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(54) Improved lubricant compositions for low-temperature internal combustion engines.

(57) In accordance with the present invention, there are provided lubricating oil compositions which comprise an oil of lubricating viscosity as the major component and as the minor component (A) a mixture of (1) at least one calcium overbased sulfonate or phenate detergent inhibitor, and (2) at least one magnesium overbased sulfonate or phenate detergent inhibitor, and (B) a mixture of (1) at least one zinc di-(primary hydrocarbyl) dithiophosphate and (2) at least one zinc di-(secondary hydrocarbyl) dithiophosphate, wherein the mixed calcium and magnesium detergent inhibitors and the mixed zinc di(primary hydrocarbyl) dithiophosphate and the zinc di(secondary hydrocarbyl) dithiophosphate antiwear agents are present in controlled ratios.

Description

IMPROVED LUBRICANT COMPOSITIONS FOR LOW-TEMPERATURE INTERNAL COMBUSTION ENGINES

FIELD OF THE INVENTION

5 This invention relates to lubricating oil compositions which exhibit marked improvements in low temperature cylinder wear. More particularly, this invention relates to lubricating oil compositions which contain minor proportions of mixtures of calcium and magnesium sulfonates with primary and secondary zinc antiwear agents, in addition to dispersant additives.

10 DESCRIPTION OF THE PRIOR ART

It is an objective of the industry to provide lubricating oil compositions which exhibit improvements in low temperature cylinder wear and ring wear, and the obtainment of concomitant improved engine life in gasoline and diesel engine vehicles. In engines which operate at low temperatures, e.g. for gasoline engines which operate without thermostats and are cooled by water in the absence of conventional antifreeze/coolant additives (such as ethylene glycol), the problem of cylinder wear is especially important. Lubrication oils which are formulated to be employed in high temperature, ethylene-glycol/water cooled gasoline engines are generally not completely satisfactory.

U.S. Patent 2,911,367 relates to mineral oil compositions adapted to preventing rusting and corrosion of metal surfaces which are exposed to moisture and comprise a major proportion of a mineral lubricating oil and a minor proportion of each of an alkali metal salt, an oil soluble sulfonic acid, a metal alkylthiophosphate, a partial ester of a fatty acid containing at least 8 carbon atoms and a polyol containing from 3 to 6 carbon atoms and from 3 to 6 hydroxyl radicals per molecule and an ethylene glycol C₆ branched-chain alkyl ether. The metal alkylthiophosphates are said to include magnesium, calcium, zinc, strontium, cadmium and barium thiophosphates, of which zinc dioctyl and zinc octyl hexyl dithiophosphates are exemplary. The sulfonate is employed in an amount of from about 1 to about 5 weight percent based on the total composition and the metal alkylthiophosphate, including the above-mentioned zinc octyl hexyl and zinc dioctyl dithiophosphate, are said to be used preferably in an amount of between about 0.1 and about 1.5 weight percent of the total composition.

U.S. Patent 3,562,159 relates to synthetic lubricants containing a carboxylic acid ester of lubricating viscosity as the basic liquid and, as additives, an alkylated alkylene polyamine (about 5 to 30 parts by weight), a basic alkaline earth metal sulfonate (about 5 to 15 parts by weight), a metal phosphorodithioate (about 5 to 70 parts by weight), a basic alkaline earth metal salt of a phosphosulfurized hydrocarbon, esters of a hydrocarbon-substituted succinic acid, and a basic alkaline earth metal salt of an alkylphenol sulfide.

U.S. Patent 3,714,042 relates to treated overbased complexes, which are disclosed as being useful as additives in lubricating oils, gasolines and other organic materials, wherein basic metal complexes selected from the class consisting of sulfonate, sulfonate-carboxylate and carboxylic complexes with up to an amount equivalent to the total basicity thereof with high molecular weight aliphatic carboxylic acid or anhydrides containing at least about 25 aliphatic carbon atoms per carboxy group under recited temperature conditions. The metal of the basic metal salt complex may be magnesium or calcium (among other recited metals). Additional additives may be used in combination with the recited compositions, including Group II metal phosphorodithioates such as zinc dicyclohexyl phosphorodithioate, and zinc dioctyl phosphorodithioate.

U.S. Patent 3,933,659 relates to lubricating oil compositions which comprise a major amount of an oil of lubricating viscosity and an effective amount of an alkenyl succinimide, a Group II metal salt of a dihydrocarbyl dithiophosphoric acid, a basic sulfurized alkaline earth metal alkylphenate, and a compound selected from the group consisting of certain fatty acid esters and fatty acid amides and amines. The Group II metal salt of the dihydrocarbyl dithiophosphoric acids are indicated to be present in an amount of from 0.5 to 1.5 weight percent of the functional fluid and the basic sulfurized alkaline earth metal alkylphenates are indicated to be present in the functional fluid in an amount of from about 0.4 to about 4 weight percent.

U.S. Patent 4,308,154 relates to mixed metal salts (especially zinc salts) of dialkylphosphorodithioic acids and carboxylic acids, which are said to be useful in lubricants and functional fluids (such as hydraulic fluids) as antioxidants and extreme pressure agents having improved thermal stability. The mixed metal salts of this invention are said to also include those of the Group I and Group II metals.

U.S. Patent 4,417,990 relates to mixed metal salts/sulfurized phenate compositions, useful in lubricants and functional fluids as antioxidants and extreme pressure agents having improved thermal stability and contains a disclosure related that of U.S. Patent 4,308,154, discussed above.

Various suggestions have been made in the prior art regarding the nature, type, and carbon content of the alkyl or aryl groups present in dialkylphosphorodithioic acids used to prepare desired metal salts. For example, U.S. Patent No. 2,344,393 taught that it was previously recognized that metal dithiophosphates should have one or more long chain alkyl groups to render them sufficiently soluble in lubricating oils to be of practical value. The patentees found, however that the zinc salt of diamyl phosphorodithioic acid was oil-soluble. U.S. Patent No. 3,318,808 discloses that the higher carbon containing alkyl groups (above 4 carbon atoms) enhance oil solubility. Thus, the patent teaches combinations of C₄ and lower primary and/or secondary alcohols with C₅ and above alcohols, and the ratio of the alcohols is selected to suit the balance between

economics and solubility.

U.S. Patent No. 3,190,833 describes oil-soluble metal phosphorodithioates which are the salts of metals in Group II of the periodic table and comprise preferably the salts of calcium, barium, strontium, zinc and cadmium with phosphorodithioic acids which contain a total of at least about 7.6 aliphatic carbon atoms per atom of phosphorus. To improve the oil solubility of the metal salts, they are reacted with up to about 0.75 mole of an epoxide.

Another patent which relates to the preparation of phosphorodithioic acid salts as useful additives in lubricants is U.S. Patent No. 3,000,822. This patent describes zinc salts of a mixture of dialkyl phosphorodithioic acids wherein the alkyl groups comprise a mixture of lower molecular weight primarily aliphatic hydrocarbon radicals having less than 5 carbon atoms and higher molecular weight primary aliphatic hydrocarbon radicals having at least 5 carbon atoms. The mole ratios of lower molecular weight radicals to higher molecular weight radicals in the zinc salt is within the range of 1:1 to 3:1.

Various suggestions have been made in the prior art for improving the utility of lower alkyl phosphorodithioic acid salts which have a tendency to be oil insoluble. U.S. Patent No. 4,306,984 describes a procedure for rendering oil insoluble metal C₂-C₃ dialkyldithiophosphates oil-soluble by forming a complex between the dithiophosphate and an alkenyl or alkyl mono-or bis-succinimide. This combination of additives is used in lubricating oils which can be employed for crankcase lubrication of internal combustion engines. Another method which has been suggested for preparing non-crystalline mixtures of basic or mixed basic and neutral zinc salts of dialkyldithiophosphates containing from 1 to 13 carbon atoms in the alkyl groups has been suggested in U.S. Patent No. 3,843,530. The mixtures of basic or mixed basic and neutral zinc salts described in this patent contain from 4 to 13 different alkyl groups, have an average carbon content of 3.5 to 4.5, and contain at least 12% by weight of zinc.

U.S. Patent 4,466,895 relates to lubricating oil compositions containing metal salt of one or more dialkylphosphorodithioic acids wherein the alkyl groups each contain from 2 to 4 carbon atoms and at least one alkyl group is a butyl group, the total number of carbon atoms per phosphorus atoms is less than 8, from about 30 to 90 mole percent of the alkyl groups are primary alkyl groups, from about 10 to 70 mole percent of the alkyl groups are secondary alkyl groups, and wherein the metal salt as zinc, copper or iron salt, mixtures thereof, or a mixture of calcium salt and one or more of said metal salts, provided that when only 2 alkyl groups are present, from about 30 to 80 mole percent of the alkyl groups are n-butyl groups, and from about 20 to 70 mole percent of said alkyl groups are isopropyl groups. The patentees disclose that these metal salts are useful in lubricating oil compositions as anti-wear agents and antioxidants. The patentees metal salts of lower dialkylphosphorodithioic acids are illustrated in combination with a conventional higher alkyl ZDDP in sufficient formulations also containing mixtures of basic calcium petroleum sulfonate and basic magnesium petroleum sulfonate.

Zinc dialkyl dithiophosphates, prepared from mixed dialkyldithiophosphoric acids, have been heretofore prepared. U.S. Patent 3,293,181 relates to mixed salts prepared from a mixture of at least two different branched chain primary alcohols, one of said alcohols being isobutyl alcohol and the other said alcohols containing at least 6 carbon atoms.

U.S. Patent 3,397,145 discloses that the alkyl groups of the alkylthiophosphoric acids can be straight or branched chain and that the alkyl groups may be primary, secondary and/or tertiary substituents (e.g., same or different alkyl groups).

U.S. Patent 3,442,804 relates to zinc phosphorodithioates, useful in lubricating compositions, in which the hydrocarbon radicals are primary alkyl radicals and consist of a mixture of lower molecular weight radicals and higher molecular weight radicals.

U.S. Patent 4,328,111 relates to modified overbased sulfonates and phenates wherein the basic compound is reacted with acidic compound comprising an organic carboxylic acid, organic carboxylic acid anhydride, phosphoric acid, phosphoric acid ester, thiophosphoric acid ester, or mixtures thereof.

U.S. Patent 4,614,602 relates to lubricant compositions containing an overbased detergent-dispersant lubricant additive comprising a reaction product of an alkaline earth metal phenate and an ammonium alkylbenzene sulfonate, which the patentees indicate can be used in combination with other conventional lubricant additives, including anti-wear agents such as ZDDP. The alkyl benzene sulfonate can comprise sulfonic acid salts derived from alkaline earth metals, such as Ca, Mg, Ba oxides or hydroxides, alone or in admixture. Exemplified as a modifying agent for reaction with overbased magnesium sulfonate is 2-ethylhexyl dithiophosphoric acid.

U.S. Patent 4,362,633 relates to lubricating oil additives containing molybdenum-containing aminated sulphurized additives. The Patentee illustrates the use of such additives in combination with mixtures containing overbased calcium phenate, overbased magnesium sulphonate and zinc dialkyldithiophosphates.

European Patent 24,146 relates to lubricating oil compositions containing copper antioxidants, and exemplifies copper antioxidants in lubricating oil compositions also containing 1.0 wt. % of a 400 TBN magnesium sulphonate (containing 9.2 wt. % magnesium), 0.3 wt. % of a 250 TBN calcium phenate (containing 9.3 wt. % of calcium) and a zinc dialkyldithiophosphate in which the alkyl groups or a mixture of such groups having between 4 and 5 carbon atoms and made by reacting phosphorous P₂S₅ with a mixture of about 65% isobutyl alcohol and 35% of amyl alcohol, to give a phosphorous level of 1.0 wt. % in lubricating oil composition.

European Patent Application 92,946 relates to lubricating oil compositions having improved fuel economy

which contain glycerol partial esters, oil-soluble organic copper compounds and oil-soluble organic copper compounds. The Patent illustrates compositions containing such combinations in admixture with basic metal detergents and anti-wear additives. The Patent discloses that the preferred detergent materials are the normal or overbased calcium or magnesium phenates, sulphurized phenates, and/or sulphonates, and further discloses that the anti-wear additives generally are the oil soluble zinc dihydrocarbyl dithiophosphates having a total of at least 5 carbon atoms.

U.S. Patent 4,104,180 relates to a process for producing overbased carbonates. Example 11 of this Patent illustrates lubricating oils containing 1.2 wt. % neutral calcium phenate, 1.2 wt. % zinc dialkyl dithiophosphate and 1.2 wt. % magnesium sulphonate.

N. E. Gallopoulos et al., ASLE Transactions, Vol. 14, pp. 1-7, (1971) investigated the interactions between a zinc dialkyl phosphoro dithioate and lubricating oil dispersants including the effect of alkaline calcium petroleum sulphonate on aging of mixtures of the sulphonate with zinc dialkyl phosphoro dithioate, and concluded that chemical reactions are likely to occur. No investigation was reported for mixtures of alkaline earth metal sulphonates.

J. A. McGeehan et al., SAE Paper 852133, 1983, pps. 879-892 investigated the effects of zinc dithiophosphates and detergents on controlling engine wear. Zinc diaryl dithiophosphates were concluded to be less effective in controlling valve wear in gasoline engines than zinc dialkyl dithiophosphates. The authors concluded that the control of engine wear requires a critical balance of zinc dithiophosphate and detergent types in order to control gasoline engine valve train wear, diesel cylinder poor polishing wear and diesel roller follower bronze pin wear, based on the authors' studies conducted with various zinc dialkyl dithiophosphates and either calcium or magnesium detergents. However, the alkyl type of these zinc dithiophosphates was not identified and mixtures of calcium and magnesium detergents were not assessed.

However, none of the above references discloses advantages to be achieved in controlling the relative amounts of mixed calcium/magnesium detergents and mixed primary/secondary zinc dithiophosphate antiwear agents.

SUMMARY OF THE INVENTION

In accordance with the present invention, there are provided cylinder and ring wear corrosion inhibiting lubricating oil compositions which comprise an oil of lubricating viscosity as the major component and as the minor component (A) a mixture of (1) at least one calcium overbased sulfonate or phenate detergent inhibitor, and (2) at least one magnesium overbased sulfonate or phenate detergent inhibitor, and (B) a mixture of (1) at least one zinc di-(primary hydrocarbyl) dithiophosphate and (2) at least one zinc di-(secondary hydrocarbyl) dithiophosphate, wherein component (A) comprises from about 0.7 to 0.9 weight percent of the lubricating oil composition, component (B) comprises from about 0.7 to 1.2 weight percent of the lubricating oil composition, and wherein the mixed calcium and magnesium detergent inhibitors are present in a weight:weight ratio of components A(1):A(2) of from about 0.3:1.0 to about 1.3:1.0, and the mixed zinc di(primary hydrocarbyl) dithiophosphate and the zinc di(secondary hydrocarbyl) dithiophosphate antiwear agents are present in a weight:weight ratio of B(1):B(2) of from about 0.7:1.0 to about 3.1:1.0.

The present invention is based on the discovery that there is a surprisingly pronounced relationship between decreased cylinder and ring wear and the proportions of mixed calcium/magnesium detergent inhibitors and mixed primary/secondary zinc antiwear agent in crank case lubricating oil composition, and that such mixtures impart a degree of decreased cylinder and ring wear per unit weight of additive not heretofore recognized by the art. Of equal significance is the fact that other desirable affects and properties of lubricating oils, e.g., compatibility, detergency and dispersancy, are not diminished.

DETAILED DESCRIPTION OF THE INVENTION

Component A

Component A is a mixture of basic (viz, overbased) Ca and Mg salt of one or more organic sulfonic acid (generally a petroleum sulfonic acid or a synthetically prepared alkaryl sulfonic acid), petroleum naphthenic acids, alkyl benzene sulfonic acids, alkyl phenols, alkylene-bis-phenols, oil soluble fatty acids and the like, such as are described in U.S. Patent Nos. 2,501,731; 2,616,904; 2,616,905; 2,616,906; 2,616,911; 2,616,924; 2,616,925; 2,617,049; 2,777,874; 3,027,325; 3,256,186; 3,282,835; 3,384,585; 3,373,108; 3,365,396; 3,342,733; 3,320,162; 3,312,618; 3,318,809; and 3,562,159. For purposes of illustration, the disclosures of the above patents are hereby incorporated in the present specification insofar as the complexes useful in this invention are described. Among the petroleum sulfonates, the most useful products are those prepared by the sulfonation of suitable petroleum fractions with subsequent removal of acid sludge and purification. Synthetic alkaryl sulfonic acids are usually prepared from alkylated benzenes such as the Friedel-Crafts reaction product of benzene and a polymer such as tetrapropylene. Suitable acids may also be obtained by sulfonation of alkylated derivatives of such compounds as diphenylene oxide thianthrene, phenolthioxine, diphenylene sulfide, phenothiazine, diphenyl oxide, diphenyl sulfide, diphenylamine, cyclohexane, decahydro naphthalene and the like.

Highly basic Ca and Mg sulfonates are frequently used as detergents. They are usually produced by heating a mixture comprising an oil-soluble sulfonate or alkaryl sulfonic acid, with an excess of alkaline earth metal compound above that required for complete neutralization of any sulfonic acid present and thereafter forming

a dispersed carbonate complex by reacting the excess metal with carbon dioxide to provide the desired overbasing. The sulfonic acids are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum by distillation and/or extraction or by the alkylation of aromatic hydrocarbons as for example those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl and the halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 30 carbon atoms. For example haloparaffins, olefins obtained by dehydrogenation of paraffins, polyolefins produced from ethylene, propylene, etc. are all suitable. The alkaryl sulfonates usually contain from about 9 to about 70 or more carbon atoms, preferably from about 16 to about 50 carbon atoms per alkyl substituted aromatic moiety.

The alkaline earth metal compounds which may be used in neutralizing these alkaryl sulfonic acids to provide the sulfonates includes the oxides and hydroxides, alkoxides, carbonates, carboxylate, sulfide, hydrosulfide, nitrate, borates and ethers of magnesium, calcium, and barium. Examples are calcium oxide, calcium hydroxide, magnesium acetate and magnesium borate. As noted, the alkaline earth metal compound is used in excess of that required to complete neutralization of the alkaryl sulfonic acids. Generally, the amount ranges from about 100 to 220%, although it is preferred to use at least 125%, of the stoichiometric amount of metal required for complete neutralization.

Various other preparations of basic alkaline-earth metal alkaryl sulfonates are known, such as U.S. Patents 3,150,088 and 3,150,089 wherein overbasing is accomplished by hydrolysis or an alkoxide-carbonate complex with the alkaryl sulfonate in a hydrocarbon solvent-diluent oil.

A preferred Mg sulfonate additive is magnesium alkyl aromatic sulfonate having a total base number ranging from about 300 to about 400 with the magnesium sulfonate content ranging from about 25 to about 32 wt. %, based upon the total weight of this additive system dispersed in mineral lubricating oil. A preferred Ca sulfonate additive is calcium alkyl aromatic sulfonate having a total base number ranging from about 300 to about 400 with the calcium sulfonate content ranging from about 25 to about 32 wt. %, based upon the total weight of this additive system dispersed in mineral lubricating oil.

As an example of a particularly convenient process for the preparation of the complexes used, an oil-soluble sulfonic acid, such as a synthetically prepared didodecylbenzene sulfonic acid, is mixed with an excess of lime (e.g., 10 equivalents per equivalent of the acid) and a promoter such as methanol, heptylphenol, or mixture thereof, and a solvent such as mineral oil, at 50°C-150°C and the process mass is then carbonated until a homogenous mass is obtained. Complexes of sulfonic acids, carboxylic acids, and mixtures thereof are obtainable by processes such as are described in U.S. Patent No. 3,312,618. Another example is the preparation of a magnesium sulfonate normal magnesium salt thereof, an excess of magnesium oxide, water, and preferably also an alcohol such as methanol.

The carboxylic acids useful for preparing sulfonate carboxylate complexes, and carboxylate complexes, i.e., those obtainable from processes such as the above wherein a mixture of sulfonic acid and carboxylic acid or a carboxylic acid alone is used in lieu of the sulfonic acid, are oil-soluble acids and include primarily fatty acids which have at least about 12 aliphatic carbon atoms and not more than about 24 aliphatic carbon atoms. Examples of these acids include: palmitic, stearic, myristic, oleic, linoleic, dodecanoic, behenic, etc. Cyclic carboxylic acids may also be employed. These include aromatic and cyclo-aliphatic acids. The aromatic acids are those containing a benzenoid structure (i.e., benzene, naphthalene, etc.) and an oil-solubilizing radical or radicals having a total of at least about 15 to 18 carbon atoms, preferably from about 15 to about 200 carbon atoms. Examples of the aromatic acids include: stearyl-benzoic acid, phenyl stearic acid, mono- or polywax-substituted benzoic or naphthoic acids wherein the wax group consists of at least about 18 carbon atoms, cetyl hydroxybenzoic acids, etc. The cycloaliphatic acids contemplated have at least about 12, usually up to about 30 carbon atoms. Examples of such acids are petroleum naphthenic acids, cetyl cyclohexane carboxylic acids, di-lauryl decahydronaphthalene carboxylic acids, di-octyl cyclopentane carboxylic acids, etc. The thiocarboxylic acid analogs of the above acids, wherein one or both of the oxygen atoms of the carboxyl group are replaced by sulfur, are also contemplated.

The ratio of the sulfonic acid to the carboxylic acid in mixtures is at least 1:1 (on a chemical equivalent basis) and is usually less than 5:1, preferably from 1:1 to 2:1.

The terms "basic salt" and "overbased salt" are used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the sulfonic acid radical.

As used in the present specification and claims, the term "complex" refers to basic metal salts which contain metal in an amount in excess of that present in a neutral or normal metal salt. The "base number" of a complex is the number of milligrams of KOH to which one gram of the complex is equivalent as measured by titration. The commonly employed methods for preparing the basic salts involve heating a mineral oil solution of the normal metal salt of the acid with a metal neutralizing agent such as the oxide, hydroxide, carbonate, bicarbonate or sulfide at a temperature above 5°C and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal is known and is preferred for the preparation of such compositions. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkyl phenols, thiophenol, sulfurized alkyl phenols, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octanol, cellosolve, carbitol, ethylene glycol, stearyl alcohol and cyclohexanol; and amines such as aniline, phenylene diamine, phenothiazine, phenol beta-naphthylamine and dodecylamine.

Usually, the basic composition obtained according to the above-described method is treated with carbon dioxide until its base number is less than about 50, as determined by ASTM procedure D2896 (TBN). In many instances, it is advantageous to form the basic product by adding the Ca or Mg base portionwise and carbonating after the addition of each portion. Products with very high metal ratios (10 or above) can be obtained by this method. As used herein, the term "metal ratio" refers to the ratio of total equivalents of alkaline earth metal in the sulfonate complex to equivalents of sulfonic acid anion therein. For example, a normal sulfonate has a metal ratio of 1.0 and a calcium sulfonate complex containing twice as much calcium as the normal salt has a metal ratio of 2.0. The compositions suitable for use as Component A have metal ratios of at least about 1.1, for example, from about 1.1 to about 30, with metal ratios of from about 2 to 20 being preferred.

It is frequently advantageous to react the basic sulfonate with anthranilic acid, by heating the two at about 140-200°C. The amount of anthranilic acid used is generally less than about 1 part (by weight) per 10 parts of sulfonate, preferably 1 part per 40-200 parts of sulfonate. The presence of anthranilic acid improves the oxidation- and corrosion-inhibiting effectiveness of the sulfonate.

Basic alkaline earth metal sulfonates are known in the art and methods for their preparation are described in a number of patents, such as U.S. Patent Nos. 3,027,325; 3,312,618; and 3,350,308. Any of the sulfonates described in these and numerous other patents are suitable for use in the present invention.

The basic Ca and Mg salts are preferably separately prepared and then admixed in the controlled amounts as provided herein. It will be generally convenient to admix such separately prepared detergent inhibitors in the presence of the diluent or solvent used in their preparation.

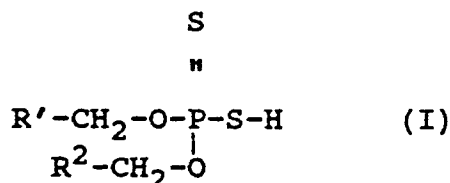
Preferably, the basic Ca detergent inhibitor and basic Mg detergent inhibitor are employed in an amount of from about 0.3 to 1.3 parts, and more preferably from about 0.8 to 1.2 parts, of the Ca detergent inhibitor per part of the Mg detergent inhibitor.

The Component A (that is, the sum of A(1) and (2)) will generally be employed in the fully formulated lubricating oil in a concentration of from about 0.7 to 0.9 wt.%.

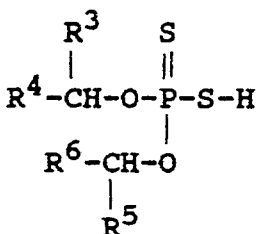
The Component A can also contain other alkaline earth and/or alkali metal detergent inhibitors, (e.g. basic or neutral Na, K and Li sulfonates, and salicylates, and basic or neutral Ba sulfonates, phenates and salicylates). Examples of each mixtures as Component A are mixtures of overbased Ca sulfonate, overbased Mg sulfonate and overbased Na sulfonate detergent inhibitors.

Component B

This component is a mixture of (1) a metal salt of a di(primary hydrocarbyl) dithiophosphoric acid and (2) a metal salt or a di(secondary hydrocarbyl) dithiophosphoric acid. The acids from which B-1 metal salts can be derived can be illustrated by acids of the formula (I)



wherein R' and R² are the same or different and are alkyl, cycloalkyl, aralkyl, alkaryl or substantially hydrocarbon radical of a similar structure. The acids from which B-2 metal salts can be derived can be illustrated by acids of the formula (II):



wherein R³, R⁴, R⁵ and R⁶ are the same or different and are alkyl, cycloalkyl, alkaryl, aralkyl, or a substantially hydrocarbon radical of a similar structure.

By "substantially hydrocarbon" is meant radicals containing substituent groups such as ether, ester, nitro or halogen which do not materially affect the hydrocarbon character of the radical.

Therefore, the acids of formula I can be seen to comprise di-primary-hydrocarbyl substituents wherein each oxygen-bonded carbon is primary, that is, $-\text{CH}_2-\text{O}$. Correspondingly, the acids of formula II can be seen to comprise di-secondary hydrocarbyl substituents wherein each oxygen bonded carbon is secondary, that is, $>\text{CH}-\text{O}$.

Specific examples of suitable R^1 through R^6 radicals include isopropyl, isobutyl, n-butyl, sec-butyl, n=hexyl, heptyl, 2-ethylhexyl, diisobutyl, isooctyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, butylphenyl, o,p-depentyphenyl, octylphenyl, polyisobutene-(molecular weight 350)-substituted phenyl, tetrapropylene-substituted phenyl, beta-octylbutyl naphthyl, cyclopentyl, cyclohexyl, phenyl, chlorophenyl, o-dichlorophenyl, bromophenyl, naphthenyl, 2-methylcyclohexyl, benzyl, chlorobenzyl, chloropentyl, dichlorophenyl, nitrophenyl, dichlorodecyl and xenyl radicals. Alkyl radicals having about 3-30 carbon atoms, and aryl radicals having about 6-30 carbon atoms, are preferred. Particularly preferred R^1 through R^6 radicals are alkyl of 3 to 18 carbons.

The phosphorodithioic acids are readily obtainable by the reaction of phosphorus pentasulfide and an alcohol or phenol. The reaction involves mixing, at a temperature of about 20-200°C, 4 moles of the alcohol or phenol with one mole of phosphorus pentasulfide. Hydrogen sulfide is liberated as the reaction takes place.

The metal salts which are useful in this invention include those salts containing Group I metals, Group II metals, aluminum, lead, tin, molybdenum, manganese, cobalt and nickel. Zinc is the preferred metal. Examples of metal compounds which may be reacted with the acid include lithium oxide, lithium hydroxide, lithium carbonate, lithium pentylate, sodium oxide, sodium hydroxide, sodium carbonate, sodium methylate, sodium propylate, sodium phenoxide, potassium oxide, potassium hydroxide, potassium carbonate, potassium methylate, silver oxide, silver carbonate, magnesium oxide, magnesium hydroxide, magnesium carbonate, magnesium ethylate, magnesium propylate, magnesium phenoxide, calcium oxide, calcium hydroxide, calcium carbonate, calcium methylate, calcium propylate, calcium pentylate, zinc oxide, zinc hydroxide, zinc carbonate, zinc propylate, strontium oxide, strontium hydroxide, cadmium oxide, cadmium hydroxide, cadmium carbonate, cadmium ethylate, barium oxide, barium hydroxide, barium hydrate, barium carbonate, barium ethylate, barium pentylate, aluminum oxide, aluminum propylate, lead oxide, lead hydroxide, lead carbonate, tin oxide, tin butylate, cobalt oxide, cobalt hydroxide, cobalt carbonate, cobalt pentylate, nickel oxide, nickel hydroxide and nickel carbonate.

In some instances, the incorporation of certain ingredients such as small amounts of the metal acetate or acetic acid used in conjunction with the metal reactant will facilitate the reaction and result in an improved product. For example, the use of up to about 5% of zinc acetate in combination with the required amount of zinc oxide facilitates the formation of a zinc phosphorodithioate.

The preparation of metal phosphorodithioates is well known in the art and is described in a large number of issued patents, including U.S. Patents 3,293,181; 3,397,145; 3,396,109; and 3,442,804, the disclosures of which are hereby incorporated by reference insofar as the preparation of metal salts of organic phosphorodithioic acids useful in this invention are described.

The relative amounts of metal salts B-1 and B-2 which are employed are critical to the present invention. Metal salt B-1 (that is, the metal salts of the di-(primary hydrocarbyl) dithiophosphoric acids of formula I) should be used in an amount of from about 0.7 to 3.1, and preferably from about 0.8 to 1.55 parts by weight per part by weight of the metal salt B-2 (that is the metal salts of the di-(secondary hydrocarbyl) dithiophosphoric acids of formula II). The Component B (that is, the sum of B(1) and B(2)) will be generally used in the fully formulated lubricating oil in a concentration of from about 0.7 to 1.2 wt.%, and preferably from about 0.8 to 1.1 wt.%.

The B-1 and B-2 metal salts are preferably made separately and then admixed to form the mixed antiwear component B. Alternatively, a mixture of primary and secondary acids I and II can be charged in the formation of mixed B-1 and B-2 metal salts in situ, to form the Component B having the desired ratio of metal salt B-1 equivalents to metal salt B-2 equivalents.

LUBRICATING COMPOSITIONS

Lubricating oil compositions, e.g., heavy duty oils suitable for gasoline and diesel engines, etc., can be prepared with the additives of the invention. Universal type crankcase oils wherein the same lubricating oil compositions can be used for both gasoline and diesel engine can also be prepared. These lubricating oil formulations conventionally contain several different types of additives that will supply the characteristics that are required in the formulations. Among these types of additives are included viscosity index improvers, antioxidants, corrosion inhibitors, other detergents, ashless dispersants, pour point depressants, other antiwear agents, etc.

In the preparation of lubricating oil formulations it is common practice to introduce the additives in the form of 10 to 80 wt. %, e.g. 20 to 80 wt. % active ingredient concentrates in hydrocarbon oil, e.g. mineral lubricating oil, or other suitable solvent. Usually these concentrates may be diluted with 3 to 100, e.g. 5 to 40 parts by weight of lubricating oil, per part by weight of the additive package, in forming finished lubricants, e.g. crankcase motor oils. The purpose of concentrates, of course, is to make the handling of the various materials less difficult and awkward as well as to facilitate solution or dispersion in the final blend. Thus, a Component A Ca/Mg hydrocarbyl sulfonate mixture or a Ca/Mg alkyl phenate would be usually employed in the form of a 40

to 50 wt. % concentrate, for example, in a lubricating oil fraction.

Components A and B of the present invention will be generally used in admixture with a lube oil basestock, comprising an oil of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof.

Components A and B can be incorporated into a lubricating oil in any convenient way. Thus, these mixtures can be added directly to the oil by dispersing or dissolving the same in the oil at the desired level of concentrations of the detergent inhibitor and antiwear agent, respectively. Such blending into the additional lube oil can occur at room temperature or elevated temperatures. Alternatively, the Components A and B can be blended with a suitable oil-soluble solvent and base oil to form a concentrate, and then blending the concentrate with a lubricating oil basestock to obtain the final formulation. Such concentrates will typically contain (on an active ingredient (A.I.) basis) from about 9 to about 18 wt. %, Component A detergent inhibitor additive, typically from about 10 to 25 wt. %, Component B antiwear agent additive, and typically from about 30 to 90 wt. %, preferably from about 40 to 60 wt. %, base oil, based on the concentrate weight.

The lubricating oil basestock for Components A and B typically is adapted to perform a selected function by the incorporation of additional additives therein to form lubricating oil compositions (i.e., formulations).

Natural oils include animal oils and vegetable oils (e.g., castor, lard oil) liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

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 polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-poly isopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of poly-ethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters and C₁₃ 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, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). 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, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic lubricants; they include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxo) disiloxane, poly(methyl) siloxanes and poly(methylphenyl) siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and rerefined oils can be used in the lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

The novel detergent inhibitor/antiwear agent mixtures of the present invention can be used with V.I improvers to form multi-grade automobile engine lubricating oils. Viscosity modifiers impart high and low temperature operability to the lubricating oil and permit it to remain relatively viscous at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures. Viscosity modifiers are generally high molecular weight hydrocarbon polymers including polyesters. The viscosity modifiers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties. These oil soluble viscosity modifying polymers will generally have number average molecular weights of from 10³ to 10⁶, preferably 10⁴ to 10⁶, e.g., 20,000 to 250,000, as determined by gel permeation chromatography or osmometry.

Examples of suitable hydrocarbon polymers include homopolymers and copolymers of two or more monomers of C₂ to C₃₀, e.g. C₂ to C₈ olefins, including both alpha olefins and internal olefins, which may be straight or branched, aliphatic, aromatic, alkyl-aromatic, cycloaliphatic, etc. Frequently they will be of ethylene with C₃ to C₃₀ olefins, particularly preferred being the copolymers of ethylene and propylene. Other polymers

can be used such as polyisobutylenes, homopolymers and copolymers of C₆ and higher alpha olefins, atactic polypropylene, hydrogenated polymers and copolymers and terpolymers of styrene, e.g. with isoprene and/or butadiene and hydrogenated derivatives thereof. The polymer may be degraded in molecular weight, for example by mastication, extrusion, oxidation or thermal degradation, and it may be oxidized and contain oxygen. Also included are derivatized polymers such as post-grafted interpolymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol, or amine, e.g. an alkylene polyamine or hydroxy amine, e.g. see U.S. Patent Nos. 4,089,794; 4,160,739; 4,137,185; or copolymers of ethylene and propylene reacted or grafted with nitrogen compounds such as shown in U.S. Patent Nos. 4,068,056; 4,068,058; 4,146,489 and 4,149,984.

The preferred hydrocarbon polymers are ethylene copolymers containing from 15 to 90 wt. % ethylene, preferably 30 to 80 wt. % of ethylene and 10 to 85 wt. %, preferably 20 to 70 wt. % of one or more C₃ to C₂₈, preferably C₃ to C₁₈, more preferably C₃ to C₈, alpha-olefins. While not essential, such copolymers preferably have a degree of crystallinity of less than 25 wt. %, as determined by X-ray and differential scanning calorimetry. Copolymers of ethylene and propylene are most preferred. Other alpha-olefins suitable in place of propylene to form the copolymer, or to be used in combination with ethylene and propylene, to form a terpolymer, tetrapolymer, etc., include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, etc.; also branched chain alpha-olefins, such as 4-methyl-1-pentene, 4-methyl-1-hexene, 4-methylpentene-1, 4,4-dimethyl-1-pentene, and 6-methylheptene-1, etc., and mixtures thereof.

Terpolymers, tetrapolymers, etc., of ethylene, said C₃-C₂₈ alpha-olefin, and a non-conjugated diolefin or mixtures of such diolefins may also be used. The amount of the non-conjugated diolefin generally ranges from about 0.5 to 20 mole percent, preferably from about 1 to about 7 mole percent, based on the total amount of ethylene and alpha-olefin present.

The polyester V.I. improvers are generally polymers of esters of ethylenically unsaturated C₃ to C₈ mono- and dicarboxylic acids such as methacrylic and acrylic acids, maleic acid, maleic anhydride, fumaric acid, etc.

Examples of unsaturated esters that may be used include those of aliphatic saturated mono alcohols of at least 1 carbon atom and preferably of from 12 to 20 carbon atoms, such as decyl acrylate, lauryl acrylate, stearyl acrylate, eicosanyl acrylate, docosanyl acrylate, decyl methacrylate, diamyl fumarate, lauryl methacrylate, cetyl methacrylate, stearyl methacrylate, and the like and mixtures thereof.

Other esters include the vinyl alcohol esters of C₂ to C₂₂ fatty or mono carboxylic acids, preferably saturated such as vinyl acetate, vinyl laurate, vinyl palmitate, vinyl stearate, vinyl oleate, and the like and mixtures thereof. Copolymers of vinyl alcohol esters with unsaturated acid esters such as the copolymer of vinyl acetate with dialkyl fumarates, can also be used.

The esters may be copolymerized with still other unsaturated monomers such as olefins, e.g. 0.2 to 5 moles of C₂ - C₂₀ aliphatic or aromatic olefin per mole of unsaturated ester, or per mole of unsaturated acid or anhydride followed by esterification. For example, copolymers of styrene with maleic anhydride esterified with alcohols and amines are known, e.g., see U.S. Patent 3,702,300.

Such ester polymers may be grafted with, or the ester copolymerized with, polymerizable unsaturated nitrogen-containing monomers to impart dispersancy to the V.I. improvers. Examples of suitable unsaturated nitrogen-containing monomers include those containing 4 to 20 carbon atoms such as amino substituted olefins as p-(beta-diethylaminoethyl)styrene; basic nitrogen-containing heterocycles carrying a polymerizable ethylenically unsaturated substituent, e.g. the vinyl pyridines and the vinyl alkyl pyridines such as 2-vinyl-5-ethyl pyridine, 2-methyl-5-vinyl pyridine, 2-vinyl-pyridine, 4-vinyl-pyridine, 3-vinyl-pyridine, 3-methyl-5-vinyl-pyridine, 4-methyl-2-vinyl-pyridine, 4-ethyl-2-vinyl-pyridine and 2-butyl-1-5-vinyl-pyridine and the like.

N-vinyl lactams are also suitable, e.g. N-vinyl pyrrolidones or N-vinyl piperidones.

The vinyl pyrrolidones are preferred and are exemplified by N-vinyl pyrrolidone, N-(1-methylvinyl) pyrrolidone, N-vinyl-5-methyl pyrrolidone, N-vinyl-3, 3-dimethylpyrrolidone, N-vinyl-5-ethyl pyrrolidone, etc.

Ashless dispersants useful in this invention comprise nitrogen or ester containing dispersants selected from the group consisting of oil soluble salts, amides, imides, oxazolines and esters, or mixtures thereof, of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides wherein said long chain hydrocarbon group is a polymer of a C₂ to C₁₀, e.g., C₂ to C₅, monoolefin, said polymer having a number average molecular weight of from about 700 to 5000.

The long chain hydrocarbonyl substituted mono or dicarboxylic acid material, i.e. acid, anhydride, or ester, used in the dispersant includes long chain hydrocarbon, generally a polyolefin, substituted with an average of from about 0.8 to 2.0, preferably from about 1.0 to 1.6, e.g., 1.1 to 1.3 moles, per mole of polyolefin, of an alpha or beta- unsaturated C₄ to C₁₀ dicarboxylic acid, or anhydride or ester thereof. Exemplary of such mono- and dicarboxylic acids, anhydrides and esters thereof are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, dimethyl fumarate, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, etc.

Preferred olefin polymers for reaction with the unsaturated dicarboxylic acids to form the dispersants are polymers comprising a major molar amount of C₂ to C₁₀, e.g. C₂ to C₅ monoolefin. Such olefins include ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene, etc. The polymers can be homopolymers such as polyisobutylene, as well as copolymers of two or more of such olefins such as copolymers of: ethylene and propylene; butylene and isobutylene; propylene and isobutylene; etc. Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is a C₄ to C₁₈ non-conjugated diolefin, e.g., a copolymer of isobutylene and butadiene: or a copolymer of

ethylene, propylene and 1,4-hexadiene; etc.

In some cases, the olefin polymer may be completely saturated, for example an ethylene-propylene copolymer made by a Ziegler-Natta synthesis using hydrogen as a moderator to control molecular weight.

The olefin polymers used in the dispersants will usually have number average molecular weights within the range of about 700 and about 5,000, more usually between about 800 and about 3000. Particularly useful olefin polymers have number average molecular weights within the range of about 900 and about 2500 with approximately one terminal double bond per polymer chain. An especially useful starting material for highly potent dispersant additives is polyisobutylene. The number average molecular weight for such polymers can be determined by several known techniques. A convenient method for such determination is by gel permeation chromatography (GPC) which additionally provides molecular weight distribution information, see W. W. Yau, J.J. Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979.

Processes for reacting the olefin polymer with the C₄₋₁₀ unsaturated dicarboxylic acid, anhydride or ester are known in the art. For example, the olefin polymer and the dicarboxylic acid material may be simply heated together as disclosed in U.S. Patents 3,361,673 and 3,401,118 to cause a thermal "ene" reaction to take place. Or, the olefin polymer can be first halogenated, for example, chlorinated or brominated to about 1 to 8 wt. %, preferably 3 to 7 wt. % chlorine, or bromine, based on the weight of polymer, by passing the chlorine or bromine through the polyolefin at a temperature of 60 to 250°C, e.g. 120 to 160°C, for about 0.5 to 10, preferably 1 to 7 hours. The halogenated polymer may then be reacted with sufficient unsaturated acid or anhydride at 100 to 250°C, usually about 180° to 235°C, for about 0.5 to 10, e.g. 3 to 8 hours, so the product obtained will contain the desired number of moles of the unsaturated acid per mole of the halogenated polymer. Processes of this general type are taught in U.S. Patents 3,087,436; 3,172,892; 3,272,746 and others.

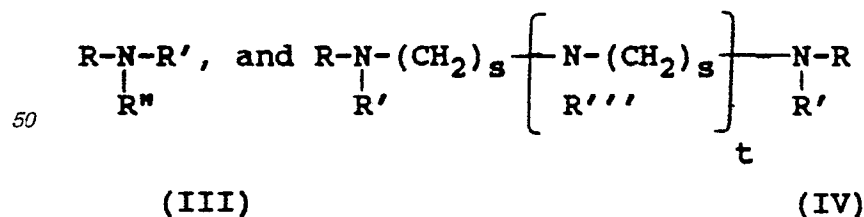
Alternatively, the olefin polymer, and the unsaturated acid material are mixed and heated while adding chlorine to the hot material. Processes of this type are disclosed in U.S. Patents 3,215,707; 3,231,587; 3,912,764; 4,110,349; 4,234,435; and in U.K. 1,440,219.

By the use of halogen, about 65 to 95 wt. % of the polyolefin, e.g. polyisobutylene will normally react with the dicarboxylic acid material. Upon carrying out a thermal reaction without the use of halogen or a catalyst, then usually only about 50 to 75 wt. % of the polyisobutylene will react. Chlorination helps increase the reactivity. For convenience, the aforesaid functionality ratios of dicarboxylic acid producing units to polyolefin, e.g., 0.8 to 2.0, etc. are based upon the total amount of polyolefin, that is, the total of both the reacted and unreacted polyolefin, used to make the product.

The dicarboxylic acid producing materials can also be further reacted with amines, alcohols, including polyols, amino-alcohols, etc., to form other useful dispersant additives. Thus, if the acid producing material is to be further reacted, e.g., neutralized, then generally a major proportion of at least 50 percent of the acid units up to all the acid units will be reacted.

Amine compounds useful as nucleophilic reactants for neutralization of the hydrocarbyl substituted dicarboxylic acid materials include mono- and (preferably) polyamines, most preferably polyalkylene polyamines, of about 2 to 60, preferably 2 to 40 (e.g. 3 to 20), total carbon atoms and about 1 to 12, preferably 3 to 12, and most preferably 3 to 9 nitrogen atoms in the molecule. These amines may be hydrocarbyl amines or may be hydrocarbyl amines including other groups, e.g. hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Hydroxy amines with 1 to 6 hydroxy groups, preferably 1 to 3 hydroxy groups are particularly useful. Preferred amines are aliphatic saturated amines, including those of the general formulas:

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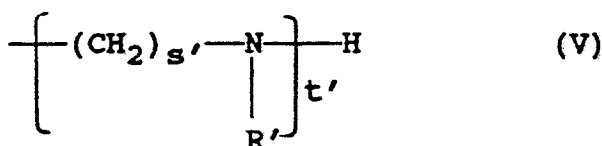


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wherein R, R', R'' and R''' are independently selected from the group consisting of hydrogen; C₁ to C₂₅ straight or branched chain alkyl radicals; C₁ to C₁₂ alkoxy C₂ to C₆ alkylene radicals; C₂ to C₁₂ hydroxy amino alkylene radicals; and C₁ to C₁₂ alkylamino C₂ to C₆ alkylene radicals; and wherein R''' can additionally comprise a moiety of the formula:

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wherein R' is as defined above, and wherein s and s' can be the same or a different number of from 2 to 6, preferably 2 to 4; and t and t' can be the same or different and are numbers of from 0 to 10, preferably 2 to 7, and most preferably about 3 to 7, with the proviso that the sum of t and t' is not greater than 15. To assure a facile reaction, it is preferred that R, R', R'', R''', s, s', t and t' be selected in a manner sufficient to provide the compounds of Formulas III and IV with typically at least one primary or secondary amine group, preferably at least two primary or secondary amine groups. This can be achieved by selecting at least one of said R, R', R'' or R''' groups to be hydrogen or by letting t in Formula IV be at least one when R''' is H or when the V moiety possesses a secondary amino group. The most preferred amine of the above formulas are represented by Formula IV and contain at least two primary amine groups and at least one, and preferably at least three, secondary amine groups.

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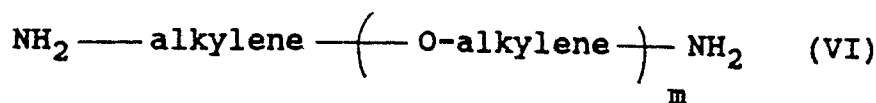
Non-limiting examples of suitable amine compounds include: 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; polypropylene amines such as 1,2-propylene diamine; di-(1,2-propylene) triamine; di-(1,3-propylene) triamine; N,N-dimethyl-1,3-diaminopropane; N,N-di-(2-aminoethyl) ethylene diamine; N,N-di(2-hydroxyethyl)-1,3-propylene diamine; 3-dodecyloxypropylamine; N-dodecyl-1,3-propane diamine; tris hydroxymethylaminomethane (THAM); diisopropanol amine; diethanol amine; triethanol amine; mono-, di-, and tri-tallow amines; amino morpholines such as N-(3-aminopropyl)morpholine; and mixtures thereof.

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Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines, and N-aminoalkyl piperazines of the general formula (Va):

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wherein p₁ and p₂ are the same or different and are each integers of from 1 to 4, and n₁, n₂ and n₃ are the same or different and are each integers of from 1 to 3. Non-limiting examples of such amines include 2-pentadecyl imidazoline; N-(2-aminoethyl) piperazine; etc.

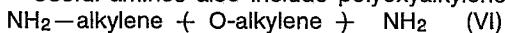
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Commercial mixtures of amine compounds may advantageously be used. For example, one process for preparing alkylene amines involves the reaction of an alkylene dihalide (such as ethylene dichloride or propylene dichloride) with ammonia, which results in a complex mixture of alkylene amines wherein pairs of nitrogens are joined by alkylene groups, forming such compounds as diethylene triamine, triethylenetetramine, tetraethylene pentamine and isomeric piperazines. Low cost poly(ethyleneamines) compounds averaging about 5 to 7 nitrogen atoms per molecule are available commercially under trade names such as "Polyamine H", "Polyamine 400", "Dow Polyamine E-100", etc.

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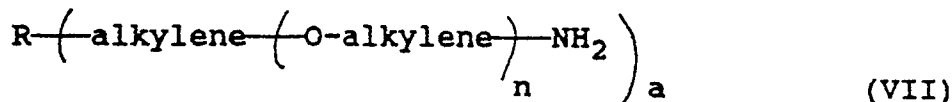
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Useful amines also include polyoxyalkylene polyamines such as those of the formulae:



where m has a value of about 3 to 70 and preferably 10 to 35; and

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where "n" has a value of about 1 to 40 with the provision that the sum of all the n's is from about 3 to about 70 and preferably from about 6 to about 35, and R is a polyvalent saturated hydrocarbon radical of up to ten carbon atoms wherein the number of substituents on the R group is represented by the value of "a", which is a number of from 3 to 6. The alkylene groups in either formula (VI) or (VII) may be straight or branched chains containing about 2 to 7, and preferably about 2 to 4 carbon atoms.

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The polyoxyalkylene polyamines of formulas (VI) or (VII) above, preferably polyoxyalkylene diamines and polyoxyalkylene triamines, may have average molecular weights ranging from about 200 to about 4000 and preferably from about 400 to about 2000. The preferred polyoxyalkylene polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines having average molecular weights ranging from about 200 to 2000. The polyoxyalkylene polyamines are commercially available and may be obtained, for example, from the Jefferson Chemical Company, Inc. under the trade name "Jeffamines D-230, D-400, D-1000, D-2000, T-403", etc.

The amine is readily reacted with the selected dicarboxylic acid material, e.g. alkenyl succinic anhydride, by heating an oil solution containing 5 to 95 wt. % of dicarboxylic acid material to about 100 to 250°C., preferably 125 to 175°C., generally for 1 to 10, e.g. 1 to 6 hours until the desired amount of water is removed. The heating is preferably carried out to favor formation of imides or mixtures of imides and amides, rather than amides and salts. Reaction ratios of dicarboxylic material to equivalents of amine as well as the other nucleophilic reactants described herein can vary considerably, depending on the reactants and type of bonds formed. Generally from 0.1 to 1.0, preferably from about 0.2 to 0.6, e.g., 0.4 to 0.6, moles of dicarboxylic acid moiety content (e.g., grafted maleic anhydride content) is used per equivalent of nucleophilic reactant, e.g., amine. For example, about 0.8 mole of a pentaamine (having two primary amino groups and five equivalents of nitrogen per molecule) is preferably used to convert into a mixture of amides and imides, the product formed by reacting one mole of olefin with sufficient maleic anhydride to add 1.6 moles of succinic anhydride groups per mole of olefin, i.e., preferably the pentaamine is used in an amount sufficient to provide about 0.4 mole (that is, 1.6 divided by (0.8 x 5) mole) of succinic anhydride moiety per nitrogen equivalent of the amine.

The nitrogen containing dispersants can be further treated by boration as generally taught in U.S. Patent Nos. 3,087,936 and 3,254,025 (incorporated herein by reference thereto). This is readily accomplished by treating the selected acyl nitrogen dispersant with a boron compound selected from the class consisting of boron oxide, boron halides, boron acids and esters of boron acids in an amount to provide from about 0.1 atomic proportion of boron for each mole of said acylated nitrogen composition to about 20 atomic proportions of boron for each atomic proportion of nitrogen of said acylated nitrogen composition. Usefully the dispersants of the inventive combination contain from about 0.05 to 2.0 wt. %, e.g. 0.05 to 0.7 wt. % boron based on the total weight of said borated acyl nitrogen compound. The boron, which appears to be in the product as dehydrated boric acid polymers (primarily $(HBO_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts e.g. the metaborate salt of said diimide.

Treating is readily carried out by adding from about 0.05 to 4, e.g. 1 to 3 wt. % (based on the weight of said acyl nitrogen compound) of said boron compound, preferably boric acid which is most usually added as a slurry to said acyl nitrogen compound and heating with stirring at from about 135°C. to 190, e.g. 140-170°C., for from 1 to 5 hours followed by nitrogen stripping at said temperature ranges. Or, the boron treatment can be carried out by adding boric acid to the hot reaction mixture of the dicarboxylic acid material and amine while removing water.

The tris(hydroxymethyl) amino methane (THAM) can be reacted with the aforesaid acid material to form amides, imides or ester type additives as taught by U.K. 984,409, or to form oxazoline compounds and borated oxazoline compounds as described, for example, in U.S. 4,102,798; 4,116,876 and 4,113,639.

The ashless dispersants may also be esters derived from the aforesaid long chain hydrocarbon substituted dicarboxylic acid material and from hydroxy compounds such as monohydric and polyhydric alcohols or aromatic compounds such as phenols and naphthols, etc. The polyhydric alcohols are the most preferred hydroxy compound and preferably contain from 2 to about 10 hydroxy radicals, for example, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, and other alkylene glycols in which the alkylene radical contains from 2 to about 8 carbon atoms. Other useful polyhydric alcohols include glycerol, mono-oleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, dipentaerythritol, and mixtures thereof.

The ester dispersant may also be derived from unsaturated alcohols such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-cyclohexene-3-ol, and oleyl alcohol. Still other classes of the alcohols capable of yielding the esters of this invention comprise the ether-alcohols and amino-alcohols including, for example, the oxy-alkylene, oxy-arylene-, amino-alkylene-, and amino-arylene-substituted alcohols having one or more oxy-alkylene, amino-alkylene or amino-arylene oxy-arylene radicals. They are exemplified by Cellosolve, Carbitol, N,N,N',N'-tetrahydroxy-trimethylene di-amine, and ether-alcohols having up to about 150 oxy-alkylene radicals in which the alkylene radical contains from 1 to about 8 carbon atoms.

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

The ester dispersant may be prepared by one of several known methods as illustrated for example in U.S. Patent 3,381,022. The ester dispersants may also be borated, similar to the nitrogen containing dispersants, as described above.

Hydroxyamines which can be reacted with the aforesaid long chain hydrocarbon substituted dicarboxylic acid materials to form dispersants include 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, p-(beta-hydroxyethyl)-aniline, 2-amino-1-propanol, 3-amino-1-propanol, 2-amino-2-methyl-1, 3-propane-diol, 2-amino-2-ethyl-1, 3-propanediol, N-(beta-hydroxy-propyl)-N'-(beta-amino-ethyl)-piperazine, tris(hydroxymethyl) amino-meth-

ane (also known as trimethylolaminomethane), 2-amino-1-butanol, ethanolamine, beta-(beta-hydroxyethoxy)ethylamine, and the like. Mixtures of these or similar amines can also be employed. The above description of nucleophilic reactants suitable for reaction with the hydrocarbyl substituted dicarboxylic acid or anhydride includes amines, alcohols, and compounds of mixed amine and hydroxy containing reactive functional groups, i.e., amino-alcohols.

A preferred group of ashless dispersants are those derived from polyisobutylene substituted with succinic anhydride groups and reacted with polyethylene amines, e.g. tetraethylene pentamine, pentaethylene hexamine, polyoxyethylene and polyoxypropylene amines, e.g. polyoxypropylene diamine, trimethylolaminomethane and pentaerythritol, and combinations thereof. One particularly preferred dispersant combination involves a combination of (i) polyisobutylene substituted with succinic anhydride groups and reacted with (ii) a hydroxy compound, e.g. pentaerythritol, (iii) a polyoxyalkylene polyamine, e.g. polyoxypropylene diamine, and (iv) a polyalkylene polyamine, e.g. polyethylene diamine and tetraethylene pentamine using about 0.3 to about 2 moles each of (ii) and (iv) and about 0.3 to about 2 moles of (iii) per mole of (i) as described in U.S. Patent 3,804,763. Another preferred dispersant combination involves the combination of (i) polyisobutenyl succinic anhydride with (ii) a polyalkylene polyamine, e.g. tetraethylene pentamine, and (iii) a polyhydric alcohol or polyhydroxy-substituted aliphatic primary amine, e.g. pentaerythritol or trimethylolaminomethane as described in U.S. Patent 3,632,511.

The antioxidants useful in this invention include oil soluble copper compounds. The copper may be blended into the oil as any suitable oil soluble copper compound. By oil soluble we mean the compound is oil soluble under normal blending conditions in the oil or additive package. The copper compound may be in the cuprous or cupric form. The copper may be in the form of the copper dihydrocarbyl thio- or dithio-phosphates wherein copper may be substituted for zinc in the compounds and reactions described above although one mole of cuprous or cupric oxide may be reacted with one or two moles of the dithiophosphoric acid, respectively. Alternatively the copper may be added as the copper salt of a synthetic or natural carboxylic acid. Examples include C₁₀ to C₁₈ fatty acids such as stearic or palmitic, but unsaturated acids such as oleic or branched carboxylic acids such as naphthenic acids of molecular weight from 200 to 500 or synthetic carboxylic acids are preferred because of the improved handling and solubility properties of the resulting copper carboxylates. Also useful are oil soluble copper dithiocarbamates of the general formula (RR'NCSS)_nCu, where n is 1 or 2 and R and R' are the same or different hydrocarbyl radicals containing from 1 to 18 and preferably 2 to 12 carbon atoms and including radicals such as alkyl, alkenyl, aryl, aralkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-heptyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl, etc. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') will generally be about 5 or greater. Copper sulphonates, phenates, and acetylacetonates may also be used.

Exemplary of useful copper compounds are copper (Cu^I and/or Cu^{II}) salts of alkenyl succinic acids or anhydrides. The salts themselves may be basic, neutral or acidic. They may be formed by reacting (a) any of the materials discussed above in the Ashless Dispersant section, which have at least one free carboxylic acid (or anhydride) group with (b) a reactive metal compound. Suitable acid (or anhydride) reactive metal compounds include those such as cupric or cuprous hydroxides, oxides, acetates, borates, and carbonates or basic copper carbonate.

Examples of the metal salts of this invention are Cu salts of polyisobutenyl succinic anhydride (hereinafter referred to as Cu-PIBSA), and Cu salts of polyisobutenyl succinic acid. Preferably, the selected metal employed is its divalent form, e.g., Cu²⁺. The preferred substrates are polyalkenyl succinic acids in which the alkenyl group has a number average molecular weight (\bar{M}_n) greater than about 700. The alkenyl group desirably has a \bar{M}_n from about 900 to 1400, and up to 2500, with a \bar{M}_n of about 950 being most preferred. Especially preferred, of those listed above in the section on Dispersants, is polyisobutylene succinic acid (PIBSA). These materials may desirably be dissolved in a solvent, such as a mineral oil, and heated in the presence of a water solution (or slurry) of the metal bearing material. Heating may take place between 70° and about 200°C. Temperatures of 110° to 140°C are entirely adequate. It may be necessary, depending upon the salt produced, not to allow the reaction to remain at a temperature above about 140°C for an extended period of time, e.g., longer than 5 hours, or decomposition of the salt may occur.

The copper antioxidants (e.g., Cu-PIBSA, Cu-oleate, or mixtures thereof) will be generally employed in an amount of from about 50-500 ppm by weight of the metal, in the final lubricating or fuel composition.

The copper antioxidants used in this invention are inexpensive and are effective at low concentrations and therefore do not add substantially to the cost of the product. The results obtained are frequently better than those obtained with previously used antioxidants, which are expensive and used in higher concentrations. In the amounts employed, the copper compounds do not interfere with the performance of other components of the lubricating composition, in many instances, completely satisfactory results are obtained when the copper compound is the sole antioxidant in addition to the ZDDP. The copper compounds can be utilized to replace part or all of the need for supplementary antioxidants. Thus, for particularly severe conditions it may be desirable to include a supplementary, conventional antioxidant. However, the amounts of supplementary antioxidant required are small, far less than the amount required in the absence of the copper compound.

While any effective amount of the copper antioxidant can be incorporated into the lubricating oil composition, it is contemplated that such effective amounts be sufficient to provide said lube oil composition

with an amount of the copper antioxidant of from about 5 to 500 (more preferably 10 to 200, still more preferably 10 to 180, and most preferably 20 to 130 (e.g., 90 to 120)) part per million of added copper based on the weight of the lubricating oil composition. Of course, the preferred amount may depend amongst other factors on the quality of the basestock lubricating oil.

5 Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition. Illustrative of corrosion inhibitors are phosphosulfurized hydrocarbons and the products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. Phosphosulfurized hydrocarbons are prepared by
10 reacting a suitable hydrocarbon such as a terpene, a heavy petroleum fraction of a C₂ to C₆ olefin polymer such as polyisobutylene, with from 5 to 30 weight percent of a sulfide of phosphorus for 1/2 to 15 hours, at a temperature in the range of 150° to 600°F. Neutralization of the phosphosulfurized hydrocarbon may be effected in the manner taught in U.S. Patent No. 1,969,324.

Oxidation inhibitors reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by
15 viscosity growth. Such oxidation inhibitors include alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, barium t-octylphenyl sulfide, dioctylphenylamine, phenylalphanaphthylamine, phosphosulfurized or sulfurized hydrocarbons, etc.

Friction modifiers serve to impart the proper friction characteristics to lubricating oil compositions such as
20 automatic transmission fluids.

Representative examples of suitable friction modifiers are found in U.S. Patent No. 3,933,659 which discloses fatty acid esters and amides; U.S. Patent No. 4,176,074 which describes molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols; U.S. Patent No. 4,105,571 which discloses glycerol esters of dimerized fatty acids; U.S. Patent No. 3,779,928 which discloses alkane phosphonic acid salts; U.S. Patent
25 No. 3,778,375 which discloses reaction products of a phosphonate with an oleamide; U.S. Patent No. 3,852,205 which discloses S-carboxy-alkylene hydrocarbyl succinimide, S-carboxy-alkylene hydrocarbyl succinamic acid and mixtures thereof; U.S. Patent No. 3,879,306 which discloses N-(hydroxy-alkyl) alkenyl-succinamic acids or succinimides; U.S. Patent No. 3,932,290 which discloses reaction products of di-(lower alkyl) phosphites and epoxides; and U.S. Patent No. 4,028,258 which discloses the alkylene oxide adduct of phosphosulfurized
30 N-(hydroxyalkyl) alkenyl succinimides. The disclosures of the above references are herein incorporated by reference. The most preferred friction modifiers are glycerol mono and dioleates, and succinate esters, or metal salts thereof, of hydrocarbyl substituted succinic acids or anhydrides and thiobis alkanols such as described in U.S. Patent No. 4,344,853.

Pour point depressants lower the temperature at which the fluid will flow or can be poured. Such
35 depressants are well known. Typical of those additives which usefully optimize the low temperature fluidity of the fluid are C₈-C₁₈ dialkylfumarate vinyl acetate copolymers, polymethacrylates, and wax naphthalene.

Foam control can be provided by an antifoamant of the polysiloxane type, e.g. silicone oil and polydimethyl siloxane.

Organic, oil-soluble compounds useful as rust inhibitors in this invention comprise nonionic surfactants
40 such as polyoxyalkylene polyols and esters thereof, and anionic surfactants such as alkyl sulfonic acids. Such anti-rust compounds are known and can be made by conventional means. Nonionic surfactants, useful as anti-rust additives in the oleaginous compositions of this invention, usually owe their surfactant properties to a number of weak stabilizing groups such as ether linkages. Nonionic anti-rust agents containing ether linkages can be made by alkoxyating organic substrates containing active hydrogens with an excess of the lower
45 alkylene oxides (such as ethylene and propylene oxides) until the desired number of alkoxy groups have been placed in the molecule.

The preferred rust inhibitors 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 ethylene oxide and propylene oxide available from Dow Chemical
50 Co.; and Tergitol, dodecylphenyl or monophenyl polyethyleneglycol ethers, and Ucon, polyalkylene glycols and derivatives, both available from Union Carbide Corp. These are but a few of the commercial products suitable as rust inhibitors 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
55 alkyl- or alkenyl-substituted succinic acids wherein the alkyl- or alkenyl group contains up to about twenty carbon atoms.

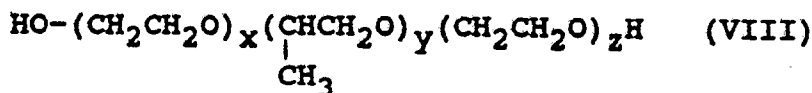
The preferred polyols are prepared as block polymers. Thus, a hydroxy-substituted compound, R-(OH)_n (wherein n is 1 to 6, and R is the residue of a mono- or polyhydric alcohol, phenol, naphthol, etc.) is reacted with propylene oxide to form a hydrophobic base. This base is then reacted with ethylene oxide to provide a
60 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 rust inhibitors suitable for use in any lubricant composition regardless of differences in the base oils and the presence of
65 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.

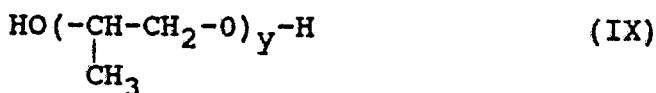
Compounds illustrative of R-(OH)_n include alkylene polyols such as the alkylene glycols, alkylene triols, alkylene tetrols, etc., such as ethylene glycol, propylene glycol, glycerol, pentaerythritol, sorbitol, mannitol, and the like. Aromatic hydroxy compounds such as alkylated mono- and polyhydric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

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

The liquid polyols available from Wyandotte Chemical Co. under the name Pluronic Polyols and other similar polyols are particularly well suited as rust inhibitors. These Pluronic Polyols correspond to the formula:



wherein x, y, and z are integers greater than 1 such that the -CH₂CH₂O- 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



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 (CH₂CH₂O) units are particularly good. Also useful are alkoxyated fatty amines, amides, alcohols and the like, including such alkoxyated fatty acid derivatives treated with C₉ to C₁₆ alkyl-substituted phenols (such as the mono- and di-heptyl, octyl, nonyl, decyl, undecyl, dodecyl and tridecyl phenols), as described in U.S. Patent 3,849,501, which is also hereby incorporated by reference in its entirety.

These compositions of our invention may also contain other additives such as those previously described, and other metal containing additives, for example, those containing barium and sodium.

The lubricating composition of the present invention may also include copper lead bearing corrosion inhibitors. Typically such compounds are the thiadiazole polysulphides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Preferred materials are the derivatives of 1,3,4 thiadiazoles such as those described in U.S. Patents 2,719,125; 2,719,126; and 3,087,932; especially preferred is the compound 2,5 bis (t-octadithio)-1,3,4 thiadiazole commercially available as Amoco 150. Other similar materials also suitable are described in U.S. Patents 3,821,236; 3,904,537; 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882.

Other suitable additives are the thio and polythio sulphenamides of thiadiazoles such as those described in U.K. Patent Specification 1,560,830. When these compounds are included in the lubricating composition, we prefer that they be present in an amount from 0.01 to 10, preferably 0.1 to 5.0 weight percent based on the weight of the composition.

Some of these numerous additives can provide a multiplicity of effects, e.g., a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

Compositions when containing these conventional additives are typically blended into the base oil in amounts effective to provide their normal attendant function. Representative effective amounts of such additives (as the respective active ingredients) in the fully formulated oil are illustrated as follows:

	<u>Compositions</u>	<u>Wt.% A.I.</u> <u>(Preferred)</u>	<u>Wt.% A.I.</u> <u>(Broad)</u>
	Total	0.7-0.9	0.7-0.9
5	Component A(1) + A(2)		
	Detergents		
	Component B	0.8-1.1	0.7-1.2
	Antiwear		
10	Agents		
	Viscosity	0.01-4	0.01-12
	Modifier		
	Corrosion	0.01-1.5	.01-5
	Inhibitor		
15	Oxidation	0.01-1.5	.01-5
	Inhibitor		
	Dispersant	0.1-8	.1-20
	Pour Point	0.01-1.5	.01-5
	Depressant		
20	Anti-Foaming	0.001-0.15	.001-3
	Agents		
	Friction	0.01-1.5	.01-5
	Modifiers		
25	Mineral Oil	Balance	Balance
	Base		

When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the novel detergent inhibitor/antiwear agent mixtures of this invention (in concentrate amounts hereinabove described), together with one or more of said other additives (said concentrate when constituting an additive mixture being referred to herein as an additive-package) whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant. Thus, the detergent inhibitor/antiwear agent mixtures of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of typically from about 2.5 to about 90%, and preferably from about 15 to about 75%, and most preferably from about 25 to about 60% by weight additives in the appropriate proportions with the remainder being base oil.

The final formulations may employ typically about 10 wt. % of the additive-package with the remainder being base oil.

All of said weight percents expressed herein (unless otherwise indicated) are based on active ingredient (A.I.) content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the A.I. weight of each additive plus the weight of total oil or diluent.

This invention will be further understood by reference to the following examples, wherein all parts are parts by weight, unless otherwise noted and which include preferred embodiments of the invention.

EXAMPLES

A series of fully formulated lubricating oils were prepared containing the selected detergent inhibitors, zinc dialkyl dithiophosphate anti-wear agents, ashless dispersants, anti-oxidants and fuel economy additives. The data thereby obtained are summarized in Table I below.

Table I

Components** (Wt. %)	Example No.						
	Compar. A	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Ca Detergent Inhibitor(1)	1.95	0.70	0.70	0.28	0.84	0.70	0.70
Mg Detergent Inhibitor (2)	0	0.66	0.66	1.05	0.79	0.66	0.66
ZDDP - 1* (3)	1.79	0.51	0.77	0.51	0.51	0.51	0.64
ZDDP - 2* (4)	0	0.52	0.26	0.52	0.52	0.77	0.52
Elemental Analysis							
(wt.%)							
Ca(5)	--	0.108	0.108	0.043	0.129	0.108	0.108
Mg(5)	--	0.060	0.060	0.097	0.072	0.061	0.061
P(6)	--	0.082	0.082	0.082	0.082	0.102	0.093
Zn(6)	--	0.091	0.091	0.091	0.091	0.113	0.103
Experimental Results*							
Rocker Pad Demerits(7)	9.7	0.0	11.1	47.2	5.6	22.2	0.0
Rocker Pad Merits(8)	9.0	10.0	8.9	5.3	9.4	7.8	10.0
Camnose Merits(9)	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Cam Wear, mls.	6.0	2.0	1.0	12.0	3.0	3.9	0.8

- NOTES:**
- (1) Overbased calcium sulphonate, 400 TBN, 15.5 wt. % calcium; 55 wt. % A.I.
 - (2) Overbased magnesium sulphonate, 400 TBN, containing 9.2 wt. % magnesium; 52 wt. % A.I.
 - (3) Zinc di(primary alkyl) dithiophosphate concentrate (75 wt. % A.I. in dilute mineral oil) in which the alkyl groups or a mixture of such groups have between 4 and 5 carbon atoms and made by reacting P_2S_5 with a mixture of about 65 wt. % isobutyl alcohol and 35 wt. % amyl alcohol.
 - (4) Zinc di(secondary alkyl)dithiophosphate concentrate (71 wt. % A.I. in dilute mineral oil) in which the alkyl groups or a mixture of such groups having between about 3 and 6 carbon atoms and made by reacting P_2S_5 with a mixture of isopropyl alcohol (30%) and methyl tertiary-butyl carbinol (70%).
 - (5) Wt. % Ca and Mg in formulated lubricating oils derived from Ca detergent inhibitor and Mg detergent inhibitor, respectively.
 - (6) Wt. % total P and Zn in formulated lubricating oil derived from ZDDP-1* and ZDDP-2*.
 - (7) 0 = best; 100 = worst
 - (8) 10 = best; 0 = worst
 - (9) 10 = best; 0 = worst
- * Experimental results obtained in Example 3 are believed to be anomalous.
- ** Added components in each formulated oil (employed at constant volumes in each formulation): (a) Ashless Dispersant (dilute mineral oil solution containing borated polyisobutenyl succinimide derived from polyisobutenyl succinic anhydride having about 1.1 succinic anhydride moieties per polyisobutenyl molecule (derived from polyisobutylene having a number average molecular weight of about 2200); (b) nonyl phenol sulfide antioxidant; (c) copper oleate antioxidant (120 ppm Cu by weight); (d) (Except Example 1) glycerol monooleate fuel economy additive; (e) multifunctional viscosity modifier (based on aminated ethylene-propylene copolymer); and (f) 150N basestock.

The data in Table I show that the improved lubricating formulation of this invention provide decreased cam wear without reduction in camnose merits as compared to the control, and that superior rocker pad demerits results can also be achieved.

EXAMPLE 7; COMPARATIVE B

An additional series of formulations were prepared and employed as lubricating oils in water-cooled, gasoline-fueled test automobiles having engines without thermostats. The data thereby obtained are summarized in Table II below.

It was surprisingly found that the oil of Example 7 provided much lower cylinder wear and lower lifter wear than the oil of Comparative B, even though the oil drain intervals and the test length for the oil of Example 7 was much longer.

<u>Table II</u>		
<u>Components*</u> <u>(wt. %)</u>	<u>Comparative</u> <u>B</u>	<u>Example</u> <u>7</u>
Ca Detergent Inhibitor (1)	0	0.74
Mg Detergent Inhibitor (2)	1.29	0.69
ZDDP-1* (3)	1.19	0.76
ZDDP-2* (4)	0	0.76
<u>Field Test</u> <u>Conditions:</u>		
SAE (5)	40	10W40
API (6)	SE/CC	SF/CC
Drain Interval, km	5,000	10,000
Test Distance, km	50,000	80,000
Test Car	(7)	(7)
<u>Test Results:</u>		
Cylinder wear, mm	(8) 0.026	(9) 0.011
Lifter wear, mm (9)	0.17	0.15

NOTES:

- (1) Overbased calcium sulphonate, 400 TBN, 16 wt. % calcium; 55 wt. % A.I.
 - (2) Overbased magnesium sulphonate, 400 TBN, containing 9.2 wt. % magnesium; 52 wt. % A.I.
 - (3) Zinc di(primary alkyl) dithiophosphate concentrate (75 wt. % A.I. in dilute mineral oil) in which the alkyl groups or a mixture of such groups have between 4 and 5 carbon atoms and made by reacting P_2S_5 with a mixture of about 65 wt. % isobutyl alcohol and 35 wt. % amyl alcohol.
 - (4) Zinc di(secondary alkyl)dithiophosphate concentrate (71 wt. % A.I. in dilute mineral oil) in which the alkyl groups or a mixture of such groups having between about 3 and 6 carbon atoms and made by reacting P_2S_5 with a mixture of isopropyl alcohol (30%) and methyl tertiary-butyl carbinol (70%).
 - (5) Society of Automotive Engineers.
 - (6) American Petroleum Institute.
 - (7) General Motors Caprice, V-6, 4.1 liter, no thermostat on engine cooling water system.
 - (8) 3-car average
 - (9) 2-car average.
- * Added components in each oil included ashless dispersant (polyisobutenyl succinimide); and copper antioxidant (120 wppm Cu) in addition to base oil. The oil of Example 7 was formulated as a multigrade oil and also contained multi- functional viscosity modifier and glycerol monooleate fuel economy additive.

The principles, preferred embodiments, and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes made by those skilled in the art without departing from the spirit of the invention.

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Claims

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1. A lubricating oil composition which comprises an oil of lubricating viscosity as the major component and as the minor component (A) a mixture of (1) at least one calcium overbased sulfonate or phenate detergent inhibitor, and (2) at least one magnesium overbased sulfonate or phenate detergent inhibitor, and (B) a mixture of (1) at least one zinc di-(primary hydrocarbyl) dithiophosphate and (2) at least one zinc di-(secondary hydrocarbyl) dithiophosphate, wherein component (A) comprises from about 0.7 to 0.9 weight percent of the lubricating oil composition, component (B) comprises from about 0.7 to 1.2 weight percent of the lubricating oil composition, and wherein the mixed calcium and magnesium detergent inhibitors are present in a weight:weight ratio of components A(1):A(2) of from 0.3:1 to 1.3:1, and the mixed zinc di(primary hydrocarbyl) dithiophosphate and the zinc di(secondary hydrocarbyl) dithiophosphate antiwear agents are present in a weight:weight ratio of B(1):B(2) of from 0.7:1 to 3.1:1.

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2. The lubricating oil composition according to claim 1 wherein the calcium detergent inhibitor comprises an overbased calcium sulfonate.

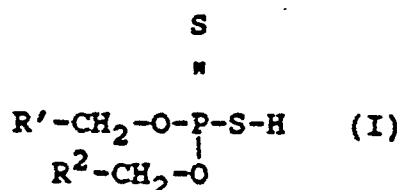
3. The lubricating oil composition according to claim 1 or claim 2, wherein the magnesium detergent inhibitor comprises an overbased magnesium sulfonate.

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4. The lubricating oil composition according to any of claims 1 to 3, wherein the calcium detergent inhibitor and magnesium detergent inhibitor are present in the lubricating oil composition in an amount of from 0.8 to 1.1 parts by weight of the calcium detergent inhibitor per part by weight of the magnesium detergent inhibitor.

5. The lubricating oil composition according to any of claims 1 to 4, wherein the zinc di(primary hydrocarbyl) dithiophosphate is derived from zinc salts of acids of the formula:

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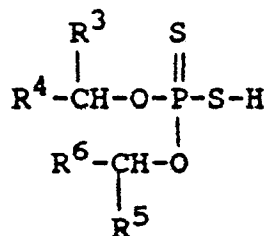
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wherein R' and R² are the same or different and are alkyl, cycloalkyl, aralkyl, alkaryl or substantially hydrocarbon radical of a similar structure.

6. The lubricating oil composition according to any of claims 1 to 5, wherein the zinc di(secondary hydrocarbyl) dithiophosphate is derived from zinc salts of acids of the formula:

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wherein R³, R⁴, R⁵ and R⁶ are the same or different and are alkyl, cycloalkyl, alkaryl, aralkyl, or a substantially hydrocarbon radical of a similar structure.

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7. The lubricating oil composition according to any of claims 1 to 6, wherein the zinc di(primary hydrocarbyl) dithiophosphate and zinc di(secondary hydrocarbyl) dithiophosphate are present in the lubricating oil composition in an amount of from 0.8 to 1.55 parts by weight of the zinc di(primary hydrocarbyl) dithiophosphate per part by weight of the zinc di(secondary hydrocarbyl) dithiophosphate.

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8. A process for forming a lubricating oil composition which comprises:

(a) providing (A) a mixture of (1) at least one calcium overbased sulfonate or phenate detergent inhibitor, and (2) at least one magnesium overbased sulfonate or phenate detergent inhibitor, wherein the mixed calcium and magnesium detergent inhibitors are present in a weight:weight ratio of components A(1):A(2) of from 0.3:1 to 1.3:1;

(b) providing (B) a mixture of (1) at least one zinc di-(primary hydrocarbyl) dithiophosphate and (2) at least one zinc di-(secondary hydrocarbyl) dithiophosphate, wherein the mixed zinc di(primary hydrocarbyl) dithiophosphate and the zinc di(secondary hydrocarbyl) di-thiophosphate antiwear agents are present in a weight:weight ratio of B(1):B(2) of from 0.7:1 to 3.1:1; and

(c) admixing mixture A and B with a major amount of a lubricating oil to provide a lubricating oil composition containing from 0.7 to 0.9 weight percent of mixture A, and from 0.7 to 1.2 weight percent of composition B.

9. A lubricating oil concentrate which comprises from 30 to 90 wt% of an oil of lubricating viscosity; from 9 to 18 wt % of (A) a mixture of (1) at least one calcium overbased sulfonate or phenate detergent inhibitor, and (2) at least one magnesium overbased sulfonate or phenate detergent inhibitor; and from 10 to 25 wt % of (B) a mixture of (1) at least one zinc di-(primary hydrocarbyl) dithiophosphate and (2) at least one zinc di-(secondary hydrocarbyl) dithiophosphate, wherein the mixed calcium and magnesium detergent inhibitors are present in a weight:weight ratio of components A(1):A(2) of from 0.3:1 to 1.3:1, and the mixed zinc di(primary hydrocarbyl) dithiophosphate and the zinc di(secondary hydrocarbyl) dithiophosphate antiwear agents are present in a weight:weight ratio of B(1):B(2) of from 0.7:1 to 3.1:1.

10. The concentrate according to claim 9 wherein the calcium detergent inhibitor and/or the magnesium detergent inhibitor and/or the zinc di(primary hydrocarbyl) dithiophosphate and/or the zinc di(secondary hydrocarbyl) dithiophosphate are as defined in any of claims 2 to 7.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
P,X	EP-A-0 277 729 (AMOCO CORP.) * Page 5, lines 1-39; page 6, lines 35-43; page 8, lines 35-43; page 9, example 1; page 20, table X; claims 1,8,13 * ---	1-10	C 10 M 163/00 // (C 10 M 163/00 C 10 M 137:10 C 10 M 137:10 C 10 M 159:22 C 10 M 159:24) C 10 N 40:00
X	EP-A-0 113 045 (HONDA MOTOR CO., LTD) * Page 2; page 6, line 7 - page 8, line 17; page 12, lines 5-30; page 13, lines 5-7; page 14, examples 4,5 * ---	1-10	
X	EP-A-0 206 748 (CHEVRON RESEARCH CO.) * Page 3, lines 16-32; page 11, line 12 - page 12, line 22; page 14, line 9 - page 15, line 12; page 16, lines 12-26; page 20; claims 13-15 * ---	1-10	
A	US-A-4 483 775 (E.S. YAMAGUCHI) * Column 1, line 50 - column 2, line 30; column 6, lines 44-59; table 1, example E * ---	1,2,5-10	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
D,A	US-A-4 466 895 (C.W. SCHROECK) * Column 3, lines 4-45; examples 1A,1B,3A,3B; column 10, line 62 - column 11, line 14; column 14, table II; examples F,G; claims 1,5,7,20,21 * ---	1-10	C 10 M
A	EP-A-0 225 580 (AMOCO CORP.) * Page 25, lines 1-15, page 28, line 21 - page 29, line 1; page 29, line 26 - page 30, line 17; page 34, line 26 - page 35, line 4; page 35, lines 22-24 * --- -/-	1-10	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21-02-1989	Examiner HILGENGA K.J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	



DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)		
D,A	EP-A-0 024 146 (EXXON RESEARCH & ENGINEERING CO.) * Page 8, line 5 - page 9, line 25; page 22, line 25 - page 23, line 4; page 29, lines 8-13; page 30, line 8 - page 31, example 1 * -----	1-10			
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)		
The present search report has been drawn up for all claims					
Place of search THE HAGUE		Date of completion of the search 21-02-1989	Examiner HILGENGA K.J.		
<table><tr><td>CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</td><td>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</td></tr></table>				CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document	T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document
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