylene oxide Sebacic acid	1	450	<−35	27.020	5.540	0.666	150
Lactic acid n-Butyl alcohol Ethylene oxide Adipic acid	1	375	<−35	22.730	4.620	0.711	136
Lactic acid n-Butyl alcohol Ethylene oxide Adipic acid	3	425	−40	38.65	7.13	0.645	143
Lactic acid n-Butyl alcohol Ethylene oxide Sebacic acid	3	(?) 375	−35	39.33	7.70	0.612	150
Lactic acid n-Butyl alcohol Ethylene oxide Adipic acid	5	365	−40	46.160	8.708	0.600	148
Lactic acid n-Butyl alcohol Ethylene oxide Sebacic acid	5	----------	−45	48.820	9.521	0.575	148
Lactic acid n-Butyl alcohol Propylene oxide Adipic acid	2.8	365	−40	46.010	7.976	0.640	139
Lactic acid n-Butyl alcohol Propylene oxide Sebacic acid	2.8	430	−40	59.052	9.651	0.620	137
Lactic acid n-Butyl alcohol Propylene Oxide Adipic acid	2.2	----------	−45	30.570	5.469	0.714	126

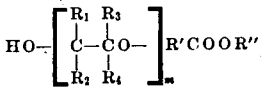
The above data indicate that the esters constituting the subject matter of the present invention possess characteristics, particularly with regard to viscosity index and the pour point, which indicate their suitability for general use as lubricating oils and particularly for use where the use of additives is not desirable. The esters of the present invention may also be blended with mineral lubricating oils to give lubricants of improved viscosity index and pour point.

What is claimed is:

1. As a new composition of matter an ester formed by fully esterifying a dicarboxylic acid of the formula—

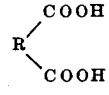


where R is a paraffinic hydrocarbon radical containing 0 to 8 carbon atoms, with a hydroxy ester of the formula—

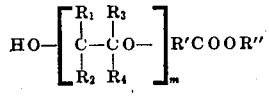


where R' is an aliphatic hydrocarbon radical containing 2 to 17 carbon atoms, R'' is an alkyl radical containing 1 to 16 carbon atoms, R_1, R_2, R_3 and R_4 each represent a member of the group consisting of hydrogen and methyl groups, not more than one such methyl group being present in R_1, R_2, R_3 or R_4, and m is an integer from 1 to 5, the components of the composition being so chosen that the molecular weight thereof is at least 300 and the viscosity at 210° F. is not greater than 150 seconds (Saybolt).

2. The process which comprises fully esterifying a dicarboxylic acid of the formula—

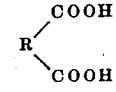


where R is a paraffinic hydrocarbon radical containing 0 to 8 carbon atoms, with a hydroxy ester of the formula—



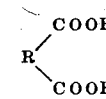
where R' is an aliphatic hydrocarbon radical containing 2 to 17 carbon atoms, R'' is an alkyl radical containing 1 to 16 carbon atoms, R_1, R_2, R_3 and R_4 each represent a member of the group consisting of hydrogen and methyl groups, only one such methyl group being present in R_1, R_2, R_3 and R_4, and m is an integer from 1 to 5, the components of the composition being so chosen that the molecular weight thereof is at least 300 and the viscosity at 210° F. is not greater than 150 seconds (Saybolt).

3. As a new composition of matter an ester formed by fully esterifying a dicarboxylic acid of the formula



where R is a paraffinic hydrocarbon radical having from 0 to 8 carbon atoms, with the product obtained by reacting one molecular proportion of an alkyl ester of a hydroxystearic acid containing 4 to 10 carbon atoms in the ester group with 1 to 5 molecular proportions of ethylene oxide.

4. As a new composition of matter an ester formed by fully esterifying a dicarboxylic acid of the formula



where R is a paraffinic group having 0 to 8 carbon atoms, with the reaction product of 1 molecular proportion of the n-butyl ester of lactic acid and 1 to 5 molecular proportions of ethylene oxide.

5. A composition according to claim 4 in which the mol ratio of ethylene oxide to the ester of lactic acid is 1:1.

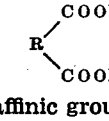
6. A composition according to claim 4 in which the dicarboxylic acid is sebacic acid.

7. A composition according to claim 4 in which the dicarboxylic acid is sebacic acid and in which the mol ratio of etheylene oxide to the ester of lactic acid is 1:1.

8. A composition according to claim 4 in which the dicarboxylic acid is sebacic acid and in which the mol ratio of ethylene oxide to the ester of lactic acid is 5:1.

9. As a new composition of matter an ester formed by fully esterifying sebacic acid with the product obtained by reacting one molecular proportion of n-butyl lactate with 2.8 molecular proportions of propylene oxide.

10. The process which comprises esterifying lactic acid with n-butyl alcohol, reacting 1 to 5 molecular proportions of ethylene oxide with one molecular proportion of the ester of lactic acid thus formed, and fully esterifying a dicarboxylic acid of the formula



where R is a paraffinic group having from 0 to 8 carbon atoms, with the product thus formed.

11. A process according to claim 10 in which the dicarboxylic acid is sebacic acid.

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No references cited.