

Description

This invention relates to novel additives for functional fluids that are derived from a norbornyl reactant and O,O-dialkyldithiophosphoric acids. It has been discovered that these additives improve the extreme pressure, antiwear and antioxidant properties of functional fluids, e.g., lubricants and fuels, for use in internal combustion engines and the machinery of motorized vehicles.

O,O-Dialkyldithiophosphoric acid adducts of a norbornene reactant have been disclosed in the art. For example, in U.S. Patent 3,023,209, various dialkyldithiophosphoric acid esters of norbornene reactants are disclosed as possessing good insecticidal, fungicidal and miticidal properties. It is also disclosed that these compounds have properties rendering them useful as corrosion inhibitors, plasticizing agents, lubricating oil additives and flotation agents, etc.

U.S. Patent 3,962,105 discloses various diesters and/or ester lactones of norbornene and norbornane systems which are useful as seal swell additives.

In U.S. Patent 4,028,258, a transmission fluid is disclosed comprising an alkylene oxide adduct of a phosphosulfurized N-(hydroxyalkyl) alkenyl succinimide.

Insecticidal alkoxy and haloalkoxyphenol-phosphinyloxy and phosphinothioxy-1,3-isoindoledones are disclosed in U.S. Patent No. 3,401,175.

In U.S. Patent 2,644,002, dialkyldithiophosphoric acid esters of succinimides are disclosed as being adaptable for various uses such as insecticides, fungicides, plasticisers, corrosion inhibitors, flotation agents, and petroleum additives.

Diesters of 1,3-bis(carboxymethyl) adamantanes which are useful as oiling agents for synthetic fibers and as synthetic lubricating oil bases are disclosed in U.S. Patent 3,849,473.

None of the foregoing disclosures teach the norbornyl dialkyldithiophosphoric acid adducts of the present invention utilized as extreme pressure agents and antiwear agents for functional fluids to be used in internal combustion engines and the machinery of a motorized vehicle.

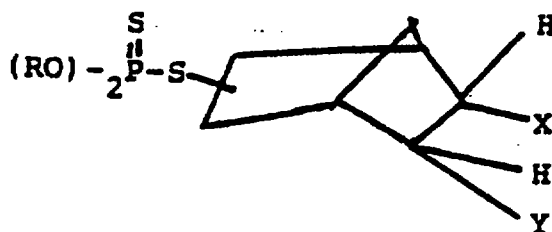
We have now found it possible to provide novel reaction products of O,O-dialkyldithiophosphoric acids with norbornene-containing reactants which have excellent activity as extreme pressure and antiwear agents.

We have also found it possible to provide functional fluids, e.g., lubricants and fuels comprising an extreme pressure and/or antiwear effective amount of the reaction products of the present invention.

Still further we have found it possible to provide additives and concentrates comprising a diluent/solvent and one or more of the norbornyl-containing reaction products of the present invention for formulating with functional fluids.

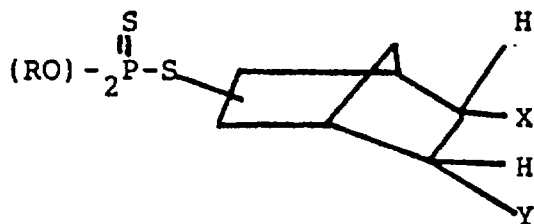
In addition, we have found it possible to provide a method for improving the load bearing characteristics of functional fluids used in motorized vehicles.

According to one aspect of the present invention, there is provided a lubricating composition comprising a major amount of an oil of lubricating viscosity and minor amount of a compound of the formula:



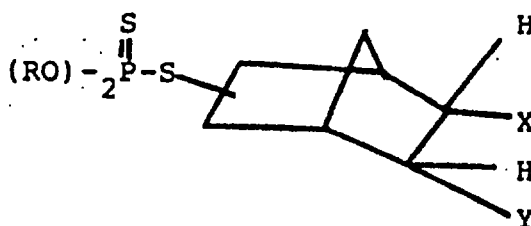
wherein R is, independently, alkyl or aryl and X and Y are independently selected from hydrogen, hydrocarbyl carboxy, a N-substituted carboxamide moiety, a thio- or dithiocarbamate moiety, a thioamide moiety, a thio acid or ester moiety, a hydrocarbyl phosphorus containing radical, or together are imide or N-hydrocarbyl substituted imide, provided that when X is alkyl carboxy, Y is not alkyl carboxy or hydrogen, and X and Y are not both hydrogen.

According to another aspect of the present invention there is provided a method for improving the load bearing properties of a lubricating composition of lubricating viscosity by admixing therewith a minor amount of an extreme pressure and antiwear agent of the formula:



wherein R is, independently, alkyl or aryl and X and Y are independently selected from hydrogen, hydrocarbyl carboxy, a N-substituted carboxamide moiety, a thio- or dithiocarbamate moiety, a thioamide moiety, a thio acid or ester moiety, a hydrocarbyl phosphorus containing radical, or together are imide or N-hydrocarbyl substituted imide, provided that when X is alkyl carboxy, Y is not alkyl carboxy or hydrogen, and X and Y are not both hydrogen.

According to a further aspect of the present invention there is provided a compound of the formula:



wherein R is, independently, alkyl or aryl and X and Y are independently selected from a N-substituted carboxamide moiety, a thioamide moiety, a thioester moiety, a dithioester moiety, a hydrocarbyl-containing dithiocarbamate moiety, hydrocarbylthio, a phosphate moiety, a phosphite moiety, a phosphonate moiety, a dithiophosphate moiety, a phosphoramidate moiety, or together represent imide or N-hydrocarbyl imide.

According to a further aspect of the present invention there is provided a lubricant additive comprising the compound of the present invention.

According to a further aspect of the present invention there is provided a concentrate for formulating lubricating compositions comprising from 1% to 99% by weight of a normally liquid, substantially inert organic solvent/diluent and at least one compound of the present invention.

According to a further aspect of the present invention there is provided a lubricating composition comprising a major amount of an oil of lubricating viscosity and a minor amount of at least one compound or at least one concentrate of the present invention.

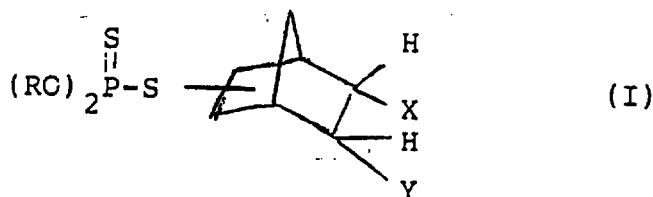
According to a further aspect of the present invention there is provided a method for improving the load bearing properties of a lubricating composition comprising admixing with a major amount of a lubricating composition, a minor amount of the compound or concentrate of the present invention.

According to a further aspect of the present invention there is provided an aqueous functional fluid comprising a minor amount of at least one compound of the present invention.

According to a further aspect of the present invention there is provided a grease composition comprising a minor amount of at least one compound of the present invention.

Various preferred features and embodiments of the invention will now be described by way of non-limiting example.

The norbornyl dialkyl dithiophosphate adducts of the present invention may be represented by the following formula:



As used herein, the terms "hydrocarbyl" or "hydrocarbon-based" denote a radical having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character within the context of this invention. Such radicals include the following:

(1) Hydrocarbon radicals; that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl or cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicyclic radicals, and the like, as well as cyclic radicals wherein the ring is completed through another portion of the molecule (that is, any two indicated substituents may together form an alicyclic radical). Such radicals are known to those skilled in the art; examples include, but are not limited to, methyl, ethyl, butyl, hexyl, octyl, decyl, dodecyl, tetradecyl, octadecyl, eicosyl, cyclohexyl, phenyl and naphthyl (all isomers being included).

(2) substituted hydrocarbon radicals; that is, radicals containing non-hydrocarbon substituents which, in the context of this invention, do not alter the predominantly hydrocarbon character of the radical. Those skilled in the art will be aware of suitable substituents (e.g, halo, hydroxy, alkoxy, carbalkoxy, nitro, alkylsulfoxy, mercapto, alkylthio, phosphono).

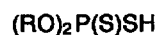
(3) Hetero radicals; that is, radicals which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, nitrogen, oxygen and sulfur.

Terms such as "alkyl-based radical," "aryl-based radical" and the like have meaning analogous to the above with respect to alkyl and aryl radicals and the like.

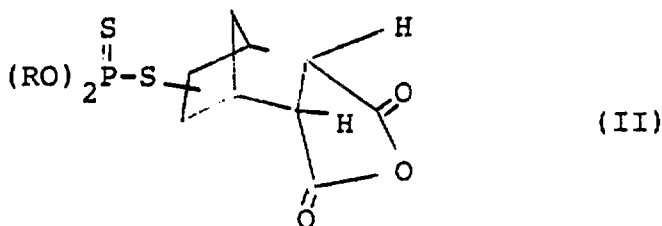
The radicals are usually hydrocarbon and especially lower hydrocarbon, the word "lower" denoting radicals containing up to ten (10) carbon atoms. They are preferably lower alkyl or aryl radicals, most often alkyl.

The preparation of the norbornyl reactant most preferably used to react with the dialkyldithiophosphoric acid, i.e., 5-norbornene-2,3-dicarboxylic anhydride is described in Onishchenko, *Diene Synthesis* (translation from the Russian by Israel Program for Scientific Translations, Jerusalem, 1964), Daniel Davey and Company, Publisher, New York (1964), pages 38, 47, 48-50 and references cited therein. In general, the preparation of 5-norbornene-2,3-dicarboxylic anhydride involves the Diels-Alder reaction or dicyclopentadiene with maleic anhydride. All isomer forms of the reaction products of the present invention are intended to be within the scope of this invention. For example, the above-referenced process may result in the production of both the exo and endo forms of this molecule. Both isomers are intended to be within the scope of the present invention.

The above norbornene dicarboxylic anhydride reactant is then reacted with a O,O-dialkyl-dithiophosphoric acid of the formula:



to form a norbornyl dialkyldithiophosphate, the structure of which may be represented by the following formula:



The alkyl group R of the dithiophosphoric acid ester may contain 1 to about 30 carbon atoms and preferably 3 to about 12 carbon atoms. As previously discussed, the anhydride group on the norbornyl ring may be in the endo or exo position or there may be mixtures thereof.

The above compound (represented by formula II) may be used as an additive for functional fluids. However, it is preferable to further react this compound with another reagent in order to enhance the properties desired to give a product represented by formula I.

Thus, II above may be reacted with various hydrocarbyl containing hydroxy, thiol, alkoxy, halo and the like reactants, as well as with basic salts, to yield products represented by the general formula I.

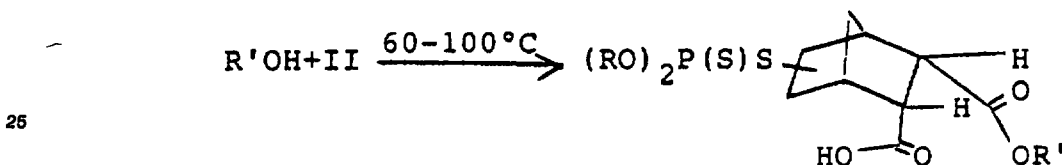
X and Y of formula I, independently, may be a primary or secondary C₂ to C₂₀₀ alkyl, aralkyl, aryl or alkylaryl (linear or branched), and may contain unsaturation, halogen or heteroatoms, alicyclic or heterocyclic rings, fused rings. It may also have pendant or incorporated functionality such as -OH, -NR₂, carbonyl in a diversity of structures (ester, carboxylic acid, aldehyde, ketone, amide or imide), corresponding thiocarbonyl moieties, thioesters, thioesters, dithioesters, thio- and dithiocarbamates), halogen, alkoxy-, alkylthio, mercapto, phosphate, phosphite, phosphonate, dithiophosphate and/or phosphoramidate moieties.

The half-ester acids may be used directly, or they may be converted to salts of metals selected from Group IA and IIA of the periodic table, as well as from the various transition series; which include Zn, Cd, Sn, Pb, Sb, Cu, Ni, Mn, Co, Fe, Cr, Ti and Zr, also the lanthanides, and the complex uranyl cation, UO₂²⁺.

Hydrolysis of the anhydride ring of structure II produces a dicarboxylic acid which may be oleophilic depending on the size and nature of the hydrocarbyl groups of the dithiophosphate ester portion of the molecule. Alternatively, this hydrolysis product may be hydrophilic if the hydrocarbyl groups of the dithiophosphate ester are lower alkyl. The hydrophilic product may be rendered water soluble by forming the corresponding salts of Group I and II metals, as well as salts of many of the metals discussed above.

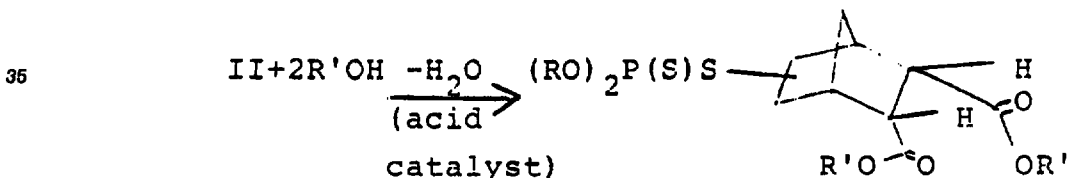
Salts of I may be made more soluble in oil or in aqueous solution by using appropriate alkyl (R) groups, and by amine complexation, where this is feasible (as with transition metal ions).

The above compounds may be prepared, in general, by reacting the particular reagent, e.g., an alcohol, an amine, an ester, a thiol or the like, with the anhydride II intermediate at an elevated temperature to obtain the desired product. For example, a monoester of II wherein Y in formula I is an acid group and X is an ester group may be prepared as illustrated below.



wherein R and R' are independently hydrocarbyl.

Diesters of II may be prepared, for example, by condensing II with two moles of alcohol, R'OH, generally using an acidic catalyst, such as methanesulfonic acid or p-toluenesulfonic acid.



wherein R' and R are independently hydrocarbyl.

It should be noted that a mixture of different alcohols may be used to give desired solubility and other properties.

Other than the carboxylic, keto, and aldehyde reaction products illustrated above, nitrogen, sulfur and phosphorus-containing derivatives are also within the scope of the present invention. In other words, where X and Y of formula I above are amide, urethane, thioamide, thioester, dithioester, mercapto, hydrocarbyl containing dithiocarbamate, phosphate, phosphite, phosphonate, dithiophosphate and/or phosphoramidate or together are imide or N-hydrocarbyl substituted imide.

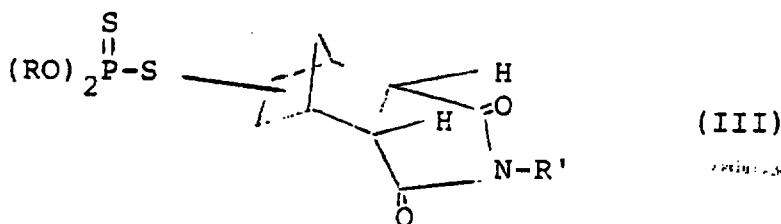
These heteroatom products may be derived from hydrocarbyl amines and amides; hydrocarbyl thiols; phosphorus containing, alcohols, esters and carbonates; hydrocarbyl alcohols; hydrocarbyl carbonates; hydrocarbyl carboxylic acids, anhydrides and esters; and hydrocarbyl halides.

It should be recognized that the end of the present invention represented products by formula (I) and species thereof may be prepared directly by reaction with the anhydride represented by formula (II) with the above discussed reactants or is a multiple step reaction which includes first reacting the anhydride of formula with another reagent, e.g., water followed by reaction with one or more of the above etc.

More specifically, the reagents that may be used to react with II include alkyl, aryl, alkenyl and heterocyclic amines such as methylamine, dimethylamine, amiline and substituted amilines, aminotriazoles, aminothiazoles, aminophenols, ethanolamine, diethanolamine, triethanolamine, morpholine, stearylamine,

oleylamine, palmylamine, lauryl-amine, eicosylamine, and the like; alkyl and alkenyl phosphites, phosphates and phosphonates such as hydroxy-methyl dibutyl phosphonate; alcohols such as ethanol, butanol, phenol, ethylene glycol, pentaerythritol as well as alkoxylated phenols, alkoxylated alcohols, alkoxylated amines, and the like; thiols such as ethanethiol, octanethiol, butanethiol and the like.

Where the specific reagent is a primary amine of formula "R'NH₂", reaction with the anhydride of structure II would be expected to produce first an amidic acid of structure I, wherein X and Y are, respectively, -CO₂H and -C(O)NHR'. Heating this product at moderate temperatures (e.g., approximately 85° to 135° C), causes the amidic acid to cyclize to the five-membered cyclic imide illustrated below



where R and R' are, independently, hydrocarbyl.

The *exo* or *endo* forms of the anhydride of formula II will form the corresponding *exo* or *endo* forms of the imides of formula III, providing that the compounds are not heated to extraordinarily high temperatures (i.e., greater than 160° C).

Other reagents known in art that fall within the above generic categories are intended to be within the scope of this invention, where as the above-listed specific reagents are presented for illustrative purposes only.

The reaction of the above-listed reagents with the norbornyl anhydride (II) is conducted under condensation conditions recognized in the art as discussed above to illustrate the preferred method for the preparation of the monoester, diester and other such derivatives. In general, the reaction is carried out in the presence of an acid or basic catalyst and/or at an elevated temperature. The product produced may otherwise be described as the reaction product of:

- (A) 5-norbornene-2,3-dicarboxylic anhydride; and
- (B) O,O-dialkyldithiophosphoric acid.

The above reaction product may then, as discussed above, further be reacted with an excess of a reactant (C) which contains a group reactive with the anhydride group of (A) or the (A)(B) adduct such that the reaction product is substantially monomeric. By monomeric, it is intended that the reaction is carried out such that the final reaction product contains substantially more to a minor amount of dimer and higher polymer products.

Alcohols are the preferred reactants, with alkylene glycols being the most preferred, particularly ethylene glycol.

Other alternative approaches to preparing the structures described above, which are depicted in formula I and II, are also feasible and in some instances may be more desirable for the preparation of certain of the structures which may contain specific groups. One such other method for preparing esters, half-esters, amidic acids or imides is to first form the corresponding esters, half-esters, amidic acids or imides of 5-norbornene-2,3-dicarboxylic anhydride, itself, followed by the reaction of the residual olefinic site with an O,O-dialkyl dithiophosphoric acid to form the desired saturated adducts.

The preparation of specific norbornyl compounds within the scope of the present invention is illustrated in the following examples. While these examples will show one skilled in the art how to operate within the scope of this invention, they are not to serve as a limitation on the scope of the invention where such scope is defined only in the claims. It is pointed out that in the following examples and elsewhere in the present specification and claims, all percentages and all parts are intended to express percent by weight and parts by weight unless otherwise clearly indicated.

EXAMPLE 1

Preparation of Adduct of Dialkylthiophosphoric Acid and 5-Norbornene-2,3-dicarboxylic Anhydride

5 A reaction flask was charged with 911 grams of 5-norbornene-2,3-dicarboxylic anhydride and 750 ml of toluene, heated to 70°C to effect dissolution. After purging the system with inert nitrogen gas, 1980 grams of O,O-di-isooctyl dithiophosphoric acid was added in a continuous manner at 80-90°C over a period of 2 hours. The homogeneous solution was held at 90°C for an additional 5 hours with stirring under a slow nitrogen sparge, during which time the strong acid number (bromphenol blue indicator) of the reaction
10 mixture decreased rapidly.

The solution was then vacuum-stripped to 90°-100°C/5 torr (665Pa) and filtered through a thin pad of diatomaceous earth to give 2723 grams (94% yield) of clear amber adduct (structure II; Risooctyl) having a bromphenol blue acid number of 2.6. The infrared spectrum of the liquid showed absorptions at 1780 and 1860cm⁻¹, indicative of 5-membered cyclic anhydride. Analysis: %S = 11.4; %P = 5.96.

EXAMPLE 2

Reaction of the Product of Example 1 with Ethanolamine

20 A reaction flask was charged with 570 grams of the product of Example 1 and 300 ml of toluene. The mixture was stirred under nitrogen while 61 grams of ethanolamine was added to the solution. The temperature rose rapidly from 25°C to 60°C over 6 min. The solution was heated at gentle reflux (ca 110°C) for 3 hours while 16.2 ml of water (90% of theory) was collected.

The reaction mixture was vacuum-stripped to 110°C/7 torr (931Pa) to provide 600 grams of amber oil.
25 Analysis: %S = 10.36. The infrared spectrum showed absorption characteristic of cyclic 5-membered imide at 1710 and 1715cm⁻¹.

EXAMPLE 3

Reaction Product of Dibutyl Hydroxymethylphosphonate with the Product of Example 1

A reaction flask was charged with 358 grams of the anhydride product of Example 1 and 142 grams of dibutyl hydroxymethylphosphonate, previously prepared by base-catalyzed condensation of paraformaldehyde and dibutyl hydrogen phosphite. The reaction mixture was stirred under nitrogen, and heated in
35 stages: 85°C for 2 hours; 100°C for 2 hours; 120°C for 2.5 hours. The mixture was filtered through diatomaceous earth to give 480 grams of product. Analysis %S = 6.5; %P = 8.8.

EXAMPLE 4

Reaction Product of Ethylene Glycol with the Product of Example 1

A reaction flask was charged with 489 grams of the product of Example 1, 400 ml of toluene, 160 grams of ethylene glycol, and 1 gram of p-toluenesulfonic acid catalyst. The reaction mixture was stirred and heated to gentle reflux with slow nitrogen sparging, and water of condensation was removed over a period
45 of 8 hours; a total of 16.6 ml of water was evolved at this point (100% of theory) for the formation of a diester of the cyclic dicarboxylic anhydride. The reaction mixture was cooled to room temperature and washed with two-500ml portions of water. The toluene solution was then vacuum-stripped at 110°C/15 torr (1995Pa) and filtered through a pad of diatomaceous earth to give 590 grams of clear yellow, viscous oil. Analysis: %S = 10.00; acid number = 10 (phenolphthalein indicator). The product had an H₂S stability, on
50 treatment with water at 100°C, greater than 8 hours.

The compounds of the present invention have been found to be useful extreme pressure agents and antiwear agents as well as antioxidants for lubricating compositions. The compounds of the present invention may also find use as additives for other such functional fluids as automatic transmission fluids and hydraulic fluids.

55 The compounds of the invention may be formulated with a lubricating oil or an automatic transmission fluid or the like by the direct blending of the composition with the particular oil or functional fluid to be formulated. The lubricating oil or other functional fluid may also be formulated with compounds of the present invention in the form of a concentrate. Such a concentrate may be prepared by adding 1% to 99%

by weight of at least 1 compound of the present invention to a substantially inert, normally liquid organic diluent or solvent such as benzene, toluene, xylene, petroleum naphtha, mineral oil, ethyleneglycol-monomethylether or the like.

5 The amount of these additives formulated with a particular lubricant may vary over a wide range and must be an amount to effectively impart extreme pressure and antiwear properties in the lubricant. As a preferred amount, the additive may range from 0.01 weight percent to about 10 weight percent of the formulated lubricant. In a most preferred embodiment, the amount may range from about 0.1 weight percent to about 5 weight percent of the formulated lubricant.

10 The compositions of the present invention formulated with the particular functional fluid may contain other additives and chemistries such as dispersants, antioxidants, and the like. Such other additives and chemistries include, for example, detergents and dispersants of the ash-producing or ashless type, corrosion- and oxidation-inhibiting agents, pour point depressing agents, auxiliary extreme pressure agents, color stabilizers and anti-foam agents. These other additives and chemistries are fully described and disclosed in U.S. Patent 3,541,012; U.S. Patent 3,697,428; and U.S. Patent 4,234,435.

15 A preferred dispersant according to the present invention is at least one substituted succinic acid or derivative thereof consisting of substituent groups wherein the substituent groups are derived from polyalkylene, said polyalkylene being characterized by a Mn value of 500 to about 10,000 and a Mw/Mn value of 1.0 to about 4.0.

20 It has also been found that the additive compounds of the present invention are useful in formulating various grease compositions. The norbornene adduct additives of the present invention are useful in both mineral and synthetic lubricating oils and greases. Synthetic oils include polyolefin oils (e.g., polybutene oil, decene oligomer, and the like), synthetic esters (e.g., dinonyl sebacate, trioctanoic acid ester of trimethylolpropane, and the like), polyglycol oils, and the like. Greases are made from these oils by adding a thickening agent such as sodium, calcium, lithium, or aluminum salts of fatty acids such as stearic acid. The oils and greases of the present invention are prepared by blending an amount of the carbamate additive of the present invention sufficient to impart extreme pressure properties and antiwear properties into the oil or grease. A useful concentration may range from about 0.1 to about 5 weight percent.

25 To further illustrate various functional fluid compositions, specifically lubricant compositions, comprising the compositions of the present invention, the following illustrative examples are provided. It is again pointed out that the following examples are provided for illustrative purposes only and are not to place any limitation on the scope of the invention where such scope is set out only in the claims. All parts and percentages are by weight.

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Typical compositions according to this invention are listed in the following table.

TABLE I

	<u>COMPONENTS</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
5	Base Oil	90.37	90.87	92.82	95.0	81.13	83.18
10	Product of Example 2						2.00
	Product of Example 3	0.11	0.11	3.86	2.50		
15	Product of Example 4					2.60	
20	Reaction Product of Polybutenyl Succinic Anhydride with Ethylene Polyamine					3.61	2.50
25	Reaction Product of Polybutenyl Succinic Anhydride with Ethylene Polyamine and Pentaerythritol						2.50
30	Reaction Product of Polybutenyl Succinic Anhydride with Ethylene Polyamine and Carbon Disulfide	2.00	2.00				
35	Reaction Product of Polybutenyl Succinic Anhydride with Ethylene Polyamine and Boric Acid	1.00	1.00				
40	Basic Calcium Alkylbenzene-sulfonate	1.79	1.79				1.10
45	Basic Magnesium Alkylbenzene-sulfonate					1.35	0.65
50	Reaction Product of Maleic Anhydride-styrene Copolymer with Alcohol and Amine	3.50	3.50	1.11		0.20	

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5	Hydrogenated Styrene- diene Block Copolymer Viscosity Improver				9.00		
	Ethylene-propylene Copolymer Viscosity Improver					7.00	
10	Sulfurized Fat	0.50					
	Reaction Product of an Organo Sulfur Cmpd. with an Epoxide	0.50	0.50				
15	Sulfurized Olefin Ester of Dimercapto- thiadiazole			2.50	1.50		
				0.17	0.10	0.06	
20	Sulfurized Diels- Alder Adduct					0.60	
	Oil Soluble Phosphorus-Containing Extreme Pressure Agent			1.47			
25	Alkylated Arylamine	0.10	0.10		0.50	0.30	
	Ethoxylated Fatty Amine	0.09	0.09				
30	Fatty Amide			0.11		0.10	
	Fatty Amine			0.39			
35	Silicone Anti- foam Agent	0.042	0.042	0.066	0.006	0.006	

40 The products of the various examples, contained in a fully formulated lubricating composition as is described in Table I, were then tested with regard to a Timken "OK" load test as well as a contact pressure test in accordance with ASTM D 2782 with the exception that in the "OK" load test the following procedural differences were made:

- 45 1. Test cup and block surfaces are merely "wetted" with test lubricant (approximately 5 drops on block). No test sample is recirculated over the surfaces during the test.
2. Test duration is 5 minutes under load.
3. This procedure is run as an "OK" Load test, determining "OK" Load as in ASTM Test D 2782 except utilizing the following load increments:
 - 50 a. "OK" Load is less than or equal to 20 lbs.: Determine "OK" Load to the nearest 1 lb.
 - b. "OK" Load is greater than 20 lbs.: Determine "OK" Load using standard load increments as described in ASTM Test D 2782.

The results from testing products of the present invention according to the above test procedure are set out in Table II below.

TABLE II

Timken Results			
Compound	# Loading	Unit Pres. psi (Pa)	Wt % ² Chem
Product of Example 2	18	13,050 (9.10 ⁷)	1.0
Product of Example 4	25	10,300 (7.1.10 ⁷)	1.12
Zn O,O-di(iso- ¹ butyl/amyI mixed alkyl)dithiophosphate	17	7,000 (4.8x10 ⁷)	0.52

¹ Comparison - a typical antiwear agent

² Percent weight of the product in the fully formulated oil;
all samples evaluated at 0.05% P, as experimental product

The invention also includes aqueous compositions characterized by an aqueous phase with at least one amine and/or metal salt of at least one dimer or polymer of the present invention dispersed or dissolved in said aqueous phase. 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, preferably from about 40% to about 65% water; and water-based functional fluids containing generally greater than about 80% by weight of water. The concentrates generally contain from about 10% to about 90% by weight of at least one of the norbornene adduct additives of the invention. The water-based functional fluids generally contain from about 0.05% to about 15% by weight of the norbornene adduct materials of the invention. The concentrates generally contain less than about 50%, preferably less than about 25%, more preferably less than about 15%, and still more preferably less than about 6% hydrocarbon oil. The water-based functional fluids generally contain less than about 15%, preferably less than about 5%, and more preferably less than about 2% hydrocarbon oil.

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, anti-foam agents and the like.

The concentrates are analogous to the water-based functional fluids except except that they contain less water and proportionately more of the other ingredients. The concentrates can be converted to water-based functional fluids by dilution with water. This dilution is usually done by standard mixing techniques. This is often a convenient procedure since the concentrate can be shipped to the point of use before additional water is added. Thus, the cost of shipping a substantial amount of the water in the final water-based functional fluid is saved. Only the water necessary to formulate the concentrate (which is determined primarily by ease of handling and convenience factors), need be shipped.

Generally these water-based functional fluids are made by diluting the concentrates with water, wherein the ratio of water to concentrate is usually in the range of about 80:20 to about 99:1 by weight. As can be seen when dilution is carried out within these ranges, the final water-based functional fluid contains, at most, an insignificant amount of hydrocarbon oil.

In various preferred embodiments of the invention, the water-based functional fluids are in the form of solutions while in other embodiments they are in the form of micelle dispersions or microemulsions which appear to be true solutions. Whether a solution, micelle dispersion or microemulsion is formed is dependent, inter alia, on the particular components employed.

Also included within this invention are methods for preparing aqueous compositions, including both concentrates and water-based functional fluids, containing other conventional additives commonly employed in water-based functional fluids. These methods comprise the steps of:

- (1) mixing at least one norbornene adduct additive of the invention with such other conventional additives either simultaneously or sequentially to form a dispersion or solution; optionally
- (2) combining said dispersion or solution with water to form said aqueous concentrate; and/or
- (3) diluting said dispersion or solution, or concentrate with water wherein, the total amount of water used is in the amount required to provide the desired concentration of the components of the invention and other functional additives in said concentrates or said water-based functional fluids.

These mixing steps are preferably carried out using conventional equipment and generally at room or slightly elevated temperatures, usually below 100°C and often below 50°C. As noted above, the concentrate can be formed and then shipped to the point of use where it is diluted with water to form the

desired water-based functional fluid. In other instances, the finished water-based functional fluid can be formed directly in the same equipment used to form the concentrate or the dispersion or solution.

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.

Among the nonionic surfactant types are the alkylene oxide-treated products, such as ethylene oxide-treated phenols, alcohols, esters, amines and amides. Ethylene oxide/propylene oxide block copolymers are also useful nonionic surfactants. Glycerol esters and sugar esters are also known to be nonionic surfactants. A typical nonionic surfactant class useful with the present invention are the alkylene oxide-treated alkyl phenols such as the ethylene oxide alkyl phenol condensates sold by the Rohm & Haas Company. A specific example of these is Triton X-100 which contains an average of 9-10 ethylene oxide units per molecule, has an HLB value of about 13.5 and a molecular weight of about 628. Many other suitable nonionic surfactants are known; see, for example, the aforementioned McCutcheon's as well as the treatise "Non-Ionic Surfactants" edited by Martin J. Schick, M. Dekker Co., New York, 1967.

As noted above, cationic, anionic and amphoteric surfactants can also be used. Generally, these are all hydrophilic surfactants. Anionic surfactants contain negatively charged polar groups while cationic surfactants contain positively charged polar groups. Amphoteric dispersants contain both types of polar groups in the same molecule. A general survey of useful surfactants is found in Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 19, page 507 et seq. (1969, John Wiley and Son, New York) and the aforementioned compilation published under the name of McCutcheon's.

Among the useful anionic surfactant types are the widely known carboxylate soaps, organo sulfates, sulfonates, sulfocarboxylic acids and their salts, and 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. Various cationic, anionic and amphoteric dispersants are available from the industry, particularly from such companies as Rohm & Haas and Union Carbide Corporation, both of America. Further information about anionic and cationic surfactants also can be found in the texts "Anionic Surfactants," Parts II and III, edited by W. M. Linfield, published by Marcel Dekker, Inc., New York, 1976, and "Cationic Surfactants," edited by E. Jungermann, Marcel Dekker, Inc., New York, 1976.

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

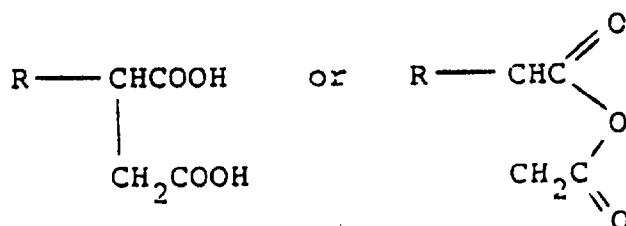
Often the aqueous compositions of this invention contain at least one thickener for thickening said compositions. Generally, these thickeners can be polysaccharides, synthetic thickening polymers, or mixtures of two or more of these. Among the polysaccharides that are useful are natural gums such as those disclosed in "Industrial Gums" by Whistler and B. Miller, published by Academic Press, 1959. Specific examples of such gums are gum agar, guar gum, gum arabic, algin, dextrans, xanthan gum and the like. Also among the polysaccharides that are useful as thickeners for the aqueous compositions of this invention are cellulose ethers and esters, including hydroxy hydrocarbyl cellulose and hydrocarbylhydroxy cellulose and its salts. Specific examples of such thickeners are hydroxyethyl cellulose and the sodium salt of carboxymethyl cellulose. Mixtures of two or more of any such thickeners are also useful.

It is a general requirement that the thickener used in the aqueous compositions of the present invention be soluble in both cold (10°C) and hot (about 90°C) water. This excludes such materials as methyl cellulose which is soluble in cold water but not in hot water. Such hot-water-insoluble materials, however, can be used to perform other functions such as providing lubricity to the aqueous compositions of this invention.

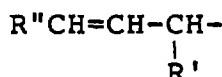
These thickeners can also be synthetic thickening polymers. Many such polymers are known to those of skill in the art. Representative of them are polyacrylates, polyacrylamides, hydrolyzed vinyl esters, water-soluble homo- and interpolymers of acrylamidoalkane sulfonates containing 50 mole percent at least of acrylamido alkane sulfonate and other comonomers such as acrylonitrile, styrene and the like. Poly-n-vinyl pyrrolidones, homo- and copolymers as well as water-soluble salts of styrene, maleic anhydride and isobutylene maleic anhydride copolymers can also be used as thickening agents.

Other useful thickeners are known to those of skill in the art and many can be found in the list in the afore-mentioned McCutcheon Publication: "Functional Materials," 1976, pp. 135-147, inclusive.

Preferred thickeners, particularly when the compositions of the invention are required to be stable under high shear applications, are the water-dispersible reaction products formed by reacting at least one hydrocarbyl-substituted succinic acid and/or anhydride represented by the formula



wherein R is a hydrocarbyl group of from about 8 to about 40 carbon atoms, with at least one water-dispersible amine terminated poly(oxyalkylene) or at least one water-dispersible hydroxy-terminated polyoxyalkylene. R preferably has from about 8 to about 30 carbon atoms, more preferably from about 12 to about 24 carbon atoms, still more preferably from about 16 to about 18 carbon atoms. In a preferred embodiment, R is represented by the formula

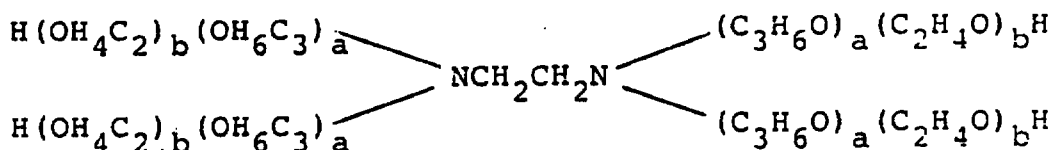


wherein R' and R'' are independently hydrogen or straight chain or substantially straight chain hydrocarbyl groups, with the proviso that the total number of carbon atoms in R is within the above-indicated ranges. Preferably R' and R'' are alkyl or alkenyl groups. In a particularly advantageous embodiment, R has from about 16 to about 18 carbon atoms, R' is hydrogen or an alkyl group of from 1 to about 7 carbon atoms or an alkenyl group of from 2 to about 7 carbon atoms, and R'' is an alkyl or alkenyl group of from about 5 to about 15 carbon atoms.

The water-dispersible amine terminated poly(oxyalkylene)s are preferably alpha omega diamino poly(oxyethylene)s, alpha omega diamino poly(oxypropylene) poly(oxyethylene) poly(oxypropylene)s or alpha omega diamino propylene oxide capped poly(oxyethylene)s. The amine-terminated poly(oxyalkylene) can also be a urea condensate of such alpha omega diamino poly(oxyethylene)s, alpha omega diamino poly(oxypropylene) poly(oxyethylene) poly(oxypropylene)s or alpha omega diamino propylene oxide capped poly(oxyethylene)s. The amine-terminated poly(oxyalkylene) can also be a polyamine (e.g., triamino, tetramino, etc.) polyoxyalkylene provided it is amine-terminated and it is water-dispersible.

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. The disclosures of these patents are incorporated herein by reference. Water-dispersible amine terminated poly(oxyalkylene)s that are useful are commercially available from the Texaco Chemical Company under the trade name "Jeffamine."

The water-dispersible hydroxy-terminated polyoxyalkylenes are constituted of block polymers of propylene oxide and ethylene oxide, and a nucleus which is derived from organic compounds containing a plurality of reactive hydrogen atoms. The block polymers are attached to the nucleus at the sites of the reactive hydrogen atoms. Examples of these compounds include the hydroxy-terminated polyoxyalkylenes which are represented by the formula



wherein a and b are integers such that the collective molecular weight of the oxypropylene chains range from about 900 to about 25,000, and the collective weight of the oxyethylene chains constitute from about 20% to about 90%, preferably from about 25% to about 55% by weight of the compound. These compounds are commercially available from BASF Wyandotte Corporation under the trade name "Tetronic." Additional examples include the hydroxy-terminated polyoxyalkylenes represented by the formula



wherein y is an integer such that the molecular weight of the oxypropylene chain is at least about 900, and x and z are integers such that the collective weight of the oxyethylene chains constitute from about 20% to about 90% by weight of the compound. These compounds preferably have a molecular weight in the range of about 1,100 to about 14,000. Those compounds are commercially available from BASF Wyandotte Corporation under the trade name "Pluronic." Useful hydroxy-terminated polyoxyalkylenes are disclosed in U.S. Patents 2,674,619 and 2,979,528.

The reaction between the carboxylic agent and the amine- or hydroxy-terminated polyoxyalkylene can be carried out at a temperature ranging from the highest of the melt temperatures of the reaction components up to the lowest of the decomposition temperatures of the reaction components or products. Generally, the reaction is carried out at a temperature in the range of about 60°C to about 160°C, preferably about 120°C to about 160°C. The ratio of equivalents of carboxylic agent to polyoxyalkylene preferably ranges from about 0.1:1 to about 8:1, preferably about 1:1 to about 4:1, and advantageously about 2:1. The weight of an equivalent of the carboxylic agent can be determined by dividing its molecular weight by the number of carboxylic functions present. The weight of an equivalent of the amine-terminated polyoxyalkylene can be determined by dividing its molecular weight by the number of terminal amine groups present. The weight of an equivalent of the amine-terminated polyoxyalkylene can be determined by dividing its molecular weight by the number of terminal amine groups present. The number of terminal amine and hydroxyl groups can usually be determined from the structural formula of the polyoxyalkylene or empirically through well-known procedures. The amine/acids and ester/acids formed by the reaction of the carboxylic agent and amine-terminated or hydroxy-terminated polyoxyalkylene can be neutralized with, for example, one or more alkali metals, one or more amines, or a mixture thereof, and thus converted to amide/salts or ester/salts, respectively. Additionally, if these amide/acids or ester/acids are added to concentrates or functional fluids containing alkali metals or amines, amide/salts or ester/salts usually form, in situ.

South African Patent 85/0978 discloses the use of hydrocarbyl-substituted succinic acid or anhydride/hydroxy-terminated poly(oxyalkylene) reaction products as thickeners for aqueous compositions. 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 surfactant. Any of the surfactants identified above under the subtitle "Surfactants" can be used in this regard. 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 preferably present at a level of up to about 70% by weight, preferably 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, preferably from about 3% to about 6% by weight of the functional fluids of the invention.

The functional additives that can be used in the aqueous systems are typically oil-soluble, water-insoluble additives which function in conventional oil-based systems as extreme pressure agents, antiwear 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 milliliters 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 can 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. Briefly, these are potential polymer forming materials which are dispersed in a liquid carrier at low concentration and which polymerize

at rubbing or contacting surfaces to form protective polymeric films on the surfaces. The polymerizations are believed to result from the heat generated by the rubbing and, possibly, from catalytic and/or chemical action of the freshly exposed surface. 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. Typically such salts are of carboxylic acids of 1 to 22 carbon atoms including both aromatic and aliphatic acids; sulfur acids such as alkyl and aromatic sulfonic acids and the like; phosphorus acids such as phosphoric acid, phosphorus acid, phosphinic acid, acid phosphate esters and analogous sulfur homologs such as the thiophosphoric and dithiophosphoric acid and related acid esters; boron acids include boric acid, acid borates and the like. Useful functional additives also include metal dithiocarbamates such as molybdenum and antimony dithiocarbamates; as well as dibutyl tin sulfide, tributyl tin oxide, phosphates and phosphites; borate amine salts, chlorinated waxes; trialkyl tin oxide, molybdenum phosphates, and chlorinated waxes.

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, New Jersey, U.S.A., 1973; and "Lubricant Additives" by C. V. Smalheer and R. K. Smith, The Lezius-Hiles Co., Cleveland, Ohio, U.S.A.

In certain of the typical aqueous compositions of the invention, the functional additive is a sulfur or chloro-sulfur extreme pressure agent, known to be useful in oil-base systems. Such materials include chlorinated aliphatic hydrocarbons, such as chlorinated wax; organic sulfides and polysulfides, such as benzyl-disulfide, bis-(chlorobenzyl)disulfide, dibutyl tetrasulfide, sulfurized sperm oil, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, sulfurized terpene, and sulfurized Diels-Alder adducts; phosphosulfurized hydrocarbons, such as the reaction product of phosphorus sulfide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, i.e., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite, dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates, such as zinc dioctyldithiocarbamate and barium heptylphenol dithiocarbamate; and Group II metal salts of a phosphorodithioic acid, such as zinc dicyclohexyl phosphorodithioate.

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.

Specific examples of functional additives useful in the aqueous systems of this invention include the following commercially available products.

TABLE I

Functional Additive Trade Name	Chemical Description	Supplier
Anglamol 32	Chlorosulfurized hydrocarbon	Lubrizol ¹
Anglamol 75	Zinc dialkyl phosphate	Lubrizol ¹
Molyvan L	A thiaphosphomolybdate	Vanderbilt ²
Lubrizol-5315	Sulfurized cyclic carboxylate ester	Lubrizol ¹
Emcol TS 230	Acid phosphate ester	Witco ³

¹ The Lubrizol Corporation, Wickliffe, Ohio, U.S.A.

² R. T. Vanderbilt Company, Inc., New York, New York, U.S.A.

³ Witco Chemical Corp., Organics Division, Houston, Texas, U.S.A.

Mixtures of two or more of any of the afore-described functional additives can also be used.

Typically, a functionally effective amount of the functional additive is present in the aqueous compositions of this invention.

The term "functionally effective amount" refers to a sufficient quantity of an additive to impart desired properties intended by the addition of said additive. For example, if an additive is a rust-inhibitor, a functionally effective amount of said rust-inhibitor would be an amount sufficient to increase the rust-inhibiting characteristics of the composition to which it is added. Similarly, if the additive is an antiwear agent, a functionally effective amount of said antiwear agent would be a sufficient quantity of the antiwear agent to improve the antiwear characteristics of the composition to which it is added.

The aqueous systems of this invention often contain at least one inhibitor for corrosion of metals. These inhibitors can prevent corrosion of either ferrous or non-ferrous metals (e.g., copper, bronze, brass, titanium, aluminum and the like) or both. The inhibitor can be organic or inorganic in nature. Usually it is sufficiently soluble in water to provide a satisfactory inhibiting action though it can function as a corrosion-inhibitor without dissolving in water, it need not be water-soluble. Many suitable inorganic inhibitors useful in the aqueous systems of the present invention are known to those skilled in the art. 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. Many suitable organic inhibitors are known to those of skill in the art. Specific examples include hydrocarbyl amine and hydroxy-substituted hydrocarbyl amine neutralized acid compound, such as neutralized phosphates and hydrocarbyl phosphate esters, neutralized fatty acids (e.g., those having about 3 to about 22 carbon atoms), neutralized aromatic carboxylic acids (e.g., 4-tertiarybutyl benzoic acid), neutralized naphthenic acids and neutralized hydrocarbyl sulfonates. Mixed salt esters of alkylated succinimides are also useful. Particularly useful amines include the alkanol amines such as ethanol amine, diethanolamine. Mixtures of two or more of any of the afore-described corrosion-inhibitors can also be used. The corrosion-inhibitor is usually present in concentrations in which they are effective in inhibiting corrosion of metals with which the aqueous composition comes in contact.

Certain of the aqueous systems of the present invention (particularly those that are used in cutting or shaping of metal) can also contain at least one polyol with inverse solubility in water. Such polyols are those that become less soluble as the temperature of the water increases. They thus can function as surface lubricity agents during cutting or working operations since, as the liquid is heated as a result of friction between a metal workpiece and work tool, the polyol of inverse solubility "plates out" on the surface of the workpiece, thus improving its lubricity characteristics.

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. Generally, these bactericides are water-soluble, at least to the extent to allow them to function as bactericides.

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 diamine tetraacetate sodium salt or nitrilo triacetic acid; odor masking agents, e.g., citronella, oil of lemon, and the like; and anti-foamants, such as the well-known silicone anti-foamant agents.

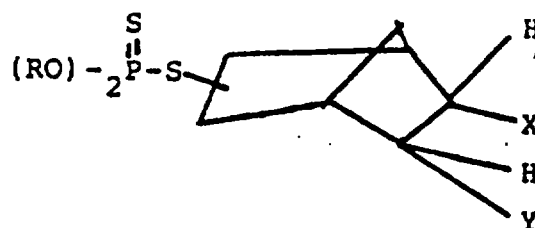
The aqueous systems of this invention may also include an antifreeze additive where it is desired to use the composition at a low temperature. Materials such as ethylene glycol and analogous polyoxyalkylene

polyols can be used as antifreeze agents. Clearly, the amount used will depend on the degree of antifreeze protection desired and will be known to those of ordinary skill in the art.

It should also be noted that many of the ingredients described above for use in making the aqueous systems of this invention are industrial products which exhibit or confer more than one property on such aqueous compositions. Thus, a single ingredient can provide several functions thereby eliminating or reducing the need for some other additional ingredient. Thus, for example, an extreme pressure agent such as tributyl tin oxide can also function as a bactericide.

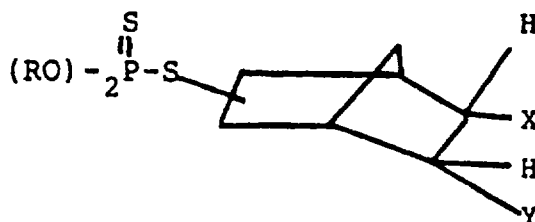
Claims

1. A lubricating composition comprising a major amount of an oil of lubricating viscosity and minor amount of a compound of the formula:



wherein R is, independently, alkyl or aryl and X and Y are independently selected from hydrogen, hydrocarbyl carboxy, a N-substituted carboxamide moiety, a thio- or dithiocarbamate moiety, a thioamide moiety, a thio acid or ester moiety, a hydrocarbyl phosphorus containing radical, or together are imide or N-hydrocarbyl substituted imide, provided that when X is alkyl carboxy, Y is not alkyl carboxy or hydrogen, and X and Y are not both hydrogen.

2. The composition according to claim 1 wherein X and Y are independently hydroxyalkyl carboxy.
3. The composition according to claim 2 wherein X and Y are the same and are hydroxyethyl carboxy.
4. A method for improving the load bearing properties of a lubricating composition of lubricating viscosity by admixing therewith a minor amount of an extreme pressure and antiwear agent of the formula:



wherein R is, independently, alkyl or aryl and X and Y are independently selected from hydrogen, hydrocarbyl carboxy, a N-substituted carboxamide moiety, a thio- or dithiocarbamate moiety, a thioamide moiety, a thio acid or ester moiety, a hydrocarbyl phosphorus containing radical, or together are imide or N-hydrocarbyl substituted imide, provided that when X is alkyl carboxy, Y is not alkyl carboxy or hydrogen, and X and Y are not both hydrogen.

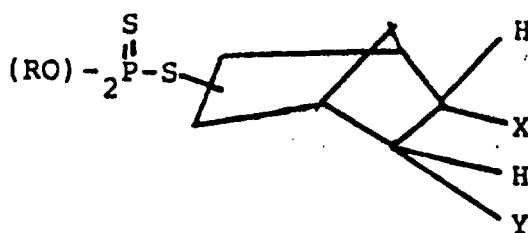
5. The method according to claim 4 wherein X and Y are the same and are hydroxy ethyl carboxy.

polyols can be used as antifreeze agents. Clearly, the amount used will depend on the degree of antifreeze protection desired and will be known to those of ordinary skill in the art.

It should also be noted that many of the ingredients described above for use in making the aqueous systems of this invention are industrial products which exhibit or confer more than one property on such aqueous compositions. Thus, a single ingredient can provide several functions thereby eliminating or reducing the need for some other additional ingredient. Thus, for example, an extreme pressure agent such as tributyl tin oxide can also function as a bactericide.

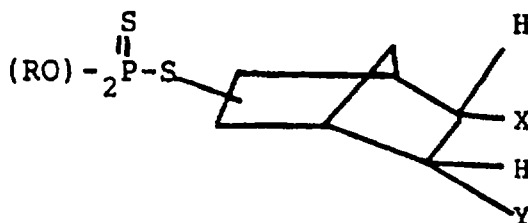
Claims

1. A lubricating composition comprising a major amount of an oil of lubricating viscosity and minor amount of a compound of the formula:



wherein R is, independently, alkyl or aryl and X and Y are independently selected from hydrogen, hydrocarbyl carboxy, a N-substituted carboxamide moiety, a thio- or dithiocarbamate moiety, a thioamide moiety, a thio acid or ester moiety, a hydrocarbyl phosphorus containing radical, or together are imide or N-hydrocarbyl substituted imide, provided that when X is alkyl carboxy, Y is not alkyl carboxy or hydrogen, and X and Y are not both hydrogen.

2. The composition according to claim 1 wherein X and Y are independently hydroxyalkyl carboxy.
3. The composition according to claim 2 wherein X and Y are the same and are hydroxyethyl carboxy.
4. A method for improving the load bearing properties of a lubricating composition of lubricating viscosity by admixing therewith a minor amount of an extreme pressure and antiwear agent of the formula:

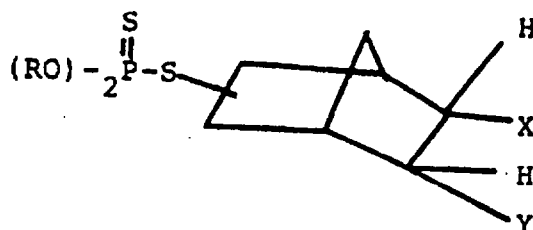


wherein R is, independently, alkyl or aryl and X and Y are independently selected from hydrogen, hydrocarbyl carboxy, a N-substituted carboxamide moiety, a thio- or dithiocarbamate moiety, a thioamide moiety, a thio acid or ester moiety, a hydrocarbyl phosphorus containing radical, or together are imide or N-hydrocarbyl substituted imide, provided that when X is alkyl carboxy, Y is not alkyl carboxy or hydrogen, and X and Y are not both hydrogen.

5. The method according to claim 4 wherein X and Y are the same and are hydroxy ethyl carboxy.



6. A compound of the formula:



wherein R is, independently, alkyl or aryl and X and Y are independently selected from a N-substituted carboxamide moiety, a thioamide moiety, a thioester moiety, a dithioester moiety, a hydrocarbyl-containing dithiocarbamate moiety, hydrocarbylthio, a phosphate moiety, a phosphite moiety, a phosphonate moiety, a dithiophosphate moiety, a phosphoramidate moiety, or together represent imide or an N-hydrocarbyl imide.

7. The compound according to claim 6 wherein X and Y are, independently, a phosphonate moiety, a N-substituted carboxamide moiety, or together are imide or N-hydrocarbyl imide.

8. A lubricant additive comprising the compound of either of claims 6 and 7.

9. A concentrate for formulating lubricating compositions comprising from 1% to 99% by weight of a normally liquid, substantially inert organic solvent/diluent and at least one compound of either of claims 6 and 7.

10. A lubricating composition comprising a major amount of an oil of lubricating viscosity and a minor amount of at least one compound of either one of claims 6 and 7 or at least one concentrate of claim 9.

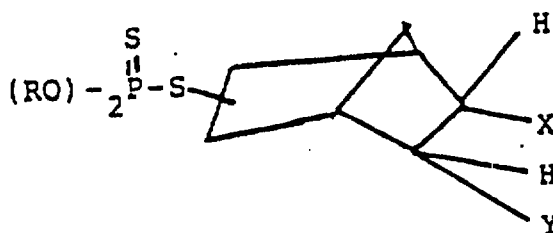
11. A method for improving the load bearing properties of a lubricating composition comprising admixing with a major amount of a lubricating composition, a minor amount of the compound or concentrate of any one of claims 6, 7 and 9.

12. An aqueous functional fluid comprising a minor amount of at least one compound set out in any one of claims 1, 2, 3, 6 and 7.

13. A grease composition comprising a minor amount of at least one compound set out in any one of claims 1, 2, 3, 6 and 7.

Patentansprüche

1. Schmiermittel, umfassend eine größere Menge eines Öls mit Schmierviskosität und eine geringere Menge einer Verbindung der Formel

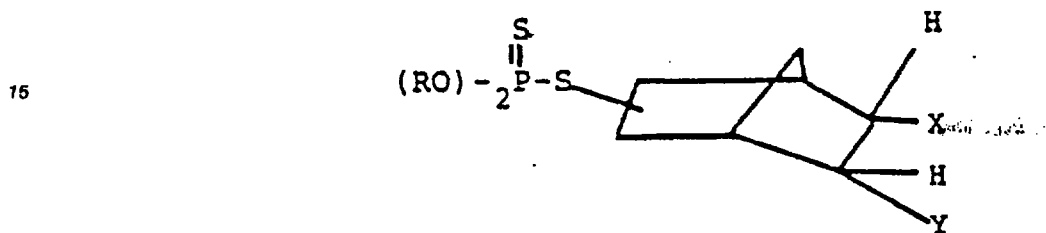


in der die Reste R unabhängig voneinander ein Alkyl- oder Arylrest sind, und X und Y unabhängig voneinander ein Wasserstoffatom, ein Kohlenwasserstoffcarboxyrest, eine N-substituierte Carboxamid-, eine Thio- oder Dithiocarbamat-, eine Thioamid-, eine Thiosäure- oder eine Estereinheit, oder ein



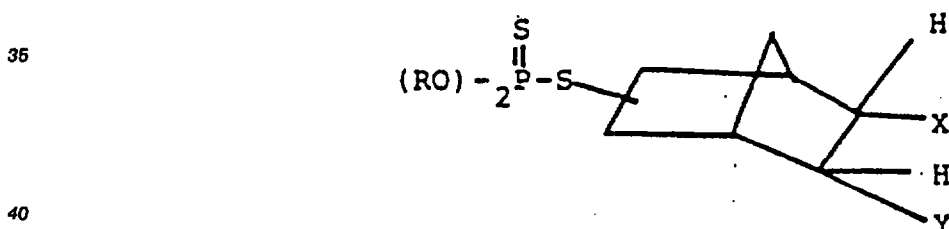
phosphorhaltiger Kohlenwasserstoffrest sind oder zusammen eine Imid- oder ein N-kohlenwasserstoff-substituierte Imidgruppe bilden, mit den Maßgaben daß, wenn X ein Alkylcarboxyrest ist, Y kein Alkylcarboxyrest oder Wasserstoffatom ist, und X und Y nicht beide Wasserstoffatome sind.

- 5 2. Mittel nach Anspruch 1, wobei X und Y unabhängig voneinander Hydroxyalkylcarboxyreste sind.
3. Mittel nach Anspruch 2, wobei X und Y gleich und eine Hydroxyethylcarboxygruppe sind.
4. Verfahren zur Verbesserung der lasttragenden Eigenschaften eines Schmiermittels mit Schmierviskosität durch Zumischen einer geringeren Menge eines Höchstdruck- und Antiverschleißmittels der Formel



in der die Reste R unabhängig voneinander ein Alkyl- oder Arylrest sind, und X und Y unabhängig voneinander ein Wasserstoffatom, ein Kohlenwasserstoffcarboxyrest, eine N-substituierte Carboxamid-, eine Thio- oder Dithiocarbamat-, eine Thioamid-, eine Thiosäure oder eine Estereinheit, oder ein phosphorhaltiger Kohlenwasserstoffrest sind, oder zusammen eine Imid- oder eine N-kohlenwasserstoff-substituierte Imidgruppe bilden, mit den Maßgaben daß, wenn X ein Alkylcarboxyrest ist, Y kein Alkylcarboxyrest oder Wasserstoffatom ist, und X und Y nicht beide Wasserstoffatome sind.

5. Verfahren nach Anspruch 4, wobei X und Y gleich und eine Hydroxyethylcarboxygruppe sind.
6. Verbindung der Formel



in der die Reste R unabhängig voneinander ein Alkyl- oder Arylrest sind und X und Y unabhängig voneinander eine N-substituierte Carboxamid-, eine Thioamid-, eine Thioester-, eine Dithioester-, oder eine kohlenwasserstoffhaltige Dithiocarbamateinheit, ein Kohlenwasserstoffthioester, eine Phosphat-, eine Phosphit-, eine Phosphonat-, eine Dithiophosphat-, oder eine Phosphoramideinheit sind oder zusammen eine Imid- oder eine N-Kohlenwasserstoffimidgruppe bilden.

7. Verbindung nach Anspruch 6, wobei X und Y unabhängig voneinander eine Phosphonat- oder eine N-substituierte Carboxamideinheit sind oder zusammen eine Imid- oder eine N-Kohlenwasserstoffimidgruppe bilden.
8. Schmierzusatz, umfassend die Verbindung nach einem der Ansprüche 6 oder 7.
9. Konzentrat zur Formulierung von Schmiermitteln, umfassend von 1 Gew.-% bis 99 Gew.-% eines normalerweise flüssigen, im wesentlichen inerten organischen Lösungsmittels oder Verdünners und mindestens eine Verbindung nach einem der Ansprüche 6 oder 7.



10. Schmiermittel, umfassend eine größere Menge eines Öls mit Schmierviskosität und eine geringere Menge von mindestens einer Verbindung nach einem der Ansprüche 6 oder 7 oder mindestens einem Konzentrat nach Anspruch 9.

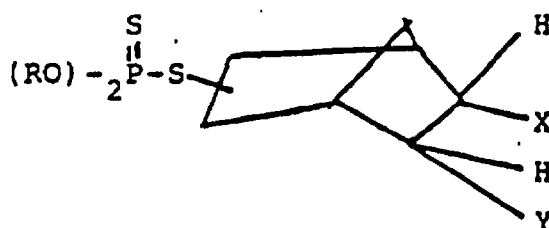
5 11. Verfahren zur Verbesserung der lasttragenden Eigenschaften eines Schmiermittels, umfassend das Zumischen einer kleineren Menge der Verbindung oder des Konzentrats nach einem der Ansprüche 6, 7 und 9 zu einer größeren Menge eines Schmiermittels.

10 12. Wässrige Arbeitsflüssigkeit, umfassend eine geringere Menge von mindestens einer Verbindung nach einem der Ansprüche 1, 2, 3, 6 und 7.

13. Schmierfett-Zusammensetzung, umfassend eine geringere Menge von mindestens einer Verbindung nach einem der Ansprüche 1, 2, 3, 6 und 7.

15 Revendications

1. Une composition lubrifiante comportant une quantité prépondérante d'une huile de viscosité lubrifiante et une quantité plus faible d'un composé de formule:

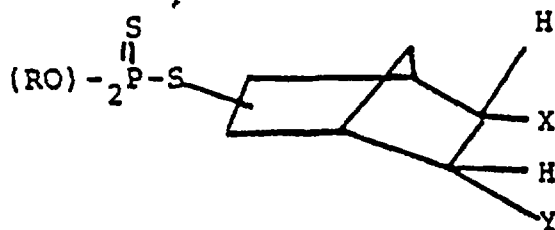


20 dans laquelle R est, indépendamment, un alkyle ou un aryle et X et Y sont indépendamment choisis parmi l'hydrogène, l'hydroxycarbyl carboxy, une partie carboxamide N-substituée, une partie thio- ou dithiocarbamate, une partie thioamide, une partie acide ou ester thio, un radical hydrocarbyle renfermant du phosphore, ou représentent conjointement un imide ou un imide à substitution N-hydrocarbyle, sous la condition que, lorsque X est un alkyl carboxyle, Y n'est pas un alkyl carboxy ni de l'hydrogène, et Y et X ne sont pas à la fois de l'hydrogène.

2. La composition selon la revendication 1, dans laquelle X et Y sont indépendamment un hydroxyalkyl carboxy.

3. La composition selon la revendication 2, dans laquelle X et Y sont identiques et sont de l'hydroxyéthyl carboxy.

4. Une méthode pour améliorer les propriétés de support de charge d'une composition lubrifiante de viscosité lubrifiante en les mélangeant avec une plus faible quantité d'un agent de pression extrême et anti-usure de formule



55 dans laquelle R est, indépendamment, un alkyle ou un aryle et X et Y sont indépendamment choisis parmi l'hydrogène, l'hydroxycarbyl carboxy, une partie carboxamide N-substituée, une partie thio- ou dithiocarbamate, une partie thioamide, une partie acide ou ester thio, un radical hydrocarbyle renfer-



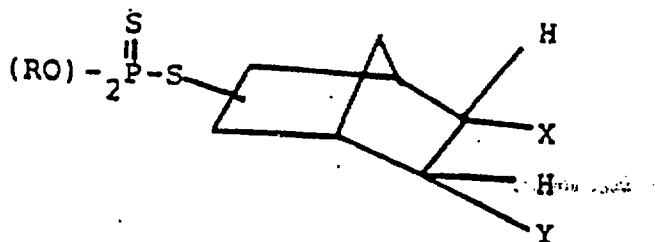
mant du phosphore, ou représentent conjointement un imide ou un imide à substitution N-hydrocarbyle, sous la condition que, lorsque X est un alkyle carboxyle, Y n'est pas un alkyl carboxy ni de l'hydrogène, et Y et X ne sont pas à la fois de l'hydrogène.

5 5. La méthode selon la revendication 4, dans laquelle X et Y sont identiques et sont de l'hydroxyéthyl carboxy.

6. Un composé de la formule:

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20 dans laquelle R est, indépendamment, un alkyle ou un aryle et X et Y sont indépendamment choisis parmi une partie carboxamide N-substituée, une partie thioamide, une partie thioester, une partie dithioester, une partie dithiocarbamate renfermant de l'hydroxycarbyle, de l'hydrocarbylthio, une partie phosphate, une partie phosphite, une partie phosphonate, une partie dithiophosphonate, une partie phosphoramidate, ou représentent conjointement un imide ou un N-hydrocarbyl imide.

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7. Le composé selon la revendication 6, dans laquelle X et Y sont, indépendamment, une partie phosphonate, une partie carboxy amide N-substituée, ou sont conjointement, un imide ou un N-hydrocarbyl imide.

30 8. Un additif lubrifiant comportant le composé de l'une quelconque des revendications 6 et 7.

9. Un concentré pour la formulation de compositions lubrifiantes, comportant de 1% à 99% en poids d'un solvant/diluant organique, pratiquement inerte et liquide dans les conditions normales et au moins un composé de l'une quelconque des revendications 6 et 7.

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10. Une composition lubrifiante comportant une quantité prépondérante d'une huile de viscosité lubrifiante et une quantité plus faible d'au moins un composé de l'une quelconque des revendications 6 et 7 ou au moins un concentré de la revendication 9.

40 11. Une méthode pour améliorer les propriétés de support de charge d'une composition lubrifiante, qui consiste à mélanger avec une quantité prépondérante d'une composition lubrifiante, une quantité plus faible du composé ou du concentré de l'une quelconque des revendications 6, 7 et 9.

45 12. Un fluide fonctionnel aqueux comportant une quantité plus faible d'au moins un composé spécifié dans l'une quelconque des revendications 1, 2, 3, 6 et 7.

13. Une composition de graisse, comportant une quantité plus faible d'au moins un composé spécifié dans l'une quelconque des revendications 1, 2, 3, 6 et 7.

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