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LUBRICANT AND FUEL COMPOSITIONS CONTAINING ESTERS

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ABSTRACT OF THE DISCLOSURE

Esters of monocarboxylic acids and polyhydric or aminoalcohols useful as additives for lubricants and fuels. The esters of a monocarboxylic acid having at least about fifty aliphatic carbon atoms exclusive of the carboxyl carbon atom and polyhydric alkanols constitute preferred embodiments.

This invention relates to novel oil-soluble compositions of matter and to fuels and lubricants containing these compositions. In particular, the invention is concerned with esters of high-molecular weight monocarboxylic acids with polyhydric alcohols or amino alcohols and to fuel and lubricant compositions containing these esters.

The esters of the invention impart sludge-dispersing properties to lubricating oils such as a crankcase lubricating oils used in internal combustion engines. The esters are effective at temperatures lower than that at which metal-containing basic detergents are effective. This is particularly advantageous in the operation of engines for short periods of time, for example, in the typical stop-and-go driving of automobiles. Under such operating conditions, the engine oil does not reach optimum temperatures and the metal-containing detergents such as the basic alkyline earth metal petrosulfonates are not completely effective. In fuels, the esters serve to reduce the formation of carbonaceous deposits within the engine such as those which accumulate on the valve points. In addition, incorporation of the esters into the fuels promotes cleanliness of the fuel system, i.e., the carburetor, fuel lines, and the like.

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

A further object of the invention is to provide oil-soluble esters of high-molecular weight monocarboxylic acids.

An additional object is to provide fuel and lubricating compositions containing the esters of the invention as additives.

These and other objects of this invention are accomplished by providing an oil-soluble ester of a carboxylic acid and an alcohol characterized by the presence within its structure of (A) a carboxylic acid moiety which is the acyl residue of a monocarboxylic acid having at least about fifty aliphatic carbon atoms and being substantially free of ethylenically unsaturation and (B) an alcohol moiety which is the oxy residue of a polyhydric alcohol or an amino alcohol. These esters are incorporated into fuels and lubricants to provide the fuel and lubricating compositions contemplated by the invention.

The esters are readily prepared by well-known conventional esterification procedures utilizing intermediates which are either readily available commercially or easily prepared applying known techniques. The preparation of the esters is discussed in more detail hereinafter.

The acyl moiety of the esters is derived from a monocarboxylic acid. One particularly important characteristic of the acyl moiety is its size. The radical should contain at least about fifty aliphatic carbon atoms exclusive of the carboxyl carbon atom. 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 moiety of the esters should be susbtantially free from oil-solubilizing pendant groups, that is, groups having more than about six aliphatic carbon atoms. Although, some such oil-solubilizing pendant groups may be present, they preferably will not exceed one such group for every twenty-five aliphatic carbon atoms in the principal hydrocarbon chain of the acyl radical.

The acyl moiety may contain polar substituents provided that the polar substituents are not present in proportions sufficiently large to alter significantly the hydrocarbon character of the moiety. 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.

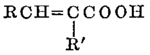
Monocarboxylic acid acylating agents suitable for preparing the esters can be prepared by procedures which are well-known in the art and have been described for example, in U.S. Pats. 3,087,936, 3,163,603, 3,172,892, 3,189,544, 3,219,666, 3,272,746, 3,288,714, 3,306,907, 3,331,776, 3,340,281, 3,341,542 and 3,346,354. In the interest of brevity, these patents are incorporated herein for their disclosure of suitable methods for preparing high molecular weight monocarboxylic acid acylating agents which can be used for preparing the esters of the present invention.

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

When preparing the carboxylic acid acylating agent according to one of these two processes, the monocarboxylic acid reactant corresponds to the general formula R_0—COOH, where R_0 contains up to about nine aliphatic carbon atoms and is characterized by the presence of at least one ethylenically unsaturated carbon-to-carbon covalent bond. Normally, the acids will correspond to the formulae

$$RCH=CH(CH_2)_nCOOH$$

or



$$RCH=\underset{R'}{\underset{|}{C}}COOH$$

where R is hydrogen or alkyl and R′ is hydrogen or methyl, with the proviso that R, R′, and *n*, are such that the total number of carbon atoms in the acid does not exceed ten. The acidic reactant can also be the corresponding carboxylic acid halide, anhydride, or other equivalent acylating agent and mixtures of one or more of these. Usually, the total number of carbon atoms in the acidic reactant will not exceed six. Preferably the acidic reactant will have at least one ethylenic linkage in an α,β-position with respect to the carboxyl function. Exemplary acidic reactants are acrylic acid, methacrylic acid, acryl chloride, allyl acetic acid, cinnamic acid, crotonic acid, angelic acid, tiglic acid, sorbic acid, 10-decenoic acid, and the like.

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

The ethylenically unsaturated hydrocarbon reactant and the chlorinated hydrocarbon reactant used in the preparation of the acylating agents are principally the high molecular weight, substantially saturated petroleum fractions and substantially saturated olefin polymers and the corresponding chlorinated products. The polymers and chlorinated polymers derived from mono-olefins having from two to about thirty carbon atoms are preferred. The especially useful polymers are the polymers of 1-mono-olefins such as ethylene, propene, 1-butene, isobutene, 1-hexane, 1-octane, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, and 2-methyl-5-proply-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. These are exemplified by 2-butene, 3-pentene, and 4-octene.

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

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

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

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

Monocarboxylic acid acylating agents may be obtained by oxidizing a monoalcohol with potassium permanganate or by reacting a halogenated high molecular weight olefin polymer with a ketene. Another convenient method for preparing monocarboxylic 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. Monocarboxylic acid acylating agents can also be obtained by reacting chlorinated monocarboxylic 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. Patent 3,340,281. The acid anhydrides are obtained by dehydrating the corresponding acid. 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. Acid halides of the 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 are generally prepared by reacting the carboxylic acid acylating agent, preferably the acid per se, its acyl chloride, or an anhydride thereof, with the desired alcohol according to conventional processes for preparing carboxylic acid esters. These alcohols are either polyhydric alcohols characterized by two to ten hydroxyl groups or amino alcohols and can be quite diverse in structure and chemical composition. Generally the polyhydric and amino alcohols will contain up to forty aliphatic carbon atoms.

Useful polyhydric alcohols include alkylene glycols and polyoxy alkylene glycols such as ethylene glycol, propylene glycol, trimethylene glycol, butylene glycol, any poly glycols such as diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, and other alkylene glycols and polyoxy alkylene glycols in which the akylene radical contains from 2 to about 8 carbon atoms. The monoethers of the polyoxy alkylene glycols are also useful in preparing esters of the present invention. These include the monoaryl ethers, monoalkyl ethers, and monoaralkyl ethers of the formula

$$HO(R_1-O)_nR_2-OR_3$$

where R_3 is aryl such as phenyl, lower alkoxy phenyl, or lower alkyl phenyl, lower alkyl such as ethyl, propyl, tert-butyl, pentyl, etc., and aralkyl such as benzyl, phenylethyl, phenylpropyl, p-ethyl phenylethyl, etc., *n* is a whole number of 2 to about 150, and R_1 and R_2 are lower alkylene of up to eight, preferably, two to four carbon atoms.

Other useful polyhydric alcohols include glycerol, monomethyl ether of glycerol, pentaerythritol, 9,10-dihydroxystearic acid, the ethyl ester of 9,10-dihydroxystearic acid, 3-chloro-1,2-propanediol, 1,2-butanediol, 1,4-butanediol, 2,3-hexanediol, 2,4-hexanediol, pinacol, erythritol, arabitol, sorbitol, mannitol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,4-(2-hydroxyethyl)cyclohexane, 1,4-dihydroxy-2-nitro-butane, 1,4-di(2-hydroxyethyl)benzene, the carbohydrates such as glucose, ramnose, mannose, lyceraldehyde, galactose, di(2-hydroxyethyl)amine, tri-(3-hydroxypropyl)amine, N,N'-di(hydroxy ethyl)ethylenediamine, copolymer of allyl alcohol and styrene, 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 monocarboxylic acid having from eight to about thirty carbon atoms such as octanoic acid, oleic acid, stearic acid, linoleic acid, dodecanoic acid, or tall oil acid. Examples of such partially esterified polyhydric alcohols are the mono-oleate of sorbitol, sorbitan mono-oleate, the mono-oleate of glycerol, the mono stearate of glycerol, the di-stearate of sorbital, and the didodecanoate of erythritol.

A preferred class of esters are those prepared from polyhydric alcohols containing up to ten carbon atoms, and especially those containing three to ten carbon atoms. This class of alcohols includes glycerol, erythritol, pentaerythritol, gluconic acid, glyceraldehyde, glucose, arabinose, 1,7-heptanediol, 2,4-heptanediol, 1,2,3-hexanetriol, 1,2,4-hexanetriol, 1,2,5-hexanetriol, 2,3,4-hexanetriol, 1,2,3-butanetriol, 1,2,4-butanetriol, quinic acid, 2,2,6,6-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 ten carbon atoms and particularly, those containing three to six carbon atoms and having at least three hydroxyl groups. Such alcohols are exemplified in the above specifically identified alcohols and are represented by glycerol, erythritol, pentaerythritol, mannitol, sorbitol, 1,2,4-hexanetriol, and the like.

The amino alcohols contemplated as suitable for preparing the esters can be monohydric or polyhydric. Examples of suitable amino alcohols are the N-hydroxy lower alkyl monoamines and polyamines such as

2-hydroxyethylamine,
3-hydroxybutylamine,
di(2-hydroxylethyl)amine,
tri(2-hydroxyethyl)amine,
di(2-hydroxypropyl)amine,
N,N,N'-tri(2-hydroxyethyl)ethylenediamine,
N,N,N',N'-tetra(2-hydroxyethyl)ethylenediamine,
N-(2-hydroxyethyl)piperazine,
N,N'-di(3-hydroxypropyl)piperazine,
N-(2-hydroxyethyl)morpholine,
N-(2-hydroxyethyl)-2-morpholinone,
N-(2-hydroxyethyl)-3-methyl-2-morpholinone,
N-(2-hydroxyethyl-(5-N-butylcarbamyl)2-piperidone,
N-(2-hydroxyethyl)-5-carbethoxy-2-piperidone,
N-(2-hydroxypropyl)5-carbethoxy-2-piperidone,
N-(2-hydroxyethyl)-5-(N-butylcarbamyl)-2-piperidone,
N-(2-hydroxyethyl)piperidine,
N-(4-hydroxybutyl)piperidine,
N,N-di(2-hydroxyethyl)glycine,

and esters thereof with aliphatic alcohols, especially lower alkanols, N,N-di(3-hydroxypropyl)glycine, and the like. Also contemplated are other mono- and poly-N-hydroxyalkyl-substituted alkylene polyamines wherein the alkylene radicals contain two to four carbon atoms and the polyamine has up to seven amino groups.

As mentioned above, the esters are prepared by mixing the alcohol and carboxylic acid acylating agent at a temperature of about 100° C. or higher and usually at 150°–300° C. The reaction is usually conducted in the presence of a substantially inert organic diluent. Suitable diluents include the aliphatic, cycloaliphatic, and aromatic hydrocarbons and their chlorinated analogs exemplified by pentane, hexane, heptane, cyclohexane, benzene, toluene, xylene, chlorobenzene, chlorohexanes, and the like. Mineral oils, naphthas, ligroin, and the like may also be used as a diluent. The diluent is preferably selected so no solubility problems will arise when the ester solution thus prepared are added to the fuel or lubricant. That is, it is desirable to prepare the ester in a diluent which is soluble in the fuel or lubricant in which it is to be used. Low-viscosity mineral oil are particularly useful diluent, either alone or in combination with other diluents.

The reaction mixture comprises at least one monocarboxylic acid acylating agent and at least one alcohol. That is, the ester compositions contemplated by the present invention include mixtures of esters prepared by reacting one or more different monocarboxylic acid acylating agents with one or more different alcohols of the general type described hereinabove. Or, the ester mixtures can be prepared by mixing two or more individually prepared esters.

The stoichiometry of the reaction requires at least one equivalent of alcohol for each equivalent of acylating agent.The acylating agents have one equivalent per mole while the number of equivalents of an alcohol per mole depends upon the number of free alcoholic hydroxy groups present therein. Thus, glycerol has three equivalents per mole; pentaerythritol, four; tri(2-hydroxyethyl)amine, three; polyoxyethyleneglycol, two; etc. Ordinarily, the total amount of acylating agent and alcohol used in the reaction mixture will vary from a ratio of about 1:1 moles to about 1:1 equivalents.

As is apparent to those skilled in the art, it is possible for up to one mole of monocarboxylic acid acylating agent to combine with each free alcoholic hydroxyl group present. Accordingly, the esters of the invention include polyesterified polyhydric alcohols. Where amino alcohols are used, it is possible that some of the acylating agent will react with primary or secondary amino groups. Compounds characterized by a group resulting from the reaction of the acylating agent with an amino group, e.g., an amide group, are not included within the scope of the present invention. Only those esters free from such groups are contemplated by the present invention.

The following examples illustrate 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

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

EXAMPLE 2

An ester is prepared by heating 658 parts of a carboxylic acid having an average molecular weight of 1018 (prepared by reacting chlorinated polyisobutene with acrylic acid) with 22 parts of pentaerythritol while maintaining a temperature of about 180°–205° C. for about 18 hours during which time nitrogen is blown through the mixture. The mixture is then filtered and the filtrate is the desired ester.

EXAMPLE 3

To a mixture comprising 408 parts of pentaerythritol and 1100 parts oil heated to 120° C., there is slowly added

2946 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%.

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—1500) with 2.5 moles of chloroacetyl chloride according to U.S. patent 3,340,281 and thereafter removing excess chloroacetyl chloride) with 3 equivalents of mannitol. After filtration, the filtrate is diluted to a mineral oil content of 40%.

(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—2200) containing about 20% propylene units and chloroacetylchloride in a molar ratio of copolymer to chloroacetylchloride of 1:2.5 following the procedure of U.S. 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. By substituting other acylating agents and alcohols of the types discussed and exemplified hereinabove for those of the table or foregoing examples, still other esters of the type contemplated by the present invention can be prepared readily.

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 trioxypropylene glycol.	1:1
12	A	Monoethyl ether of polyoxy ethylene 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.	1:1
18	A	N,N-di-(2-hydroxyethyl)glycine.	1:2

NOTE: A=Acylating agent of Example 1.
B=Acylating agent of Example 4(A).
C=Acylating agent of Example 4(B).

As mentioned before, the esters of this invention are useful as additives in lubricants and fuels. When employed as lubricating oil additives they are usually present in amounts of from about 0.01% to about 30% by weight in the final lubricating composition. Ordinarily, when used as additives for lubricating oil compositions, the esters will be present in amounts of from about 0.5% to about 10% by weight although under unusually adverse conditions, such as in the operation of certain diesels, they may comprise up to about 30% by weight of the lubricant. The products are particularly useful as dispersants in lubricating oil compositions used in the crankcase of various internal combustion engines. Although they can be used effectively in gear and transmission lubricants, hydraulic fluids and the like. When employed in lubricating oils, the esters may be used alone or in combination with other dispersants or detergents. In addition, the lubricating composition may contain rust inhibitors, oxidation inhibitors, viscosity index improving agents, extreme pressure additives, and the like. Typical examples of these additional additives are contained in the above-identified patents disclosing the carboxylic acid acylating agents useful in preparing the esters of the present invention.

The additives of this invention can be effectively employed in a variety of lubricating compositions based on natural or synthetic lubricating oils or on combinations of miscible or mutually soluble natural and synthetic oils. The term "miscible" is intended to describe the situation where the oils are soluble in each other whereas the terminology "mutually soluble" is intended to describe a 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 normally be satisfactory for a combination use due to solubility problems. The lubricating compositions contemplated are principally lubricating oils for both spark-ignition and compression-ignition internal combustion engines. However, other lubricating compositions can benefit from the incorporation of these additives including lubricants for automatic transmissions, gear lubricants, metal-working lubricants, and hydraulic fluids. While the above lubricating compositions are normally liquids, it is also anticipated that they may be converted to "thickened" lubricants or greases for specific applications by application of conventional grease-forming procedures without departing from the scope of this invention.

Natural oils include castor oil, lard oil, and 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. Other synthetic lubricating oils include hydrocarbon oils such as polymerized olefins (e.g., polybutylenes, polypropylenes, etc.); alkyl benzenes (e.g., dodecyl benzenes, tetradecyl benzenes, dinonyl benzenes, di-(2-ethylhexyl) benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyls, etc.); and the like. Alkylene oxide polymers 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 propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene ether having an average molecular weight of 1000, diphenylether of polyethylene glycol having a molecular weight of 500–1000, diethylether of polypropylene glycol having a molecular weight of 1000–1500, etc.) or the lower alkanoyl esters thereof such as the acetic esters. Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acids, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, etc.). Specific examples of these esters include dibutyl adipate, di-(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, dioctylphthalate, didecyl phthalate, dieicosyl sebacate, and the like. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, diethyl ester of decane phosphonic acid, etc.), alkyl diphenyl ethers; and polymerized tetrahydrofuranes. Silicone-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, and polyaryl-oxy-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-pentoxy)disiloxane, poly(methyl(siloxanes, poly(methylphenyl)siloxanes, etc.). This identification of certain oils is not intended to be inclusive but is merely illustrative of the type of base oils contemplated by this invention.

In fuels, the esters promote engine cleanliness by reducing or eliminating harmful deposits in the fuel system, engine, and exhaust system. Their presence promotes carburetor and fuel line cleanliness and reduces or eliminate the deposition of carbonaceous deposits in internal parts of the engine such as on exhaust parts. Normally, the esters used in fuels will be derived from acids having an average molecular weight of about 700–2000 and alcohols containing not more than about ten carbon atoms. The esters 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, antiscreen clogging agents, demulsifiers, smoke suppressants and the like.

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

EXAMPLE A

SAE 30 mineral oil containing 1% of the product of Example 1 and 0.5% of the product of Example 8.

EXAMPLE B

SAE 20 mineral oil containing 0.75% of the product of Examples 2 and 0.15% of the zinc salt of an equimolar mixture of di-cyclohexylphosphorodithioic acid and di-isobutylphosphorodithioic acid.

EXAMPLE C

SAE 10W–30 mineral lubricating oil containing 4% of the product of Example 3.

EXAMPLE D

SAE 10W–30 mineral lubricating oil containing 1.5% of the product of Example 11, 0.075% of phosphorus as the adduct obtained by heating di-nonylphosphorodithioate with 0.25 mole of 1,2-hexene 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) antifoam agent, and 0.5% lard oil.

EXAMPLE E

SAE 20 mineral lubricating oil containing 2.5% of the product of Example 18, 0.75% of phosphorus as the dioctylphosphorodithioate, 2% of a barium detergent prepared by neutralizing with barium hydroxide a hydrolyzed reaction product of a propylene (molecular weight 2000) with one mole of phosphorus pentasulfide and one mole of sulfur, 3% of a barium sulfonate detergent prepared by carbonating a mineral oil solution of mahogany acid and a 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 0.75% of the product of Example 8.

EXAMPLE G

Diesel fuel containing 0.2% of the product of Example 17.

EXAMPLE H

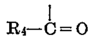
Kerosene containing 0.15% of the product of Example 9.

EXAMPLE I

Gasoline containing 0.007% of the product of Example 16.

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 esters used in these fuels and lubricants with an equal amount of other esters of the present invention. Obviously, optimum amounts for any application will depend upon the particular additive or additive combination selected, the specific fuel or lubricant, 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.

As is apparent to those skilled in the art, the terminology "carboxylic acid moiety" and "acyl residue of a monocarboxylic acid" as used in the specification and claims is intended to describe the carboxylic acid acyl radical of the esters of the invention, (e.g.,



$$R_4-\overset{|}{C}=O$$

where R_4 contains at least about fifty aliphatic carbon atoms. Similarly, "alcoholic moiety" and "oxy residue" are intended to describe the alcohol radical of the ester, that is, the oxy radical corresponding to the esterified alcohol absent one or more hydrogens from alcoholic hydroxy groups (e.g., $-OCH_2CHOHCH_2O-$,

$$-OCH_2CH_2N(CH_2CH_2OH)_2$$

etc.

I claim:

1. A lubricant or fuel composition comprising, respectively, a major amount of a lubricating oil or a normally liquid petroleum distillate fuel and an amount sufficient to impart sludge-dispersing properties to said composition of an oil-soluble ester of a carboxylic acid and an alcohol characterized by the presence within its structure of (A) a carboxylic acid moiety which is the acyl residue of a hydrocarbon monocarboxylic acid having at least about fifty aliphatic carbon atoms and which is substantially free from ethylenic unsaturation and (B) an alcohol moiety which is the oxy residue of a polyhydric alcohol containing two to ten hydroxyl groups or an amino alcohol, with the proviso that the hydrocarbon carboxylic acid moiety may contain polar substituents provided the polar substituents do not exceed 10% by weight of the hydrocarbon portion of the carboxylic acid moiety exclusive of the carboxyl group.

2. A lubricant or fuel composition according to claim 1 wherein the hydrocarbon monocarboxylic acid has an average molecular weight of about 700 to about 5,000 exclusive of the carboxyl group and the alcohol moiety contains up to about forty aliphatic carbon atoms.

3. A lubricant or fuel composition according to claim 2 wherein the alcohol moiety is an oxy residue of a polyhydric amino alcohol.

4. A lubricant or fuel composition according to claim 2 wherein the alcohol moiety is the oxy residue of a polyhydric alkanol containing three to ten aliphatic carbon atoms.

5. A lubricant or fuel composition according to claim 1 wherein the carboxylic acid moiety is the acyl residue of a hydrocarbon-substituted monocarboxylic acid having at least about fifty aliphatic carbon atoms with the proviso that the hydrocarbon substituent may contain polar substituents provided the polar substituents do not exceed 10% by weigh of the hydrocarbon portion of the carboxylic acid moiety exclusive of the carboxyl group.

6. A lubricant or fuel composition according to claim 5 wherein the alcohol moiety is an oxy residue of a polyhydric alkanol containing up to ten aliphatic carbon atoms and at least three hydroxyl groups.

7. A lubricant or fuel composition according to claim 1 wherein the carboxylic acid moiety is the acyl residue

of an aliphatic hydrocarbon-substituted monocarboxylic acid substantially free of ethylenic unsaturation which has an average molecular weight of about 700 to about 5,000 exclusive of the carboxyl groups, said hydrocarbon-substituted monocarboxylic acid having been prepared by reacting a 1-mono-olefin or chlorinated 1-mono-olefin polymer with an α,β-ethylenically unsaturated monocarboxylic acid containing up to six carbon atoms.

8. A lubricant or fuel composition according to claim **7** wherein the alcohol moiety is an oxy residue of a polyhydric alkanol containing at least three hydroxyl groups and three to six carbon atoms.

9. A lubricant or fuel according to claim **8** wherein the alcohol moiety is an oxy residue of a polyhydric alkanol selected from the class consisting of glycerol, erythritol, pentaerythritol, sorbitol, and mannitol.

10. A lubricant or fuel according to claim **7** wherein the alcohol moiety is an oxy residue of an N-hydroxyalkylamine.

11. A lubricant or fuel composition according to claim **10** wherein the alcohol moiety is an oxy residue of an N-hydroxyalkyl monoamine.

12. A lubricant or fuel according to claim **10** wherein the alcohol moiety is an oxy residue of an N-hydroxyalkyl-alkylene polyamine having up to four carbon atoms in the alkylene groups and up to seven amino groups.

13. A lubricant or fuel composition comprising, respectively, a major amount of a lubricating oil or a normally liquid petroleum distillate fuel and an amount sufficient to impart sludge-dispersing properties thereto of an oil-soluble ester of a carboxylic acid and an alcohol characterized by the presence within its structure of (A) a carboxylic acid moiety which is the acyl residue of an aliphatic hydrocarbon-substituted monocarboxylic acid which is substantially free from ethylenic unsaturation and which has an average molecular weight of about 700 to about 5,000 exclusive of the carboxyl group and (B) an alcohol moiety which is an oxy residue of a member selected from the class consisting of polyoxyalkylene glycols having up to 150 oxyalkylene groups and the mono-aryl, mono-alkyl, or mono-aralkyl ethers of said poyloxyalkylene glycols, with the proviso that the hydrocarbon substituent may contain polar substituents provided the polar substituents do not exceed 10% by weight of the hydrocarbon portion of the carboxylic acid moiety exclusive of the carboxyl group.

14. A lubricant or fuel composition according to claim **13** wherein the alcohol moiety is an oxy residue of said polyoxyalkylene glycols.

15. A lubricant composition according to claim **1** wherein the lubricating oil is a synthetic lubricating oil.

16. A lubricating composition according to claim **2** wherein the lubricating oil is a mineral lubricating oil.

17. A lubricating composition according to claim **4** wherein the lubricating oil is a mineral lubricating oil.

18. A lubricant composition according to claim **5** wherein the lubricating oil is a mineral lubricating oil.

19. A lubricant composition according to claim **6** wherein the lubricating oil is a mineral lubricating oil.

20. A lubricant composition according to claim **7** wherein the lubricating oil is a mineral lubricating oil.

21. A lubricating composition according to claim **8** wherein the lubricating oil is a mineral lubricating oil.

22. A lubricating composition according to claim **9** wherein the lubricating oil is a mineral lubricating oil.

23. A lubricating composition according to claim **10** wherein the lubricating oil is a mineral lubricating oil.

24. A lubricating composition according to claim **11** wherein the lubricating oil is a mineral lubricating oil.

25. A lubricating composition according to claim **13** wherein the lubricating oil is a mineral lubricating oil.

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252—56; 44—66, 70, 71