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(54) Lubricants and fluids containing thiocarbamates and phosphonates

(57) Oil based compositions including a compound of the structure $R_1R_2N - C(X)S - (CR_3R_4)_aY$, where R_1, R_2, R_3, and R_4 are hydrogen or hydrocarbyl groups, X is oxygen or sulfur, Y is an activating group such as an ester, and a is 1 or 2; a sulfur-containing phosphonic acid or a salt thereof, and optionally a surfactant, exhibit good anti-wear performance.

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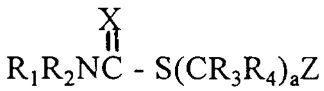
Description

BACKGROUND OF THE INVENTION

The present invention relates to additives and compositions useful as lubricants and functional fluids with good extreme pressure and antiwear properties.

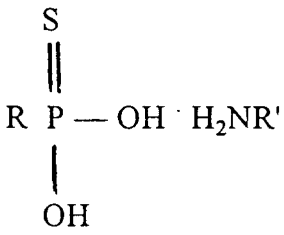
Dithiocarbamate compounds are known and useful as lubricant additives. U.S. Patent 4,758,362, Butke, July 19, 1988, discloses carbamate additives for low phosphorus or phosphorus free lubricating compositions. The additive has the formula



$$R_1R_2N\overset{X}{\overset{\|}{C}} - S(CR_3R_4)_aZ$$

where X is O or S and Z one of several listed groups. These additives are said to impart improved extreme pressure and anti-wear properties to lubricant compositions. The compositions can contain other additives and chemistries.

Likewise, phosphonic acid salts are known as lubricant additives. U.S. Patent 3,185,728, Schallenberg et al., May 25, 1965, discloses amine salts of hydrocarbyl thiophosphonic acids, represented by, e.g., the formula



$$R\ \underset{\underset{OH}{|}}{\overset{\overset{S}{\|}}{P}} - OH \cdot H_2NR'$$

where R is a hydrocarbyl radical and R' is an aliphatic hydrocarbyl radical containing preferably 5-22 carbon atoms. R is usually an olefinic radical containing 12 to 100 carbon atoms. The amines involved in the formation of the salts can be Primene™ 81-R (a mixture of branched chain t-alkylamines said to contain 11-14 carbon atoms). The salts are useful as ashless detergents for lubricating oils and dispersants for fuels.

U.S. Patent 4,804,456, Forester, Feb. 14, 1989, discloses a petrochemical or hydrocarbon to which is added 0.5 to 10,000 ppm of an amine salt of polyalkenylthiophosphonic acid, to control fouling during processing at elevated temperatures. Alkenyl polymers are reacted with P_2S_5 at 100-320°C in the presence of elemental sulfur. The product is then steam hydrolyzed at 100-260°C. The preferred material is polyisobutenylthiophosphonic acid wherein the polyisobutenyl moiety of the acid has a molecular weight of about 1300. Amines/fatty amines may be used to form the amine addition salts.

Moreover, surfactants of various types have found use in lubricating applications. U.S. Patent 4,959,168, Schroeck, September 25, 1990, discloses sulfurized mixtures which include at least one partial fatty acid ester of a polyhydric alcohol and at least one other listed material. The ester can be glycerol monooleate. Other additives can also be present. In one example, a composition is described which includes a C_{11-14} t-alkylamine salt of the reaction product of P_2O_5 with hydroxypropyl O,O-di(4-methyl-2-pentyl) phosphorodithioate and a borated reaction product of an ethylenepolyamine with polyisobutenyl succinic anhydride, a fatty amide, and a sulfurized isobutylene.

SUMMARY OF THE INVENTION

The present invention provides a composition which exhibits good antiwear performance. The invention includes a composition of matter comprising:

(a) an oil of lubricating viscosity;

(b) a compound of the structure

$$R_1R_2N - C(X)S - Q$$

where R_1 and R_2 are independently hydrogen or hydrocarbyl groups; X is an oxygen or sulfur atom; and Q is an alkyl group or an alkyl group containing at least one substituent selected from the group consisting of activating groups, hydrocarbyl groups, hetero groups, or -SC(X)-NR_1R_2 groups, groups R_1, R_2, and Q containing in total at least 4 carbon atoms; and

(c) A sulfur-containing phosphonic acid or a salt thereof.

A preferred embodiment of the composition further comprises (d) a surfactant.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a composition which can serve as a functional fluid such as a power transmission fluid and, in particular, a tractor hydraulic fluid, with improved properties. Specifically, the compositions exhibit improved anti-wear performance, good rust inhibition, good water tolerance, and good oxidation performance. Certain formulations, in particular, are capable of passing the JDQ-95 spiral bevel test, a test standard for tractor hydraulic fluids, established by John Deere & Company Engineering Standards Department, John Deere Rd., Moline, IL 61265. Other applications in which the present composition or equivalents thereof can be advantageously used include crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, including automibile and truck engines, two-cycle engines, aviation piston engines, and marine and railroad diesel engines. They can also be used in gas engines and stationary power engines and turbines. Automatic or manual transmission fluids, transaxle lubricants, gear lubricants, including open and enclosed gear lubricants, tractor lubricants, metal-working lubricants, hydraulic fluids, and other lubricating oil and grease composition can also benefit from the incorporation therein of the compositions of the present invention. They can also be used as wirerope, walking cam, way, rock drill, chain and conveyor belt, worm gear, bearing, and rail and flange lubricants.

The first and major component of this invention is an oil of lubricating viscosity. The oils of lubricating viscosity include natural or synthetic lubricating oils and mixtures thereof. Natural oils include animal oils, mineral lubricating oils, and solvent or acid treated mineral oils. Synthetic lubricating oils include hydrocarbon oils (polyalpha-olefins), halo-substituted hydrocarbon oils, alkylene oxide polymers, esters of dicarboxylic acids and polyols, esters of phosphorus-containing acids, polymeric tetrahydrofurans and silicon-based oils. Preferably, the oil of lubricating viscosity is a hydrotreated mineral oil or a synthetic lubricating oil, such as a polyolefin. Examples of useful oils of lubricating viscosity include XHVI basestocks, such as 100N isomerized wax basestock (0.01% sulfur/ 141 VI), 120N isomerized wax basestock (0.01% sulfur/ 149 VI), 170N isomerized wax basestock (0.01% sulfur/ 142 VI), and 250N isomerized wax basestock (0.01% sulfur/ 146 VI); refined basestocks, such as 250N solvent refined paraffinic mineral oil (0.16% sulfur/89 VI), 200N solvent refined naphthenic mineral oil (0.2% sulfur/ 60 VI), 100N solvent refined/ hydrotreated paraffinic mineral oil (0.01% sulfur/98 VI), 240N solvent refined/ hydrotreated paraffinic mineral oil (0.01% sulfur/ 98 VI), 80N solvent refined/ hydrotreated paraffinic mineral oil (0.08% sulfur/ 127 VI), and 150N solvent refined/ hydrotreated paraffinic mineral oil (0.17% sulfur/ 127 VI). For further description of oils of lubricating viscosity, attention is directed to U.S. Patent 4,582,618 (column 2, line 37 through column 3, line 63, inclusive).

In one embodiment, the oil of lubricating viscosity is a polyalpha-olefin (PAO). Typically, the polyalpha-olefins are derived from monomers having from about 4 to about 30, or from about 4 to about 20, or from about 6 to about 16 carbon atoms. Examples of useful PAOs include those derived from decene. These PAOs may have a viscosity from about 3 to about 150, or from about 4 to about 100, or from about 4 to about 8 cSt at 100°C. Examples of PAOs include 4 cSt polyolefins, 6 cSt polyolefins, 40 cSt polyolefins and 100 cSt polyalphaolefins.

In one embodiment, the lubricating composition contains an oil of lubricating viscosity which has an iodine value of less than about 9, determined according to ASTM D-460. In one embodiment, the oil of lubricating viscosity has a iodine value less than about 8, or less than about 6, or less than about 4.

In one embodiment, the oils of lubricating viscosity are selected to provide lubricating compositions with a kinematic viscosity of at least about 3.5 cSt, or at least about 4.0 cSt at 100°C. In one embodiment, the lubricating compositions have an SAE gear viscosity grade of at least about SAE 75W. The lubricating composition may also have a so-called multigrade rating such as SAE 75W-80, 75W-90, 75W-140, 80W-90, 80W-140, 85W-90, or 85W-140. Multigrade lubricants may include a viscosity improver which is formulated with the oil of lubricating viscosity to provide the above lubricant grades. Useful viscosity improvers include but are not limited to polyolefins, such as ethylene-propylene copolymers, or polybutylene rubbers, including hydrogenated rubbers, such as styrene-butadiene or styrene-isoprene rubbers; or polyacrylates, including polymethacrylates. In one embodiment, the viscosity improver is a polyolefin or polymethacrylate. Viscosity improvers available commercially include Acryloid™ viscosity improvers available from Rohm & Haas; Shellvis™ rubbers available from Shell Chemical; Trilene™ polymers, such as Trilene™ CP-40, available commercially from Uniroyal Chemical Co., and Lubrizol 3100 series and 8400 series polymers, such as Lubrizol® 3174 available from The Lubrizol Corporation.

In one embodiment, the oil of lubricating viscosity includes at least one ester of a dicarboxylic acid. Typically the esters containing from about 4 to about 30, preferably from about 6 to about 24, or from about 7 to about 18 carbon atoms in each ester group. Here, as well as elsewhere, in the specification and claims, the range and ratio limits may be combined. Examples of dicarboxylic acids include glutaric, adipic, pimelic, suberic, azelaic and sebacic. Example of ester groups include hexyl, octyl, decyl, and dodecyl ester groups. The ester groups include linear as well as branched ester groups such as iso arrangements of the ester group. A particularly useful ester of a dicarboxylic acid is diisodecyl azelate. The lubricating oil in the invention will normally comprise the major amount of the composition. Thus it will normally be at least 50% by weight of the composition, preferably about 83 to about 98%, and most preferably about 88 to about 96%. As an alternative embodiment, however, the present invention can provide an additive concentrate in which the oil can be 0 to about 20% by weight, preferably about 1 to about 10%, and the other components, described in greater detail below, are proportionately increased.

The second component (b) of the present composition is a compound of the structure R_1R_2N - C(X)S - Q where R_1 and R_2 are independently hydrogen or hyrdrocarbyl groups; X is an oxygen or sulfur atom; and Q is an alkyl group or an alkyl group containing at least one substituent selected from the group consisting of hydrocarbyl groups, hetero groups (that is, a group attached through a heteroatom such as O, N, or S), additional -SC(X)-NR_1R_2 groups, or, preferably, activating groups. Groups R_1, R_2, and Q should contain in total at least 4, preferably at least 6, and more preferably at least 8 carbon atoms. In a preferred embodiment, Q is $(CR_3R_4)_aY$, wherein R_3 and R_4 are independently hydrogen or hydrocarbyl groups, a is 1 or 2, and Y is the hydrocarbyl group, hetero group, -SC(X)-NR_1R_2 group, or activating group.

As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

(1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical);

(2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

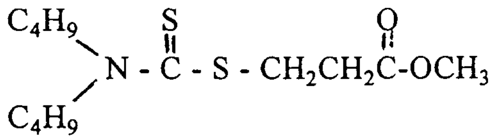
(3) heteroatom-containing substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

When a in the above formula is 2, Y is preferably an activating group. In describing Y as an "activating group," what is meant is a group which will activate an olefin to which it is attached toward nucleophilic addition by, e.g., CS_2 or COS derived intermediates. (This is reflective of the method by which the material of this component is normally prepared, by reaction of an activated olefin with CS_2 and an amine.) The activating group Y can be, for instance, an ester group, typically but not necessarily a carboxylic ester group of the structure -$COOR_5$. It can also be an ester group based on a non-carbon acid, such as a sulfonic or sulfinic ester or a phosphonic or phosphinic ester. The activating group can also be any of the acids or salts corresponding to the aforementioned esters. Y can also be an amide group, that is, based on the condensation of an acid group, preferably a carboxylic acid group, with an amine. In that case the -$(CR_3R_4)_aY$ group could be suitably derived from acrylamide. Y can also be an ether group, -OR_5; a carbonyl group, that is, an aldehyde or a ketone group; a cyano group, -CN, or an aryl group. In a preferred embodiment Y is an ester group of the structure, -$COOR_5$, where R_5 is a hydrocarbyl group. R_5 can preferably comprise 1 to 18 carbon atoms, preferably 1 to 6 carbon atoms. Most preferably R_5 is methyl so that the activating group is -$COOCH_3$. R_5 can be a hydrocarbyl group derived from a mono- or a polyalcohol; in the latter instance, the polyfunctional R_5 alcohol can be reacted with a plurality of R_1R_2N-C(X)S-$(CR_3R_4)_a$COO- groups.

When a is 1, Y need not be an activating group, because the molecule is generally prepared by methods, described below, which do not involve nucleophilic addition to an activated double bond.

Groups R_3 and R_4 are preferably independently hydrogen or methyl or ethyl groups. When a is 2, at least one of R_3 and R_4 is normally hydrogen so that this component will be R_1R_2N-C(S)S-$CR_3R_4CR_3HCOOR_5$. Preferably most or all of the R_3 and R_4 groups are hydrogen so that this component of the composition will be R_1R_2N-C(S)S-$CH_2CH(CH_3)COOCH_3$ or preferably R_1R_2N-C(S)S-$CH_2CH_2COOCH_3$. (These materials can be seen as derivable from methyl methacrylate and methyl acrylate, respectively.) These and other materials containing appropriate activating groups are disclosed in greater detail in PCT publication WO87/05622, equivalent to U.S. Patent 4,758,362.

The substituents R_1 and R_2 on the nitrogen atom are likewise hydrogen or hydrocarbyl groups, but at least one should preferably be a hydrocarbyl group. It is generally believed that at least one such hydrocarbyl group is desired in order to provide suitable oil-solubility to the molecule. However, R_1 and R_2 can both be hydrogen, provided the other groups in the molecule provide sufficient oil solubility. In practice this means that one of the groups R_3 or R_4 could be a hydrocarbyl group of at least 4 carbon atoms. R_1 or R_2 are preferably alkyl groups of 1-18 carbon atoms, preferably alkyl groups of 1-8 carbon atoms. In a particularly preferred embodiment, both R_1 and R_2 are butyl groups. Thus a particularly preferred embodiment of this component of the composition has the formula



(I)

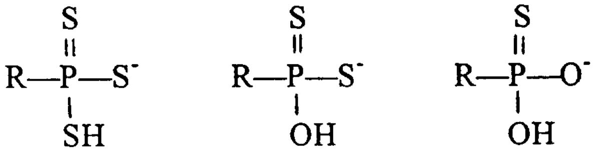
Materials of this type can be prepared by a process more fully described in PCT publication WO87/05622. The materials are derived from an amine such as those described in detail below, carbon disulfide or carbonyl sulfide, or source materials for these reactants, and a reactant containing an activated, ethylenically-unsaturated bond or derivatives thereof. These reactants are charged to a reactor and stirred, generally without heating, since the reaction is normally exothermic. Once the reaction reaches the temperature of the exotherm (typically 40-65°C), the reaction mixture is held at temperature to insure complete reaction. After a reaction time of typically 3-5 hours, the volatile materials are removed under reduced pressure and the residue is filtered to yield the final product.

The relative amounts of the reactants used to prepare the compounds of this component are not particularly critical. The charge ratios to the reactor can vary where economics and the amount of the product desired are controlling factors. Thus, the charge ratio of the amine to the CS_2 or COS reactant to the ethylenically unsaturated reactant may vary in the ranges 5:1:1 to 1:5:1 to 1:1:5. As a preferred embodiment, the charge ratios of these reactants will be 1:1:1.

In the case where a is 1, the activating group Y is separated from the sulfur atom by a methylene group. Materials of this type can be prepared by reaction of sodium dithiocarbamate with a chlorine substituted material. Such materials are described in greater detail in U.S. Patent 2,897,152.

It is preferred that the amount of component (b) in the composition of the present invention will be 0.1 to 10 percent by weight; more preferably 0.5 to 5% by weight. The amount of this component will be proportionately increased if the composition takes the form of a concentrate.

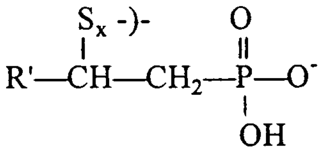
The third major component (c) of the composition of the present invention is a salt of a sulfur-containing phosphonic acid. The sulfur-containing phosphonic acid can be a monothio- or di- or tri-thiophosphonic acid, in which the sulfur replaces one or more of the oxygen atoms in the phosphonic acid group, e.g.,



$$R-\underset{\underset{SH}{|}}{\overset{\overset{S}{\|}}{P}}-S^- \qquad R-\underset{\underset{OH}{|}}{\overset{\overset{S}{\|}}{P}}-S^- \qquad R-\underset{\underset{OH}{|}}{\overset{\overset{S}{\|}}{P}}-O^- \qquad \text{(II)}$$

and isomers thereof.

Alternatively, and preferably, the sulfur can be contained elsewhere in the phosphonic acid molecule, for instance, principally within or associated with the R group, i.e. the hydrocarbyl group. In this preferred embodiment materials of the structure (II) will not be present in readily detectable amounts, although small amounts may nevertheless be present. The sulfur-containing materials may be speculated to have substantially the structure of a sulfurized and possibly crosslinked olefin, such as



$$\mathrm{R'-\overset{\overset{S_x\text{ -)-}}{|}}{C}H-CH_2-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O^-} \qquad \text{(III)}$$

where the bond emanating from the sulfur atom indicates the possibility of any of a number of structures, including mercapto groups, thioalkoxy groups, or bridging groups. The x indicates that there may be a single sulfur atom or a chain of two or more sulfur atoms.

In the above structures R or R' indicates a hydrocarbyl group, preferably an alkyl group containing, for R, 8 to 24 carbon atoms, more preferably 16 to 18 carbon atoms, although materials with longer hydrocarbyl chains can be used. Thus polymeric chains, such as polyalkenes prepared from olefins of 2-30 carbon atoms, for instance, polyisobutylene, with number average molecular weight of 900 or 1000 to 2000, are also permitted. (R', in the structure written, would in each case contain 2 fewer carbon atoms than R.) It is to be understood that an alkyl group containing 16-18 carbon atoms generally means a mixture of alkyl groups, the average chain length being 16-18. Most often this will comprise a mixture of C_{16} and C_{18} alkyl groups, although minor amounts of shorter and longer-chain alkyl groups can also be present.

Component (c) is a salt, which indicates that a positively charged ion is associated with the above anions. This can be a metal ion, derived from the neutralization of the phosphonic acid with a metal-containing base. However, since the composition is in one embodiment a largely ashless or metal-free composition, it is preferred that the positively charged ion is an ion derived from an organic base such as an amine. Suitable amines include monoamines and polyamines. The amines can be aliphatic, cycloaliphatic, aromatic, or heterocyclic, including mixtures thereof, and can be saturated or unsaturated. The amines can also generally contain non-hydrocarbon substituents or groups. Such non-hydrocarbon substituents or groups include lower alkoxy, lower alkylmercapto, nitro, interrupting groups such as -O- and -S- (e.g., as in such groups as $-CH_2CH_2-X-CH_2CH_2-$ where X is -O- or -S-). In general, the amines can be characterized by the formula $NR^7R^8R^9$ wherein R^7, R^8, and R^9 are each independently hydrogen or hydrocarbon, amino-substituted hydrocarbon, hydroxy-substituted hydrocarbon, alkoxy-substituted hydrocarbon, amino, carbamyl, thiocarbamyl, guanyl, or acylimidoyl groups, provided that not all of R^7, R^8, and R^9 are hydrogen. In a preferred embodiment R^7 is an aliphatic hydrocarbyl group having 6-22 carbon atoms, while R^8 and R^9 are each independently hydrogen or C_{1-4} aliphatic hydrocarbyl groups, where hydrocarbyl is defined as above.

With the exception of the branched polyalkylenepolyamines, the polyoxy-alkylenepolyamines, and the high molecular weight hydrocarbyl-substituted amines described more fully hereafter, the amines ordinarily contain less than about 40 carbon atoms in total and usually not more than about 20 carbon atoms in total.

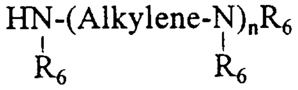
Aliphatic monoamines include mono-aliphatic, di-aliphatic, and tri-aliphatic substituted amines wherein the aliphatic group can be saturated or unsaturated and straight or branched chain. Thus, they are primary, secondary, or tertiary aliphatic amines. Specific examples of such monoamines include ethylamine, diethylamine, triethylamine, n-butylamine, di-n-butylamine, tri-n-butylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyllaurylamine, oleylamine, N-methyl-octylamine, dodecylamine, and octadecylamine.

Cycloaliphatic monoamines are those monoamines wherein there is one cycloaliphatic substituent attached directly to the amino nitrogen. Examples of cycloaliphatic monoamines include cyclohexylamines, cyclopentylamines, cyclohexenylamines, cyclopentenylamines, N-ethyl-cyclohexylarnine, dicyclohexylamines, and the like. Heterocyclic monoamines are monoamines in which the amine nitrogen forms a part of the cyclic ring structure. Examples include piperidine, pyrrolidine, and morpholine.

Aromatic amines include those monoamines wherein a carbon atom of the aromatic ring structure is attached directly to the amino nitrogen. The aromatic ring will usually be a mononuclear aromatic ring (i.e., one derived from benzene) but can include fused aromatic rings, especially those derived from naphthalene. Examples of aromatic monoamines include aniline, di-(paramethylphenyl)amine, naphthylamine, and N,N-di(butyl)aniline. Examples of aliphatic-substituted, cycloaliphatic-substituted, and heterocyclic-substituted aromatic monoamines are para-ethoxyaniline, para-dodecylaniline, cyclohexyl-substituted naphthylamine, and thienyl-substituted aniline.

The amine which forms the salt in the present invention can also be a polyamine. The polyamine can be aliphatic, cycloaliphatic, heterocyclic or aromatic. Examples of the polyamines include alkylenepolyamines, hydroxy-containing polyamines, arylpolyamines, and heterocyclic polyamines.

Alkylene polyamines are represented by the formula



$$\underset{\displaystyle R_6}{\mathrm{HN}}\text{-(Alkylene-}\underset{\displaystyle R_6}{\mathrm{N}})_n R_6 \qquad \text{(IV)}$$

wherein n has an average value from 1 or 2 to 10, 7, or 5, and the "Alkylene" group has from 1 or 2 to 10, 6, or 4 carbon atoms. Each R_6 is independently hydrogen, or an aliphatic or hydroxy-substituted aliphatic group of up to 30 carbon atoms.

Such alkylenepolyamines include methylenepolyamines, ethylenepolyamines, propylenepolyamines, butylenepolyamines, and pentylenepolyamines. The higher homologues and related heterocyclic amines such as piperazines and N-aminoalkyl-substituted piperazines are also included. Specific examples of such polyamines are ethylenediamine, diethylenetriamine (DETA), triethylenetetramine (TETA), tris-(2-aminoethyl)amine, propylenediamine, trimethylenediamine, tripropylenetetramine, tetraethylenepentamine, hexaethyleneheptamine, and pentaethylenehexamine.

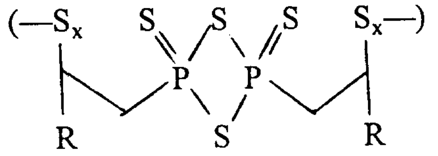
Higher homologues obtained by condensing two or more of the above-noted alkylene amines are similarly useful as are mixtures of two or more of the aforedescribed polyamines.

Ethylenepolyamines are described in detail under the heading Ethylene Amines in Kirk Othmer's "Encyclopedia of Chemical Technology," 2d Edition, Vol. 7, pages 22-37, Interscience Publishers, New York (1965). Ethylenepolyamine mixtures are also useful. Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures to leave as residue what is often termed "polyamine bottoms."

A highly preferred class of amines in the present application is the alkyl primary amine, preferably branched primary amines, such as in particular C_{8-18} tertiary alkyl primary amines. Preferably the alkyl group contains 11-14 or 12-14 carbon atoms. One such material is sold under the trade name Primene™ 81R, available from Rohm and Haas Company, which is believed to be a mixture of C_{12-14} tertiary alkyl primary amines. Other related materials include Primene™ JMT, which is a mixture of C_{18-22} tertiary alkyl primary amines. Tertiary aliphatic primary amines and methods for their preparation are known in the art and are described in U.S. Patent 2,945,749.

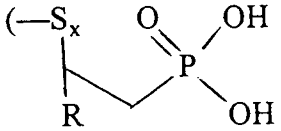
The materials comprising component (c) of the present invention can be prepared by reacting an olefinic material with phosphorus pentasulfide followed by treatment with water (or, conveniently, steam) and reaction of the product with a basic material such as an amine, to form the salt. Olefins or olefinic materials are well-known substances, which include ethylene and other olefins having 3 to 40, preferably 4 to 24, carbon atoms. The olefins are preferably alpha-olefins (sometimes referred to as mono-1-olefins or terminal olefins) or isomerized alpha-olefins. Examples of alpha-olefins include 1-octene, 1-nonene, 1-decene, 1-ridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, and 1-tetracosene. Commercially available alpha-olefin fractions that can be used include the C_{15-18} alpha-olefins, C_{12-16} alpha-olefins, C_{14-16} alpha-olefins, C_{14-18} alpha olefins, C_{16-18} alpha-olefins, C_{16-20} alpha-olefins, C_{18-24} alpha olefins, and C_{22-28} alpha-olefins. Olefins can also be polyolefins including diolefins such as 1,3-butadiene and isoprene.

For purposes of illustration, a mixture of C_{16-18} olefins (1000 parts by weight, 4.26 equivalents) can be heated to 145 to 170°C, preferably 150-160°C. Phosphorus pentasulfide, P_2S_5 (472.3 parts, 4.26 equivalents) is added in increments over a period of 1.5 to 4.5 hours, preferably about 3 hours. The resulting mixture is further heated to 150-180°C, preferably 160-170°C, and maintained at temperature for an additional 3 to 12 hours, preferably 3-5 hours. The reaction product is purified by filtration through a filter aid (FAX-5™) while the mixture is still warm (130 - 155°C, preferably 140-150°C). Without intending to be bound by the following interpretation, the resulting sulfur- and phosphorus-containing intermediate is speculated to have a variety of structures which can be approximately designated by:



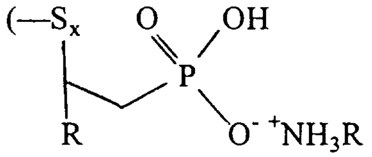
(V)

where, as above, the bonds emanating from the sulfur atoms represent a variety of possible structures such as mercapto groups, thioalkoxy groups, or bridging groups, and the x indicates that there may be a single sulfur atom or a chain of two or more sulfur atoms. Component (V) is optionally mixed with diluent oil (30%), then heated to 170-190°C and hydrolyzed by treatment with steam. The steam treatment is continued for 6 to 12 hours, until the acid neutralization number to bromophenol blue indicator (NNA_{bpb}) is about 100. The structure of the hydrolyzed material is not precisely known but is speculated to be a mixture of materials having a general structure which can be designated as



(VI)

Intermediate (VI) is purged with nitrogen at temperature for about 1 hour, then cooled to 110-120°C, at which time a suitable amine (such as Primene™ 81R, 893 parts, 4.68 equivalents) is added dropwise over a period of 1-4 hours. The mixture is thereafter maintained at 110-160°C, preferably 130-140°C for a suitable time, e.g. an additional 1-6 hours (preferably about 3 hours) to permit complete reaction. The product is isolated by filtration through Fax-5™ filter aid while hot, yielding a product speculated to comprise at least in part materials having structures which can be designated by



(VII)

and other isomers and related structures. Structures which retain phosphorus-sulfur bonds may also be present.

Example A.

A 5L, 4-necked flask equipped with stirrer, thermowell, solids addition funnel, and water-cooled condenser with exit to two 50% aqueous sodium hydroxide traps and a NaOCl final trap with aspirator vacuum source is charged with 1848 g (7.86 moles) of a C_{16-18} alpha olefin mixture. The olefin mixture is heated to 155°C, after which time P_2S_5 (888 g, 4.0 moles) is added in increments over about 1 hour. The mixture exhibits a mild exotherm to 175°C. The mixture is stirred at 170°C for four hours, then filtered at 100°C through FAX-5™.

The above isolated product, 1059 g (1.6 moles) is returned to a similar flask to which is added 450 g of SSO-99 diluent oil. The material is heated to 190-200°C and steam is added via a subsurface tube for a period of 6-8 hours. The material is analyzed by NNA_{bpb} and found to have a value of 99, indicating substantially complete reaction. The material is stirred for an additional 1 hour at 190°C to remove residual water. The material is then cooled to 100°C and decanted.

A 2L, 4-necked flask equipped with a stirrer, addition funnel, nitrogen purge, and water-cooled condenser is charged with 600 g (1.06 moles) of the above steam-blown intermediate. The material is heated to 85°C and 201.4 g (1.06 moles) of Primene™ 81R is added dropwise through an addition funnel over a period of about 1 hour. A mild exotherm is noted (to 105°C). An additional 20 g of Primene™ 81R is added at 100 - 135°C followed by stirring for 1 hour. The product is isolated by filtration.

Example B.

A 12L, 4-necked flask equipped with a stirrer, thermowell, two Claisen adapters, a powder addition funnel, and two vents attached to two 50% aqueous sodium hydroxide traps and a NaOCl final trap is charged with 2745 g (11.7 moles) C_{16-18} α-olefins. The material is heated to 155°C, whereupon 1296.5 g P_2S_5 (11.7 equivalents) is added in 40 g increments over a 1.5 hour period. An exotherm to 165°C is controlled by rate of addition of the P_2S_5. After complete addition, the mixture is stirred for 2.5 hours at 170°C, whereupon 1742 g diluent oil is added in one portion. Stirring of the mixture is continued at 170°C for 1 hour, and thereafter allowed to cool overnight. The mixture is heated to 180°C and steam is slowly blown into the mixture over a 4.5 hour period at which time the material is analyzed to have a NNA_{bpb} of about 100, indicating complete reaction. The material is cooled under a nitrogen purge to 135°C. Primene™ 81R, 2009 g (10.57 equivalents) is added via an addition funnel over a 1.5 hour period, followed by stirring for 0.5 hours. The mixture is vacuum stripped at 135°C at 4 kPa (30 mm Hg) to remove traces of water, then filtered through a filter aid to yield the product.

Example C.

The steam blown intermediate from Example A, 1455 g, is reacted with an equimolar amount of oleylamine by adding the oleylamine dropwise at 100°C over a period of about 3-4 hour, followed by heating with stirring at 145°C for 4-5 hours. A few drops of an antifoam agent are included in the mixture.

Example D.

The steam blown intermediate from Example A, 293g, is reacted with an equimolar amount of succinimide dispersant (1500 g, including 43% diluent oil) by adding the steam blown product in one portion to the succinimide dispersant. The succinimide dispersant is the reaction product of polyisobutylene substituted succinic anhydride (polyisobutylene number average molecular weight about 1000) with polyethyleneamines (comprising about 20% diethylenetriamine and 80% amine bottoms), the product containing about 1.5% nitrogen and a carbonyl:nitrogen ratio of about 1:1.1. The mixture is heated to 100°C for 3 hours and 130°C for 2 hours.

Example E.

The steam blown intermediate from Example A, 500 g, is reacted with 20.4 g of tetraethylenepentamine (TEPA), by heating the intermediate to 100°C and adding the TEPA dropwise over 1/2 hour, followed by stirring for 2 hours and heating to 140°C, and filtration through a filter aid.

Example F.

The steam-blown intermediate from Example A, 800 g, is reacted with 1179 g of a succinimide dispersant similar to that of Example D (containing 60% chemical and 40% diluent oil; having a carbonyl:nitrogen ratio of 1:2 and 2.5% nitrogen in the composition), by a route comparable to that of Example E.

Example G.

Example A is substantially repeated except in place of the C_{16-18} olefins a polypropylene containing residual unsaturation (equivalent weight 386) 1500 g is reacted with 431 g P_2S_5. The initial reaction temperature is 150-200°C; reaction time is 1.5 hours (at 200°C), followed by heating and stirring at 220-250°C over 5 hours. The isolated intermediate is treated with steam, as in Example A, for 6 hours. The resulting material is reacted with mixed tertiary alkyl (C_{11-14}) aliphatic primary amine to form the salt. The final product contains about 25% diluent oil.

Example H.

Example A is substantially repeated using polyisobutylene having residual unsaturation, equivalent weight 1000. The polyisobutylene, 3000 g, is reacted with 333 g P_2S_5. The resulting mixture has a milky appearence which clarifies upon heating to 260°C. The isolated intermediate is treated with steam for 9 hours, isolated, and reacted with the amine of Example G.

Example I.

A portion of steam-treated intermediate prepared as in Example H, 504 g, is reacted with 7.2 g tetraethylenepentamine, using essentially the procedure of Example E.

Example J.

A sample of steam-treated polyisobutylene-P_2S_5 product, 625 g, is placed with 200 g toluene in a 2 L flask equipped with a stirrer, a cold water condenser, caustic traps, a powder funnel, and a nitrogen inlet. To this mixture is added 14.6 g zinc oxide, at room temperature. The mixture is heated slowly to 135°C (under a nitrogen flow) and maintained at temperature for 2.5 hours, collecting water and toluene. After cooling to room temperature, 10 mL water, 100 mL acetic acid, and 1 mL toluene are added ad the mixture heated at reflux at 95° for 2 hours. The product is vacuum stripped (135°C, 20 mm Hg, 1/2 hour), then filtered using filter aid. The filtrate is the product.

Example K.

Example J is substantially repeated except that in place of the zinc oxide 30 g 50% aqueous sodium hydroxide is added. The mixture is reacted at 125°C for 1 hour (collecting water) and thereafter 145°C for 1 hour (collecting toluene). An intermediate is isolated by vacuum stripping; to this intermediate is added an additional 5 g 50% sodium hydroxide, followed by treatment at 145°C for 1 hour, vacuum stripping at 145°C for 1/2 hour, and isolation of the product.

It is preferred that the amount of component (c) in the composition of the present invention will be 0.05 to 8 percent by weight; more preferably 0.1 to 3 percent by weight. The amount of this component will be proportionately increased if the composition takes the form of a concentrate.

A fourth component of the composition of the present invention, which is a preferred component, is (d) a surfactant. Surfactants (sometimes more narrowly referred to as dispersants) are well-known materials, which can be generally classified as anionic, cationic, zwitterionic, or non-ionic. Anionic surfactants include substances containing a long lipophilic tail bonded to a water-soluble (hydrophilic) group, wherein the hydrophilic group contains an anionic moiety derived from a carboxylic acid, sulfonic acid, or phenol, by neutralizing with an alkali metal or an amine. The lipophilic tail is preferably an alkyl group, typically having about 8 to about 21 carbon atoms.

Typical anionic surfactants include carboxylic acid salts such as fatty acid salts having the formula R_1COOZ wherein R_1 is a straight chain, saturated or unsaturated, hydrocarbon radical of about 8 to about 21 carbon atoms and Z is a base-forming radical such as Li^+, Na^+, K^+, or NH_4^+ which makes the detergent-like surfactant soluble in water or increases its affinity to water. Alternatively Z may be a divalent or polyvalent metal, in which case the appropriate number of acid groups are normally present in order to provide the neutral salt. Multivalent metal ions can be derived from metals including Mg, Ca, Sr, Ba, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn, Pb, and others. Typical fatty acid salts include sodium stearate, sodium palmitate, ammonium oleate, and triethanolammonium palmitate. Additional carboxylic acid salts useful as anionic surfactants include salts, and especially sodium and potassium salts, of coconut oil fatty acids and tall oil acids as well as other carboxylic acids salt compounds including amine salts such as triethanolamine salts, acylated polypeptides, and salts of N-lauryl sarcosine such as N-dodecanoyl-N-methylglycine sodium salt.

Other anionic surfactants include aryl and alkaryl sulfonates such as linear and branched alkylbenzene sulfonates, sodium tetrapropylene benzene sulfonate, sodium dodecylbenzene sulfonate, toluene-, xylene-, and cumene sulfonates, lignin sulfonates, petroleum sulfonates, paraffin sulfonates, secondary n-alkanesulfonates, α-olefin sulfonates, alkylnaphthalene sulfonates, N-acyl-N-alkyltaurates, sulfosuccinate esters, isethionates, alkyl sulfates having the formula R_1OSO_3Z wherein R_1 and Z are defined above, such as lithium dodecyl sulfate, sodium dodecyl sulfate, potassium dodecyl sulfate, and sodium tetradecyl sulfate, alkyl sulfonates having the formula R_1SO_3Z wherein R_1 and Z are as defined above, such as sodium lauryl sulfonate, sulfated and sulfonated amides and amines, sulfated and sulfonated esters such as lauric monoglyceride sodium sulfate, sodium sulfoethyl oleate, and sodium lauryl sulfoacetate, sulfuric acid ester salts such as sulfated linear primary alcohols, sulfated polyoxyethylenated straight chain alcohols and sulfated triglyceride oils, phosphoric and polyphosphoric acid esters, perfluorinated carboxylic acids, and polymeric anionic surfactants such as alginic acids.

Also included are polymeric anionic surfactants such as salts of polymers of alkyl acrylates and/or alkyl methacrylates and acrylic and/or methacrylic acid, and salts of partial esters of maleic anhydride-styrene copolymers.

Another group of materials which can be classified as anionic surfactants are those materials known as overbased or superbased materials. These are basic metal salts, preferably alkali or alkaline earth metal salts, of acidic organic compounds (carboxylic acids, sulfonic acids, phosphonic acids, phenols, and so on). Overbased materials are generally single phase homogeneous Newtonian systems characterized by a metal content in excess of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, preferably carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (mineral oil, naphtha, toluene, xylene, etc.) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter such as a phenol or alcohol.

The acidic organic material will normally have a sufficient number of carbon atoms to provide a degree of solubility in oil and to provide a measure of surfactant activity to the product. The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound: a neutral metal salt has a metal ratio of one; a salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5.

Overbased materials are commonly used as lubricant additives and are well known to those skilled in the art. While they are useful for some applications, the scope of their utility may be different from that of other surfactants. Patents describing techniques for making basic salts of sulfonic acids, carboxylic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109. Overbased materials are not generally preferred for use in the present invention, however, because one advantage of the present invention is that it provides a useful fluid even in the absence of overbased materials, i.e., in the absence of relatively large amounts of metal salts. The present materials likewise provide a material with good antiwear properties even in the absence of typical zinc compounds such as zinc dialkyldithiophosphates. Accordingly, to fully exploit the advantages of the present invention, overbased materials would not be employed as the surfactant, nor would zinc compounds be added. Thus these materials will, in one embodiment, be present, if at all, in amounts of less than about 3% by weight, more preferably less than 1%. In another embodiment the composition of the present invention will be substantially free from (e.g., less than 3% or 1%) dispersants of the type used in crankcase lubricants (e.g., polyalkenylsuccinimide types or Mannich dispersant types), olefin copolymer viscosity index improvers, or halogenated olefins or halogenated waxes.

Cationic surfactants are similar to anionic surfactants except that the surface-active portion of the molecule has a positive charge. Examples of cationic surfactants include salts of long-chain amines such as primary amines derived from animal and vegetable fatty acids and tall oil and synthetic C_{12}-C_{18} primary, secondary, or tertiary amines; diamines and their salts, quaternary ammonium salts including tetraalkylammonium salts and imidazolinium salts derived from e.g. tallow or hydrogenated tallow, or N-benzyl-N-alkyldimethylammonium halides; polyoxyethylenated long-chain amines; quaternized polyoxyethylenated long-chain amines; and amine oxides such as N-alkyldimethylamine oxides (which may be considered zwitterionic) such as cetyl dimethylamine oxide or stearyl dimethylamine oxide.

Zwitterionic surfactants include amino acids such as β-N-alkylaminopropionic acids, N-alkyl-β-iminodipropionic acids, imidazoline carboxylates, N-alkylbetaines, sulfobetaines, and sultaines.

Nonionic surfactants, which are preferred for the present invention, are similar materials in which the polar functionality is not provided by an anionic or cation group, but by a neutral polar group such as typically an alcohol, amine, ether, ester, ketone, or amide function. Typical nonionic surfactants include polyoxyethylenated alkylphenols such as polyoxyethylenated p-nonylphenol, p-octylphenol, or p-dodecylphenol, polyoxyethylenated straight-chain alcohols derived from coconut oil, tallow, or synthetic materials including oleyl derivatives; polyoxyethylenated polyoxypropylene glycols (block copolymers of ethylene oxide and propylene oxide), typically having molecular weights of 1000 to 30,000; polyethylene glycol; polyoxyethylenated mercaptans; long-chain carboxylic acid esters including glyceryl and polyglyceryl esters of natural fatty acids, propylene glycol esters, sorbitol esters, polyoxyethylenated sorbitol esters, polyoxyethylene glycol esters, and polyoxyethylenated fatty acids; alkanolamine "condensates" e.g. the condensates made by reaction of methyl or triglyceride esters of fatty acids with equimolar or twice equimolar amounts of alkanolamine; tertiary acetylenic glycols; polyoxyethylenated silicones, prepared by reaction of a reactive silicone intermediate with a capped alkylene or polyalkylene oxide such as propylene oxide or mixed ethylene oxide/propylene oxide copolymer; N-alkylpyrrolidinones, and alkylpolyglycosides (long chain acetals of polysaccharides). Many of these and other ionic and non-ionic surfactants are discussed in Rosen, "Surfactants and Interfacial Phenomena," John Wiley & Sons, pp. 7-31, 1989.

Further nonionic surfactants more specifically include ethoxylated coco amide, oleic acid, t-dodecyl mercaptan, modified polyester dispersants, ester, amide, or mixed ester-amide dispersants based on polyisobutenyl succinic anhydride, dispersants based on polyisobutyl phenol, ABA type block copolymer nonionic dispersants, acrylic graft copolymers, octylphenoxypolyethoxyethanol, nonylphenoxypolyethoxyethanol, ethoxylated amines, borated olefin epoxides, alkyl aryl ethers, alkyl aryl polyethers, amine polyglycol condensates, modified polyethoxy adducts, modified terminated alkyl aryl ethers, modified polyethoxylated straight chain alcohols, terminated ethoxylates of linear primary alcohols, high molecular weight tertiary amines such as 1-hydroxyethyl-2-alkyl imidazolines, oxazolines, perfluoralkyl sulfonates, sorbitan fatty acid esters, polyethylene glycol esters, aliphatic and aromatic phosphate esters. Also included are the reaction products of hydrocarbyl-substituted succinic acylating agents and amines. These reaction products and methods for preparing them are described in U.S. Patents 4,234,435; 4,952,328; 4,938,881; and 4,957,649.

Other nonionic surfactants include functionalized polysiloxanes. These materials contain functional groups such as amino, amido, imino, sulfonyl, sulfoxyl, cyano, hydroxy, hydrocarbyloxy, mercapto, carbonyl (including aldehydes and ketones), carboxy, epoxy, acetoxy, phosphate, phosphonyl, and haloalkyl groups. These polysiloxanes can be linear or branched and generally have molecular weight above 800, i.e. up to 10,000 or 20,000. The functionality can be randomly distributed on the polymer chain or present in blocks. The functionality can be present as alkyl or alkaryl groups as well as groups such as $-(C_2H_4O)_a-(C_3H_6O)_b-R$ where a and b are independently numbers from 0 to about 100 provided that at least one of a or b is at least 1, and R is H, acetoxy, or a hydrocarbyl group. Other suitable substituent groups can include C_3H_6X, where X is OH, SH, or NH_2. Examples of such materials include SILWET™ surfactants from Union Carbide and Tegopren™ silicone surfactants from Goldschmidt Chemical Corp., Hopewell, VA.

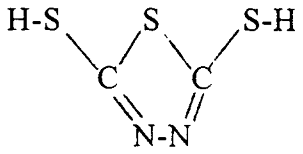
Preferred nonionic surfactants include esters of polyols, in particular, partial esters of glycerol where the acid moiety of the ester is a fatty acid of 8 to 24 carbon atoms, preferably about 18 carbon atoms. Particularly preferred are surfactants which comprise in large part glycerol monooleate.

It is preferred that the amount of the surfactant (d) in the composition of the present invention will be 0.05 to 8 percent by weight; more preferably 0.1 to 3% by weight. The amount will be proportionately increased if the present invention is used as a concentrate.

Whether the present invention is used as a concentrate or as a fully formulated material, the relative amounts of (b), (c), and (d) employed will preferably be within the relative weight ratios of b:c:d = 1-10:0.2-3:0.3-3, and more preferably within the relative weight ratios of b:c:d: = 1-3:0.2-1:0.3-1.

Other additives can also be used in compositions of the present invention in conventional amounts, including the additives listed below. Antioxidants, corrosion inhibitors, extreme pressure and anti-wear agents include but are not limited to chlorinated aliphatic hydrocarbons, boron-containing compounds including borate esters, and molybdenum compounds. Other additives are viscosity improvers, which include but are not limited to polyisobutenes, polymethacrylate esters, polyacrylate esters, diene polymers, polyalkylstyrenes, alkenylaryl conjugated diene copolymers polyolefins and multifunctional viscosity improvers. Also included are pour point depressants, which are often included in the lubricating oils described herein. See for example, page 8 of "Lubricant Additives" by C. V. Smalheer and R. Kennedy Smith (Lesius-Hiles Company Publishers, Cleveland, Ohio, 1967). Anti-foam agents can be used to reduce or prevent the formation of stable foam, and include silicones or organic polymers. A particularly suitable antifoam agent is poly(dimethylsiloxane), which is preferably present in an amount of 0.0004 to 0.4 weight percent, preferably 0.001 to 0.1 weight percent, in a fully formulated composition. Examples of these and additional anti-foam compositions are described in "Foam Control Agents," by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162. Sulfurized organic materials can also be present. Materials which may be sulfurized to form the sulfurized organic compositions include oils, fatty acids or esters, olefins or polyolefins made thereof, terpenes, or Diels-Alder adducts. Sulfurized olefins can be produced by reacting sulfur monochloride with a low carbon atom olefin, treating the resulting product with an alkali metal sulfide in the presence of free sulfur, and reacting that product with an inorganic base, as described by reference to U.S. Patent 3,471,404. Alternatively, organic polysulfides can be prepared by reacting, optionally under superatmospheric pressure, an olefin with a mixture of sulfur and hydrogen sulfide in the presence or absence of a catalyst, such as an alkyl amine catalyst, followed by removal of low boiling materials. For suitable olefins, sulfurized olefins, and methods of preparing the same, reference is made to U.S. Patents 4,119,549, 4,199,550, 4,191,659, and 4,344,854.

Another additive which can be present is a dimercaptothiadiazole or a derivative thereof, which can be used as a copper corrosion inhibitor. These materials are prepared by reaction of CS_2 with hydrazine. Dimercaptothiadiazoles consist of a five-membered ring having the structure


(VIII)

The carbon atoms are substituted by sulfur-containing groups, in particular -S-H (as shown), -S-R, or -S-S-R groups, where R is hydrocarbyl group. Substitution by -S-R groups can be obtained by condensation of (VIII) with an alcohol or by addition of above material to an activated olefin such as an alkyl acrylate; substitution by -S-S-R can be obtained by reaction with an alkyl mercaptan.

These and other additives are described in greater detail in U.S. Patent 4,582,618 (column 14, line 52 through column 17, line 16, inclusive).

EXAMPLES

Examples 1-27. Compositions are prepared by mixing the following components in the amounts indicated in Table I:

Oil: A: A mixture of mineral oils from Sun Oil Company, comprising 70% Sun™ 70 neutral oil and 30% Sun™ 60 neutral oil. (The oil composition used also contains maleic anhydride-styrene viscosity improver and pour point depressant in an amount of 3.29 percent by weight.) This and the other oil compositions listed may contain small amount of other oils normally introduced along with the other ingredients as diluents.

B: A mixture of sunflower oil and 2-ethylhexyl adipate ester (BASF Glisso-fluid A-9™)
C: Mineral oil, Sun™ 70 neutral, without additives.

Dithiocarbamate esters:

G: The material of formula (I) prepared from methyl acrylate
H: Methylene-bis(di-n-butyldithiocarbamate)
J: A material akin to formula (I) prepared from the reaction of diethylamine, carbon disulfide, and methyl acrylate
K: A material akin to (J), prepared using butyl acrylate
L: A material akin to (J), prepared from dipropylamine as the amine

M: A material akin to (J), prepared from di-2-ethylhexylamine as the amine.

N. A material akin to (J), prepared from hexylamine as the amine and butyl acrylate as the activated olefin reactant.

S-containing phosphonate:

O: The material of Example A
P: Material akin to Example A but prepared as the acid, i.e., without reaction with the amine.
Q: Material akin to Example A where the amine is oleyl amine
R: Material akin to Example A where the amine is 2-ethylhexyl amine
S: Material prepared from reacting Primene 81R™ with the reaction product of α-pinene and phosphorus pentasulfide.

Surfactant:

V: Glycerol monooleate
W: Borated C_{16} α-olefin epoxide
X: Alkyl hydrogen phosphite from oleyl alcohol
Y: 1-hydroxyethyl-2-heptadecenyl imidazoline
Z: ethoxylated fatty (tallow) amine (Ethomeen T12™)
AA: Calcium carbonate-overbased fatty acid carboxylate
AB: Reaction product of C_{18-24} alkenyl succinic anhydride with diethanolamine
AC: Calcium carbonate-overbased alkyl salicylate
AD: Oleylamide

Table I

Ex.	Oil:		DTC ester:		Phosphonate		Surfactant	
	type[a]	%	type	%	type	%	type	%
1	A	95.2	G	3.0	O	0.83	V	1.0
2	A	95.3	G	2.0	O	1.24	V	1.5
3	A	96.1	G	2.0	O	0.41	V	1.5
4	A	97.1	G	2.0	O	0.41	V	0.5
5	A	96.3	G	2.0	O	1.24	V	0.5
6	A	95.1	G	4.0	O	0.41	V	0.5
7	A	94.3	G	4.0	O	1.24	V	0.5
8	A	94.1	G	4.0	O	0.41	V	1.5
9	A	93.3	G	4.0	O	1.24	V	1.5
10	A	96.0	H	2.2	O	0.83	V	1.0
11	A	93.8	G	3.0	P	2.17	V	1.0
12	A[b]	94.9	G	3.0	Q	1.08	V	1.0
13	A	95.0	G	3.0	R	1.05	V	1.0
14	A	95.7	J	2.43	O	0.83	V	1.0
15	A	97.1	G	2.0	O	0.41	W	0.5
16	A	97.1	G	2.0	O	0.41	X	0.5
17	A	97.1	G	2.0	O	0.41	Y	0.5
18	A	97.1	G	2.0	O	0.41	Z	0.5
19	A	97.1	G	2.0	O	0.41	AA	0.21
20	A	96.6	G	1.5	O	0.83	AB	1.06
21	A	96.5	G	1.5	O	0.83	AC	1.2
22	A	96.7	H	1.5	O	0.83	V + AD	0.95 0.05
23	A	96.9	G	1.5	S	0.56	V	1.0
24	B	88.9	K	0.1	O	8.0	V	3.0
25	B	88.5	L	0.5	O	3.0	V	8.0
26	C	94.9	M	5.0	O	0.1	--	0
27	C	89.8	N	10	P	0.05	V	0.1

a: The oil, except in Examples 12 and 24-27, also contains 0.02% dimercaptothiadiazole condensate and 0.2% silicone foam inhibitor.

b: Contains 0.05% dimercaptothiadiazole condensate.

Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil which may be customarily present in the commercial material, unless otherwise indicated. As used herein, the expression "consisting essentially of" permits the inclusion of substances which do not materially affect the basic and novel characteristics of the composition under consideration.

Claims

1. A composition of matter comprising:

   (a) an oil of lubricating viscosity;
   (b) a compound of the structure

   $$R_1R_2N - C(X)S - Q$$

   where R_1 and R_2 are independently hydrogen or hydrocarbyl groups; X is an oxygen or sulfur atom; and Q is an alkyl group or an alkyl group containing at least one substituent selected from the group consisting of activating groups, hydrocarbyl groups, hetero groups, and $-SC(X)-NR_1R_2$ groups, groups R_1, R_2, and Q containing in total at least 4 carbon atoms; and
   (c) A sulfur-containing phosphonic acid or a salt thereof.

2. The composition of claim 1 wherein component (b) is

   $$R_1R_2N - C(S)S - CR_3R_4CR_3HC(O)OR_5$$

   where R_1 and R_2 are independently C_1 to C_8 alkyl groups, R_3 and R_4 are independently hydrogen, methyl, or ethyl groups, and R_5 is a C_1 to C_6 alkyl group.

3. The composition of claim 1 or 2 wherein (c) is a salt of a sulfur-containing phosphonic acid prepared by the reaction of an olefin with a phosphorus sulfide followed by treatment with water or steam.

4. The composition of claim 3 wherein the salt is an amine salt.

5. The composition of claim 3 wherein the olefin is C_{8-24} olefin.

6. The composition of claim 3 wherein the sulfur-containing phosphonic acid contains a dimeric, oligomeric, or cyclic species having sulfur-bridges between hydrocarbyl radicals derived from the olefin.

7. The composition of any one of claims 1 to 6 wherein the amount of component (b) is about 0.1 to about 10 percent by weight and the amount of component (c) is about 0.05 to about 8 percent by weight.

8. The composition of any one of claims 1 to 7 further comprising (d) a surfactant.

9. The composition of claim 8 wherein the amount of component (d) is about 0.05 to about 8 percent by weight.

10. The composition of any one of claims 1 to 9 substantially free from overbased detergent and zinc compounds.

11. A power transmission fluid comprising the composition of any of claims 1-10.

12. A tractor hydraulic fluid comprising the composition of any of claims 1-10.

13. The use of the composition of any of claims 1 to 10 as a power transmission fluid.

14. The use of the composition of any of claims 1 to 10 as a tractor hydraulic fluid.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 7730

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.6)
X	EP-A-0 604 232 (THE LUBRIZOL CORPORATION) * page 9, line 9 * * page 14, line 33 - line 34 * * page 15, line 55 * * page 16, line 7 * * page 19; example IX * ---	1,2,7-9, 11,13	C10M141/10 //(C10M141/10, 129:76,135:18, 137:14), C10N30:06, C10N40:04, C10N40:08
A	US-A-2 882 228 (F.J. WATSON) * column 3, line 41 - line 42 * * column 5, line 37 - line 40 * * column 6, line 13 * ---	1,8-11, 13	
A	US-A-3 143 506 (E. E. SCHALLENBERG) * column 1, line 61 - column 2, line 1 * ---	1,3-5	
A	US-A-5 019 284 (LIENPAO FARNG) * claim 1 * ---	1	
D,A	US-A-4 609 480 (HITOSHI HATA) -----		**TECHNICAL FIELDS SEARCHED (Int.Cl.6)** C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 January 1996	Hilgenga, K

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
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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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