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3,579,450

LUBRICANTS AND FUELS CONTAINING EPOXIDE TREATED ESTERS

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No Drawing. Continuation of application Ser. No. 712,606, Mar. 13, 1968, which is a continuation-in-part of applications Ser. No. 567,052, now Patent No. 3,522,179, and Ser. No. 567,320, now Patent No. 3,381,022, both July 22, 1966. This application Oct. 3, 1969, Ser. No. 866,084

Int. Cl. C10m 1/26

U.S. Cl. 252—56

19 Claims

ABSTRACT OF THE DISCLOSURE

A process for post-treating oil-soluble esters of mono- or polycarboxylic acids and polyhydric alcohols with organic epoxides. The acyl moiety of the esters is derived from mono- or polycarboxylic acids containing at least about fifty aliphatic carbon atoms exclusive of the carboxyl carbon atoms. The products are useful as lubricant and fuel additives. A typical example of the process would be the post-treatment of a diester of polyisobutenyl-substituted succinic acid and sorbitol with propylene oxide.

This is a continuation of application Ser. No. 712,606, filed Mar. 13, 1968, and now abandoned, which is a continuation-in-part of applications Ser. No. 567,052, now Pat. No. 3,522,179, and Ser. No. 567,320, now Pat. No. 3,381,022, both filed July 22, 1966, which in turn are respectively a continuation-in-part and continuation of application Ser. No. 274,905, filed Apr. 23, 1963, and now abandoned.

This invention relates to a process for treating carboxylic acid esters, to the compositions of matter resulting from this process, and to lubricants and fuels containing these compositions of matter. In particular, the invention is concerned with the post-treatment of esters of high molecular weight carboxylic acids with organic epoxides, the compositions of matter which results from treating the esters with the epoxides, and to lubricants and fuels containing these compositions.

The prior art discloses many esters of high molecular weight carboxylic acids as useful additives in fuel and lubricant compositions, for example, French patent 1,396,645; British patents 981,850 and 1,055,337; and U.S. patents 3,255,108; 3,311,558; 3,331,776; and 3,346,354. The present invention is directed to a process for post-treating esters of this general type with at least one organic epoxide to provide novel compositions of matter also useful as additives in lubricant and fuel compositions.

In accordance with the foregoing, it is a principal object of this invention to provide a novel chemical process.

A further object of the invention is to provide a process for post-treating certain esters with organic epoxides.

An additional object is to provide novel compositions of matter resulting from the post-treatment of certain carboxylic acid esters with organic epoxides.

A still further object is to provide lubricants and fuels containing compositions produced by post-treating certain esters with organic epoxides.

These and other objects of this invention are accomplished by providing a process comprising contacting (A) at least one oil-soluble ester of a mono- or polycarboxylic acid and a polyhydric alcohol where the carboxylic acid moiety of the ester is characterized by at least about fifty aliphatic carbon atoms exclusive of the carboxyl carbon atoms and the alcohol moiety contains up to about forty aliphatic carbon atoms with (B) at least one organic

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epoxide, the amount of (A) to (B) in the reaction mixture being such that the ratio of equivalents alcohol present in the ester to equivalents of epoxide is about 1:0.05 to about 1:5. The compositions produced by this process, the process, and lubricants and fuels containing the compositions are described in more detail hereinafter.

The esters to be post-treated with the organic epoxides according to the process of the present invention are esters of mono- and polycarboxylic acids containing at least about fifty aliphatic carbon atoms exclusive of the carboxyl carbon atoms. The alcohol moiety of the esters contemplated is derived from a polyhydric alcohol containing up to about forty aliphatic carbon atoms. These esters are known in the prior art or can be readily prepared from available intermediates according to conventional procedures. Since the foregoing enumerated patents disclose many esters of this type and various processes for their preparation, these patents are incorporated herein for the sake of brevity.

For the most part, these patents are directed to esters of substituted succinic acids and aliphatic polyhydric alcohols. However, the present invention contemplates the post-treatment of similar esters prepared from monocarboxylic acids as well as polycarboxylic acids other than succinic acids. Such esters can be prepared from these mono- and polycarboxylic acid acylating agents and the appropriate aliphatic alcohols by following the same general procedure as used in the preparation of the succinic acid esters in the above patents.

The acyl radical of the esters to be treated by the process of this is derived from a mono- or polycarboxylic acid. One particularly important characteristic of the acyl radical is its size. Thus, the radical should contain at least about fifty aliphatic carbon atoms exclusive of the carboxylic carbon atoms. This limitation is based upon both oil-solubility considerations and the effectiveness of the compositions as additives in lubricants and fuels. Another important aspect of the acyl radical is that it preferably should be substantially saturated, i.e., at least about 95% of the total number of the carbon-to-carbon covalent linkages therein preferably should be saturated linkages. In an especially preferred aspect of the invention, at least about 98% of these covalent linkages are saturated. Obviously, all of the covalent linkages may be saturated. A greater degree of unsaturation renders the esters more susceptible to oxidation, degradation, and polymerization and this lessens the effectiveness of the final products as lubricant and fuel additives.

In addition, the acyl radical of the esters should be substantially free from oil-solubilizing pendant groups, that is, groups having more than about six aliphatic carbon atoms. Although, some such oil-solubilizing pendant groups may be present, they preferably will not exceed one such group for every twenty-five aliphatic carbon atoms in the principal hydrocarbon chain of the acyl radical.

The acyl radical may contain polar substituents provided that the polar substituents are not present in proportions sufficiently large to alter significantly the hydrocarbon character of the radical. Typical suitable polar substituents are halo, such as chloro and bromo, oxo, oxy, formyl, sulfonyl, sulfinyl, thio, nitro, etc. Such polar substituents, if present, preferably will not exceed 10% by weight of the total weight of the hydrocarbon portion of the carboxylic acid radical exclusive of the carboxyl group.

Carboxylic acid acylating agents suitable for preparing the esters are well-known in the art and have been described in detail, for example, in U.S. Patents 3,087,936; 3,163,603; 3,172,892; 3,189,544; 3,219,666; 3,272,746; 3,288,714; 3,306,907; 3,331,776; 3,340,281; 3,341,542; and 3,346,354. In the interest of brevity, these patents are incorporated herein for their disclosure of suitable mono- and polycarboxylic acid acylating agents

which can be used for the preparation of the esters used as starting materials in the present invention.

As disclosed in the foregoing patents, there are several processes for preparing the acids. Generally, the process involves the reaction of (1) an ethylenically unsaturated carboxylic acid, acid halide, or anhydride with (2) an ethylenically unsaturated hydrocarbon containing at least about fifty aliphatic carbon atoms or a chlorinated hydrocarbon containing at least about fifty aliphatic carbon atoms at a temperature within the range of about 100°–300° C. The chlorinated hydrocarbon or ethylenically unsaturated hydrocarbon reactant can, of course, contain polar substituents, oil-solubilizing pendant groups, and be unsaturated within the general limitations explained hereinabove. It is these hydrocarbon reactants which provides most of the aliphatic carbon atoms present in the acyl moiety of the final products.

When preparing the carboxylic acid acylating agent according to one of these two processes, the carboxylic acid reactant usually corresponds to the formula



where R_o is characterized by the presence of at least one ethylenically unsaturated carbon-to-carbon covalent bond and n is an integer from one to six and preferably one or two. The acidic reactant can also be the corresponding carboxylic acid halide, anhydride, ester, or other equivalent acylating agent and mixtures of one or more of these. Ordinarily, the total number of carbon atoms in the acidic reactant will not exceed ten and generally will not exceed six. Preferably the acidic reactant will have at least one ethylenic linkage in an α,β -position with respect to at least one carboxyl function. Exemplary acidic reactants are acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, glutaric acid, chloromaleic acid, aconitic acid, crotonic acid, methylcrotonic acid, sorbic acid, 3-hexenoic acid, 10-decenoic acid, and the like. Due to considerations of economy and availability, these acid reactants usually employed are acrylic acid, methacrylic acid, maleic acid, and maleic anhydride.

As is apparent from the foregoing discussion, the carboxylic acid acylating agents may contain cyclic and/or aromatic groups. However, the acids are essentially aliphatic in nature and in most instances, the preferred acid acylating agents are aliphatic mono- and polycarboxylic acids, anhydrides and halides.

The substantially saturated aliphatic hydrocarbon-substituted succinic acid and anhydrides are especially preferred as acylating agents in the preparation of the esters used as starting materials in the present invention. These succinic acid acylating agents are readily prepared by reacting maleic anhydride with a high molecular weight olefin or a chlorinated hydrocarbon such as a chlorinated polyolefin. The reaction involves merely heating the two reactants at a temperature of about 100°–300° C., preferably, 100°–200° C. The product from such a reaction is a substituted succinic anhydride where the substituent is derived from the olefin or chlorinated hydrocarbon as described in the above cited patents. The product may be hydrogenated to remove all or a portion of any ethylenically unsaturated covalent linkages by standard hydrogenation procedures, if desired. The substituted succinic anhydrides may be hydrolyzed by treatment with water or steam to the corresponding acid and either the anhydride or the acid may be converted to the corresponding acid halide or ester by reacting with phosphorus halide, phenols, or alcohols.

The ethylenically unsaturated hydrocarbon reactant and the chlorinated hydrocarbon reactant used in the preparation of the acylating agents are principally the high molecular weight, substantially saturated petroleum fractions and substantially saturated olefin polymers and the corresponding chlorinated products. The polymers and chlorinated polymers derived from mono-olefins having from

two to about thirty carbon atoms are preferred. The especially useful polymers are the polymers of 1-mono-olefins such as ethylene, propene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. These are exemplified by 2-butene, 3-pentene, and 4-octene.

The interpolymers of 1-mono-olefins such as illustrated above with each other and with other interpolymerizable olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins, are also useful sources of the ethylenically unsaturated reactant. Such interpolymers include for example, those prepared by polymerizing isobutene with styrene, isobutene with butadiene, propene with isoprene, propene with isobutene, ethylene with piperylene, isobutene with chloroprene, isobutene with p-methyl-styrene, 1-hexene with 1,3-hexadiene, 1-octene with 1-hexene, 1-heptene with 1-pentene, 3-methyl-1-butene with 1-octene, 3,3-dimethyl-1-pentene with 1-hexene, isobutene with styrene and piperylene, etc.

For reasons of oil-solubility and stability, the interpolymers contemplated for use in preparing the acylating agents of this invention should be substantially aliphatic and substantially saturated, that is, they should contain at least about 80% and preferably about 95%, on a weight basis, of units derived from aliphatic mono-olefins. Preferably, they will contain no more than about 5% olefinic linkages based on the total number of the carbon-to-carbon covalent linkages present.

The chlorinated hydrocarbons and ethylenically unsaturated hydrocarbons used in the preparation of the acylating agents can have molecular weights of from about 700 up to about 100,000 or even higher. The preferred reactants are the above described polyolefins and chlorinated polyolefins having an average molecular weight of about 700 to about 5,000. When the acylating agent has a molecular weight in excess of about 10,000, the acylated nitrogen composition also possess viscosity index improving qualities.

In lieu of the high molecular weight hydrocarbons and chlorinated hydrocarbons discussed above, hydrocarbons containing activating polar substituents which are capable of activating the hydrocarbon molecule in respect to reaction with an ethylenically unsaturated acid reactant may be used in the above-illustrated reactions for preparing the acylating agents. Such polar substituents include sulfide and disulfide linkages, and nitro, mercapto, carbonyl, and formyl radicals. Examples of these polar-substituted hydrocarbons include polypropylene sulfide, dipolyisobutene disulfide, nitrated mineral oil, di-polyethylene sulfide, brominated polyethylene, etc.

The acylating agents may also be prepared by halogenating a high molecular weight hydrocarbon such as the abovedescribed olefin polymers to produce a poly-halogenated product, converting the poly-halogenated product to a poly-nitrile, and then hydrolyzing the poly-nitrile. They may be prepared by oxidation of a high molecular weight polyhydric alcohol with potassium permanganate, nitric acid, or a similar oxidizing agent. Another method for preparing such poly-carboxylic acids involves the reaction of an olefin or a polar-substituted hydrocarbon such as a chloropolyisobutene with an unsaturated poly-carboxylic acid such as 2-pentene-1,3,5-tricarboxylic acid prepared by dehydration of citric acid. Mono-carboxylic acid acylating agents may be obtained by oxidizing a mono-alcohol with potassium permanganate or by reacting a halogenated high molecular weight olefin polymer with a ketene. Another convenient method for preparing mono-carboxylic acid involves the reaction of metallic sodium with an acetoacetic ester or a malonic ester of an alkanol to form a sodium derivative of the ester and the subsequent reaction of the sodium derivative with a halogenated high molecular weight hydrocarbon such as brominated wax or brominated polyisobutene.

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Mono-carboxylic and poly-carboxylic acid acylating agents can also be obtained by reacting chlorinated mono- and poly-carboxylic acids, anhydrides, acyl halides, and the like with ethylenically unsaturated hydrocarbons or ethylenically unsaturated substituted hydrocarbons such as the polyolefins and substituted polyolefins described hereinbefore in the manner described in 3,340,281.

The mono-carboxylic and poly-carboxylic acid anhydrides are obtained by dehydrating the corresponding acids. Dehydration is readily accomplished by heating the acid to a temperature above about 70° C., preferably in the presence of a dehydration agent, e.g. acetic anhydride. Cyclic anhydrides are usually obtained from poly-carboxylic acids having acid radicals separated by no more than three carbon atoms such as substituted succinic or glutaric acid, whereas linear anhydrides are obtained from poly-carboxylic acids having the acid radicals separated by four or more carbon atoms.

The acid halides of the mono-carboxylic and polycarboxylic acids can be prepared by the reaction of the acids or their anhydrides with a halogenating agent such as phosphorus tribromide, phosphorus pentachloride, or thionyl chloride.

The esters which are to be post-treated are generally prepared by reacting the carboxylic acid acylating agent, preferably the acid per se, its acyl chloride, or an anhydride thereof, with an aliphatic polyhydric alcohol containing up to about forty aliphatic carbon atoms according to conventional processes for preparing carboxylic acid esters. These alcohols are characterized by two to ten hydroxyl groups and can be quite diverse in structure and chemical composition. Typical alcohols are alkylene glycols such as ethylene glycol, propylene glycol, trimethylene glycol, butylene glycol, and poly glycols such as diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, and other alkylene glycols and polyalkylene glycols in which the alkylene radical contains from 2 to about 8 carbon atoms. Other useful polyhydric alcohols include glycerol, monomethyl ether of glycerol, pentaerythritol, 9,10-dihydroxystearic acid, the ethyl ester of 9,10-dihydroxystearic acid, 3-chloro-1,2-propanediol, 1,2-butanediol, 1,4-butanediol, 2,3-hexanediol, 2,4-hexanediol, pinacol, erythritol, arabitol, sorbitol, mannitol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,4-(2-hydroxyethyl)-cyclohexane, 1,4-dihydroxy-2-nitrobutane, 1,4-di(2-hydroxyethyl)-benzene, the carbohydrates such as glucose, mannose, mannose, glyceraldehyde, and galactose, and the like, amino alcohols such as di(2-hydroxyethyl)amine, tri-(3-hydroxypropyl)amine, N,N'-di(hydroxyethyl)ethylenediamine, copolymer of allyl alcohol and styrene, etc.

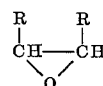
Included within the group of aliphatic alcohols are those polyhydric alcohols containing at least three hydroxyl groups, at least one of which has been esterified with a monocarboxylic acid having from eight to about thirty carbon atoms such as octanoic acid, oleic acid, stearic acid, linoleic acid, dodecanoic acid, or tall oil acid. Examples of such partially esterified polyhydric alcohols are the mono-oleate of sorbitol, the mono-oleate of glycerol, the mono-stearate of glycerol, the di-stearate of sorbitol, and the di-dodecanoate of erythritol.

A preferred class of esters are those prepared from aliphatic alcohols containing up to ten carbon atoms, and especially those containing three to ten carbon atoms. This class of alcohols includes glycerol, erythritol, pentaerythritol, gluconic acid, glyceraldehyde, glucose, arabinose, 1,7-heptanediol, 2,4-heptanediol, 1,2,3-hexanetriol, 1,2,4-hexanetriol, 1,2,5-hexanetriol, 2,3,4-hexanetriol, 1,2,3-butanetriol, 1,2,4-butanetriol, quinic acid, 2,2,6,6-tetraakis-(hydroxymethyl)cyclohexanol, 1,10-decanediol, digitolose and the like. The esters prepared from aliphatic alcohols containing at least three hydroxyl groups and up to ten carbon atoms are particularly preferred.

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As especially preferred class of polyhydric alcohols for preparing the esters used as starting materials in the present invention are the polyhydric alkanols containing three to six carbon atoms and having at least three hydroxyl groups. Such alcohols are exemplified in the above specifically identified alcohols and are represented by glycerol, erythritol, pentaerythritol, mannitol, sorbitol, 1,2,4-hexanetriol, and the like.

The organic epoxides used in the post-treatment of the esters can have up to about forty carbon atoms and may be represented by the formula



where each R is independently hydrogen or an aliphatic, cycloaliphatic, or aromatic radical. Normally R will be hydrogen or an alkyl, haloalkyl, cycloalkyl, halocycloalkyl, aryl, or haloaryl radical having no more than one halogen radical for every three carbon atoms. The lower alkylene and haloalkylene epoxides, including the cycloalkylene epoxides, containing from two to eight carbon atoms are especially preferred for post-treating the esters. The arylenes and haloarylenes epoxides contemplated are those containing from one to two resonant ring structures such as phenyl, naphthyl, or substituted phenyl and naphthyl such as alkyl phenyl or halophenyl (e.g., tolyl, cresyl, xylyl, methyl naphthyl, chlorophenyl, etc.). Phenyl and halophenyl radicals are the preferred R groups among the aryl epoxides. The epoxides in which at least one of the carbon atoms attached to the oxygen in the oxirane ring is also attached to two hydrogen atoms are especially preferred. Those epoxides are designated as terminal epoxides.

Specific examples of the organic epoxides useful in the process of this invention are ethylene oxide, propylene oxide, 1,2-epoxybutane, 1,2-epoxy-3-butane, 1,2-epoxypentane, 1,2-epoxyheptane, 1,2-epoxydodecane, 2,3-epoxybutane, 1,2-epoxy-5-hexane, 1,2-epoxycyclohexane, 2,3-epoxyheptane, 1,2-epoxyoctane, epichlorohydrin, 1,2-epoxy-4-chlorobutane, styrene oxide, p-methylstyrene oxide, p-chloro-styrene oxide, epoxidized soyabean oil, methyl ester of 9,10-epoxy-stearic acid, and epoxidized fatty acid esters in which the fatty acid radical has up to about thirty aliphatic carbon atoms and the alcohol radical is derived from an aliphatic alcohol having up to about eight carbon atoms. Ethylene oxide, propylene oxide and epichlorohydrin are particularly preferred for post-treating the esters.

The post-treatment process involves contacting the ester or mixture of esters with an epoxide or mixture of epoxides, usually in the presence of an inert diluent, while maintaining a temperature of about 25° C. up to the decomposition temperature of the ester or epoxide involved and usually at a temperature within a range of about 50°-250° C. Good results are achieved when the post-treatment is conducted at a temperature of about 70°-200° C. The esters and epoxides are easily brought into contact simply by mixing them in any convenient manner. It is usually desirable to employ some type of mechanical agitation to facilitate thorough contact of the esters and epoxides.

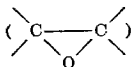
Any substantially inert organic liquid can be used as a diluent. Suitable diluents include the aliphatic, cycloaliphatic, and aromatic hydrocarbons and their chlorinated analogs exemplified by pentane, hexane, heptane, cyclohexane, benzene, toluene, xylene, chlorobenzene, chlorohexanes, and the like. Mineral oils, naphthas, ligroin, and the like may also be used as a diluent. In many instances, the esters are prepared as oil-solutions and these oil-solutions can be used in the post-treating process, the oil functioning as a diluent.

The precise means by which this process improves the dispersancy characteristics of the esters is not known.

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The epoxides are believed to react with nonesterified hydroxyl groups although they may also react with any free carboxyl groups present. In a preferred aspect of the invention, the esters will be substantially free from unreacted carboxyl groups, for example, the diesters of the succinic acids as opposed to the monoesters. This can be achieved by using a stoichiometric equivalent or an excess of alcohol in preparing the esters. An ester is considered substantially free from free carboxyl groups when not more than about 10% of the number of carboxyl functions present are free carboxyl groups, i.e., —COOH . Ordinarily the number of free carboxyl groups will be less than about 5% of the total number in the ester composition being treated in this preferred aspect of the invention. When free carboxyl groups are present, the amount of epoxide employed can be increased to provide up to about one equivalent of epoxide for each equivalent of free carboxyl group in addition to that used for post-treating the ester.

The esters and epoxides should be contacted in an amount such that the ratio of equivalents of alcohol present in the ester to the equivalents of epoxide will be about 1:0.05 to about 1:5 and preferably 1:0.1 to about 1:2. For purposes of using this ratio, the equivalent weight of an alcohol is deemed to be its molecular weight divided by the number of hydroxyl groups present whether or not they are esterified. Similarly, the equivalent weight of an epoxide is deemed to be the molecular weight of the epoxide divided by the number of oxirane rings



present in the epoxy molecule. By way of example, if the ester to be treated contains one mole of pentaerythritol in the alcoholic moiety, the ester contains four equivalents of alcohol. According to the present process, such an ester would be contacted with 0.2 to 20, preferably 0.4 to 8 equivalents of epoxide. This equivalent ratio is offered merely as a guideline to define the effective ratios of ester and epoxide and is in no way intended to imply that all the epoxide used will react with the ester. However, within this ratio, it is possible to determine the optimum ratio of ester and epoxide for any given ester or combination of esters and any given epoxide or combination of epoxides through routine evaluation.

The following examples illustrate the preferred embodiments of this invention. As used in these examples and elsewhere in the specification and claims, "percentage," and "parts" refer to percent by weight and parts by weight unless otherwise indicated.

EXAMPLE 1

An ester is prepared by reacting 600 parts of polyisobutenyl-substituted succinic anhydride (average molecular weight—1100) with 230 parts of polypropylene glycol (average molecular weight—425) in the presence of 547 parts of a mineral oil for about 17 hours at 150°–160° C. while blowing the reaction mixture with nitrogen. Then 32.8 parts of an acidified clay (commercially available as Super Filtrol from Filtrol Corporation) is added and the mixture heated to about 200° C. for an additional 11 hours with hydrogen blowing and subsequently filtered. The filtrate is an oil solution of the desired ester.

To the filtrate there is added 43.2 parts of propylene oxide and this mixture is heated at 85°–90° C. for 17 hours. The reaction mixture is then stripped to 85° C. at a pressure of 80 mm. (Hg). The resulting material is an oil solution of the desired propylene oxide treated ester.

EXAMPLE 2

(A) A carboxylic acid ester is prepared by slowly adding 3240 parts of a high molecular weight carboxylic acid (prepared by reacting chlorinated polyisobutylene and acrylic acid in a 1:1 equivalent ratio and having an average molecular weight of 982) to a mixture of 200

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parts of sorbitol and 1000 parts of diluent oil over a 1.5-hour period while maintaining a temperature of 115°–125° C. Then 400 parts of additional diluent oil are added and the mixture is maintained at about 195°–205° C. for 16 hours while blowing the mixture with nitrogen. An additional 755 parts of oil are then added, the mixture cooled to 140° C., and filtered. The filtrate is an oil solution of the desired ester.

(B) The above ester is post-treated with propylene oxide by adding 108 parts of propylene oxide to 5105 parts of the filtrate and 25 parts of pyridine while maintaining a temperature of 80°–90° C. Then the mixture is heated to 110°–120° C. for 2 to 3 hours and stripped to 170° C. at a pressure of 15 mm. (Hg). The stripped product is the desired epoxide treated product.

EXAMPLE 3

(A) An ester is prepared by heating 658 parts of a carboxylic acid having an average molecular weight of 1018 (prepared by reacting chlorinated polyisobutene with acrylic acid) with 22 parts of pentaerythritol while maintaining a temperature of about 180°–205° C. for about 18 hours during which time nitrogen is blown through the mixture. The mixture is then cooled to about 90° C. and maintained at 90°–100° C. for about 2 hours while 14 parts of ethylene oxide are slowly added. The mixture is subsequently heated to about 190°–200° C. for about 4.5 hours while slowly adding an additional 16 parts of ethylene oxide to the mixture. This mixture is then maintained at this latter temperature for an additional 2 hours, then stripped to 150° C. at a pressure of 18 mm. (Hg), and filtered. The filtrate is an oil solution of the desired ethylene oxide treated ester.

(B) The ester of A is post-treated with epichlorohydrin following the same general procedure but substituting an equivalent amount of epichlorohydrin for the ethylene oxide.

EXAMPLE 4

(A) An ester is prepared by heating 3318 parts of polyisobutenyl-substituted succinic anhydride (average molecular weight—1100), 408 parts of pentaerythritol, and 2445 parts of diluent oil at 150° C. for 5 hours and thereafter at 200°–210° C. for an additional 5 hours. The reaction mixture is then filtered, the filtrate being an oil solution of the desired ester.

(B) The foregoing ester is post-treated with an epoxide by heating 2500 parts of the filtrate to about 80° C. and thereafter adding 123 parts of propylene oxide over a period of 4 hours while maintaining a temperature at 80°–90° C. Upon completion of the addition of the propylene oxide, the resulting mixture is heated an additional 3 hours at a temperature of 80°–90° C. and subsequently stripped to 150° C. at a pressure of 20 mm. (Hg). The residue of this stripping step is an oil solution of the desired propylene oxide-treated ester.

EXAMPLE 5

Following the procedure of Example 1, a polyisopropenyl-substituted succinic anhydride (where the polyisopropenyl substituent has an average molecular weight of about 750) is reacted with mannitol in an equivalent ratio of anhydride to mannitol of 1:3. An oil solution containing 1000 parts of the ester is post-treated with 145 parts of butylene oxide.

EXAMPLE 6

Following the general procedure of Example 3(A), the ester is post-treated with an equivalent amount of styrene oxide in lieu of ethylene oxide.

EXAMPLE 7

Following the general procedure of Example 4, an ester is prepared by reacting one mole of polyisobutenyl-substituted succinic anhydride (average molecular weight—3200) simultaneously with one-half mole of gly-

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erol and one-half mole of pentaerythritol and the resulting ester (1000 parts in a 40% oil solution) is post-treated with 58 parts of propylene oxide.

EXAMPLE 8

An ester is prepared by reacting 2000 parts of the carboxylic acid of Example 2(A), 1200 parts of the anhydride of Example 1, and 300 parts of sorbitol in 1400 parts of oil following the general procedure of Example 2(A). Thereafter, the filtrate is post-treated with 300 parts of propylene oxide following the general procedure of Example 2(B).

EXAMPLE 9

An ester is prepared from 1000 parts of the acid of Example 2(A) and 92 parts of glycerol and thereafter post-treated with 180 parts of propylene oxide following the general procedure of Example 2(A).

EXAMPLE 10

The ester of Example 4(A) is post-treated with 100 parts of propylene oxide and 25 parts of epichlorohydrin following the general procedure of Example 4.

EXAMPLE 11

A mixture of 340 grams (0.3 mole) of alcohol (prepared by copolymerizing equi-molar proportions of styrene and allyl alcohol to a copolymer having a molecular weight of 1150 and containing an average of 5 hydroxyl radicals per mole), 1.5 moles of a polyisobutene-substituted succinic anhydride as described in Example 1, and 500 grams of xylene is heated at 80°–115° C., diluted with mineral oil, heated to remove xylene, and filtered. The filtrate is post-treated with propylene oxide (about one equivalent per equivalent of alcohol used) at 70°–150° C. under reflux. The product is diluted with oil to an oil solution having an oil content of 40%.

As mentioned before, the post-treated esters produced by the process of this invention are useful as additives in lubricants and fuels in the same manner as the ester starting materials. They function effectively as sludge-dispersants in both lubricants and fuels. When employed as lubricating oil additives they are usually present in amounts of from about 0.01% to about 30% by weight in the final lubricating composition. Ordinarily, when used as additives for lubricating oil compositions, the post-treated esters will be present in amounts of from about 0.5% to about 10% by weight although under unusually adverse conditions, such as in the operation of certain diesels, they may comprise up to about 30% by weight of the lubricant. The products are particularly useful as dispersants in lubricating oil compositions used in the crankcase of various internal combustion engines.

When employed in lubricating oils, the post-treated esters may be used alone or in combination with other dispersants or detergents. In addition, the lubricating composition may contain rust inhibitors, oxidation inhibitors, viscosity index improving agents, extreme pressure additives, and the like. Typical examples of these additional additives are contained in the above-identified patents disclosing the carboxylic acid acylating agents useful in preparing the products of the present invention. The post-treated esters can be used effectively in both mineral oil-based lubricating compositions (i.e., petroleum distillates of lubricating oil viscosity) and synthetic oil-based lubricating compositions although they will probably find greater use in the former since mineral oil lubricating compositions are more prevalent.

In fuels, the post-treated esters serve to promote engine cleanliness by reducing or eliminating harmful deposits in the fuel system, engine, and exhaust system. They are primarily intended for use in the normally liquid petroleum distillate fuels, that is, the petroleum distillates which boil in the range characteristic of petroleum fuels such as gasolines, fuel oils, diesel fuels, aviation fuels, kerosene, and the like. When employed in fuels, they are generally

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employed in lower concentrations than in lubricants, for example, in amounts of from about 0.001% to about 2% by weight and generally in amounts of from about 0.01% to about 1% by weight. As in the case of lubricants, other conventional additives can be present in the fuel compositions contemplated by the present invention. Additional additives include lead scavengers, deicers, antiscreen clogging agents, demulsifiers, and the like.

The following are examples of the lubricating and fuel compositions contemplated by the present invention.

EXAMPLE A

SAE 20 mineral oil containing 1% of the product of Example 1.

EXAMPLE B

SAE 30 mineral oil containing 0.4% of the product of Example 2(B) and 0.15% of the zinc salt of an equimolar mixture of di-cyclohexylphosphorodithioic acid and di-isobutylphosphorodithioic acid.

EXAMPLE C

SAE 10W-30 mineral lubricating oil containing 4% of the product of Example 3(A).

EXAMPLE D

SAE 10W-30 mineral lubricating oil containing 1.5% of the product of Example 4(B), 0.075% of phosphorus as the adduct obtained by heating di-nonylphosphorodithioate with 0.25 mole of 1,2-hexane oxide at 100° C., a sulfurized methyl ester of tall oil acid having a sulfur content of 15%, 6% of a polyisobutene viscosity index improver having an average molecular weight of about 100,000, 0.005% of poly-(alkylmethacrylate) anti-foam agent, and 0.5% lard oil.

EXAMPLE E

SAE 20 mineral lubricating oil containing 2.5% of the product of Example 4, 0.75% of phosphorus as the zinc dioctylphosphorodithioate, 2% of a barium detergent prepared by neutralizing with barium hydroxide a hydrolyzed reaction product of a propylene (molecular weight 2000) with one mole of phosphorus pentasulfide and one mole of sulfur, 3% of a barium sulfonate detergent prepared by carbonating a mineral oil solution of mahogany acid and a 500% stoichiometrically excess amount of barium hydroxide in the presence of octylphenol as the promoter at 180° C., 3% of a supplemental ashless dispersant prepared by copolymerizing a mixture of 95% by weight of decylmethacrylate, 5% by weight of diethylaminoethyl acrylate.

EXAMPLE F

A di-2-ethylhexyl sebacate lubricating composition comprising 0.25% of the product of Example 2(B).

EXAMPLE G

Diesel fuel containing 0.2% of the product of Example 4.

EXAMPLE H

Kerosene containing 0.15% of the product of Example 1.

EXAMPLE I

Gasoline containing 0.003% of the product of Example 4.

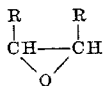
The foregoing compositions illustrate types of compositions contemplated by the present invention. Many additional compositions apparent to those skilled in the art are available simply by replacing all or part of the high-molecular weight esters used in fuels and lubricants described in the above-patents with an equal amount of the post-treated esters of the present invention. Obviously, optimum amounts for any application will depend upon the particular additive or additive combination selected and the specific environment in which the fuel or lubricant is to be used. These optimum amounts can be as-

certained through conventional evaluation techniques common-place in the industry.

The foregoing examples are illustrative of the present invention and in no way are intended to be limiting as many other obvious modifications and embodiments will be obvious to those skilled in the art.

What is claimed is:

1. A composition comprising a major amount of a lubricating oil or a normally liquid petroleum distillate fuel and a minor amount sufficient to impart dispersancy thereto of a composition produced by a process comprising contacting at a temperature of from about 25° C. up to about the decomposition temperature (A) at least one oil-soluble ester of a mono- or polycarboxylic acid and a polyhydric alcohol characterized by the presence of at least three hydroxyl groups where the carboxylic acid moiety of the ester is characterized by at least about fifty aliphatic carbon atoms exclusive of the carboxyl carbon atoms and the alcohol moiety contains up to about forty aliphatic carbon atoms with (B) at least one organic epoxide of the formula



where each R is independently hydrogen or an aliphatic, cycloaliphatic or aromatic radical, the amount of (A) and (B) in the reaction mixture being such that the ratio of equivalents of alcohol present in the ester to equivalents of epoxide is about 1:0.05 to about 1:5.

2. A composition according to claim 1 where (A) and (B) are contacted at a temperature within the range of about 50°–250° C. and (B) is at least one organic epoxide wherein each R is independently hydrogen, alkyl, haloalkyl, cycloalkyl, halocycloalkyl, aryl, haloaryl where the haloalkyl, halocycloalkyl, and haloaryl groups have no more than one halogen radical for every three carbon atoms.

3. A composition according to claim 2 where (B) is at least one aliphatic epoxide containing two to eight carbon atoms.

4. A composition according to claim 3 where (B) is at least one terminal aliphatic epoxide.

5. A composition according to claim 4 where (A) is at least one ester of a monocarboxylic acid and (A) and (B) are contacted at a temperature of about 70°–200° C.

6. A composition according to claim 5 where (A) is an ester of a polyhydric aliphatic alcohol of up to ten carbon atoms, and characterized by the presence of at least three hydroxyl groups.

7. A composition according to claim 6 wherein the polyhydric aliphatic alcohol is a polyhydric alkanol of up to six carbon atoms, the aliphatic epoxide is ethylene oxide or propylene oxide, and said ratio of equivalents is about 1:0.1 to about 1:2.

8. A composition according to claim 7 wherein the polyhydric aliphatic alcohol is selected from the class comprising glycerol, erythritol, pentaerythritol, mannitol, and sorbitol.

9. A composition according to claim 4 where (A) is at least one ester of a dicarboxylic acid and (A) and (B) are contacted at a temperature of about 70°–200° C.

10. A composition according to claim 9 where (A) is an ester of a hydrocarbon-substituted or chlorinated hydrocarbon-substituted succinic acid wherein the substituent is substantially saturated and contains at least about fifty aliphatic carbon atoms.

11. A composition according to claim 10 where (A) is a diester of a polyolefin-substituted succinic acid wherein the polyolefin substituent has a molecular weight of about 700 to about 5000 and not more than 5% of the carbon-

to-carbon covalent linkages in this substituent are unsaturated linkages.

12. A composition according to claim 11 where (A) is a diester of a polyhydric aliphatic alcohol of up to ten carbon atoms and characterized by the presence of at least three hydroxyl groups.

13. A composition according to claim 12 wherein the polyhydric aliphatic alcohol is a polyhydric alkanol of up to six carbon atoms, the aliphatic epoxide is ethylene oxide or propylene oxide, and said ratio of equivalents is about 1:0.1 to about 1:2.

14. A composition according to claim 13 where (A) is a diester of polyisobutene-substituted succinic acid with a polyhydric alkanol selected from the class consisting of glycerol, erythritol, pentaerythritol, mannitol, and sorbitol.

15. A lubricating composition according to claim 4 containing 0.01% to 30% by weight of the composition produced by contacting (A) with (B) where (A) is at least one ester of a mono- or polycarboxylic acid where the acyl moiety of said mono- or polycarboxylic acid corresponds to the acyl moiety derived from the reaction at a temperature within the range of about 100°–300° C. of (1) an unsaturated carboxylic acid of the formula $R_0-(\text{COOH})_n$ or the corresponding acyl halides or anhydrides where R_0 is characterized by the presence of at least one ethylenically unsaturated carbon-to-carbon covalent bond and n is an integer of one to six with (2) an ethylenically unsaturated hydrocarbon containing at least about fifty aliphatic carbon atoms or a chlorinated hydrocarbon containing at least about fifty aliphatic carbon atoms, wherein (A) and (B) are contacted at a temperature of about 70°–200° C.

16. A composition according to claim 15 where the acyl moiety is derived from the reaction of (1) an unsaturated carboxylic acid of the formula $R_0-(\text{COOH})_n$ or its corresponding acyl halides or anhydrides where R_0 is characterized by the presence of at least one ethylenically unsaturated carbon-to-carbon covalent bond in an α,β -position with respect to at least one carboxyl function, n is one or two and the total number of carbon atoms in $R_0-(\text{COOH})_n$ does not exceed ten with (2) polymerized 1-mono-olefins or chlorinated polymerized 1-mono-olefins.

17. A composition according to claim 16 where (A) is at least one ester of a polyhydric aliphatic alcohol of up to ten carbon atoms characterized by the presence of at least three hydroxyl groups.

18. A composition according to claim 17 containing about 0.5% to about 10% by weight of the composition produced by contacting (A) with (B) wherein the total number of carbon atoms in $R_0-(\text{COOH})_n$ does not exceed six and where (2) is polyisobutylene or chlorinated polyisobutylene.

19. A composition according to claim 18 where (A) is at least one ester of a polyhydric alkanol of up to six carbon atoms and (B) is selected from the group consisting of ethylene oxide or propylene oxide, the ratio of equivalents of (A) to (B) being about 1:0.1 to about 1:2.

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U.S. Cl. X.R.

44—70; 252—54

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,579,450 Dated May 18, 1971

Inventor(s) William M. LeSuer

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Claim 11, line 4, "than 5%" should be
--than about 5%--.

Signed and sealed this 24th day of August 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents