

[54] **REACTION PRODUCTS OF HIGH
MOLECULAR WEIGHT CARBOXYLIC
ACID ESTERS AND CERTAIN
CARBOXYLIC ACID ACYLATING
REACTANTS**

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[56]

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[57]

ABSTRACT

High molecular weight, oil-soluble, mono- and poly-carboxylic acid esters are post-treated with mono- or polycarboxylic acid acylating reactants to provide compositions useful as dispersants in lubricants and fuels. Esters of polyisobutenyl-substituted succinic anhydride and pentaerythritol post-treated with maleic anhydride exemplify the process and compositions of this invention.

13 Claims, No Drawings

REACTION PRODUCTS OF HIGH MOLECULAR WEIGHT CARBOXYLIC ACID ESTERS AND CERTAIN CARBOXYLIC ACID ACYLATING REACTANTS

This is a continuation-in-part copending application of Ser. No. 717,429 filed Mar. 29, 1968 now abandoned.

This invention relates to a process for treating oil-soluble 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 mono- or poly- carboxylic acid acylating reactants, the compositions of matter produced by treating the esters with these acylating reactants 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; and commonly assigned copending applications Ser. No. 567,320, filed July 22, 1966, now U.S. Pat. No. 3,381,022, and Ser. No. 712,627 filed Mar. 13, 1968, now U.S. Pat. No. 3,542,678. The present invention is directed to a process for post-treating esters of this general type with at least one carboxylic acid acylating reactant to provide novel compositions of matter also useful as additives in lubricants and fuels.

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 carboxylic acid acylating reactants.

An additional object is to provide novel compositions of matter produced by post-treating of certain carboxylic acid esters with carboxylic acid acylating reactants.

A still further object is to provide novel lubricants and fuels containing compositions produced by post-treating certain esters with carboxylic acid acylating reactants.

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 acylating reactant selected from mono- or polycarboxylic acids having one to about 30 carbon atoms, anhydrides thereof, acyl halides thereof, or mixtures of two or more such acylating reactants. 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 C_1 - C_{30} carboxylic acid acylating reactants according to the present invention are esters of mono- and polycarboxylic acids containing at least about 50 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 post-treated 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 50 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 percent 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 percent 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 percent 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; 3,331,776; 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 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 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 $R_o-(COOH)_n$, 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 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, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, glutaconic 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 an-

hydrides 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 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-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 percent and preferably about 95 percent, on a weight basis, of units derived from aliphatic mono-olefins. Preferably, they will contain no more than about 5 percent 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 hydrocar-

bons include polypropylene sulfide, di-polysobutene 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 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 chloropolisobutene 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.

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 U.S. Pat No. 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 poly-carboxylic 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 10 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 polyglycols 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 two to about eight 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, 2,3-hexanediol, pinacol, erythritol, arabitol, sorbitol, mannitol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,4-(2-hydroxyethyl)-cyclohexane, 1,4-dihydroxy-2-nitro-butane, 1,4-di(2-hydroxyethyl)-benzene, the carbohydrates such as glucose, ramnose, 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, N,N-di-(2-hydroxyethyl) glycine and esters thereof with lower mono- and polyhydric aliphatic alcohols etc.

Included within this group of aliphatic alcohols are those polyhydric alcohols containing at least three hydroxyl 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, 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 10 carbon atoms, and especially those containing three to 10 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-tetrakis-(hydroxymethyl)-cyclohexanol, 1,10-decanediol, digitalose, and the like. The esters prepared from aliphatic alcohols containing at least three hydroxyl groups and up to ten 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 containing three to 10, especially 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 acylating reactants used in the post-treatment process are the C₁-C₃₀ mono- or polycarboxylic acids, their halides, anhydrides, or mixtures thereof. The acids may be aromatic, acyclic, or alicyclic acids and they may contain one or more substituents such as halo e.g., Br, Cl, I, lower alkoxy e.g., methoxy, ethoxy, butoxy, pentoxy, lower alkyl e.g., methyl, isopropyl, isobutyl, heptyl, lower alkylthio e.g., propylmercapto, hexylmercapto, ethylmercapto, nitro, amino, lower alkylamino, di(lower alkyl)amino, and the like. Illustrative acylating reactants include formic acid, acetic acid, chloroacetic acid, acetic anhydride, butyric acid, cyclohexanoic acid, tetrapropylene-substituted suc-

cinic acid, fumaric acid, benzoic acid, m-toluic acid, salicylic acid, phthalic acids, 4-propoxy-benzoic acid, phenyl acetic acid, β -phenyl-propionic acid, and the like.

However, the C_1 to C_{30} saturated or unsaturated aliphatic mono- or dicarboxylic acids, acid halides, or anhydrides constitute a preferred class of acylating reactants. These acids are generally free from non-hydrocarbon substituents and can be straight or branched chain aliphatic acids. Examples of this class of acylating reactants are formic acid, acetic acid, hexanoic acid, maleic anhydride, tetrapropylene-substituted succinic anhydride, oxalic acid, adipic acid, lauric acid, oleic acid, linoleic acid, stearic acid, tall oil acid, dodecanoic acid, octanoic acid, 2-ethyl-hexanoic acid, undecanoic acid, octadecanoic acid, eicosanoic acid, docosanoic acid, triacontanoic acid, acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, sorbic acid, malonic acid, succinic anhydride, glutaric acid, pimelic acid, azelaic acid, sebacic acid, glutaconic acid, citraconic acid, itaconic acid, mesaconic acid, allylsuccinic acid, cetylmalonic acid, and the like. Such acylating reactants having up to six aliphatic carbon atoms, including the carboxyl carbon atoms, are a particularly preferred class of acylating reactants. The dicarboxylic acids in this latter class of acylating reactants, particularly maleic acid, maleic anhydride, succinic anhydride, succinic acid, and fumaric acid are especially useful.

The specific nature of post-treatment process is not completely understood but it is believed that the C_1 - C_{30} acylating reactants esterify free-hydroxyl groups present in the alcoholic moiety of the esters and/or with unesterified polyhydric alcohol present in the ester. Such free-hydroxyl groups could be present as a result of using less than at least a stoichiometrically equivalent amount of acylating agent relative to polyhydric alcohol when preparing the ester e.g., a ratio of equivalents of high molecular weight acylating agent to polyhydric alcohol of about 1:1.05 to about 1:6; generally about 1:1.1 to about 1:4). Or the esterification process may have been terminated before all the hydroxyl groups could react even assuming the presence of sufficient acylating agent to react with all the hydroxyl groups in the polyhydric alcohol. Moreover, the size of a given high-molecular weight acylating agent may hinder reaction with all of the hydroxyl groups on a given polyhydric alcohol due to spatial considerations, e.g., steric hinderance. In addition, the acylating reactant can react with other groups present in the esters which are subject to acylation. For example, esters derived from amino-alcohols may form salts or amides with the acylating reactants. Obviously, polycarboxylic acylating reactants may combine with unesterified hydroxyl groups, amino groups, etc., on different ester molecules to form larger ester molecules bridged by a polycarboxylic acid acylating reactant.

This invention includes as the subsequent post-treatment of esters which have been first post-treated with organic epoxides particularly alkylene oxides such as ethylene oxide and propylene oxide. Such esters are disclosed in detail in commonly assigned application Ser. No. 712,606 filed Mar. 13, 1968, now abandoned. This application is incorporated herein by reference for its disclosure of epoxide post-treated esters.

Since the specific nature of the post-treatment is not

understood, it is not possible to identify a specific ratio of ester and acylating reactant which will give the best results in all cases. However, if the ratio of equivalents of ester to total equivalents of acylating reactant employed in the post-treatment process is maintained at about 1:0.5 to 1:5 and preferably, about 1:0.1 to 1:1, the post-treating process will impart improved properties to the ester, particularly improved dispersant properties. Within these ratios, the optimum ratios for a given ester or mixture of esters and a given acylating reactant or mixture of acylating reactants can be determined by routine evaluation. It is not meant to imply that all of the acid used in the post-treatment process must react. Excess acylating reactant which is not soluble in the post-treated ester or an oil-solution thereof can be removed by conventional procedures such as decantation or filtration as appropriate. Soluble excess acylating reactant can remain in the product.

For purposes of further defining the invention only, the number of equivalents in an ester corresponds to the number of alcoholic hydroxyl groups in the alcohol moiety regardless of whether or not they are esterified. Similarly, the number of equivalents in an acylating reactant corresponds to the number of carboxylic acid, acid halide, or anhydride groups present. Thus, an ester prepared from pentaerythritol has four equivalents per mole; from mannitol, six; from tri-(2-hydroxyethyl)amino, three. When, for example, the acylating reactant is acetic acid, octanoyl chloride, or phenylacetic acid, it has one equivalent per mole; when maleic acid or maleic anhydride, two equivalents per mole; etc.

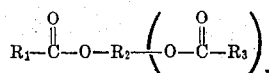
The post-treatment process involves merely contacting the ester and acylating reactant. This "contacting" is preferably accomplished by forming a reaction mixture of the ester and acylating reactant and maintaining this reaction mixture at a temperature of about 50°C. up to a temperature just below the decomposition temperature of the reactant in the reaction mixture having the lowers decomposition temperature. Temperatures of about 100°C. to about 250°C., however, are preferred with temperatures of about 190°-220°C. being particularly suitable. Agitation of the reaction mixture also facilitates the reaction.

The post-treatment process is normally conducted in the presence of a substantially inert liquid diluent such as liquid hydrocarbons and halo hydrocarbons, ethers, mixtures of these, and the like. Specific suitable diluents include mineral oil, naphthas, benzene, toluene, xylene, chlorobenzenes, cyclohexane, hexane, heptane, 1-chlorohexane, 1-bromooctane, n-amyl-ether, dimethylformamide, dimethylacetamide, etc. These same diluents are normally employed in the preparation of the esters. In fact, the usual procedure is to prepare the ester in a diluent comprising in part, at least, a synthetic or mineral lubricating oil since they are soluble in such diluents and can be added to the lubricant or fuel in the form of a lubricating oil solution. The acylating reactants can be mixed with such solutions in order to carry out the post-treating process of the invention.

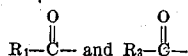
As is obvious to those skilled in the art, the duration of the post-treating process can vary depending on the type and quantity of ester and acylating reactant, agitation of the reaction mixture, temperature, and the like.

It will be understood by those skilled in the art the

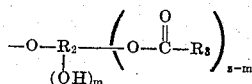
carboxylic acid moiety of an ester refers to the carboxylic acid acyl radical of the ester while the alcoholic moiety refers to the oxy radical of the alcohol from which the ester is derived. Thus, in the illustrative formula



where R_1 and R_3 are the residues of the carboxylic acid acylating agents used to prepare the esters, the acyl moiety is



while the alcoholic moiety is $-O-R_2-(O-)_z$. The variable z in the illustrative formula represents the total number of esterified hydroxyl groups minus one. Of course, only one hydroxy group of the alcohol may be esterified so that the alcoholic moiety may be represented as $-O-R_2-(OH)_z$. Or only a portion of the hydroxyl groups may be esterified in which case the alcohol moiety could be represented as



The following examples further illustrate the present invention. Unless otherwise indicated, "parts" and "percentages" refer to parts by weight and percent by weight in these examples and elsewhere in the specification and claims.

EXAMPLE 1

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 1,000 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.

EXAMPLE 2

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 filtered and the filtrate is the desired ester.

EXAMPLE 3

To a mixture comprising 408 parts of pentaerythritol and 1,100 parts oil heated to 120°C., there is slowly added 2,946 parts of the acid of Example 1 which has been preheated to 120°C., 225 parts of xylene, and 95

parts of diethylene glycol dimethylether. The resulting mixture is heated at 195°–205°C., under a nitrogen atmosphere and reflux conditions for eleven hours, stripped to 140°C. at 22 mm (Hg.) pressure, and filtered. The filtrate comprises the desired ester. It is diluted to a total oil content of 40 percent.

EXAMPLE 4

A. An ester is prepared following the general procedure of Example 1 by reacting 1 equivalent of a carboxylic acid chloride (prepared by reacting 1 mole of polyisobutene (average molecular weight —1,500) with 2.5 moles of chloroacetyl chloride according to U.S. Pat. No. 3,340,281 and thereafter removing excess chloroacetyl chloride) with 3 equivalents of man-
nitrol. After filtration, the filtrate is diluted to a mineral oil content of 40 percent. B. The procedure of Example 4(A) is repeated but the acid chloride is replaced with 1 equivalent of an acid chloride prepared by reacting an isobutylene: propylene copolymer (average molecular weight —2,200) containing about 20 percent propylene units and chloroacetylchloride in a molar ratio of copolymer to chloroacetylchloride of 1:2.5 following the procedure of U.S. Pat. No. 3,340,281.

Following the general procedure of Example 1, esters are prepared from the acylating agents and alcohols indicated in the following table in the equivalent ratio shown. Obviously, more or less diluent can be used as desired to facilitate handling, etc.

TABLE

example	acylating agent (X)	alcohol (Y)	equivalent ratio of (X):(Y)
5	A	Polyoxyethylene Glycol (Average M.W.—400)	1:1
6	A	Polyoxypropylene Glycol (Average M.W.—425)	1.5:2
7	A	Polyoxypropylene Glycol (Average M.W.—1,025)	1:2
8	B	Glycerol	2:3
9	A	Di-(2-hydroxyethyl) amine	1:1
10	A	Sorbitan Mono-Oleate	1:1
11	A	Monophenyl Ether of Trioxypolypropylene Glycol	1:1
12	A	Monoethyl Ether of Polyoxyethylene Glycol (Average M.W.—430)	1:1
13	A	1,4-Di-(2-hydroxyethyl) piperazine	1:1
14	C	Mannitol	1:2
15	A	Monobenzyl Ether of Polyoxypropylene Glycol (Average M.W.—510)	1:1
16	A	N-(2-hydroxyethyl) morpholine	1:1
17	A	N,N'-Di(2-hydroxyethyl) ethylene diamine	1:2
18	A	N,N-Di-(2-hydroxyethyl) glycine	1:2

A = Acylating agent of Example 1.

B = Acylating agent of Example 4(A).

C = Acylating agent of Example 4(B).

EXAMPLE 19

An ester is prepared by reacting 600 parts of polyisobutenyl-substituted succinic anhydride (average molecular weight —1,100) 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.

EXAMPLE 20

The above ester of Example 1 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 170°C. at a pressure of 15 mm. (Hg.). The stripped product is an epoxide treated ester.

EXAMPLE 21

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.

EXAMPLE 22

Following the procedure of Example 19, 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.

EXAMPLE 23

Following the general procedure of Example 21, an ester is prepared by reacting one mole of polyisobutenyl-substituted succinic anhydride (average molecular weight —3,200) simultaneously with one-half mole of glycerol and one-half mole of pentaerythritol.

EXAMPLE 24

An ester is prepared by reacting 2,000 parts of the carboxylic acid of Example 1, 1,200 parts of the anhydride of Example 19, and 300 parts of sorbitol in 1,400 parts of oil following the general procedure of Example 1.

EXAMPLE 25

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 1,150 and containing an average of 5 hydroxyl radicals per mole), 1.5 moles of a polyisobutene-substituted succinic anhydride as described in Example 19, 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 desired epoxide post-treated product is diluted with oil to an oil solution having an oil content of 40 percent.

EXAMPLE I

An ester is prepared according to the general procedure of Example 21 by reacting the polyisobutenyl-substituted succinic acid anhydride and pen-

taerythritol in a 1:1 mole ratio. The oil content of the ester-containing filtrate is adjusted to about 40 percent.

A. A reaction mixture containing 2,008 parts of the above oil solution and 73.5 parts of maleic anhydride (the ratio of equivalents of ester to maleic anhydride is about 1:0.37) is heated to 200°C. over a 1.5 hour period, and maintained at 200°–210°C. for 5.5 hours. During the last 1.5 hour period of heating, the reaction mixture is blown with nitrogen. The mixture is then stripped to 190°C. at 40 mm. (Hg.). Thereafter, the reaction mixture is filtered. The filtrate is an oil solution of the desired post-treated ester.

B. Following the general procedure of (A), 1,506 parts of the ester solution is contacted with 73.5 parts of maleic anhydride. The ratio of equivalents of ester to maleic anhydride is about 1:0.5. Again, the desired post-treated ester is recovered in the form of an oil solution i.e., the filtrate).

C. Following the general procedure of (A), 1,506 parts of the ester solution is contacted with 147 parts of maleic anhydride producing a ratio of equivalents of ester to maleic anhydride of about 1:1/ The reaction mixture is permitted to cool to room temperature and thereafter filtered to remove unreacted precipitated maleic anhydride.

EXAMPLE II

An ester is prepared by following the general procedure of Example 21 by reacting the polyisobutenyl-substituted succinic anhydride with pentaerythritol in a 1:2 molar ratio. The filtrate thus produced is adjusted to an oil content of about 40 percent.

A. Following the general procedure of Example I(A), 1,670 parts of the above oil solution of the ester is contacted with 73.5 parts of maleic anhydride resulting in a reaction mixture having a ratio of equivalents of ester to anhydride of 1:0.25. Upon completion of the heating, 583 parts of mineral oil are added and the resulting mixture is filtered. The filtrate is an oil solution of the desired post-treated ester.

B. Following the general procedure of Example I(A), 1,670 parts of the above oil solution of the ester is contacted with 147 parts of maleic anhydride producing a reaction mixture having a ratio of equivalents of acid to anhydride of 1:0.5. After the heating step is completed, 906 parts of mineral oil are added and the resulting mixture is filtered. The filtrate is an oil solution of the desired post-treated ester.

The foregoing examples illustrate the preferred embodiment of the present invention. Following the general procedures of Examples I and II, other useful embodiment of the invention are achieved readily by substituting for all or a portion of the esters and acylating reactants used therein one or more esters or acylating reactants described hereinabove. The following table illustrates additional embodiments prepared following the general procedure of Examples I and II but using the indicated esters and acylating reactants.

TABLE

example	ester of example (X)	Acylating Reactant (Y)	equivalent Ratio of (X):(Y)
III	No. 1	Succinoyl chloride	1:0.33
IV	No. 3	Acetic Anhydride	1:0.75
V	No. 7	Pentanoic Acid	1:0.5

VI	No. 9	Phthalic Anhydride	1:0.1
VII	No. 11	Chloromaleic Anhydride	1:0.05
VIII	No. 14	Lauric Acid	1:0.33
IX	No. 16	Maleic Anhydride	1:0.1
X	No. 17	Equimolar Mixture of Formic Acid and maleic Anhydride	1:2
XI	No. 20	Adipic Acid	1:0.4
XII	No. 24	Oleic Acid	1:0.15

The manner in which the post-treatment improves the properties of the esters is not understood. It is believed that the acylating reactants provide increased "polarity" to the ester molecules. Thus, the ester molecules are characterized by an essentially non-polar portion (the portion of the acyl moiety characterized by at least about 50 aliphatic carbon atoms) and a polar portion of the ester groups. The reaction of additional acid possibly provides additional polarity through the formation of more ester groups, amide groups, amine salt groups and the like. The additional polarity could account for the improved sludge-dispersing capabilities. Moreover, when the acylating reactant is a polycarboxylic acid acylating agent, cross-linking is possible. This would result in higher molecular weight esters and this might also account for improvements in dispersancy as well as improved oil solubility. Some of the post-treated esters derived from very high-molecular weight acids, for example molecular weights above about 10,000, are characterized by enhanced viscosity-index improving capabilities after post-treatment with polycarboxylic acid acylating reactants.

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 percent to about 30 percent 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 percent to about 10 percent by weight although under unusually adverse conditions, such as in the operation of certain diesels, they may comprise up to about 30 percent 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.

The additives of this invention can be effectively employed in a variety of lubricating compositions based on diverse oils of lubricating viscosity such as a natural or synthetic lubricating oil, a mixture of miscible or mutually soluble natural oils or synthetic oils, or a mixture of miscible or mutually soluble natural and synthetic oils. The term "miscible" is intended to describe that situation where two or more oils are sufficiently soluble to be compatible as a base oil, whereas the terminology "mutually soluble" is intended to describe the situation where a suitable common solvent, perhaps another lubricating oil, permits the use of two or more lubricating oils in combination where they would not otherwise be compatible due to solubility problems. Typical examples of natural and synthetic oils are identified hereafter. These examples are illustrative and not intended to be exhaustive.

The lubricating compositions contemplated include principally crankcase lubricating oils for spark-ignited

and compression-ignited internal combustion engines including automobile and truck engines, aviation piston engines, marine and railroad diesel engines, and the like. However, automatic transmission fluids, transaxle lubricants, gear lubricants, metal-working lubricants, hydraulic fluids, and other lubricating compositions can benefit from the incorporation of the present additives. It is also anticipated that the lubricating compositions will be thickened or converted to greases by conventional techniques well-known in the art to form lubricating greases.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as solvent-refined or acid-refined mineral lubricating oils of the paraffinic, naphthenic, or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils. Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylene, propylene-isobutylene copolymers, chlorinated polybutylenes, etc.); alkyl benzenes (e.g., dodecylbenzenes, tetradecylbenzene, dinonyl benzenes di-(2-ethylhexyl)benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyls, etc.); and the like. Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether having an average molecular weight of 1,000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1,000, diethyl ether of polypropylene glycol having a molecular weight of 1,000-1,500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters, or the C₁₃ oxo acid diester of tetraethylene glycol. Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, pentaerythritol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diis decyl azelate, dioctyl phthalate, didecylphthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid, and the like. Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl-silicate, tetraisopropyl-silicate, tetra-(2-ethylhexyl)-silicate, tetra-(4-methyl-2-tetraethyl)-silicate, tetra-(p-tert-butylphenyl)-silicate, hexyl-(4-methyl-2-pentoxo)-disiloxane, poly(methyl)-siloxanes, poly(methylphenyl)-siloxanes, etc.). Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid, etc.), polymeric tetra-hydrofurans, and the like.

The post-treated esters may be used along in a lubricating oil composition although they are normally used in conjunction with other conventional lubricating oil additives of the type illustrated in the above-identified U.S. Pat. applications, patents, and British specification. The conventional additives include extreme pressure agents, metal containing detergents such as normal and basic oil-soluble alkaline earth metal phenates and petrosulfonates, viscosity index improving agents, oxidation inhibitors, antifoam agents, ashless dispersants, corrosion inhibitors, and the like.

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 percent to about 2 percent by weight and generally in amounts of from about 0.01 percent to about 1 percent 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, anti-screen clogging agents, demulsifiers, and the like.

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

Composition A

SAE 10W-30 mineral lubricating oil containing 1.5 percent of the product of Example I(A) and 0.05 percent of phosphorus as the zinc salt of a phosphorodithioic acid prepared by the reaction of phosphorus pentasulfide with a mixture of 60 percent (mole) p-butylphenol and 40 percent (mole) of N-pentyl alcohol.

Composition B

SAE 10W-30 mineral lubricating oil containing 0.75 percent of the product of Example I(B).

Composition C

SAE 30 mineral lubricating oil containing 5 percent of the product of Example II(A), 0.1 percent of phosphorus as the zinc salt of a mixture of equimolar amounts of diisopropyl phosphorodithioic acid and di-n-decyl phosphorodithioic acid, and 2.5 percent of sulfate ash as a basic barium detergent prepared by carbonating at 160°C. a mixture comprising mineral oil, barium di-dodecyl-benzenesulfonate, and 1.5 moles of barium hydroxide in the presence of a small amount of water and 0.7 mole of octylphenol as the promoter.

Composition D

SAE 10 mineral lubricating oil containing 2 percent of the product of Example II(B), 0.07 percent of phosphorus zinc dioctyl phosphorodithioate, 2 percent of a barium detergent prepared by neutralizing with barium hydroxide the hydrolyzed reaction product of polypropylene (molecular weight 2,000) with one mole of phosphorus pentasulfide and one mole of sulfur, 3 percent of a barium sulfonate detergent prepared by carbonating a mineral oil solution of mahogany acid, and a 500 percent stoichiometrically

excess amount of barium hydroxide in the presence of a phenol as the promoter at 180°C., 3 percent of a supplemental ashless detergent prepared by copolymerizing a mixture of 95 percent (weight) of decylmethacrylate and 5 percent (weight) of diethylaminoethyl acrylate.

Composition E

SAE 10 mineral lubricating oil containing 2 percent of the product of Example IV, 0.075 percent of phosphorus as the adduct of zinc di-cyclohexyl phosphorodithioate treated with 0.3 mole of ethylene oxide, 2 percent of sulfurized sperm oil having a sulfur content of 10 percent, 3.5 percent of a poly-(alkyl methacrylate) viscosity index improver, 0.02 percent of a poly(alkylmethacrylate), pour point depressant, and 0.003 percent of a poly-(alkylsiloxane) anti-foam agent.

Composition F

SAE 80 mineral lubricating oil containing 2 percent of Example XI, 0.1 percent of phosphorus as zinc di-n-hexyl phosphorodithioate, 10 percent of a chlorinated paraffin wax having a chlorine content of 40 percent, 2 percent of di-butyl tetrasulfide, 2 percent of sulfurized dipentene, 0.2 percent of oleyl amide, 0.003 percent of an anti-foam agent, 0.02 percent of a pour point depressant, and 3 percent of a viscosity index improver.

Composition G

SAE 20W-30 mineral lubricating oil containing 5 percent of the product of Example IX.

Composition H

A synthetic lubricating oil which is the complex esters formed by reacting 1 mole of sebacic acid with 2 moles of tetraethylene glycol and 2 moles of 2-ethyl-hexanoic acid and 3 percent of the product of Example I(A).

Composition I

A synthetic lubricating oil composition with a lubricating oil is the ester of 2-ethylhexyl alcohol and azelaic acid containing 1 percent of the product of Example II(B).

Composition J

A diesel fuel containing 0.015 percent of the product of Example I(A).

Composition K

Gasoline containing 0.075 percent of the product of Example X.

Composition L

Kerosene containing 0.05 percent of the product of Example VIII.

The foregoing description of the invention is directed primarily to the preparation and use of the resulting post-treated esters as additives in lubricants and fuels. However, these post-treated esters may themselves be further treated to enhance their dispersant characteristics. For example, if as a result of the acid post-treatment, the post-treated composition contains unreacted carboxylic acid acylating groups, further treatment of these products with sufficient amine or epoxide to neutralize these groups may be desirable. The alkylene oxides, particularly ethylene oxide and propylene oxide, are especially useful for this purpose. Likewise, the alkylenepolyamines are also very useful in neutralizing residual acidity. The ethylene-polyamines (ethylene diamine, penta-ethylenhexamine, and the like) or mixtures thereof are preferred for this purpose.

What is claimed is:

1. An oil-soluble reaction product produced by a process comprising contacting at a temperature of about 50°C. up to just below the decomposition temperature (A) at least one oil-soluble ester of aliphatic mono- or polycarboxylic acid and a polyhydric alcohol characterized by the presence of unesterified free hydroxyl groups in the alcohol moiety which alcohol moiety contains up to about forty aliphatic carbon atoms, where the carboxylic acid moiety of the ester is substantially saturated and is substantially free from oil-soluble pendant groups and is further characterized by containing at least about fifty aliphatic carbon atoms exclusive of the carboxyl carbon atoms, with (B) at least one acylating reactant selected from mono- or polycarboxylic acids having one to about thirty carbon atoms, anhydrides thereof, acyl halides thereof, or mixture of two or more of these acylating reactants, in an equivalent ratio of (A) to (B) of about 1:0.05 to about 1:5.

2. An oil-soluble reaction product according to Claim 1 where at least a portion of said oil-soluble ester (A) is characterized by the presence of unreacted hydroxyl groups in the alcoholic moiety as a result of preparing said oil-soluble ester (A) by reacting aliphatic mono- or polycarboxylic acid acylating agent and polyhydric alcohol in an equivalent ratio of acylating agent to polyhydric alcohol of about 1:105 to about 1:6.

Claim 2 where said oil-soluble ester (A) is at least one ester of a mono- or polycarboxylic acid or anhydride with at least one polyhydric alcohol having three to ten aliphatic carbon atoms and at least hydroxyl groups wherein the mono- or polycarboxylic acid or anhydride is one derived from the reaction of a poly(1-monoolefin) or chlorinated poly(1-monoolefin) having an average molecular weight of about 700 to about 5,000 with an α,β -ethylenically unsaturated mono- or polycarboxylic acid or anhydride and wherein said contacting of (A) and (B) is carried out at a temperature of about 100°C. to about 250°C.

4. An oil-soluble reaction product according to Claim 3 where said acylating reactant (B) is an aliphatic acylating reactant containing one to six carbon atoms.

5. An oil-soluble reaction product according to Claim 4 wherein said polyhydric alcohol is a poly-

hydric alkanol and said acylating reactant (B) is selected from maleic anhydride, maleic acid, succinic anhydride, succinic acid, or fumaric acid.

6. An oil-soluble reaction product according to Claim 5 wherein said polyhydric alkanol is selected from the class consisting of glycerol, erythritol, pentaerythritol, mannitol, and sorbitol.

7. An oil-soluble reaction product according to Claim 2 wherein said equivalent ratio of acylating agent to polyhydric alcohol is about 1:1.1 to about 1:4.

8. An oil soluble reaction product according to Claim 7 where said oil-soluble ester (A) is at least one ester of a substituted succinic acid wherein the substituent is a substantially saturated aliphatic substituent containing at least about fifty aliphatic carbon atoms.

9. An oil-soluble reaction product according to Claim 8 where said oil-soluble ester (A) is a diester of a polyolefin-substituted succinic acid wherein the polyolefin substituent has a molecular weight of about 700 to about 5,000 and not more than about 5 percent of the carbon-to-carbon covalent linkages in this substituent are unsaturated linkages.

10. An oil-soluble reaction product according to Claim 9 wherein the acylating reactant (B) is an aliphatic acylating reactant containing one to six carbon atoms.

11. An oil-soluble reaction product according to Claim 10 wherein said oil-soluble ester (A) is an ester of a polyhydric aliphatic alcohol of up to ten carbon atoms characterized by the presence of at least three hydroxyl groups.

12. An oil-soluble reaction product according to Claim 11 wherein the polyhydric alcohol is a polyhydric alkanol, the acylating reactant (B) is selected from the class consisting of maleic anhydride, maleic acid, succinic anhydride, succinic acid, and fumaric acid.

13. An oil-soluble reaction product according to Claim 12 wherein said oil-soluble ester (A) is a diester of polyiso-butenyl-substituted succinic acid and a polyhydric alkanol selected from the class consisting of glycerol, erythritol, pentaerythritol, mannitol, and sorbitol.

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