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LUBRICATING COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Improved lubricating compositions containing a lubricating oil, a dispersant which is a derivative of a substituted succinic acid where the substituent contains at least 50 aliphatic carbon atoms, and a demulsifier. These improved compositions reduce or eliminate the formation of sludge on the internal metal surfaces of internal combustion engines. Polyoxyalkylene polyols are preferred demulsifiers.

This is a continuation-in-part of application Ser. No. 669,282, filed Sept. 20, 1967, now abandoned.

This invention relates to improvements in lubricating oil compositions. Specifically, this invention relates to improvements in lubricating oil compositions containing at least one dispersant derived from a substituted succinic acid.

In recent years, there has been developed in the lubricating industry a new class of dispersants based on the derivatives of essentially hydrocarbon-substituted succinic acids. Specifically, the esters, acidic esters, half esters-half amides, acidic amides, amides, imides, amidines, amine salts, and metal salts of substituted succinic acids, the substituent being a hydrocarbon or essentially hydrocarbon radical containing at least about fifty aliphatic carbon atoms, have found widespread commercial use as dispersants in lubricating oil compositions.

In the majority of internal combustion engines, these dispersant additives function without undesirable side effects. However, in a few types of automobile engines, it has been found that a mayonnaise-like sludge forms on metal surfaces in areas of the engine where water vapors can condense when lubricants containing these dispersants are employed. For example, these sludges have been found in the rocker arm covers an oil-fill caps of these engines, particularly smaller car engines. In these areas of the engine, moisture can condense from the air. As these metal parts also come into contact with the lubricating oil, the oil and water form the sludge deposit in the presence of the succinic acid dispersant. It is obviously desirable to eliminate or reduce the amount of sludge formed in the engine.

It has now been found that this sludge accumulation can be eliminated or greatly reduced by incorporating demulsifiers for water-in-oil emulsions into lubricating compositions containing dispersants derived from substituted succinic acids. This is surprising since it would appear that the presence of such demulsifiers would counteract the dispersant capabilities of succinic acid dispersants.

Thus, it has been suggested that one reason this class of dispersants is effective is that they are capable of forming stable water-in-oil emulsions. The presence of a demulsifier for water-in-oil emulsions, therefore, would be expected to neutralize or greatly diminish the properties of the dispersant. However, it has been found that these demulsifiers effectively reduce or eliminate the sludge formations without adversely affecting the dispersant capabilities of the succinic acid derivatives. This would seem to negate the theory that the dispersant capabilities arise out of whatever ability these dispersants may have for forming stable water-in-oil emulsions.

In addition, the use of the demulsifiers in combination with the ashless dispersants inhibits rust formation on ferrous metal surfaces coming into contact with lubricants containing such combinations. The polyoxyalkylene glycols, described more fully below, in combination with acylated nitrogen containing dispersants derived from alkenyl-substituted succinic acids or anhydrides and amines such as alkylene polyamines in particular exhibit improved rust-resisting capabilities.

Accordingly, it is a principal object of the present invention to provide improved lubricating compositions.

Another object is to provide improved lubricating compositions comprising at least one dispersant derived from substituted succinic acid and a demulsifier for water-in-oil emulsions.

A further object is to provide improved lubricating compositions capable of eliminating or substantially reducing sludge formation on metal surfaces in internal combustion engines.

A still further object of this invention is to provide improved lubricating compositions comprising polyoxyalkylene polyols as demulsifiers.

These and other objects of the invention are accomplished by incorporating demulsifiers for water-in-oil emulsions into lubricating compositions comprising at least one dispersant derived from a substituted succinic acid. The presence of such demulsifiers in amounts of from about 0.01 to about 5% by weight based on the total weight of composition results in an improved lubricating composition.

The lubricating oil compositions contemplated by the present invention are those which contain a minor but effective amount of a dispersant derived from a substituted succinic acid. Specifically, the lubricating compositions contemplated by the present invention are those containing at least one dispersant selected from the class consisting of the esters, acidic esters, half esters-half amides, acidic amides, amides, imides, amidines, amine salts, and metal salts of substituted succinic acids wherein the substituent contains at least about fifty aliphatic carbon atoms. As mentioned above, these compounds comprise a well known class of recently developed dispersants.

The substituent on the succinic acid dispersant is generally a saturated or unsaturated aliphatic hydrocarbon group although it may contain pendant aryl groups or polar groups as substituents. However, the polar groups should not be present in sufficiently large numbers to alter the hydrocarbon character of the substituent. Exemplary polar groups include halo, keto, ether, aldehyde, nitro, phosphosulfur groups, sulfur, etc. The upper limit

of polar groups is about 10% by weight based on the weight of the hydrocarbon portion of the substituent.

The hydrocarbon substituents on the succinic acid dispersants should contain no more than about 5% olefinic linkages based on the total number of carbon-to-carbon covalent linkages present in the substituent. Preferably, the number of olefinic linkages will not exceed about 2%.

The source of the hydrocarbon substituent on the succinic acid moiety of the dispersants include principally the high molecular weight substantially saturated petroleum fractions and substantially saturated olefin polymers, particularly polymers of the olefins having from two to thirty 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 useful. 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 olefinic substances such as aromatic olefins, cyclic olefins, polyolefins, etc. Such interpolymers include for example those prepared by polymerizing isobutene with styrene; isobutene with butadiene, propene with isopropene; 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 monoolefins 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 aliphatic monoolefins.

Specific examples of such interpolymers include a copolymer of 95% of isobutene and 5% of styrene; terpolymer of 98% of isobutene with 1% of piperylene and 1% of chloroprene; terpolymer of 95% of isobutene, 2% of 1-butene and 3% of 1-hexene; terpolymer of 80% of isobutene with 10% of 1-pentene and 10% of 1-octene; a 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 a copolymer of 80% of ethylene and 20% of propene. The percentages refer to the percent by weight of total polymer weight attributable to the indicated monomer.

Another source of hydrocarbon substituents are saturated aliphatic hydrocarbons, e.g., highly refined high molecular weight white oils or synthetic alkanes such as are obtained by hydrogenation of the high molecular weight olefin polymers illustrated above or other high molecular weight olefinic substances.

Olefin polymers having molecular weights from about 750 to about 10,000 are a preferred source of hydrocarbon substituent with those having molecular weights of about 700 to 5,000 being especially preferred. High molecular weight olefin polymers having molecular weights of from about 10,000 to about 100,000 or more can be used alone or in combination with the lower molecular weight polymers to prepare substituted succinic acid reactants from which the dispersants are prepared. These higher molecular weight substituents can impart viscosity index improving properties to the improved lubricating compositions of this invention.

The substituted succinic acids are readily available from the reaction of maleic anhydride with a suitable olefin, olefin polymer, chlorinated hydrocarbon, and the like. The reaction involves merely heating the two reactants at a temperature of about 100° to 200° C. The product of such a reaction is a succinic anhydride having a large hydrocarbon substituent. The hydrocarbon substituent may contain olefinic linkages which may be converted, if desired, to saturated paraffinic linkages by hydrogenation. The anhydride can be hydrolyzed by treatment with water or steam to the corresponding acid. It will be noted in this regard that the anhydride is equivalent to the acid insofar as its utility in the preparation of the dispersants utilized in the improved compositions of this invention. The anhydride is often more reactive than the acid and is often preferred over the acid in preparing the dispersants. Either the anhydride or the acid may be transformed into the corresponding acid halide or ester by reacting with phosphorus halide, phenols, and alcohols according to known procedures.

In lieu of the olefins of chlorinated hydrocarbons, other hydrocarbons containing an activating polar substituent, i.e., a substituent which is capable of activating a hydrocarbon molecule in respect to reaction with maleic acid or maleic anhydride, may be used in the above-illustrated reaction for preparing the substituted succinic acids. Such polar substituents are exemplified by sulfide, disulfide, nitro, mercaptan, halo, keto, or aldehyde radicals. Examples of such polar-substituted hydrocarbons include polypropene sulfide, di-polyisobutene disulfide, nitrated mineral oil, dipolyethylene sulfide, brominated polyethylene, etc. Another useful method for preparing succinic acids and anhydrides involves the reaction of itaconic acid with a high molecular weight olefin or a polar-substituted hydrocarbon at a temperature usually within the range of from about 100° to about 200° C. Similarly, chloromaleic acid or chloromaleic anhydride may be used in lieu of succinic acid, succinic anhydride, or itaconic acid.

The dispersants prepared from the reaction of polyolefin-substituted succinic acids or anhydrides and mono- or polyamines, particularly polyalkylene polyamines having up to about ten amino nitrogens, are especially suitable dispersants. The reaction products generally comprise amides, imides, amine salts, amidines or mixtures thereof resulting from the reaction of amino nitrogen with succinic acid acyl group. The reaction products of polyisobutene-substituted succinic anhydride and polyethylene polyamines containing an average of up to about ten amino nitrogens are particularly good dispersants. Generally, the polyalkylene polyamine is reacted with the acid or anhydride in an amount such that the reaction mass contains from about 0.5 equivalent to about 2 moles of polyamine for each equivalent of acid. The reaction product prepared by reacting polyisobutenyl- (molecular weight—750 to about 1100) substituted succinic anhydride with polyethylene polyamines containing an average of from about 3–7 amino nitrogens per polyamine wherein the ratio of equivalents of anhydride to amine is about 1:1 are particularly effective dispersants.

As mentioned above, these dispersants are well known in the art. Thus, the reaction products of the substituted succinic acid or anhydrides with amines are disclosed in the following U.S. Patents: 3,018,250; 3,024,195; 3,172,892; 3,216,936; 3,219,666; 3,272,746. Also included within this class of dispersants derived from succinic acid are those products prepared by post-treating the reaction product of an amine and a substituted anhydride with formic or other carboxylic acids, aldehydes, carbon disulfide, a boron compound, an alkyl nitrile, urea, thiourea, guanidine, alkylene oxides, and the like as disclosed in 3,087,936; 3,185,704; 3,200,107; 3,216,936; 3,254,025; 3,256,185; 3,278,550; 3,281,428; 3,312,619; and British specification 1,053,577. These patents are expressly incorporated herein by reference for their disclosure of suitable dispersants.

The metal salt of the substituted succinic acids are disclosed in U.S. Patent 3,271,310. The metal moiety of the salts is preferably a Group I or II metal, aluminum, lead, tin, cobalt, nickel, or zinc.

The esters of these substituted succinic acids are also

useful dispersants. These esters are prepared by reacting the substituted acid or anhydride with a mono- or polyhydric alcohol, phenol, or naphthol according to standard procedures for preparing esters of carboxylic acids. Alternatively, the ester can be formed by first reacting maleic anhydride, itaconic acid, or the like with an alcohol, phenol, naphthol, or alkylene oxide to produce an ester. This ester can be subsequently reacted with a chlorinated hydrocarbon or polyolefin to produce ester dispersants. Typical esters of this type are disclosed in British specification 981,850, U.S. Patent 3,311,558, and copending application Ser. No. 567,052 filed July 22, 1966, now Patent 3,381,022.

The preferred esters are the esters of the polyolefin-substituted succinic acid or anhydrides and polyhydric aliphatic alcohols containing 2 to 10 hydroxy groups and up to about 40 aliphatic carbon atoms. Such alcohols include ethylene glycol, glycerol, sorbitol, erythritol, mannitol, polyethylene glycol, diethanolamine, triethanolamine, N,N'-di(hydroxyethyl)-ethylenediamine, and the like.

If the alcohol reactant contains reactive amino hydrogens (or if an amine reactant contains reactive hydroxyl groups), it is obvious that a mixture comprising the reaction products of a substituted succinic acid reactant and both the hydroxyl and amino functional groups is possible. Such reaction products can include half-ester half-amides, half-amine salt half amide, half amine salt half ester, esters, imides, and the like. See, for example, U.S. Patent 3,342,033.

Since the dispersants themselves and lubricating compositions containing them are old in the art, the foregoing patents, printed specifications, and co-pending application are incorporated herein by reference in the interest of brevity. These prior disclosures contain detailed descriptions of the various dispersants based on substituted succinic acids as well as providing additional data regarding their preparation. In addition, these prior disclosures describe lubricating compositions containing these dispersants. It is lubricating compositions of this type which are improved according to the present invention.

Ordinarily, the lubricating compositions contemplated by the present invention will contain from 0.01% to about 20% by weight of the succinic acid dispersant. Generally, dispersant will be present in amount of from about 0.1% to about 10% by weight.

The demulsifiers for oil-in-water emulsions contemplated for use in the present invention are preferably at least partially soluble in the lubricating oil base. The demulsifier can be employed in amounts of from about 0.01% to about 5% by weight based on the weight of lubricating composition. However, one of the unusual aspects of the present invention is that very small amounts of demulsifier are effective. In most instances, concentrations of demulsifier in amounts of 0.01% to about 1%, usually 0.02% to 0.5%, give satisfactory performance. This means that those demulsifiers which have only very limited solubility in the lubricating oil compositions to which they are added can be readily employed with satisfactory results.

Many commercially available demulsifiers can be used in the improved lubricating oil compositions of the invention. For example, General Aniline and Film Corporation supplies a line of surface-active agents sold under the name GAFAC which are suitable demulsifiers. The preferred GAFAC demulsifiers are the alkyl phenoxypoly-(ethyleneoxy)ethyl mono- and diesters of phosphoric acid such as GAFAC RE-610 and RE-960. Other useful demulsifiers are the reaction products of various organic amines, carboxylic acid amides, and quaternary ammonium salts with ethyleneoxide. These polyoxyethylated amines, amides, and quaternary salts are available from Armour Industrial Chemical Co. under the names Ethoduomeen T/20, an ethyleneoxide condensation product of an N-alkyl alkylenediamine produced by Armour under the name Duomeen T; Ethomeen, tertiary amines which are ethyleneoxide condensation products of primary fatty amines; Ethomid, ethyleneoxide condensates of fatty acid amides; and Ethoquad, polyoxy ethylated quaternary ammonium salts such as quaternary ammonium chlorides.

The preferred demulsifiers are polyoxyalkylene polyols and derivatives thereof. This class of materials are commercially available from various sources: Pluronic Polyols from Wyandotte Chemicals Corporation; Polyglycol 112-2, a liquid triol derived from ethyleneoxide and propyleneoxide available from Dow Chemical Co.; and Tergitol, dodecylphenyl or nonophenyl polyethylene glycol ethers, and Ucon, polyalkylene glycols and derivatives, both available from Union Carbide Corp. These are but a few of the commercial products suitable as demulsifiers in the improved composition of the present invention.

In addition to the polyols per se, the esters thereof obtained by reacting the polyols with various carboxylic acids are also suitable. Acids useful in preparing these esters are lauric acid, stearic acid, succinic acid, and alkyl-for alkenyl-substituted succinic acids wherein the alkyl-for alkenyl group contains up to about twenty carbon atoms.

The preferred polyols are prepared as block polymers. Thus, a hydroxy-substituted compound, R—(OH)n (where n is 1 to 6, and R is the residue of a mono- or polyhydric alcohol, phenol, naphthol, etc.) is reacted with propylene oxide to form a hydrophobic base. This base is then reacted with ethylene oxide to provide a hydrophylic portion resulting in a molecule having both hydrophobic and hydrophylic portions. The relative sizes of these portions can be adjusted by regulating the ratio of reactants, time of reaction, etc., as is obvious to those skilled in the art. Thus it is within the skill of the art to prepare polyols whose molecules are characterized by hydrophobic and hydrophylic moieties which are present in a ratio rendering demulsifiers suitable for use in any lubricant composition regardless of differences in the base oils and the presence of other additives.

If more oil-solubility is needed in a given lubricating composition, the hydrophobic portion can be increased and/or the hydrophylic portion decreased. If greater oil-in-water emulsion breaking ability is required, the hydrophylic and/or hydrophobic portions can be adjusted to accomplish this.

Compounds illustrative of R—(OH)n include alkylene polyols such as the alkylene glycols, alkylene triols, alkylene tetrols, etc., such as ethylene glycol, propylene glycol, glycerol, pentaerylthritol, sorbitol, mannitol, and the like. Aromatic hydroxy compounds such as alklated mono- and polyhydric phenols and naphthols can also be used, e.g., heptylphenol, dodecylphenol, etc.

Other suitable demulsifiers include the esters disclosed in U.S. Patent 3,098,827 and 2,674,619.

The liquid polyols available from Wyandotte Chemicals Co. under the name Pluronic Polyols and other similar polyols are particularly well suited as demulsifiers. These Pluronic Polyols correspond to the Formula I:

$$HO-(CH_2CH_2O)_x(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_y(CH_2CH_2O)_z-H$$

wherein x, y, and z are integers greater than 1 such that the CH_2CH_2O groups comprise from about 10% to about 40% by weight of the total molecular weight of the glycol, the average molecule weight of said glycol being from about 1000 to about 5000.

These products are prepared by first condensing propylene oxide with propylene glycol to produce the hydrophobic base

$$(-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2-O)_y$$

This condensation product is then treated with ethylene oxide to add hydrophylic portions to both ends of the molecule. For best results, the ethylene oxide units should comprise from about 10 to about 40% by weight of the molecule. Those products wherein the molecular weight of the polyol is from about 2500 to 4500 and the ethylene oxide units comprise from about 10% to about 15% by weight of the molecule are particularly suitable. The polyols having a molecular weight of about 4000 with about 10% attributable to (CH_2CH_2O) units are particularly good.

This invention is not limited to mineral oil-based lubricating compositions. Other lubricating oils, natural and synthetic, can be used as the base for the improved lubricant compositions of this invention.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as solvent-refined or acid-refined mineral lubricating oils of the paraffinic, naphthenic, or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils. Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, etc.); alkyl benzenes (e.g., dodecylbenzenes, tetradecylbenzene, dinonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polyphenyls (e.g., bi-phenyls, terphenyls, etc.); and the like. Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc.; constitute another class of known synthetic lubricating oils. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500–1000, diethyl ether of polypropylene glycol having a molecular weight of 1000–1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_3–C_8 fatty acid esters, or the C_{13} Oxo acid diester of tetraethylene glycol. Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, pentaerythritol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, and the like. Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl-silicate, tetraisopropyl-silicate, tetra-(2-ethylhexyl)-silicate, tetra-(4-methyl-2-tetraethyl)- silicate, tetra-(p-tert-butylphenyl) - silicate, hexyl-(4-methyl-2-pentoxy) - disiloxane, poly(methyl) - siloxanes, poly(methyl phenyl)-siloxanes, etc.). Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid, etc.), polymeric tetrahydrofurans, and the like.

As mentioned supra, the present invention contemplates the presence of other additives in the lubricating compositions in addition to the succinic acid dispersants and the demulsifiers. Such additives include, for example, detergents of the ash-containing type, viscosity index improving agents, pour point depressants, anti-foam agents, extreme pressure agents, rust inhibitors, oxidation and corrosion inhibitors, and the like.

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 phosphorous acids characterized by at least one direct carbon-to-phosphorous 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 phosphorous trichloride, phosphorous heptasulfide, phosphorous pentasulfide, phosphorous trichloride and sulfur, white phosphorous and a sulfur halide, or phosphorothioate 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 radicals. 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 a metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature above about 50° C. and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid in the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promotor include phenolic substances such as phenol, naphthol, alkylphenols, thiophenols, sulfurized alkylphenols, condensation products of formaldehyde with such phenolic substances, alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve, Carbitol, ethylene glycol, cyclohexyl alcohol; amines such as aniline, phenylene diamine, phenothiazine, phenyl-beta-napthylamine, 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° to 200° C.

Extreme pressure agents and corrosion-inhibiting and oxidation-inhibiting agents are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyldisulfide, bis-(chlorobenzyl)-disulfide, dibutyl tetrasulfide, sulfurized sperm oil, sulfurized methyl ester of oleic acid, sulfurized alkylphenol ,sulfurized dipentene, and sulfurized terpene; phosphosulfurized hydrocarbons such as the reaction product of phosphorus sulfide with turpentine or methyloleate; phosphorous esters including principally dihydrocarbon and tri-hydrocarbon phosphites such as dibutylphosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite, dipentyl phenyl phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentyl phenyl phosphite, polypropylene- (molecular weight 500) substituted phenyl phosphite, diisobutyl-substituted phenyl phosphite; metal thiocarbamates such as zinc dioctyl-dithiocarbamate and barium heptylphenyl dithiocarbamate; Group II metal phosphorodithioates such as zinc dicyclohexyl phosphorodithioate, zinc dioctyl phosphorodithioate, barium di(heptylphenyl)-phosphorodithioate, cadmium dinonyl phosphorodithioate, and a zinc salt of a phosphorodithioic acid produced by the reaction of phosphorus pentasulfide with an equal molar mixture of isopropyl alcohol and n-hexyl alcohol.

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

The following examples are illustrative of the improved

lubricating compositions of the present invention. All percentages refer to percent by weight of total composition unless otherwise stated.

Composition A

A polyisobutenyl succinic anhydride having an acid number of 105 and an equivalent weight of 540 is prepared by reacting chlorinated polyisobutylene having an average molecular weight of 1050 and a chlorine content of 4.3% with maleic anhydride. To a mixture of 300 parts by weight of the polyisobutenyl succinic anhydride and 160 parts by weight of mineral oil, there is added at 65–95° C. an equivalent amount of polyalkylene polyamine (25 parts by weight of Polyamine H, an ethylene amine mixture having an average composition corresponding to that of tetraethylene pentamine and available from Carbide and Carbon). This mixture is then heated to 150° C. to distill water formed during the reaction. Nitrogen is bubbled through the mixture at this temperature to insure removal of all water. The residue is diluted by 79 parts by weight of mineral oil and this oil solution has a nitrogen content of 1.6% by weight.

The above described succinic acid dispersant is then incorporated into the following improved lubricating composition of the invention.

(1) SAE 20 mineral lubricating oil containing 0.5% of the succinic acid product and 0.2% of a polyoxyalkylene glycol corresponding to Formula I above and having a molecular weight of about 4000 and an ethyleneoxy content of about 10% by weight based on the total weight of the molecule.

(2) SAE 10W–30 mineral lubricating oil containing 1.0% of the above succinic dispersant product and 0.3% of GAFAC RE–960 identified hereinbefore.

(3) SAE 10 mineral lubricating oil containing 0.06% of Dow Polyglycol 112–1, 2% of the above succinic acid dispersant, 0.07% of phosphorus as zinc dioctyl-phosphorodithioate, 2% of a barium detergent prepared by neutralizing with barium hydroxide the hydrolyzed reaction product of a polypropylene (molecular weight 2000) with one mole of phosphorus pentasulfide and one mole of sulfur, 3% of a barium sulfonate detergent prepared by carbonating a mineral oil solution of mahogany sulfonic acid and a 500% stoichiometric excess of barium hydroxide in the presence of phenol as the promoter at 180° C., and 3% of a supplemental ashless detergent prepared by copolymerizing a mixture of 95% by weight of decylmethacrylate and 5% by weight of diethylaminoethyl acrylate.

(4) SAE 80 mineral lubricating oil containing 2% of the above succinic dispersant, 0.1% of phosphorus as zinc di-n-hexyl phosphorodithioate, 10% of a chlorinated paraffin wax having a chlorine content of 40%, 2% of di-butyltetrasulfide, 2% of sulfurized dipentene, 0.2% of oleyl amide, 0.003% of an anti-foam agent, 0.02% of a pour point depressant, 3% of a viscosity index improver, and, as the demulsifier, 1.0% of the ester formed by reacting dodecyl-substituted succinic acid with a polyoxypropylene condensation product of pentaerylthritol having an average molecular weight of about 600.

Composition B

SAE 10W–30 mineral lubricating oil containing 5% of the succinic acid dispersant prepared by reacting diethanolamine and an alkenyl-substituted succinic acid wherein the alkenyl group is a polyisobutene group having a molecular weight of 1100 according to U.S. Patent 3,324,033 and 0.5% of the polyol available as Dow 112–2.

Composition C

SAE 10W–40 mineral lubricating oil containing 3% of the dispersant of Composition A above, 3% of the diester of polyisobutenyl-substituted succinic anhydride and pentaerythritol disclosed in U.S. Patent 3,331,776 where the polyisobutenyl substituent has a molecular weight of about 1100, and 0.06% of Pluronic L–101.

Composition D

SEA 20W mineral lubricating oil containing (a) 2.5% of a succinic acid dispersant prepared by reacting polyisobutenyl (average molecular weight: 900–1000) substituted succinic anhydride with an ethylene polyamine mixture having an average composition corresponding to that of tetraethylenepentamine in an equivalent ratio of anhydride to polyamine of about 1:1.5 following the procedure of Example 5 of U.S. Patent 3,219,666 to form an acylated nitrogen composition and subsequently post-treating this product with about 0.2–0.6% by weight (based on the total weight of acylated nitrogen composition) of formic acid at about 145°–155° C. for about one-half to one and one-half hours and (b) about 1.2% of Pluronic L-101. This combination is an example of a lubricant having improved rust-resistant capabilities when compared to a similar lubricant lacking the demulsifier.

Composition E

SAE 10W–30 mineral lubricating oil containing 4.5% of the ester produced by reacting equimolar amounts of polyisobutenyl- (average molecular weight: 850–950) substituted succinic anhydride and pentaerythritol for five hours at about 150° C. and 2% of Dow Polyglycol 112–1.

The foregoing examples are merely illustrative of the improved compositions of the invention. Obviously, the other demulsifiers identified herein can be substituted for all or a portion of the demulsifiers in the foregoing illustrative examples. Similarly, other succinic acid dispersants of the type previously described above can be substituted for all or a portion of the succinic acid dispersants in the foregoing illustrative compositions.

The effectiveness of the demulsifiers is shown by the following test results. The test procedure used in arriving at this data is as follows:

The test engine (a 1964 Ford Falcon six-cylinder engine having a 170 cubic inch displacement) is operated on a cycling procedure consisting of 45 minutes at idle 500 r.p.m., no load, followed by 120 minutes at 2500 r.p.m., 31 BHP. During the cycle the blow-by is passed through a condenser and the condensate is returned to the crank case. The cycle is repeated five times in succession each day (for 13¾ hours of engine operation), and then the engine is shut down for the remainder of the day (for 10¼ hours). This completes a day's running. The test is run on a day-to-day basis with the maximum test length being five days. Daily test evaluation consists of rating the rocker arm cover for emulsion deposits on a numerical scale. The test engine is modified by providing for water cooling of the rocker arm covers in order that the temperature of the rocker arm cover can be maintained at 105°–115° F. by regulating the water flow.

The rocker arm cover is removed and inspected after each 13¾ hours of engine operation. The rocker arm cover is rated for emulsion deposits on a 10 to 1 numerical scale with 10 representing maximum cleanliness. Immediately after evaluation, the cover is replaced if the test is to continue.

TABLE I

Composition Number [1]	Demulsifier Type	Amount of Demulsifier	Rating at End of Daily Test				
			1st Day	2nd Day	3rd Day	4th Day	5th Day
I-(1)	None		5	5			
I-(2)	Ploy oxyalkylene polyol (Dow Polyol 112-2).	0.02	8.5	5.5			
II-(1)	None		5.0	4.5			
II-(2)	Polyoxyalkylene polyol (Wyandotte Pluronic L-101).	0.06	9.0	9.0	7.0	6.0	4.5
III-(1)	None		5.5	4.0			
III-(2)	Same as II-(2)	0.06	9.5	9.0	6.5	6.0	5.0
IV-(1)	None		3.5				
IV-(2)	Same as II-(2)	0.06	8.0	6.5	5.5	5.0	[2] 4.0

[1] Each composition I-IV is a typical commercial mineral lubricating oil containing as the succinic acid dispersant the reaction product of polyisobutylene-substituted succinic anhydride and a commercial mixture of ethylene polyamines. Compositions I-IV differ one from the other in the concentration and type of additive present. However, in a given composition, e.g., I-(1) and I-(2), (1) and (2) differ only in the presence of the indicated demulsifier.

[2] While the test is normally terminated on or before the 5th day, this test was continued to the 7th day. The rating on the 7th day was 3.5.

What is claimed is:

1. In a lubricating composition comprising a major amount of a lubricating oil and a minor amount of at least one dispersant selected from the class consisting of the metal salts, amine salts, amides, imides, amidines, and esters of substituted succinic acids having a substituent containing at least about fifty aliphatic carbon atoms, the improvement in said lubricating composition comprising the presence therein of from 0.01% to about 5% by weight of a polyoxyalkylene polyol demulsifier for water-in-oil emulsions wherein said polyoxyalkylene polyol is characterized by an average molecular weight of about 1000 to about 5000.

2. The improvement according to claim **1** wherein the demulsifier is a polyoxyalkylene polyol block copolymer the molecules of which consist essentially of a hydrophobic portion comprising

$$-\mathrm{CHCH_2O}-$$
$$\mathrm{CH_3}$$

groups and at least one hydrophylic portion comprising

$$-\mathrm{CH_2CH_2O}-$$

groups.

3. The improvement according to claim **2** wherein the $-\mathrm{CH_2CH_2O}-$ groups comprise from about 10% to about 40% by weight of the polyoxyalkylene polyol.

4. The improvement according to claim **3** in which the dispersant comprises at least one reaction product of a polyolefin-substituted succinic acid anhydride and an alkylene polyamine wherein the anhydride and polyamine are reacted in a ratio of about one-half equivalent to about two moles of polyamine per equivalent of anhydride.

5. The improvement according to claim **4** wherein the dispersant comprises at least one reaction product of a polyisobutylene-substituted succinic acid anhydride and a polyethylene polyamine.

6. The improvement according to claim **3** wherein the demulsifier is a polyoxyalkylene glycol.

7. The improvement according to claim **6** wherein said polyoxyalkylene glycol corresponds to the formula:

$$\mathrm{HO(-CH_2CH_2O-)_x(-CHCH_2O-)_y(-CH_2CH_2O-)_zH}$$
$$\mathrm{CH_3}$$

wherein x, y, and z are such that the $-\mathrm{CH_2CH_2O}-$ groups comprise from about 10% to about 15% of the total molecular weight of the glycol.

8. The improvement according to claim **7** wherein the average molecular weight of said glycol is about 2500 to 4000.

9. The improvement according to claim **8** in which the dispersant comprises at least one reaction product of a polyolefin-substituted succinic acid anhydride and an alkylene polyamine wherein the anhydride and polyamine are reacted in a ratio of about one-half equivalent to about two moles of polyamine per equivalent of anhydride.

10. The improvement according to claim **9** wherein the dispersant comprises at least one reaction product of a polyisobutylene-substituted succinic acid anhydride and a polyethylene polyamine.

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