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REDUCTION OF ACIDITY IN SYNTHETIC ESTER LUBES WITH OLEFIN OXIDES

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11 Claims. (Cl. 260—484)

This invention relates to complex synthetic ester lubricating oil. Particularly this invention relates to a process for neutralizing synthetic lubricatinng oil of the complex ester type using an olefin oxide as the neutralizing agent.

In an effort to obtain superior lubricating oils having specific and unusual characteristics, new synthetic lubricants have been developed. One class of material which has attracted unusual interest as synthetic lubricants are the complex esters. In general these lubricating oils are characterized by higher viscosity indices and lower pour points than mineral oils of corresponding viscosity. 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 "prop-jet" type. Mineral oil lubricants containing added viscosity index improvers, pour point depressors, or other highly nonvolatile additives are undesirable for use in such engines because of their tendency to leave a residue which accumulates and interferes with the operation of the engine. In addition the high pour points and low flash points of such compositions are undesirable. The synthetic lubricants of the complex ester type are especially adaptable to use under such conditions since these lubricants contain no additive and have a desirable combination of high flash points, low pour points, and high viscosities. In addition they thus tend to leave no residue upon volatilizaton.

In the preparation of these complex ester synthetic lubricating oils, manufacturers are faced with the problem of lowering the final acidity of the oil to a point where the synthetic lubricant will be acceptable for use in engines at high temperatures. In the past this residual acidity has been reduced by washing with aqueous alkali or by percolating through beds of alkali or alkali impregnated on less active materials. Washing with alkalies, however, frequently results in the formation of stable emulsions and washing alone frequently does not reduce the acidity to a point low enough to be practical. The percolation method, on the other hand, may reduce the acidity to the desired point, however, estersoluble alkali salts of organic acids apparently result since the ester lubricants so treated have been found to possess a high and undesirable ash content.

It has now been found, and forms the object of this invention, that the acidity of these complex ester synthetic lubricating oils may be reduced to the desired point by treatment with an olefin oxide. In addition to being extremely effective, the process of this invention has the further advantage of introducing no ash into the synthetic lubricant or contaminating the oil in any way with traces of inorganic materials. As a result the complex ester synthetic lubricant oils which have been treated according to the process of this invention need not be subsequently washed or filtered before stripping to the desired viscosity or flash point. Moreover, the amount of the olefin oxide introduced into the synthetic lubricating oil is so small that the physical properties of the final lubricating oil such as viscosity, flash point, fire point and extreme pressure properties are not altered.

The synthetic ester lubricating oils operable in the concept of this invention are those complex esters, distillable or not distillable, which are formed by the interaction of two or more of the following compounds

in which at least one polyfunctional alcohol and one polyfunctional acid are employed:

(*a*) Monohydric alcohols
(*b*) Monobasic acids
(*c*) Dibasic acids
(*d*) Glycols
(*e*) Polyhydric alcohols
(*f*) Poilybasic acids

The synthetic lubricating oils of the complex ester type contemplated by this invention are grouped under one of four types as follows:

TYPE I

Monobasic acid-glycol-dibasic acid-glycol-monobasic acid

This complex ester may be considered to have the following structural formula:

$$R_1\text{–C–O–O–}R_2\text{–O–O–C–}R_3\text{–C–O–O–}R_4\text{–O–O–C–}R_5$$

wherein R_1 and R_5 are the alkyl radicals of the monobasic acids,
R_2 and R_4 are the alkyl radicals from the glycols, and
R_3 is the alkyl radical from the dibasic acid.

The esters of this type are prepared by admixing the calculated amounts of the various compounds and carrying out a straightforward esterification of the reaction. The reaction conditions are continued with an occasional sample of the product being tested for acidity until the minimum acidity is attained.

TYPE II

Alcohol-dibasic acid-glycol-dibasic acid-alcohol

This material may be represented by the following formula:

$$R_1\text{–O–O–C–}R_2\text{–C–O–O–}R_3\text{–O–O–C–}R_4\text{–C–O–O–}R_5$$

wherein R_1 and R_5 are the combining radicals of the alcohol,
R_2 and R_4 are the alkyl radicals of the dibasic acids, and
R_3 is the alkyl radical of the glycol.

These esters are prepared in the manner similar to those of Type I.

TYPE III

Alcohol-dibasic acid-glycol-monobasic acid

These esters are prepared by reacting a dibasic acid and a glycol under such conditions that one hydroxyl group of the glycol combines with one carboxyl group of the dibasic acid, in other words, a half ester is formed. This half ester is then reacted with a molar proportion each of an aliphatic alcohol and a monobasic acid. These materials may be said to have the general formula

$$R_1\text{—O—O—C—}R_2\text{—C—O—O—}R_3\text{—O—O—C—}R_4$$

wherein R_1 is the combining radical of the aliphatic alcohol,
R_2 the alkyl radical of the dibasic acid,
R_3 the alkyl radical of the glycol, and
R_4 the alkyl radicals of the monobasic acid.

The preparation of these ester materials is specifically set out in copending application Serial No. 52,428, now Patent No. 2,575,195.

TYPE IV

Alcohol-dibasic acid-glycol-dibasic acid-alcohol

These materials may be said to have the type formula

$$R_1\text{–O–O–C–}R_2\text{–C–O–O–}R_3\text{–O–O–C–}R_4\text{–C–O–O–}R_5$$

wherein R_1 and R_5 are the combining alkyl radicals of the alcohol,
R_2 and R_4 the alkyl radicals of the dibasic acid, and
R_3 is the alkyl radical of the glycol.

It will be noted that the esters of Type IV have the same structural formula as Type II. However, these complex esters are prepared by reacting an alcohol with a dibasic acid under such conditions that a half ester is formed and reacting two moles of such an ester with

one mole of a glycol. The preparation of this type of synthetic ester lubricating oil is set out in detail in copending application Serial No. 52,429.

TYPE V

Monobasic acid-glycol-dibasic acid-glycol-monobasic acid

These synthetic esters may be said to have the general formula:

$$R_1\text{–}C\text{–}O\text{–}O\text{–}R_2\text{–}O\text{–}O\text{–}C\text{–}R_3\text{–}C\text{–}O\text{–}O\text{–}R_4\text{–}O\text{–}O\text{–}C\text{–}R_5$$

wherein R_1 and R_5 are the alkyl radicals of the monobasic acid,
R_2 and R_4 are the alkyl radicals of the glycol, and
R_3 is the alkyl radical of the dibasic acid.

It will be noted that these synthetic esters are the same as those appearing above under Type I except that this type is prepared by reacting a monobasic acid with a glycol under such conditions that a half ester is formed and reacting two moles of such ester with one mole of a dibasic acid. The details of the preparation of this type of synthetic ester are set out in copending application Serial No. 52,430, now Patent No. 2,575,196.

As is stated above, at various stages in the preparation of the complex esters samples are removed from the reaction vessel and are titrated with a standardized basic solution to determine the acidity. It has been determined that the minimum allowable residual acidity in the ester oils is in the vicinity of 0.1 mg. of potassium hydroxide/g. In the preparation of these synthetic esters, while it is theoretically possible to completely neutralize the acids, as a practical matter it is found impossible to lower the acidity to below 1.5 mg. of potassium hydroxide per gram.

As was set out above, these complex ester materials are prepared by a combination of an alcohol, a monobasic acid, a dibasic acid, and a glycol in various fashions.

Operable C_1 to C_{18} alcohols include 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 thioether
Propylene glycol mono-n-dodecyl thioether
n-Butylmercaptoethoxyethanol
tert.-octylmercaptoethoxyethanol
n-Butylmercaptopropoxypropanol
tert.-octylmercaptopropoxypropanol
n-Dodecylmercaptopropoxypropanol
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
Propylene glycol monoisopropyl ether
Dipropylene glycol monoisopropyl ether
Tripropylene glycol monoisopropyl ether

Many of the above lister 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. Materials such as diisobutylene and C_7 olefins are suitable for this purpose; also higher and lower molecular weight olefinic materials are sometimes employed. The alcohols obtained in this manner normally have a branched chain structure.

Among the monobasic acids which may be employed in the preparation of the esters of the present invention, the following C_2 to C_{18} acids may be listed as illustrative:

Acetic acid
Propionic acid
Butyric acid
Valeric acid
Caproic acid
Caprylic 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
Any of the various "Oxo" acids

Illustrative examples of C_2 to C_{24} dibasic acids, or particularly C_4 to C_{10} 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
Carbon-alkyl derivatives of the above acids as e. g. 2-methyl adipic acid.

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

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

$$HO(CH_2CH_2O)_nCH_2CH_2OH$$

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

$$HO(\underset{\displaystyle R_1}{\underset{|}{CH}}\text{–}\underset{\displaystyle R_2}{\underset{|}{CHO}})_nCH\text{–}CHOH$$

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 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.

In carrying out the process of this invention these complex esters are placed in a pressure bomb and the calculated amount of the desired olefin oxide is added. The bomb is sealed, the temperature raised to the desired point, and the reaction allowed to proceed until the minimum final acidity is attained.

As the olefin oxide used, a material corresponding to the type formula

$$R_1\text{–}CH\text{—}CH\text{–}R_2$$
$$\qquad\quad\diagdown\;\diagup$$
$$\qquad\quad\;\;O$$

wherein R_1 and R_2 are either hydrogen or a CH_3 group

may be used. Also applicable are oxides such as styrene oxide, glycidic esters, trimethylene oxide, tetrahydrofuran, and epichlorohydrin. In the preferred embodiment of the invention the commercially available propylene or ethylene oxide is used. Especially preferred is ethylene oxide.

The amounts of the olefin oxide used to neutralize the residual acidity in the complex ester lubricating oils will depend, of course, upon the final residual acidity of the ester. It has been found that amounts varying between about 2% and 20% by weight based on the weight of the ester material is sufficient in most instances. Amounts in the range of from 4 to 8% are especially preferred.

As was stated above the synthetic lubricating oil is placed within a pressure bomb and the desired amount of the desired olefin oxide is admixed therewith. The temperature at which the reaction best occurs will lie within the range of from 150 to 300° C., preferably 200 to 250° C. The time of the reaction is a function of both the residual acidity of the synthetic ester and the temperature at which the reaction is carried out. It is necessary, therefore, to maintain the reaction until such time as the desired residual acidity is attained. For temperatures within a range of from 200 to 250° C. it has been found that from 2 to 6 hours is sufficient.

In order to more specifically illustrate the process of the instant invention the following examples are given. It is to be understood that these examples are illustrative only and are not considered to be limiting in any way upon the concept of this invention.

EXAMPLE I

528 g. of "isooctyl" alcohol, 304 g. of triethylene glycol, 408 g. of sebacic acid, and 288 g. of adipic acid were placed in a round bottomed flask equipped with a reflux condenser and a water trap. 100 c. c. of xylene was added as an entraining agent for the water of esterification. The reaction mixture was heated to reflux temperature and maintained at that temperature until the theoretical amount of water resulting from complete esterification was removed. Samples of the final product were removed and titrated with standardized potassium hydroxide to check the acidity. The acidity was found to be 1.1 mg. KOH/g.

200 g. of this ester product was placed in a one liter bomb, 32 g. of ethylene oxide was added, the bomb sealed, and heated to a temperature of about 200° C. After 3 hours of reaction the residual acidity was found to be at the value, 0.1 mg. KOH/g.

EXAMPLE II

Using the procedure outlined in Example I above a synthetic oil was prepared from the following formulation:

572 g. "isooctyl" alcohol
330 g. triethylene glycol
576 g. adipic acid

The residual acidity of this synthetic oil was 2.2 mg. KOH/g. After treatment with 16% ethylene oxide at 250° C. for 3 hours in a one liter bomb the residual acidity was 0.08 mg. KOH/g.

EXAMPLE III

Following the procedure of Example I a synthetic lubricant was prepared from the following:

679 g. "isodecyl" alcohol
133 g. diethylene glycol
576 g. adipic acid

The residual acidity of this synthetic lubricant was 1.1 mg. KOH/g. By treatment with 16% ethylene oxide for 3 hours at 250° C. in a one liter bomb the residual acidity was reduced to .06 mg. KOH/g.

EXAMPLE IV

In accordance with the procedure of Example I above a synthetic lubricant was prepared from the following:

729 g. butanediol-1,3
576 g. caprylic acid
292 g. adipic acid

The residual acidity of this ester was 0.88 mg. KOH/g. After treatment in a one liter bomb for 3 hours at 250° C. in the presence of 16% ethylene oxide the residual acidity was reduced to .08 mg. KOH/g.

EXAMPLE V

In accordance with the procedure of Example I above a synthetic lubricant was prepared from the following:

232 g. butanediol-1,3
670 g. "isooctyl" alcohol
536 g. diglycollic acid

The residual acidity of this ester was 2.1 mg. KOH/g. After 3 hours treatment in a one liter bomb at 250° C. with 8% ethylene oxide this residual acidity was 0.1 mg. KOH/g.

EXAMPLE VI

In accordance with the procedure of Example I above a synthetic lubricant was prepared from the following:

1142 g. "isooctyl" alcohol
660 g. triethylene glycol
1150 g. adipic acid

The residual acidity of this ester was 2.1 mg. KOH/g. After treatment for 3 hours at 250° C. in a one liter bomb with 19% of ethylene oxide the residual acidity was reduced to .13 mg. KOH/g.

EXAMPLE VII

In accordance with the procedure of Example I above a synthetic lubricant was prepared from the following:

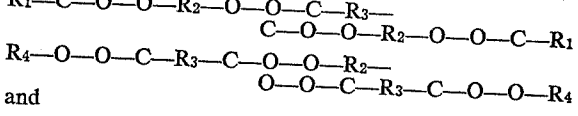
203 g. tetramethylene glycol
585 g. "isooctyl" alcohol
584 g. adipic acid

The residual acidity of this ester was 2.7 mg. KOH/g. After treatment for three hours at 225° C. with 8 wt. per cent propylene oxide the acidity was 0.5 mg. KOH/g.

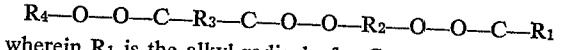
It will be seen by examination of the data given in the examples above that the instant invention is a very satisfactory process for the reduction of the residual acidity of synthetic ester type lubricating oils.

What is claimed is:

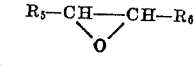
1. A process for the reduction of the residual acidity of complex ester synthetic lubricating oils selected from the group consisting of materials of the formula



and



wherein R_1 is the alkyl radical of a C_2 to C_{18} monobasic acid, wherein R_2 is the alkyl radical of a glycol containing from 2 to 18 carbon atoms, wherein R_3 is the alkyl radical of a C_2 to C_{24} dibasic acid and wherein R_4 is the alkyl radical of an alcohol containing from 1 to 18 carbon atoms, which comprises reacting the complex ester with an olefin oxide having the general formula

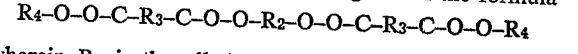


wherein R_5 and R_6 are selected from the class consisting of H— and CH_3, said reaction occurring under pressure at a temperature within a range of between 150 and 300° C., for a period of time sufficient to reduce the residual acidity of the complex ester below about 0.5 mg. KOH/g.

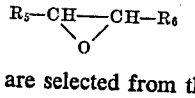
2. A process according to claim 1 wherein said olefin oxide is ethylene oxide.

3. A process according to claim 1 wherein said olefin oxide is propylene oxide.

4. A process for the reduction of the residual acidity of complex ester synthetic lubricating oils of the formula



wherein R_2 is the alkyl radical of a glycol containing from 2 to 18 carbon atoms, wherein R_3 is the alkyl radical of a C_4 to C_{10} dibasic acid and wherein R_4 is the alkyl radical of an alcohol containing from 1 to 18 carbon atoms, which process comprises reacting the complex ester with an olefin oxide having the general formula



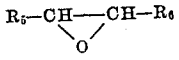
wherein R_5 and R_6 are selected from the class consisting

of H- and CH_3, said reaction occurring under pressure at a temperature within a range of between 150 and 300° C., for a period of time sufficient to reduce the residual acidity of the complex ester below about 0.5 mg. KOH/g.

5. A process for the reduction of the residual acidity of complex ester synthetic lubricating oils of the formula

$$R_1\text{–C–O–O–}R_2\text{–O–O–C–}R_3\text{–C–O–O–}R_2\text{–O–O–C–}R_1$$

wherein R_1 is the alkyl radical of a C_2 to C_{18} monobasic acid, wherein R_2 is the alkyl radical of a glycol containing from 2 to 18 carbon atoms and where R_3 is the alkyl radical of a C_4 to C_{10} dibasic acid, which process comprises reacting the complex ester with an olefin oxide having the general formula

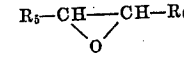


wherein R_5 and R_6 are selected from the class consisting of H- and CH_3, said reaction occurring under pressure at a temperature within a range of between 150 and 300° C., for a period of time sufficient to reduce the residual acidity of the complex ester below about 0.5 mg. KOH/g.

6. A process for the reduction of the residual acidity of complex ester synthetic lubricating oils of the formula

$$R_4\text{–O–O–C–}R_3\text{–C–O–O–}R_2\text{–O–O–C–}R_1$$

wherein R_1 is the alkyl radical of a C_2 to C_{18} monobasic acid wherein R_2 is the alkyl radical of a glycol containing from 2 to 18 carbon atoms, wherein R_3 is the alkyl radical of a C_4 to C_{10} dibasic acid and wherein R_4 is the alkyl radical of an alcohol containing from 1 to 18 carbon atoms, which process comprises reacting the complex ester with an olefin oxide having the general formula



wherein R_5 and R_6 are selected from the class consisting of H- and CH_3, said reaction occurring under pressure at a temperature wtihin a range of between 150 and 300° C., for a period of time sufficient to reduce the residual acidity of the complex ester below about 0.5 mg. KOH/g.

7. A process according to claim 4 wherein said complex ester has the formula

$$R_4\text{–O–O–C–}R_3\text{–C–O–O–}R_2\text{–O–O–C–}R_3\text{–C–O–O–}R_4$$

wherein R_2 is the alkyl radical of tri-ethylene glycol, wherein R_3 is the alkyl radical of adipic acid and wherein R_4 is the alkyl radical of iso-octyl alcohol.

8. A process according to claim 4 wherein said complex ester has the formula

$$R_4\text{–O–O–C–}R_3\text{–C–O–O–}R_2\text{–O–O–C–}R_3\text{–C–O–O–}R_4$$

wherein R_2 is the alkyl radical of di-ethylene glycol, wherein R_3 is the alkyl radical of adipic acid and wherein R_4 is the alkyl radical of iso-decyl alcohol.

9. A process according to claim 4 wherein said complex ester has the formula

$$R_4\text{–O–O–C–}R_3\text{–C–O–O–}R_2\text{–O–O–C–}R_3\text{–C–O–O–}R_4$$

wherein R_2 is the alkyl radical of butane diol-1,3, wherein R_3 is the alkyl radical or diglycolic acid and wherein R_4 is the alkyl radical of iso-octyl alcohol.

10. A process according to claim 4 wherein said complex ester has the formula

$$R_4\text{–O–O–C–}R_3\text{–C–O–O–}R_2\text{–O–O–C–}R_3\text{–C–O–O–}R_4$$

wherein R_2 is the alkyl radical of tri-ethylene glycol, wherein R_3 is the alkyl radical of sebacic acid and wherein R_4 is the alkyl radical of iso-octyl alcohol.

11. A process according to claim 5 wherein said complex ester has the formula

$$R_1\text{–C–O–O–}R_2\text{–O–O–C–}R_3\text{–C–O–O–}R_2\text{–O–O–C–}R_1$$

wherein R_1 is the alkyl radical of caprylic acid, wherein R_2 is the alkyl radical of butane diol-1,3 and wherein R_3 is the alkyl radical of adipic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,372,244	Adams et al.	Mar. 27, 1945
2,575,195	Smith	Nov. 13, 1951
2,575,196	Smith	Nov. 13, 1951