PRODUCTS PRODUCED BY POST-TREATING OIL-SOLUBLE ESTERS OF MONO- OR POLYCARBOXYLIC ACIDS AND POLYHYDRIC ALCOHOLS WITH EPOXIDES

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ABSTRACT
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 polyisobutene1-substituted succinic acid and sorbitol with propylene oxide.

19 Claims, No Drawings
PRODUCTS PRODUCED BY POST-TREATING OIL-SOLUBLE ESTERS OF MONO- OR POLYCARBOXYLIC ACIDS AND POLYHYDRIC ALCOHOLS WITH EPOXIDES

This is a continuation of copending application Ser. No. 826,015 filed May 19, 1969 now abandoned which, in turn is a division of application Ser. No. 712,606 filed Mar. 13, 1968, now abandoned, which is a continuation-in-part of my earlier filed applications Ser. No. 567,052 and 567,320 filed on July 22, 1966, these being, respectively, a continuation-in-part and a continuation of application Ser. No. 274,905, filed Apr. 23, 1963, and now abandoned. Ser. No. 567,320 has issued Apr. 30, 1968, as U.S. Pat. No. 3,381,022, and Ser. No. 567,052, issued July 28, 1970, as U.S. Pat. No. 3,522,179. Lubricants and fuels containing the compositions of this invention are the subject of application Ser. No. 866,084 filed Oct. 3, 1969, now U.S. Pat. No. 3,579,450; Ser. No. 866,084 being a continuation of Ser. No. 712,606.

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 Pat. No. 1,396,645; British Pat. Nos. 981,850 and 1,055,337; and U.S. Pat. Nos. 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 40 aliphatic carbon atoms with (B) at least one organic 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 40 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 30 aliphatic carbon atoms exclusive of the carboxyl 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 25 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. Pat. Nos. 3,087,936; 3,163,603; 3,172,892; 3,189,544; 3,219,666; 3,272,746; 3,288,714; 3,306,907; 3,311,776; 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 poly-
carboxylic 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 sev-
eral processes for preparing the acids. Generally,
the process involves the reaction of (1) an ethylenically un-
saturated carboxylic acid, acid halide, or anhydride
with (2) an ethylenically unsaturated hydrocarbon con-
taining at least about 50 aliphatic carbon atoms or a
chlorinated hydrocarbon containing at least about 50
aliphatic carbon atoms at a temperature within the
range of about 100°-300°C. The chlorinated hydrocar-
bon 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 Rₙ-
(COOH)ₙ, where R₂ 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
10 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, fu-
maric acid, itaconic acid, itaconic anhydride, citra-
conic acid, citraconic anhydride, mesaconic acid, glut-
aconic acid, chloromaleic acid, aconitic acid, cyro-
nic acid, methylcyroonic acid, sorbic acid, 3-hexenoic acid,
10-decenonic acid, and the like. Due to considerations
of economy and availability, these acid reactants usu-
ally employed are acrylic acid, methacrylic acid, maleic
acid, and maleic anhydride.

As is apparent from the foregoing discussion, the car-
boxylic acid acylating agents may contain cyclic and/or
aromatic groups. However, the acids are essentially al-
phatic in nature and in most instances, the preferred
acid acylating agents are aliphatic mono- and poly-
carboxylic 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 inven-
tion. These succinic acid acylating agents are readily
prepared by reacting maleic anhydride with a high mo-
lecular 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 pro-
duct from such a reaction is a substituted succinic anhy-
dride 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 proce-
dures, 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 petro-
leum fractions and substantially saturated olefin poly-
mers and the corresponding chlorinated products. The
polymers and chlorinated polymers derived from mono-
olefins having from 2 to about 30 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-prop-
yl-1-hexene. Polymers of medial olefins, i.e., olefins in
which the olefinic linkage is not at the terminal posi-
tion, likewise are useful. These are exemplified by 2-
butene, 3-pentene, and 4-octene.

The interpolymer of 1-mono-olefins such as illustrat-
ed above with each other and with other interpolymerizable olefinic substances such as aro-
matic olefins, cyclic olefins, and polyeolefins, are also
useful sources of the ethylenically unsaturated reac-
tant. Such interpolymers include for example, those
prepared by polymerizing isobutene with styrene, iso-
butene 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-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 inter-
polymers contemplated for use in preparing the acylat-
ing agents of this invention should be substantially al-
phatic 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 un-
saturated 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 polyelefin
and chlorinated polyolefins having an average molecu-
lar weight of about 700 to about 5,000. When the acyl-
ating 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, hydro-
carbons 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 reac-
tions for preparing the acylating agents. Such polar
substituents include sulfide and disulfide linkages, and
nitro, mercapto, carbonyl, and formyl radicals. Ex-
amples of these polar-substituted hydrocarbons include
polypropene sulfide, di-polyisobutene disulfide, ni-
trated mineral oil, di-polyethylene sulfide, brominated polyethylene, etc.

The acylating agents may also be prepared by halo-
genating a high molecular weight hydrocarbon such as the above described 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 dehy-
dration of citric acid. Mono-carboxylic acid acylating
agents may be obtained by oxidizing a mono-alcohol
with potassium permanganate or by reacting a haloge-
nated high molecular weight olefin polymer with a ke-
tone. Another convenient method for preparing mono-
carboxylic acid acylating agents is to react a metal
chloride 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 ha-
logenated high molecular weight hydrocarbon such as
brominated wax or brominated polyisobutene.

Mono-carboxylic and poly-carboxylic acid acylating
agents can also be obtained by reacting chlorinated
mono- and poly-carboxylic acids, anhydrides, acyl ha-
lides, and the like with ethylenically unsaturated hydro-
carbons or ethylenically unsaturated substituted hydro-
carbons such as the polyolefins and substituted polyole-
fins described hereabove in the manner described in

The mono-carboxylic and poly-carboxylic acid anhy-
drides are obtained by dehydrating the corresponding
acids. Dehydration is readily accomplished by heating
the acid to a temperature above about 70°C., prefera-
bly 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 poly-
carboxylic acids can be prepared by the reaction of the
acids on their anhydrides with a halogenating agent
such as phosphorus tribromide, phosphorus pentachlo-
ride, 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 acid to about 40 aliphatic carbon atoms ac-
gording to conventional processes for preparing car-
boxylic acid esters. These alcohols are characterized by
two to 10 hydroxy 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, tripolypropylene
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 gly-
erol, monomethyl ether of glycerol, pentaerythritol,
9,10-dihydroxystearic acid, the ethyl ester of 9,10-
dihydroxy-stearic acid, 3-chloro-1,2-propanediol, 1,2-
butanediol, 1,4-butanediol, 2,3-hexanediol, 2,4-
hexanediol, pinacol, erythritol, arabitol, sorbitol, man-
nitol, 1,2-cyclohexanediol, 1,4-cyclo-hexanediol, 1,4-
(2-hydroxyethyl)-cyclohexane, 1,4-dihydroxy-2-nitro-
butane, 1,4-di-(2-hydroxyethyl)-benzene, the carboxy-
drates such as glucose, ramnose, mannose, glyceralde-
hyde, and galactose, and the like, amino alcohols such as
di(2-hydroxyethyl)amine, tri-(3-hydroxypropyl)ami-
mine, N,N'-di-(hydroxyethyl)ethylendiamine, copoly-
mer of allyl alcohol and styrene, etc.

Included within this group of aliphatic alcohols are
those polyhydric alcohols containing at least three hy-
droxyl groups, at least one of which has been esterified
with a mono-carboxylic acid having from eight to about
30 carbon atoms such as octanoic acid, oleic acid, ste-
aric acid, linoleic acid, dodecanoic acid, or tall oil acid.
Examples of such partially esterified polyhydric alco-
hol esters are the mono-oleate of sorbitol, the mono-oleate
of glycerol, the glycerol tri-oleate, the di-oleate of sorbitol, and the
di-dodecanoate of erythritol.

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

An especially preferred class of polyhydric alcohols
for preparing the esters used as starting materials in the
present invention are the polyhydric alkanols contain-
ing 3 to 6 carbon atoms and having at least three hy-
droxyl groups. Such alcohols are exemplified in the
above specifically identified alcohols and are repre-
sented by glycerol, erythritol, pentaerythritol, manni-
tol, 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

$$\begin{align*}
\text{R} & \quad \text{R} \\
\text{CH} & \quad \text{CH} \\
\text{O} &
\end{align*}$$

where each R is independently hydrogen or an al-
phatic, cyclo-aliphatic, or aromatic radical. Normally R
will be hydrogen or an alkyl, haloalkyl, cycloalkyl,
halo-cycloalkyl, aryl, or haloaryl radical having no more
than one halogen radical for every 3 carbon atoms.
The lower alkylene and haloalkylene epoxides, including
the cycloalkylene epoxides, containing from 2 to 8 car-
bon atoms are especially preferred for post-treating the
esters. The arylene and haloarylene epoxides contem-
plated 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, xylol, methyl naphthyl, chloro-
phenyl, etc.). Phenyl and halophenyl radicals are the
preferred R groups among the aryl epoxides. The epoxi-
ides 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-epoxyhexane, 1,2-epoxyheptane, 1,2-epoxyoctane, 1,2-epoxynonane, 1,2-epoxydecane, and 1,2-epoxyparacresine. These epoxides are used in the process at a ratio of up to about 30 mole per cent of carbon atoms and the alcohol radical is derived from an aliphatic alcohol having up to about 8 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, chloroform, and the like. Mineral oils, naphthas, lignin, and the like may also be used as a diluent. In many instances the ester is 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. 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 epoxide 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 3,240 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 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 5,105 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
EXAMPLE 3
A. An ester is prepared by heating 658 parts of a carboxylic acid having an average molecular weight of 1,018 (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 3,318 parts of polyisobutenyl-substituted succinic anhydride (average molecular weight — 1,100), 408 parts of pentaerythritol, and 2,445 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 1,000 parts of the ester is post-treated with 145 parts of butylene oxide.

EXAMPLE 6
Following the general procedure at Example 3(A), the ester 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 glycerol and one-half mole of pentaerythritol and the resulting ester (1,000 parts in a 40% oil solution) is post-treated with 58 parts of propylene oxide.
mer 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 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, antiscrreen 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 percent 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-oxene 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 diocylphosphorodithioate, 2% of a barium detergent prepared by neutralizing with barium hydroxide a hydrolyzed reaction product of a propylene (molecular weight 2,000) 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 5% 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 ascertained through conventional evaluation techniques commonplace 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. An oil-soluble reaction product 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 polyfunctional acid and a polyhydric alcohol having at least three hydroxyl groups wherein the carboxylic acid moiety of the ester is characterized by a substantially saturated, aliphatic hydrocarbon radical, which is substantially free of oil-solubilizing pendant groups and has at least about 50 aliphatic carbon atoms exclusive of the carboxyl carbon atoms, and the alcohol moiety contains up to about 40 aliphatic carbon atoms; with (B) at least one organic epoxide having up to about 40 carbon atoms and corresponding to the formula

\[
\begin{align*}
R & \quad \text{R} \\
\text{O} & \quad \text{R} \\
\text{O} & \quad \text{OH} \\
\end{align*}
\]

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. An oil-soluble reaction product according to claim 1 where (A) and (B) are contacted at a temperature within the range of about 50°C-250°C. and (B) is at least one organic epoxide wherein each R is independently hydrogen, alkyl, haloalkyl, cycloalkyl, halocycloalkyl, aryl, haloaryl where the haloaryl, halocycloalkyl, and haloaryl groups have no more than one halogen radical for every 3 carbon atoms.

3. An oil-soluble reaction product according to claim 2 where (B) is at least one aliphatic epoxide containing 2 to 8 carbon atoms.

4. An oil-soluble reaction product according to claim 3 where (B) is at least one terminal aliphatic epoxide.
5. An oil-soluble reaction product according to claim 4 where (A) is at least one ester of a monocarboxylic acid and (B) are contacted at a temperature of about 70°-200°C.

6. An oil-soluble reaction product according to claim 5 where (A) is an ester of a polyhydric aliphatic alcohol of up to 10 carbon atoms, and characterized by the presence of at least three hydroxyl groups.

7. An oil-soluble reaction product according to claim 6 wherein the polyhydric aliphatic alcohol is a polyhydric alkanol of up to 6 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. An oil-soluble reaction product according to claim 7 wherein the polyhydric aliphatic alcohol is selected from the class comprising glycerol, erythritol, pentaerythritol, mannitol, and sorbitol.

9. An oil-soluble reaction product 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. An oil-soluble reaction product 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. An oil-soluble reaction product 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 about 5% of the carbon-to-carbon covalent linkages in this substituent are unsaturated linkages.

12. An oil-soluble reaction product according to claim 11 where (A) is a diester of a polyhydric aliphatic alcohol up to 10 carbon atoms which alcohol is characterized by the presence of at least three hydroxyl groups.

13. An oil-soluble reaction product according to claim 12 wherein the polyhydric aliphatic alcohol is a polyhydric alkanol of up to 6 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. An oil-soluble reaction product according to claim 13 where (A) is a diester of polyisobutenesubstituted succinic acid with a polyhydric alkanol selected from the class consisting of glycerol, erythritol, pentaerythritol, mannitol, and sorbitol.

15. An oil-soluble reaction product according to claim 14 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 \( \text{R} - (\text{COOH})_n \) or the corresponding acyl halides or anhydrides where \( \text{R} \) is characterized by the presence of at least one ethylenically unsaturated carbon-to-carbon covalent bond in an \( \alpha,\beta \)-position with respect to at least one carboxyl function 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 50 aliphatic carbon atoms, wherein (A) and (B) are contacted at a temperature of about 70°-200°C.

16. An oil-soluble reaction product according to claim 15 wherein the acyl moiety is derived from the reaction of (1) an unsaturated carboxylic acid of the formula \( \text{R} - (\text{COOH})_n \) or its corresponding acyl halides or anhydrides where \( \text{R} \) is characterized by the presence of at least one ethylenically unsaturated carbon-to-carbon covalent bond in an \( \alpha,\beta \)-position with respect to at least one carboxyl function, \( n \) is one or two and the total number of carbon atoms in \( \text{R} - (\text{COOH})_n \) does not exceed 10 with (2) polymerized 1-monoolesins or chlorinated polymerized 1-monoolesins.

17. An oil-soluble reaction product according to claim 16 where (A) is at least one ester of a polyhydric aliphatic alcohol of up to 10 carbon atoms characterized by the presence of at least three hydroxyl groups.

18. An oil-soluble reaction product 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 \( \text{R} - (\text{COOH})_n \) does not exceed six and where (2) is polyisobutylene or chlorinated polyisobutylene.

19. An oil-soluble reaction product according to claim 18 where (A) is at least one ester of a polyhydric alkanoal of up to 6 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.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,859,318 Dated January 7, 1975

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:

At column 13, line 37, that is Claim 12, line 3, "alcohol up to" should be -- alcohol of up to --.

Signed and Sealed this second Day of September 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks