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3,016,353

ESTER TYPE SYNTHETIC LUBRICANTS

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This invention relates to synthetic lubricating compositions and to a process for their preparation. In general, the invention pertains to a process for preparing synthetic lubricants comprising a mixture of complex and simple esters characterized by high viscosity indices and very low pour points.

The present invention is directed to an ester interchange reaction between either (1) a diester of a dicarboxylic acid and a monohydric alcohol, (2) a diester of a glycol and a monocarboxylic acid, or (3) an ester of a monocarboxylic acid and a monohydric alcohol, with a glycol and a dibasic or monobasic acid in the presence of an esterification catalyst.

Complex ester type synthetic lubricating oils prepared by combinations of glycols, dibasic acids, monobasic acids and alcohols are well known in the synthetic lubricant art. Esters of this type are described in detail among others in U.S. Patents 2,575,195 and 2,575,196.

The complex esters are of the following general types:

- (I) Glycol centered complex esters, i.e. alcohol-dibasic acid-(glycol-dibasic acid)_x alcohol.
- (II) Dibasic acid centered complex esters, i.e. monobasic acid-glycol-(dibasic acid-glycol)_x monobasic acid.
- (III) Alcohol-acid terminated complex esters, i.e. monobasic acid (glycol-dibasic acid)_x alcohol.

wherein *x* is a number greater than zero, preferably about 1 to 6. The preferred complex esters of this invention are included within the group listed above as type I. Nevertheless, the preparation of complex esters of type II and III is also contemplated as being within the scope of the present invention.

The preferred method of this invention relates to an improved process for preparing synthetic lubricating compositions containing from about 3 to 90% of a complex ester preferably of the formula:



with about 10 to 97% of a simple ester of the formula:

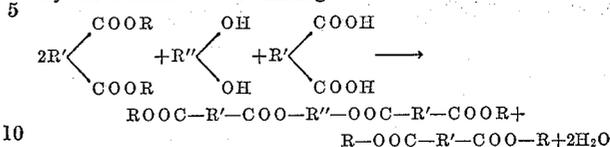


wherein the group R contains 1 to 12 carbon atoms, preferably 6 to 10 carbon atoms, and wherein the group R' contains 0 to 20 carbon atoms, preferably 6 to 8 carbon atoms. The R'' group represents a glycol radical and consists of a saturated aliphatic hydrocarbon group, straight chain or branched, containing 2 to 24 carbon atoms, or preferably a series of saturated aliphatic hydrocarbon radicals interlinked by oxygen or sulfur atoms, or by both oxygen and sulfur atoms, provided that there are at least two carbon atoms between each carboxyl group and the nearest oxygen or sulfur atom and at least two carbon atoms between each pair of oxygen and/or sulfur atoms in the chain, provided further that the total number of carbon, oxygen and sulfur atoms in each radical is from 4 to 80 and the number of sulfur atoms in each radical is not greater than two.

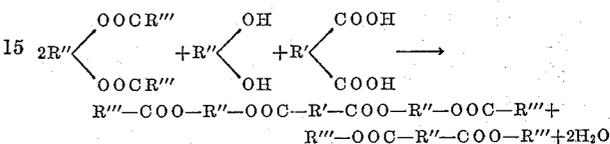
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The exact nature of the over-all reaction is not entirely known, but in general it is believed to be as follows:

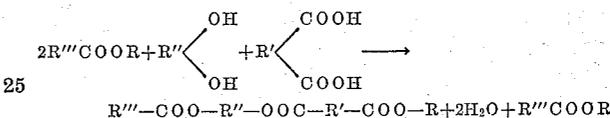
(a) A diester of a dicarboxylic acid and a monohydric alcohol as the starting material:



(b) A diester of a glycol and a monocarboxylic acid as the starting material:



(c) An ester of a monocarboxylic acid and a monohydric alcohol as the starting material:



the R''' group represents a monobasic acid radical having from about 1 to 18 carbon atoms.

Illustrative examples of the alcohol which may be employed in the preparation of the esters of the present invention are as follows:

- Methyl alcohol
- Ethyl alcohol
- n-Butyl alcohol
- n-Hexyl alcohol
- 2-ethyl butyl 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-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 thioether
- Propylene glycol mono-n-dodecyl thioether
- n-Butylmercaptoethoxyethanol
- Tert.-octylmercaptoethoxyethanol
- n-Dodecylmercaptoethoxyethanol
- n-Butylmercaptopropoxypropanol
- Tert.-octylmercaptopropoxypropanol
- Propylene glycol mono-n-butyl ether
- Dipropylene glycol monomethyl ether
- Dipropylene glycol monoethyl ether
- Dipropylene glycol mono-n-butyl ether
- Tripropylene glycol monomethyl ether
- Tripropylene glycol monoethyl ether
- Tripropylene glycol mono-n-butyl ether

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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 as "Dowanols," "Carbitols" or "Cellosolves."

Another group of alcohols especially adapted for use in connection with the present invention are the so-called Oxo alcohols, prepared by the carbonylation of olefins with carbon monoxide and hydrogen in the presence of a cobalt catalyst. Suitable olefins include those obtainable from petroleum products. Diisobutylene and C₇ olefins as well as higher and lower molecular weight olefinic materials can also be employed. The alcohols obtained in this manner normally have a branched chain structure.

The preferred alcohols have the formula ROH wherein R is a branched chain alkyl group having from 4 to 12 carbon atoms.

Among the monobasic 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
Caprylic acid
Pelargonic acid
Lauric acid
Palmitic acid
Stearic acid
Oleic acid
 β -Methoxypropionic acid
 β -Ethoxypropionic acid
 β -tert.-Octoxypropionic acid
 β -Ethylmercaptpropionic acid
 β -tert.-Octylmercaptpropionic acid
 β -tert.-Dodecylmercaptpropionic acid
Any of the various Oxo acids

Preferred monobasic acids have the formula R'''COOH, wherein R''' is an alkyl group having from 1 to 18 carbon atoms.

Illustrative examples of the dibasic acids which may be employed in the synthesis of the complex esters of the present invention are the following:

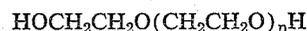
Oxalic acid
Malonic acid
Succinic acid
Glutaric acid
Adipic acid
Pimelic acid
Suberic acid
Azelaic acid
Sebacic acid
Brassylic acid
Pentadecanedicarboxylic acid
Tetracosanedicarboxylic acid
C₄—C₂₄ Alkenylsuccinic acids
Diglycolic acid
Thiodiglycolic acid
Carbon-alkyl derivatives of the above acids, as, e.g., 2-methyl adipic acid, iso sebacic acid, α , α' diethyl adipic acid.

The C₄—C₂₄ alkenylsuccinic acids listed above are prepared by condensing olefins or mixtures of olefins with maleic anhydride. Preferred dibasic acids have the formula HOOC(CH₂)_xCOOH where x is a number of from 2 to 10.

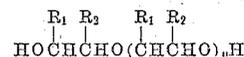
The glycols employed in preparing the esters of the present invention include ethylene glycol and any of the paraffinic homologues of the same containing up to 18 carbon atoms. These may include, for example, ethylene

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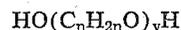
glycol, propylene glycol, butylene glycols, pinacol, trimethylene glycol, tetramethylene glycol, pentamethylene glycol and the like. Compounds such as diethylene glycol, triethylene glycol, the polyethylene glycols of the formula:



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



where either R₁ or R₂ is a methyl group and the other is hydrogen, and where n is 1 to 20, may be employed. Glycols containing sulfur atoms in thioether linkages may also be employed, and these include compounds as thiodiglycol and 1,2-bis (2-hydroxy-ethylmercapto) 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. Preferred glycols have the formula



wherein n and y are numbers of from 1 to 6.

Aliphatic or simple esters of aliphatic dicarboxylic corresponding to the general formula



wherein the group R contain 1 to 12 carbon atoms, preferably 6 to 10 carbon atoms, and the group R' contains 0 to 20 carbon atoms, preferably 6 to 8 carbon atoms, are also known as lubricants for various purposes. It is also known that such diesters may advantageously be blended with complex esters of the type described above to prepared synthetic lubricants having better properties than either of its components.

The present invention provides an improved method of preparing a complex ester, and in general comprises the steps of effecting an alkyl interchange between a diester of a dicarboxylic acid and a glycol, or other polyhydric alcohol, in the presence of a dibasic or monobasic acid; the various reactants being selected from the above lists. The ester interchange is preferably carried out with the aid of an acid or basic esterification catalyst, such as sodium bisulfate, sulfuric acid, toluene sulfonic acid, calcium oxide, lithium oxide, the alkali metal alcoholates such as sodium and potassium alcoholates, and metal salts such as calcium sebacate, zinc stearate, etc. It is also possible to charge metallic sodium to the reaction zone to react with the alcohol or acid present to form the desired catalytic material. The acid type catalysts, such as sodium bisulfate and toluene sulfonic acid, are preferred and are employed in amounts ranging from 0.001 to 1%. It may also be advantageous to employ minor amounts of an oxidation inhibitor such as, for example, phenothiazine in amounts varying between about 0.01 to about 2.0 weight percent, based on the theoretical weight of the complex ester formed.

More particularly, the inventive process comprises admixing a diester, which has been formed by esterifying a dicarboxylic acid with an aliphatic alcohol, with a glycol and a dibasic acid and carrying out an alkyl interchange reaction in the presence of an acid catalyst, preferably sodium bisulfate. The reaction mixture is initially heated to a temperature within the range of 100 to 250° C., preferably 175 to 225° C., at a pressure of between about 5 to 800 mm. Hg., and preferably atmospheric pressure, for from about 1 to 5 hours. The pressure is then reduced to about 10 to 20 mm. Hg. and the heating is continued at a temperature within the range of about 220 to 270° C., preferably 230 to 250° C., for about 1 to 5 hours. An oxidation inhibitor such as phenothiazine and an inert reaction medium or water-entraining medium such as naphtha, benzene, hexane, heptane, or the like can be added to the reaction mixture. During the heating stages the water-entraining me-

dium and other volatile matter are removed from the reaction mixture.

The relative proportions of reactants employed in the process of this invention will range from about 1 to 6 mols of dibasic acid and 1 to 6 mols of glycol for each mol of starting ester. In addition, an excess of from one to six mols of ester is employed. In the preferred method of operation the preformed diester of a dicarboxylic acid will be present in amounts of about 2 mols along with 1 mol of a dibasic acid and 1 mol of a glycol.

In conventional alcoholysis reactions wherein an ester is reacted with a hydroxy compound, i.e. an alcohol or a glycol, the more volatile alcohol portion of the ester is evolved. Simultaneously it is replaced by the added hydroxy compound which is less volatile. The removal of the more volatile alcohol drives the reaction to completion. For example, an esterinterchange reaction has been carried out by reacting di-2-ethylhexyl sebacate with polyethylene glycol while evolving 2-ethylhexanol until the desired viscosity is obtained.

In accordance with the present invention it has now been unexpectedly found that a reaction similar to that described above can be carried out in the presence of a dibasic or monobasic acid. As a result of having the latter material present, the more volatile alcohol portion of the diester does not escape the reaction mass but is completely converted immediately into the corresponding diester or into additional complex ester. The reaction products thus obtained are blends of complex as well as simple esters, and they constitute as such synthetic lubricating compositions having outstanding low temperature properties. In addition, the simplified synthesis technique of this invention wherein the more volatile alcohol portion of the diester undergoing esterinterchanging is reacted with dibasic or monobasic acids present in the reaction mass instead of being recovered as well as the direct preparation of a blend of complex and simple esters contribute toward making the process economically attractive. Another important feature is that ester blends of any viscosity can be obtained by simply varying the relative amounts of added glycol and dibasic acid.

The invention will be more fully understood by reference to the following examples and table:

EXAMPLE I

In accordance with the inventive process, the following materials were charged to a 3-liter flask equipped with a stirrer, thermometer, water trap and condenser:

Di-2-ethylhexyl sebacate	3 mols, 1278 g.
Polyethylene glycol (6% excess)	1.59 mols, 302 g.
Sebacic acid	1.5 mols, 303 g.
Phenothiazine (pure) (0.5% on theoretical 1829 g. ester)	9.1 g.
Heptane	60 g.
NaHSO ₄ catalyst (0.4% on 1829 g. ester)	7.3 g.

The above reaction mass was heated with stirring and at atmospheric pressure for three hours at a temperature of 225° C. during which time 58 cc. of water was collected in the water trap. The pressure was then reduced to 10 mm. and the temperature raised to about 230 to 235° C., and heating was continued for another three hours. During this latter period 86 cc. (63 g.) of water-entraining medium was recovered. The crude ester mixture had a Neutralization No. of 2.0 and a Hydroxyl No. of 2.7 indicating essentially complete esterification and alcoholysis, part of the Neutralization No. being due to the acidity of the catalyst employed which was not filtered off. The mixture was diluted with 200 cc. heptane and washed with 900 cc. of 10% Na₂CO₃ solution containing 900 cc. isopropanol, then with 900 cc. water plus 700 cc. heptane and finally with 720 cc. water containing 540 cc. isopropanol. The material was stripped free of water and solvents by heating to 170° C. and depressurizing to about 5 mm. The stripped material

was then filtered to give 1906 grams of the final ester product. The composition and properties of the final product are listed in column one of the table.

EXAMPLE II

A complex ester type lubricant was also prepared via conventional esterification technique for comparison. This was done by charging to a 3-liter flask equipped with stirrer, thermometer, water trap and condenser the following materials:

2-ethylhexanol	6.48 mols, 843 gms.
Sebacic acid	4.64 mols, 937 gms.
Tetraethylene glycol	1.82 mols, 364 gms.
Phenothiazine	9.1 gms.
Heptane	63 gms.
NaHSO ₄ catalyst (0.4%)	5.6 gms.

The reaction mixture was treated according to the procedure as described in Example I above. The composition and properties of the final product are listed in column two of the table.

The ester compositions of Examples I and II were submitted to a series of tests to determine their utility as synthetic lubricants. These tests include the standard ASTM viscosity determinations at 210° F., 100° F., 0° F. and -40° F. There is also included the data obtained on a second viscosity measurement at -40° F. after the lubricant was held at that temperature for four hours. Viscosity index calculations were made and the standard ASTM flash, fire, and pour points were measured. The samples were also submitted to a lead corrosion test which may be described as follows:

500 gms. of the test oil was placed in a beaker. A stainless steel stirrer shaft on which was fastened a weighed lead strip was immersed in the oil and served as a stirrer. A strip of copper of comparable size was placed on the other side of the shaft and likewise stirred in the oil sample. The copper strip served as a catalyst to promote degradation. The sample was heated to 325° F. and air was bubbled through the oil. After one hour the lead strip was removed, cleaned and its weight loss determined. A loss in the weight of the lead strip of less than 30 mgs. is considered satisfactory. A load carrying determination was also run on the samples using the standard SAE load testing machine at a 3.4:1 gear ratio. After an initial run-in period of two minutes at 50 lbs., incremental 50 pound weight loads were added every 10 seconds until the bearings running in the test oil were scuffed. The results reported are the total load carried without scuffing.

The data obtained on these tests are set forth below:

Table

	Example I	Example II
Viscosity, Cs. @ ° F.:		
210	8.11	8.16
100	39.13	39.68
0	1.034	1.048
-40	12.470	12.740
V.I.	156	155
Pour Point, ° F.	<-75	<-75
Flash Point, ° F.	530	465
Fire Point, ° F.	550	540
1 Hr. SOD Lead Corrosion Loss, mg.	23	166
SAE-SOD Test (Load, lbs.)	650	625
Neut. No.	0.19	0.36
Hydroxyl No.	3.6	1.9
Diester Content, Wt. percent.	51.7	41.3
Complex ester Content, Wt. percent.	48.3	58.7
Properties of Diester recovered by distillation from the reaction product:		
Viscosity, Cs. @ ° F.—		
210	3.36	3.39
100	13.00	12.53
Properties of Complex Ester portion of the reaction product:		
Viscosity, Cs. @ ° F.—		
210	17.86	15.49
100	109.5	91.0

It is noted that the reaction products of Examples I

and II have nearly the same properties although each was prepared by an entirely different process. As indicated in the table the two products were distilled in order to detect possible differences, but the distillates were essentially identical and consisted of di-2-ethylhexyl sebacate. The amount of residue or complex ester in the product prepared according to the inventive process was, however, somewhat smaller than that found in ester product of Example II prepared according to the teachings of the prior art. This difference in complex ester content can be attributed to the fact that during the preparation of Example I ester the formation of the diester would be the favored reaction, and that slightly more diester than complex ester would be formed from the "evolved" alcohol. It is to be noted particularly that the initial diester content of 1278 gms. in Example I was 70% by weight of the total original ingredients, exclusive of the water of reaction. By distillation, as recorded in the table, the final product was shown to contain about 52% diester. Therefore, a quantity of the original diester, representing 18% of the total ingredients and distinct from any diester that may have been formed from the "evolved" alcohol, entered into the constitution of the complex ester portion of the lubricant. In the process of this invention, therefore, at least 25% of the simple diester enters into the reaction to form complex ester.

The more viscous nature of the complex ester portion of the product of this invention indicates that the complex esters have a slightly longer chain length than those prepared according to the method described in Example II.

The above data further shows that the ester compositions constituting the subject matter of the present invention possess characteristics, particularly with respect to viscosity index and pour point, which indicate their suitability for general use as lubricating oils. These synthetic lubricants of this invention may also be blended with either mineral or synthetic lubricating compositions known to the art to give lubricants of improved viscosity index and pour point. They also furnish a satisfactory base for the preparation of lubricating grease compositions.

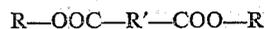
In addition the diester may be removed from the reaction products by conventional methods such as extraction, distillation, etc., and the complex ester recovered and employed either alone or blended with mineral and synthetic lubricating oils as a lubricant.

Special characteristics of the ester compositions of the invention may be enhanced by the incorporation of various well-known lubricant additives, such as the oxidation inhibitors represented by phenothiazine and the like, extreme pressure resisting agents, such as tricresyl phosphate, etc., viscosity index improvers such as polybutenes, polymerized acrylate and methacrylate esters, etc., pour point depressants, such as polymerized fumarate and maleate esters, and copolymers of such esters with other polymerizable compounds, especially vinyl acetate.

In summary, the preferred embodiment of this invention comprises the steps of admixing a diester of a dicarboxylic acid with a glycol and a dibasic acid, and

subjecting the reaction mixture to a temperature of about 225 to 270° C. for about 3 to 6 hours at atmospheric to subatmospheric pressure. The alkyl interchange-esterification reaction is usually carried out in the presence of an esterification catalyst, preferably acid in nature such as sodium bisulfate.

The dicarboxylic acid diester preferred as the starting material has the general formula:

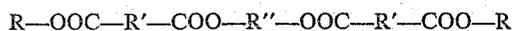


where R' is a hydrocarbon radical having from about 4 to 12 carbon atoms and R is an alkyl group of from about 4 to 12 carbon atoms in preferably branched chain arrangement.

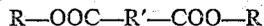
The foregoing description and examples are not to be taken as in any way limiting but merely illustrative of the present invention for many variations may be made by those skilled in the art without departing from the spirit or scope of the following claims.

What is claimed is:

1. A process for the preparation of an ester blend useful as a synthetic lubricant and comprising complex ester typified by the formula:



and diester of the formula:



wherein R is a C₆ to C₁₀ alkyl group, R' is a C₆ to C₈ saturated aliphatic hydrocarbon group and R'' is an aliphatic hydrocarbon group containing interlinked oxygen atoms in ether groupings, which comprises reacting together under esterinterchanging conditions and in the presence of an esterification catalyst at a temperature within the range of about 225 to 270° C. for about 3 to 6 hours at atmospheric to subatmospheric pressure, about 2 molar proportions of diester, about one molar proportion of a glycol and about one molar proportion of a dicarboxylic acid.

2. A process according to claim 1 wherein said diester is di-2-ethylhexyl sebacate, said glycol is polyethylene glycol, and said dicarboxylic acid is sebacic acid.

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