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(71) Applicant : **THE LUBRIZOL CORPORATION**
29400 Lakeland Boulevard
Wickliffe, Ohio 44092-2298 (US)

(72) Inventor : **Vinci, James N.**
131 Chatham Way
Mayfield Heights, Ohio 44124 (US)
Inventor : **Butke, Betsy J.**
6642 Pear Tree Lane
Mentor, Ohio 44060 (US)
Inventor : **Schwind, James J.**
Charnwood,
Church Lane
Doveridge, Derbyshire DE6 5NN (GB)

(74) Representative : **Crisp, David Norman et al**
D. YOUNG & CO.
21 New Fetter Lane
London EC4A 1DA (GB)

(54) Lubricating compositions, greases, and aqueous fluids containing the combination of a dithiocarbamate compound and an organic polysulfide.

(57) This invention relates to a lubricating composition comprising an oil of lubricating viscosity, (A) at least one dithiocarbamate compound, and (B) at least one organic polysulfide. The invention also relates to greases and aqueous compositions which contain this combination. The compositions have good antiwear or extreme pressure properties. The combination also provides improved oxidation resistance and thermal stability to fluids.

Jouve, 18, rue Saint-Denis, 75001 PARIS

This invention relates to lubricating compositions, greases, and aqueous fluids containing a dithiocarbamate compound and an organic polysulfide. These compositions possess improved antiwear or extreme pressure properties.

Lubricating compositions, greases, and aqueous fluids are used to maintain a film of lubricant between surfaces that are moving with respect to each other. The compositions minimize contact of the moving surfaces thus preventing harmful wear to the surfaces. The compositions generally also lower the coefficient of friction. To be effective, the compositions should have sufficient antiwear, antiweld, and extreme pressure properties to minimize metal damage from metal-to-metal contact under high load conditions.

Polysulfides have been used to provide extreme pressure protection to lubricating compositions. High levels of polysulfides generally lead to higher extreme pressure protection. However, high levels of polysulfides can lead to copper corrosion, seal compatibility, oxidation stability, and thermal stability problems. It is beneficial to find a material that when combined with a polysulfide has good extreme pressure properties without the adverse effects caused by high levels of polysulfide.

Dithiocarbamate acid esters and their preparation have been described in U.S. Patent 2,710,872 (Thompson et al.), 2,897,152 (Elliott et al.), 3,890,360 (Malec), 3,833,496 (Malec), 4,064,265 (Varsanyi et al.), 4,758,362 (Butke), 4,885,365 (Lam), and 4,957,643 (Lam).

The sulfurized compositions prepared from unsaturated compounds and olefinic compounds have been described in U.S. Patents 4,119,549 (Davis), 4,119,550 (Davis et al.), 4,191,659 (Davis), and 4,344,854 (Davis et al.).

The invention provides a lubricating composition comprising (A) at least one dithiocarbamate compound, (B) at least one organic polysulfide, optionally, (C) a phosphorus or boron antiwear or extreme pressure agent, and (D) a base fluid selected from (i) an oil of lubricating viscosity, (ii) water and a surfactant or thickener, and (iii) an oil of lubricating viscosity and a thickener.

In one aspect, the invention relates to a lubricating composition generally comprising a major amount of an oil of lubricating viscosity, (A) at least one dithiocarbamate compound, and (B) at least one organic polysulfide. The invention also relates to greases and aqueous compositions which contain the combination of (A) and (B). The compositions of the invention have good antiwear or extreme pressure properties. The combination also provides improved oxidation resistance and thermal stability to fluids.

Various preferred features and embodiments of the invention are described below by way of non-limiting illustration.

The term "hydrocarbyl" includes hydrocarbon as well as substantially hydrocarbon groups. Substantially hydrocarbon describes groups which contain heteroatom substituents which do not alter the predominantly hydrocarbon nature of the group. Examples of hydrocarbyl groups include the following:

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

(2) substituted hydrocarbon substituents, i.e., those substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; those skilled in the art will be aware of such groups (e.g., halo (especially chloro and fluoro), hydroxy, mercapto, nitro, nitroso, sulfoxy, etc.);

(3) heteroatom substituents, i.e., substituents which will, while having a predominantly hydrocarbon character within the context of this invention, contain an atom other than carbon present in a ring or chain otherwise composed of carbon atoms (e.g., alkoxy or alkylthio). Suitable heteroatoms will be apparent to those of ordinary skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as, e.g., pyridyl, furyl, thienyl, imidazolyl, etc.

In general, no more than about 2, preferably no more than one, hetero substituent will be present for every ten carbon atoms in the hydrocarbyl group. Typically, there will be no such hetero atom substituents in the hydrocarbyl group. Therefore, such a hydrocarbyl group is purely hydrocarbon.

As described above, the compositions include the combination of (A) a dithiocarbamate compound and (B) an organic polysulfide. Generally, from about 0.25 up to about 2, or from about 0.5 up to about 1.8, or from about 0.75 up to about 1.5 parts of the dithiocarbamate compound (A) are used with each part of the organic polysulfide (B). Here as well elsewhere in the specification, the ratio and range limits may be combined.

Dithiocarbamate compounds include reaction products of a dithiocarbamic acid or salt and an unsaturated amide, carboxylic acid, anhydride, or ester, or ether, alkylene-coupled dithiocarbamate, and bis(S-alkyldithiocarbamoyl) disulfides. In one embodiment, the dithiocarbamate compounds are ashless, i.e. metal free. The dithiocarbamate compounds (A) may be prepared by reacting a dithiocarbamic acid or salt with an unsaturated compound. The dithiocarbamate compounds may also be prepared by simultaneously reacting an amine, carbon disulfide and an unsaturated compound. Generally, the reaction occurs at a temperature from about 25°C, or from about 50°C to about 125°C, or to about 100°C. U. S. Patents 4,758,362 and 4,997,969 describe dithiocarbamate compounds and methods of making the same.

The dithiocarbamic acid or salt which may be used to prepare the dithiocarbamate compounds may be prepared by reacting an amine with carbon disulfide. The amine may be a primary or a secondary amine. The amines may be primary or secondary amines, with secondary amines most preferred. The amines generally may contain hydrocarbyl groups. Each hydrocarbyl group may independently contain from one up to about 40, or from about two up to about 30, or from three up to about 24, or even up to about 12 carbon atoms.

In one embodiment, the amines are primary amines. Examples of primary amines useful in the present invention include ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine, and dodecylamine.

In one embodiment, the primary amine is a fatty (C_{8-30}) amine which include n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, oleyamine, etc. Also useful fatty amines include commercially available fatty amines such as "Armeen" amines (products available from Akzo Chemicals, Chicago, Illinois), such as Akzo's Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as cocoa, oleyl, tallow, or stearyl groups.

Other useful primary amines include primary ether amines, such as those represented by the formula, $R''(OR')_XNH_2$, wherein R' is a divalent alkylene group having about 2 to about 6 carbon atoms; x is a number from one to about 150, or from about one to about five, or one; and R" is a hydrocarbyl group of about 5 to about 150 carbon atoms. An example of an ether amine is available under the name SURFAM® amines produced and marketed by Mars Chemical Company, Atlanta, Georgia. Preferred etheramines are exemplified by those identified as SURFAM P14B (decyloxypropylamine), SURFAM P16A (linear C_{16}), SURFAM P17B (tridecyloxypropylamine). The carbon chain lengths (i.e., C_{14}, etc.) of the SURFAMS described above and used hereinafter are approximate and include the oxygen ether linkage.

In one embodiment, the amine is a tertiary-aliphatic primary amine. Generally, the aliphatic group, preferably an alkyl group, contains from about 4 to about 30, or from about 6 to about 24, or from about 8 to about 22 carbon atoms. Usually the tertiary alkyl primary amines are monoamines represented by the formula R_1-$C(R_1')_2$-NH_2, wherein R_1 is a hydrocarbyl group containing from one to about 27 carbon atoms and each R_1' is independently a hydrocarbyl group containing from 1 to about 12 carbon atoms. Such amines are illustrated by tert-butylamine, tert-hexylamine, 1-methyl-1-amino-cyclohexane, tert-octylamine, tert-decylamine, tert-dodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetracosanylamine, and tert-octacosanylamine.

Mixtures of amines are also useful for the purposes of this invention. Illustrative of amine mixtures of this type are "Primene 81R" which is a mixture of C_{11}-C_{14} tertiary alkyl primary amines and "Primene JMT" which is a similar mixture of C_{18}-C_{22} tertiary alkyl primary amines (both are available from Rohm and Haas Company). The tertiary alkyl primary amines and methods for their preparation are known to those of ordinary skill in the art. The tertiary alkyl primary amine useful for the purposes of this invention and methods for their preparation are described in U.S. Patent 2,945,749.

In another embodiment, the amine is a secondary amine. Specific of secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, methylethylamine, ethylbutylamine, ethylamylamine and the like. In one embodiment, the secondary amines may be cyclic amines such as piperidine, piperazine, morpholine, etc.

In one embodiment, the dithiocarbamate compound (A) is prepared by reacting one or more dithiocarbamic acids or salts with an unsaturated amide. Examples of unsaturated amides include acrylamide, N,N'-methylene bis(acrylamide), methacrylamide, crotonamide, and the like. In one embodiment, the dithiocarbamate containing composition is derived from the reaction product of a diamylamine or dibutylamine with carbon disulfide which forms a dithiocarbamic acid or a salt which is ultimately reacted with a acrylamide. If the reaction products of the dithiocarbamic acid or salt and an unsaturated amide has additional NH group which are capable of reacting, then the reaction product may be further reacted with a linking or a coupling compound, such as formaldehyde or paraformaldehyde. The reaction products of dithiocarbamic acids and salts with unsaturated amides are disclosed in U.S. Patents 4,758,362 (Butke) and 4,997,969 (Luciani).

In one embodiment, the dithiocarbamate compound (A) is a reaction product of a dithiocarbamic acid or salt with an unsaturated acid, anhydride or ester. Examples of unsaturated carboxylic acids and anhydrides include acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, and maleic anhydride. If an unsaturated carboxylic acid or anhydride is used, an ester may then be formed by subsequent reaction of the dithiocarbamate-unsaturated carboxylic acid or anhydride adduct with an alcohol such as those alcohols discussed herein. In one embodiment, the alcohol has from 1 to about 12 carbon atoms.

In one embodiment, the unsaturated carboxylic acid, or anhydride or ester includes maleic, fumaric, acrylic, methacrylic, itaconic, citraconic acids and esters. The ester may be represented by one of the formulae: $(R_2)_2C=C(R_2)C(O)OR_3$, or $R_3O\text{-}(O)C\text{-}HC=CH\text{-}C(O)OR_3$, wherein each R_2 and R_3 are independently hydrogen or a hydrocarbyl group having 1 to about 18, or to about 12, or to about 8 carbon atoms, R_2 is hydrogen or an alkyl group having from 1 to about 6 carbon atoms. In one embodiment, R_2 is preferably hydrogen or a methyl group.

Examples of unsaturated carboxylic esters include methyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, ethylmethacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, ethyl maleate, butyl maleate and 2-ethylhexyl maleate. The above list includes mono- as well as diesters of maleic, fumaric, and itaconic acids and anhydrides. In one embodiment, the dithiocarbamate acid or salt is formed from diethylamine or dibutylamine and carbon disulfide. The resulting dithiocarbamic acid is then reacted with methyl acrylate.

In another embodiment, the unsaturated carboxylic ester is a vinyl ester. The vinyl ester may be represented by the formula $R_4CH=CH\text{-}O(O)CR_5$, wherein R_4 is a hydrocarbyl group having from 1 to about 30, or to about 12 carbon atoms, preferably hydrogen, and R_5 is a hydrocarbyl group having 1 to about 30, or to about 12, or to about 8 carbon atoms. Examples of vinyl esters include vinyl acetate, vinyl 2-ethylhexanoate, vinyl butanoate, etc.

In one embodiment, the dithiocarbamate compound (A) is a reaction product of a dithiocarbamic acid or salt and a vinyl ether. The vinyl ether is represented by the formula $R_6\text{-}CH=CH\text{-}OR_7$ wherein R_6 is independently hydrogen or a hydrocarbyl group having from 1 up to about 30, or up to about 24, or up to about 12 carbon atoms. R_7 is a hydrocarbyl group defined the same as R_5. Examples of vinyl ethers include methyl vinyl ether, propyl vinyl ether, 2-ethylhexyl vinyl ether and the like.

In one embodiment, the dithiocarbamate compound (A) is an alkylene-coupled dithiocarbamate. Alkylene-coupled dithiocarbamates useful in the present invention may be prepared by the reaction of a salt of a dithiocarbamic acid, described above, with a suitable dihalogen containing hydrocarbon. The reaction is generally carried out at a temperature within the range from about 25°C up to about 150°C, or up to about 100°C. U.S. Patent 3,876,550 issued to Holubec describes alkylene dithiocarbamate compounds, and U.S. Patents 1,726,647 and 1,736,429, issued to Cadwell describe, phenylmethylene bis(dithiocarbamates) and methods of making the same. In one embodiment, the alkylene-coupled dithiocarbamate is derived from di-n-butyl amine, carbon disulfide and methylene dichloride.

In another embodiment, the dithiocarbamate compound is a bis(S-alkyldithiocarbamoyl) disulfide. These materials have previously been referred to as sulfur-coupled dithiocarbamates. The disulfides may be prepared by (A) reacting a sulfur halide with about a stoichiometric equivalent of (i) at least one olefinic hydrocarbon, or (ii) an aldehyde or ketone, at a temperature and for a period of time sufficient to produce a di(halohydrocarbyl)sulfur intermediate or a dialdehyde or diketo sulfur intermediate, and (B) reacting the intermediate with a salt of a dithiocarbamate in an amount sufficient generally to replace both halo groups with the dithiocarbamate groups or to react with both carbonyl groups of the dialdehyde or diketone. The sulfur halide utilized in the first step (A) may be sulfur monochloride (i.e., S_2Cl_2), sulfur dichloride, sulfur monobromide, sulfur dibromide, or mixtures of any of the above sulfur halides with elemental sulfur in varying amounts.

The sulfur halide utilized in the first step (A) may be sulfur monochloride (i.e., S_2Cl_2), sulfur dichloride, sulfur monobromide, sulfur dibromide, or mixtures of any of the above sulfur halides with elemental sulfur in varying amounts. Various olefins and olefin mixtures may be used as the starting material in step (A). The olefins are disclosed below for the organic polysulfide. Specific examples of aldehydes that may be reacted with sulfur halides include, for example, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, 2-ethyl-hexanal, and cyclohexanecarboxaldehyde . Examples of ketones include dimethyl ketone, methyl ethyl ketone, diethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, etc.

The reaction between the sulfur intermediate and the dithiocarbamate salts generally is conducted from ambient temperature to the reflux temperature of the mixture. The reaction is conducted until the reaction is completed which is generally from about 5 to about 24 hours. At the end of the reaction, the aqueous phase is separated, and the product is recovered from the organic phase.

The bis(S-alkyldithiocarbamoyl) disulfides also may be prepared by a process which comprises the steps of (A) reacting an olefinic hydrocarbon with a halogen to produce a halogen-containing intermediate, and (B) reacting said intermediate with an alkali metal sulfide and a salt of a dithiocarbamate in an amount sufficient to replace the halogen groups present partially with dithiocarbamate groups and/or partially with sulfide groups. The bis(S-alkyldithiocarbamoyl) disulfides are described in U.S. Patent 2,599,350, issued to Rudel et al.

In the compositions of the present invention, the dithiocarbamate compounds (A) esters are used in combination with (B) an organic polysulfide. The organic polysulfides are generally characterized as having sulfide linkages having from at least 2 to about 10 sulfur atoms, or from 2 to about 6 sulfur atoms, or from 2 to about

4 sulfur atoms. The organic polysulfides are generally di-, tri- or tetrasulfide compositions with trisulfide compositions preferred. The organic polysulfides may be a mixture of di-, tri- or tetrasulfide materials with materials having a majority of trisulfide being preferred. Materials having at least 70% trisulfide are preferred, with materials containing greater than 80% trisulfide more preferred.

The organic polysulfides of the present invention provide from about 1% to about 3% sulfur to the lubricating compositions. Generally, the organic polysulfides contain from about 10% to about 60% sulfur, or from 20% to about 50%, and or from about 35% to about 45% sulfur. Materials which may be sulfurized to form the organic polysulfides include oils, fatty acids or esters, or olefins, or polyolefins.

Oils which may be sulfurized are natural or synthetic oils including mineral oils, lard oil, carboxylate esters derived from aliphatic alcohols and fatty acids or aliphatic carboxylic acids (e.g., myristyl oleate and oleyl oleate), and synthetic unsaturated esters or glycerides.

Fatty acids generally contain from about 8 up to about 30, or from about 12 up to about 24 carbon atoms. Examples of fatty acids include such as palmitoleic, oleic, ricinoleic, linoleic, oleostearic, etc. Sulfurized fatty acid esters prepared from mixed unsaturated fatty acid esters such as are obtained from animal fats and vegetable oils including tall oil, linseed oil, rape oil, fish oil, etc., also are useful.

The olefinic compounds which may be sulfurized are diverse in nature. They contain at least one olefinic double bond, which is defined as a non-aromatic double bond; that is, one connecting two aliphatic carbon atoms. In its broadest sense, the olefin may be defined by the formula

$$R^{*1}R^{*2}C{=}CR^{*3}R^{*4}$$

wherein each of R^{*1}, R^{*2}, R^{*3} and R^{*4} is independently hydrogen or an organic group. In general, the R groups in the above formula which are not hydrogen may be satisfied by such groups as $-C(R^{*5})_3$, $-COOR^{*5}$, $-CON(R^{*5})_2$, $-COON(R^{*5})_4$, -COOM, -CN, -X, $-YR^{*5}$ or -Ar, wherein: each R^{*5} is independently hydrogen, alkyl, alkenyl, aryl, substituted alkyl, substituted alkenyl or substituted aryl, with the proviso that any two R^{*5} groups can be alkylene or substituted alkylene whereby a ring of up to about 12 carbon atoms is formed; M is one equivalent of a metal cation (preferably Group I or II, e.g., sodium, potassium, barium, calcium); X is halogen (e.g., chloro, bromo, or iodo); Y is oxygen or divalent sulfur; Ar is an aryl or substituted aryl group of up to about 12 carbon atoms. Any two of R^{*1}, R^{*2}, R^{*3} and R^{*4} may also together form an alkylene or substituted alkylene group; i.e., the olefinic compound may be alicyclic.

The olefinic compound is usually one in which each R* group which is not hydrogen is independently alkyl, alkenyl or aryl group. Monoolefinic and diolefinic compounds, particularly the former, are preferred, and especially terminal monoolefinic hydrocarbons; that is, those compounds in which R^{*3} and R^{*4} are hydrogen and R^{*1} and R^{*2} are alkyl or aryl groups, especially alkyl groups (that is, the olefin is aliphatic) having 1 up to about 30, or up to about 16, or up to about 8, and or up to about 4 carbon atoms. Olefinic compounds having about 3 to about 30 and especially about 3 to about 16 (most often less than about 9) carbon atoms are particularly desirable.

Isobutene, propylene and their dimers, trimers and tetramers, and mixtures thereof are especially preferred olefinic compounds. Of these compounds, isobutylene and diisobutylene are particularly desirable because of their availability and the particularly high sulfur containing compositions which can be prepared therefrom.

In one embodiment, the organic polysulfide comprises a sulfurized olefin, where the olefins are described above. For example, organic poly-sulfides may be prepared by the sulfochlorination of olefins containing four or more carbon atoms and further treatment with inorganic higher polysulfides according to U.S. Patent 2,708,199.

In one embodiment, sulfurized olefins are produced by (1) reacting sulfur monochloride with a stoichiometric excess of a lower olefin, e.g. containing less than eight carbon atoms, (2) treating the resulting product with an alkali metal sulfide in the presence of free sulfur in a mole ratio of no less than 2:1 in an alcohol-water solvent, and (3) reacting that product with an inorganic base. This procedure is described in U.S. Patent 3,471,404. Generally, the olefin reactant generally contains from about 2 to 5 carbon atoms and examples include ethylene, propylene, butylene, isobutylene, amylene, etc.

The sulfurized olefins which are useful in the compositions of the present invention also may be prepared by the reaction, under superatmospheric pressure, of olefinic compounds with a mixture of sulfur and hydrogen sulfide in the presence of a catalyst, followed by removal of low boiling materials. This procedure for preparing sulfurized compositions which are useful in the present invention is described in U.S. Patents 4,119,549, 4,119,550, 4,191,659, and 4,344,854.

The following non-limiting example relates to organic polysulfides.

Example 1

Sulfur (526 parts, 16.4 moles) is charged to a jacketed, high-pressure reactor which is fitted with an agitator and internal cooling coils. Refrigerated brine is circulated through the coils to cool the reactor prior to the introduction of the gaseous reactants. After sealing the reactor, evacuating to about 2 torr and cooling, 920 parts (16.4 moles) of isobutene and 279 parts (8.2 moles) of hydrogen sulfide are charged to the reactor. The reactor is heated using steam in the external jacket, to a temperature of about 182°C over about 1.5 hours. A maximum pressure of 1350 psig is reached at about 168°C during this heat-up. Prior to reaching the peak reaction temperature, the pressure starts to decrease and continues to decrease steadily as the gaseous reactants are consumed. After about 10 hours at a reaction temperature of about 182°C, the pressure is 310-340 psig and the rate of pressure change is about 5-10 psig per hour. The unreacted hydrogen sulfide and isobutene are vented to a recovery system. After the pressure in the reactor has decreased to atmospheric, the sulfurized mixture is recovered as a liquid.

The mixture is blown with nitrogen at about 100°C to remove low boiling materials including unreacted isobutene, mercaptans and monosulfides. The residue after nitrogen blowing is agitated with 5% Super Filtrol and filtered, using a diatomaceous earth filter aid. The filtrate is the desired sulfurized composition which contains 42.5% sulfur.

Phosphorus or Boron Agents (C):

In one embodiment, the combination of a dithiocarbamate compound (A) and organic polysulfide (B) is used with (C) at least one phosphorus or boron containing antiwear or extreme pressure agent. In this embodiment, the phosphorus or boron containing antiwear or extreme pressure agent (C) is conveniently present in an amount sufficient to impart antiwear, antiweld, and/or extreme pressure properties to the lubricants and functional fluids. The phosphorus or boron antiwear or extreme pressure agents (C) are typically present in the lubricants and functional fluids at a level of up to about 20% by weight, preferably up to about 10% by weight, based on the total weight of the lubricant, functional fluid, or grease. Typically, the phosphorus or boron containing antiwear or extreme pressure agent is present in the lubricants and functional fluids at a level from about 0.01%, or from about 0.05%, or from about 0.08% by weight. The phosphorus or boron containing antiwear or extreme pressure agent is present in an amount up to about 10%, or up to about 3%, or up to about 2% by weight. In one embodiment, the lubricating compositions, functional fluids, and greases contain more than 0.01% phosphorus, or greater than 0.05% phosphorus.

Examples of phosphorus or boron containing antiwear or extreme pressure agents (C) include a metal thiophosphate; a phosphoric acid ester or salt thereof; a phosphite; a phosphorus-containing carboxylic acid, ester, ether, or amide; a borated dispersant; an alkali metal borate; a borated overbased metal salt; a borated fatty amine; a borated phospholipid; and a borate ester. The phosphorus acids include the phosphoric, phosphonic, phosphinic and thiophosphoric acids including dithiophosphoric acid as well as the monothiophosphoric acid, thiophosphinic and thiophosphonic acids.

In one embodiment, phosphorus or boron containing antiwear or extreme pressure agent (C) is a phosphorus acid ester prepared by reacting one or more phosphorus acid or anhydride with an alcohol containing from one, or from about 3 carbon atoms. The alcohol generally contains up to about 30, or up to about 24, or up to about 12 carbon atoms. The phosphorus acid or anhydride is generally an inorganic phosphorus reagent, such as phosphorus pentoxide, phosphorus trioxide, phosphorus tetroxide, phosphoric acid, phosphorous acid, phosphorus halide, lower phosphorus esters, or a phosphorus sulfide, including phosphorus pentasulfide, and the like. Lower phosphorus acid esters generally contain from 1 to about 7 carbon atoms in each ester group. The phosphorus acid ester may be a mono-, di- or triphosphoric acid ester. Alcohols used to prepare the phosphorus acid esters include butyl, amyl, 2-ethylhexyl, hexyl, octyl, and oleyl alcohols, and phenols, such as cresol. Examples of commercially available alcohols include Alfol 810 (a mixture of primarily straight chain, primary alcohols having from 8 to 10 carbon atoms); Alfol 1218 (a mixture of synthetic, primary, straight-chain alcohols containing 12 to 18 carbon atoms); Alfol 20+ alcohols (mixtures of C_{18}-C_{28} primary alcohols having mostly C_{20} alcohols as determined by GLC (gas-liquid-chromatography)); and Alfol 22+ alcohols (C_{18}-C_{28} primary alcohols containing primarily C_{22} alcohols). Alfol alcohols are available from Continental Oil Company.

Another example of a commercially available alcohol mixtures are Adol 60 (about 75% by weight of a straight chain C_{22} primary alcohol, about 15% of a C_{20} primary alcohol and about 8% of C_{18} and C_{24} alcohols) and Adol 320 (oleyl alcohol). The Adol alcohols are marketed by Ashland Chemical.

A variety of mixtures of monohydric fatty alcohols derived from naturally occurring triglycerides and ranging in chain length of from C_8 to C_{18} are available from Procter & Gamble Company. These mixtures contain various amounts of fatty alcohols containing mainly 12, 14, 16, or 18 carbon atoms. For example, CO-1214 is a fatty alcohol mixture containing 0.5% of C_{10} alcohol, 66.0% of C_{12} alcohol, 26.0% of C_{14} alcohol and 6.5% of C_{16} alcohol.

Another group of commercially available mixtures include the "Neodol" products available from Shell Chemical Co. For example, Neodol 23 is a mixture of C_{12} and C_{13} alcohols; Neodol 25 is a mixture of C_{12} and C_{15} alcohols; and Neodol 45 is a mixture of C_{14} to C_{15} linear alcohols. Neodol 91 is a mixture of C_9, C_{10} and C_{11} alcohols.

Fatty vicinal diols also are useful and these include those available from Ashland Oil under the general trade designation Adol 114 and Adol 158. The former is derived from a straight chain alpha olefin fraction of C_{11}-C_{14}, and the latter is derived from a C_{15}-C_{18} fraction.

Examples of useful phosphorus acid esters include the phosphoric acid esters prepared by reacting a phosphoric acid or anhydride with cresol alcohols. An example of these phosphorus acid esters is tricresylphosphate.

In another embodiment, the phosphorus or boron antiwear or extreme pressure agent (C) is a thiophosphorus acid ester or salt thereof. The thiophosphorus acid ester may be prepared by reacting a phosphorus sulfide, such as those described above, with an alcohol, such as those described above. The thiophosphorus acid esters may be mono- or dithiophosphorus acid esters. Thiophosphorus acid esters are also referred to generally as thiophosphoric acids.

In one embodiment, the phosphorus acid ester is a monothiophosphoric acid ester or a monothiophosphate. Monothiophosphates may be prepared by the reaction of a sulfur source with a dihydrocarbyl phosphite. The sulfur source may for instance be elemental sulfur. The sulfur source may also be a monosulfide, such as a sulfur coupled olefin or a sulfur coupled dithiophosphate. Elemental sulfur is a preferred sulfur source. The preparation of monothiophosphates is disclosed in U.S. Patent 4,755,311 and PCT Publication WO 87/07638. Monothiophosphates may also be formed in a lubricant blend by adding a dihydrocarbyl phosphite to a lubricating composition containing a sulfur source, such as a sulfurized olefin. The phosphite may react with the sulfur source under blending conditions (i.e., temperatures from about 30°C. to about 100°C. or higher) to form the monothiophosphate.

In another embodiment, the phosphorus or boron antiwear or extreme pressure agent (C) is a dithiophosphoric acid or phosphorodithioic acid. The dithiophosphoric acid may be represented by the formula $(R_8O)_2PSSH$ wherein each R_8 is independently a hydrocarbyl group containing from about 3 to about 30 carbon atoms, or up to about 18, or to about 12, or to about 8. Examples R_8 include isopropyl, isobutyl, n-butyl, sec-butyl, the various amyl, n-hexyl, methylisobutyl carbinyl, heptyl, 2-ethylhexyl, isooctyl, nonyl, behenyl, decyl, dodecyl, and tridecyl groups. Illustrative lower alkylphenyl R_8 groups include butylphenyl, amylphenyl, heptylphenyl, etc. Examples of mixtures of R_8 groups include: 1-butyl and 1-octyl; 1-pentyl and 2-ethyl-1-hexyl; isobutyl and n-hexyl; isobutyl and isoamyl; 2-propyl and 2-methyl-4-pentyl; isopropyl and sec-butyl; and isopropyl and isooctyl.

In one embodiment, the dithiophosphoric acid may be reacted with an epoxide or a glycol. This reaction product may be used alone, or further reacted with a phosphorus acid, anhydride, or lower ester. The epoxide is generally an aliphatic epoxide or a styrene oxide. Examples of useful epoxides include ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, styrene oxide, etc. Propylene oxide is preferred. The glycols may be aliphatic glycols having from 1 to about 12, or from about 2 to about 6, or from 2 or 3 carbon atoms, or aromatic glycols. Glycols include ethylene glycol, propylene glycol, catechol, resorcinol, and the like. Dithiophosphoric acids, glycols, epoxides, inorganic phosphorus reagents and methods of reacting the same are described in U.S. patent 3,197,405 and U.S. patent 3,544,465.

The following Examples P-1 and P-2 exemplify the preparation of useful phosphorus acid esters.

Example P-1

Phosphorus pentoxide (64 grams) is added at 58°C over a period of 45 minutes to 514 grams of hydroxypropyl O,O-di(4-methyl-2-pentyl)phosphorodithioate (prepared by reacting di(4-methyl-2-pentyl)-phosphorodithioic acid with 1.3 moles of propylene oxide at 25°C). The mixture is heated at 75°C for 2.5 hours, mixed with a diatomaceous earth and filtered at 70°C. The filtrate contains 11.8% by weight phosphorus, 15.2% by weight sulfur, and an acid number of 87 (bromophenol blue).

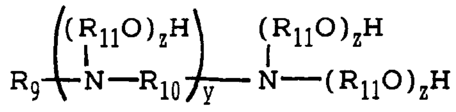
Example P-2

A mixture of 667 grams of phosphorus pentoxide and the reaction product of 3514 grams of diisopropyl phosphorodithioic acid with 986 grams of propylene oxide at 50°C is heated at 85°C for 3 hours and filtered. The filtrate contains 15.3% by weight phosphorus, 19.6% by weight sulfur, and an acid number of 126 (bromophenol blue).

Acidic phosphoric acid esters may be further reacted with an amine compound or metallic base to form an amine or metal salt. The salts may be formed separately and then the salt of the phosphorus acid ester may be added to the lubricating composition. Alternatively, the salts may also be formed in situ when the acidic phosphorus acid ester is blended with other components to form a fully formulated lubricating composition.

The amine salts of the phosphorus acid esters may be formed from ammonia, or an amine, including monoamines and polyamines. The amines may be primary amines, secondary amines or tertiary amines. Useful amines include those amines disclosed in U.S. Patent 4,234,435 at Col. 21, line 4 to Col. 27, line 50. The amines have been described above. Examples of monoamines include methylamine, ethylamine, propylamine, butylamine, octylamine, and dodecylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, methylbutylamine, ethylhexylamine, trimethylamine, tributylamine, methyldiethylamine, ethyl dibutylamine, etc.

In another embodiment, the amines may be hydroxyhydrocarbyl amines, such as those represented by the formula



$$R_9\left(\overset{(R_{11}O)_zH}{\overset{|}{N}}-R_{10}\right)_y-\overset{(R_{11}O)_zH}{\overset{|}{N}}-(R_{11}O)_zH$$

wherein: R_9 is a hydrocarbyl group generally containing from about 6 to about 30 carbon atoms; R_{10} is an alkylene group having from about two to about twelve carbon atoms, or an ethylene or propylene group; R_{11} is an alkylene group containing up to about 5 carbon atoms; y is zero or one; and each z is independently a number from zero to about 10, with the proviso that at least one z is zero.

Useful hydroxyhydrocarbyl amines wherein y in the above formula is zero include 2-hydroxyethylhexylamine; 2-hydroxyethyloctylamine; 2-hydroxyethylpentadecylamine; 2-hydroxyethyloleylamine; 2-hydroxyethylsoyamine; bis(2-hydroxyethyl) hexylamine; bis(2-hydroxyethyl) oleylamine; and mixtures thereof. Also included are the comparable members wherein in the above formula at least one x is at least 2, as for example, 2-hydroxyethoxyethylhexylamine.

A number of hydroxyhydrocarbyl amines wherein y in the above formula is zero are available from Akzo Chemical, under the general trade designations "Ethomeen" and "Propomeen". Specific examples of such products include: Ethomeen C/15 which is an ethylene oxide condensate of a cocoamine containing about 5 moles of ethylene oxide; Ethomeen C/20 and C/25 which are ethylene oxide condensation products from cocoamine containing about 10 and 15 moles of ethylene oxide, respectively; Ethomeen O/12 which is an ethylene oxide condensation product of oleylamine containing about 2 moles of ethylene oxide per mole of amine; Ethomeen S/15 and S/20 which are ethylene oxide condensation products with stearylamine containing about 5 and 10 moles of ethylene oxide per mole of amine, respectively; Ethomeen T/12, T/15 and T/25 which are ethylene oxide condensation products of tallowamine containing about 2, 5 and 15 moles of ethylene oxide per mole of amine, respectively; and Propomeen O/12 which is the condensation product of one mole of oleylamine with 2 moles propylene oxide.

Commercially available examples of alkoxylated amines where y in the above formula is one include Ethoduomeen T/13 and T/20 which are ethylene oxide condensation products of N-tallowtrimethylenediamine containing 3 and 10 moles of ethylene oxide per mole of diamine, respectively.

The fatty diamines include mono- or dialkyl, symmetrical or asymmetrical ethylene diamines, propane diamines (1,2, or 1,3), and polyamine analogs of the above. Suitable commercial fatty diamines are Duomeen C (N-coco-1,3-diaminopropane), Duomeen S (N-soya-1,3-diaminopropane),DuomeenT(N-tallow-1,3-diaminopropane), and Duomeen O (N-oleyl-1,3-diaminopropane). "Duomeens" are commercially available from Armak Chemical Co., Chicago, Illinois. In one embodiment, the secondary amines may be cyclic amines such as piperidine, piperazine, morpholine, etc.

The metal salts of the phosphorus acid esters may be prepared by the reaction of a metal base with the phosphorus acid ester. The metal base may be any metal compound capable of forming a metal salt. Examples of metal bases include metal oxides, hydroxides, carbonates, sulfates, borates, or the like. The metals of the metal base include Group IA, IIA, IB through VIIB, and VIII metals (CAS version of the Periodic Table of the Elements). These metals include the alkali metals, alkaline earth metals and transition metals. In one embodiment, the metal is a Group IIA metal, such as calcium or magnesium, Group IIB metal, such as zinc, or a Group VIIB metal, such as manganese. In one embodiment, the metal is magnesium, calcium, manganese or zinc. Examples of metal compounds which may be reacted with the phosphorus acid include zinc hydroxide, zinc oxide, copper hydroxide, copper oxide, etc.

In one embodiment, the phosphorus or boron containing antiwear or extreme pressure agent (C) is a metal thiophosphate, preferably a metal dithiophosphate. The metal thiophosphate is prepared by means known to those in the art. Examples of metal dithiophosphates include zinc isopropyl, methylamyl dithiophosphate, zinc isopropyl isooctyl dithiophosphate, barium di(nonyl) dithiophosphate, zinc di(cyclohexyl) dithiophosphate, zinc di(isobutyl) dithiophosphate, calcium di(hexyl) dithiophosphate, zinc isobutyl isoamyl dithiophosphate, and zinc isopropyl secondary-butyl dithiophosphate.

The following Examples P-3 to P-6 exemplify the preparation of useful phosphorus acid ester salts.

Example P-3

A reaction vessel is charged with 217 grams of the filtrate from Example P-1. A commercial aliphatic primary amine (66 grams), having an average molecular weight of 191 in which the aliphatic radical is a mixture of tertiary alkyl radicals containing from 11 to 14 carbon atom, is added over a period of 20 minutes at 25-60°C. The resulting product has a phosphorus content of 10.2% by weight, a nitrogen content of 1.5% by weight, and an acid number of 26.3.

Example P-4

The filtrate of Example P-2 (1752 grams) is mixed at 25-82°C with 764 grams of the aliphatic primary amine used in of Example P-3. The resulting product has 9.95% phosphorus, 2.72% nitrogen, and 12.6% sulfur.

Example P-5

Phosphorus pentoxide (852 grams) is added to 2340 grams of isooctyl alcohol over a period of 3 hours. The temperature increases from room temperature but is maintained below 65°C. After the addition is complete the reaction mixture is heated to 90°C and the temperature is maintained for 3 hours. Diatomaceous earth is added to the mixture, and the mixture is filtered. The filtrate has 12.4% phosphorus, a 192 acid neutralization number (bromophenol blue) and a 290 acid neutralization number (phenolphthalein).

The above filtrate is mixed with 200 grams of toluene, 130 grams of mineral oil, 1 gram of acetic acid, 10 grams of water and 45 grams of zinc oxide. The mixture is heated to 60-70°C under a pressure of 30 mm Hg. The resulting product mixture is filtered using a diatomaceous earth. The filtrate has 8.58% zinc and 7.03% phosphorus.

Example P-6

Phosphorus pentoxide (208 grams) is added to the product prepared by reacting 280 grams of propylene oxide with 1184 grams of O,O'-di-isobutylphosphorodithioic acid at 30-60°C. The addition is made at a temperature of 50-60°C and the resulting mixture is then heated to 80°C and held at that temperature for 2 hours. The commercial aliphatic primary amine identified in Example P-3 (384 grams) is added to the mixture, while the temperature is maintained in the range of 30-60°C. The reaction mixture is filtered through diatomaceous earth. The filtrate has 9.31% phosphorus, 11.37% sulfur, 2.50% nitrogen, and a base number of 6.9 (bromophenol blue indicator).

In another embodiment, the phosphorus or boron antiwear or extreme pressure agent (C) is a metal salt of (a) at least one dithiophosphoric acid and (b) at least one aliphatic or alicyclic carboxylic acid. The dithiophosphoric acids are described above. The carboxylic acid may be a monocarboxylic or polycarboxylic acid, usually containing from 1 to about 3, or just one carboxylic acid group. The preferred carboxylic acids are those having the formula $R_{12}COOH$, wherein R_{12} is an aliphatic or alicyclic hydrocarbyl group preferably free from acetylenic unsaturation. R_{12} generally contains from about 2 up to about 40, or from about 4 up to about 24, or to up about 12 carbon atoms. In one embodiment, R_{12} contains fromabout 4 up to about 12, or from about 6 up to about 8 carbon atoms. In one embodiment, R_{12} is an alkyl group. Suitable acids include the butanoic, pentanoic, hexanoic, octanoic, nonanoic, decanoic, dodecanoic, octodecanoic and eicosanoic acids, as well as olefinic acids such as oleic, linoleic, and linolenic acids and linoleic acid dimer. A preferred carboxylic acid is 2-ethylhexanoic acid.

The metal salts may be prepared by merely blending a metal salt of a dithiophosphoric acid with a metal salt of a carboxylic acid in the desired ratio. The ratio of equivalents of dithiophosphoric acid to carboxylic acid is from about 0.5 up to about 400 to 1. The ratio may be from 0.5 up to about 200, or up to about 100, or up to about 50, or up to about 20 to 1. In one embodiment, the ratio is from 0.5 up to about 4.5 to one, or about 2.5 up to about 4.25 to one. For this purpose, the equivalent weight of a dithiophosphoric acid is its molecular weight divided by the number of -PSSH groups therein, and the equivalent weight of a carboxylic acid is its molecular weight divided by the number of carboxy groups therein.

A second and preferred method for preparing the metal salts useful in this invention is to prepare a mixture of the acids in the desired ratio, such as those described above for the metal salts of the individual metal salts, and to react the acid mixture with one of the above described metal compounds. When this method of preparation is used, it is frequently possible to prepare a salt containing an excess of metal with respect to the number of equivalents of acid present; thus the metal salts may contain as many as 2 equivalents and especially up to about 1.5 equivalents of metal per equivalent of acid may be prepared. The equivalent of a metal for this purpose is its atomic weight divided by its valence. The temperature at which the metal salts are prepared is generally between about 30°C and about 150°C, or up to about 125°C. U.S. Patents 4,308,154 and 4,417,990 describe procedures for preparing these metal salts and disclose a number of examples of such metal salts.

In another embodiment, the phosphorus or boron containing antiwear or extreme pressure agent (C) is a phosphite. The phosphite may be a di-or trihydrocarbyl phosphite. Generally, each hydrocarbyl group independently has from 1 up to about 24, or from about 2 up to about 18, or up to about 8 carbon atoms. Examples of specific hydrocarbyl groups include propyl, butyl, hexyl, heptyl, octyl, oleyl, linoleyl, stearyl, phenyl, naphthyl, heptylphenol, and mixtures of two or more of thereof. In one embodiment, each hydrocarbyl group is independently propyl, butyl, pentyl, hexyl, heptyl, oleyl, or phenyl. Phosphites and their preparation are known and many phosphites are available commercially. Particularly useful phosphites are dibutyl phosphite, trioleyl phosphite and triphenyl phosphite.

In one embodiment, the phosphorus or boron containing antiwear or extreme pressure agent (C) is a phosphorus containing amide. Phosphorus containing amides may be prepared by the reaction of one of the above describe phosphorus acids, preferably a dithiophosphoric acid, with an one of the above described unsaturated amides. The reaction product of the phosphorus acid and the unsaturated amide may be further reacted with a linking or a coupling compound, such as formaldehyde or paraformaldehyde. Phosphorus containing amides are known in the art and are disclosed in U.S. Patents 4,670,169, 4,770,807, and 4,876,374.

In one embodiment, the phosphorus or boron antiwear or extreme pressure agent (C) is a phosphorus containing carboxylic ester. Phosphorus containing carboxylic esters may be prepared by reaction of one of the above-described phosphorus acids, preferably a dithiophosphoric acid, and one of the above described unsaturated carboxylic acids or esters. If a carboxylic acid is used, the ester may then be formed by subsequent reaction of the phosphoric acid-unsaturated carboxylic acid adduct with an alcohol, such as those described herein.

In one embodiment, the phosphorus or boron containing antiwear or extreme pressure agent (C) is a reaction product of a phosphorus acid, preferably a dithiophosphoric acid, and one of the above described vinyl ethers.

In another embodiment, the phosphorus or boron containing antiwear or extreme pressure agent (C) is an alkali metal borate. Alkali metal borates are generally a hydrated particulate alkali metal borate which are known in the art. Alkali metal borates include mixed alkali and alkaline earth metal borates. These alkali metal borates are available commercially. Representative patents disclosing suitable alkali metal borates and their methods of manufacture include U.S. 3,997,454; 3,819,521; 3,853,772; 3,907,601; 3,997,454; and 4,089,790.

In another embodiment, the phosphorus or boron containing antiwear or extreme pressure agent (C) is a borated overbased metal salt. Borated overbased compounds are generally prepared by reacting an overbased metal salt, such as a carbonated overbased metal salt with a boron compound. The boron compounds include boron oxides, boron acids, boric acid, boron anhydrides, boron amides and various borate esters, such as mono-, di-, and tri-organic esters of boric acid with alcohols or phenols. Preferred borate esters are those derived from alcohols having less than about 8 carbon atoms.

The overbased metal salts include basic salts (i.e., overbased salts) of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, phenols or organic phosphorus acids. The phosphorus acids include those prepared by the treatment of a polyalkene with a phosphorizing agent, such as phosphorus pentasulfide. The most commonly used metals are sodium, potassium, lithium, calcium, and magnesium. The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The overbased salts and borated overbased salts are prepared by means known to those in the art. Examples of borated overbased compounds include borated overbased sodium alkylbenzene sulfonate, sodium borated overbased polybutenyl ($\overline{M}n$=950) substituted succinate, and borated overbased magnesium alkylbenzene sulfonate.

Patents describing overbased salts, methods of making the salts and components for making the same include U.S. Patents 2,501,731; 2,616,911; 2,777,874; 3,384,585; 3,320,162; 3,488,284 and 3,629,109. Borated overbased compositions, lubricating compositions contain the same and methods of preparing borated overbased compositions are found in U.S. Patents 4,744,920, 4,792,410, and PCT publication WO 88/03144.

In another embodiment, the phosphorus or boron antiwear or extreme pressure agent (C) is a borated fatty amine. Borated amines may be prepared by reacting one or more of the above boron compounds, such as boric acid or borate ester, with a fatty amine, e.g. an amine having from about four to about eighteen carbon atoms. Borated fatty amines may be prepared by reacting the amine with the boron compound at about 50°C to about 300°C, preferably about 100°C to about 250°C, and at a ratio of 3:1 to 1:3 equivalents of amine to equivalents of boron compound.

In another embodiment, the phosphorus or boron containing antiwear or extreme pressure agent (C) is a borated epoxide. Borated fatty epoxides are generally the reaction products of one or more of the above boron compounds, with at least one epoxide. The epoxide is generally an aliphatic epoxide having at least 8, or at least about 10, or at least about 12, up to about 24, or up to about 20 carbon atoms. Examples of useful aliphatic epoxides include heptyl oxide, octyl oxide, stearyl oxide, oleyl oxide and the like. Mixtures of epoxides may also be used, for instance commercial mixtures of epoxides having from about 14 to about 16 carbon atoms and from about 14 to about 18 carbon atoms. The borated fatty epoxides are generally known and are disclosed in U.S. Patent 4,584,115.

In another embodiment, the phosphorus or boron containing antiwear or extreme pressure agent (C) is a borated phospholipid. Borated phospholipids may be prepared by reacting a combination of a phospholipid and a boron compound. Optionally, the combination may include an amine, an acylated nitrogen compound, such as reaction products of carboxylic acrylating agents and polyamines, a carboxylic ester, such as reaction products of carboxylic acrylating agents and alcohols and optionally amines, a Mannich reaction product, or a basic or neutral metal salt of an organic acid compound. Phospholipids, sometimes referred to as phosphatides and phospholipins, may be natural or synthetic. Naturally derived phosliholipids include those derived from fish, fish oil, shellfish, bovine brain, chicken eggs, sunflowers, soybean, corn, and cottonseed. Phospholipids may be derived from microorganisms, including blue-green algae, green algae, and bacteria.

The reaction of the phospholipid, the boron compound, and the optional components usually occurs at a temperature from about 60°C, or about 90°C up to about 200°C, up to about 150°C. The reaction is typically accomplished in about 0.5, or about 2 up to about 10 hours. Generally, from one equivalent to about three equivalents of the phospholipid are reacted with each boron atom of the boron compound. An equivalent of phospholipid is determined by the number of phosphorus atoms in the phospholipid. The equivalent of boron compound is determined by the number of boron atoms in the boron compound. When the combination includes additional components, one atom of the boron compound is reacted with from one to about three equivalents of the combination. The equivalents of the combination is determined by the total equivalents of the phospholipid and the additional component.

Lubricants

As previously indicated, the combination of a dithiocarbamate compound (A) and an organic polysulfide (B) is useful in lubricants where they can function primarily as antiwear, antiweld, extreme pressure, anticorrosion, antioxidation and/or friction modifying agents. They can be employed in a variety of lubricants based on diverse oils of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. These lubricants include crankcase lubricating oils for sparkignited and compression-ignited internal combustion engines, including automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad diesel engines, and the like. They can also be used in gas engines, stationary power engines and turbines and the like. 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 compositions can also benefit from the incorporation therein of the compositions of the present invention. They may also be used in lubricants for wirerope, walking cam, way, rock drill, chain and conveyor belt, worm gear, bearing, and rail and flange applications.

The combination of the dithiocarbamate containing compound and the organic polysulfide may be used in lubricants or in concentrates. A concentrate may contain the combination or other components used in preparing fully formulated lubricants. A concentrate generally also contains a substantially inert organic diluent, which may be selected from kerosene, mineral distillates, or one or more of the oils of lubricating viscosity discussed below. In one embodiment, the concentrates contain from about 0.01%, or from about 0.1%, or from about 1% up to about 70% or up to about 80%, even up to about 90% by weight of the combination.

The dithiocarbamate compound (A) and the organic polysulfide (B) may be present in a final product, blend, or concentrate in any amount effective to act as an antiwear, antiweld, and/or extreme pressure agent in lubricating compositions. Generally the components are each independently present in the lubricating composition in an amount from about 0.01%, or from about 0.1%, or from about 0.5%, or from about 1% up to about 10%, or up to about 5% by weight. In one embodiment, when the components are used in oils, such as gear oils, they are each preferably present in an amount from about 0.5%, or from about 1%, or from about 1.5%

up to about 8%, or up to 5%, by weight of the lubricating composition. When the dithiocarbamate compound and the organic polysulfide are used in hydraulic fluids, they are each generally present in an amount from about 0.01%, or from about 0.3% up to about 2%, or up to about 1% by weight of the hydraulic fluid.

In one embodiment, the lubricating composition contains less than about 2%, or less than about 1.5%, or less than about 1.0%, or less than about 0.5% by weight of reaction product of a polyisobutenyl substituted succinic anhydride and a polyalkylene polyamine. In another embodiment, the lubricating compositions, such as gear lubricants, contain less than 2%, or less than 1.5%, or less than 1% by weight of a dispersant, such as those described herein. The dispersants may include carboxylic dispersants, amine dispersants, Mannich dispersants, post-treated dispersants and polymeric dispersants.

The lubricating compositions and methods of this invention may employ an oil of lubricating viscosity, including natural or synthetic lubricating oils and mixtures thereof. Natural oils include animal oils, vegetable oils, mineral lubricating oils, and solvent or acid treated mineral oils. Synthetic lubricating oils include hydrocarbon oils (polyalphaolefins), halo-substituted hydrocarbon oils, alkylene oxide polymers, esters of dicarboxylic acids and polyols, esters of phosphorus-containing acids, polymeric tetrahydrofurans and silicon-based oils. Unrefined, refined, and rerefined oils, either natural or synthetic, may be used in the compositions of the present invention. A description of oils of lubricating viscosity occurs in U.S. Patent 4,582,618 (column 2, line 37 through column 3, line 63, inclusive).

In one embodiment, the oil of lubricating viscosity or a mixture of 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 number of at least about SAE 65, or at least about SAE 75. The lubricating composition may also have a so-called multigrade rating such as SAE 75W-80, 75W-90, 75W-90, or 80W-90. 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. Preferably the viscosity improver is a polyolefin or polymethacrylate, more preferably polymethacrylate. Viscosity improvers available commercially include Acryloid™ viscosity improvers available from Rohm & Haas; Shellvi™ rubbers available from Shell Chemical; and Lubrizol 3174 available from The Lubrizol Corporation.

In another embodiment, the oil of lubricating viscosity is selected to provide lubricating compositions for crankcase applications, such as for gasoline and diesel engines. Typically, the lubricating compositions are selected to provide an SAE crankcase viscosity number of 10W, 20W, or 30W lubricants. The lubricating composition may also have a so called multigrade rating such as SAE 5W-30, 10W-30, 10W-40, 20W-50, etc. As described above, multi-grade lubricants include a viscosity improver which is formulated with the oil of lubricating viscosity to provide the above lubricant grades.

Other Additives

The invention also contemplates the use of other additives together with the combination of a dithiocarbamate compound and an organic polysulfide. Such additives include, for example, detergents and dispersants, corrosion- and oxidation-inhibiting agents, pour point depressing agents, extreme pressure agents, antiwear agents, color stabilizers and anti-foam agents.

The detergents are exemplified by oil-soluble neutral and basic salts (i.e. overbased salts) of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, phenols or organic phosphorus acids, such as those described above. The oil-soluble neutral or basic salts of alkali or alkaline earth metal salts may also be reacted with a boron compound. Boron compounds are described above. The overbased and borated overbased metal salts are described above.

Dispersants are known in the art and the following are illustrative.

(1) "Carboxylic dispersants" are the reaction products of carboxylic acids (or derivatives thereof) containing at least about 34 or at least about 54 carbon atoms and nitrogen containing compounds (such as amine), organic hydroxy compounds (such as phenols and alcohols), and/or basic inorganic materials. These reaction products include imide, amide, and ester reaction products of carboxylic acylating agents. The carboxylic dispersants are generally prepared by reacting one or more of hydrocarbyl substituted carboxylic acylating agent with an amine, such as a polyethylenepolyamine, or hydroxy containing compound such as an alcohol. The hydrocarbyl group may be derived from a polyalkene having a number average molecular weight from about 800 up to about 5000, or up to about 2500. Examples of these materials include succinimide dispersants and carboxylic ester dispersants. Examples of these "carboxylic dispersants" are described in British Patent 1,306,529 and in many U.S. Patents including the following: 3,219,666,

3,316,177, 3,340,281, 3,351,552, 3,381,022, 3,433,744, 3,444,170, 3,467,668, 3,501,405, 3,542,680, 3,576,743, 3,632,511, 4,234,435, and Re 26,433.

(2) "Amine dispersants" are the reaction products of relatively high molecular weight aliphatic or alicyclic halides and amines, preferably polyalkylene substituted polyamines. Examples thereof are described for example, in the following U.S. Patents: 3,275,554, 3,438,757, 3,454,555, and 3,565,804.

(3) "Mannich dispersants" are the reaction products of alkylphenols and aldehydes (especially formaldehyde) and amines (especially amine condensates and polyalkylenepolyamines). The materials described in the following U.S. Patents are illustrative: 3,036,003, 3,236,770, 3,414,347, 3,448,047, 3,461,172, 3,539,633, 3,586,629, 3,591,598, 3,634,515, 3,725,480, 3,726,882, and 3,980,569.

(4) "Post-treated dispersants" are the products obtained by post-treating the carboxylic, amine or Mannich dispersants with reagents such as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, phosphorus compounds or the like. Exemplary materials of this kind are described in the following U.S. Patents: 3,200,107, 3,282,955, 3,367,943, 3,513,093, 3,639,242, 3,649,659, 3,442,808, 3,455,832, 3,579,450, 3,600,372, 3,702,757,and 3,708,422.

(5) "Polymeric dispersants" are interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides and poly-(oxyethylene)-substituted acrylates. Polymeric dispersants include esters of styrene-maleic anhydride copolymers. Examples thereof are disclosed in the following U.S. Patents: 3,329,658, 3,449,250, 3,519,656, 3,666,730, 3,687,849, and 3,702,300.

Auxiliary extreme pressure agents and corrosion- and oxidation-inhibiting agents which may be included in the lubricants of the invention are exemplified by chlorinated aliphatic hydrocarbons, such as chlorinated wax; sulfurized alkylphenol; phosphosulfurized hydrocarbons, such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium diheptylphenyl dithiocarbamate. Many of the above-mentioned extreme pressure agents and corrosion- and oxidation-inhibitors also serve as antiwear agents.

Pour point depressants are additives often included in the lubricating oils described herein. Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and polymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants useful for the purposes of this invention, techniques for their preparation and their uses are described in U.S. Patents 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,878; and 3,250,715.

Antifoam agents are used to reduce or prevent the formation of stable foam. Typical antifoam agents include silicones or organic polymers. Additional antifoam compositions are described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162.

The following examples relate to lubricating compositions containing the combination of a dithiocarbamate compound and an organic polysulfide.

Example I

A lubricant is prepared by incorporating 2% by weight of the dithiocarbamate compound prepared by reacting dibutyl amine, carbon disulfide and methyl acrylate and 2% by weight of the product of Example 1 into a SAE 10W-40 lubricating oil mixture.

Example II

A gear lubricant is prepared by incorporating 2.5% by weight of the product of Example 2 and 2% of the product of Example 1 into an SAE 80W-90 lubricating oil mixture.

Example III

A gear lubricant is prepared by incorporating 2% by weight of the dithiocarbamic compound of Example I, 1.9% by weight of the product of Example 1; 1.5% by weight of the product of Example P-3 into an SAE 80W-90 lubricating oil mixture.

Example IV

A lubricant is prepared as described in Example III except a SAE 10W-40 lubricating oil mixture is used in place of the SAE 80W-90 lubricating oil mixture.

Example V

A gear lubricant is prepare by incorporating 2.2% by weight of a dithiocarbamate compound prepared by reacting diamylamine, carbon disulfide and acrylamide, 2% by weight of the product of Example 1, and 1% by weight of a borated overbased compound prepared by reacting boric acid with a sodium overbased alkyl benzene sulfonic acid, having a metal ratio of 19, into an SAE 80W-90 lubricating oil mixture.

Example VI

A lubricant is prepared as described in Example V except 0.8% by weight of a borated dispersant prepared by a reacting boric acid with the reaction product of a polybutenyl ($\overline{M}$n 950) substituted succinic acylating agent and a polyalkylene polyamine is included in the lubricant.

Example VII

A hydraulic fluid is prepared by incorporating 0.5% by weight of the dithiocarbamate compound of Example V, 0.1% by weight of the product of Example 1, 0.005% by weight tolyltriazole, and 0.25% by weight of 2-6-di-tertiary butyl phenol into a hydraulic base stock lubricating oil mixture.

Example VIII

A oil based metalworking fluid is prepared by incorporating 2.5% parts by weight of the dithiocarbamate compound of Example I and 2.5% by weight of the product of Example 1 into a metalworking lubricating oil mixture.

Grease

Where the lubricant is to be used in the form of a grease, the lubricating oil generally is employed in an amount sufficient to balance the total grease composition and, generally, the grease compositions will contain various quantities of thickeners and other additive components to provide desirable properties. The dithiocarbamate compound and the organic polysulfide are each independently present in an amount from about 0.5% up to about 10%, or from about 1% up to about 5% by weight.

A wide variety of thickeners can be used in the preparation of the greases of this invention. The thickener is conveniently employed in an amount from about 0.5 to about 30 percent, and preferably from 3 to about 15 percent by weight of the total grease composition. Including among the thickeners are alkali and alkaline earth metal soaps of fatty acids and fatty materials having from about 12 to about 30 carbon atoms. The metals are typified by sodium, lithium, calcium and barium. Examples of fatty materials include stearic acid, hydroxystearic acid, stearin, oleic acid, palmitic acid, myristic acid, cottonseed oil acids, and hydrogenated fish oils.

Other thickeners include salt and salt-soap complexes, such as calcium stearate-acetate (U.S. Patent 2,197,263), barium stearate-acetate (U.S. Patent 2,564,561), calcium stearate-caprylate-acetate complexes (U.S. Patent 2,999,066), calcium salts and soaps of low-intermediate- and high-molecular weight acids and of nut oil acids, aluminum stearate, and aluminum complex thickeners. Useful thickeners include hydrophilic clays which are treated with an ammonium compound to render them hydrophobic. Typical ammonium compounds are tetraalkyl ammonium chlorides. These clays are generally crystalline complex silicates. These clays include bentonite, attapulgite, hectorite, illite, saponite, sepiolite, biotite, vermiculite, zeolite clays and the like.

Example G-1

A grease is prepared by incorporating 0.5% by weight of the dithiocarbamate compound of Example I and 0.5% by weight of the product of Example 1 into a Southwest Petro-chem Lithium 12 hydroxy base grease.

Example G-2

A grease is prepared by incorporating 0.25% by weight of the dithiocarbamate compound of Example I, 0.25% by weight of the product of Example 1, 0.5% by weight of the product of Example P-3, and 1% by weight of tolyltriazole into a Southwest Petro-Chem Lithium 12 hydroxy base grease.

Aqueous Compositions

The invention also includes aqueous compositions generally characterized by an aqueous phase with the combination of the dithiocarbamate compound and the organic polysulfide dispersed or dissolved in said aqueous phase. The water-based functional fluids may be in the form of solutions; or micelle dispersions or microemulsions which appear to be true solutions. Preferably, this aqueous phase is a continuous aqueous phase although, in some embodiments, the aqueous phase can be a discontinuous phase.

These aqueous compositions usually contain at least about 25% by weight water. Such aqueous compositions encompass both concentrates containing about 25% to about 80% by weight, or from about 40% to about 65% water; and water-based functional fluids containing generally over about 80% by weight of water. The concentrates generally contain less than about 50%, or less than about 25%, or less than about 15%, and or less than about 6% hydrocarbon oil. The hydrocarbon oil may be one or more of the above oils of lubricating viscosity. The water-based functional fluids generally contain less than about 15%, or less than about 5%, and or less than about 2% hydrocarbon oil. The dithiocarbamate compound and the organic polysulfide are preferably each independently present in the aqueous compositions in an amount from about 0.2%, or about 0.5%, or about 0.75% up to about 10%, or to about 5%, or to about 2.5% of the aqueous composition.

These concentrates and water-based functional fluids can optionally include other conventional additives commonly employed in water-based functional fluids. These other additives include surfactants; thickeners; oil-soluble, water-insoluble functional additives such as antiwear agents, extreme pressure agents, dispersants, etc.; and supplemental additives such as corrosion-inhibitors, shear stabilizing agents, bactericides, dyes, water-softeners, odor masking agents, antifoam agents and the like.

The surfactants that are useful in the aqueous compositions of the invention can be of the cationic, anionic, nonionic or amphoteric type. Many such surfactants of each type are known to the art. See, for example, McCutcheon's "Emulsifiers & Detergents", 1981, North American Edition, published by McCutcheon Division, MC Publishing Co., Glen Rock, New Jersey, U.S.A. Specific nonionic surfactant types include alkylene oxide treated products, such as ethylene oxide treated phenols and ethylene oxide/propylene oxide block copolymers, alcohols, esters, such as glycerol esters, amines, such as the above hydroxy amines, and amides. Examples of surfactants include alkylene oxide treated alkylphenols, sold commercially under the tradename of Triton® such as Triton® X-100, available commercially from Union Carbide Chemical Company; alkoxylated amines available from Akzo Chemie under the names ETHODUOMEEN® (polyethoxylated diamines), ETHOMEEN® (poly-ethoxylated aliphatic amines), ETHOMID® (polyethoxylated amides), and ETHOQUAD (polyethoxylated quaternary ammonium chlorides); tall oil acids, sold under the trade name Unitol DT/40 (available from Union Camp Corp); and the above described hydroxyhydrocarbyl amines.

Among the useful anionic surfactant types are the widely known carboxylate soaps, metal organosulfates, metal sulfonates, metal sulfonylcarboxylates, and metal phosphates. Useful cationic surfactants include nitrogen compounds such as amine oxides and the well-known quaternary ammonium salts. Amphoteric surfactants include amino acid-type materials and similar types.

Surfactants are generally employed in effective amounts to aid in the dispersal of the various additives, particularly in the functional additives discussed below of the invention. Preferably, the concentrates can contain up to about 75% by weight, or from about 10% to about 75% by weight of one or more of these surfactants. The water-based functional fluids can contain up to about 15% by weight, or from about 0.05% to about 15% by weight of one or more of these surfactants.

Often the aqueous compositions of this invention contain at least one thickening agent. Generally, these thickening agents can be polysaccharides, including cellulose ethers and esters, such as hydroxyethyl cellulose and the sodium salt of carboxymethyl cellulose, synthetic thickening polymers, or mixtures of two or more of these. Specific examples of such gums are gum agar, guar gum, gum arabic, algin, dextrans, xanthan gum and the like. A thickener can also be synthetic thickening polymers. Representative of them are polyacrylates, polyacrylamides, hydrolyzed vinyl esters, water-soluble homo- and interpolymers of acrylamidoalkane sulfonates and other comonomers such as acrylonitrile, styrene and the like.

Preferred thickening agents include the water- dispersible reaction products formed by reacting at least one hydrocarbyl-substituted succinic acid and/or anhydride wherein the hydrocarbyl group has from about 8, or about 12, or about 16, up to about 40, or to about 30, or to about 24, about 18 carbon atoms, with at least one water-dispersible amine terminated poly(oxyalkylene) or at least one water-dispersible hydroxy-terminated polyoxyalkylene. Examples of water-dispersible amine-terminated poly(oxyalkylene)s that are useful in accordance with the present invention are disclosed in U.S. Patents 3,021,232; 3,108,011; 4,444,566; and Re 31,522. Water-dispersible amine terminated poly(oxyalkylene)s that are useful are commercially available from the Texaco Chemical Company under the trade name Jeffamine®. Water-dispersible hydroxy-terminated polyoxyalkylenes are commercially available from BASF Wyandotte Corporation under the tradename "Tetronic" and "Pluronic". Useful hydroxy-terminated polyoxyalkylenes are disclosed in U.S. Patents 2,674,619 and 2,979,528.

The reaction between the succinic acid and/or anhydride and the amine- or hydroxy-terminated polyoxyalkylene is described in U.S. Patent 4,659,492.

When the thickener is formed using an amine-terminated poly(oxyalkylene), the thickening characteristics of said thickener can be enhanced by combining it with at least one of the above surfactant. When such surfactants are used, the weight ratio of thickener to surfactant is generally in the range of from about 1:5 to about 5:1, preferably from about 1:1 to about 3:1.

Typically, the thickener is present in a thickening amount in the aqueous compositions of this invention. When used, the thickener is generally present at a level of up to about 70% by weight, or from about 20% to about 50% by weight of the concentrates of the invention. The thickener is preferably present at a level in the range of from about 1.5% to about 10% by weight, or from about 3% to about 6% by weight of the functional fluids of the invention.

The functional additives that may also be included in the aqueous systems are typically oil-soluble, water-insoluble additives which function in conventional oil-based systems as extreme pressure agents, anti-wear agents, load-carrying agents, dispersants, friction modifiers, lubricity agents, etc. They can also function as anti-slip agents, film formers and friction modifiers. As is well known, such additives can function in two or more of the above-mentioned ways; for example, extreme pressure agents often function as load-carrying agents.

The term "oil-soluble, water-insoluble functional additive" refers to a functional additive which is not soluble in water above a level of about 1 gram per 100 parts of water at 25°C, but is soluble in mineral oil to the extent of at least 1 gram per liter at 25°C. These functional additives may also include certain solid lubricants such as graphite, molybdenum disulfide and polytetrafluoroethylene and related solid polymers. These functional additives can also include frictional polymer formers, which form materials which are dispersed in a liquid are believed to polymerize under operating conditions. A specific example of such materials is dilinoleic acid and ethylene glycol combinations which can form a polyester frictional polymer film. These materials are known to the art and descriptions of them are found, for example, in the journal "Wear", Volume 26, pages 369-392, and West German Published Patent Application 2,339,065.

Typically these functional additives are known metal or amine salts of organo sulfur, phosphorus, boron or carboxylic acids which are the same as or of the same type as used in oil-based fluids and are described above.

Many such functional additives are known to the art. For example, descriptions of additives useful in conventional oil-based systems and in the aqueous systems of this invention are found in "Advances in Petroleum Chemistry and Refining", Volume 8, edited by John J. McKetta, Interscience Publishers, New York, 1963, pages 31-38 inclusive; Kirk-Othmer "Encyclopedia of Chemical Technology", Volume 12, Second Edition, Interscience Publishers, New York, 1967, page 575 et seq.; "Lubricant Additives" by M.W. Ranney, Noyes Data Corporation, Park Ridge, N.J., U.S.A., 1973; and "Lubricant Additives" by C.V. Smallheer and R.K. Smith, The Lezius-Hiles Co., Cleveland, Ohio, U.S.A.

The functional additive can also be a film former such as a synthetic or natural latex or emulsion thereof in water. Such latexes include natural rubber latexes and polystyrene-butadienes synthetic latex.

The functional additive can also be an anti-chatter or anti-squawk agent. Examples of the former are the amide-metal dithiophosphate combinations such as disclosed in West German Patent 1,109,302; amine salt-azomethene combinations such as disclosed in British Patent Specification 893,977; or amine dithiophosphate such as disclosed in U.S. Patent 3,002,014. Examples of anti-squawk agents are N-acyl-sarcosines and derivatives thereof such as disclosed in U.S. Patents 3,156,652 and 3,156,653; sulfurized fatty acids and esters thereof such as disclosed in U.S. Patents 2,913,415 and 2,982,734; and esters of dimerized fatty acids such as disclosed in U.S. Patent 3,039,967.

Typically, the functional additive is present in a functionally effective amount. The term "functionally effective amount" refers to a sufficient quantity of an additive to impart desired properties intended by the addition of said additive.

The aqueous systems of this invention often contain at least one optional inhibitor for corrosion of either ferrous or non-ferrous metals or both. The inhibitor can be organic or inorganic in nature. Included are those described in "Protective Coatings for Metals" by Burns and Bradley, Reinhold Publishing Corporation, Second Edition, Chapter 13, pages 596-605. Specific examples of useful inorganic inhibitors include alkali metal nitrites, sodium di- and tripolyphosphate, potassium and dipotassium phosphate, alkali metal borate and mixtures of the same. Specific examples of organic inhibitors include hydrocarbyl amine and hydroxy-substituted hydrocarbyl amine neutralized acid compounds, such as neutralized phosphates and hydrocarbyl phosphate esters, neutralized fatty acids, neutralized aromatic carboxylic acids (e.g., 4-tertiarybutyl benzoic acid), neutralized naphthenic acids and neutralized hydrocarbyl sulfonates. Particularly useful amines include the alkanolamines such as ethanolamine, diethanolamine.

The aqueous systems of the present invention can also include at least one bactericide. Such bactericides are well known to those of skill in the art and specific examples can be found in the aforementioned McCutcheon publication "Functional Materials" under the heading "Antimicrobials" on pages 9-20 thereof.

The aqueous systems of the present invention can also include such other materials as dyes, e.g., an acid green dye; water softeners, e.g., ethylene- diaminetetraacetate sodium salt or nitrilotriacetic acid; odor masking agents, e.g., citronella, oil of lemon; antifreeze additive, e.g., ,ethylene glycol and analogous polyoxyalkylene polyols; and antifoamants, such as the well-known silicone antifoamant agents.

Discussion of aqueous compositions and components of aqueous systems occurs in U.S. Patent 4,707,301.

Examples IX-X

The following examples relate to aqueous compositions containing the combination of the dithiocarbamate compound and the organic polysulfide. The examples are prepared by mixing the components in a homogenizer.

	IX	X
100 neutral mineral oil	4.0	4.0
Water	95.0	95.0
Reaction product of diethylethanolamine and a polybutenyl-($\bar{M}n$=950)-substituted succinic anhydride	0.8	0.8
Dithiocarbamate of Example I	0.1	0.15
Product of Example 1	0.1	0.05

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification.

Claims

1. A lubricating composition comprising (A) at least one dithiocarbamate compound, (B) at least one organic polysulfide, optionally, (C) a phosphorus or boron antiwear or extreme pressure agent, and (D) a base fluid selected from (i) an oil of lubricating viscosity, (ii) water and a surfactant or thickener, and (iii) an oil of lubricating viscosity and a thickener.

2. The composition of claim 1 wherein (A) is a reaction product of (i) a dithiocarbamic acid or salt, and (ii) an unsaturated amide, acid, anhydride ester or ether.

3. The composition of either of claims 1 and 2 wherein (A) is a reaction product of (i) a dithiocarbamic acid or salt, and (ii) an acrylic ester of the formula $R^6R^7C=C(R^8)COOR^9$, wherein each R^6, R^7, and R^8 is independently hydrogen or a hydrocarbyl group, and R^9 is hydrogen, or a hydrocarbyl group containing from 1 to 24 carbon atoms.

4. The composition of any one of claims 1-3 wherein (A) is a reaction product of (i) a dithiocarbamic acid or salt, and (ii) methylacrylate, ethylacrylate, butylacrylate, pentylacrylate, hexylacrylate, methylmethacrylate, ethylmethacrylate, butylmethacrylate, pentylmethacrylate, or hexylmethacrylate.

5. The composition of any one of claims 1-4 wherein (B) is derived from an oil, a fatty acid or ester, an olefin, or a polyolefin.

6. The composition of any one of claims 1-5 wherein (B) is derived from an olefin is represented by the formula

$$R^{*1}R^{*2}C{=}CR^{*3}R^{*4},$$

wherein each of R^{*1}, R^{*2}, R^{*3} and R^{*4} is independently hydrogen, hydrocarbyl, $-C(R^{*5})_3$, $-COOR^{*5}$, $-CON(R^{*5})_2$, $-COON(R^{*5})_4$, -COOM, -CN, -X, $-YR^{*5}$ or -Ar, wherein each R^{*5} is independently hydrogen or hydrocarbyl group, with the proviso that any two R^{*5} groups can be hydrocarbylene or substituted hydrocarbylene whereby a ring of up to 12 carbon atoms is formed; M is one equivalent of a metal cation; X is halogen; Y is oxygen or divalent sulfur; Ar is an aryl or substituted aryl group of up to 12 carbon atoms.

7. The composition of any one of claims 1-6 wherein (B) is derived from an olefin containing from 2 to 8 carbon atoms.

8. The composition of any one of claims 1-7 wherein (C) is selected from (i) a phosphoric acid ester prepared by reacting a dithiophosphoric acid with an epoxide to form an intermediate, and the intermediate is further reacted with a phosphorus acid or anhydride, or a salt of the phosphoric acid ester, (ii) a phosphoric acid ester prepared by reacting a phosphorus acid or anhydride with at least one alcohol wherein each alcohol independently contains from 1 to 30 carbon atoms, or a salt of the phosphoric acid ester, (iii) a triarylphosphate, (iv) a phosphite, (v) a borated dispersant, (vi) an alkali metal or a mixed alkali metal, alkaline earth metal borate, (vii) a borated epoxide, (viii) a borated amine, (ix) a borated overbased metal salt, (x) a borated phospholipid; and (xi) a borate ester.

9. The composition of any one of claims 1-7 wherein (C) is selected from (i) an ammonia or amine salt of a phosphoric acid ester prepared by reacting a dithiophosphoric acid with an epoxide to form an intermediate, and the intermediate is further reacted with a phosphorus acid or anhydride, (ii) an ammonia or amine salt of a phosphoric acid ester prepared by reacting a phosphorus acid or anhydride with at least one alcohol wherein each alcohol independently contains from 1 to 30 carbon atoms, (iii) tricresylphosphate, and (iv) a dihydrocarbyl or trihydrocarbyl phosphite independently having from 1 to 30 carbon atoms in each hydrocarbyl group.

10. The composition of claim 8 or claim 9 wherein the dithiophosphoric acid is a dihydrocarbyl dithiophosphoric acid independently having from 1 to 24 carbon atoms in each hydrocarbyl group.

11. The composition of claims 9 wherein the amine is a tertiary aliphatic primary amine.

12. The composition of any one of claims 1-11 wherein the lubricating composition is a metal working fluid, a hydraulic fluid, a grease composition, an aqueous fluid, or a gear oil composition.

13. A concentrate comprising a substantially inert organic diluent and from 0.01 to 90% by weight of a combination of components (A) and (B) as defined in claim 1.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 5742

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	WO-A-87 05622 (THE LUBRIZOL CORPORATION) * page 9; examples IV,V,VI * * page 13; examples D,E,F; table I *	1-6,12,13	C10M135/00 C10M141/10 C10M141/12 C10M163/00 //(C10M135/00, 135:02,135:04, 135:18), (C10M141/10, 135:02,135:04, 135:18,137:02, 137:04, 137:10), (C10M141/12, 135:02,135:04, 135:18, 139:00), C10N40:04, C10N40:08,
D	& US-A-4 758 362 (B.BUTKE) ---		
X	US-A-4 609 480 (H. HATA) * column 2, line 5 - line 35 * * column 3, line 39 * * column 3, line 47 - line 55 * * column 3, line 44 - line 49 * ---	1-7,12,13	
X	EP-A-0 041 597 (R.T. VANDERBILT COMPANY) * claim 1 * * page 4, line 15 * * page 4, line 31 * * page 7; example 11 * ---	1,5-7,12,13	
X	WO-A-86 04601 (THE LUBRIZOL CORPORATION) * page 5, line 1 - line 11 * * page 9, line 24 - line 28 * * page 72, line 14 - line 19 * ---	1,5-9,12,13	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)** C10M
X	WO-A-86 04602 (THE LUBRIZOL CORPORATION) * page 4, line 17 - page 5, line 11 * * page 34, line 4 - line 7 * * page 34, line 25 - line 28 * ---	1,12,13	
P,X	US-A-5 246 605 (P.F. VARTANIAN) * claims 1,4,5 * ---	1,5,8,12	
P,X	EP-A-0 604 232 (THE LUBRIZOL CORPORATION) * page 19; example IX * * claims 7-9 * -----	1-6,8-13	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 November 1994	Hilgenga, K

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 5742

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)
			C10N40:20, C10N50:10
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 November 1994	Hilgenga, K

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X : particularly relevant if taken alone
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A : technological background
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