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3,281,356 THERMALLY STABLE WATER-IN-OIL EMULSIONS

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This invention relates to novel compositions and to emulsions, and in a more particular sense, it relates to compositions which are useful as additives in hydrocarbon oils and especially to stable water-in-oil emulsions which are suitable for use as lubricants and hydraulic fluids.

Emulsions, especially water-in-oil emulsions, find use as lubricants and particularly as fire-resistant hydraulic fluids. Fire-resistant lubricants are necessary wherever equipment failure exposes the lubricant to an ignition source such as a hot object, spark, or fire itself. Thus, these lubricants find particular use in the die casting industry and in the hydraulic systems of steam turbine plants, cotton gins, furnace charging devices in steel mills, and coal mining machinery. It is a well established fact that petroleum base hydraulic fluids have caused many serious fires in coal mines and steel mills. Fire-resistant water-in-oil emulsions have been studied extensively in recent years as a substitute for the flammable petroleum base fluids and a number of these have been prepared which possess the necessary properties, in addition to fire-resistance, of lubricity, and oxidation and thermal stability. The thermal stability of hydraulic fluids is especially important in those systems operating at extremes of temperature and pressure. Because of the presence of a substantial amount of water in the emulsions, the use of these emulsions is not generally recommended at temperatures above 200° F. since the water is readily lost by evaporation. The water-in-oil emulsions suffer the additional disadvantage of instability when subjected to low temperatures such as 0° C. When the heretofore known emulsions are subjected to such low temperatures, separation of a water layer occurs which is quickly converted to ice. The accompanying expansion has resulted, on many occasions, in the destruction of valuable equipment and pipe lines which are exposed at one point or another to low temperatures. It is important, therefore, that emulsions be stable over a wide range of temperatures and under conditions of intermittent freezing and thawing. Attempts have been made to alleviate this problem by the addition of minor amounts of additives which are known to reduce the freezing point of water such as the polyhydric alcohols, and more specifically, ethylene glycol and propylene glycol. It has been generally found, however, that the addition of such agents has a detrimental effect on the overall stability of the hydraulic emulsion. The water-in-oil emulsions should be characterized also by noncorrosiveness, detergency, suitable frictional characteristics, anti-bacterial properties, and wear-reducing properties. The requirement of these properties poses a difficult problem in the formulation of emulsions which are economically feasible for commercial production.

Accordingly, it is an object of this invention to provide novel compositions.

It is another object to provide compositions which are suitable as additives in lubricating oils and emulsions.

It is another object of this invention to provide stable water-in-oil emulsions.

It is another object of this invention to provide emulsions having extended room temperature stability.

It is another object of this invention to provide emulsions suitable for use as lubricants and hydraulic fluids.

It is another object of this invention to provide emulsions which are suitable for use as fire-resistant hydraulic fluids.

It is another object of this invention to provide emulsions which are suitable for use under conditions of intermittent low and high temperatures.

These and other objects are accomplished in accordance with this invention by providing a composition comprising from about 0.2 to 10 parts of a succinic ester of a substantially saturated hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the substituent and a polyhydric alcohol, and from about 0.1 to 5 parts of an alkaline earth metal salt of a fatty acid having at least about 12 aliphatic carbon atoms in the fatty radical, said metal salt having a metal ratio of at least 1.

The compositions of this invention are useful as additives in lubricants such as automatic transmission fluids and especially as stabilizers in water-in-oil emulsions as described hereafter. Use of the compositions of this invention in water-in-oil emulsions improves the low temperature stability of the emulsions and reduces the possibility of water separation and the subsequent freezing of the water.

It will be noted that the succinic esters contemplated for use in the invention are characterized by the presence of a relatively large substituent on the succinic radical which contains at least about 50 aliphatic carbon atoms. The sources of this substituent include principally the high molecular weight petroleum fractions and olefin polymers, particularly polymers of monoolefins having from 2 to about 30 carbon atoms. The especially useful polymers are the polymers of 1-mono-olefins such as ethylene, propene, 1-butene, isobutene, 1-hexane, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. They are illustrated by 2-butene, 3-pentene, and 4-octene.

The polymers include also the interpolymers of the olefins such as those illustrated above with other interpolymerizable olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins. The relative proportions of the mono-olefins to the other olefinic monomers in the interpolymers influence the stability and effectiveness of the succinic esters derived therefrom in the emulsions of this invention. Thus, the interpolymers 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 unsaturated linkages based upon the total number of carbon-to-carbon covalent linkages.

Examples of such interpolymers include copolymer of 95% (by weight) of isobutene with 5% of styrene; terpolymer of 98% of isobutene with 1% of piperylene and 1% of chloroprene; terpolymer of 95% of isobutene with 2% of 1-butene and 3% of 1-hexene; terpolymer of 60% of isobutene with 20% of 1-pentene and 20% of 1-octene; copolymer of 80% of 1-hexene and 20% of 1-heptene; terpolymer of 90% of isobutene with 2% of cyclohexene and 8% of propene; and copolymer of 80% of ethylene and 20% of propene.

Succinic esters in which the substituent is derived from an olefin polymer having a molecular weight of about 750–5000 are preferred. Those from polymers of higher molecular weight, i.e., from about 10,000 to about 100,000 or higher, likewise are useful.

Another source of the substituent comprises petroleum fractions such as high molecular weight white oils and synthetic alkanes such as are obtained by hydrogenation of high molecular weight olefins or fats.

The methods of preparing the polymers and interpolymers from which the succinic esters are derived are known.

A particularly useful method comprises the treatment of an olefin (e.g., isobutene) or a mixture of olefins at a temperature from about —60° C. to about 20° C. in the presence of a Friedel-Crafts catalyst (e.g., boron trifluoride). The use of a solvent to facilitate mixing and the transfer of the heat of polymerization is advantageous. Solvents are exemplified by n-butane, isobutane, n-hexane, naphtha, carbon tetrachloride, and ethane.

The succinic esters contemplated for use in the emulsions of this invention may be prepared directly from the appropriately substituted succinic acids or from compounds capable of yielding such succinic acids, the latter being illustrated by the acid anhydrides, halides, and esters of volatile alcohols or phenols, etc. These succinic acid-producing compounds can be prepared by, e.g., the reaction of maleic anhydride with a high molecular weight olefin or a chlorinated hydrocarbon such as the olefin polymer described herein-above. The reaction involves merely heating the two reactants at a temperature preferably about 100°–200° 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.

In lieu of the olefins or chlorinated hydrocarbons, other hydrocarbons containing an activating polar substitutent, i.e., a substituent which is capable of activating the hydrocarbon molecule in respect to reaction with maleic acid or anhydride, may be used in the above-illustrated reaction for preparing the succinic acid-producing compounds. Such polar substituents are illustrated by sulfide, disulfide, nitro, mercaptan, bromine, ketone, or aldehyde radicals. Examples of such polar-substituted hydrocarbons include polypropylene sulfide, dipolyisobutene disulfide, nitrated mineral oil, di-polyethylene sulfide, brominated polyethylene, etc. Another method useful for preparing the succinic acids and their compounds involve the reaction of itaconic acid with an olefin or a polar-substituted hydrocarbon at a temperature usually within the range from about 100° C. to about 200° 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. The esters of such acids can be prepared simply by the reaction of the acids or the anhydrides with an alcohol or a phenolic compound such as methanol, ethanol, phenol, naphthol, etc. The esterification is usual promoted by the use of an alkaline catalyst such as sodium hydroxide or sodium alkoxide or an acidic catalyst such as sulfuric acid. The nature of the alcoholic or phenolic portion of the ester radical appears to have little influence on the utility of such esters as the reactants in the process described herein-above. In most instances the esters derived from volatile alcohols or phenols are preferred.

The succinic acid esters of polyhydric alcohols are most conveniently prepared by the reaction of the succinic acid or anhydride with the alcohol under esterification conditions. An alternative method involves the transesterification of a succinic acid ester of a relatively volatile alcohol or phenol with the polyhydric alcohol. Both the esterification and the transesterification reactions are promoted by a small amount of a catalyst such as sodium methoxide, potassium hydroxide, or sulfuric acid, although in most instances the reaction proceeds readily simply upon heating of the reactants.

The polyhydric alcohols are preferably those containing from 2 to 6 alcoholic radicals of which at least 1 is unsubstituted. The unsubstituted polyhydric alcohols include principally ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, glycerol, erythritol, pentaerythritol, arabitol, adonitol, xylitol, mannitol, sorbitol, neopentyl and glycol. Higher molecular weight polyhydric alcohols are also useful. Examples of such alcohols include the various polyethylene glycols, and polypropylene glycols.

Partially acylated polyhydric alcohols likewise are contemplated for use herein. The partially acylated polyhydric alcohols are preferably those containing from 2 to 6 alcoholic radicals of which at least one but not all are acylated with an aliphatic carboxylic acid having from about 8 to about 30 carbon atoms. Examples are glycerol mono-oleate, glycerol di-stearate, sorbitan monostearate, sorbitan di-decanoate, sorbitan tristearate, sorbitan di-behenate, erythritol mono-oleate, 1,1,1-trimethylol propane mono-myristate, pentaerythritol di-linoleate, ribitol mono-(9,10-dichloro stearate), sorbitan mono-oleate, etc.

The polyhydric alcohols may also contain ether linkages within their molecular structure. The ether-containing polyhydric alcohols may be obtained by dehydrating a polyhydric alcohol. Examples of such derivative are sorbitan and mannitan. The ether-containing polyhydric alcohols may also be obtained by reacting a polyhydric alcohol with an epoxide. The epoxides are for the most part hydrocarbon epoxides and substantially hydrocarbon epoxides. The hydrocarbon epoxide may be an alkylene oxide or an aryl-alkylene oxide. The aryl-alkylene oxides are exemplified by styrene oxide, para-ethylstyrene oxide and para-chlorostyrene oxide. The alkylene oxides include principally the lower alkylene oxides such as ethylene oxide, propylene oxide, 1,2-butene oxide and 1,2-hexene oxide. The substantially hydrocarbon epoxides may contain polar substituents. The polar substituent is usually a halo radical such as chloro, fluoro, bromo, or iodo; an ether radical such as methoxy or phenoxy; or an ester radical such as carbomethoxy. Examples of such epoxides are epichlorohydrin and butyl 9,10-epoxy-stearate. The number of ether linkages in the product is determined by the amount of epoxide added. Thus it is possible to react a polyhydric alcohol such as sorbitol with 1, 2, 3 or more equivalents of an epoxide such as propylene oxide.

The polyhydric alcohols contemplated for use in this invention may also be ether-containing acylated polyhydric alcohols. These may be prepared by a number of methods. A polyhydric alcohol may be dehydrated and subsequently acylated or an alcoholic radical may be acylated first followed by dehydration of other alcoholic radicals. As mentioned previously, the ether linkage may also be introduced by the reaction of an epoxide with the polyhydric alcohol either before or after acylation. Examples of ether-containing acylated polyhydric alcohols include polyoxyethylene sorbitan mono-oleate, polyoxyethylene sorbitan tri-stearate, polyoxyethylene glycerol distearate, polyoxypropylene sorbitan di-linoleate, and polyoxypropylene pentaerythritol mono-oleate.

The reaction of a succinic acid-producing compound with the above-illustrated polyhydric alcohols is generally carried out at a temperature of at least 100° C., preferably above 130° C. The use of a solvent such as benzene, toluene, naphtha, mineral oil, xylene, n-hexane, or the like is often desirable in the above reaction to facilitate the control of the reaction temperature.

The relative proportions of the succinic acid-producing reactant and of the polyhydric alcohol reactant usually are such that at least about one-tenth and preferably one-half of a stoichiometrically equivalent amount of the alcohol reactant is used for each equivalent of the acid-producing reactant. In this regard it will be noted that the equivalent weight of the polyhydric alcohols is based on the number of unsubstituted hydroxy radicals in the molecular structure. Thus, ethylene glycol has two equivalents per mole, pentaerythritol has 4 equivalents per mole, and sorbitan mono-oleate has 3 equivalents per mole. The number of equivalents per mole of epoxide treated polyhydric alcohols is determined analytically.

The succinic esters likewise can be obtained from succinic acid halides or other succinic acid-producing compounds. For example, the sorbitan mono-oleate ester is

formed by heating a mixture of sorbitan mono-oleate with the dihalide of an appropriately substituted succinic acid.

The following examples illustrate the methods for preparing the succinic esters of this invention (parts are by weight unless otherwise indicated):

Example A

A polyisobutenyl succinic anhydride is prepared by the reaction of a chlorinated polyisobutene with maleic anhydride at 200° C. The chlorinated polyisobutene is prepared by blowing chlorine gas through polyisobutene having an average molecular weight of 1000 at a temperature of 104–110° C. until the chlorine content reaches 4.3%. The resulting alkenyl succinic anhydride is found to have a saponification number of 109 (corresponding to an equivalent weight of 514). To 770 parts (1.5 equivalents) of this polyisobutenyl succinic anhydride there is added 126 parts (1.5 equivalents) of a commercial mixture of polyol fatty acid esters, predominantly sorbitan mono-oleate, 588 parts of mineral oil, 9 parts of paratoluene sulfonic acid monohydrate and 500 parts (by volume) of xylene. The mixture is heated to reflux at 140° C. and is held at this temperature for 12 hours to remove water. The reaction mixture is then washed with water and dried by heating to 150° C./20 mm. The residue is found to have a saponification number of 68.

Example B

A mixture of 514 parts (1 equivalent) of the polyisobutenyl succinic anhydride of Example A, 234 parts (1 equivalent) of a commercial mixture of ethylene oxide treated polyol fatty acid esters, predominantly polyoxyethylene sorbitan mono-oleate, 492 parts of mineral oil, 7 parts of para-toluene sulfonic acid monohydrate and 500 parts (by volume) of xylene is heated at reflux for 10 hours while removing water. The mixture is then washed with water and dried by heating to 150° C./20 mm. The residue is found to have a saponification number of 53.

Example C

The procedure of Example A is repeated except that the sorbitan mono-oleate is replaced with 1 equivalent of a commercial mixture of polyol fatty acid esters which are predominantly sorbitan tristearate.

Example D

The procedure of Example A is repeated except that the sorbitan mono-oleate is replaced with 1 equivalent of a commercial mixture of ethylene oxide treated polyol fatty acid esters which are predominantly polyoxyethylene sorbitan tristearate.

Example E

A polyisobutenyl succinic anhydride having an equivalent weight of 518 is prepared according to the procedure of Example A. To a mixture of 518 parts (1 equivalent) of this polyisobutenyl succinic anhydride there is added 200 parts (1 equivalent) of commercial polyethylene glycol, 7.2 parts of paratoluene sulfonic acid monohydrate, and 400 parts of xylene. The mixture is heated at 140–150° C. for 10 hours while water is removed. The volatile components are then removed by heating to 105° C./4 mm. and 471 parts of mineral oil are added and the products filtered to remove solid impurities. The filtrate is found to have a saponification number of 50.

Example F

To a mixture of 300 parts (0.545 equivalent) of a polyisobutenyl succinic anhydride prepared as in Example A there is added 279 parts (0.545 equivalent) of commercial polypropylene glycol, 382 parts of mineral oil, and 28.5 parts of an acid activated bleaching earth. The mixture is heated to 150° C. and purged with nitrogen for 20 hours at this temperature. The mixture is filtered while hot and the filtrate is found to have a saponification number of 35.

Example G

A mixture of 600 parts (1.09 equivalents) of a polyisobutenyl succinic anhydride prepared as in Example A, 232 parts (1.09 equivalents) of a commercial polypropylene glycol, 547 parts of mineral oil, and 40 parts of acid activated bleaching earth is heated to 115° C. The mixture is purged with nitrogen and heated to 150°–160° C. for 17 hours and 200° C. for 4 hours. The mixture is filtered and 43.2 parts (0.745 equivalent) of propylene oxide is added to the cooled filtrate. This mixture is heated at 85°–90° C. for 16 hours whereupon the temperature of the mixture is maintained at 85° C. while reducing to 80 mm. of pressure. The residue is the product and is found to have a saponification number of 48.

Example H

A mixture of 3,318 parts (3 moles) of a polyisobutenyl succinic anhydride prepared as in Example A and having a saponification number of 101, 408 parts (3 moles) of pentaerythritol, and 2,445 parts of mineral oil is heated to 150° C. for 5 hours. The mixture is then heated to 200°–210° C. for 5 hours and filtered. The filtrate is the product and is found to have a saponification number of 50.

Example I

A mixture of 544 parts (0.5 mole) of a polyisobutenyl succinic anhydride prepared as in Example A and having a saponification number of 103, 90.6 parts (0.5 mole) of sorbitol and 417 parts of mineral oil is heated to 200° C. The mixture is purged with nitrogen at a rate of 2 cubic feet per hour while maintaining the mixture at a temperature of 200°–210° C. for 3.5 hours. The mixture is filtered hot and the filtrate is the product which is found to have a saponification number of 55.

Example J

A mixture of 895 parts (1.6 equivalents) of a polyisobutenyl succinic anhydride prepared as in Example A and having a saponification number of 100, 181 parts (0.744 equivalent) of the polyoxyethylene sorbitan mono-oleate mixture of Example B, and 714 parts of mineral oil is heated to 150° C. in 4 hours. The mixture is then purged with nitrogen for 7 hours at this temperature. Ten parts of a filter aid is added and the mixture filtered while hot. The filtrate is the product and is found to have a saponification number of 54.

Example K

A mixture of 544 parts (1 equivalent) of a polyisobutenyl succinic anhydride prepared as in Example A and having a saponification number of 103, 358 parts (4 equivalents) of the sorbitan mono-oleate mixture of Example A, and 594 parts of mineral oil is heated to 150° C. in one hour. The mixture is held at this temperature for 3 hours while being purged with nitrogen. The mixture is filtered while hot, and the filtrate is found to have a saponification number of 76.

Example L

Sodium (0.5 part) is dissolved in 60.8 parts (2 equivalents) of melted sorbitol while stirring in an atmosphere of nitrogen, and 348.6 parts (6 equivalents) of propylene oxide is added over a period of 20 hours at a temperature of 150°–210° C. The mixture is heated an additional hour at 175° C. giving the product which is found to have a hydroxyl content of 9.26%.

A mixture of 358 grams (2 equivalents) of this propylene oxide treated sorbitol, 272 grams (0.5 equivalent) of a polyisobutenyl succinic anhydride prepared as in Example A and having a saponification number of 103, and 418 parts of mineral oil is heated to 150° C. and purged with nitrogen at this temperature for 3.5 hours. The hot

solution is filtered and the filtrate is found to have a saponification number of 25.

Example M

Sodium (0.5 part) is added to 182 parts (6 equivalents) of melted sorbitol in a nitrogen atmosphere and the mixture is stirred for 0.5 hour. Propylene oxide (348.6 parts, 6 equivalents) is added to the mixture over a period of 20 hours at a temperature of 150–200° C. This mixture is heated an additional hour at 120–140° C. to give the product which has a hydroxyl content of 16.2%.

A mixture of 210 parts (2 equivalents) of this propylene oxide treated sorbitol, 272 parts (0.5 equivalent) of a polyisobutenyl succinic anhydride prepared as in Example A and having a saponification number of 103, and 318 parts of mineral oil is heated to 130° C. The reaction temperature is then raised to 150° C. while purging with nitrogen, and the mixture is maintained at this temperature for 3.5 hours. The mixture is filtered and the filtrate is found to have a saponification number of 36.

Example N

A mixture of 1156 parts (2 equivalents) of polyisobutenyl succinic anhydride prepared according to the procedure of Example A, 61 parts (2 equivalents) of glycerol, and 800 parts of xylene is heated to 140° C. The mixture is heated at this temperature for 16 hours while removing the water which is formed in the reaction. The xylene is removed by heating to 150° C./20 mm. and the residue is the product having a saponification number of 93.

Example O

A mixture of 555 parts (1 equivalent) of a polyisobutenyl succinic anhydride prepared according to the procedure of Example A and 45 parts (1 equivalent) of 1,4-butane diol is heated to 135° C. The mixture is maintained at a temperature of 135–190° C. for 11 hours while removing the water as it is formed. Fifty parts of a filter aid and 250 parts of mineral oil are added to the warm mixture which is then filtered. The filtrate is the product and is found to have a saponification number of 68.

Example P

A mixture of 544 parts (1 equivalent) of a polyisobutenyl succinic anhydride prepared according to the procedure of Example A, 90.6 parts (3 equivalents) of mannitol, and 417 parts of mineral oil is heated to 200° C. The mixture is purged with nitrogen while heating at 200–210° C. for 3.5 hours. The mixture is filtered while hot and the filtrate is found to have a saponification number of 56.

The fatty acid compound which is included in the compositions of this invention is an alkaline earth metal salt of a fatty acid having at least about 12 aliphatic carbon atoms in the fatty radical. The fatty acids include principally, lauric acid, stearic acid, oleic acid, myristic acid, palmitic acid, oleostearic acid, linoleic acid, linolenic acid, behenic acid, dichlorostearic acid, or a mixture of such acids such as are obtained from the hydrolysis of tall oil, sperm oil, or other commercial fats. It is of critical importance that the acids should contain at least about 12 aliphatic carbon atoms, preferably from 16 to 30 carbon atoms. The criticality is based upon the oil-solubility and the effectiveness of the metal salts of such acids as additives in the emulsions of this invention.

The alkaline earth metal salts of the fatty acids include those of magnesium, calcium, strontium, and barium. The calcium and barium salts are especially preferred. The term "metal salt" as used here includes both normal and basic metal salts.

The ratio of the total chemical equivalents of the metal in the metal salt to the chemical equivalents of the metal which is in the form of a normal salt, i.e., a neutral salt of the acid, is designated as the "metal ratio." To illustrate, a metal salt having 5 equivalents of metal per equivalent of the organic acid radical has a metal ratio of 5. A neutral metal salt has a metal ratio of 1.

The neutral metal salts are exemplified by the following: calcium stearate, magnesium palmitate, barium linoleate, and barium oleate. Although the metal salt which is contemplated for use in this invention has a metal ratio of at least 1, the use of salts having a metal ratio between about 1 and 25 has been found to be advantageous. An especially preferred range of metal ratios is from 2 to 10.

A convenient process for preparing the basic metal salts of the fatty acids comprises carbonating a substantially anhydrous mixture of the fatty acid reactant with more than 1 equivalent of an alkaline earth metal base in the presence of a promoting agent. When a commercial fat such as sperm oil is utilized, it is hydrolyzed by the addition of water to the reaction mixture and the water is subsequently removed before the carbonation step.

The metal base may be an alkaline earth metal oxide or hydroxide. It is preferably an oxide or hydroxide of barium or calcium.

The promoting agent is, for the most part, a hydroxy compound such as an alcohol or a phenol. It may be, for example, ethanol, methanol, isopropanol, cyclohexanol, dodecanol, behenyl alcohol, ethylene glycol, diethylene glycol, hexamethylene glycol, glycerol, pentaerythritol, benzyl alcohol, phenol, naphthol, cresol, catechol, para-tertiary-butylphenol, 4,4'-methylene bis-phenol, hexatriacontanyl alcohol, and furfuryl alcohol. Alcohols having up to about 12 carbon atoms are especially effective for use as promoting agents. Phenol and alkylated phenols having 1 to 3 alkyl substituents each of which has up to about 50 carbon atoms are also preferred. Mixtures of alcohols, such as mixtures of methanol, and n-pentanol; mixtures of methanol, isobutanol, n-pentanol, and cyclohexanol, mixtures of methanol and glycerol; mixtures of methanol and isooctanol; etc., are particularly useful.

The amount of the promoting agent to be used in the reaction mixture is best defined in terms of its chemical equivalents per equivalent of the acid. The amount may be as little as 0.1 equivalent or as much as 10 equivalents or even more per equivalent of the acid reactant. The preferred amount is from about 0.25 to 5 equivalents per equivalent of the acid reactant. It will be noted that the equivalent weight of the promoting agent is based upon the number of alcoholic or phenolic hydroxyl radicals in the molecule. To illustrate, the equivalent weight of a monohydric alcohol is its molecular weight; that of a trihydric alcohol is one-third of its molecular weight, and that of a bis-phenol is one-half of its molecular weight.

The carbonation temperature depends to a large measure upon the promoting agent used. When a phenol is used as a promoting agent, the temperature usually ranges from about 80° C. to about 300° C., preferably from about 100° C. to 200° C. When an alcohol is used the temperature usually will not exceed about 100° C. The carbonation temperature may be as low as about 20° C.

After carbonation, the promoting agent, if it is a volatile substance, may be removed from the product by distillation. If the promoting agent is a relatively non-volatile substance it is usually allowed to remain in the product without any adverse effect. Ordinarily, it is convenient to prepare the carbonated, basic metal salt in a mineral oil so that the product is a fluid oil solution or concentrate which readily mixes with additional quantities of mineral oil. If the carbonation is carried out in the presence of a volatile solvent such as xylene or naphtha, the product may be dissolved in a mineral oil and the resulting oil solution heated to remove the solvent. It will be noted that upon mixing of the alkaline earth metal base, the acid forms a metal salt so that the process mixture contains a metal salt of the acid and a larger excess of the metal base. Such a mixture is heterogeneous primarily because of the presence of the large excess of the

insoluble metal base. As carbonation proceeds, the metal base becomes solubilized in the organic phase and the carbonated product eventually becomes a homogeneous composition containing an unusually large amount of the metal. The mechanism of the formation of the homogeneous product is not fully understood. It is believed, however, that carbonation converts the excess metal base to a carbonate or bicarbonate which forms a complex with the metal salt of the acid reactant. It is not necessary for all of the metal base to be so converted by carbonation to produce a soluble homogeneous product. In many instances a homogeneous product is obtained when as little as 75% of the excess metal base is carbonated.

The preferred fatty acid salts are those obtained by the carbonation of a substantially anhydrous mixture of the fatty acids obtained from the hydrolysis of commercial fats such as sperm oil and an alkaline earth oxide or hydroxide in the presence of a phenolic promoter such as phenol and heptyl phenol. Calcium and barium are the preferred metals and these are usually present in a ratio of from 1 to 20 equivalents per equivalent of acid. From 0.25 to 5 equivalents of phenolic promoter is generally present in the reaction mixture and the carbonation is carried out at temperatures from 100° C. to 200° C. and higher.

The following examples illustrate the methods of preparing the basic metal salts of this invention.

Example Q

A mixture of 423 grams (1.0 equivalent) of sperm oil, 124 grams (0.6 equivalent) of diisobutylphenol, 520 grams of mineral oil and 146 grams of water is heated to 70° C. and then treated with 308 grams (4.0 equivalents) of barium oxide. The mixture is refluxed for an hour, dried by heating to 150° C., and carbonated by treatment with carbon dioxide at this temperature until it is slightly acidic. Filtration of this material yields a clear, light brown, non-viscous liquid having the following analyses: percent sulfate ash, 31.2; neutralization number, 0.4; metal ratio, 3.7.

Example R

The procedure of Example Q is repeated except that the barium oxide is replaced, on an equivalent basis, with calcium oxide.

Example S

A mixture of 423 grams (1 equivalent) of sperm oil, 123 grams (0.602 equivalent) of a heptylphenol, 1214 grams of mineral oil and 452 grams of water is treated at 70° C. with 612 grams (8 equivalents) of barium oxide. This mixture is stirred at the reflux temperature for 1 hour and then at 150° C. while carbon dioxide is bubbled beneath the surface. Filtration yields a clear liquid having the following analyses: percent sulfate ash, 35; neutralization number (basic), 10; metal ratio, 7.3.

Example T

A mixture of 423 grams (1.0 equivalent) of sperm oil, 31 grams (0.15 equivalent) of diisobutylphenol, 520 grams of mineral oil and 146 grams of water is heated to 70° C. and then treated with 290 grams (3.75 equivalents) of barium oxide. The mixture is refluxed for 1 hour, then dried by heating to 150° C., and carbonated by treatment with carbon dioxide at this temperature until it is slightly acidic. Filtration of this material yields a liquid product having the following analyses: percent sulfate ash, 30.4; neutralization number (acidic), 0.5; metal ratio, 3.5.

Example U

To a mixture of 4,022 grams of mineral oil, 310 grams (1.6 equivalents) of heptylphenol, and 1108 grams (12.9 equivalents) of barium hydroxide heated to 75° C. there is added 764 grams (2.7 equivalents) of stearic acid. The mixture is heated to 110° C. whereupon 400 grams of isooctanol is added. The mixture is heated to 150° C. and held at this temperature while a stream of carbon dioxide is bubbled through the mixture until it is slightly acidic. A vacuum of 15 mm. is then applied to remove the volatile constituents and the residue is filtered. The filtrate is the desired product having the following analyses: percent sulfate ash, 20.63; metal ratio, 3.6.

Example V

A mixture of 576 grams (2 equivalents) of oleic acid, 524 grams of mineral oil, 60 grams of isooctanol, and 222 grams (6 equivalents) of calcium hydroxide is prepared at room temperature and 98 grams of methanol is added. The mixture is heated to 45–55° C. and treated with carbon dioxide at this temperature for 5 hours. The mixture is dried by heating to 150° C. under a vacuum of 30 mm. The residue is filtered and the filtrate is the product having the following analyses: percent sulfate ash, 24.5; metal ratio, 2.4.

Example W

A mixture of 212 grams (0.5 equivalent) of sperm oil, 58 grams (0.3 equivalent) of heptylphenol, 867 grams of mineral oil, and 192 grams of water is heated to 70° C. whereupon 612 grams (8 equivalents) or barium oxide is added and the mixture heated to 150° C. The mixture is held at this temperature and treated with carbon dioxide until the mixture is slightly acidic to phenolphthalein. The mixture is filtered and the filtrate is the desired product having the following analyses: percent sulfate ash, 48.4; neutralization number (basic), 1; metal ratio, 15.8.

Example X

A mixture of 212 grams (0.5 equivalent) of sperm oil, 58 grams (0.3 equivalent) of heptylphenol, 636 grams of mineral oil and 120 grams of water is heated to 70° C. whereupon 490 grams (6.4 equivalents) of barium oxide is added. The mixture is heated to 150° C. and treated with carbon dioxide at this temperature until the mixture is slightly acidic to phenophthalein. The mixture is filtered and the filtrate is the desired product having the following analyses: percent sulfate ash, 46.2; metal ratio, 12.3.

Example Y

A mixture of 134 grams (6.65 equivalents) of magnesium oxide, 500 grams of isooctanol, 96 grams (0.5 equivalent) of heptylphenol, and 583 grams of mineral oil is prepared and 234 grams (0.83 equivalent) of oleic acid is added. The mixture is heated to 150° C. whereupon carbon dioxide and steam are bubbled simultaneously through the mixture until it is slightly acidic. The mixture is dried by applying a vacuum of 30 mm. while maintaining the temperature at about 150° C. The residue is filtered and the filtrate is the product having a metal ratio of 3.4.

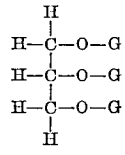
The oil of the emulsion may be a hydrocarbon oil having viscosity values from 50 SUS (Saybolt Universal Seconds) at 100° F. to 200 SUS at 210° F. Mineral oils having lubricating viscosities (e.g., SAE 5–90 grade oils) are especially advantageous for use in the emulsion. A mixture of oils of different sources likewise is useful. Such a mixture is available from mineral oils, vegetable oils, animal oils, synthetic oils of the silicon type, synthetic oils of the polyolefin type, synthetic oils of the polyester type, etc.

The emulsions of this invention contain from 1 to 80 parts of water and from 20–99 parts of oil. (All parts in this specification and claims are expressed in terms of weight unless otherwise indicated). However, emulsions having the most desirable properties are composed of from 30 to 50 parts of water and 50 to 70 parts of oil. Also, emulsions intended for use as fire-resistant hydraulic fluids should contain at least about 30% of water. The concentration of the succinic ester in the emulsions is from 0.2 to 10 parts, more often from 1 to 5 parts, per 100 parts of the emulsion. The principal function of

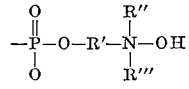
the succinic ester is that of an emulsifier, although it also imparts detergency to the emulsion. The concentration of fatty acid metal salt is from 0.1 to 5 parts, more often from 0.5 to 3 parts, per 100 parts of the emulsion. The fatty acid metal salt is utilized in the invention because of its wear-reducing properties, for the improved freeze-thaw stability which it imparts to the emulsions, and as a buffer.

The emulsions can be prepared simply by mixing water, oil, the succinic ester, the fatty acid metal salt, and any other ingredient which may be desirable, in a homogenizer or any other efficient blending device. Heating the emulsion during or after it is prepared is not necessary. The order of mixing of the ingredients is not critical, although it is convenient first to prepare an oil concentrate containing from about 50 to 95 parts of the oil-soluble ingredients and from about 5 to 50 parts of oil and then to emulsify the concentrate with water in appropriate proportions.

Although the emulsions described herein-before are, in themselves, useful, they nevertheless are susceptible to improvement by the incorporation of chemical additives which impart properties desired for various specific applications. One such additive is an emulsion stabilizer which functions to improve the stability of the emulsion against deterioration due to temperature, pressure, oxidation of the oil, and other harmful environments. Stabilizers include phosphatides, especially those having the structural formula



wherein G is selected from the class consisting of fatty acyl radicals and phosphorus-containing radicals having the structural grouping



wherein R′ is a lower alkylene radical having from 1 to about 10 carbon atoms and R″ and R‴ are lower alkyl radicals having from 1 to 4 carbon atoms, and at least one but no more than two of the G radicals being said phosphorus-containing radical. The fatty acyl radicals are for the most part those derived from fatty acids having from 8 to 30 carbon atoms in the fatty radicals such as octanoic acid, stearic acid, oleic acid, palmitic acid, behenic acid, myristic acid, and oleostearic acid. Especially desirable radicals are those derived from commercial fatty compounds such as soyabean oil, cotton seed oil, and castor seed oil. A particularly effective phosphatide is soyabean lecithin which is described in detail in Encyclopedia of Chemical Technology, Kirk and Othmer, volume 8, pages 309–326 (1952).

The emulsion stabilizer may be an aliphatic glycol or a mono-aryl ether of an aliphatic glycol. The aliphatic glycol may be a polyalkylene glycol. It is preferably one in which the alkylene radical is a lower alkylene radical having from 1 to 10 carbon atoms. Thus, the aliphatic glycol is illustrated by ethylene glycol, trimethylene glycol, propylene glycol, tetramethylene glycol, 1,2-butylene glycol, 2,3-butylene glycol, tetramethylene glycol, hexamethylene glycol, or the like. Specific examples of the ethers inculde monophenyl ether of ethylene glycol, mono-(heptylphenyl)ether of triethylene glycol, mono-(alpha-octyl-beta-naphthyl)ether of tetrapropylene glycol, mono-(polyisobutene(molecular weight of 1000)-substituted phenyl) ether of octapropylene glycol, and mono-(o,p-dibutylphenyl) ether of polybutylene glycol, mono-(heptylphenyl) ether of trimethylene glycol and mono-(3,5-dioctylphenyl) ether of tetra-trimethylene glycol, etc. The mono-aryl ethers are obtained by the condensation of a phenolic compound such as an alkylated phenol or naphthyl with one or more moles of an epoxide such as ethylene oxide, propylene oxide, trimethylene oxide, or 2,3-hexalene oxide. The condensation is promoted by a basic catalyst such as an alkali or alkaline earth metal hydroxide, alcoholate, or phenate. The temperature at which the condensation is carried out may be varied within wide ranges such as from room temperature to about 250° C. Ordinarily it is preferably 50–150° C. More than one mole of the epoxide may condense with the phenolic compound so that the product may contain in its molecular structure one or more of the radicals derived from the epoxide. A polar-substituted alkylene oxide such as epichlorohydrin or epibromohydrin likewise is useful to prepare the mono-aryl ether product and such product likewise is useful as the emulsion stabilizer in this invention.

Likewise useful as the emulsion stabilizers are the mono-alkyl ethers of the aliphatic glycols in which the alkyl radical is, e.g., octyl, nonyl, dodecyl, behenyl, etc. The fatty acid esters of the mono-aryl or mono-alkyl ethers of aliphatic glycols also are useful. The fatty acids include, e.g., acetic acid, formic acid, butanoic acid, hexanoic acid, oleic acid, stearic acid, behenic acid, decanoic acid, iso-stearic acid, linolenic acid, as well as commercial acid mixtures such as are obtained by the hydrolysis of tall oils, sperm oils, etc. Specific examples are the oleate of mono-(heptylphenyl)ether of tetraethylene glycol and the acetate of mono-(polypropene(having molecular weight of 1000)-substituted phenyl) ether of tri-propylene glycol.

The alkali metal and ammonium salts of sulfonic acids likewise are emulsion stabilizers. The acids are illustrated by decylbenzene sulfonic acid, di-dodecylbenzene sulfonic acid, mahogany sulfonic acid, heptylbenzene sulfonic acid, polyisobutene sulfonic acid (molecular weight of 750), and decylnaphthalene sulfonic acid, and tri-decylbenzene sulfonic acid. The salts are illustrated by the sodium, potassium, or ammonium salts of the above acids.

Also useful as supplementary emulsion stabilizers are the neutral alkali metal salts of fatty acids having at least 12 aliphatic carbon atoms in the fatty radical. These fatty acids include, principally, lauric acid, stearic acid, oleic acid, myristic acid, palmitic acid, linoleic acid, linolenic acid, behenic acid, or a mixture of such acids such as are obtained from the hydrolysis of tall oil, sperm oil, and other commercial fats. It is of critical importance that the acids should contain at least about 12 aliphatic carbon atoms, preferably from 16 to 30 carbon atoms; the criticality is based upon the oil-solubility and the effectiveness of the metal salts of such acids as additives in the emulsions of this invention.

Only a small amount of the stabilizer is necessary for the purpose. It may be as little as 0.01 part and seldom exceeds 2 parts per 100 parts of the emulsion. In most instances it is within the range from 0.1 to 1 part per 100 parts of the emulsion.

Another additive which finds use in the emulsion is an extreme pressure agent, i.e., one which improves the load-carrying properties of the emulsion. It is illustrated by a lead or nickel or a Group II metal phosphorodithioate in which the metal may be magnesium, calcium, barium, strontium, zinc, or cadmium. Zinc is an especially preferred metal. Specific examples of the metal phosphorodithioates include zinc di(4-methyl-2-pentyl)phosphorodithioate, zinc O-methyl-O′-dodecylphosphorodithioate,

barium diheptylphosphorodithioate, barium di(n-butylphenyl)phosphorodithioate, magnesium di-cyclohexylphosphorodithioate, cadmium salt of an equal molar mixture of dimethylphosphorodithioic acid and di-octylphosphorodithioic acid, zinc di-n-nonylphosphorodithioate, zinc di-dodecylphosphorodithioate, lead di-pentyl phosphorodithioate, nickel di-octylphosphorodithioate, and zinc di-(heptylphenyl)phosphorodithioate.

Methods for preparing the phosphorodithioic acids are known in the art, including, for example, the reaction of an alcohol or a phenol with phosphorus pentasulfide. Likewise known are the methods for preparing the Group II metal salts of phosphorodithioic acids. Such methods are illustrated by the neutralization of phosphorodithioic acids or mixtures of such acids with zinc oxide.

Other extreme pressure agents useful in the emulsions of this invention include the chlorinated waxes; sulfurized or phosphosulfurized fatty acid esters; di- and tri-hydrocarbon phosphites and phosphates; di-hydrocarbon polysulfides; and metal dithiocarbamates. The chlorinated waxes are exemplified by chlorinated eicosane having a chlorine content of 50% or other chlorinated petroleum waxes having a chlorine content of 5%–60%. The sulfurized fatty esters are obtained by the treatment of a lower alkyl ester of a fatty acid having at least about 12 carbon atoms with a sulfurizing agent such as sulfur, sulfur mono-chloride, sulfur dichloride, or the like. The fatty acid esters are illustrated by methyl oleate, methyl stearate, isopropyl myristate, cyclohexyl ester of tall oil acid, ethyl palmitate, isooctyl laurate, diester of ethylene glycol with stearic acid, etc. Commercial mixtures of esters likewise are useful. They include, for example, sperm oil, Menhaden oil, glycerol trioleate, etc. The sulfurization is effected most conveniently at temperatures between 100° C. and 250° C. More than one atom of sulfur can be incorporated into the ester and for the purpose of this invention sulfurized esters having as many as four or five atoms of sulfur per molecule have been found to be useful. Examples include sulfurized sperm oil having a sulfur content of 5%, sulfurized tall oil having a sulfur content of 9%, sulfurized methyl oleate having a sulfur content of 3%, and sulfurized stearyl stearate having a sulfur content of 15%.

The phosphosulfurized fatty acid esters are obtained by the treatment of the esters illustrated above with a phosphorus sulfide such as phosphorus pentasulfide, phosphorus sesquisulfide, or phosphorus heptasulfide. The treatment is illustrated by mixing an ester with from about 0.5% to 25% of a phosphorus sulfide at a temperature within the range from about 100° C. to 250° C. The products contain both phosphorus and sulfur but the precise chemical structure of such products is not clearly understood.

The phosphites and phosphates useful herein are the di- and tri-esters of phosphorus or phosphoric acid in which the ester radical is derived from a substantially hydrocarbon radical including aryl, alkyl, alkaryl, arylalkyl, or cycloalkyl radical as well as a hydrocarbon radical having a polar substituent such as chloro, nitro, bromo, ether, or the like. Particularly desirable phosphites and phosphates are those in which the ester radicals are phenyl, alkylphenyl or alkyl radicals containing from 6 to 30 carbon atoms. Examples are: dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, di-(pentylphenyl)phosphite, bis-(dipentylphenyl)phosphite, tridecyl phosphite, di-stearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentylphenyl phosphite, triphenyl phosphite, bis-(hexapropylene-substituted phenyl)phosphite, tri(n-chloro-3-heptylphenyl)phosphite, triphenyl phosphate, tricresyl phosphate, tri(p-chlorophenyl)phosphate, and triheptylphenyl)phosphate.

The metal dithiocarbamates include principally those of zinc, lead, strontium, nickel, cadmium, and palladium with N,N-dialkyldithiocarbamic acids in which the alkyl radical contains from 3 to about 30 carbon atoms. Examples are zinc N,N-dioctyl dithiocarbamate, lead N,N-dicyclohexyl dithiocarbamate, cadmium N,N-dibehenyl dithiocarbamate, lead N,N-didodecyl dithiocarbamate, and mixtures thereof.

The concentration of the extreme pressure agent is usually within the range from about 0.05 to about 5 parts, although it is seldom necessary to employ more than 2 parts of this agent per 100 parts of the emulsion.

Another type of additive which finds use in the emulsion is a rust-inhibiting agent. The most effective rust-inhibiting agents in the emulsions of this invention are aliphatic amines, especially aliphatic primary amines having at least 8 carbon atoms in the molecule. The aliphatic amines are preferably tertiary-alkyl primary amines having from about 12 to about 30 carbon atoms. The amines include stearyl amine, oleyl amine, myristyl amine, palmityl amine, n-octyl amine, dodecyl amine, octadecyl amine, and other commercial primary amine mixtures such as the mixture in which the aliphatic radical is a mixture of tertiary-alkyl radical having from 11 to 14 carbon atoms and an average of 12 carbon atoms, and the mixture in which the aliphatic radical is a mixture of tertiary-alkyl radicals having from 18 to 24 carbon atoms.

Also effective as rust-inhibiting agents are the salts of an aromatic acid such as benzoic acid, toluic acid, naphthoic acid, phthalic acid, or terephthalic acid with any of the aliphatic amines listed above. Salts derived from other acids such as p-aminobenzoic acid and o-chlorobenzoic acid likewise are useful.

The salts of amines with the aromatic acids are prepared simply by mixing the reactants at a temperature below the dehydration temperature, i.e., below 90° C. In most instances the reaction is exothermic and heating is not necessary. A solvent such as benzene, toluene, naphtha, and chlorobenzene may be used.

Still another class of rust-inhibiting agents are the hydroxy-alkyl amines, especially the long chain (i.e., C_{8-30}) aliphatic amines containing one or two hydroxy-alkyl substituents on the amine nitrogen atom. Examples are N-(2-hydroxyethyl)octylamine, N,N-di - (2-hydroxy - 1-propyl)dodecylamine, N-(3 - hydroxy-1-pentyl)octadecylamine, and N,N-di-(2-hydroxy-3-butyl)decylamine.

Also useful as the rust-inhibiting agents are the nitrous acid salts of the long chain aliphatic amines illustrated above. Such salts are obtained simply by mixing at ordinary temperatures such as room temperature an amine with nitrous acid. Specific examples include the nitrous acid salt of the tertiary-alkyl (C_{11-14}) primary amine and the nitrous acid salt of octadecylamine.

The concentration of rust-inhibiting agent in the emulsion depends to some extent upon the relative concentration of water in the emulsion. Ordinarily from about 0.01 part to about 2 parts of a rust-inhibiting agent per 100 parts of the emulsion is sufficient.

Still another type of additive which finds use in these emulsions is a foam-inhibitor which may be a commercial dialkyl siloxane polymer or a polymer of an alkyl methacrylate. Freezing point depressants, i.e., water-soluble polyhydric alcohols such as glycerol or other polar substances such as Cellosolve are also useful. The concentration of these additives usually is less than 5 parts per 100 parts of the emulsion.

Bactericides are also useful in the emulsions of this invention. They are illustrated by nitro-bromo-alkanes (such as 3-nitro-1-propyl bromide), nitro-hydroxy-alkanes (such as tri-(hydroxymethyl)nitromethane, 2-nitro-2-ethyl-1,3-propan-diol, and 2-nitro-1-butanol), and boric acid esters (such as glycerol borate). The concentration of the bactericide may be 0.001 to 1 part per 100 parts of the emulsion.

Oxidation-inhibitors useful in the emulsions of this invention include the hindered phenols such as 2,4-di-tert-butyl-6-methylphenol, 4,4′ - methylene - (2,6-di-tert-pentylphenol), and 2,6 - di - tert-octyl-4-sec-butylphenol.

The concentration of the oxidation-inhibitors is usually 0.01 to 2 parts per 100 parts of the emulsion.

The following examples illustrate the concentrates and emulsions containing the oil-soluble substituted succinic esters and fatty acid metal salts of this invention.

Example 1 (Emulsion)

	Parts by weight
The product of Example J	9.0
Soyabean lecithin	1.8
A tertiary-alkyl primary amine having a molecular weight of 191 in which the tertiary-alkyl radical is a mixture of radicals having from 11 to 14 carbon atoms	0.6
Zinc di-(heptylphenyl)phosphorodithioate	2.0
The basic barium salt of Example S	3.0
SAE 40 mineral lubricating oil	284.1
Silicone anti-foam agent	0.0075
Water	200

Example 2 (Emulsion)

The product of Example J	9.0
Soyabean lecithin	1.8
The tertiary-alkyl primary amine of Example 1	0.6
The basic barium salt of Example S	3.0
Zinc diisooctyl phosphorodithioate	1.5
SAE 40 mineral lubricating oil	284.1
Silicone anti-foam agent	0.0075
Water	200

Example 3 (Emulsion)

The product of Example J	9.0
Soyabean lecithin	1.8
The tertiary-alkyl primary amine of Example 1	0.6
The basic barium salt of Example S	3.0
Zinc di-(heptylphenyl)phosphorodithioate	1.5
Zinc diisooctyl phosphorodithioate	1.5
SAE 40 mineral lubricating oil	282.6
Silicone anti-foam agent	0.0075
Water	200

Example 4 (Emulsion)

The product of Example J	9.0
Soyabean lecithin	1.8
The tertiary-alkyl primary amine of Example 1	0.6
Zinc di-(heptylphenyl)phosphorodithioate	3.0
An amide mixture consisting of, by weight, 91% oleamide, 6% stearamide, and 3% linoleamide	0.6
The basic barium salt of Example S	3.0
SAE 40 mineral lubricating oil	282.0
Silicone anti-foam agent	0.0075
Water	200

Example 5 (Emulsion)

The product of Example J	9.5
Soyabean lecithin	3.5
The tertiary-alkyl primary amine of Example 1	0.642
Zinc diisooctyl phosphorodithioate	3.28
The basic barium salt of Example S	3.18
SAE 40 mineral lubricating oil	292.4
Water	240

Example 6 (Concentrate)

The product of Example E	9.0
Soyabean lecithin	1.8
A tertiary-alkyl primary amine having a molecular weight of 330 in which the tertiary-alkyl radical is a mixture of radicals having 18 to 24 carbon atoms	0.6
Lead diamyl dithiocarbamate	3.0
Sulfurized sperm oil having a sulfur content of 10%	3.0
The basic barium salt of Example W	1.0
SAE 20 mineral lubricating oil	281.6
Silicone anti-foam agent	0.0045

Example 7 (Emulsion)

The product of Example H	9.0
Soyabean lecithin	1.8
The tertiary-alkyl primary amine of Example 1	0.6
The basic barium salt of Example S	3.0
Zinc di-(heptylphenyl)phosphorodithioate	3.7
SAE 40 mineral lubricating oil	281.9
Silicone anti-foam agent	0.0045
Water	200

Example 8 (Emulsion)

The product of Example F	18.0
Soyabean lecithin	3.6
The nitrous acid salt of the tertiary-alkyl primary amine of Example 1	1.2
Sulfurized sperm oil having a sulfur content of 10%	18.0
The basic calcium salt of Example R	2.2
4-methyl 2,6-di-tertiary butylphenol	3.0
SAE 5 mineral lubricating oil	534.0
Silicone anti-foam agent	0.015
Water	400

Example 9 (Emulsion)

The product of Example C	30
The basic magnesium salt of Example Y	10
SAE 20 mineral lubricating oil	560
Water	400

Example 10 (Emulsion)

The product of Example 9	49.5
Zinc di-(heptylphenyl)phosphorodithioate	0.5

Example 11 (Concentrate)

The product of Example K	3.0
Soyabean lecithin	0.6
The tertiary-alkyl primary amine of Example 1	0.2
The basic barium salt of Example S	1.0
Zinc di-(heptylphenyl)phosphorodithioate	1.25
SAE 40 mineral lubricating oil	93.95
Silicone anti-foam agent	0.015

Example 12 (Emulsion)

The product of Example 11	600
Water	400

Example 13 (Emulsion)

The product of Example L	9.0
Soyabean lecithin	1.8
The tertiary-alkyl primary amine of Example 6	0.6
The basic barium salt of Example U	3.0
Zinc di-(heptylphenyl)phosphorodithioate	3.75
SAE 40 mineral lubricating oil	271.8
Silicone anti-foam agent	0.0075
Water	200

Example 14 (Emulsion)

The product of Example M	9.0
Soyabean lecithin	1.8
The tertiary-alkyl primary amine of Example 1	0.6
Zinc di-(heptylphenyl)phosphorodithioate	3.75
The basic barium salt of Example U	3.5
SAE 40 mineral lubricating oil	268.3
Silicone anti-foam agent	0.0075
Water	200

Example 15 (Emulsion)

The product of Example J	9.0
Soyabean lecithin	1.8
The benzoic acid salt of the tertiary-alkyl primary amine of Example 1	0.6

	Parts by weight
Dipentene disulfide having a sulfur content of 36%	6.0
The basic calcium salt of Example V	4.0
SAE 40 mineral lubricating oil	278.6
Silicone anti-foam agent	0.0075
Water	200

Example 16 (Concentrate)

The product of Example I	9.0
The mono-(heptylphenyl)ether of tetra-ethylene glycol	1.8
The tertiary-alkyl primary amine of Example 1	0.6
Zinc di-(heptylphenyl)phosphorodithioate	1.5
Zinc diamyl dithiocarbamate	1.5
The basic barium salt of Example X	1.5
SAE 20 mineral lubricating oil	284.1
Silicone anti-foam agent	0.0045

Example 17 (Emulsion)

The product of Example J	9.0
The basic barium salt of Example S	4.8
The tertiary-alkyl primary amine of Example 1	0.6
Zinc diisooctyl phosphorodithioate	3.0
SAE 40 mineral lubricating oil	282.6
Silicone anti-foam agent	0.0075
Water	200

Example 18 (Emulsion)

The product of Example 10	49.7
The tertiary-alkyl primary amine of Example 1	0.1
Soyabean lecithin	0.2

Example 19 (Emulsion)

The product of Example 5	970
Ethylene glycol	30

Example 20

The product of Example J	45.0
Zinc di-(heptylphenyl)phosphorodithioate	18.7
Soyabean lecithin	9.0
The tertiary-alkyl primary amine of Example 1	3.0
The basic barium salt of Example S	15.0
SAE 40 mineral lubricating oil	9.3
Silicone anti-foam agent	0.022

Example 21

The product of Example 20	6.0
SAE 40 mineral lubricating oil	94.0

As indicated previously the emulsions of this invention are useful as lubricants as well as hydraulic fluids, especially fire-resistant hydraulic fluids for use in mining, die-casting and injection molding, welding equipment, cotton gins, etc. A specific illustration of such utility is as follows: an emulsion prepared from a mixture consisting of 95 parts (by weight) of an SAE 20 mineral lubricating oil, 2 parts of the polyisobutene-substituted succinic ester of Example J, 0.5 part of the basic barium salt of Example S, and 5 parts of water is useful as the power-transmitting fluid in a hydraulic pump.

Other advantages of the emulsions of this invention include, for example, thermal stability, wear-reducing properties, fire-resistance, rust-inhibiting properties, and antibacterial properties. Thus, for instance, the emulsion of Example 1 is found to pass the Heat Stability Test, in which a 55-cc. sample of the emulsion in a container is immersed in boiling water. (The emulsion is said to pass the test if no appreciable amount of water separates from the emulsion at the end of one hour of heating.)

The lubricating properties, especially the improved wear-reducing properties, of the emulsion of this invention are shown by the results of a proposed ASTM wear test. In the test, the emulsion is placed in a hydraulic pump (in this particular test, Vickers 104E Vane Pump) which is operated under the following conditions: motor speed, 1200 r.p.m.; approximate fluid flow rate, 2 gallons per minute; pressure 1000 p.s.i.; and sump temperature, 150° F. The results of the test are shown in Table I. The same emulsion, not containing the metal salt of a fatty acid, and a commercial fluid are also evaluated for the purpose of comparison.

TABLE I

Hydraulic Emulsion Fluid	Test Duration (Hours)	Percent Wear				
		Vanes	Ring	Side Plate	Rotor	Total
Emulsion containing 0.6% of the product of Example S	400	0.071	0.204	0.042	0.030	0.071
Do	400	0.054	0.201	0.039	0.027	0.067
Do	1,000	0.091	0.294	0.054	0.045	0.101
The same emulsion without the metal salt	400	0.217	0.811	0.080	0.051	0.223
Do	1,000	0.663	1.170	0.123	0.090	0.345
Commercial fluid	84	4.31	0.575	0.012	0.472	0.460

The fire-resistance of the emulsions of this invention is shown by the fact that the emulsion prepared according to Example 1 is found to pass the fire-resistance test for hydraulic fluids as required by the Bureau of Mines of the U.S. Government (test procedure described in Federal Register, December 17, 1959, volume 24, number 245, title 30, part 35, and sections 35.1–35.23).

The rust-inhibiting properties of the emulsions of this invention are shown by the results of a rust test in which one-half of a steel strip is immersed in a 50-cc. sample of the emulsion. At the end of five weeks, the strip is inspected for rust. The results are summarized in Table II.

TABLE II

Emulsion Tested	Rust Result	
	Portion of Strip Immersed in Emulsion	Portion of Strip Exposed to Vapor of the Emulsion
Emulsion of Example 5	Clean	Clean.
Commercial emulsion hydraulic fluid (for purpose of comparison).	do	Heavy Rust.

The low temperature stability of the emulsions of this invention is shown by the results of a freeze-thaw test. In this test, a 200-cc. sample of the emulsion is placed in a jar which is sealed and stored in a compartment maintained at a temperature of 0° C. for 24 hours. The jar is removed from the compartment and the emulsion is examined for water separation and to determine if the emulsion is sufficiently fluid to be poured or pumped. The emulsion is warmed to room temperature and again examined as above. The cycle is repeated until there is water separation or the emulsion solidifies when cooled to 0° C. An emulsion prepared according to Example 1 is found to successfully withstand eight such cycles before solidifying at 0° C. Emulsions which do not contain the fatty acid metal salts of this invention solidify at 0° C. after three cycles or less. This added low temperature

stability which is characteristic of the emulsions of this invention is especially important when the emulsion is to be used in equipment which will be subject to intermittent low and normal temperatures over an extended period.

What is claimed is:

1. A composition consisting essentially of from about 0.2 to about 10 parts of a succinic ester of a hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the substituent and a polyhydric alcohol, and from about 0.1 to 5 parts of an alkaline earth metal salt of a fatty acid having at least about 12 aliphatic carbon atoms in the fatty radical, said metal salt having a metal ratio of at least 1.

2. A hydrocarbon lubricating oil composition consisting essentially of from about 1 to 80 parts of a hydrocarbon oil, from about 0.2 to about 10 parts of a succinic ester of a hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the substituent and a polyhydric alcohol, and from about 0.1 to 5 parts of an alkaline earth metal salt of a fatty acid having at least about 12 aliphatic carbon atoms in the fatty radical, said metal salt having a metal ratio of at least 1.

3. A hydrocarbon lubricating oil composition consisting essentially of from about 1 to 80 parts of a hydrocarbon oil, from about 0.2 to 10 parts of a succinic ester of a hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the substituent and a polyhydric alcohol, and from about 0.1 to 5 parts of an alkaline earth metal salt of a fatty acid having at least about 12 aliphatic carbon atoms in the fatty radical, said metal salt having a metal ratio of at least 1, from about 0.1 to 5 parts of a zinc phosphorodithioate, from about 0.1 to 5 parts of an aliphatic primary amine in which the aliphatic radical is a tertiary alkyl radical having from 8 to 30 carbon atoms, and from about 0.01 to 5 parts of a phosphatide.

4. The hydrocarbon oil composition of claim 3 characterized further in that the alkaline earth metal salt of the fatty acid has a metal ratio of from 1 to about 20.

5. A stable water-in-oil emulsion suitable for use as a lubricant and a hydraulic fluid consisting essentially of from about 1 to 80 parts of water, from about 20 to 99 parts of mineral oil, from about 0.2 to about 10 parts of the succinic ester of a hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the substituent and a polyhydric alcohol, and from about 0.1 to 5 parts of an alkaline earth metal salt of a fatty acid having at least about 12 aliphatic carbon atoms in the fatty radical, said metal salt having a metal ratio of at least 1.

6. The emulsion of claim 5 characterized further in that the alkaline earth metal salt of the fatty acid has a metal ratio of from 1 to about 20.

7. The emulsion of claim 5 characterized further in that it contains from about 0.05 to 5 parts of a zinc phosphorodithioate.

8. The emulsion of claim 5 characterized further in that it contains from about 0.1 to about 5 parts of an aliphatic primary amine in which the aliphatic radical is a tertiary alkyl radical having from 8 to 30 carbon atoms.

9. The emulsion of claim 5 characterized further in that it contains from about 0.01 to 5 parts of a phosphatide.

10. A stable water-in-oil emulsion suitable for use as a lubricant and a hydraulic fluid consisting essentially of from about 1 to 80 parts of water, from about 20 to 99 parts of mineral oil, from about 0.2 to about 10 parts of a succinic ester of a hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the substituent and a polyhydric alcohol, from about 0.1 to 5 parts of an alkaline earth metal salt of a fatty acid having at least about 12 aliphatic carbon atoms in the fatty radical, said metal salt having a metal ratio of from 1 to about 20, from about 0.1 to 5 parts of an aliphatic primary amine in which the aliphatic radical is a tertiary alkyl radical having from 8 to 30 carbon atoms, and from about 0.01 to about 5 parts of a phosphatide.

11. The emulsion of claim 10 characterized further in that it contains from about 0.05 to 5 parts of a zinc phosphorodithioate.

12. A stable water-in-oil emulsion suitable for use as a lubricant and a hydraulic fluid consisting essentially of from about 20 to 50 parts of water, from about 50 to 80 parts of a mineral oil, and from about 1 to 5 parts of a succinic ester of a hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the substituent and a partially acylated polyhydric alcohol, and from about 0.1 to 5 parts of an alkaline earth metal salt of a fatty acid having at least about 12 aliphatic carbon atoms in the fatty radical, said metal salt having a metal ratio of from 1 to about 20.

13. A stable water-in-mineral oil emulsion suitable for use as a lubricant and a hydraulic fluid consisting essentially of from about 20 to 50 parts of water, from about 50 to 80 parts of a mineral oil, and from about 1 to 5 parts of a succinic ester of a hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the substituent and at least about 0.1 equivalent of polyoxyethylene sorbitan monooleate, and from about 0.1 to 5 parts of a basic alkaline earth metal salt of a fatty acid having at least about 12 aliphatic carbon atoms in the fatty radical, said metal salt having a metal ratio of from 1 to about 20.

14. The emulsion of claim 13 characterized further in that it contains from about 0.1 to 3 parts of a tertiary-alkyl primary amine having from about 11 to 14 carbon atoms in the alkyl radical, and from about 0.1 to about 3 parts of a phosphatide.

15. The emulsion of claim 14 characterized further in that it contains from about 0.1 to 2 parts of zinc phosphorodithioate.

16. A stable water-in-mineral oil emulsion suitable for use as a lubricant and a hydraulic fluid consisting essentially of from about 20 to 50 parts of water, from about 50 to 80 parts of a mineral oil, from about 1 to 5 parts of a succinic ester of a hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the substituent and about 0.5 equivalent of polyoxyethylene sorbitan monooleate, from about 0.1 to 5 parts of a basic barium salt of a fatty acid having about 18 carbon atoms in the fatty radical, prepared by carbonating a mixture of an ester of said fatty acid, an alkyl phenol, and a stoichiometric excess of barium oxide, said barium salt having a metal ratio of from about 2 to 10, from about 0.1 to 2 parts of zinc di(heptylphenyl) phosphorodithioate, from about 0.1 to 1 part of a tertiary-alkyl primary amine having a molecular weight of 191 in which the tertiary-alkyl radical is a mixture of radicals having from about 11 to 14 carbon atoms, and from about 0.1 to 3 parts of soyabean lecithin.

17. A stable water-in-mineral oil emulsion suitable for use as a lubricant and a hydraulic fluid consisting essentially of from about 20 to 50 parts of water, from about 50 to 80 parts of a mineral oil, from about 1 to 5 parts of a succinic ester of a hydrocarbon-substituted succinic acid having at least about 50 aliphatic carbon atoms in the substituent and about 0.5 equivalent of polyoxyethylene sorbitan monooleate, from about 0.1 to 5 parts of a basic barium salt of a fatty acid having about 18 carbon atoms in the fatty radical, prepared by carbonating a mixture of an ester of said fatty acid, an alkyl phenol, and a stoichiometric excess of barium oxide, said barium salt having a metal ratio of from about 2 to 10, from about 0.1 to 2 parts of zinc diisoctyl phosphorodithioate, from about 0.1 to 1 part of a tertiary-alkyl primary amine having a molecular weight of 191 in which the tertiary-alkyl radical is a mixture of radicals having from about 11 to 14 carbon atoms, and from about 0.1 to 3 parts of soyabean lecithin.

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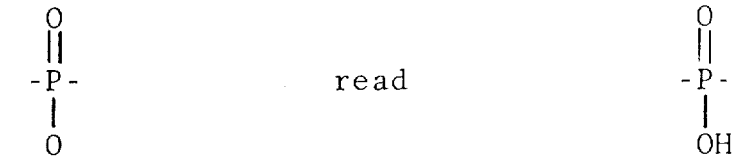
CERTIFICATE OF CORRECTION

Patent No. 3,281,356 October 25, 1966

Lester E. Coleman

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 48, for "usual" read -- usually --; column 10, line 24, for "or barium" read -- of barium --; column 11, lines 45 to 48, for that portion of the formula reading



column 14, line 13, after "least" insert -- about --; column 17, line 72, for "55-cc." read -- 50-cc. --; column 20, line 68, for "diisoctyl" read -- diisooctyl --.

Signed and sealed this 24th day of December 1968.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents