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LUBRICANT COMPOSITION AND METHOD OF REFINING

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ABSTRACT OF THE DISCLOSURE

A method of refining synthetic ester lubricants by adding glycidyl esters of various aliphatic acids, preferably neo-acids to the unrefined ester lubricant. The glycidyl esters, acting an acid scavengers, react with the free acid of the synthetic ester lubricants to reduce the acid value. Additional lubricant materials fully compatible with the ester lubricant are formed in the reaction. The metal corrosion properties of the lubricant are enhanced by either adding additional glycidyl ester to the lubricant or leaving a certain amount of excess glycidyl ester in after refining.

Background of the invention

This invention relates to a method for refining synthetic lubricants, more particularly to a method for reducing the acid value of synthetic ester lubricants, and to new lubricant compositions.

Ester lubricants which are prepared by lubricant manufacturers generally contain an excessive amount of acidity in the form of unreacted acids used in the preparation of the ester. The excess acidity results from (1) incomplete esterification caused by the discontinuance of the esterification reaction before completion can be achieved, it being uneconomical and unfeasible from a time standpoint to allow the reaction to go to virtually 100% completion, (2) the hydrolysis of the esters after they have been formed by the water by-product of the esterification reaction (water is removed during the esterification reaction; however, it is not economically or technically feasible to remove it entirely and thus the residual water causes hydrolysis of the esters to the original alcohol and acid reactants), and (3) the use of unequal equivalents of acid and alcohol. Because of reaction kinetics, it is sometimes desirable to use an excess of acid in order to drive the reaction toward completion. The excess acid above that which can be easily distilled off remains in solution. If an attempt is made to remove all of the acid or alcohol by distillation, excessive losses of the ester product often result and the ester lubricant product frequently undergoes some decomposition resulting in an undesirable darkened product.

A number of methods have been attempted in the past to reduce the acidity of ester lubricants. One of the most popular methods has been the treatment of the acid-alcohol reaction product (ester lubricant) with an aqueous alkali solution such as potassium carbonate or sodium hydroxide or the percolating of the ester reaction product through an alkaline bed. While being effective in reducing the acid value, the alkali treatment has not been entirely satisfactory for a number of reasons. The alkali treatment results in formation of alkali salts which give the end lubricant product a high and undesirable ash content unless copious and time consuming water washing steps are performed. Furthermore, the alkali salts or soaps formed in alkali refining cause emulsions which are difficult or impossible to break and result in a loss of lubricant product.

Another method which has been used for the removal of excess acidity from ester lubricants has been the treatment of the unrefined ester lubricant with short chain alkylene oxides, such as propylene oxide or ethylene oxide. One of the drawbacks to this latter-mentioned process is that the reaction product of alkylene oxides, particularly the lower alkylene oxides, and the free acid is a material which is generally unstable under the high temperature operating conditions to which ester lubricants are normally subjected and either decomposes resulting in the contamination of the lubricant composition or gives a lubricant having excessive volatility. Another problem connected with the use of alkylene oxides is their tendency to polymerize causing the introduction into the lubricant composition of undesirable polymeric materials which are difficult to remove.

Epoxidized oils in which the epoxy group is contained in an internal position have also been used to reduce the free acidity of organic ester solutions. The primary problem with epoxidized oils has been that they are not capable of reducing the acidity to the low levels desired in ester lubricants. The lack of effectiveness of the epoxidized oils is probably attributable to the internal positioning of the epoxy compound within the expodized oil which causes them to be less reactive.

It is impossible to alkali refine some synthetic ester lubricants such as those prepared from polymerized fatty acids, such as polymerized oleic or linoleic acid, often referred to as dimer acids because they are predominantly dibasic C_{36} acids resulting from the combining of two C_{18} acids. Dimer acid forms a salt (or soap) which is more soluble in the ester than in water and thus cannot be removed when conventional alkali refining is attempted.

Ester lubricants must be refined to an acid value of at least 0.1 and preferably 0.05 or lower in order to eliminate the corrosive activity of the lubricant. It has been found that the glycidyl esters used in the process of this invention are highly effective in reducing the acid value to exceptionally low levels, e.g. as low as 0.01, making the esters well suited for lubricant use.

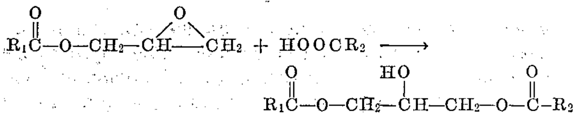
The process of the present invention overcomes the above-noted problems connected with ester lubricant refining by providing a method for reducing the acid values in which the agent used to lower the acid value, a terminal epoxy compound, forms an ester which is in itself a good lubricant additive and which is fully compatible with the principal ester lubricant compositions.

The glycidyl esters used in the present invention are also effective in reducing the metal corrosion, particularly lead corrosion properties, of lubricants, both synthetic ester lubricants and petroleum lubricants.

Description of the invention

This invention is concerned with a method for refining synthetic ester lubricants in which the acid value of the ester lubricant is lowered by the addition of terminal epoxy-containing glycidyl esters of C_5 to C_{22} straight or branched acids preferably the latter in the form of neo-acids. The terminal epoxy group-containig glycidyl esters are reacted with the free acid remaining from the preparation of the synthetic ester lubricants to reduce the acid value and thus the corrosive tendencies of the ester lubricant.

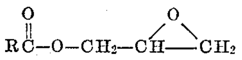
The process is performed by introducing to the unrefined synthetic ester lubricant a sufficient amount of a glycidyl ester to enable removal of the entire residual acid content of the unrefined lubricant. The glycidyl esters react with the free acid in the lubricant to form a hydroxy ester compound with the basic reaction being as follows:



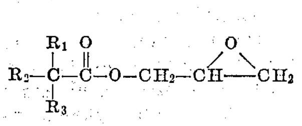
wherein R_1 is a branched or straight chain alkyl group having from about 4 to 21 carbon atoms preferably having a neo structure and from about 7 to about 9 carbon atoms, and R_2 is the residue of a monocarboxylic acid, a dicarboxylic acid, a half ester of a monohydric alcohol and a dicarboxylic acid or carboxyl terminated polyester.

In carrying out the process, the acid value of the unrefined ester lubricant is determined and then at least a stoichiometric amount of glycidyl ester, but preferably an excess of from about 5 to 100 equivalent percent over the stoichiometric amount required for reaction with all of the free carboxyl groups is added. The reaction may be carried out over a wide temperature range but because it is desirable from an economic standpoint to have the reaction proceed as fast as possible, a temperature of 150–250° C. should be used and preferably 190–210° C. The time of the reaction is dependent upon the temperature used and the amount of acid which was present at the beginning of the reaction. Normally, at a temperature of about 200° C., the reaction is carried out for a period of about three hours. After the acid scavenging reaction has been completed, the point of completion being the point at which essentially all free acid has been reacted, the excess glycidyl ester remaining in the ester lubricant solution may be stripped at a temperature of about 250° C. and at a pressure of from about 1 to 5 torr.

The glycidyl esters which may be used as acid scavengers in the present invention include the glycidyl esters of aliphatic acids having from 5 to 22 carbon atoms. The acids may be normal although it is preferable that they be branched and more preferable that they be neo-acids, that is, acids in which the alpha carbon atoms are completely substituted with alkyl groups. The glycidyl esters useful in the present invention are formed by the reaction of epichlorohydrin and an alkali metal salt of the acid of the type described above and should have the general formula:



wherein R is a branched or straight chain alkyl group having from 4 to 21 carbon atoms. The preferred acid scavenging glycidyl ester is a compound having the general formula:



wherein R_1, R_2, and R_3 are all saturated alkyl groups and contain a total of about 7 to 9 carbon atoms. The glycidyl esters having this structure produce, when reacted with the free acid of the ester lubricant, materials which are particularly stable and compatible with the lubricant system. Among other glycidyl esters which may be used in the present invention in addition to the neo-acid esters are the glycidyl esters of pelargonic acid, heptanoic acid, valeric acid, isostearic acid, and oleic acid.

The process of the present invention may be used in reducing the acid value in most if not all synthetic ester lubricants including those prepared from various combinations of aliphatic monocarboxylic acids and dicarboxylic acids having from about 6 to about 36 carbon atoms and monohydric and polyhydric aliphatic alcohols having from about 4 to 20 carbon atoms. Among the ester lubricants which may be refined are simple esters such as dioctylazelate, di(2-ethylhexyl) azelate, di(2-ethylhexyl)sebacate, di(2-ethylhexyl)adipate, dilaurylsuccinate, di-2-ethoxyethylsebacate, di-2-(2'-butoxy-ethoxy) ethylsebacate, pentaerythritoltetracaproate, pentaerythritoltetraisostearate, di(2-ethylhexyl)dimerate, and complex esters having a structural formula such as:

X—Y—Z—Y—X

wherein X is a monohydric alcohol residue, Y is a dibasic acid residue, and Z is a glycol residue, or a structural formula such as A—B—C—B—A wherein A is a monocarboxylic acid residue, B is a glycol residue, and C is a dicarboxylic acid residue. Examples of complex esters which may be treated are the reaction products of 2-ethyl-1,3-hexanediol, sebacic acid, and 2-ethylhexanoic acid; adipic acid, diethylene glycol, and 2-ethylhexanoic acid; sebacic acid, trimethylolpropane, and pelargonic acid; sebacic acid, trimethylolethane, and hexanoic acid; and sebacic acid, 1,3,5,7-octanetetraol and pentanoic acid.

The hydroxy ester products formed in the process of this invention are fully compatible with the ester lubricants and have excellent high performance lubricant qualities themselves and thus do not detract from the ester lubricant capacity of the refined ester lubricant and in fact they supplement it while alleviating, because of their stability or lack of volatility, the usual need for removal of the free acid reaction product. The process of this invention is effective in refining both synthetic ester lubricating oils and greases.

Following the method described herein, it has been possible to lower the acid value of synthetic ester lubricants to the point no carboxyl content is detectible. One of the advantages of the present process is that it is possible to refine the lubricant in the same vessel in which it is prepared in the initial esterification reaction and thus alleviate the need for additional handling and equipment. This is possible because of the relatively short time which is required to accomplish the reduction of the acid value to the desired level and the simplicity of the process.

The metal corrosion particularly lead corrosion properties of lubricants are markedly improved using the glycidyl esters heretofore described. The esters are effective over a broad range but preferably should be added to the lubricant in amounts of from 0.1 to 5.0 percent by weight based on the total weight of the lubricant. They are effective in reducing the metal corrosion properties of both petroleum and synthetic ester lubricants.

The glycidyl esters when utilized as metal corrosion inhibitors may be added directly to the lubricant after refining, or when refining has been accomplished using the esters in the manner described herein, excess glycidyl ester may be used and can be left in the lubricant after refining.

To further illustrate the method of the present invention, the following examples are provided. It is to be understood that these examples are illustrative only and are not to be considered limitative of the scope of the invention.

EXAMPLE I

1500 grams of a synthetic ester lubricant, 2-ethylhexyl dimerate prepared from the reaction of 2-ethylhexyl alcohol and dimeric acid (a dibasic polymerized oleic acid having about 36 carbon atoms) was prepared. The acid value of the 2-ethylhexyl dimerate was determined to be 2.20. A reaction vessel containing the di(2-ethylhexyl)-dimerate was charged with 30 grams of the glycidyl ester of a neo-acid (sold under the trade name Carbura E), the glycidyl ester having a molecular weight average of 245. The 30 grams represented a 100% excess over the stoichiometric amount required to react with all of the free acid contained within the synthetic ester lubricant. The reaction vessel was heated to a temperature of 215–230° C. for a period of 6 hours after which the excess glycidyl ester was stripped off at a temperature of about

230° C. while subjecting the reaction vessel to a pressure of 1 to 2 torr. The resulting ester lubricant had an acid value of 0.05.

EXAMPLE II

A 1200 lb. batch of di(2-ethylhexyl)dimerate was prepared and the acid value was determined to be 3.2. 34 lbs. of the same glycidyl ester as was used in Example I and representing a 100% excess over the stoichiometric amount required to completely remove the free acid content of the ester lubricant was added. The resulting mixture was heated for 3 hours at a temperature of from 209–215° C. after which time the acid value had been reduced to 0.04. The excess Cardura E was then stripped for a period of 5 hours at a temperature of 211–219° C. and at a pressure of 5 torr.

EXAMPLE III

A 95 lb. batch of di(2-ethylhexyl)dimerate lubricant, the dimer acid being a high purity dimer acid having from 95–98% dimer acid with the remaining portion being substantially trimer acid was prepared and the acid value was determined to be 4.0. 3 lbs. of the glycidyl ester used in Example I and representing a 100% excess over the stoichiometric amount required for complete removal of the free acid content of the di(2-ethylhexyl)-dimerate was added and the mixture was heated for 3 hours at temperatures ranging from 203–213° C. The pressure was reduced to 5 torr to strip off the excess glycidyl ester. The stripping operation was continued for 3 hours after which time the lubricant was cooled and the acid value was determined to be 0.05.

EXAMPLE IV

1800 grams of a synthetic ester lubricant, pentaerythritol tetraisostearate was prepared by the esterification of pentaerythritol with isostearic acid, a branched fatty acid described in United States Patent No. 2,812,342, and the acid value of the pentaerythritol tetraisostearate was determined to be 3.50. To the unrefined lubricant was added 34.5 grams of the glycidyl ester described in Example I which represented an excess of 25% over the stoichiometric amount required to reduce the acid value to 0. The resulting mixture was heated for 1 hour at 220° C., at which point the acid value had been reduced to 2.09. Heating was continued for another hour at 220° C. after which an additional 30 grams of the glycidyl ester were added and then the heating was continued at 230° C. for 4 hours after which time the acid value had been reduced to 0.07. The refined lubricant was then stripped of the excess glycidyl ester by heating for approximately 1 hour at 245° C. and at a pressure of 4 torr.

EXAMPLE V

150 grams of an unrefined lubricant ester, di(2-ethylhexyl)dimerate having an acid value of 3.2 was treated with 6.41 grams (representing a 200% excess) of the glycidyl ester of heptanoic acid (2,3-epoxy-propylheptanote) for 2 hours at a temperature of 230° C. The resulting lubricant had an acid value of 0.05.

EXAMPLE VI

150 grams of the same unrefined ester lubricant as was used in Example V was reacted with 10 grams (representing a 300% excess) of 2,3-epoxy propyloleate. The reaction was conducted at a temperature of 230° C. for a period of 3 hours after which the acid value was determined to be 0.04.

EXAMPLE VII

A pentaerythritol tetraisostearate lubricant having an acid value of 6.4 such as is described in Example IV was prepared and divided into two portions one of which was treated with the same glycidyl ester and in the same manner as described in Example IV with the final refined product having an acid value of 0.08. The product contained approximately 6% by weight of the reaction product of the glycidyl ester and free acid materials contained within the ester lubricant prior to refining. The second portion of pentaerythritol tetraisostearate was refined with sodium hydroxide in the following manner. The unrefined ester was first diluted with an equal volume of toluene, then sodium hydroxide equivalent to about 300% excess of the stoichiometric amount required to react with the free acid was added as a 10% aqueous solution. After vigorous agitation, the excess caustic solution including the soap heel was allowed to settle from the organic layer and drawn off. The organic solution was then washed with copious quantities of distilled water until the wash water drained from the solution was neutral to phenolphthalein. The organic layer was then heated in vacuo to distill off the toluene and last traces of moisture. The alkali refining was accomplished with great difficulty and considerable loss of product. The end acid value was 0.04.

The glycidyl ester refined and the alkali refined lubricants were then subjected to a Falex Extreme Pressure Test for evaluation of the load bearing properties of the two materials. No additives such as anticorrosive or extreme pressure agents were incorporated within the lubricants when the test was conducted. The tests were performed using a Fayville-LaValle lubricant tester. The test is described on pp. 58 and 59 of the Lubrication Engineers Manual, United States Steel Corporation, Pittsburgh, Pa. The test was conducted at 290 r.p.m. for 2 minutes at 300 lbs. load, 1 minute for 500 lbs. load, and 1 minute at each 250 lbs. increment thereafter. The results of the tests are shown in Table I below. Failure was detected by shearing of the brass pin of the test equipment.

TABLE I

	Glycidyl ester refined pentaerythritol tetra-isostearate		Alkali refined pentaerythritol tetraisostearate	
Load, lbs.	Start torque, lb.-in.	Finish torque, lb.-in.	Start torque, lb.-in.	Finish torque, lb.-in.
300	14	13	13	13
500	16	15	16	16
750	19	19	20	19
1,000	21	21	21	20
1,250	24	23	22	21
1,500	26	32	24	24
1,750	35	29	30	Failed.
2,000	34	Failed		

The above data shows that an ester lubricant, which has been refined with a glycidyl ester and contains as a minor portion of the lubricant the reaction product of the glycidyl ester with free acids and partial esters resulting from incomplete esterification of the ester lubricant, has good load-bearing properties which are equivalent to or exceed the load-bearing properties of an alkali refined lubricant ester.

EXAMPLES VIII AND IX

A metal corrosion test was performed in the following manner. The refined lubricant composition of Example I containing 0.5% part by weight of phenothiazine as an oxidation inhibitor was heated to 375° F. and agitated with a polished and preweighted lead coupon of standard size for one hour. During the test dry air was bubbled through the test liquid at a rate of 2 cubic feet per hour. The coupon was solvent washed, dried and reweighed after the conclusion of the test.

The above test was repeated in all particulars except 1% by weight of the glycidyl ester of a neo-acid having 7 to 9 carbon atoms and sold under the trademark Cardura E was added to the refined ester of Example I before the corrosion test was conducted. The weight loss or gain is reported in mgs./in.^{2} in Table II below for each test.

TABLE II

Example	Material	Acid value	Lead coupon weight loss (mgs./in.^{2})
8	Refined ester	0.05	25.1
9	Refined ester + 1% by weight of glycidyl ester.*		5.4

* Cardura E.

The above corrosion test results demonstrate the effectiveness of the glycidyl esters as corrosion inhibitors inasmuch as the corrosion properties of the lubricant were markedly diminished by the inclusion in the lubricant of the glycidyl ester.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore, only those limitations should be imposed as are indicated in the appended claims.

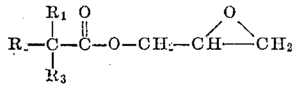
We claim:

1. A method for refining an ester lubricant containing free carboxyl groups which comprises reacting said free carboxyl groups in said lubricant with a glycidyl ester of an aliphatic acid having from 5 to 22 carbon atoms.

2. The method of claim **1** wherein the acid value of said lubricant is reduced to a value below about 0.10.

3. The method of claim **2** wherein said aliphatic acid is a branched acid.

4. The method of calim **3** wherein said glycidyl ester has the structure:



wherein R_1, R_2 and R_3 are the same or different saturated alkyl groups having a total of from 7 to 9 carbon atoms.

5. The method of claim **1** wherein said lubricant is a polymerized fatty acid ester.

6. A lubricant composition comprising as a major component a synthetic ester and as a minor component the reaction product of a glycidyl ester of an aliphatic acid having from 5 to 22 carbon atoms and a carboxylic acid.

7. The composition of claim **6** wherein said carboxylic acid is selected from the group consisting of aliphatic monocarboxylic acids, aliphatic dibasic carboxylic acids, partial esters of aliphatic dibasic acids, carboxyl-terminated polyesters and mixtures thereof.

8. The composition of claim **7** wherein said reaction product comprises up to 5% by weight of said lubricant.

9. The composition of claim **7** wherein said aliphatic acid component of the glycidyl ester is a branched acid.

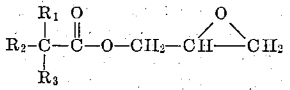
10. The composition of claim **8** wherein said aliphatic acid is a neo-acid having from about 9 to about 11 carbon atoms.

11. The composition of claim **7** wherein said major component is an ester of a polymerized fatty acid and a polyol.

12. A method of inhibiting the metal corrosion properties of a lubricant member of the group consisting of ester lubricants and petroleum lubricants which comprises adding to said lubricant a glycidyl ester of a carboxylic acid.

13. The method of claim **12** wherein said aliphatic acid is a branched acid.

14. The method of claim **13** wherein said glycidyl ester has the structure:



wherein R_1, R_2, and R_3 are the same or different saturated alkyl groups having a total of from 7 to 9 carbon atoms.

15. The method of claim **12** wherein from about 0.1 to about 5% by weight of said glycidyl ester is added to said lubricants.

16. The method of claim **15** wherein said lubricant is a synthetic ester.

17. The method of claim **15** wherein said lubricant is a petroleum lubricant.

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