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3,522,179
**LUBRICATING COMPOSITION CONTAINING
ESTERS OF HYDROCARBON-SUBSTITUTED
SUCCINIC ACID**

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25 Claims

ABSTRACT OF THE DISCLOSURE

Lubricating compositions comprising a major amount of a lubricating oil and a minor proportion of an ester derivative of a hydrocarbon-substituted succinic acid wherein the hydrocarbon substituent contains at least about fifty aliphatic carbon atoms, the substituent being further characterized by having no more than about 5% olefinic linkages therein based on the total number of carbon-to-carbon covalent linkages in the substituent. The esters include the acidic esters, diesters, metal salt-esters, and mixtures of these wherein the ester moiety is derived from monohydric and polyhydric alcohols, phenols, and naphthols.

This is a continuation-in-part of application Ser. No. 274,905, filed Apr. 23, 1963, now abandoned.

This invention relates to novel compositions of matter and processes for preparing the same. In a more particular sense this invention relates to composition useful as plasticizers, detergents, anti-rust agents, emulsifiers, and additives in lubricating compositions, fuels, hydrocarbon oils, and power transmitting fluids.

Deterioration of lubricating oils, especially mineral oils, has been a great concern in the formulation of lubricating compositions for use in internal combustion engines, transmissions, gears, etc. Deterioration of the oil results in the formation of products which are corrosive to the metal surfaces with which the oil comes into contact. It also results in the formation of products which agglomerate to form sludge- and varnish-like deposits. The deposits cause sticking of the moving metal parts and obstruct their free movement. They are a principal cause of malfunctioning and premature break-down of the equipment which the oil lubricates.

It is known that water is a common contaminant in the crankcase lubricant of an engine. It may result from the decomposition of the lubricating oil or come from the combustion chamber as a blow-by product of the burning of the fuel. The presence of water in the lubricant seems to promote the deposition of a mayonnaise-like sludge. This type of sludge is more objectionable because it clings tenaciously to metal surfaces and is not removed by oil filters. If the engine is operated under conditions such that the crankcase lubricant temperature is continuously high the water will be eliminated about as fast as it accumulates and only a very small amount of the mayonnaise-like sludge will be formed. On the other hand, if the crankcase lubricant temperature is intermittently high and low or consistently low the water will accumulate and a substantial quantity of the mayonnaise-like sludge will be deposited in the engine.

High operating temperatures are characteristic of an engine that is run consistently at a relatively high speed. However, where an automobile is used primarily for trips of short distance such as is characteristic of urban, home to work use, a significant portion of the operation occurs before the engine has reached its optimum high tempera-

ture. An ideal environment thus obtains for the accumulation of water in the lubricant. In this type of operation the problem of mayonnaise-like sludge has been especially troublesome. Its solution has been approached by the use in the lubricant of detergents such as metal phenates and sulfonates which have been known to be effective in reducing deposits in engines operated primarily at high temperatures. Unfortunately, such known detergents have not been particularly effective in solving the problems associated with low temperature operation particularly those problems which are associated with crankcase lubricants in engines operated at low or intermittently high and low temperatures.

It is accordingly a principal object of this invention to provide novel compositions of matter.

It is also an object of this invention to provide compositions which are suitable for use as additives in hydrocarbon oils.

It is also an object of this invention to provide compositions which are effective as additives in lubricating compositions.

It is another object of this invention to provide compositions effective as detergents in lubricating compositions intended for use in engines operated at low or intermittently high and low temperatures.

It is another object of this invention to provide a process of preparing additives useful as additives in hydrocarbon oils and lubricating compositions.

It is another object of this invention to provide lubricating compositions.

It is further an object of this invention to provide fuel compositions.

These and other objects are attained in accordance with this invention by means of an ester of a substantially saturated hydrocarbon-substituted succinic acid wherein the substantially hydrocarbon substituent has at least about 50 aliphatic carbon atoms. A critical aspect of this invention is the size and the chemical constitution of the substantially hydrocarbon substituent of the succinic radical. Thus, only the esters of substituted succinic acids in which the substituent is substantially saturated and has at least about 50 aliphatic carbon atoms are contemplated as being within the scope of this invention. This lower limit for the size of the substituent is based upon a consideration not only of the oil-solubility of the esters but also of their effectiveness in applications contemplated by this invention.

The substantially hydrocarbon substituent of the succinic radical may contain polar groups, provided, however, that the polar groups are not present in proportions sufficiently large to alter significantly the hydrocarbon character of the substituent. The polar groups are exemplified by the chloro, bromo, keto, ether, aldehyde, nitro, etc. The upper limit with respect to the portion of such polar groups in the substituent is approximately 10% based on the weight of the hydrocarbon portion of the substituent.

The sources of the substantially hydrocarbon substituent include principally the high molecular weight substantially saturated petroleum fractions and substantially saturated olefin polymers, particularly polymers of mono-olefins having from 2 to 30 carbon atoms. 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 helpful. They are illustrated by 2-butene, 3-pentene, and 4-octene.

Also useful are the interpolymers of the olefins such as those illustrated above with other interpolymerizable ole-

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finic substances such as aromatic olefins, cyclic olefins, and polyolefins. Such interpolymers include, for example, those prepared by polymerizing isobutene with styrene; isobutene with butadiene; propene with isoprene; 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.

The relative proportions of the mono-olefins to the other monomers in the interpolymers influence the stability and oil solubility of the final products derived from such interpolymers. Thus, for reasons of oil-solubility and stability the interpolymers contemplated for use in this invention should be substantially aliphatic and substantially saturated, i.e., they should contain at least about 80%, preferably at least about 95%, on a weight basis, of units derived from the aliphatic mono-olefins and no more than about 5% of olefinic linkages based on the total number of carbon-to-carbon covalent linkages. In most instances, the percentage of olefinic linkages should be less than about 2% of the total number of carbon-to-carbon covalent linkages.

Specific examples of such interpolymers include the copolymer of 95% (by weight) of isobutene with 5% of styrene; the terpolymer of 98% of isobutene with 1% of piperylene and 1% of chloroprene; the terpolymer of 95% of isobutene with 2% of 1-butene and 3% of 1-hexene; the terpolymer of 80% of isobutene with 10% of 1-pentene and 10% of 1-octene; the copolymer of 80% of 1-hexene and 20% of 1-heptene; the terpolymer of 90% of isobutene with 2% of cyclohexene and 8% of propene; and the copolymer of 80% of ethylene and 20% of propene.

Another source of the substantially hydrocarbon radical comprises saturated aliphatic hydrocarbons such as highly refined high molecular weight white oils or synthetic alkanes such as are obtained by hydrogenation of high molecular weight olefin polymers illustrated above or high molecular weight olefinic substances.

The use of olefin polymers having molecular weights of about 700-5000 is preferred. Higher molecular weight olefin polymers having molecular weights from about 10,000 to about 100,000 or higher have been found to impart viscosity index improving properties to the final products of this invention. The use of such higher molecular weight olefin polymers often is desirable.

The esters of this invention are those of the above-described succinic acids with hydroxy compounds which may be aliphatic compounds such as monohydric and polyhydric alcohols or aromatic compounds such as phenols and naphthols. The aromatic hydroxy compounds from which the esters of this invention may be derived are illustrated by the following specific examples: phenol, beta-naphthol, alpha-naphthol, cresol, resorcinol, catechol, p,p'-dihydroxybiphenyl, 2-chlorophenol, 2,4-dibutylphenol, propene tetramer-substituted phenol, didodecylphenol, 4,4'-methylene-bis-phenol, alpha-decyl-beta-naphthol, polyisobutene (molecular weight of 1000)-substituted phenol, the condensation product of heptylphenol with 0.5 mole of formaldehyde, the condensation product of octylphenol with acetone, di(hydroxyphenyl) oxide, di(hydroxyphenyl)sulfide, di(hydroxyphenyl) disulfide, and 4-cyclohexylphenol. Phenol and alkylated phenols having up to three alkyl substituents are preferred. Each of the alkyl substituents may contain 100 or more carbon atoms.

The alcohols from which the esters may be derived preferably contain up to about 40 aliphatic carbon atoms. They may be monohydric alcohols such as methanol, ethanol, isooctanol, dodecanol, cyclohexanol, cyclopentanol, behenyl alcohol, hexatriacontanol, neopentyl alcohol, isobutyl alcohol, benzyl alcohol, beta-phenylethyl alcohol, 2-methylcyclohexanol, beta-chloroethanol, monomethyl ether of ethylene glycol, monobutyl ether of ethylene

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glycol, monopropyl ether of diethylene glycol, monododecyl ether of triethylene glycol, mono-oleate of ethylene glycol, monostearate of diethylene glycol, sec-pentyl alcohol, tert-butyl alcohol, 5-bromo-dodecanol, nitro-octadecanol and dioleate of glycerol. The polyhydric alcohols preferably contain from 2 to about 10 hydroxy radicals. They are illustrated by, for example, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, and other alkylene glycols in which the alkylene radical contains from 2 to about 8 carbon atoms. Other useful polyhydric alcohols include glycerol, mono-oleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, 9,10-dihydroxy stearic acid, methyl ether of 9,10-dihydroxy stearic acid, 1,2-butanediol, 2,3-hexanediol, 2,4-hexanediol, pinacol, erythritol, arabitol, sorbitol, mannitol, 1,2-cyclo-hexanediol, and xylylene glycol. Carbohydrates such as sugars, starches, celluloses, etc., likewise may yield the esters of this invention. The carbohydrates may be exemplified by a glucose, fructose, sucrose, rhamose, mannose, glyceraldehyde, and galactose.

An especially preferred class of polyhydric alcohols are those having at least three hydroxy radicals, some of which have been esterified with a monocarboxylic acid having from about 8 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, distearate of sorbitol, mono-oleate of glycerol, monostearate of glycerol, di-dodecanoate of erythritol.

The esters of this invention may also be derived from unsaturated alcohols such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-cyclohexen-3-ol, an oleyl alcohol. Still other classes of the alcohols capable of yielding the esters of this invention comprises the ether-alcohols and amino-alcohols including, for example, the oxy-alkylene-, oxy-arylene-, amino-alkylene-, and amino-arylene-substituted alcohols having one or more oxy-alkylene, amino-alkylene or amino-arylene oxy-arylene radicals. They are exemplified by Cellosolve, Carbitol, phenoxy-ethanol, heptylphenyl-(oxypropylene)₈-H, octyl-(oxyethylene)₃₀-H, phenyl-(oxyoctylene)₂-H, mono(heptylphenyl-oxypropylene)-substituted glycerol, poly(styrene oxide), aminoethanol, 3-amino ethylpentanol, di(hydroxyethyl) amine, p-aminophenol, tri(hydroxypropyl) amine, N-hydroxyethyl ethylene diamine, N,N,N',N'-tetrahydroxy-trimethylene diamine, and the like. For the most part, the ether-alcohols having up to about 150 oxy-alkylene radicals in which the alkylene radical contains from 1 to about 8 carbon atoms are preferred.

The esters of this invention may be di-esters of succinic acids or acidic esters, i.e., partially esterified succinic acids; as well as partially esterified polyhydric alcohols or phenols, i.e., esters having free alcoholic or phenolic hydroxyl radicals. Mixtures of the above-illustrated esters likewise are contemplated within the scope of this invention.

A suitable class of esters for use in the lubricating compositions of this invention are those diesters of succinic acid and an alcohol having up to about nine aliphatic carbon atoms and having at least one substituent selected from the class consisting of amino and carboxy groups wherein the hydrocarbon substituent of the succinic acid is a polymerized butene substituent having a molecular weight of from about 700 to about 5000.

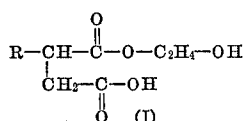
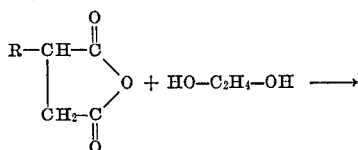
The esters of this invention may be prepared by one of several methods. The method which is preferred because of convenience and superior properties of the esters it produces, involves the reaction of a suitable alcohol or phenol with a substantially hydrocarbon-substituted succinic anhydride. The esterification is usually carried out at a temperature above about 100° C., preferably between 150° C. and 300° C.

The water formed as a by-product is removed by distillation as the esterification proceeds. A solvent may be

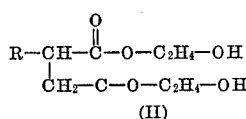
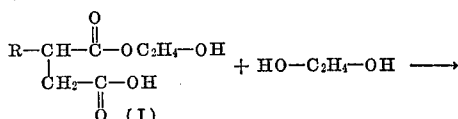
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used in the esterification to facilitate mixing and temperature control. It also facilitates the removal of water from the reaction mixture. The useful solvents include xylene, toluene, diphenyl ether, chlorobenzene, and mineral oil. The esterification is illustrated by the reaction of ethylene glycol with a substituted succinic anhydride as represented by the equations below.

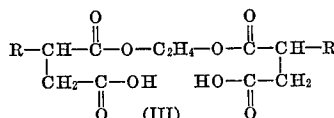
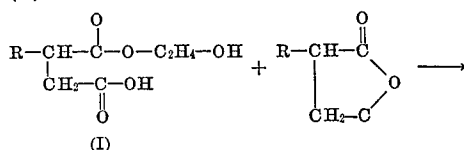
(A)



(B)



(C)



wherein R is a substantially hydrocarbon radical having at least about 50 aliphatic carbon atoms. It will be readily appreciated that the above equations are merely illustrative. Other products not represented by Formulas I, II, and III may be formed. Polymeric esters formed by the condensation of two or more molecules of each of the succinic acid reactant and the polyhydric alcohol reactant likewise may be formed. In most cases the product is a mixture of esters, the precise chemical composition and the relative proportions of which in the product are difficult to determine. Consequently, the product of such reaction is best described in terms of the process by which it is formed.

A modification of the above process involves the replacement of the substituted succinic anhydride with the corresponding succinic acid. However, succinic acids readily undergo dehydration at temperatures above about 100° C. and are thus converted to their anhydrides which are then esterified by the reaction with the alcohol reactant. In this regard, succinic acids appear to be the substantial equivalent of their anhydrides in the process.

The relative proportions of the succinic reactant and the hydroxy reactant which are to be used depend to a large measure upon the type of the product desired and the number of hydroxyl groups present in the molecule of the hydroxy reactant. For instance, the formation of a half ester of a succinic acid, i.e., one in which only one of the two acid radicals is esterified, involves the use of one mole of a monohydric alcohol for each mole of the substituted succinic acid reactant, whereas the formation of a diester of a succinic acid involves the use of two moles

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of the alcohol for each mole of the acid. On the other hand, one mole of a hexahydric alcohol may combine with as many as six moles of a succinic acid to form an ester in which each of the six hydroxyl radicals of the alcohol is esterified with one of the two acid radicals of the succinic acid. Thus, the maximum proportion of the succinic acid to be used with a polyhydric alcohol is determined by the number of hydroxyl groups present in the molecule of the hydroxy reactant. For the purposes of this invention, it has been found that esters obtained by the reaction of equi-molar amounts of the succinic acid reactant and hydroxy reactant have superior properties and are therefore preferred.

In some instances it is advantageous to carry out the esterification in the presence of a catalyst such as sulfuric acid, pyridine hydrochloride, hydrochloric acid, benzene sulfonic acid, p-toluene sulfonic acid, phosphoric acid, or any other known esterification catalyst. The amount of the catalyst in the reaction may be as little as 0.01% (by weight of the reaction mixture), more often from about 0.1% to about 5%.

The esters of this invention likewise may be obtained by the reaction of a substituted succinic acid or anhydride with an epoxide or a mixture of an epoxide and water. Such reaction is similar to one involving the acid or anhydride with a glycol. For instance, the product represented by the structural Formula I above may be prepared by the reaction of a substituted succinic acid with one mole of ethylene oxide. Similarly, the product of Formula II may be obtained by the reaction of a substituted succinic acid with two moles of ethylene oxide. Other epoxides which are commonly available for use in such reaction include, for example, propylene oxide, styrene oxide, 1,2-butylene oxide, 2,3-butylene oxide, epichlorohydrin, cyclohexene oxide, 1,2-octylene oxide, epoxidized soya bean oil, methyl ester of 9,10-epoxystearic acid, and butadiene mono-epoxide. For the most part, the epoxides are the alkylene oxides in which the alkylene radical has from 2 to about 8 carbon atoms; or the epoxidized fatty acid esters in which the fatty acid radical has up to about 30 carbon atoms and the ester radical is derived from a lower alcohol having up to about 8 carbon atoms.

In lieu of the succinic acid or anhydride, a substituted succinic acid halide may be used in the processes illustrated above for preparing the esters of this invention. Such acid halides may be acid dibromides, acid dichlorides, acid monochlorides, and acid monobromides. The substituted succinic anhydrides and acids can be prepared by, for example, the reaction of maleic anhydride with a high molecular weight olefin or a halogenated hydrocarbon such as is obtained by the chlorination of an olefin polymer described previously. The reaction involves merely heating the reactants at a temperature preferably from about 100° C. to about 250° C. The product from such a reaction is an alkenyl succinic anhydride. The alkenyl group may be hydrogenated to an alkyl group. The anhydride may be hydrolyzed by treatment with water or steam to the corresponding acid. Another method useful for preparing the succinic acids or anhydrides involves the reaction of itaconic acid or anhydride with an olefin or a chlorinated hydrocarbon at a temperature usually within the range from about 100° C. to about 250° C. The succinic acid halides can be prepared by the reaction of the acids or their anhydrides with a halogenation agent such as phosphorus tribromide, phosphorus pentachloride, or thionyl chloride. These and other methods of preparing the succinic compounds are well known in the art and need not be illustrated in further detail here.

Still other methods of preparing the esters of this invention are available. For instance, the esters may be obtained by the reaction of maleic acid or anhydride with an alcohol such as is illustrated above to form a mono- or di-ester of maleic acid and then the reaction of this

ester with an olefin or a chlorinated hydrocarbon such as is illustrated above. They may also be obtained by first esterifying itaconic anhydride or acid and subsequently reacting the ester intermediate with an olefin or a chlorinated hydrocarbon under conditions similar to those described hereinabove.

Still another method of preparing the esters of this invention involves the reaction of a substituted succinic acid or anhydride with a halogenated alcohol or epoxide such as 2-chloro-ethanol, 3-bromopropanol, 2-chloro-cyclohexanol, epichlorohydrin, p-benzyl alcohol or the like. The resulting ester has a halogen substituent which is susceptible to modification by reaction with an amino compound such as ammonia, aniline, toluidine, methylamine, dimethylamine, cyclohexylamine, N-methyldodecylamine, N-methylaniline ethylenediamine, diethylene triamine, pentaethylene hexamine, behenylamine, etc. The modification results in the replacement of the halogen group with an amino group so that the ester is characterized by the presence of an amino hydrocarbon-containing ester group. Such amino hydrocarbon-substituted esters, especially those in which the amino radical is an unsubstituted amino radical or one having hydrocarbon substituents or one being free of any high molecular weight succinic radical attached directly to the amino nitrogen atom, are especially useful for the purpose of the present invention.

The following examples illustrate the esters of this invention and the processes for preparing such esters.

EXAMPLE 1

A substantially hydrocarbon-substituted succinic anhydride is prepared by chlorinating a polyisobutene having a molecular weight of 1000 to a chlorine content of 4.5% and then heating the chlorinated polyisobutene with 1.2 molar proportions of maleic anhydride at a temperature of 150°–220° C. The succinic anhydride thus obtained has an acid number of 130. A mixture of 874 grams (1 mole) of the succinic anhydride and 104 grams (1 mole) of neopentyl glycol is mixed at 240°–250° C./30 mm. for 12 hours. The residue is a mixture of the esters resulting from the esterification of one and both hydroxy radicals of the glycol. It has a saponification number of 101 and an alcoholic hydroxyl content of 0.2%.

EXAMPLE 2

The di-methyl ester of the substantially hydrocarbon-substituted succinic anhydride of Example 1 is prepared by heating a mixture of 2185 grams of the anhydride, 480 grams of methanol, and 1000 cc. of toluene at 50°–65° C. while hydrogen chloride is bubbled through the reaction mixture for 3 hours. The mixture is then heated at 60°–65° C. for 2 hours, dissolved in benzene, washed with water, dried and filtered. The filtrate is heated at 150° C./60 mm. to rid it of volatile components. The residue is the defined di-methyl ester.

EXAMPLE 3

The substantially hydrocarbon-substituted succinic anhydride of Example 1 is partially esterified with an ether-alcohol as follows. A mixture of 550 grams (0.63 mole) of the anhydride and 190 grams (0.32 mole) of a commercial polyethylene glycol having a molecular weight of 600 is heated at 240°–250° C. for 8 hours at atmospheric pressure and 12 hours at a pressure of 30 mm. Hg until the acid number of the reaction mixture is reduced to 28. The residue is an acidic ester having a saponification number of 85.

EXAMPLE 4

A mixture of 926 grams of a polyisobutene-substituted succinic anhydride having an acid number of 121, 1023 grams of mineral oil, and 124 grams (2 moles per mole of the anhydride) of ethylene glycol is heated at 50°–170° C. while hydrogen chloride is bubbled through the reaction mixture for 1.5 hours. The mixture is then heated

to 250° C./30 mm. and the residue is purified by washing with aqueous sodium hydroxide followed by washing with water, then dried and filtered. The filtrate is a 50% oil solution of an ester having a saponification number of 48.

EXAMPLE 5

A mixture of 438 grams of the polyisobutene-substituted succinic anhydride prepared as is described in Example 1 and 333 grams of a commercial polybutylene glycol having a molecular weight of 1000 is heated for 10 hours at 150°–160° C. The residue is an ester having a saponification number of 73 and an alcoholic hydroxyl content of 0.7%.

EXAMPLE 6

The acidic ester of Example 3 (250 grams) is neutralized by mixing with 11 grams (10% excess on a chemical equivalent basis) of barium oxide, 20 grams of methanol, and 267 grams of mineral oil at 50°–60° C. The mixture is then heated to 150° C. to distill off volatile components and the residue is filtered. The filtrate is a mineral oil solution of a mixed ester-metal salt having a saponification number of 17 and a barium sulfate ash content of 4.6%.

EXAMPLE 7

A mixture of 645 grams of the substantially hydrocarbon-substituted succinic anhydride prepared as is described in Example 1 and 44 grams of tetramethylene glycol is heated at 100°–130° C. for 2 hours. To this mixture there is added 51 grams of acetic anhydride (esterification catalyst) and the resulting mixture is heated under reflux at 130°–160° C. for 2.5 hours. Thereafter the volatile components of the mixture are distilled by heating the mixture to 196°–270° C./30 mm. and then at 240° C./0.15 mm. for 10 hours. The residue is an acidic ester having a saponification number of 121 and an acid number of 58.

EXAMPLE 8

A mixed ester-metal salt is prepared as follows. A mixture of 1545 grams (1.5 moles) of the substituted succinic anhydride having an acid number of 110 and prepared as is described in Example 1 and 46 grams (0.5 mole) of glycerol is heated at 120°–150° C. for 3 hours whereupon the acid number of the reaction mixture is reduced to 68. It is then heated at 150°–190° C. until the acid number is reduced to 53. To this mixture there is added portionwise 125 grams (1.63 moles) of barium oxide together with 1500 grams of mineral oil and 50 cc. of water. The resulting mixture is heated to 90°–100° C., diluted with 25 cc. isopropyl alcohol and 100 cc. of benzene (solvent mixture), and heated under reflux for 3 hours. Volatile components are then removed by heating the mixture to 160° C./35 mm. and the residue filtered. The filtrate is a mineral oil solution of the mixed ester-barium salt having a barium sulfate content of 5.6%.

EXAMPLE 9

A mixed ester-metal salt is prepared by the procedure of Example 8 except that pentaerythritol (51 grams, 0.38 mole) is used in place of glycerol. The product has a barium sulfate ash content of 4.9%.

EXAMPLE 10

A mixed ester-metal salt is prepared as follows. A mixture is prepared from 1545 grams (1.5 moles) of a polyisobutene-substituted succinic anhydride having an acid number of 110 and 152 grams (0.19 mole) of an ether-alcohol prepared by the reaction of sucrose with 8 moles of propylene oxide. The mixture is heated at 139°–180° C. for 3 hours whereupon the acid number of the mixture is reduced to 45. It is diluted with 320 grams of mineral oil and heated at 170°–195° C. for 3.5 hours until the acid number is 42. To this mixture there are added 1180 grams of mineral oil, 50 grams of water, 50 cc. of isopropanol, and 128 grams (0.83 mole)

of barium oxide at 70° C. The resulting mixture is heated at 90°–105° C. for 3 hours and dried at 158° C. The residue is filtered. The filtrate is a mineral oil solution of the mixed ester-barium salt having a barium sulfate ash content of 5.6%.

EXAMPLE 11

A mixture of 456 grams of a polyisobutene-substituted succinic anhydride prepared as is described in Example 1 and 350 grams (0.35 mole) of the monophenyl ether of a polyethylene glycol having a molecular weight of 1000 is heated at 150°–155° C. for 2 hours. The product is an ester having a saponification number of 71, an acid number of 53, and an alcoholic hydroxyl content of 0.52%.

EXAMPLE 12

An ester is prepared by heating at the reflux temperature for 10 hours a xylene solution of an equi-molar mixture of the polyisobutene-substituted succinic anhydride of Example 1 and a commercial polystyrene oxide having a molecular weight of 500 while water is removed by azeotropic distillation. The mixture is then heated to 160° C./18 mm. The residue is an ester having a saponification number of 67, an acid number of 45, and an alcoholic hydroxyl content of 1.2%.

EXAMPLE 13

A di-oleyl ester is prepared as follows: A mixture of 1 mole of a polyisobutene-substituted succinic anhydride, 2 moles of a commercial oleyl alcohol, 305 grams of xylene, and 5 grams of p-toluene sulfonic acid (esterification catalyst) is heated at 150°–173° C. for 4 hours whereupon 18 grams of water is collected as the distillate. The residue is washed with water and the organic layer dried and filtered. The filtrate is heated to 175° C./20 mm. and the residue is the defined ester.

EXAMPLE 14

A di-oleyl ester is prepared by the procedure of Example 13 except that the substituted succinic anhydride used is prepared by the reaction of a chlorinated petroleum oil having a molecular weight of 800 with maleic anhydride.

EXAMPLE 15

An ether-alcohol is prepared by the reaction of 9 moles of ethylene oxide with 0.9 mole of a polyisobutene-substituted phenol in which the polyisobutene substituent has a molecular weight of 1000. A substantially hydrocarbon-substituted succinic acid ester of this ether-alcohol is prepared by heating a xylene solution of an equi-molar mixture of the two reactants in the presence of a catalytic amount of p-toluene sulfonic acid at 157° C. The ester is found to have a saponification number of 25 and an acid number of 10.

EXAMPLE 16

A polyhydric alcohol is prepared by copolymerizing equimolar proportions of styrene and allyl alcohol to a copolymer having a molecular weight of 1150 and containing an average of 5 hydroxyl radicals per mole. An ester of this alcohol is prepared as follows. A mixture of 340 grams (0.3 mole) of the alcohol and 1.5 moles of a polyisobutene-substituted succinic anhydride as is prepared in Example 1 in 500 grams of xylene is heated at 80°–115° C., diluted with mineral oil, then heated to distill off xylene, and filtered. The filtrate is further esterified by heating with propylene oxide (one equivalent per equivalent of the unesterified anhydride) at 70°–150° C. under reflux. The product is diluted with oil to an oil solution having an oil content of 40%.

EXAMPLE 17

A substantially hydrocarbon-substituted succinic acid is prepared by chlorinating a polyisobutene having a molecular weight of 50,000 to a chlorine content of 3.9%, 75

reacting the chlorinated polyisobutene with maleic anhydride to form a substituted succinic anhydride having an acid number of 20, and hydrolyzing the anhydride by treatment with steam at 102°–133° C. to the corresponding acid. A mixture of 315 grams of the acid (0.06 mole) and 10 grams (0.17 mole) of propylene oxide is heated at 90°–102° C. for 1 hour. The residue is then heated at 100°–110° C./1 mm. The above treatment with propylene oxide is repeated twice. The final product is found to have a saponification number of 20.

EXAMPLE 18

An ester of an ether-alcohol is prepared by heating a toluene solution of an equi-molar mixture of the substantially hydrocarbon-substituted succinic anhydride of Example 1 and a commercial polyethylene glycol at 97°–102° C. for 6 hours and then at 110° C./16 mm. The ester has a saponification number of 37 and an acid member of 26.

EXAMPLE 19

A di-(hydroxypropyl)ester is prepared as follows: propylene oxide (58 grams, 1 mole) is added dropwise to a mixture of 0.5 mole of the substantially hydrocarbon-substituted succinic anhydride of Example 1 and 8 grams (0.1 mole, esterification catalyst) of pyridine at 80°–90° C. The mixture is heated at reflux for 1 hour, diluted with 400 grams of mineral oil and heated to 170° C./40 mm. The residue is filtered. The filtrate is a 40% mineral oil solution of the defined ester.

EXAMPLE 20

An ester is obtained by heating a mixture of 525 grams of the substantially hydrocarbon-substituted succinic anhydride of Example 1, 422 grams of butyl 9,10-epoxystearate, and 9.5 grams of pyridine (esterification catalyst) at 100°–200° C. for 2.5 hours. The mixture is diluted with 630 grams of mineral oil and heated to 210° C./20 mm. The residue is a mineral oil solution of the ester having a saponification number of 70, an acid number of 1.4, and an alcoholic hydroxyl content of 0.3%.

EXAMPLE 21

An ester is prepared by the procedure of Example 20 except that the butyl 9,10-epoxystearate is replaced with dipentene di-epoxide (0.64 mole per mole of the anhydride used). A 40% mineral oil solution of the ester obtained has a saponification number of 54 and an acid number of 0.4.

EXAMPLE 22

A partial ester of sorbitol is obtained by heating a xylene solution containing the substantially hydrocarbon substituted succinic anhydride of Example 1 and sorbitol (0.5 mole per mole of the anhydride) at 150°–155° C. for 6 hours while water is removed by azeotropic distillation. The residue is filtered and the filtrate is heated at 170° C./11 mm. to distill off volatile components. The residue is an ester having a saponification number of 97 and an alcoholic hydroxyl content of 1.5%.

EXAMPLE 23

An ester is obtained by heating an equi-molar mixture of dibutyl itaconate and chlorinated polyisobutene having a chlorine content of 4.7% and a molecular weight of 700 at 190°–220° C. for 7 hours and then at 200° C./3 mm. The residue is filtered. The filtrate is the ester having a saponification number of 74.

EXAMPLE 24

An ester is obtained by the further esterification of sorbitol mono-oleate with a substituted succinic anhydride as follows: a mixture of 126 grams of sorbitol mono-oleate, 770 grams of the substantially hydrocarbon substituted succinic anhydride of Example 1, 588 grams of mineral oil, 500 cc. of xylene and 9 grams of p-toluene sulfonic acid (esterification catalyst) is heated at

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140° C. while water is removed by azeotropic distillation. The residue is washed with water and dried at 150° C./20 mm. The product is a 40% mineral oil solution of an ester having a saponification number of 68.

EXAMPLE 25

An ester is obtained by the procedure of Example 24 except that sorbitol tri-oleate (272 grams) is used in place of sorbitan mono-oleate. The product is a 40% oil solution of the ester having a saponification number of 79.

EXAMPLE 26

A substantially hydrocarbon-substituted succinic anhydride is prepared as is described in Example 1 except that a copolymer of 90 weight percent of isobutene and 10 weight percent of piperylene having a molecular weight of 66,000 is used in lieu of the polyisobutene used. The anhydride has an acid number of 22. An ester is prepared by heating a toluene solution of an equi-molar mixture of the above anhydride and a commercial alkanol consisting substantially of C₁₂₋₁₄ alcohols at the reflux temperature for 7 hours while water is removed by azeotropic distillation. The residue is heated at 150° C./3 mm. to remove volatile components and diluted with mineral oil. A 50% oil solution of the ester is found to have a saponification number of 17 and an acid number of 5.7.

EXAMPLE 27

A substantially hydrocarbon-substituted succinic anhydride having an acid number of 25 is obtained from maleic anhydride and a copolymer of 90 weight percent of isobutene with 10 weight percent of piperylene having a molecular weight of 20,000. An ester of the above anhydride with allyl alcohol is prepared by heating a toluene solution containing the anhydride and allyl alcohol (4 moles per mole of the anhydride) in the presence of a catalytic amount of p-toluene sulfonic acid at 110°-125° C. The residue is then treated with calcium hydroxide and filtered. The solvent is then removed from the filtrate and the residue is dissolved in a mineral oil to make up a 50% oil solution.

EXAMPLE 28

An ester is obtained by the procedure of Example 24 except that 234 grams of a poly(oxyethylene)substituted sorbitol mono-oleate having a molecular weight of 234 is used in place of sorbitol mono-oleate. The ester has a saponification number of 53.

The esters of this invention are useful for a wide variety of purposes, as pesticides, plasticizers, rust-inhibiting agents, corrosion-inhibiting agents, extreme pressure agents, detergents, etc.

A principal utility of the esters is as additives in lubricants. It has been discovered in accordance with this invention that when used for such purpose the esters depend for their effectiveness upon the size of the substantially hydrocarbon substituent in the succinic radical. More particularly, it has been found that esters in which the substantially hydrocarbon substituent contain more than about 50 aliphatic carbon atoms are effective to impart detergent properties to a lubricant, especially under low temperature, or intermittently high and low temperature, service conditions. It has been further found that the detergent properties of the esters diminish sharply when the size of this substituent is less than about 50 aliphatic carbon atoms, so that esters having less than about 35 aliphatic carbon atoms in this substituent are relatively ineffective for the purposes of this invention.

The lubricating oils in which the esters of this invention are useful as additives may be of synthetic, animal, vegetable, or mineral origin. Ordinarily, mineral lubricating oils are preferred by reason of their availability, general excellence, and low cost. For certain applications, oils belonging to one of the other three groups may be pre-

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ferred. For instance, synthetic polyester oils such as didodecyl adipate and di-2-ethylhexyl sebacate are often preferred as jet engine lubricants. Normally, the lubricating oils preferred will be fluid oils ranging in viscosity from about 40 Saybolt Universal seconds at 100° F. to about 200 Saybolt Universal seconds at 210° F.

The concentration of the esters as additives in lubricants usually ranges from about 0.01% to about 10% by weight. The optimum concentration for a particular application depends to a large extent upon the type of service to which the lubricants are to be subjected. Thus, for example, lubricants for use in gasoline engines may contain from about 0.5 to about 5% of the additive whereas lubricating compositions for use in gears and diesel engines may contain as much as 10% or even more of the additive.

This invention contemplates also the presence of other additives in the lubricating compositions. Such additives include, for example, supplemental detergents of the ash-containing type, viscosity index improving agents, pour point depressing agents, anti-foam agents, extreme pressure agents, rust-inhibiting agents, and supplemental oxidation and corrosion-inhibiting agents.

The ash-containing detergents are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, or organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage such as those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium, and barium.

The term "basic salt" is used to designate the metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involves heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature about 50° C. and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance, alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve, Carbitol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; amines such as aniline, phenylenediamine, phenothiazine, phenyl - beta naphthyl-amine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent, a phenolic promoter compound, and a small amount of water and carbonating the mixture at an elevated temperature such as 60°-200° C.

The preparation of a basic sulfonate detergent is illustrated as follows: A mixture of 490 parts (by weight) of a mineral oil, 110 parts of water, 61 parts of heptylphenol, 340 parts of barium mahogany sulfonate, and 227 parts of barium oxide is heated at 100° C. for 0.5 hour and then to 150° C. Carbon dioxide is then bubbled into the mixture until the mixture is substantially neutral. The mixture is filtered and the filtrate found to have a sulfate ash content of 25%.

The preparation of a basic barium salt of a phosphorus acid is illustrated as follows: A polyisobutene having a molecular weight of 50,000 is mixed with 10% by weight of phosphorus pentasulfide at 200° C. for 6 hours. The resulting product is hydrolyzed by treatment with steam at 160° C. to produce an acidic intermediate. The acidic

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EXAMPLE VI

SAE 20W-30 mineral lubricating oil containing 5% of the product of Example 24.

EXAMPLE VII

SAE 10W-30 mineral lubricating oil containing 1.5% of the product of Example 2 and 0.05% of phosphorus as the zinc salt of a phosphorodithioic acid prepared by the reaction of phosphorus pentasulfide with a mixture of 60% (mole) of p-butylphenol and 40% (mole) of n-pentyl alcohol.

EXAMPLE VIII

SAE 50 mineral lubricating oil containing 3% of the product of Example 26 and 0.1% of phosphorus as the calcium salt of di-hexylphosphorodithioate.

EXAMPLE IX

SAE 10W-30 mineral lubricating oil containing 2% of the product of Example 2, 0.06% of phosphorus as zinc di-n-octylphosphorodithioate, and 1% of sulfate ash as barium mahogany sulfonate.

EXAMPLE X

SAE 30 mineral lubricating oil containing 5% of the product of Example 10, 0.1% of phosphorus as the zinc salt of a mixture of equi-molar amounts of di-isopropylphosphorodithioic acid and di-n-decylphosphorodithioic acid, and 2.5% of sulfate ash as a basic barium detergent prepared by carbonating at 150° C. a mixture comprising mineral oil, barium di-dodecylbenzene sulfonate 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.

EXAMPLE XI

SAE 10W-30 mineral lubricating oil containing 6% of the product of Example 17, 0.075% of phosphorus as zinc di-n-octylphosphorodithioate, and 5% of the barium salt of an acidic composition prepared by the reaction of 1000 parts of a polyisobutene having a molecular weight of 60,000 with 100 parts of phosphorus pentasulfide at 200° C. and hydrolyzing the product with steam at 150° C.

EXAMPLE XII

SAE 10 mineral lubricating oil containing 2% of the product of Example 25, 0.075% of phosphorus as the adduct of zinc di-cyclohexylphosphorodithioate treated with 0.3 mole of ethylene oxide, 2% of a sulfurized sperm oil having a sulfur content of 10%, 3.5% of a poly-(alkyl methacrylate) viscosity index improver, 0.02% of a poly-(alkyl methacrylate) pour point depressant, 0.003% of a poly-(alkyl siloxane) anti-foam agent.

EXAMPLE XIII

SAE 10 mineral lubricating oil containing 1.5% of the product of Example 14, 0.075% of phosphorus as the adduct obtained by heating zinc dinonylphosphorodithioate with 0.25 mole of 1,2-hexene oxide at 120° C., a sulfurized methyl ester of tall oil acid having a sulfur content of 15%, 6% of a polybutene viscosity index improver, 0.005% of a poly-(alkyl methacrylate) anti-foam agent, and 0.5% of lard oil.

EXAMPLE XIV

SAE 20 mineral lubricating oil containing 1.5% of the product of Example 2, 0.5% of di-dodecyl phosphite, 2% of the sulfurized sperm oil having a sulfur content of 9%, a basic calcium detergent prepared by carbonating a mixture comprising mineral oil, calcium mahogany sulfonate and 6 moles of calcium hydroxide in the presence of an equi-molar mixture (10% of the mixture) of methyl alcohol and n-butyl alcohol as the promoter at the reflux temperature,

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EXAMPLE XV

SAE 10 mineral lubricating oil containing 25% of the product of Example 9, 0.07% of phosphorus as zinc di-octylphosphorodithioate, 2% of a barium detergent prepared by neutralizing with barium hydroxide the hydrolyzed reaction product of a polypropylene (molecular weight of 2000) with 1 mole of phosphorus pentasulfide and 1 mole of sulfur, 3% of a barium sulfonate detergent prepared by carbonating a mineral oil solution of mahogany acid, and a 500% stoichiometrically excess amount of barium hydroxide in the presence of phenol as the promoter at 180° C., 3% of a supplemental ashless detergent prepared by copolymerizing a mixture of 95% (weight) of decyl-methacrylate and 5% (weight) of diethylaminoethylacrylate.

EXAMPLE XVI

SAE 80 mineral lubricating oil containing 2% of the product of Example 20, 0.1% of phosphorus as zinc di-n-hexylphosphorodithioate, 10% of a chlorinated paraffin wax having a chlorine content of 40%, 2% of di-butyl tetrasulfide, 2% of sulfurized dipentene, 0.2% oleyl amide, 0.003% of an anti-foam agent, 0.02% of a pour point depressant, and 3% of a viscosity index improver.

EXAMPLE XVII

SAE 10 mineral lubricating oil containing 3% of the product of Example 2, 0.075% of phosphorus as the zinc salt of a phosphorodithioic acid prepared by the reaction of phosphorus pentasulfide with an equi-molar mixture of n-butyl alcohol and dodecyl alcohol, 3% of a barium detergent prepared by carbonating a mineral oil solution containing 1 mole of sperm oil, 0.6 mole of octylphenol, 2 moles of barium oxide, and a small amount of water at 150° C.

EXAMPLE XVIII

SAE 20 mineral lubricating oil containing 2% of the product of Example 12 and 0.07% of phosphorus as zinc di-n-octylphosphorodithioate.

EXAMPLE XIX

SAE 30 mineral lubricating oil containing 3% of the product of Example 14 and 0.1% of phosphorus as zinc di-(isobutylphenyl)-phosphorodithioate.

EXAMPLE XX

SAE 50 mineral lubricating oil containing 2% of the product of Example 15.

EXAMPLE XXI

SAE 90 mineral lubricating oil containing 3% of the product of Example 18 and 0.2% of phosphorus as the reaction product of 4 moles of turpentine with 1 mole of phosphorus pentasulfide.

EXAMPLE XXII

SAE 90 mineral lubricating oil containing 3% of the product of Example 19 and 0.2% of 4,4'-methylene-bis-(2,6-di-tert-butylphenol).

EXAMPLE XXIII

SAE 30 mineral lubricating oil containing 2% of the product of Example 22 and 0.1% of phosphorus as phenylethyl dicyclohexylphosphorodithioate.

EXAMPLE XXIV

SAE 90 mineral lubricating oil containing 5% of the product of Example 2 and 1% of the calcium salt of the sulfurized phenol obtained by the reaction of 2 moles of heptylphenol with 1 mole of sulfur.

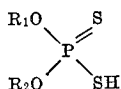
The above lubricants are merely illustrative and the scope of the invention includes the use of all of the additives previously illustrated as well as others within the broad concept of this invention described herein.

The effectiveness of the esters of this invention as deter-

intermediate is then converted to a basic salt by mixing with twice its volume of mineral oil, 2 moles of barium hydroxide and 0.7 mole of phenol and carbonating the mixture at 150° C. to produce a fluid product.

The esters of this invention are especially adapted for use in combination with extreme pressure and corrosion-inhibiting additives such as metal dithiocarbamates, xanthates, the Group II metal phosphorodithioates and their epoxide adducts, hindered phenols, sulfurized cycloalkanes, di-alkyl polysulfides, sulfurized fatty esters, phosphosulfurized fatty esters, alkaline earth metal salts of alkylated phenols, dialkyl phosphites, triaryl phosphites, and esters of phosphorodithioic acids. Combinations of the esters of this invention with any of the above-mentioned additives are especially desirable for use in lubricants which must have superior extreme pressure and oxidation-inhibiting characteristics.

The Group II metal phosphorodithioates are the salts of acids having the formula



in which R₁ and R₂ are substantially hydrocarbon radicals. The metals for forming such salts are exemplified by barium, calcium, strontium, zinc, and cadmium. The barium and zinc phosphorodithioates are especially preferred. The substantially hydrocarbon radicals in the phosphorodithioic acid are preferably low or medium molecular weight alkyl radicals and alkylphenyl radicals, i.e., those having from about 1 to about 30 carbon atoms in the alkyl group. Illustrative alkyl radicals include methyl, ethyl, isopropyl, isobutyl, n-butyl, sec-butyl, the various amyl alcohols, n-hexyl methylisobutyl carbonyl, heptyl, 2-ethylhexyl, diisobutyl, isooctyl, nonyl, behenyl, decyl, etc. Illustrative lower alkylphenyl radicals include butylphenyl, amylphenyl, di-amylphenyl, octylphenyl, etc. Cycloalkyl radicals likewise are useful and these include chiefly cyclohexyl and the lower alkyl-cyclohexyl radicals. Other substantially hydrocarbon radicals likewise are useful such as tetradecyl, octadecyl, eicosyl, butyl-naphthyl, hexyl-naphthyl, octyl-naphthyl, cyclohexylphenyl, naphthenyl, etc. Many substituted hydrocarbon radicals may also be used, e.g., chloropentyl, dichlorophenyl, and dichlorodecyl.

The availability of the phosphorodithioic acids from which the Group II metal salts of this invention are prepared is well known. They are prepared by the reaction of phosphorous pentasulfide with an alcohol or phenol. The reaction involves four moles of the alcohol or phenol per mole of phosphorus pentasulfide, and may be carried out within the temperature range from about 50° C. to about 200° C. Thus the preparation of O,O-di-n-hexyl phosphorodithioic acid involves the reaction of phosphorus pentasulfide with four moles of n-hexyl alcohol at about 100° C. for about 2 hours. Hydrogen sulfide is liberated and the residue is the defined acid. The preparation of the zinc or barium salt of this acid may be effected by reaction with zinc oxide or barium oxide. Simply mixing and heating these two reactants is sufficient to cause the reaction to take place and the resulting product is sufficiently pure for the purposes of this invention.

Especially useful Group II metal phosphorodithioates can be prepared from phosphorodithioic acids which in turn are prepared by the reaction of phosphorus pentasulfide with mixtures of alcohols. The use of such mixtures enables the utilization of cheaper alcohols which in themselves do not yield oil-soluble phosphorodithioic acids. Thus a mixture of isopropyl and hexyl alcohols can be used to produce a very effective, oil-soluble metal phosphorodithioate. For the same reason mixtures of simple phosphorodithioic (i.e., acids prepared from one

alcohol) acids can be reacted with zinc oxide or barium oxide to produce less expensive, oil-soluble salts.

Another class of the phosphorothioate additives contemplated for use in the lubricating compositions of this invention comprises the adducts of the metal phosphorodithioates described above with an epoxide. The metal phosphorodithioates useful in preparing such adducts are for the most part the zinc phosphorodithioates. The epoxides may be alkylene oxides or arylalkylene oxides. The arylalkylene oxides are exemplified by styrene oxide, p-ethylstyrene oxide, alpha-methylstyrene oxide, 3-betanaphthyl-1,3-butylene oxide, m-dodecylstyrene oxide, and p-chlorostyrene oxide. The alkylene oxides include principally the lower alkylene oxides in which the alkylene radical contains 6 or less carbon atoms. Examples of such lower alkylene oxides are ethylene oxide, propylene oxide, 1,2-butene oxide, trimethylene oxide, tetramethylene oxide, butadiene monoepoxide, 1,2-hexene oxide, and propylene epichlorohydrin. Other epoxides useful herein include, for example, butyl 9,10-epoxy-stearate, epoxidized soya bean oil, epoxidized tung oil, and epoxidized copolymer of styrene with butadiene.

The adduct may be obtained by simply mixing the phosphorodithioate and the epoxide. The reaction is usually exothermic and may be carried out within wide temperature limits from about 0° C. to about 200° C. Because the reaction is exothermic it is best carried out by adding one reactant, usually the epoxide, in small increments to the other reactant in order to obtain convenient control of the temperature of the reaction. The reaction may be carried out in a solvent such as benzene, mineral oil, naphtha, or n-hexane.

The chemical structure of the adduct is not known. More than one mole, sometimes as many as four moles, of the epoxide can be made to combine with the phosphorodithioate to form products useful herein. However, adducts obtained by the reaction of one mole of the phosphorodithioate with from about 0.25 mole to about 1 mole of a lower alkylene oxide, particularly ethylene oxide and propylene oxide, have been found to be especially useful and therefore are preferred.

The lubricating compositions may contain metal detergent additives in amounts usually within the range of from about 0.1% to about 20% by weight. In some applications such as in lubricating marine diesel engines the lubricating compositions may contain as much as 30% of a metal detergent additive. They may contain extreme pressure addition agents, viscosity index improving agents, and pour point depressing agents, each in amounts within the range from about 0.1% to about 10%.

The following examples are illustrative of the lubricating compositions of this invention: (all percentages are by weight).

EXAMPLE I

SAE 20 mineral lubricating oil containing 0.5% of the product of Example 1.

EXAMPLE II

SAE 30 mineral lubricating oil containing 0.75% of the product of Example 2 and 0.1% of phosphorus as the barium salt of di-n-nonylphosphorodithioic acid.

EXAMPLE III

SAE 10W-30 mineral lubricating oil containing 0.4% of the product of Example 3.

EXAMPLE IV

SAE 90 mineral lubricating oil containing 0.1% of the product of Example 4 and 0.15% of the zinc salt of an equi-molar mixture of di-cyclohexylphosphorodithioic acid and di-isobutyl phosphorodithioic acid.

EXAMPLE V

SAE 30 mineral lubricating oil containing 2% of the product of Example 12.

gent additives in lubricating compositions is shown by the results in Table I of the modified CRC-EX-3 engine test (the modification consists of extending the test period from the specified 96 hours to 144 hours, thus making the test more severe). The test is recognized in the field as an important test by which lubricants can be evaluated for use under relatively light duty or intermittently high and low temperature service conditions such as are encountered in the operation of automobiles in urban use. In this test, the lubricant is used in the crankcase of a 1954 6-cylinder Chevrolet Power-Glide engine operated for 144 hours under recurring cyclic conditions, each cycle consisting of: 2 hours at engine speed of 500 r.p.m. under no load, oil sump temperature of 100°-125° F., and air:fuel ratio of 10:1; and 2 hours at an engine speed of 2500 r.p.m. under a load of 40 brake horsepower, oil sump temperature of 240-280° F., and an air:fuel ratio of 16:1. At the end of the test the lubricant is rated in terms of (1) the extent of piston filling, (2) the amount of sludge formed in the engine (rating scale of 80-0, 80 being indicative of no sludge and 0 being indicative of extremely heavy sludge), (3) the total amount of engine deposits, i.e., sludge and varnish formed in the engine (rating scale of 100-0, 100 being indicative of no deposit and 0 being indicative of extremely heavy deposits). The lubricating oil base used in the lubricants tested is a SAE 20 mineral lubricating oil.

TABLE I

Additive of this Invention		Engine Test Result		
		Percent ring filling	Sludge rating	Deposit rating
Lubricant sample:				
A.....	1.6% by weight of the product of Example 6.....	6	69.4	87.2
B.....	1.32% by weight of the product of Example 10.....	8	69.6	85.5
C.....	2% by weight of the product of Example 16.....	1	78.1	97.4

What is claimed is:

1. A lubricating composition comprising a major proportion of a lubricating oil and a minor proportion of an ester of hydrocarbon-substituted succinic acid sufficient to improve the detergency of the lubricating composition wherein the hydrocarbon substituent has at least 50 aliphatic carbon atoms, optionally contains polar groups provided the polar groups in total do not exceed about 10% by weight of the hydrocarbon portion of the hydrocarbon substituent, and has no more than about 5% olefinic linkages based on the total number of carbon-to-carbon covalent linkages in said substituent, said ester being selected from the group consisting of acidic esters, diesters, and mixtures thereof, excluding esters having a nitrogen atom attached directly to a succinic radical.

2. A lubricating composition according to claim 1 wherein said ester is an ester of said hydrocarbon-substituted succinic acid with a member selected from the class consisting of monohydric and polyhydric alcohols.

3. A lubricating composition according to claim 2 wherein said ester is an ester of a member selected from the class consisting of monohydric and polyhydric alcohols of up to forty aliphatic carbon atoms and said hydrocarbon substituent is derived from polymerized lower monoolefin having a molecular weight of from about 700 to about 5000.

4. A lubricating composition according to claim 3 wherein said ester comprises 0.01-10% by weight of the composition.

5. A lubricating composition according to claim 2 wherein said ester is an ester of a polyhydric alcohol of from 2 to 10 hydroxy radicals and up to about forty aliphatic carbon atoms and said hydrocarbon substituent is derived from polymerized lower mono-olefin of a molecular weight of from about 700 to about 5000.

6. A lubricating composition according to claim 5

wherein said ester comprises from about 0.01 to about 10% by weight of the composition and said oil is a mineral lubricating oil.

7. A lubricating composition according to claim 5 wherein said hydrocarbon substituent is a polybutene substituent.

8. A lubricating composition according to claim 5 wherein said hydrocarbon substituent is a polyisobutene substituent.

9. A lubricating composition according to claim 5 wherein said ester is an ester of a member selected from a class consisting of neopentyl glycol, ethylene glycol, glycerol, pentaerythritol, and sorbitol.

10. The lubricating composition according to claim 9 wherein the hydrocarbon substituent is a polyisobutene substituent, the oil is a mineral lubricating oil, and the ester comprises from about 0.5% to about 5% by weight of the composition.

11. A lubricating composition according to claim 2 wherein the ester is an ester of an alcohol of at least three hydroxyl radicals, at least one hydroxyl radical being esterified with a monocarboxylic acid of 8 to 30 carbon atoms and the hydrocarbon substituent is derived from polymerized lower mono-olefin having a molecular weight of about 700 to about 5000.

12. A lubricating composition according to claim 11 wherein the ester comprises from about 0.01% to about

10% by weight of the composition and said oil is a mineral lubricating oil.

13. A lubricating composition according to claim 11 wherein the ester is an ester of sorbitol mono-oleate and said hydrocarbon substituent is a polyisobutene substituent having a molecular weight of about 700 to about 5000.

14. A lubricating composition according to claim 12 wherein the ester is an ester of a polyoxyalkylene alcohol and wherein said hydrocarbon substituent is derived from polymerized lower mono-olefin having a molecular weight of from about 700 to about 5000.

15. A lubricating composition according to claim 14 wherein the ester comprises from about 0.01% to about 10% by weight of the composition.

16. A lubricating composition according to claim 2 wherein the ester is an ester of a mono-alkyl or a mono-aryl ether of a poly(oxyalkylene) glycol and wherein the hydrocarbon substituent is derived from polymerized lower mono-olefin having a molecular weight of from about 700 to about 5000.

17. A lubricating composition according to claim 2 wherein the ester is an ester of an alcohol having at least one substituent selected from the class consisting of carboxy, and amino groups and wherein the hydrocarbon substituent is derived from a polymerized lower mono-olefin having a molecular weight of about 700 to about 5000.

18. A lubricating composition according to claim 2 wherein the ester is a diester of an alcohol having up to about nine aliphatic carbon atoms and having at least one substituent selected from the class consisting of amino and carboxy groups and a butene polymer substituted succinic acid.

19. A composition according to claim 18 wherein the

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ester comprises from about 0.01% to about 10% by weight of the composition.

20. A lubricating composition comprising a major proportion of a lubricating oil and a minor proportion of an ester sufficient to improve the detergency of the lubricating composition produced by reacting at a temperature above about 100° C. one mole of a polyhydric alcohol having 2 to about 10 hydroxy radicals with from about 0.5 to about 10 moles of a hydrocarbon-substituted succinic acid reactant wherein the hydrocarbon substituent has at least about 50 aliphatic carbon atoms, optionally contains polar groups provided the polar groups in total do not exceed about 10% by weight of the hydrocarbon portion of the substituent, and has no more than about 5% olefinic linkages based on the total number of carbon-to-carbon covalent linkages in said substituent and is derived from a polymerized lower monoolefin having a molecular weight of from about 700 to about 5000; said succinic acid reactant being selected from the class consisting of succinic acids, the anhydrides, and the halides thereof; said ester being selected from the group consisting of acidic esters, diesters, and mixtures thereof, excluding esters having a nitrogen atom attached directly to a succinic radical.

21. A lubricating composition according to claim 20 wherein the succinic acid reactant is an anhydride and the reaction temperature is from about 150° C. to about 300° C.

22. A lubricating composition according to claim 21 wherein said hydrocarbon substituent is a polyisobutene group.

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23. A lubricating composition according to claim 22 wherein the polyhydric alcohol is selected from the class consisting of glycerol, pentaerythritol, and sorbitol.

24. A lubricating composition according to claim 22 wherein it is a mineral oil composition and the ester comprises from about 0.01% to about 10% by weight of the composition.

25. A lubricating composition according to claim 23 wherein the lubricating oil is a mineral lubricating oil and the ester comprises from about 0.5% to about 5% by weight of the composition.

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PATRICK P. GARVIN, Primary Examiner

U.S. Cl. X.R.

252—56, 57, 39

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,522,179

July 28, 1970

William M. Le Suer

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

Column 17, line 45, "at least 50" should read -- at least about 50 --. Column 18, line 47, "12" should read -- 2 --.

Signed and sealed this 2nd day of March 1971.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents