

1

2,723,286

REDUCTION OF ACIDITY IN SYNTHETIC ESTER LUBES WITH ETHYLENE CARBONATE

David W. Young, Westfield, and Delmer L. Cottle, Highland Park, N. J., assignors to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Application October 6, 1951,
Serial No. 250,184

8 Claims. (Cl. 260—485)

This invention relates to complex synthetic ester lubricating oils. Particularly this invention relates to a process for neutralizing synthetic lubricating oil of the complex ester type using ethylene carbonate 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 high viscosity indices and lower pour points than mineral oils of corresponding viscosity. Lubricants possessing such properties are of special value in the lubricating of engines which are subjected to high temperatures such as combustion turbine engines, particularly those of the "prop-jet" type. Mineral oil lubricants are generally less desirable for use in such engines because of their tendency to leave a higher percentage of carbonaceous residue which accumulates and interferes with the operation of the engine. In addition the relatively 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 may contain no additive and have a desirable combination of high flash points, low pour points, and high viscosities.

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 alkalis, 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. Although the percolation method may reduce the acidity to the desired point, ester-soluble 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 ethylene carbonate. 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 because of the presence 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 ethylene carbonate 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 con-

2

cept 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) Polybasic acids
- (g) Hydroxy acids

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

I. Monobasic acid-glycol-dibasic acid-glycol-monobasic acid

This complex ester may be represented by the following structural formula:



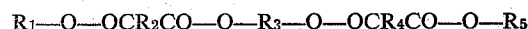
wherein:

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

II. Alcohol-dibasic acid-glycol-dibasic acid-alcohol

This material may be represented by the following formula:



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 I.

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:



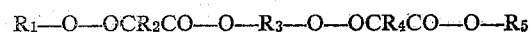
wherein:

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.

IV. Alcohol-dibasic acid-glycol-dibasic acid-alcohol

These materials may be said to have the general formula



wherein:

R₁ and R₅ are the combining alkyl radicals of the alcohol, R₂ and R₄ the alkyl radicals of the dibasic acid, and R₃ is the alkyl radical of the glycol.

It will be noted that the esters of IV have the same structural formula as 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 mols of such an ester with one mol 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, now Patent No. 2,703,811.

V. Monobasic acid-glycol-dibasic acid-glycol-monobasic acid

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



wherein:

R₁ and R₅ are the alkyl radicals of the monobasic acid, R₂ and R₄ are the alkyl radicals of the glycol, and R₃ is the alkyl radical of the dibasic acid.

It will be noted that these synthetic esters are the same as those appearing above under 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 mols of such ester with one mol 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 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-n-butyl thioether
Propylene glycol mono-tert.-octyl thioether
Propylene glycol mono-n-dodecyl thioether
n-Butylmercaptoethoxyethanol
Tert.-octylmercaptoethoxyethanol
n-Dodecylmercaptoethoxyethanol
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 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. Materials such as diisobutylene and C₇ 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 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 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.

The C₄-C₂₄ alkenylsuccinic acids listed above are prepared by condensing olefins or mixtures of olefins with maleic anhydride.

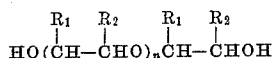
The glycols employed in preparing the esters of the present invention include ethylene glycol and any of the paraffinic homologues of the same containing up to 18 carbon atoms. These may include, for example, ethylene glycol, propylene glycol, butylene glycols, pinacene, trimethylene glycol, tetramethylene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

5

glycol, triethylene glycol, the polyethylene glycols of the formula



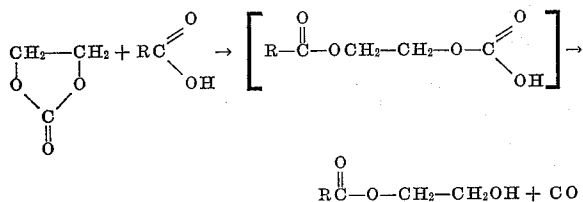
where n is 1 to 26, and the polypropylene glycols of the general formula



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 thioether linkages may also be employed, and these include such compounds as thiodiglycol and 1,2-bis(2-hydroxyethyl-mercapto) 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 suitable reaction equipment and the calculated amount of ethylene carbonate is placed therein. The temperature is raised to the desired point and the reaction allowed to proceed until the minimum acidity is attained.

The reaction probably proceeds through the formation of an intermediate alkyl carbonate as follows:



The amounts of the ethylene carbonate 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 0.5 and 20% by weight based on the weight of the ester material are sufficient in most instances. Amounts in the range of from 4 to 10% are especially preferred. Unreacted carbonate may be recovered and recycled to the next batch.

The temperature at which the reaction best occurs will lie within the range of from 100° to 300° C., preferably 125° to 200° 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 100 to 200° 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

74 g. of adipic acid, 65.6 g. of isooctyl alcohol, and 22.7 g. of 1-4 butylene glycol were placed in a round bottomed flask equipped with a reflux condenser and a water trap. 50 cc. 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 standard potassium hydroxide solution to check the acidity. The final product was found to require 0.50 mg. KOH/g. for neutralization.

100 g. of this ester product were admixed with 8 g. (8.0%) of ethylene carbonate and were heated for 4 hours at 160° C. After this treatment the residual acidity was tested and 0.05 mg. KOH/g. were needed for neutralization.

6

Example II

Following the procedure outlined in Example I above a second complex ester synthetic lubricant was prepared from 74 g. of adipic acid, 65.6 g. of isooctyl alcohol and 22.7 g. of 1-3 butylene glycol.

Titration of this final product showed a residual acidity equivalent to 0.79 mg. KOH/g.

100 g. of this product was admixed with 10 g. ethylene carbonate and heated for 4 hours at a temperature of 160° C. The resulting residual acidity was reduced to an equivalent of 0.02 mg. KOH/g.

Example III

Following the procedure outlined in Example I above a third complex ester synthetic lubricant was prepared from 74 g. of adipic acid, 65.6 g. of 2-ethylhexyl alcohol and 22.7 g. of 1-3 butylene glycol.

Titration of this final product showed a residual acidity equivalent to 0.89 mg. KOH/g.

100 g. of this product was admixed with 12.0% ethylene carbonate and heated for 4.4 hours at 204° C. The resulting residual acidity was reduced to an equivalent of 0.04 mg. KOH/g.

What is claimed is:

1. A process for the reduction of the residual acidity of a synthetic lubricating oil of the complex ester type which comprises reacting the complex ester with ethylene carbonate, said reaction occurring at a temperature within a range of between 100° C. and 250° C. for a period of time sufficient to reduce the residual acidity of the complex ester to an equivalent of below about 0.5 mg. KOH/g.

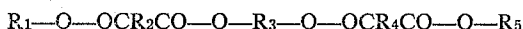
2. A process according to claim 1 wherein the synthetic lubricating oil has the general formula



wherein:

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

3. A process according to claim 1 wherein the synthetic lubricating oil has the general formula



wherein:

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

4. A process according to claim 1 wherein the synthetic lubricating oil has the general formula



wherein:

R_1 is the combining radical of aliphatic alcohols, R_2 the alkyl radical of dibasic acids, R_3 the alkyl radical of a glycol, and R_4 the alkyl radicals of a monobasic acid.

5. A process for the reduction of a residual acidity of a synthetic lubricating oil of a complex ester type which comprises reacting said complex ester with from 0.5% to 20% by weight based on the weight of the ester of ethylene carbonate, said reaction occurring at a temperature within a range of between 100° and 300° C. for a period of time sufficient to reduce the residual acidity of the complex ester to an equivalent of below about 0.5 mg. KOH/g.

6. A process for the reduction of the residual acidity of a synthetic lubricating oil of a complex ester type which comprises reacting said complex ester with from 6% to 12% by weight based on the weight of the ester of ethylene carbonate, said reaction occurring at a temperature within a range of between 150° and 250° C. for a period of time sufficient to reduce the residual acidity of the complex ester to an equivalent of below about 0.5 mg. KOH/g.

7

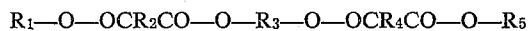
7. A process according to claim 6 wherein said synthetic ester has the general formula



wherein:

R₁ and R₅ are the alkyl radicals of monobasic acid, R₂ and R₄ are the alkyl radicals from glycols, and R₃ is the alkyl radical from a dibasic acid.

8. A process according to claim 6 wherein said synthetic ester has the general formula



8

wherein:

R₁ and R₅ are the combining radicals of alcohols, R₂ and R₄ are the alkyl radicals of dibasic acids, and R₃ is the alkyl radical of a glycol.

5

References Cited in the file of this patent

UNITED STATES PATENTS

1,817,898	Martin	Aug. 4, 1931
2,537,890	Gearhart et al.	Jan. 9, 1951

10