

Description

This invention relates to dithiophosphates and to lubricating oils containing them.

Zinc dialkyl dithiophosphates (ZDDPs) have been used for many years as antiwear and antioxidant additives in lubricating oils and are typically prepared by reacting a dialkyl dithiophosphoric acid with a basic zinc compound. The dialkyl dithiophosphoric acid is usually made by reacting phosphorous pentasulphide with an alcohol. In order to increase the surface activity of ZDDPs and hence their antiwear activity, it has been thought possible to prepare ZDDPs from dithiophosphoric acids formed by phosphorous pentasulphide with not the usual C₄ to C₁₀ alcohol, but an alcohol having a polar group. Patents suggesting this include U.S. 3654329, U.S. 3290246, U.S. 4410434, U.S. 4288335, U.S. 4253973, U.S. 4253978, U.S. 3288819 and U.S. 2631132. However, difficulties have arisen because these ZDDPs made from the alcohols containing a polar group are often oil-insoluble.

EP-A-54804 describes a broad class of ZDDPs prepared from mixed alcohols for use in aqueous hydraulic fluids.

ZDDPs are multifunctional additives and act as antioxidants, antiwear agents and bearing corrosion inhibitors. ZDDPs are frequently used in the presence of other additives such as polar hydroxy compounds - hydroxyesters (glyceryl mono oleate) imidazolines, alkylphenol/ethylene oxide condensates (Plexol 305) and the hydroxyester formed by esterification of a dimer acid of linoleic acid and diethylene glycol - which act as friction modifiers, fuel economy additives or rust inhibitors. Due to their polar nature, additives of this type may have poor oil solubility, which can limit the treat levels at which they are used. Also, when these polar additives have been tried in certain packages or blends, compatibility problems have been experienced involving sediment formation during storage and this precludes the use of these additives in specific packages.

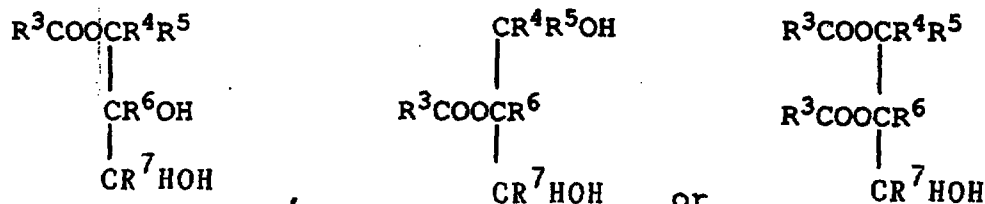
These polar hydroxy compounds are substituted alcohols which could be reacted with phosphorous pentasulphide and then zinc oxide to form a ZDDP, but such a ZDDP would be a highly viscous liquid, or a solid, with poor handling properties and poor oil solubility. It has now been found that by reacting a mixture of a simple C₄ - C₁₀ alcohol together with a certain more polar substituted alcohol, in appropriate proportions, liquid oil-soluble functionalised or friction-modified ZDDPs with excellent handling properties can be made.

An advantage of the friction-modified ZDDPs is that they overcome the compatibility problems previously associated with friction modifiers when used alone. A further advantage is that the friction-modified ZDDPs provide a potential source of higher levels of friction modifier in a blend than were previously obtained when the polar friction modifiers themselves were used, due to their low oil solubility.

A still further advantage is that the introduction of polar groups into a ZDDP usually provides an improvement in antiwear activity.

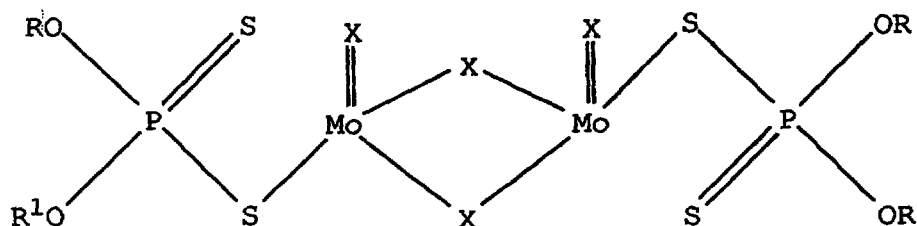
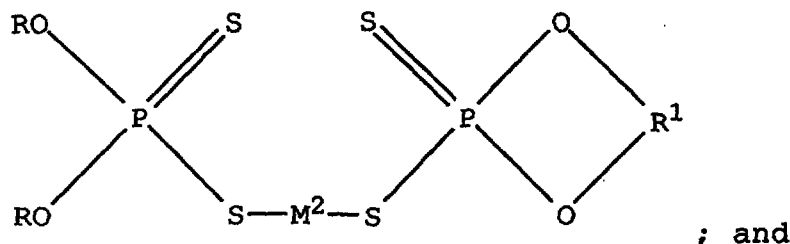
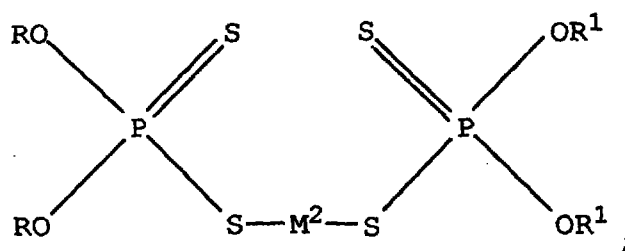
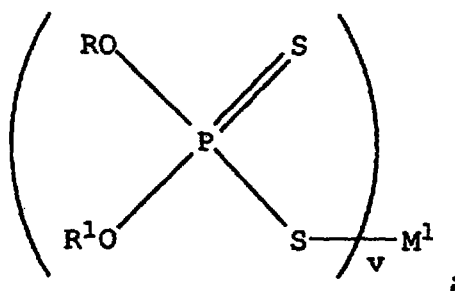
Accordingly, this invention provides a lubricating oil composition comprising a lubricating oil and a minor proportion by weight of a metal dithiophosphate obtainable by reacting a base zinc or copper compound or a molybdenum compound with a dithiophosphoric acid, said dithiophosphoric acid being obtainable by reacting phosphorous pentasulphide with a mixture of alcohols ROH and R¹(OH)_m where m is 1 or 2. The group R is an aliphatic hydrogen- and carbon-containing group having at least 4 carbon atoms or is an alkaryl group, R¹ is a hydrogen- and carbon-containing group containing at least 12 carbon atoms which group R¹ includes either (a) a > C = N or (b) the group -(C_nH_{2n-p}R_p²O)_q, R² being an alkyl group, n being an integer of from 2 to 5, p being zero or an integer of from 1 to 5 and q being an integer of 2 or more with the proviso that p is less than 2n.

Alternatively R¹(OH)_m is a glyceryl derivative and has the formula



where R³ is an aliphatic hydrogen - and carbon - containing group containing at least 9 carbon atoms and R⁴, R⁵, R⁶ and R⁷ are hydrogen or alkyl groups.

The metal dithiophosphates include those of the formulae



where M^1 is cuprous or cupric copper or zinc, M^2 is cupric copper or zinc, v being the valency of the metal and X is S or O .

This invention also provides the use of the above defined metal dithiophosphates in a lubricating oil as an antioxidant.

The invention provides certain of the above defined metal dithiophosphates per se being those wherein the group R^1 does not contain a polyalkyleneoxide group $-(\text{C}_n\text{H}_{2n-p}\text{R}_p^2\text{O})_q-$.

The dithiophosphate is derived from the reaction of the alcohols ROH and $\text{R}^1(\text{OH})_m$ with P_2S_5 . Usually there are four equivalents plus a slight excess of ROH and $\text{R}^1(\text{OH})_m$ reacted with P_2S_5 . Usually there is more of ROH than $\text{R}^1(\text{OH})_m$ on a molar basis so as to ensure that a mobile liquid oil-soluble product is formed.

Since the dithiophosphates are prepared by the reaction of P_2S_5 with an alcohol the groups R and R^1 are derived from the corresponding alcohols ROH and $\text{R}^1(\text{OH})_m$.

In the above formulae the group R may be an aliphatic hydrogen- and carbon-containing group having at least 4 carbon atoms, e.g. 4 to 10 carbon atoms. This may for example be an alkenyl group but preferably it is C_4 to C_{10} alkyl and may for example be a *n*-butyl, *i*-butyl, *sec*-butyl, amyl, *sec*-hexyl, *n*-

heptyl, n-octyl, i-octyl or n-decyl. Preferably R is 2-ethyl hexyl. Alternatively R can be an alkaryl group and this is preferably an alkyl phenyl group, especially a C₇ to C₁₂ alkyl phenyl group, e.g. branched nonyl phenyl or branched dodecyl phenyl. R may be a mixture, i.e. derived from a mixture of alcohols ROH.

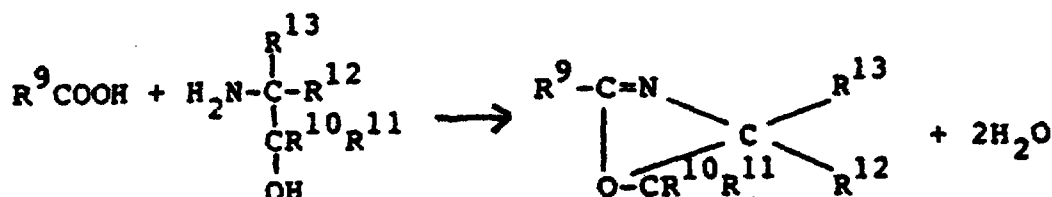
R¹ is a hydrogen- and carbon-containing group containing at least 12 carbon atoms and may contain a > C=N- group.

The > C=N- group is preferably an oxazoline group, i.e.



Preferred oxazolines are prepared by reacting substantially equivalent proportions of a monocarboxylic acid and 2-amino diol or triol.

Thus



where R⁹ is alkyl or alkenyl, R¹⁰ and R¹¹ are hydrogen or alkyl and R¹² and R¹³ are alkyl or hydroxy alkyl provided at least one of them is hydroxyalkyl.

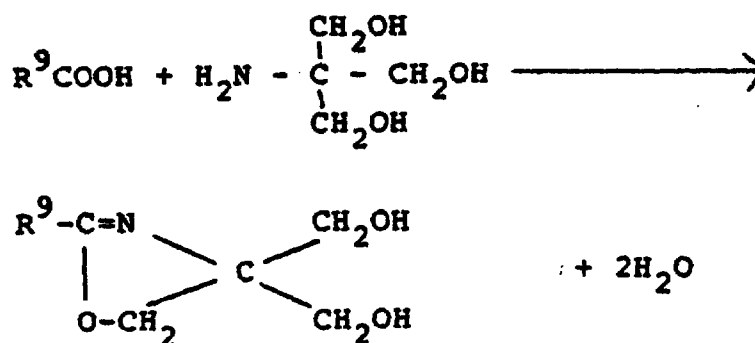
The carboxylic acid R⁹COOH may have from 9 to 50 carbon atoms. These acids include decanoic, dodecanoic, tetradecanoic, octadecanoic and eicosanoic acids as well as unsaturated acids such as oleic or linoleic acids.

R¹⁰ and R¹¹ are preferably hydrogen but one of them may for example be a low alkyl such as methyl or ethyl.

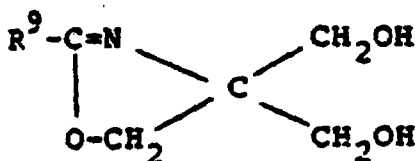
When a 2-amino diol is reacted it is preferred that R¹² be hydrogen or a low alkyl such as methyl or ethyl. R¹³ is then preferably hydroxy-(C₁-C₁₀) alkyl, for example, hydroxy-methyl, hydroxy-butyl or hydroxy-octyl. When a 2-amino triol is reacted it is preferred that R¹² and R¹³ each be hydroxy-(C₁-C₁₀) alkyl, e.g. hydroxy-methyl.

A particularly preferred amino-triol is 2-amino-2-(hydroxymethyl)-1,3-propane diol.

Thus



In this case $R^1(OH)_2$ is



The reaction between the monocarboxylic acid R^3COOH and the 2-amino diol or triol can be carried out by heating the reactants at from $80^\circ C$ to $250^\circ C$, preferably from $120^\circ C$ to $190^\circ C$.

The group R^1 may contain the polyalkyleneoxide group $-(C_nH_{2n-p}R_p^2O)_q-$ where n , p and q and R^2 are as previously defined.

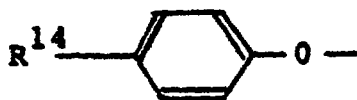
R^1OH may therefore be a polyalkylene oxide derivative of an alcohol, a phenol or a fatty acid.

These compounds are of the general formula



wherein n is preferably in the range of from 2 to 12. Preferably R^2 is a low alkyl, eg methyl as in polyoxypropylene or is hydrogen as in polyoxyethylene $-C_nH_{2n-p}R_p^2-$ is an alkylene radical of 2-5 carbon atoms representing the hydrocarbyl portion of the one or more alkylene oxide units incorporated into the molecule. Preferably it is the propylene oxide unit $-CH(CH_3)CH_2O-$, or most preferably, the ethylene oxide unit $-CH_2CH_2O-$.

Y can take various forms and it is preferred that Y is the phenoxy fragment having the formula



wherein R^{14} is an aliphatic hydrocarbyl radical having at least 4 carbon atoms. If R^{14} is an alkyl group, and $-C_nH_{2n-p}R_p^2$ is $-CH_2CH_2-$, then the compound is an alkyl phenoxy poly(oxyethylene)ethanol.

R^{14} is preferably a saturated C_8 or C_{12} branched alkyl radical derived from tripropylene or tetrapropylene, but it could be a linear alkyl radical. The R^{14} group can be derived from synthetic or natural sources. Illustrative R^{14} groups are isooctyl, nonyl, dodecyl, tetradecyl, hexadecyl and octadecyl. R^{14} can be polyisobutenyl or other polymers of olefin monomers of from 2 to 6 carbon atoms, and preferably from 3 to 4 carbon atoms.

Examples of the polyalkoxylated phenoxy compounds are isooctyl phenoxy tetraethoxy ethanol, nonylphenoxy poly(oxyethylene)ethanol, dodecyl phenoxy poly(oxyethylene)ethanol, dodecyl phenoxy poly(oxypropylene)propanol, and hexadecadienyl phenoxy poly(oxyethylene)ethanol.

Alternatively Y can be the fatty acid fragment $R^{14}COO-$ and $Y(C_nH_{2n-p}R_p^2O)_qH$ is a polyoxyalkylene fatty acid ester. As another alternative Y is the alcoholic fragment, $R^{14}CH_2O-$ and $Y(C_nH_{2n-p}R_p^2O)_qH$ is an alkyl or alkenyl poly(oxyalkylene)alkanol.

Alkyl poly(oxyalkylene)alkanols and alkenyl poly(oxyalkylene)alkanols include decyl poly(oxyethylene)ethanol, dodecyl poly(oxypropylene)propanol, and octadecenyl poly(oxyethylene)ethanol, all of the general formula, $R^{14}\{C_nH_{2n-p}R_p^2O\}_q$. Of these, the alkyl poly(oxyethylene)ethanols are the preferred embodiment.

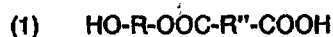
Illustrative poly(oxyalkylene) fatty acid esters which are included within the scope of this invention are of the general formula $R^{14}COO(C_nH_{2n-p}R_p^2O)_qH$ and include poly(oxyethylene) stearate, poly(oxyethylene) laurate, poly(oxyethylene)oleate, and poly(oxypropylene)stearate.

The most preferred alkoxylated group R^1 is of the formula



where R^{14} is C_8 or C_9 alkyl and γ is 3 or 4.

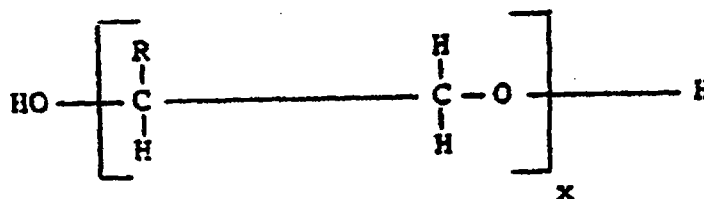
Another class of alcohols $R'(OH)_m$ are hydroxy esters derived from the esterification of a polycarboxylic acid with a polyglycol. Such an ester may be a partial, di- or polyester with typical formulae of the ester represented by the following general formulae when using a polyglycol:



wherein R'' is the hydrocarbon radical of said acid and each R and R' may be the same or different hydrocarbon radicals associated with the polyglycol an hereinafter defined. It will, of course, be appreciated that esters of the type illustrated by the foregoing formulae can be obtained by esterifying a polycarboxylic acid, or a mixture of such acids, with a polyglycol or mixture of such polyglycols.

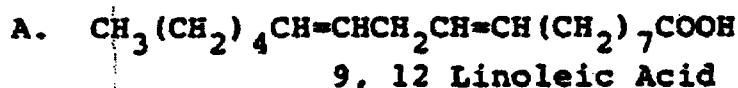
Suitable carboxylic acids include mono- and poly-carboxylic acids. Preferably they are poly-carboxylic acids and they may be aliphatic, saturated or unsaturated and will generally have a total of 24 to 90, preferably 24 to 60 carbon atoms and 2 to 4, preferably 2 or 3 and more preferably 2 carboxylic acid groups with at least 9 up to 42 carbon atoms, preferably 12 to 42 and more preferably 16 to 22 carbon atoms between the carboxylic acid groups.

The oil insoluble polyglycol which is reacted with the polycarboxylic acid such as one of those described above may be a polyalkylene glycol, straight chain or branched. The oxa-alkane diol will, generally, have from 4 to 200, preferably 4 to 100 carbon atoms per molecule. The oxa-alkane diol (polyalkylene glycol) will, of course, contain periodically repeating groups of the formula:



wherein R may be H , CH_3 , C_2H_5 or C_3H_7 , and x is 2 to 100, preferably 2 to 25. The preferred oxa-alkane diol or polyalkylene glycol is diethylene glycol.

Although any of the esters as set forth above can be effectively used, best results are, however, obtained with such compounds wherein the carboxyl groups of the polycarboxylic acid are separated from each other by from about 16 to about 22 carbon atoms and wherein the hydroxy groups are separated from the closest carboxyl group by from about 2 to about 12 carbon atoms. Particularly desirable results have been obtained with additives prepared by esterifying a dimer of a fatty acid particularly those containing conjugated unsaturation with a polyhydroxy compound. Such dimers are clearly taught in U.S. Patent 3,180,832 and U.S. Patent 3,429,817 and as there indicated, the hydrocarbon portion of the dimer or dicarboxylic acid thus obtained may contain a six member ring. The formation of the dimer from linoleic acid, oleic acid, and mixtures of these acids is illustrated by the following:

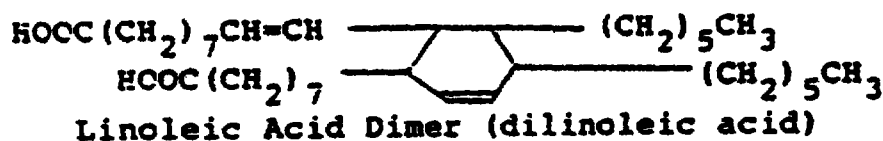


2 molecules
 9-11 acid



Diels-Alder

9, 11 Linoleic Acid

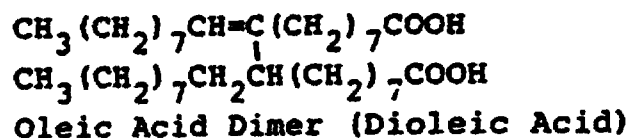


2 molecules
 oleic acid



Diels Alder

Oleic Acid



Diels Alder

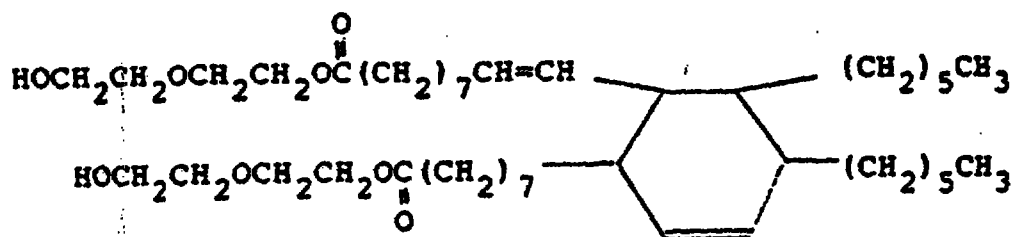


Mixed Dimer

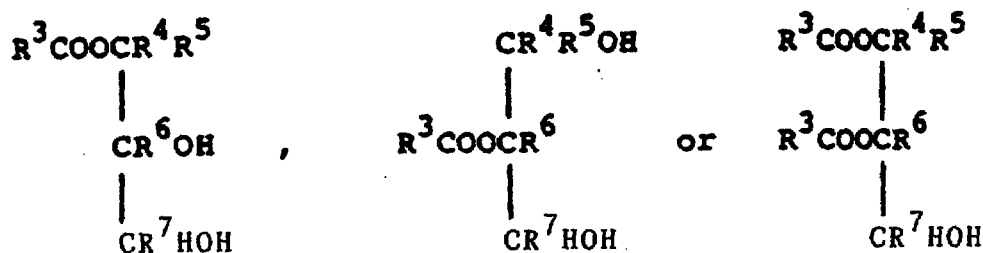
It will, of course, be appreciated that although the reactions illustrated produce the dimers, commercial application of the reactions will, generally, lead to trimer formation and in some cases the product thus obtained will contain minor amounts of unreacted monomer or monomers. As a result, commercially available dimer acids may contain as much as 25% trimer and the use of such mixtures is within the scope of the present invention.

The preferred hydroxy-substituted esters are the reaction product of a dimerized fatty acid, such as those illustrated, and an oil insoluble polyglycol and may be produced by various techniques. As previously pointed out, the preferred acid dimers are the dimers of linoleic acid, oleic acid or the mixed dimer of linoleic and oleic acids, which may also contain some monomer as well as trimer. Other specifically satisfactory polyglycols in addition to polyethylene polyglycol are, for example polypropylene glycol, and polybutylene glycol.

Particularly preferred is the hydroxy ester formed by esterification of a dimer acid of linoleic acid and diethylene glycol having the formula



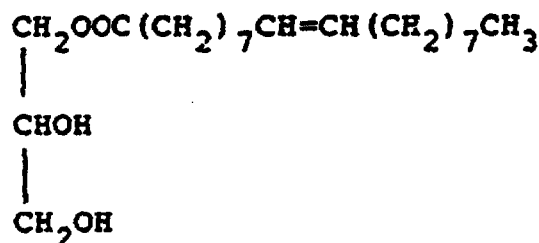
As a third alternative $\text{R}^1(\text{OH})_m$ is a glyceryl derivative and has the formula



Although R^4 , R^5 , R^6 and R^7 may be alkyl groups they are preferably hydrogen atoms. If alkyl it is preferred that only one or two of them are alkyl and the alkyl group is preferably a C_1 to C_5 alkyl, for example methyl or ethyl.

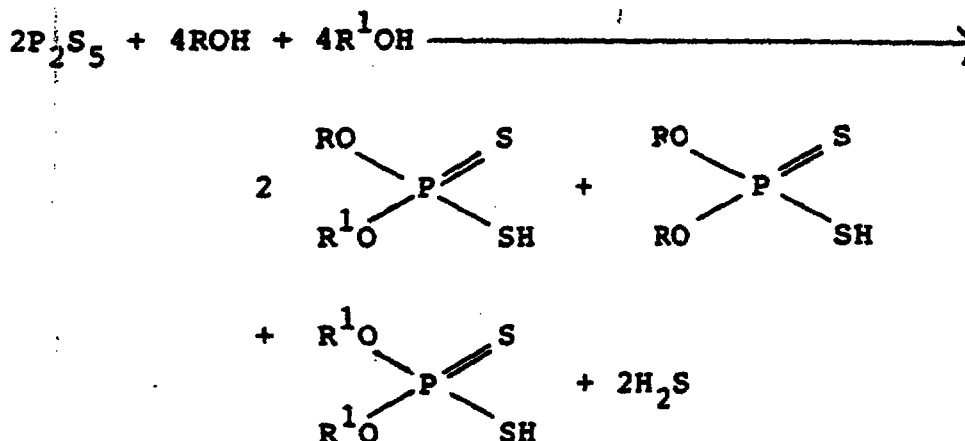
R^3 is an aliphatic hydrogen- and carbon - containing group and it preferably alkyl or alkenyl. Usually it has 9 to 26 carbon atoms, for example 12 to 22 carbon atoms. Thus it may for example be lauryl, myristyl, palmityl, stearyl, behenyl, oleyl, linoleyl or linolenyl.

Particularly preferred is glyceryl mono oleate i.e.



The dithiophosphoric acid from which the dithiophosphate is prepared can be obtained by reacting phosphorus pentasulphide with a mixture of the alcohols ROH and R^1OH .

Thus, for a substantially equimolar mixture of alcohols ROH and R¹OH:



A mixture of acids is thereby obtained and although it would be possible to separate them, e.g. by chromatography, in practice it is not necessary or even particularly desirable to separate them before preparing the metal dithiophosphate.

The maximum ratio of R¹(OH)_m to ROH is limited by the need to produce a liquid oil-soluble ZDDP. If R¹(OH)_m/ROH is high and gives a viscous liquid ZDDP which is difficult to handle, this can be thinned with diluent oil. The maximum R¹(OH)_m/ROH has to be determined by experiment for each case but usually it cannot be more than 50/50 wt %.

The metal dithiophosphate is obtained by reacting the dithiophosphoric acid with a basic compound of zinc or copper or a molybdenum compound, e.g. molybdic acid or ammonium molybdate. The basic compounds are preferably the oxides, e.g. ZnO, but other salts of the metals can be used provided that the anion can be replaced by the anion of the dithiophosphoric acid. Cuprous oxide is preferred to cupric oxide or cupric hydroxide.

Other basic metal compounds which may be used are preferably soluble in the dithiophosphoric acid. Examples of other suitable basic compounds are the carboxylates, e.g. the stearates, acetates and the carbonates.

When forming the metal dithiophosphate it is often desired to use a promoter. Suitable promoters are carboxylic acids, metal carboxylates and other metal salts, particularly the salts of zinc and copper, eg nitrates, phosphates, sulphates or halides. Especially preferred are the zinc salts, particularly zinc carboxylates, zinc chloride, zinc phosphate, zinc nitrate and zinc sulphate. The preferred carboxylic acids for use as such or as their carboxylates are C₁ and C₂₀ monocarboxylic acids, eg acetic acid, propionic acid, decanoic acid, stearic acid and oleic acid. The most preferred promoter is zinc acetate.

The amount of promoter used is usually less than 10 weight %, for example between 0.1 and 10 weight % of the total weight of the metal compound.

The metal dithiophosphate is simply prepared by heating together the dithiophosphoric acid with the metal compound and if used, the promoter. The acid may be slowly added to the metal compound which is generally used in the form of a slurry, for example with mineral oil. Alternatively, the metal compound, and promoter if used, are added to about half the acid and then the remainder of the acid added. The reactants are usually heat soaked eg at 40°C to 60°C and then heated to a temperature of between 60°C and 100°C for example about 85°C and the remainder of the acid added, if only some acid has been used hitherto. As indicated above the metal compound may be slurried in a liquid vehicle, for example a mineral oil, before reacting with the acid. The amount of vehicle can be quite low, for example 5-10% of the total reaction mixture and it is advantageous to use small amounts because this results in lower treat rates when the metal dithiophosphate is used as a lubricating oil additive.

After maintaining the reactants at the reaction temperature for 1 to 4 hours, eg about 1.0 to 3.0 hours the reaction mixture is preferably cooled, flocculant is added and the mixture is stripped and filtered. The filtrate is the desired product.

The lubricating oil to which the metal dithiophosphate can be added includes mineral lubricating oils and synthetic lubricating oils and mixtures thereof. The synthetic oils include polyalpha olefins, diester oils such as di(2-ethylhexyl) sebacate, azelate and adipate, complex ester oils such as those formed from dicarboxylic acids, glycols and either monobasic acids or monohydric alcohols and silicone oils.

The lubricating oil base stock for the antioxidant additives of the present invention typically is adapted to perform a selected function by the incorporation of additives therein to form lubricating oil compositions (i.e. formulations).

Representative additives typically present in such formulations include viscosity modifiers, corrosion inhibitors, other oxidation inhibitors, other friction modifiers, dispersants, anti-foaming agents, anti-wear agents, pour point depressants, detergents, rust inhibitors and the like.

Viscosity modifiers impart high and low temperature operability to the lubricating oil and permit it to remain shear stable at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures.

Viscosity modifiers are generally high molecular weight hydrocarbon polymers including polyesters. The viscosity modifiers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties.

These oil soluble viscosity modifying polymers will generally have number average molecular weights of from 10^3 to 10^6 , preferably 10^4 to 10^5 , e.g., 20,000 to 250,000, as determined by gel permeation chromatography or membrane osmometry.

Representative examples of suitable viscosity modifiers are any of the types known to the art including polyisobutylene, copolymers of ethylene and propylene, polymethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and vinyl compound, interpolymers of styrene and acrylic esters, and styrene/isoprene copolymers.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition. Illustrative of corrosion inhibitors are phosphosulphurized hydrocarbons and the products obtained by reaction of a phosphosulphurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. Phosphosulphurized hydrocarbons are prepared by reacting a suitable hydrocarbon such as terpene, a heavy petroleum fraction of a C_2 to C_6 olefin polymer, such as polyisobutylene, with from 5 to 30 wt.% of a sulfide of phosphorus for 1/2 to 15 hours, at a temperature in the range of 150° to 600° F. Neutralization of the phosphosulphurized hydrocarbon may be effected in the manner taught in U.S. Patent No. 1,969,324.

Oxidation inhibitors reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include ZDDP's, aromatic amines such as alkylated diphenylamines and phenyl alpha naphthylamine, hindered phenols, copper compounds, alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, eg, calcium nonylphenol sulphide, barium t-octylphenyl sulphide, dioctylphenyl-amine, phenylalphanaphthylamine, phosphosulphurized or sulphurized hydrocarbons, etc.

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

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

Dispersants maintain oil insolubles, resulting from oxidation during use, in suspension in the fluid thus preventing sludge flocculation and precipitation or deposition on metal parts. Suitable dispersants include high molecular weight alkenyl succinimides, the reaction product of oil-soluble polyisobutylene succinic anhydride with ethylene amines such as tetraethylene pentamine and borated salts thereof.

Pour point depressants lower the temperature at which the fluid will flow or can be poured. Such depressants are well known. Typically of those additives which usefully optimize the low temperature fluidity of the fluid are C_8 - C_{18} dialkylfumarate vinyl acetate copolymers, polymethacrylates, and wax naphthalene. Foam control can be provided by an antifoamant of the polysiloxane type, eg, silicone oil and polydimethyl siloxane.

Detergents and metal rust inhibitors include the metal salts of sulphonic acids, alkyl phenols, sulphurized alkyl phenols, alkyl salicylates, naphthenates and other oil soluble mono- and di-carboxylic acids.

Highly basic (viz, overbased) metals salts, such as highly basic alkaline earth metal sulphonates (especially Ca and Mg salts) are frequently used as detergents.

5 Copper and lead corrosion inhibitors and antiwear agents include borate esters, thiadiazoles such as derivatives of 2, 5 dimercapto 1,3,4-thiadiazole and benzotriazoles.

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

10 Compositions when containing these conventional additives are typically blended into the base oil in amounts which are effective to provide their normal attendant function. Representative effective amounts of such additives are illustrated as follows:

Additive	Vol %	Wt % a.i.
Viscosity Modifier	.01-4	.01-4
Corrosion Inhibitor	0.01-1	.01-1.5
Oxidation inhibitor	0.01-1	.01-1.5
Dispersant	0.1 -7	0.1 -8
Pour Point Depressant	0.01-1	.01-1.5
20 Anti-Foaming Agents	0.001-0.1	.001-0.15
Anti-Wear Agents	0.001-1	.001-1.5
Friction Modifiers	0.01 - 1	.01 - 1.5
Detergents/Rust Inhibitors	.01-2.5	.01-3
Mineral Oil Base	Balance	Balance

25 When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the dispersant (in concentrate amounts hereinabove described), together with one or more of said other additives (said concentrate when constituting an additive mixture being referred to herein as an additive-package) whereby several additives
30 can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the dispersant additive and optional additional additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount
35 of base lubricant. Thus, the dispersant of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of typically from about 2.5 to about 90%, and preferably from about 5 to about 75%, and most preferably from about 8 to about 50% by weight additives in the appropriate proportions with the remainder being base oil.

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

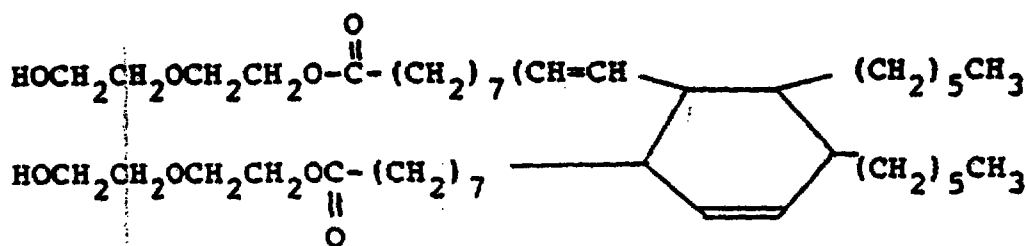
All of said weight percents expressed herein are based on active ingredient (a.i.) content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the a.i. weight of each additive plus the weight of total oil or diluent.

45 The amount of the mixture of dithiophosphate added to the lubricating oil is a minor proportion by weight, preferably less than 20% by weight, more preferably 0.2 to 2.0 and especially 0.5 to 1.5 % by weight.

Additives for lubricating oils are generally supplied as concentrates in solvent (eg oil) for incorporation into the bulk lubricant. According to this invention a concentrate comprises a solvent and 20 to 90 weight %
50 of the metal dithiophosphate of this invention. Suitable solvents include kerosene, aromatic naphthas, mineral lubricating oils etc. Such concentrates may contain one or more other lubricant additives such as described above to form a package which may be diluted with lubricant basestock to form a lubricating oil composition.

55 Example 1

In this Example a zinc dithiophosphate was prepared from a dithiophosphoric acid derived from 2-ethyl hexanol and an alcohol having the formula



hereinafter referred to as alcohol A.

111g of phosphorus pentasulphide was added to a mixture of 253g of 2-ethyl hexanol and 75g of alcohol A over 2 hours at a temperature of 120°C, followed by a 1 hour heat soak at 85°C. The reaction mixture was cooled and filtered. The resulting dithio phosphoric acid had a content of phosphorus of 7.2 weight %.

To prepare the zinc dithiophosphate with a Zn/P molar ratio of 1:1 a reaction vessel was charged with 90g of the acid mixture followed by the addition of 34.7g of ZnO over several minutes. The temperature rose from 22 to 55°C and after 0.5 hr/50°C heat soak, the temperature was raised to 80°C and the rest of the acid (260g) was added over 2 hours, followed by a 1 hour soak at 85°C.

After stripping and filtration, a clear filtrate was obtained (basic Zn 0.85%) which was soluble in a mineral oil at 1.5% at ambient temperature and at 0°C. This product contained the equivalent of about 16% (wt) of alcohol A. Its analysis was Zn = 8.4 wt%, P = 8.1 wt% and S = 16.7 wt%.

Example 2

The product (X) obtained in Example 1 was tested in the four ball friction tests. (1 rpm, 5 kg, 110°C). The results shown below indicate that X has good friction properties

Composition	1	2
Succinimide dispersant	4.5	4.5
Overbased Mg sulphonate	1.0	1.0
ZDDP(1)	1.4	-
X	-	1.5
Mineral Oil	93.1	93.0
μ	0.24, 0.21	0.061

(1) zinc bis(2-ethylhexyl) dithiophosphate.

It is seen that composition 2 containing X has much better friction properties than composition 1 which contains a previously known ZDDP.

Example 3

A mixture of Plexol 305 (a mixture of polyoxyethylene alkyl phenols having 3 and 4 oxyethylene groups) (102g) and isooctanol (238g) was heated to 110°C and P₂S₅ (110g) added over 2 hours. The dithiophosphoric acid thus obtained was heat soaked for 1 hr/85°C, cooled and filtered. The P content was 7.1 wt%. Part of the acid (100g) was charged to a reaction pot at ambient temperature and ZnO (34.1g) and zinc acetate (1.0g) added. The temperature rose to 50°C and stirring continued for 30 mins. The temperature was increased to 85°C and a further 250g of the acid added over 1.5 hours. The ZDDP was heat soaked for 2 hours at 85°C, flocculated, stripped and filtered to give a clear mobile liquid (this analysed as Zn = 7.2; P = 6.4; S = 12.1 wt%) with good oil solubility.

Example 4

2-Ethylhexanol (218g) and glyceryl monooleate (93g) were heated to 85°C and P₂S₅ (111g) added over 2 hours. The acid was heat soaked for 2 hours, cooled and filtered. The acid was found to contain 7.4 wt% P. 100g of the acid was charged to a reaction pot and 30g ZnO plus 0.8g zinc acetate were added. The

temperature rose to 44°C, and the mixture was heat soaked for 30 mins. at 50°C. The temperature was then raised to 50°C and a further 200g of the dithiophosphoric acid added over 1 hour. The ZDDP thus obtained was heat soaked for 2 hours at 85°C, flocculated, stripped and filtered to give a clear mobile liquid oil-soluble product containing Zn 7.9; P 7.3; S 13.1 wt%.

Example 5

Storage Stability Tests

These were carried out on fully formulated oil containing dispersant, detergent and V.I. improver, the only difference being in one case a conventional C₈ ZDDP and friction modifier A (alcohol A of Example 1) was used whereas in the other case the new ZDDP with built-in friction modifier (product X of Example 1) used:

1		2	
C ₈ ZDDP	1.3 wt%	Modified C ₈ ZDDP	
Friction modifier A	0.10 "	(product X)	1.4%
Storage Stability			
<u>25°C</u>	<u>60°C</u>	<u>25°C</u>	<u>60°C</u>
Hazy (3 days)	13% flocculated		
	(3 days)		
18% flocculated	9% flocculated	clear and bright	
(8 days)	(8 days)	(8 days)	

It is noted that the modified C₈ ZDDP in 2 effectively provides 0.5% of friction modifier A, yet still had much better storage stability. It is not possible to dissolve more than 0.1% friction modifier A itself into a blend because of solubility problems.

Example 6

Wear Testing

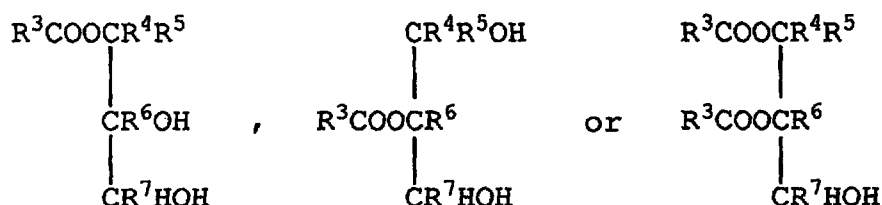
Wear tests were carried out using a reciprocating piston liner section running on a fixed piston ring section at a load of 120 kg for 2 hours. Lower rates of wear were obtained for the two friction modified ZDDPs. The same fully formulated oil, apart from the ZDDP, was used in all cases, and the ZDDPs were compared at 0.1% P treat.

	Wear μm	
	1 hour	2 hours
C ₈ ZDDP	3.2	2.0
C ₈ ZDDP modified with A (Product X of Example 1)	2.2	1.1
C ₄ /C ₅ ZDDP	10.6	2.2
C ₄ /C ₅ ZDDP modified with A (Contained the equivalent of about 21 wt% of A)	3.1	1.4



Claims

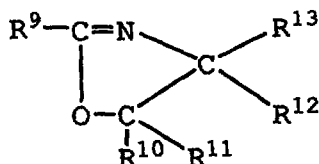
1. A lubricating oil composition comprising a lubricating oil and a minor proportion by weight of a metal dithiophosphate obtainable by reacting a basic zinc or copper compound or a molybdenum compound with a dithiophosphoric acid, said dithiophosphoric acid being obtainable by reacting phosphorous pentasulphide with a mixture of alcohols ROH and R¹(OH)_m where m is 1 or 2, the group R is an aliphatic hydrogen- and carbon-containing group having at least 4 carbon atoms or is an alkaryl group, and R¹ is a hydrogen- and carbon-containing group containing at least 12 carbon atoms which group R¹ includes either (a) a >C=N- group or (b) the group -(C_nH_(2n-p)R²_pO)_q-, R₂ being an alkyl group, n being an integer of from 2 to 5, p being zero or an integer of from 1 to 5 and q being an integer of 2 or more with the proviso that p is less than 2n or R¹(OH)_m is a glyceryl derivative having the formula



where R³ is an aliphatic hydrogen- and carbon-containing group containing at least 9 carbon atoms and R⁴, R⁵, R⁶ and R⁷ are hydrogen or alkyl groups.

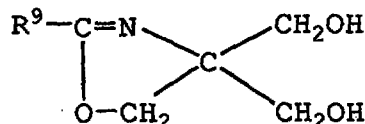
2. A lubricating oil composition according to claim 1 wherein R is 2-ethyl hexyl.

3. A lubricating oil composition according to either of claims 1 and 2 wherein R¹(OH)_m is an oxazoline of the formula



where R⁹ is alkyl or alkenyl, R¹⁰ and R¹¹ are hydrogen or alkyl and R¹² and R¹³ are alkyl or hydroxy alkyl provided at least one of them is hydroxy alkyl.

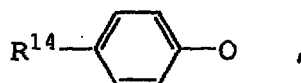
4. A lubricating oil composition according to claim 3 wherein R¹(OH)_m is



5. A lubricating oil composition according to either of claims 1 and 2 wherein R¹(OH)_m is a compound of the formula



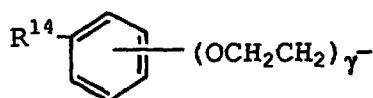
wherein Y has the formula



$R^{14}\text{COO}-$ or $R^{14}\text{CH}_2\text{O}-$

wherein R^{14} is an aliphatic hydrocarbyl radical having at least 4 carbon atoms subject to R^1 containing at least 12 carbon atoms.

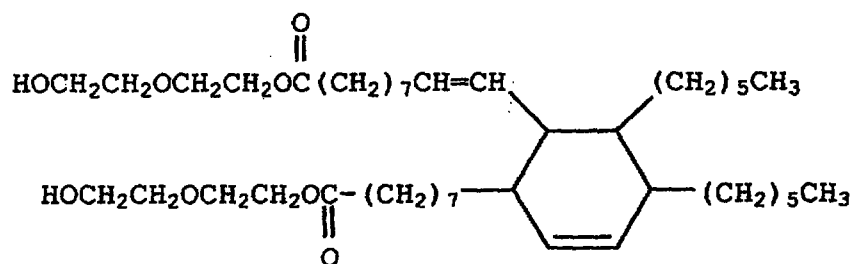
6. A lubricating oil composition according to claim 5 wherein R^1 is of the formula



where R^{14} is C_8 or C_9 alkyl and γ is 3 or 4.

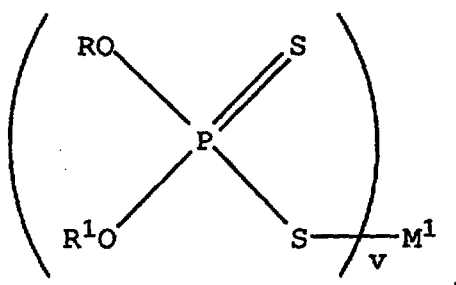
7. A lubricating oil composition according to either of claims 1 and 2 wherein $R^1(\text{OH})_m$ is a hydroxy ester derived from the esterification of a polycarboxylic acid with a polyglycol.

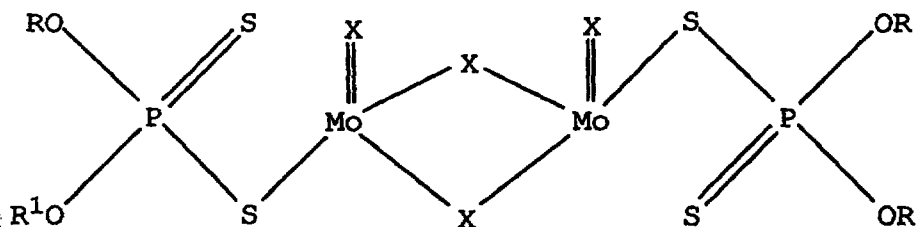
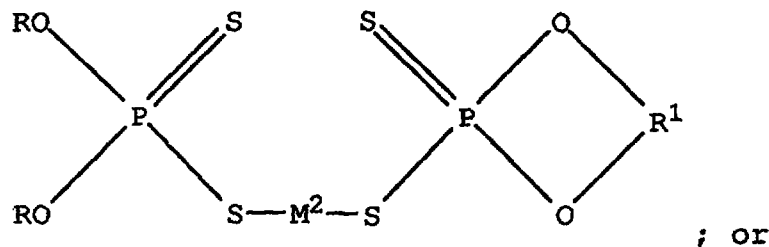
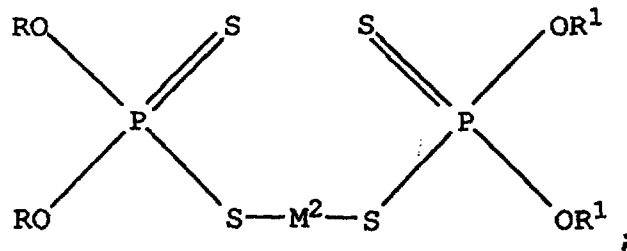
8. A lubricating oil composition according to claim 7 wherein $R^1(\text{OH})_m$ is a hydroxy ester of the formula



9. A lubricating oil composition according to either of claims 1 and 2 wherein $R^1(\text{OH})_m$ is glyceryl mono oleate.

10. A lubricating oil composition according to any of the preceding claims wherein the metal dithiophosphate is





where M^1 is cuprous or cupric copper or zinc, M^2 is cupric copper or zinc, v being the valency of the metal and X is S or O.

11. A composition according to any of claims 1 to 10 which contains 0.2 to 2.0 weight % of the metal dithiophosphate.

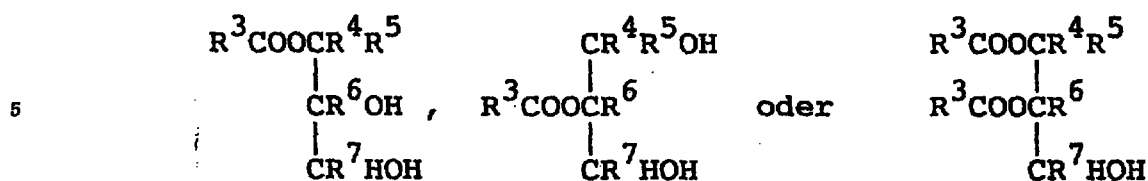
12. A concentrate comprising a solvent compatible in lubricant oils and 20 to 90 weight % of the metal dithiophosphate defined in any one of claims 1 to 10.

13. The use in a lubricating oil as an antiwear additive of the metal dithiophosphate defined in any one of claims 1 to 10.

14. The metal dithiophosphate as defined in any of claims 1 to 4 and 7 to 10, wherein the group R^1 does not contain a polyalkyleneoxide group $-(\text{C}_n\text{H}_{2n-p}\text{R}_p^2\text{O})_q^-$.

Patentansprüche

- Schmierölzusammensetzung, die ein Schmieröl und einen geringen Gewichtsanteil eines Metaldithiophosphats enthält, das durch Umsetzung einer basischen Zink- oder Kupferverbindung oder einer Molybdänverbindung mit einer Dithiophosphorsäure erhältlich ist, wobei die Dithiophosphorsäure durch Umsetzung von Phosphorpentasulfid mit einer Mischung aus Alkoholen ROH und $\text{R}^1(\text{OH})_m$ erhältlich ist, wobei m 1 oder 2 ist, die Gruppe R eine aliphatische Wasserstoff und Kohlenstoff enthaltende Gruppe mit mindestens 4 Kohlenstoffatomen oder eine Alkarylgruppe ist, und R^1 eine Wasserstoff und Kohlenstoff enthaltende Gruppe mit mindestens 12 Kohlenstoffatomen ist, wobei die Gruppe R^1 entweder (a) eine $>\text{C}=\text{N}$ -Gruppe oder (b) die Gruppe $-(\text{C}_n\text{H}_{2n-p}\text{R}_p^2\text{O})_q^-$ einschließt, wobei R^2 eine Alkylgruppe ist, n eine ganze Zahl von 2 bis 5 ist, p 0 oder eine ganze Zahl von 1 bis 5 ist und q eine ganze Zahl von 2 oder mehr ist, mit der Maßgabe, daß p weniger als $2n$ ist, oder $\text{R}^1(\text{OH})_m$ ein Glycerinderivat mit der Formel



ist, wobei R^3 eine aliphatische Wasserstoff und Kohlenstoff enthaltende Gruppe mit mindestens 9 Kohlenstoffatomen ist und R^4 , R^5 , R^6 und R^7 Wasserstoff oder Alkylgruppen sind.

2. Schmierölzusammensetzung nach Anspruch 1, bei der R 2-Ethylhexyl ist.
3. Schmierölzusammensetzung nach einem der Ansprüche 1 oder 2, bei der $R^1(\text{OH})_m$ ein Oxazolin mit der Formel



ist, wobei R^9 Alkyl oder Alkenyl ist, R^{10} und R^{11} Wasserstoff oder Alkyl sind und R^{12} und R^{13} Alkyl oder Hydroxyalkyl sind, vorausgesetzt, daß mindestens einer von ihnen Hydroxyalkyl ist.

4. Schmierölzusammensetzung nach Anspruch 3, bei der $R^1(\text{OH})_m$



ist.

5. Schmierölzusammensetzung nach einem der Ansprüche 1 oder 2, wobei $R^1(\text{OH})_m$ eine Verbindung mit der Formel



ist, wobei Y die Formel

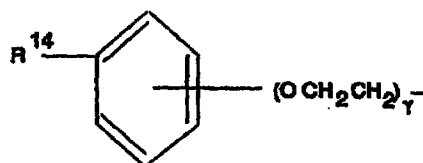


$R^{14}\text{COO}-$ oder $R^{14}\text{CH}_2\text{O}-$

hat, wobei R^{14} ein aliphatischer Kohlenwasserstoffrest mit mindestens 4 Kohlenstoffatomen ist, vorausgesetzt, daß R^1 mindestens 12 Kohlenstoffatome enthält.



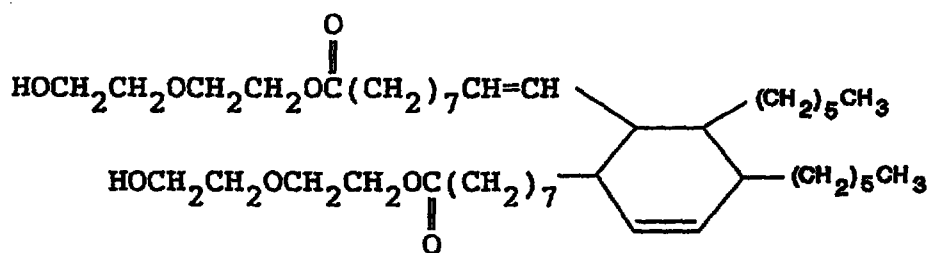
6. Schmierölszusammensetzung nach Anspruch 5, wobei R^1 die Formel



besitzt, in der R^{14} C_8 - oder C_9 -Alkyl ist und γ 3 oder 4 ist.

7. Schmierölszusammensetzung nach einem der Ansprüche 1 oder 2, bei der $R^1(\text{OH})_m$ ein aus der Veresterung von Polycarbonsäure mit Polyglykol stammender Hydroxyester ist.

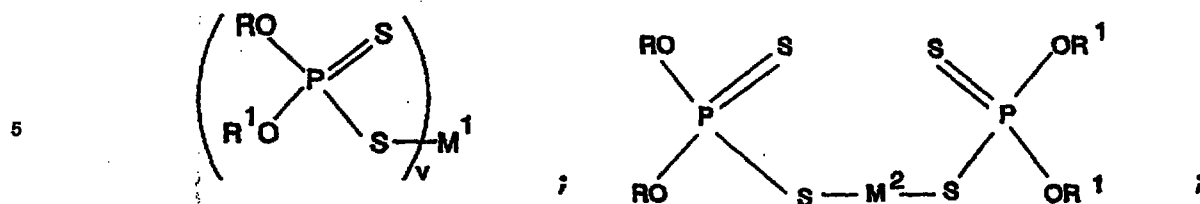
8. Schmierölszusammensetzung nach Anspruch 7, bei der $R^1(\text{OH})_m$ ein Hydroxyester mit der Formel



ist.

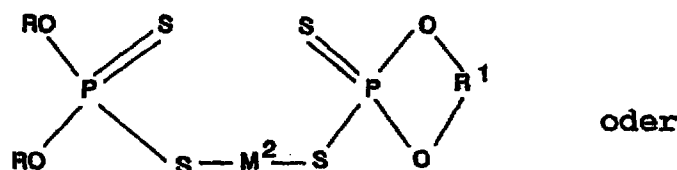
9. Schmierölszusammensetzung nach einem der Ansprüche 1 oder 2, wobei $R^1(\text{OH})_m$ Glycerinmonooleat ist.

10. Schmierölszusammensetzung nach einem der vorhergehenden Ansprüche, bei der das Metaldithiophosphat



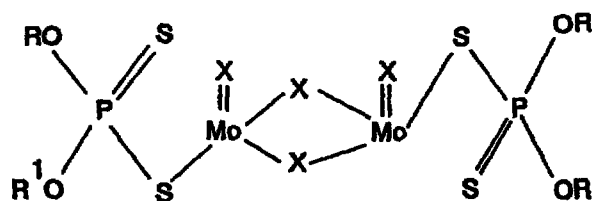
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ist, wobei M^1 Kupfer in ein- oder zweiwertiger Form oder Zink ist, M^2 Kupfer in zweiwertiger Form oder Zink ist, v die Wertigkeit des Metalls ist und X S oder O ist.

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11. Zusammensetzung nach einem der Ansprüche 1 bis 10, die 0,2 bis 2,0 Gew.% des Metaldithiophosphats enthält.

40

12. Konzentrat, das ein mit Schmierölen verträgliches Lösungsmittel und 20 bis 90 Gew.% des in einem der Ansprüche 1 bis 10 definierten Metaldithiophosphats enthält.

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13. Verwendung des in einem der Ansprüche 1 bis 10 definierten Metaldithiophosphats als Antiverschleißadditiv in Schmieröl.

14. Metaldithiophosphate wie in einem der Ansprüche 1 bis 4 und 7 bis 10 definiert, wobei die Gruppe R^1 keine Polyalkylenoxidgruppe $-(\text{C}_n\text{H}_{2n-p}\text{R}_p\text{O})_q-$ enthält.

45 Revendications

1. Composition d'huile lubrifiante comprenant une huile lubrifiante et une faible proportion en poids d'un dithiophosphate métallique pouvant être obtenu par réaction d'un composé de zinc ou de cuivre basique ou d'un composé de molybdène avec un acide dithiophosphorique, ledit acide dithiophosphorique pouvant être obtenu par réaction du pentasulfure de phosphore avec un mélange d'alcools de formules ROH et $\text{R}^1(\text{OH})_m$

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où m est égal à 1 ou 2,

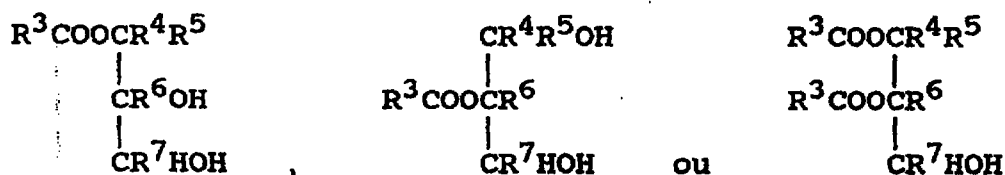
le groupe R est un groupe aliphatique contenant de l'hydrogène et du carbone, renfermant au moins 4 atomes de carbone, ou bien représente un groupe alkyle, et

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R^1 représente un groupe contenant de l'hydrogène et du carbone, renfermant au moins 12 atomes de carbone, groupe R^1 qui comprend (a) un groupe $>\text{C}=\text{N}-$, ou (b) le groupe $-(\text{C}_n\text{H}_{(2n-p)}\text{R}_p\text{O})_q-$, R_2 représente un groupe alkyle, n étant un nombre entier de 2 à 5, p étant égal à 0 ou à un nombre entier de 1 à 5 et q étant un nombre entier égal ou supérieur à 2, sous réserve que p soit inférieur à $2n$,

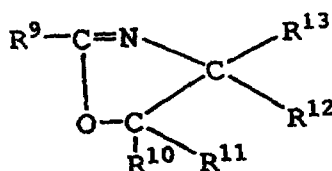


ou bien $R^1(OH)_m$ représente un dérivé de glycéryle répondant à la formule



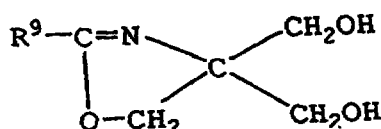
dans laquelle R^3 représente un groupe aliphatique contenant de l'hydrogène et du carbone, renfermant au moins 9 atomes de carbone, et R^4 , R^5 , R^6 et R^7 représentent des atomes d'hydrogène ou des groupes alkyle.

2. Composition d'huile lubrifiante suivant la revendication 1, dans laquelle R représente un groupe 2-éthylhexyle.
3. Composition d'huile lubrifiante suivant l'une et l'autre des revendications 1 et 2, dans laquelle $R^1(OH)_m$ représente une oxazoline de formule



dans laquelle R^9 représente un groupe alkyle ou alcényle, R^{10} et R^{11} représentent l'hydrogène ou des groupes alkyle et R^{12} et R^{13} représentent des groupes alkyle ou hydroxyalkyle, sous réserve qu'au moins l'un d'entre eux soit un groupe hydroxyalkyle.

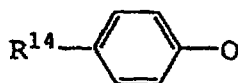
4. Composition d'huile lubrifiante suivant la revendication 3, dans laquelle $R^1(OH)_m$ répond à la formule



5. Composition d'huile lubrifiante suivant l'une et l'autre des revendications 1 et 2, dans laquelle $R^1(OH)_m$ est un composé de formule



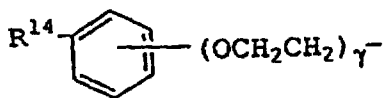
dans laquelle Y répond à la formule



$R^{14}COO-$ ou $R^{14}CH_2O-$ dans laquelle R^{14} représente un radical hydrocarbyle aliphatique possédant au moins 4 atomes de carbone, sous réserve que R^1 contienne au moins 12 atomes de carbone.

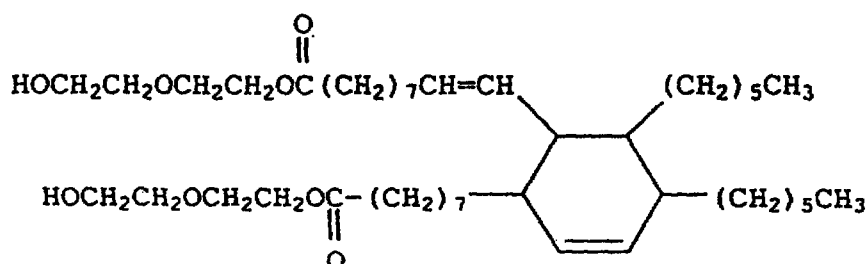


6. Composition d'huile lubrifiante suivant la revendication 5, dans laquelle R¹ répond à la formule

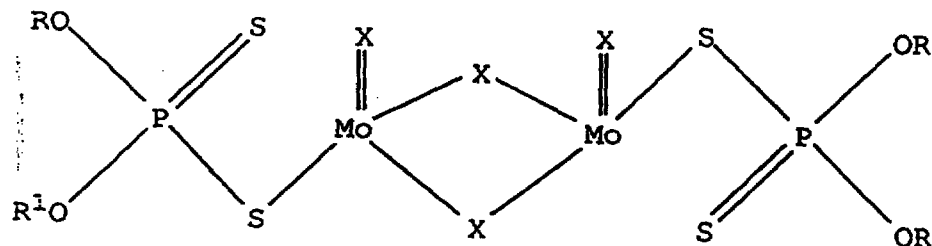
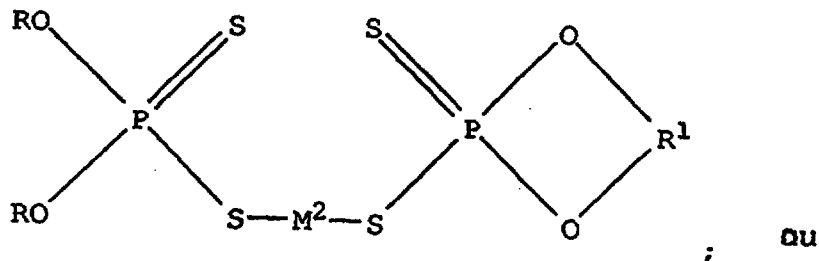
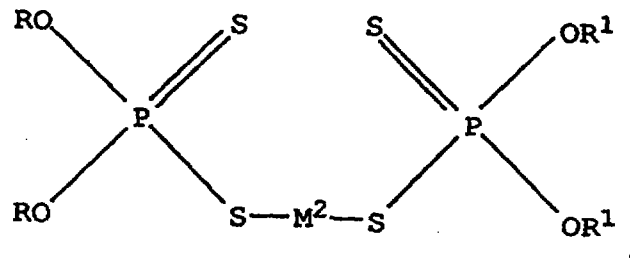
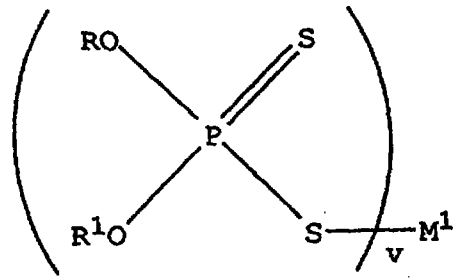


dans laquelle R¹⁴ représente un groupe alkyle en C₈ ou C₉ et γ est égal à 3 ou 4.

7. Composition d'huile lubrifiante suivant l'une et l'autre des revendications 1 et 2, dans laquelle R¹(OH)_m est un hydroxyester obtenu par estérification d'un acide polycarboxylique avec un polyglycol.
8. Composition d'huile lubrifiante suivant la revendication 7, dans laquelle R¹(OH)_m est un hydroxyester de formule



9. Composition d'huile lubrifiante suivant l'une et l'autre des revendications 1 et 2, dans laquelle R¹(OH)_m représente le monooléate de glycéryle.
10. Composition d'huile lubrifiante suivant l'une quelconque des revendications précédentes, dans laquelle le dithiophosphate métallique répond à la formule



dans laquelle M¹ est le cuivre cuivreux ou cuivrique ou le zinc, M² est le cuivre cuivrique ou le zinc, v étant la valence du métal et X représente S ou O.

11. Composition suivant l'une quelconque des revendications 1 à 10, qui contient 0,2 à 2,0 % en poids du dithiophosphate métallique.

12. Concentré comprenant un solvant compatible avec les huiles lubrifiantes et 20 à 90 % en poids du dithiophosphate métallique défini dans l'une quelconque des revendications 1 à 10.

13. Utilisation dans une huile lubrifiante, comme additif anti-usure, du dithiophosphate métallique défini dans l'une quelconque des revendications 1 à 10.

14. Dithiophosphate métallique défini dans l'une quelconque des revendications 1 à 4 et 7 à 10, dans lequel le groupe R¹ ne contient pas un groupe polyalkylèneoxyde $-(\text{C}_n\text{H}_{2n-p}\text{R}_p^2\text{O})_q-$