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LUBRICATING COMPOSITIONS CONTAINING ISATOIC ANHYDRIDE

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This invention relates to lubricant compositions and in a more particular sense to mineral oil compositions having improved resistance to deterioration under service conditions. The lubricant compositions are useful in internal combustion engines, especially engines of the diesel type.

The problem of deterioration of lubricating oils and formation of harmful deposits under service conditions has been the cause of much concern in providing satisfactory lubrication of internal combustion engines. The problem is especially acute in lubricating engines of the diesel type where the lubricant encounters temperatures above 700° F. and pressures above 1200 pounds per square inch. In recent years, it has been common practice to incorporate into a lubricating oil, detergent additives which are capable of preventing the deposition of the products of oil degradation. Such additives include the metal salts of sulfonic acids, carboxylic acids and organic phosphorus acids. The basic metal salts, i.e., those in which the metal is present in stoichiometrically greater amounts than the organic acid radical, are especially effective for this purpose. Unfortunately, however, these metal detergents tend to promote oxidation of the oil. Thus, while lubricant compositions containing such additives are improved wth respect to their detergent properties, they are usually also characterized by a marked susceptibility to oxidative degradation.

Accordingly, it is an object of this invention to provide a means for reducing the oxidation tendencies of lubricant compositions having incorporated therein metal-containing detergent additives.

It is also an object of this invention to provide lubricant compositions adapted for use in internal combustion engines.

It is further an object of this invention to provide lubricant compositions adapted especially for use in diesel engines.

These and other objects are accomplished by providing a lubricating composition comprising a major proportion of mineral lubricating oil, from about 0.1% to about 20% of an oil-soluble alkaline earth metal salt of an acidic composition selected from the class consisting of sulfonic acids and phosphorus acids derived from the reaction of an aliphatic hydrocarbon with an inorganic phosphorus reagent, and a small amount, sufficient to increase the resistance to deterioration of said lubricating composition, of isatoic anhydride.

The amount of the detergent additive to be used in a lubricant composition of this invention will depend primarily upon the degree of detergency desired in the lubricant composition and the type of service to which the lubricant composition is to be subjected. For example, a lubricant for use in a gasoline engine of a passenger automobile may contain from 0.5% to 5% by weight of the detergent additive, whereas a lubricant for use in a diesel engine may contain as much as 20% or more of the detergent additive. In other applications

such as in two-cycle outboard motor type engines, a lubricant may contain only 0.2% or even less of the detergent additive.

The isatoic anhydride is used in the lubricant compositions of this invention to reduce the oxidation-promoting tendencies of the metal detergent additive. Hence, the amount of isatoic anhydride to be used depends to a large extent upon the amount and the type of the detergent additive used. A small amount of a detergent additive will usually require a correspondingly small amount of isatoic anhydride. In most instances, from 0.01% to 0.5%, more often in the neighborhood of 0.02%–0.2%, by weight of isatoic anhydride in a final lubricant will suffice to counteract the oxidation tendencies of a lubricant containing a detergent additive.

Isatoic anhydride is not readily soluble in mineral oil and its solubilization may require a short period of heating accompanied by stirring. For the purposes of this invention it is preferable to add it to a mineral oil which already contains the detergent additive. The isatoic anhydride dissolves easily in such a medium and there are thus no solubility difficulties.

The sulfonic acids from which the detergent additives of this invention are derived may be either petroleum sulfonic acids (e.g., mahogany acids) or alkylaryl sulfonic acids prepared by the treatment of alkylated aromatic compounds with a sulfonating agent such as sulfur trioxide, chlorosulfonic acid, sulfuric acid or the like. The organic radical of the sulfonic acid should contain at least about 12 aliphatic carbon atoms in order to impart oil-solubility.

The organic phosphorus acids from which the detergent additives are derived are principally those prepared by the treatment of a polymer of a lower monoolefin such as ethylene, propene, isobutene or 1-butene with a phosphorizing agent such as phosphorus pentasulfide, phosphorus heptasulfide, phosphorus sesquisulfide, phosphorus trichloride, phosphorus trichloride and sulfur, elemental phosphorus and a sulfur chloride, phosphorothioic chloride, etc. They may also be prepared by chlorinating an olefin polymer and treating the chlorinated polymer with a phosphorizing agent. The phosphorized polymer may be hydrolyzed (effected by, e.g., water addition, water washing, or preferably, steam blowing at a temperature of from about 100° C. to about 260° C.) first before conversion to the metal salts. Interpolymers of the above-illustrated lower monoolefins, aromatic olefins or diolefins likewise are useful for preparing the organic phosphorus acids provided that at least about 95% by weight of the interpolymer is composed of the lower monoolefin units. Examples of the olefin polymers include polyisobutenes, polypropenes, polyethylenes, copolymer of 90% of isobutene and 10% of styrene, copolymer of 98% of isobutene and 2% of chloroprene, copolymer of 99% of propene and 1% of piperylene, terpolymer of 98% of isobutene, 1% of butadiene and 1% of n-hexene, etc. Polymers of isobutene are most frequently used because of their ready availability. The molecular weights of the polymers may vary within wide ranges such as, for example, from 200 to 100,000 or even higher. Polymers of intermediate molecular weights, i.e., 500–10,000 are especially useful.

As noted above the phosphorus acids are prepared from an aliphatic hydrocarbon. The aliphatic hydrocarbons may contain incidental proportions of aromaticity and only such substituents as do not materially affect the aliphatic character of the molecule.

The alkaline earth metals from which the metal detergents of this invention are derived include magnesium, calcium, strontium, and barium. Of these, calcium and barium are preferred because of the particular effectiveness of their salts as detergent additives in the lubricant compositions of this invention.

The calcium sulfonates and the barium salts of the sulfonic acids and organic phosphorus acids may be neutral or basic salts obtained by treatment of the acid with at least a stoichiometric amount of an alkaline earth metal neutralizing agent such as the metal oxide, metal hydroxide, metal carbonate, metal alcoholate, metal phenate, etc. The term "basic metal salts" is used to designate the metal salts of organic acids wherein the metal is present in a larger amount than is stoichiometrically equivalent to the organic acid radical. Examples of such metal salts include those prepared by the processes described in U.S. Patents 2,616,905, 2,723,234, 2,921,901, 2,902,105, 2,906,709, 2,902,448, 2,865,956, 2,861,272, 2,316,080, and 2,316,081.

The most commonly employed methods for preparing the basic metal salts involve heating a mixture of an acid wth a stoichiometric excess of an alkaline earth neutralizing agent at a temperature above about 50° C. and filtering the reaction mass in a diluent such as mineral oil to obtain a fluid product. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess amount of metal is likewise known. Examples of such promoter compounds include phenolic substances such as phenol, naphthol, alkyl phenol, thiophenol, sulfurized phenol and condensation products of formaldehyde and a phenol; alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve, carbitol, ethylene glycol, stearyl alcohol, cyclohexyl alcohol; amines such as aniline, phenylenediamine, phenothiazine, phenyl-β-naphthylamine, dodecyl amine, etc. A particularly efficient method comprises mixing an acid with an excess of a neutralizing agent, a promoter compound and a small amount of water, and carbonating the mixture at an elevated temperature, e.g., 60°–150° C.

The present invention also contemplates the use of a corrosion inhibitor in conjunction with isatoic anhydride and the metal detergent additive in a lubricant composition. Corrosion inhibitors which are particularly effective for use in the lubricant compositions of this invention include the oil-soluble alkaline earth metal salts of alkylated phenolic compounds such as, e.g., alkyl phenols, alkyl naphthols, sulfurized alkyl phenols or naphthols, and condensation products of such phenolic compounds with aldehydes or ketones. The alkyl phenols and naphthols used in the preparation of the alkaline earth metal salts may be substituted with one or more alkyl radicals. To impart oil-solubility, the alkyl radical in the phenolic compound should contain at least seven carbon atoms.

The condensation products of phenolic compounds with aldehydes or ketones, for example, formaldehyde, are prepared by the process comprising the steps of reacting a mixture comprising one mole of an alkyl phenol and about one to about two moles of a formaldehyde-producing reagent in the presence of a catalyst at a temperature of from about 10° C. to about 99° C. and thereafter reacting said mixture with about one mole of an alkaline earth metal hydroxide or oxide at a temperature of at least about 30° C. Although this second step is generally carried out at a temperature between 30° C. and the decomposition temperature of the alkaline earth metal salt, the usual temperature range for the second step is from about 70° C. to about 175° C.

The catalyst used in the process for preparing these condensation products may be an inorganic metal hydroxide or other suitable catalyst. Such catalysts include ammonium hydroxide, amines, and the oxides or hydroxides of alkali or alkaline earth metals. Examples of the latter include lithium hydroxide, sodium hydroxide, barium oxide, and calcium oxide or hydroxide. The amount of catalysts used is within the range from about 0.01 mole to about 0.06 mole per mole of alkyl phenol.

Specific examples of such corrosion inhibitors include: the barium salt of cetyl phenol, the calcium salt of octyl phenol, the strontium salt of heptylphenol, the barium salt of bis-(hydroxyphenyl) sulfide, the calcium salt of the condensation product of heptylphenol with 0.5 mole of formaldehyde, the calcium salt of bis(hydroxyphenyl) di-sulfide, etc. Likewise useful are the basic alkaline earth metal salts of the alkylated phenolic compounds wherein the metal is present in stoichiometrically larger amounts than the phenolic radical. These basic salts may be prepared by heating a mixture of a phenolic compound with an excess of an alkaline earth metal neutralization agent, or treating such mixtures with carbon dioxide at a temperature of about 100°–200° C.

Another class of corrosion inhibitors contemplated for use in the lubricant compositions of this invention are the Group II metal salts of organic phosphorodithioic acids, especially the zinc and barium salts of dialkyl phosphorodithioic and dialkaryl phosphorodithioic acids. In addition to serving as corrosion inhibitors, these metal salts are effective as extreme pressure additives and prevent "valve train" wear, that is, wear on the cam surfaces, the valve lifter faces, the valve tip, the rocker arm tips, etc. The phosphorodithioic acids are preferably those in which the total number of the carbon atoms in the two alkyl radicals is at least about 7.6 per each phosphorus atom. The metal salts of such acids may be illustrated by, e.g., zinc dipentyl phosphorodithioic, zinc dicyclohexyl phosphorodithioate, barium di(p-heptylphenyl) phosphorodithioate, the barium salt of propyl heptyl phosphorodithioic acid, the zinc salt of heptyl cresyl phosphorodithioic acid, etc.

Another class of phosphorodithioate additives contemplated for use in the lubricating compositions of this invention comprises the adducts of the metal phosphorodithioates described above obtained by mixing the phosphorodithioate with up to 4 moles of an epoxide. Generally, from 1 to 2 moles of epoxide is used per mole of phosphorodithioate. The reaction is usually exothermic and may be carried out within wide temperature limits from about 0° to about 300° C. Because the reaction is exothermic it is best carried out by adding one reactant, usually the epoxide, in small increments to the other reactant in order to obtain convenient control of the temperature of the reaction. The reaction may be carried out in a solvent such as benzene, mineral oil, naphtha, or n-hexane.

The phosphorodithioates useful in preparing such adducts are for the most part the zinc phosphorodithioates. The epoxides may be alkylene oxides or arylalkylene oxides. The arylalkylene oxides are exemplified by styrene oxide, p-ethyl styrene oxide, alpha-methylstyrene oxide, 3-beta-naphthyl-1,3-butylene oxide, m-dodecylstyrene oxide, and p-chlorostyrene oxide. The alkylene oxides include principally the lower alkylene oxides in which the alkylene radical contains 6 or less carbon atoms. Examples of such lower alkylene oxides are ethylene oxide, propylene oxide, 1,2-butene oxide, trimethylene oxide, tetramethylene oxide, butadiene monoepoxide, 1,2-hexene oxide, and epichlorohydrin. Other epoxides useful herein include, for example, butyl 9,10-epoxystearate, epoxidized soyabean oil, epoxidized tung oil, and the epoxidized copolymer of styrene with butadiene.

The chemical nature of the adduct is not known. For the purpose of this invention adducts obtained by the reaction of 1 mole of the phosphorodithioate with from about 0.25 mole to about 4 moles of a lower alkylene oxide, particularly ethylene oxide and propylene oxide, have been found to be especially useful and therefore are preferred.

The amount of phosphorodithioate corrosion inhibitor to be used in the lubricant composition of this invention

may be varied within the range from abut 0.001% to about 2% of phosphorus. As mentioned previously, the amount of corrosion inhibitor to be used is determined by the amount of metal detergent used in the lubricant. That is, the greater the amount of the metal detergent the greater the amount of corrosion inhibitor.

Still another class of corrosion inhibitors includes the sulfurized or phosphosulfurized hydrocarbons or fatty materials such as the reaction products of alpha-pinene with sulfur or phosphorus pentasulfide, the reaction products of methyl oleate with phosphorus sesquisulfide, the reaction products of sperm oil with sulfur, dibutyl tetrasulfide, dipentyl trisulfide, etc.

Other corrosion inhibitors are the metal salts of organic thiocarbamic acids such as zinc diheptylphenyl dithiocarbamate, zinc dipentyl dithiocarbamate, cadmium cyclohexyl thiocarbamate, etc.

Yet another class of corrosion inhibitors consists of organic phosphites, especially diaryl- and dialkyl phosphites having the formula, $(RO)_2P(O)H$, wherein R is an aryl or an alkyl radical containing 4–30 carbon atoms. They may be prepared by the reaction of an alcohol or phenol or a mixture of alcohols or phenols with phosphorus trichloride. Examples of such phosphites include: dicyclohexyl phosphite, di(4-methyl-2-pentyl)phosphite, propyl octyl phosphite, methylcyclohexylpentyl phosphite, diphenyl phosphite, etc. Other phosphites such as triphenyl phosphite, tributyl phosphite, and hexyl dicresyl phosphite are likewise contemplated.

While any of the above-mentioned corrosion inhibitors may be used, the particular combination of an alkaline earth metal salt of an alkylated phenolic compound with isatoic anhydride and a metal detergent has been found to produce lubricants which show unexpectedly high resistance to oxidative degradation. Accordingly, such a combination is preferred for use in preparing the lubricants of this invention.

The amount of corrosion inhibitor to be used in the lubricant compositions of this invention may be varied within the range from about 0.1% to about 5% by weight, more often within the range of from about 1% to about 3% by weight.

The use in a lubricant composition of this invention of other types of additives such as anti-foam agents, rust-inhibitors, pour point and viscosity index improving agents, etc., is likewise contemplated.

The following examples illustrate more specifically the additives useful in a lubricant composition of this invention. All parts are by weight.

Example 1.—Neutral calcium detergent additive: A mineral oil solution containing 50% by weight of a sodium petroleum sulfonate (molecular weight 500) is heated at 90° C. for 2 hours with a 20% stoichiometrically excessive amount of calcium chloride and 10% by weight of water. The mixture is then dehydrated by heating to 150° C. and the inorganic chlorides removed by filtration. The filtrate is an oil solution of a neutral calcium petroleum sulfonate.

Example 2.—Basic calcium detergent additive: A mixture of 520 parts of a mineral oil, 480 parts of a sodium petroleum sulfonate (molecular weight of 480) and 84 parts of water is heated at 100° C. for 4 hours. The mixture is then heated with 88 parts of a 76% aqueous solution of calcium chloride and 72 parts of lime (90% purity) at 100° C. for 2 hours, dehydrated by heating to a water content of less than 0.5%, cooled to 50° C., mixed with 130 parts of methyl alcohol and blown with carbon dioxide at 50° C. until substantially neutral. The mixture is then heated to 150° C. to distill off methyl alcohol and water and the resulting oil solution of the basic calcium sulfonate filtered. The filtrate is found to have a sulfate ash of 16%.

Example 3.—Basic calcium detergent additive: A mixture of 300 grams of mineral oil, 690 grams (0.5 mole) of neutral calcium mahogany sulfonate, 75 grams of water and 29 grams of lime (90% purity) is heated at 100° C. for 2 hours and then to 150° C. during a period of 7 hours. The mixture is blown with carbon dioxide at 150° C. until substantially neutral and filtered. The filtrate is found to have a sulfate ash content of 8.2%.

Example 4.—Basic barium detergent additive: A mixture of 490 parts of a mineral oil, 110 parts of water, 61 parts of heptylphenol, 340 parts of neutral barium mahogany sulfonate and 227 parts of barium oxide is heated at 100° C. for 0.5 hour and then to 150° C. Carbon dioxide is then bubbled into the mixture until the mixture is substantially neutral. The mixture is filtered and the filtrate found to have a sulfate ash content of 25%.

Example 5.—Basic barium detergent additive: To 900 parts of a chlorinated polyisobutene having a chlorine content of 4.3% and a molecular weight of 1000 there is added 150 parts of phosphorus trichloride at 110°–190° C. during a period of 15 hours. The mixture is heated at 200° C. for 2 hours, at 180°–190° C./660 mm. for 1.5 hours, and then blown with nitrogen at 170° C. for 2 hours. The residue is hydrolyzed with steam to form an acidic intermediate. A basic barium salt is prepared by adding 400 parts of the acidic intermediate to a mixture of 495 parts of a mineral oil, 100 parts of heptylphenol, 38 parts of water and 62 parts of barium oxide at 90°–95° C. during 1.5 hours. The mixture is heated at this temperature for 0.5 hour, mixed with 257 parts of barium oxide and carbonated at 130°–140° C. until it is substantially neutral. The resulting mixture is diluted with 280 parts of mineral oil and filtered. The filtrate is found to have a sulfate ash content of 25%.

Example 6.—Basic magnesium detergent additive: A methyl alcohol suspension containing 14% by weight of suspended magnesium methoxide is blown with carbon dioxide at 40° C. until it is acidic to alpha-naphtholbenzein indicator, whereupon a homogeneous solution is obtained. The solution (200 parts by weight) is added dropwise to 27 parts of an alkylated benzene-sulfonic acid having a molecular weight of 450, 123 parts of a mineral oil and 75 parts of water, and the resulting mixture is heated to 150° C. The residue is filtered and the filtrate contains 40% by weight of sulfate ash.

Example 7.—Neutral barium detergent additive: A polypropene having a molecular weight of 2000 is mixed with 10% by weight of phosphorus pentasulfide at 190° C. for 6 hours. The resulting phospho-sulfurized polypropene is hydrolyzed by treatment with steam at 160° C. to produce an acidic intermediate which is then converted to the neutral barium salt by treatment with a stoichiometric amount of barium hydroxide.

Example 8.—Basic barium detergent additive: To a mixture of 1000 parts of a chlorinated polyisobutene having a chlorine content of 4.3% and a molecular weight of 1000 and 110 parts of phosphorus trichloride, there is added portionwise throughout a period of 0.5 hour 61 parts of heptylphenol at 210° F. The mixture is heated to 390° F. whereupon an additional 110 parts of phosphorus trichloride is added throughout a period of 6 hours. The mixture is heated at 390° F. for 0.5 hour, blown with nitrogen at 360°–390° F./100 mm. for 2 hours, and then with steam at 300°–320° F. for 3 hours. To a mixture of 270 parts of mineral oil, 18 parts of water and 15 parts of barium oxide, there are added 143 parts of the above steam-hydrolyzed product and 38 parts of heptylphenol at 190°–195° F., and then 125 parts of barium oxide at 200°–230° F. The mixture is heated to 270°–280° F. and blown with carbon dioxide until substantially neutral. The residue is diluted with 120 parts of mineral oil, blown with nitrogen at 310° F. for 0.5 hour, and filtered. The filtrate has a sulfate ash content of 25%.

Example 9.—Basic barium detergent additive: To a mixture of 6,245 grams (12.5 equivalents) of barium petroleum sulfonate, 1,460 grams (7.5 equivalents) of heptyl phenol and 2,100 grams of water in 8,045 grams of mineral oil there is added at 180° F., 7,400 grams (96.5

equivalents) of barium oxide. The addition of barium oxide causes the temperature to rise to 290° F. and this temperature is maintained until all of the water has been distilled away. The mixture then is blown with carbon dioxide until it is substantially neutral. 5,695 grams of mineral oil is added and the mixture filtered through a siliceous filter aid. The filtrate is diluted further with mineral oil to a barium content of 38.5% as sulfate ash.

Example 10.—Basic calcium detergent additive: (Same as Example 2 except that sodium polydodecylbenzene sulfonate is used in the place of sodium mahogany sulfonate).

Example 11.—Neutral strontium detergent additive: A copolymer of isobutene and styrene (molar ratio of 10.5:1 respectively) having a molecular weight of 1000 is heated with 8.6% by weight of sulfur to 200° C. whereupon 37% by weight of phosphorus trichloride is added to the mixture at 170°–200° C. during a period of 5 hours. The mixture is then subjected to distillation at 170° C./50 mm. for 1 hour, and the residue diluted with 44% by weight of a mineral oil. The oil solution is found to contain 3% of phosphorus, 4.7% of sulfur, and 2.7% of chlorine. Steam is passed into the oil solution to produce an acidic intermediate which is then treated with a stoichiometric amount of strontium hydroxide to produce a neutral strontium salt of an organic phosphorus acid.

Example 12.—Calcium phenolic corrosion inhibitor: A mineral oil solution containing 50% of cetyl phenol is heated with a stoichiometric amount of calcium oxide and 10% by weight of water at 150°–170° C. for 8 hours. The mixture is then dried at 150° C./15 mm. pressure.

Example 13.—Calcium phenolic corrosion inhibitor: A mixture of 315 parts of mineral oil, 125 parts of heptylphenol and 26.4 parts of lime is heated at 105°–108° F. for 10 minutes and to this mixture there is then added 5.8 parts of aqueous ammonium hydroxide and 29.3 parts of paraformaldehyde at 115°–120° F. The mixture is maintained at 155°–180° F. for 1 hour and then heated to 300° F. in 5 hours whereupon the water is removed by distillation. The residue is dried by heating at 300°–305° F. for 1 hour, mixed with 18 parts of a filter aid and filtered. The filtrate has a sulfate ash content of 6.2.

Example 14.—Calcium phenolic corrosion inhibitor: A mineral oil solution containing 50% by weight of a mixture of stoichiometrically equivalent amounts of bis(heptylphenyl) sulfide and hydrated lime is heated at 200° C. for 6 hours and filtered. The filtrate is the neutral calcium salt.

Example 15.—Barium phenolic corrosion inhibitor: A mixture of 400 grams of heptylphenol, 54 grams of water, 1150 grams of mineral oil and 163 grams of barium oxide is heated at 160°–170° C. for 2 hours and filtered. The filtrate has a barium content of 4.8%.

Example 16.—Magnesium phenolic corrosion inhibitor: A mineral oil solution containing 40% by weight of dipentylphenol is mixed with a 20% stoichiometric excess of magnesium methoxide suspended in methyl alcohol. The mixture is heated at reflux temperature for 15 hours and then distilled to remove any volatile components. The residue is filtered to yield as the filtrate, an oil solution of the magnesium salt.

Example 17.—Barium phenolic corrosion inhibitor: A mixture of 309 grams (1.5 equivalents) of octylphenol, 1500 grams of mineral oil, 344 grams (4.5 equivalents) of barium oxide and 180 grams (10 equivalents) of water is stirred at reflux temperature for an hour, then heated to 150° C. and held at 150°–160° C. for an hour. Carbon dioxide is bubbled into the mixture for 35 minutes at 150° C. and the hot mixture is filtered. The filtrate has the following analysis: percent sulfate ash: 21.2; Neutralization No.: 16.7 (basic).

Example 18.—Zinc phosphorodithioate corrosion inhibitor: A phosphorodithioic acid prepared by the reaction of phosphorus pentasulfide with four moles of an equimolar mixture of sec-butyl alcohol and cyclohexyl alcohol is neutralized by treatment with a 20% stoichiometric excess of zinc oxide at 80° C. The resulting zinc phosphorodithioate is filtered.

Example 19.—Phosphosulfurized cyclic hydrocarbon corrosion inhibitor: A solution of 250 grams of pinene in 250 grams of mineral oil is heated with 100 grams of phosphorus pentasulfide at 120°–150° C. for 2 hours. The mixture is filtered and the filtrate has a phosphorus content of 4.8% and a sulfur content of 13%.

Example 20.—Zinc phosphorodithioate-propylene oxide adduct corrosion inhibitor: To 394 parts of zinc dioctyl phosphorodithioate having a phosphorus content of 7% there is added at 75°–85° C., 13 parts of propylene oxide (0.5 mole per mole of zinc phosphorodithioate) over a period of 20 minutes. The mixture is heated at 82°–85° C. for one hour and filtered. The filtrate (399 parts) is found to contain 6.7% phosphorus, 7.4% zinc, and 4.1% sulfur.

Example 21.—Zinc phosphorodithioate-ethylene oxide adduct corrosion inhibitor: Ethylene oxide (21 parts, 0.5 mole) is added to 323 parts (0.5 mole) of the zinc salt of a phosphorodithioic acid prepared by the reaction of phosphorus pentasulfide with a mixture of 65% (by weight) of isobutyl alcohol and 35% of primary-pentyl alcohol at 90°–100° C. over a period of one hour. The mixture is heated at this temperature for six hours, then to 90° C./20 mm. and filtered. The filtrate is the desired product.

Example 22.—Calcium phenolic corrosion inhibitor: Water (50 parts) is added to a mixture of 2,250 parts of mineral oil and 960 parts (5 moles) of heptylphenol at 27° C. To this reaction mixture at 41° C. there is added 231 parts (7 moles) of 91% paraformaldehyde over a period of 0.75 hour. Lime (6.6 parts, 0.16 mole) is added to the reaction mixture at 41°–43° C. and the mixture is heated to 80° C. over a period of 1.1 hours. Additional lime (200 parts, 4.8 moles) is added to the reaction mixture at 80°–90° C. over a period of 0.75 hour. The mixture is heated to 149° C. over a period of five hours, blown with nitrogen and heated at 150°–155° C. for seven hours, mixed with a filter aid and filtered. The filtrate has a calcium content of 7.6% measured as sulfate ash.

Example 23.—Calcium phenolic corrosion inhibitor: The procedure of Example 22 is repeated except that 610 parts (7.5 moles) of 37% aqueous formaldehyde is used in lieu of the paraformaldehyde and water, and 1170 parts (5 moles) of decylphenol is used in lieu of the heptylphenol.

The following examples illustrate the lubricant compositions of this invention:

	Parts by weight
Lubricant I:	
SAE 20 mineral oil	100
Calcium detergent additive of Example 2	6
Isatoic anhydride	0.02
Lubricant II:	
SAE 10W 30 mineral oil	100
Calcium detergent additive of Example 1	10
Isatoic anhydride	0.05
Lubricant III:	
SAE 30 mineral oil	100
Basic barium detergent additive of Example 4	15
Calcium phenolic corrosion inhibitor of Example 12	3
Isatoic anhydride	0.3
Lubricant IV:	
SAE 40 mineral oil	100
Neutral barium detergent additive of Example 7	3
Phosphosulfurized cyclic hydrocarbon corrosion inhibitor of Example 19	2
Isatoic anhydride	0.075

Lubricant V:	
SAE 10W–30 mineral oil	100
Basic barium detergent additive of Example 4	10
Calcuim phenolic corrosion inhibitor of Example 13	2
Isatoic anhydride	0.1
Polyalkylsiloxane anti-foam agent	0.003
Polyalkylmethacrylate viscosity index improving agent	1.5
Lubricant VI:	
SAE 30 mineral oil	100
Basic magnesium detergent additive of Example 6	2
Calcium phenolic corrosion inhibitor of Example 14	0.5
Isatoic anhydride	0.075
Lubricant VII:	
SAE 30 mineral oil	100
Neutral strontium detergent additive of Example 11	3
Zinc phosphorodithioic corrosion inhibitor of Example 18	1
Isatoic anhydride	0.05
Lubricant VIII:	
SAE 30 mineral oil	100
Basic calcium detergent additive of Example 10	11.2
Basic barium detergent additive of Example 9	2.4
Calcium phenolic corrosion inhibitor of Example 13	2.3
Isatoic anhydride	0.09
Lubricant IX:	
SAE 40 mineral oil	100
Basic barium detergent additive of Example 5	4.5
Zinc phosphorodithioate corrosion inhibitor of Example 18	2
Isatoic anhydride	0.8
Lubricant X:	
SAE 30 mineral oil	100
Neutral barium detergent additive of Example 7	4
Isatoic anhydride	0.5
Lubricant XI:	
SAE 30 mineral oil	100
Basic barium detergent additive of Example 5	6
Propylene oxide adduct of zinc phosphorodithioate of Example 20	1
Isatoic anhydride	0.09
Lubricant XII:	
SAE 20 mineral oil	100
Basic barium detergent additive of Example 8	14
Propylene oxide adduct of zinc phosphorodithioate of Example 20	1.5
Isatoic anhydride	0.1
Polyalkyl acrylate anti-foam agent	0.005
Lubricant XIII:	
SAE 30 mineral oil	100
Basic magnesium detergent additive of Example 6	10
Barium phenolic corrosion inhibitor of Example 15	2
Isatoic anhydride	0.075
Lubricant XIV:	
SAE 40 mineral oil	100
Basic barium detergent additive of Example 9	8
Magnesium phenolic corrosion inhibitor of Example 16	1
Isatoic anhydride	0.1
Lubricant XV:	
SAE 30 mineral oil	100
Basic barium detergent additive of Example 4	8
Basic calcium detergent additive of Example 2	3
Barium phenolic corrosion inhibitor of Example 15	3
Isatoic anhydride	0.05
Lubricant XVI:	
SAE 30 mineral oil	100
Basic calcium detergent additive of Example 3	7.5
Calcium phenolic corrosion inhibitor of Example 22	2.5
Isatoic anhydride	0.075
Lubricant XVII:	
SAE 20 mineral oil	100
Basic calcium detergent additive of Example 3	7
Basic barium detergent additive of Example 9	2
Calcium phenolic corrosion inhibitor of Example 23	2
Isatoic anhydride	0.1

The above lubricants are, of course, merely illustrative and the scope of the invention includes the use of all of the detergent additives and inhibitors previously illustrated as well as many others within the broad definition of the combination of the invention.

The oxidation resistance of the lubricants of this invention is shown by the results of the Air Oxidation Test summarized in Table I. The test consists of bubbling air at a rate of 1 cubic foot per hour into 300 grams of a lubricant having immersed therein a sheet of copper (2 x 8 x 0.33 inches) as an oxidation promoter at 300°±5° F., and measuring the viscosity increase of the lubricant at 24-hour intervals until a sharp increase in viscosity occurs. The results are expressed in terms of percent of viscosity increase. It will be readily appreciated that a smaller increase in viscosity indicates a greater resistance to oxidative degradation of the lubricant. The Air Oxidation Test results summarized in Table I illustrate the effectiveness of isatoic anhydride to increase the resistance to deterioration of lubricating compositions containing metal detergents.

TABLE I

AIR OXIDATION TEST RESULTS

Test Sample	Lubricant	Percent viscosity increase at end of test period of—						
		120 hrs.	144 hrs.	166 hrs.	192 hrs.	216 hrs.	240 hrs.	264 hrs.
1	VIII	10	------	12	15	------	62	160
2	Same as test sample 1 but without isatoic anhydride.	------	8	10	58	142	248	------

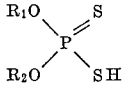
What is claimed is:

1. A lubricating composition comprising a major proportion of lubricating oil, from about 0.1% to about 20% of an oil-soluble alkaline earth metal salt of an acidic composition selected from the class consisting of sulfonic acids and phosphorus acids derived from the reaction of an aliphatic hydrocarbon with an inorganic phosphorus reagent, and a small amount, sufficient to increase the resistance to deterioration of said lubricating composition, of isatoic anhydride.

2. The lubricating composition of claim 1 characterized further in that it contains from about 0.01% to about 5% of a corrosion inhibitor.

3. The lubricating composition of claim 2 characterized further in that the corrosion inhibitor is an alkaline earth metal salt of an alkylated phenol.

4. The lubricating composition of claim 1 characterized further in that it contains from about 0.001% to about 2% of phosphorus as a phosphorothioate additive selected from the class consisting of oil-soluble Group II metal salts of phosphorodithioic acids having the formula



wherein R_1 and R_2 are aliphatic radicals and contain at least about 7.6 aliphatic carbon atoms per atom of phosphorus, and adducts of said metal salts with an epoxide.

5. The lubricating composition of claim 4 characterized further in that the phosphorothioate additive is a zinc phosphorodithioate.

6. The lubricating composition of claim 4 characterized further in that the phosphorothioate additive is an adduct of a zinc dialkyl phosphorodithioate with an alkylene oxide.

7. A lubricating composition comprising a major proportion of a mineral lubricating oil, from about 0.1% to about 20% of an alkaline earth metal salt of a hydrocarbon sulfonic acid and a small amount, sufficient to increase the resistance to deterioration of said lubricating composition, of isatoic anhydride.

8. The lubricating composition of claim 7 characterized further in that the hydrocarbon sulfonic acid is a mahogany acid.

9. A lubricating composition comprising a major proportion of a mineral lubricating oil, from about 0.1% to about 20% of an oil-soluble alkaline earth metal salt of a phosphorus acid derived from the reaction of an aliphatic hydrocarbon with an inorganic phosphorus reagent selected from the class consisting of phosphorus sulfide and phosphorus halides, and a small amount, sufficient to increase the resistance to deterioration of said lubricating composition, of isatoic anhydride.

10. The lubricating composition of claim 9 characterized further in that the aliphatic hydrocarbon is an olefin polymer.

11. A lubricating composition comprising a major proportion of a mineral lubricating oil, from about 0.1% to about 10% of an oil-soluble calcium sulfonate, from about 0.1% to about 10% of an oil-soluble barium sulfonate, and a small amount, sufficient to increase the resistance to deterioration of said lubricating composition, of isatoic anhydride.

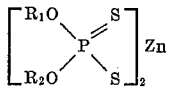
12. The lubricating composition of claim 11 characterized further in that the calcium sulfonate and barium sulfonate are each derived from a mahogany acid.

13. The lubricating composition of claim 11 characterized further in that the calcium sulfonate and barium sulfonate are each derived from an alkylaryl sulfonic acid.

14. The lubricating composition of claim 11 characterized further in that it contains from about 0.01% to about 5% of an alkaline earth metal salt of an alkylated phenol.

15. The lubricating composition of claim 11 characterized further in that it contains from about 0.1% to about 5% of a calcium salt of an alkyl phenol-formaldehyde condensation product.

16. The lubricating composition of claim 11 characterized further in that it contains from about 0.001% to about 2% by weight of phosphorus of a zinc phosphorodithioate having the formula



wherein R_1 and R_2 are aliphatic radicals and contain at least about 7.6 aliphatic carbon atoms per atom of phosphorus.

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