

Description

The present invention relates to lubricating compositions, especially automobile crankcase lubricants, containing low or zero amounts of phosphorus and zinc.

There is currently a drive to reduce the amounts of phosphorus in lubricants because of the deleterious effect phosphorus has on catalysts commonly used in catalytic converters used for emission control. Levels of phosphorus have typically been of the order of 0.1% but there is an increasing need to reduce phosphorus levels to below 0.05 wt % or remove it altogether. However, zinc dialkyl dithiophosphates (ZDDP) and other phosphorus containing additives have been widely used as anti-wear and/or anti-oxidant additives and simply reducing or removing such components results in lubricants with poor engine performance.

This invention provides lubricant compositions and concentrates with low or zero amounts of phosphorus and zinc, and which comprise copper, sulphur, and a bearing corrosion inhibitor, which compositions have been found to have remarkable engine performance.

US-A-2356661 deals with lubricating oils containing 50 to 1000 parts per million of copper as an oil-soluble organic compound such as copper dialkyl dithiocarbamates and including phosphorus containing compounds together with from 0.1 to 0.5 wt % of total sulphur in the oil, sulphur being provided as oil-soluble organic sulphur compounds such as thiocarbamates.

US-A-2343756 discloses the addition of copper compounds including phosphorus-containing copper complexes in conjunction with sulphur compounds, to lubricating oils. Amounts of from 0.1 to 0.5 wt % of sulphur are disclosed, with amounts in excess of 0.5 wt % sulphur described as being potentially detrimental. In US-A-2552580, cuprous thiophosphates are included in lubricant compositions at relatively high levels, which will give high phosphorus level in the oils. In US-A-3346493, a wide variety of metal-containing polymeric amine-metal reactants are employed as detergents in lubricant compositions. In an isolated example, a lubricant is described containing inter alia, a copper salt of an acylated nitrogen compound, 0.075% phosphorus as a ZDDP reacted with hexene oxide, and a sulphurized methyl ester of a tall oil acid. Other copper containing lubricants either contain more phosphorus or no sulphur. US-A-4122033 discloses the entire group of transition metal compounds as antioxidation stabilizers in conjunction with amines, selenides, phosphines or phosphites and may be used in various applications including as additives for lubricants. None of the foregoing documents describe fully formulated lubricant oils which would be appropriate to meet the requirements for modern lubricants and none specifically address the reduction of phosphorus levels while maintaining performance in antiwear, antioxidation and corrosion inhibition.

EP-A-24148 discloses lubricant compositions containing an ashless dispersant and/or polymeric viscosity index improver dispersant and copper which may be in the form of a dithiocarbamate, but requires the presence of from 0.01 to 0.5 wt% zinc and from 0.01 to 0.5 wt % phosphorus. Thiadiazole polysulphides are an optional component.

US-A-4330420 describes oils with reduced phosphorus content (but only to 0.05%P) using mixtures of dialkyldiphenylamine and a sulphurized polyolefin to compensate for reduction in the amount of ZDDP. There is no disclosure of the use of copper or thiadiazole polysulphides.

EP-A-89844 describes reaction products of 4,4'-methylene-(2,6-di-t-butyl phenol) and tri-Sec-C₄-₁₂ alkyl orthoborate and their use in lubricants to enable the amount of ZDDP to be reduced to provide from 0.05 to 0.11 wt % p.

US-A-4490265 describes lubricating oils comprising boron-containing heterocyclic compounds which may be in the form of a metal salt including a copper salt, thiadiazole polysulphides, terephthalic acid and as an oxidation inhibitor either a bis(dithiobenzil) metal derivative where the metal may inter alia be copper or a sulphur-bridged, bis hindered phenol. The desirability of reducing or eliminating phosphorus is not disclosed and all the Examples of lubricants contain 0.05 wt% P. US-A-4623474 contains a similar disclosure. US-A-4627930 also describes boron-containing heterocyclic compounds which may be in the form of a copper salt and may be sulphurized. Thiadiazole polysulphides and copper carboxylates are also disclosed. Although the boron-containing heterocyclic compounds are described as phosphorus-free, there is no disclosure of a fully formulated oil containing less than 0.05 wt % P. US-A-4 629 580 contains a similar disclosure, as does US-A-4 595 514. US-A-4 629 579 discloses boron and metal-boron derivatives for use as extreme pressure, anti-wear and friction reducing additives for lubricating oils and compositions including one containing no ZDDP, but there is disclosure of a composition containing low or zero amounts of phosphorus, with sulphur and copper.

GB-A-779825 discloses an antioxidant for hydrocarbon oils, the antioxidant comprising a copper compound and a relatively small amount (0.4 % in the Examples) of an iron, nickel or cobalt derivative of

an alkyldithio acid or acids.

WO-A-8707291 relates to the use of low concentrations of an oil-soluble transition metal compound for ameliorating low temperature thickening in automatic transmission fluids and high temperature thickening in gear lubricants, copper compounds being mentioned in this context. Lubricant compositions which exhibit improved resistance to high temperature thickening and a dramatic reduction in the formation of insoluble resins are disclosed.

Each of WO-A-8604601 and WO-A-8604602 indicates that the compositions disclosed therein may contain a dithiocarbamate of any monovalent or polyvalent metal and lists the alkaline earth metals, zinc, cadmium, magnesium, tin, molybdenum, iron, copper, nickel, cobalt, chromium and lead as examples of suitable polyvalent metals, the Group II metals being preferred. Each specification indicates that the compositions may contain ZDDPs, and indicates a low level of phosphorus as being less than 0.1%.

The invention seeks to provide lubricants having antiwear, corrosion inhibition and antioxidant performance appropriate to modern oil requirements with reduced or zero amounts of zinc and phosphorus and without the need for large amounts and/or expensive forms of antioxidant. Lubricants with reduced or zero amounts of phosphorus are disclosed and claimed in European Application No. 88.301 712.1.

The term "modern oil" as used herein in relation to automobile crankcase lubricants refers to oil which can meet the current requirements for crankcase lubricants in the major industrial countries. High performance engines, increased lifetime requirements resulting from longer periods between oil changes and higher operating temperatures all contribute to the increased performance required from lubricants. This invention is particularly concerned with automobile lubricants which can meet and exceed the requirements for the SF API Engine Service Category for service station oils and/or the CD requirements for the CD/API Engine Service Category for Commercial Oils (Diesel Engines) established jointly by API, SAE and ASTM.

In one aspect, this invention provides a lubricant composition comprising a major amount of a lubricating oil, 5 to 500 parts per million by weight (ppm) of added copper present in oil-soluble form, one or more added oil-soluble sulphur-containing compounds such that the composition preferably comprises from greater than 0.5 to 2.0 wt % of total sulphur, more preferably 0.5 to 1.0 wt % of total sulphur, and an effective amount of a bearing corrosion inhibitor, the composition containing less than 0.05 wt % phosphorus and less than 0.01 wt% zinc, preferably being substantially phosphorus-free and zinc-free.

In particularly preferred embodiments of the invention, the lubricant composition will also contain one or more ashless dispersants and/or one or more viscosity index improver dispersants and/or one or more overbased additives which function as antacid and anti-rust agents, such as overbased calcium or magnesium sulphonates or phenates.

The use of copper in the invention enables a low phosphorus oil with performance meeting the requirements for modern oils to be obtained economically and with good control of oxidation, which in an automobile engine is catalysed by metal accumulated in the oil by wear or corrosion, with iron being a particular oxidation catalyst. At unduly low concentrations of copper, the anti-oxidant effect may not be sufficient for some applications. At unduly high concentrations the ash level of the oil will be increased and an increased tendency to bearing corrosion may be observed. The amount of added copper in the compositions will generally be within the range of 10 to 400 ppm, typically 10 to 300 ppm, preferably 10 to 200 ppm, e.g. 60 to 200 ppm.

The ability of the compositions of the invention comprising low amounts of oil-soluble copper compounds and very low or zero amounts of phosphorus to provide adequate antioxidant and antiwear performance for the stringent requirements of modern engine tests is surprising. Copper is known to act in many situations as an oxidation promoter or catalyst, and closely related metals, such as cobalt and chromium, are not effective lubricant anti-oxidants. EP-A-24146 teaches the presence of at least 0.01 wt % of each of phosphorus and zinc.

It is also surprising that the copper compound functions effectively in compositions which may contain zinc and other metal compounds, such as calcium or magnesium overbased additives, which have an inherent pro-oxidant activity.

The copper compounds used as anti-oxidants in this invention may be chosen from those described in EP-A-24146 as suitable for lubricants provided that the copper compounds are substantially free of phosphorus.

Thus, the copper may be blended into the oil as the oil soluble copper salt of a synthetic or natural carboxylic acid. Examples of suitable carboxylic acids include C₁₀ to C₁₈ fatty acids such as stearic or palmitic acid, unsaturated acids such as oleic acid, branched carboxylic acids such as naphthenic acids of molecular weight from 200 to 500, neodecanoic or 2-ethylhexanoic acid and alkyl or alkenyl substituted dicarboxylic acids such as polyalkene substituted succinic acids, e.g. octadecenyl succinic acids,

dodecenyl succinic acids and polyisobutenyl succinic acids.

The copper may be blended into the oil as oil-soluble copper dithiocarbamates of the general formula $(RR'NCSS)_nCu$, where n is 1 or 2 and R and R' are the same or different hydrocarbyl radicals containing 1 to 18, preferably 2 to 12 carbon atoms such as alkyl, alkenyl, aryl, aralkyl, alkaryl and cycloalkyl radicals. Other copper and sulphur containing compounds such as copper mercaptides, disulphides and thioxanthates are suitable for use in the invention. Copper sulphonates, phenates, and acetylacetonates may also be used.

Alternatively the copper may be introduced in the oil in an oil-insoluble form provided that in the finished lubricant composition the copper is in the form of an oil-soluble compound. The term "added copper" is intended to exclude copper present in the oil as a result of accumulation of copper in the oil during use, e.g. by wear or corrosion of copper-containing components.

The lubricant compositions of the invention contain an added oil-soluble sulphur compound. One preferred class of such sulphur compounds are the dithiocarbamates, preferably of the formula: $(RR'NCSS)_nM$, wherein R, R' and n are as defined hereinbefore and M is a suitable metal such as molybdenum or (as indicated above) copper or a optionally substituted hydrocarbyl radical. Preferred dithiocarbamates are dialkyl dithiocarbamates preferably containing 2 to 12 carbon atoms such as diamyl dithiocarbamates.

Sulphur may also be introduced as a mercaptide particularly the mercaptides of aliphatic mercaptans (including copper mercaptides as indicated above), sulphurized unsaturated organic compounds including sulphurized olefins (e.g. US-A-4119549, US-A-4119550, US-A-4191659 and US-A-4147640), sulphurized Diels-Alder adducts (e.g. US-A-3632566, US-A-3498915 and US-E-27331) and particularly sulphurized unsaturated alcohols and esters such as sperm oil substitutes, sulphides including di- and polysulphides, thioethers, thiophenols, thioxanthates (including copper thioxanthates as indicated above), sulphurized esters, thioesters, thioamides, thiazoles such as benzothiazoles, and particularly mercaptobenzothiazoles, and thiadiazoles.

Mineral lubricating oils contain sulphur, whereas synthetic oils may be sulphur-free, so that the amount of sulphur added as a sulphur-containing compound varies according to the basestock and the sulphur contents of other components in the lubricating composition, more preferably so as to give a sulphur content of greater than 0.5 to 1.0 wt % total sulphur. The lubricant compositions of the invention advantageously contain from 0.5 to 0.7 wt % total S, and most preferably 0.1 to 0.5 wt % S as added oil-soluble sulphur-containing compound preferably in the form of a sulphurized ester.

The bearing corrosion inhibitor is a corrosion inhibitor effective at inhibiting corrosion effects on bearings such as Cu/Pb bearings, where effects such as copper staining and high weight loss can be encountered. Such additives have been found to promote the anti-wear performance of the oil. Preferred bearing corrosion inhibitors are borate esters such as $B(OR)_3$, $(RO)_2B-O-B(OR)_2$ or $(ROBO)_3$, $(RO)_2BOR'OB(OR)_2$ and mixtures (wherein R is a substituted or unsubstituted alkyl, aryl or aralkyl group or two groups R together form a substituted or unsubstituted alkylene group and R' is a substituted or unsubstituted alkylene group) and these materials may be derived, for example, from alcohols such as alkoxyalkanols (both short chain alkanols and longer chain alcohols as in US-A-4440656) and polyetheralkanols; mono-, di- and trihydroxy alkanols, e.g. 2-ethylhexanol, 2-ethylhexan-1,3-diol, butane-1,2-diol, butane-1,3-diol glycerol and the acyclic polyols of US-A-2866811; hydroxy esters such as glyceryl mono-oleate; oxazolines derived for example from oleic acid and tris(hydroxymethyl)-aminomethane; sulphur-containing alcohols such as may be obtained by reacting epoxides with mercaptans e.g. 1-dodecyl-mercaptoethanol; amino alcohols such as alkanolamines e.g. triethanolamine and tri-isopropanolamine, hydroxyamines made by reacting a primary amine (e.g. oleylamine) or secondary amine with ethylene or propylene oxide and the compounds of US-A-4406802. Preferred alcohols are 2-methylpentan-1,3-diol, butane-1,2-diol, butane-1,3-diol and similar 1,2 and 1,3 diols, and ethoxyethanol.

In a preferred aspect the invention contains from 0.01 to 10 wt %, preferably 0.1 to 5 wt %, of a borate ester especially an ester of an alkoxyalkanol or a polyetheralkanol, e.g. a tris(ethoxyethyl) orthoborate ester or metaborate ester, or a diborate of a diol such as butane-1,3-diol.

As an alternative, the bearing corrosion inhibitor is a thiadiazole mercaptan, especially a thiadiazole polysulphide containing from 5 to 50 carbon atoms, a derivative or polymer thereof. Preferred materials are the derivatives of 1,3,4 thiadiazole polysulphides such as those described in US-A-2719125, 2719126 and 3087932. Especially preferred is the compound 2,5-bis (t-octadithio)-1,3,4-thiadiazole commercially available as Amoco 150 or 2,5-bis(nonyldithio)-1,3,4-thiadiazole available as Amoco 158. Other similar materials also suitable are described in US-A-3821236, 3904537, 4097387, 4107059, 4136043, 4188299 and 4193882. Derivatives of thiadiazole mercaptans may be used such as esters, condensation products with halogenated carboxylic acids, reaction products with aldehydes and amines, alcohols or mercaptans, amine salts, dithiocarbamates, reaction products with ashless dispersants (e.g. US-A-4140643 and US-A-4136043) and

reaction products with sulphur halides and olefins.

These materials are preferably present in an amount of from 0.01 to 10 wt %, more preferably 0.1 to 5.0 wt % of the lubricant composition.

The lubricating compositions may comprise small amounts of phosphorus, less than 0.05 wt %, preferably less than 0.01 wt %, more preferably less than 0.005 wt %, but more preferably the lubricating compositions are substantially free of phosphorus.

In a preferred aspect the lubricating composition further comprises:

(A) from 1 to 10 wt % of an ashless dispersant compound which is:

an ashless nitrogen or ester containing dispersant compound preferably selected from:

- (i) oil soluble salts, amides, imides, oxazolines and esters, or mixtures thereof, of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides;
- (ii) long chain aliphatic hydrocarbon having a polyamine attached directly thereto; and
- (iii) Mannich condensation products formed by condensing a molar proportion of long chain hydrocarbon substituted phenol with 1 to 2.5 moles of formaldehyde and 0.5 to 2 moles of polyalkylene polyamine; wherein said long chain hydrocarbon group is a polymer of a C₂ to C₅ monoolefin, said polymer having a molecular weight of 700 to 5000; and/or

(B) from 0.3 to 10 wt %, of a nitrogen or ester containing polymeric viscosity index improver dispersant which may include

- (a) polymers comprised of C₄ to C₂₄ unsaturated esters of vinyl alcohol or C₃ to C₁₀ unsaturated mono- or di-carboxylic acid with unsaturated nitrogen containing monomers having 4 to 20 carbons;
- (b) polymers of C₂ to C₂₀ olefin with unsaturated C₃ to C₁₀ mono- or di-carboxylic acid neutralised with amine, hydroxy amine or alcohols; and
- (c) polymers of ethylene with a C₃ to C₂₀ olefin further reacted either by grafting C₄ to C₂₀ unsaturated nitrogen containing monomers thereon or by grafting an unsaturated acid onto the polymer backbone and then reacting said carboxylic acid groups with amine, hydroxy amine or alcohol.

The nitrogen containing dispersant additives are those known in the art as sludge dispersants for crankcase motor oils, e.g. such as shown in US-A-3275554, US-A-3585804, US-A-3442808, US-A-3442808, GB-A-983040 or BE-A-658236.

The most commonly used dispersants are those formed by reacting alkenyl succinic anhydride, e.g. polyisobutenyl succinic anhydride, and an amine described in US-A-3202678, 3154580, 3172892, 3024195, 3024237, 3219666, 3216936 and BE-A-662875.

Alternatively the ashless dispersants may be esters derived from long chain hydrocarbon substituted carboxylic acids and from hydroxy compounds such as monohydric and polyhydric alcohols or aromatic compounds such as phenols and naphthols as prepared for example in US-A-3522179.

Hydroxyamines which can be reacted with any of the aforesaid long chain hydrocarbon substituted carboxylic acids to form dispersants include 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, p-(beta-hydroxyethyl)-aniline, 2-amino-1-propanol, 3-amino-1-propanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol, N-(beta-hydroxy-propyl)-N'-(beta-aminoethyl)-piperazine, tris(hydroxymethyl) aminomethane (also known as trimethylolaminomethane), 2-amino-1-butanol, ethanolamine, beta-(beta-hydroxyethoxy)-ethylamine, and the like. Mixtures of these or similar amines can also be employed.

Preferred dispersants are those derived from polyisobutenyl succinic anhydride and polyethylene amines, e.g. tetraethylene pentamine, polyoxyethylene and polyoxypropylene amines, e.g. polyoxypropylene diamine, trimethylolaminomethane and pentaerythritol, and combinations thereof. One particularly preferred dispersant combination involves a combination of (A) polyisobutenyl succinic anhydride with (B) a hydroxy compound, e.g. pentaerythritol, (C) a polyoxyalkylene polyamine, e.g. polyoxypropylene diamine, and (D) a polyalkylene polyamine, e.g. polyethylene diamine and tetraethylene pentamine using about 0.01 to about 4 equivalents of (B) and (D) and about 0.01 to about 2 equivalents of (C) per equivalent of (A) as described in US-A-3894763. Another preferred dispersant combination involves the combination of (A) polyisobutenyl succinic anhydride with (B) a polyalkylene polyamine, e.g. tetraethylene pentamine, and (C) a polyhydric alcohol or polyhydroxy-substituted aliphatic primary amine, e.g. pentaerythritol or trimethylolaminomethane as described in US-A-3632511.

The alkenyl succinic polyamine type dispersants can be further modified with a boron compound such as boron oxide, boron halides, boron acids and ester of boron acids in an amount to provide 0.1 to 10 atomic proportions of boron per mole of the acylated nitrogen compound as generally taught in US-A-3087936 and 3254025. Mixtures of dispersants can also be used such as those described in US-A-4113639.

The oils may contain from 1.0 to 10 wt %, more preferably 2.0 to 7.0 wt % of these dispersants.

The dispersancy may be provided by 0.3 to 10% of a polymeric Viscosity Index improver dispersant,

for example copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminoalkyl methacrylate, alkyl fumarate-vinyl acetate N-vinyl pyrrolidone copolymers, post-grafted interpolymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine, such as in US-A-4149984; or styrene/maleic anhydride polymers post-reacted with

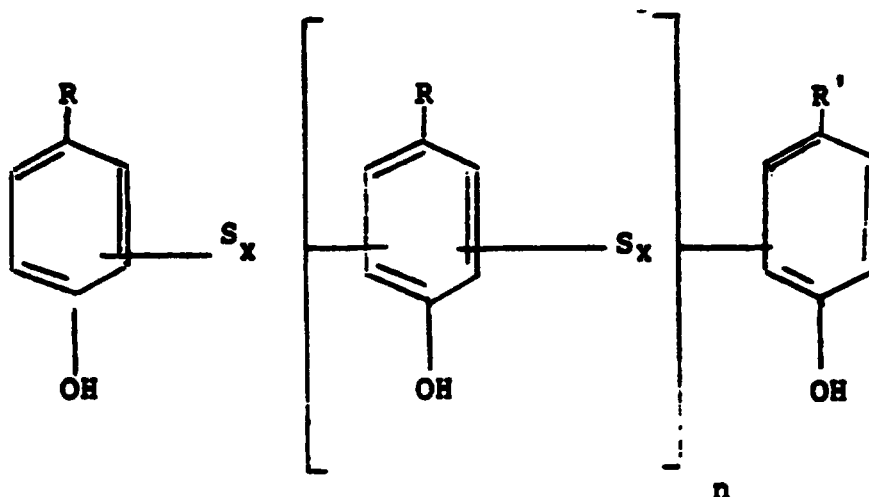
alcohols and amines, ethoxylated derivatives of acrylate polymers such as in US-A-3702300.

Magnesium and/or calcium containing additives are frequently included in lubricating compositions either alone or in combination with other alkali metal or alkaline earth metal additives such as those containing sodium. These may be present for example as the metal salts of sulphonic acids, alkyl phenols, sulphurised alkyl phenols, alkyl salicylates, naphthenates, and other oil soluble mono- and di-carboxylic acids.

Highly basic alkaline earth metal alkaryl sulfonates are generally known for example in US-A-3150088 and 3150089. For the purposes of this invention, a preferred alkaline earth sulfonate is magnesium alkyl aromatic sulfonate having a total base number (TBN, as measured by the procedure of ASTM D2896) ranging from 300 to 400.

Polyvalent metal alkyl salicylate and naphthenate materials may also be included, such as the methylene and sulfur bridged materials which are readily derived from alkyl substituted salicylic or naphthenic acids or mixtures of either or both with alkyl substituted phenols. Basic sulfurized salicylates and a method for their preparation are shown in US-A-3595791.

The sulfurized metal phenates can be considered the "metal salt of a phenol sulfide" which thus refers to a metal salt, whether neutral or basic, of a compound typified by the general formula:



where $x = 1$ or 2 , $n = 0, 1$ or 2

or a polymeric form of such a compound, where R is an alkyl radical, n and x are each integers from 1 to 4, and the average number of carbon atoms in all of the R groups is at least about 9 in order to ensure adequate solubility in oil. The individual R groups may each contain from 5 to 40, preferably 8 to 20, carbon atoms. The metal salt is prepared by reacting an alkyl phenol sulfide with a sufficient quantity of metal containing material to impart the desired alkalinity to the sulfurized metal phenate.

The sulfurized alkyl phenol is converted by reaction with a metal containing material including oxides, hydroxides and complexes in an amount sufficient to neutralize said phenol and, if desired, to overbase the product to a desired alkalinity by procedures well known in the art. Preferred is a process of neutralization utilizing a solution of metal in a glycol ether.

Magnesium and calcium containing additives such as described above although beneficial in other respects can increase the tendency of the lubricating oil to oxidise. This is especially true of the highly basic sulphonates.

According to a preferred embodiment the invention therefore provides a crankcase lubricating composition also containing from 2 to 8000 parts per million of calcium and/or magnesium.

The magnesium and/or calcium is generally present as basic or neutral detergents such as the sulphonates and phenates, and preferred additives are basic magnesium or calcium sulphonates. Preferably the oils contain from 500 to 5000 parts per million of calcium and/or magnesium from such additives.

These compositions of our invention may as an alternative or in addition contain other similar metal-

containing detergent additives, for example, those containing barium, sodium, potassium or lithium.

The lubricating oil used in the lubricant composition may be a mineral lubricating oil or a synthetic lubricating oil or a mixture thereof. Suitable synthetic oils include diester oils such as di(2-ethyl-hexyl) sebacate, azelate and adipate; complex ester oils such as those formed for dicarboxylic acids, glycols and either monobasic acids or monohydric alcohols; silicone oils; sulfide esters; organic carbonates; hydrocarbon oils and other synthetic oils known to the art. The invention is particularly useful in mineral lubricating oils and has the added benefit that it may allow use of base stock oils that have inferior antioxidant properties to those currently used.

The lubricating compositions of the present invention may and usually will contain other traditional lubricant additives provided that they are substantially zinc-free and phosphorus-free - for example, rust inhibitors such as oleic acid and its derivatives such as N-oleylsarcosine, and oleic acid dimers and trimers, lecithin, sorbitan mono-oleate, dodecyl succinic anhydride or ethoxylated alkyl phenols; pour point depressants such as copolymers of vinyl acetate with fumaric acid esters of coconut oil alcohols; and viscosity index improvers such as olefin copolymers or polymethacrylates.

In copper-free oils other antioxidants in addition to the zinc dialkyldithiophosphate are sometimes required to improve the oxidative stability of the oil. These supplementary antioxidants are included especially when the basestock has poor oxidative stability; and typically the supplementary antioxidant is added to the oil in amounts from 0.1-1.5 wt %. The supplementary antioxidants that are used include phenols, hindered-phenols, bis-phenols, and sulphurised phenols, catechol, alkylated catechols and sulphurised alkyl catechols, diphenylamine and alkyl diphenylamines and phenyl-1-naphthylamine and its alkylated derivatives.

The inclusion of small amounts of copper generally removes the need for these supplementary antioxidants. It would, however, still be within the scope of our invention for a supplementary antioxidant to be included especially for oils operating under particularly severe conditions where the presence of such supplementary antioxidants may be beneficial, provided that substantially no phosphorus is thereby introduced.

Additives for lubricating oils are generally supplied as concentrates in oil for incorporation into the bulk lubricant. The present invention therefore provides concentrates comprising an oil solution containing:

- (1) less than 0.1 wt % of phosphorus and less than 0.1 wt % of zinc;
- (2) from 1 to 50 wt % of an oil-soluble sulphur-containing compound;
- (3) from 0.005 to 2 wt % of copper; and
- (4) from 0.1 to 20 wt % of a bearing corrosion inhibitor,

and optionally a dispersant selected from the group consisting of:

- (a) 0 to 60, e.g. 10 to 60 wt % of an ashless dispersant compound,
- (b) 0 to 40, e.g. 3 to 40% of a polymeric viscosity index improver dispersant, although it is usual to add any viscosity index improver separately.

The concentrate may also contain other additives such as the detergents and viscosity index improvers previously described. A particularly preferred concentrate also contains a magnesium and/or calcium containing additive and the invention therefore provides a concentrate which further comprises from 0.1 to 8 wt % of calcium and/or magnesium.

The following Examples are now given, though only by way of illustration, to show certain aspects of the invention in more detail.

Comparative Examples I-VI and Examples 1 and 2

In the following Comparative Examples and Examples of the invention, formulations are prepared with the combinations and amounts of additives set out in Table 1, with the balance being a diluent oil suitable for lubricating compositions and comprising 0.3 wt % sulphur. The additives used are as follows:

A is a dispersant V.I. additive comprising an oil solution containing 21% of a multifunctional ethylene-propylene copolymer and containing 0.29 wt % N.

B is an ashless dispersant comprising a 50 wt % oil solution of borated polyisobutenyl succinimide having a polyisobutenyl radical with a molecular weight of approximately 950 and containing 1.6 wt % N and 0.35 wt % B.

C is an oil solution of an overbased magnesium sulphonate having a TBN of 400 and a magnesium content of 9.2 wt % and a sulphur content of 1.7 wt %.

D is an oil solution of an overbased calcium sulphonate having a TBN of 300 and a calcium content of 11.9 wt % and a sulphur content of 1.9 wt %

E is an oil solution of copper oleate containing 4 wt % copper.

F is a 30 wt % solution in oil of a hindered methylene bis-phenol antioxidant.

G is an alkylated diphenylamine antioxidant, commercially available as Irganox L-57 from Ciba-Geigy.

H is a 50 wt % oil solution of a zinc diamyl dithiocarbamate containing 6 wt % of zinc and 12 wt % sulphur.

J is an orthoborate ester made from ethoxyethanol comprising 5 to 6 wt % of boron.

K is 2,5-bis(nonyldithio)-1,3,4-thiadiazole, commercially available as Amoco 158 from Amoco Chemical Company, comprising 33 wt % sulphur.

L is an oil solution containing 12 wt % of molybdenum as the octoate.

M is a sulphurized ester sperm oil substitute, commercially available as Emery 9844 from Emery Corporation, and comprising 11.5 wt % sulphur.

The formulations were tested in the following standard tests:

Seq. IIID engine test according to ASTM STP 315M Part II in which the maximum and average cam plus lifter wear are measured. A pass in this test is achieved with maximum wear of 0.02 cm (0.008 in.) or better, and an average wear of 0.01 cm (0.004 in.) or better.

Kinematic viscosity increase in the IIID was measured at 40°C as a percentage increase in 64 hours. A pass is achieved in this test by achieving a viscosity increase in 64 hours of not more than 375%.

CRC-L-38 Screener engine test based on ASTM STP 509A PE IV in which the bearing weight loss (BWL) is measured. A pass in this test is achieved with BWL of not more than 40 mg.

The results are shown in Table 2. These results show the invention provides a surprising advantage in lubricants which have excellent antioxidant, anti-wear, and bearing corrosion inhibition with substantial absence of phosphorus and zinc. Comparative Examples I, II, and III show that in the absence of a bearing corrosion inhibitor, wear performance was inadequate. Comparative Example IV shows that the addition of a molybdenum additive did not improve wear performance. Comparative Example V shows that in the absence of copper antioxidant performance was inadequate even with conventional amounts of other known antioxidants.

The Examples of the invention show that the performance of the formulations is not merely summation of the performance of individual additive, but gives a surprising improvement in antiwear, antioxidant and bearing corrosion performance, while having phosphorus levels below those commercially employed in conventional oils.

Table 1

Example:	I	II	III	IV	V	VI	1	2
Additives (wt %)								
A	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5
B	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
C	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
D	-	-	-	-	-	0.9	-	-
E	0.3	0.3	0.3	0.15	-	0.3	0.3	0.3
F	-	-	-	-	1.0	1.0	-	-
G	-	-	-	-	0.4	0.4	-	-
H	1.5	2.0	1.0	1.5	1.5	1.5	-	-
J	-	-	-	-	1.0	-	1.0	-
K	-	-	-	-	-	-	-	0.5
L	-	-	-	0.03	-	-	-	-
M	-	-	-	-	-	-	3.0	3.0
Added Sulphur content (%)	0.51	0.57	0.45	0.51	0.51	0.53	0.67	0.84
Copper content (%)	0.012	0.012	0.012	0.006	0	0.012	0.012	0.012
Zinc content (%)	0.09	0.12	0.06	0.09	0.09	0.09	0	0
Phosphorus content (%)	0	0	0	0	0	0	0	0
Boron content (%)	0.01	0.01	0.01	0.01	0.06	0.01	0.06	0.01
Mg(Ca) (%)	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
						(0.11)		

Table 2

Example	I	II	III	IV	V	VI	1	2
Seq. IIID								
max. wear (cm)	0.027 F	0.0546 F	P*	0.0290 F	0.0028 P	0.33 F	0.0056 P	0.0013 P
ave. wear (cm)	0.012 F	0.0236 F	P*	0.0163 F	0.0015 P	0.02 F	0.0023 P	0.0008 P
Viscosity inc. (%) at 64 hours	102 P	66 P	*	104 P	400 +/-48 hr P	65 P	-	67 P
CRC-L-38 BWL (mg)	-	88.3 F	-	-	-	5 P	-	3.3 P

P = Pass

F = Fail

* = Test not completed, failure after 4 hours.

- = Not tested.

55 Concentrates - Typical concentrates for providing the above formulations.

	<u>Component</u>	<u>wt %</u>	<u>%S</u>	<u>%Cu</u>	<u>%B</u>
5	<u>Example 1</u>				
	B	33.7			0.12
	C	18.0	0.31		
	E	3.4		0.16	
10	J	11.2			0.56
	M	<u>33.7</u>	<u>3.88</u>	<u> </u>	<u> </u>
		100.0	4.19	0.16	0.68
15	<u>Example 2</u>				
	B	35.7			
	C	19.1	0.32		0.13
	E	3.6		0.14	
20	K	5.9	1.95		
	M	<u>35.7</u>	<u>4.09</u>	<u> </u>	<u> </u>
		100.0	6.36	0.14	0.13

Concentrates may also contain some dilute oil to improve handling (reduce viscosity).

Claims

30 Claims for the following Contracting States : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE

1. A crankcase lubricant composition for use in automobile engines comprising a major amount of a lubricating oil, 5 to 500 parts per million by weight (ppm) of added copper present in oil-soluble form, one or more added oil-soluble sulphur-containing compounds such that the composition comprises from greater than 0.5 to 2.0 wt % of total sulphur and a bearing corrosion inhibitor, the composition containing less than 0.05 wt % phosphorus and less than 0.01 wt% zinc.
2. A composition as claimed in claim 1, in which the amount of added copper in the composition is from 10 to 400 ppm.
3. A composition as claimed in claim 2, in which the amount of added copper in the composition is from 10 to 200 ppm.
4. A composition as claimed in claim 3, in which the amount of added copper in the composition is from 60 to 200 ppm.
5. A composition as claimed in any of the preceding claims, in which copper may be blended into the oil as the copper salt of a C₁₀ to C₁₈ fatty acid, an unsaturated carboxylic acid, a naphthenic acid of molecular weight from 200 to 500 or an alkyl or alkenyl substituted dicarboxylic acid, an oil-soluble copper dithiocarbamates of the general formula (RR'NCSS)_nCu, where n is 1 or 2 and R and R' are the same or different hydrocarbonyl radicals containing 1 to 18 carbon atoms, a copper sulphonate, a copper phenate, or a copper acetylacetonate.
6. A composition as claimed in any of the preceding claims, in which the oil-soluble sulphur compound is a dithiocarbamate of the formula: (RR'NCSS)_n M (wherein R, R' and n are as defined in claim 5 and M is a metal) or a mercaptide, a sulphurized unsaturated organic compound, a sulphide, a thioether, a thiophenol, a thioxanthate, a sulphurized ester, a thioester, a thioamide, a thiazole or a thiadiazole.



	<u>Component</u>	<u>wt %</u>	<u>%S</u>	<u>%Cu</u>	<u>%B</u>
5	<u>Example 1</u>				
	B	33.7			0.12
	C	18.0	0.31		
	E	3.4		0.16	
10	J	11.2			0.56
	M	<u>33.7</u>	<u>3.88</u>	<u> </u>	<u> </u>
		100.0	4.19	0.16	0.68
15	<u>Example 2</u>				
	B	35.7			
	C	19.1	0.32		0.13
	E	3.6		0.14	
20	K	5.9	1.95		
	M	<u>35.7</u>	<u>4.09</u>	<u> </u>	<u> </u>
		100.0	6.36	0.14	0.13

Concentrates may also contain some dilute oil to improve handling (reduce viscosity).

Claims

30 Claims for the following Contracting States : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE

1. A crankcase lubricant composition for use in automobile engines comprising a major amount of a lubricating oil, 5 to 500 parts per million by weight (ppm) of added copper present in oil-soluble form, one or more added oil-soluble sulphur-containing compounds such that the composition comprises
35 from greater than 0.5 to 2.0 wt % of total sulphur and a bearing corrosion inhibitor, the composition containing less than 0.05 wt % phosphorus and less than 0.01 wt% zinc.
2. A composition as claimed in claim 1, in which the amount of added copper in the composition is from 10 to 400 ppm.
3. A composition as claimed in claim 2, in which the amount of added copper in the composition is from 10 to 200 ppm.
4. A composition as claimed in claim 3, in which the amount of added copper in the composition is from
45 60 to 200 ppm.
5. A composition as claimed in any of the preceeding claims, in which copper may be blended into the oil as the copper salt of a C₁₀ to C₁₈ fatty acid, an unsaturated carboxylic acid, a naphthenic acid of molecular weight from 200 to 500 or an alkyl or alkenyl substituted dicarboxylic acid, an oil-soluble copper dithiocarbamates of the general formula (RR'NCSS)_nCu, where n is 1 or 2 and R and R' are the
50 same or different hydrocarbyl radicals containing 1 to 18 carbon atoms, a copper sulphonate, a copper phenate, or a copper acetylacetonate.
6. A composition as claimed in any of the preceding claims, in which the oil-soluble sulphur compound is a dithiocarbamate of the formula: (RR'NCSS)_n M (wherein R, R' and n are as defined in claim 5 and M is a metal) or a mercaptide, a sulphurized unsaturated organic compound, a sulphide, a thioether, a thiophenol, a thioxanthate, a sulphurized ester, a thioester, a thioamide, a thiazole or a thiadiazole.



7. A composition as claimed in claim 6, in which the oil-soluble sulphur compound is a dialkyl dithiocarbamate containing 2 to 12 carbon atoms.

8. A composition as claimed in any of the preceding claims, which contains from greater than 0.5 to 1.0 wt % total S, including from 0.1 to 0.5 wt % S as added oil-soluble sulphur-containing compound.

9. A composition as claimed in any of the preceding claims, which is substantially zinc-free.

10. A composition as claimed in claim 6 which contains from 0.5 to 3 wt % sulphurized ester.

11. A composition as claimed in any of the preceding claims, in which the bearing corrosion inhibitor comprises one or more borate esters of the formula:



(wherein R is a substituted or unsubstituted alkyl, aryl or aralkyl group or two groups R together form a substituted or unsubstituted alkylene group and R¹ is a substituted or unsubstituted alkylene group) and/or a thiadiazole polysulphide containing from 5 to 50 carbon atoms, a derivative or polymer thereof.

12. A composition as claimed in claim 11, which contains from 0.01 to 10 wt % of a borate ester.

13. A composition as claimed in claim 11 or claim 12, in which the borate ester is a tris(ethoxyethyl) orthoborate ester or a diborate of butane-1,3-diol.

14. A composition as claimed in claim 11 which contains from 0.01 to 10 wt % of 2,5-bis(t-nonyldithio)-1,3,4-thiadiazole.

15. A composition as claimed in any of the preceding claims, which contains less than 0.005 wt % of phosphorus.

16. A composition as claimed in claim 15 which is substantially free of phosphorus.

17. A composition as claimed in any of the preceding claims, which further comprises:

(A) from 1 to 10 wt % of an ashless dispersant compound and/or

(B) from 0.3 to 10 wt %, of a nitrogen or ester containing polymeric viscosity index improver dispersant.

18. A composition as claimed in any of the preceding claims, which comprises from 2 to 8000 parts per million of calcium and/or magnesium.

19. A composition as claimed in claim 18, which comprises from 500 to 5000 parts per million of calcium and/or magnesium as a basic calcium and/or magnesium sulphonate.

20. A composition as claimed in any of the preceding claims, which further comprises one or more of rust inhibitors, pour point depressants, additional anti-oxidants and viscosity index improvers.

21. A concentrate comprising an oil solution containing:

(1) less than 0.1 wt % of phosphorus; and less than 0.1 wt % of zinc;

(2) from 1 to 50 wt % of an oil-soluble sulphur-containing compound;

(3) from 0.005 to 2 wt % of copper;

(4) from 0.1 to 20 wt % of a bearing corrosion inhibitor; and

(5) from 0 to 60 wt % of an ashless dispersant and/or from 0 to 40 wt % of a polymeric viscosity index improver dispersant.

22. A concentrate as claimed in claim 21, which further comprises from 0.01 to 8 wt % of calcium and/or magnesium.

23. The use of oil-soluble copper as antioxidant in a zinc-free and phosphorus-free lubricant composition



comprising an oil-soluble sulphur-containing compound such that the composition comprises from greater than 0.5 to 2.0 wt. % of total sulphur, a bearing corrosion inhibitor, an ashless dispersant and/or a polymeric viscosity index improver dispersant, and a calcium and/or magnesium containing detergent, the copper being used in such an amount that the composition contains 5 to 500 ppm of added copper present in oil-soluble form.

24. The use in a crankcase lubricant composition for automobile engines which contains less than 0.05 wt % phosphorus and less than 0.01 wt % zinc, of 5 to 500 ppm of added copper present in an oil-soluble form, from greater than 0.5 to 2.0 wt % of total sulphur, and a bearing corrosion inhibitor to control oxidation, wear and corrosion and meet at least the quality standard of category SF and/or CD of the API Engine Service Categories.

Claims for the following Contracting State : ES

1. A crankcase lubricant composition for use in automobile engines comprising a major amount of a lubricating oil, 5 to 500 parts per million by weight (ppm) of added copper present in oil-soluble form, one or more added oil-soluble sulphur-containing compounds such that the composition comprises from greater than 0.5 to 2.0 wt % of total sulphur and a bearing corrosion inhibitor, the composition containing less than 0.05 wt % phosphorus and less than 0.01 wt% zinc.
2. A composition as claimed in claim 1, in which the amount of added copper in the composition is from 10 to 400 ppm.
3. A composition as claimed in claim 2, in which the amount of added copper in the composition is from 10 to 200 ppm.
4. A composition as claimed in claim 3, in which the amount of added copper in the composition is from 60 to 200 ppm.
5. A composition as claimed in any of the preceding claims, in which copper may be blended into the oil as the copper salt of a C₁₀ to C₁₈ fatty acid, an unsaturated carboxylic acid, a naphthenic acid of molecular weight from 200 to 500 or an alkyl or alkenyl substituted dicarboxylic acid, an oil-soluble copper dithiocarbamates of the general formula (RR'NCSS)_nCu, where n is 1 or 2 and R and R' are the same or different hydrocarbonyl radicals containing 1 to 18 carbon atoms, a copper sulphonate, a copper Phenate, or a copper acetylacetonate.
6. A composition as claimed in any of the preceding claims, in which the oil-soluble sulphur compound is a dithiocarbamate of the formula: (RR'NCSS)_n M (wherein R, R' and n are as defined in claim 5 and M is a metal) or a mercaptide, a sulphurized unsaturated organic compound, a sulphide, a thioether, a thiophenol, a thioxanthate, a sulphurized ester, a thioester, a thioamide, a thiazole or a thiadiazole.
7. A composition as claimed in claim 6, in which the oil-soluble sulphur compound is a dialkyl dithiocarbamate containing 2 to 12 carbon atoms.
8. A composition as claimed in any of the preceding claims, which contains from greater than 0.5 to 1.0 wt % total S, including from 0.1 to 0.5 wt % S as added oil-soluble sulphur-containing compound.
9. A composition as claimed in any of the preceding claims, which is substantially zinc-free.
10. A composition as claimed in claim 6 which contains from 0.5 to 3 wt % sulphurized ester.
11. A composition as claimed in any of the preceding claims, in which the bearing corrosion inhibitor comprises one or more borate esters of the formula:



(wherein R is a substituted or unsubstituted alkyl, aryl or aralkyl group or two groups R together form a substituted or unsubstituted alkylene group and R¹ is a substituted or unsubstituted alkylene group)



and/or a thiadiazole polysulphide containing from 5 to 50 carbon atoms, a derivative or polymer thereof.

12. A composition as claimed in claim 11, which contains from 0.01 to 10 wt % of a borate ester.

13. A composition as claimed in claim 11 or claim 12, in which the borate ester is a tris(ethoxyethyl) orthoborate ester or a diborate of butane-1,3-diol.

14. A composition as claimed in claim 11 which contains from 0.01 to 10 wt % of 2,5-bis(t-nonyldithio)-1,3,4-thiadiazole.

15. A composition as claimed in any of the preceding claims, which contains less than 0.005 wt % of phosphorus.

16. A composition as claimed in claim 15 which is substantially free of phosphorus.

17. A composition as claimed in any of the preceding claims, which further comprises:

(A) from 1 to 10 wt % of an ashless dispersant compound and/or

(B) from 0.3 to 10 wt %, of a nitrogen or ester containing polymeric viscosity index improver dispersant.

18. A composition as claimed in any of the preceding claims, which comprises from 2 to 8000 parts per million of calcium and/or magnesium.

19. A composition as claimed in claim 18, which comprises from 500 to 5000 parts per million of calcium and/or magnesium as a basic calcium and/or magnesium sulphonate.

20. A composition as claimed in any of the preceding claims, which further comprises one or more of rust inhibitors, pour point depressants, additional anti-oxidants and viscosity index improvers.

21. A concentrate comprising an oil solution containing:

(1) less than 0.1 wt. % of phosphorus; and less than 0.1 wt. % of zinc;

(2) from 1 to 50 wt. % of an oil-soluble sulphur-containing compound;

(3) from 0.005 to 2 wt. % of copper;

(4) from 0.1 to 20 wt. % of a bearing corrosion inhibitor; and

(5) from 0 to 60 wt. % of an ashless dispersant and/or from 0 to 40 wt. % of a polymeric viscosity index improver dispersant.

22. A concentrate as claimed in claim 21, which further comprises from 0.01 to 8 wt. % of calcium and/or magnesium.

23. A process for preparing a crankcase lubricant composition for use in automobile engines, which comprises mixing a major amount of a lubricating oil, added copper such that the composition comprises 5 to 500 parts per million by weight (ppm) of added copper present in oil-soluble form, one or more added oil-soluble sulphur-containing compounds such that the composition comprises from greater than 0.5 to 2.0 wt. % of total sulphur, and a bearing corrosion inhibitor, the substances to be mixed being chosen such that the composition contains less than 0.05 wt. % phosphorus and less than 0.01 wt. % Zn.

24. A process as claimed in claim 23, in which the amount of added copper in the composition is from 60 to 200 ppm.

25. A process as claimed in claim 23 or claim 24, in which the oil-soluble sulphur compound is a dialkyl dithiocarbamate containing 2 to 12 carbon atoms.

26. A process as claimed in any one of claims 23 to 25, wherein the proportion of added oil-soluble sulphur-containing compound(s) is such that the composition contains from greater than 0.5 to 1.0 wt. % total S, including from 0.1 to 0.5 wt. % S as added oil-soluble sulphur-containing compound.



27. A process as claimed in any one of claims 23 to 26, wherein the substances to be mixed are chosen such that the composition is substantially zinc-free.

28. A process as claimed in any one of claims 23 to 27, in which the bearing corrosion inhibitor comprises one or more borate esters of the formula:



(wherein R is a substituted or unsubstituted alkyl, aryl or aralkyl group or two groups R together form a substituted or unsubstituted alkylene group and R' is a substituted or unsubstituted alkylene group) and/or a thiadiazole polysulphide containing from 5 to 50 carbon atoms, a derivative or polymer thereof, the borate ester or thiadiazole preferably being admixed in a proportion of 0.01 to 10 wt. %, based on the final composition.

29. A process as claimed in any one claims 23 to 28, wherein the substances to be mixed are chosen such that the composition is substantially free of phosphorus.

30. A process as claimed in any one of claims 23 to 29, wherein one or more of (A), (B), (C) and (D) is/are also incorporated in the composition:

(A) from 1 to 10 wt. % of an ashless dispersant compound;

(B) from 0.3 to 10 wt. %, of a nitrogen or ester containing polymeric viscosity index improver dispersant;

(C) from 2 to 8000 parts per million of calcium and/or magnesium; and

(D) one or more of rust inhibitors, pour point depressants, additional anti-oxidants and viscosity index improvers.

31. A process for preparing a concentrate which comprises mixing with oil, to form a solution, one or more oil-soluble sulphur-containing compounds, one or more copper-containing compounds, a bearing corrosion inhibitor, and, optionally, one or more additional substances selected from phosphorus-containing compounds, ashless dispersants, calcium compounds and magnesium compounds, the proportions of the substances mixed being such that the concentrate contains:

(1) less than 0.1 wt. % of phosphorus; and less than 0.1 wt % of zinc;

(2) from 1 to 50 wt. % of an oil-soluble sulphur-containing compound;

(3) from 0.005 to 2 wt. % of copper;

(4) from 0.1 to 20 wt. % of a bearing corrosion inhibitor;

(5) from 0 to 60 wt. % of an ashless dispersant and/or from 0 to 40 wt. % of a polymeric viscosity index improver dispersant; and, optionally,

(6) from 0.01 to 8 wt. % of calcium and/or magnesium.

32. The use of oil-soluble copper as antioxidant in a zinc-free and phosphorus-free lubricant composition comprising an oil-soluble sulphur-containing compound such that the composition comprises from greater than 0.5 to 2.0 wt. % of total sulphur, a bearing corrosion inhibitor, an ashless dispersant and/or a polymeric viscosity index improver dispersant, and a calcium and/or magnesium containing detergent, the copper being used in such an amount that the composition contains 5 to 500 ppm of added copper present in oil-soluble form.

33. The use, in a crankcase lubricant composition for automobile engines which contains less than 0.05 wt. % phosphorus and less than 0.01 wt. % zinc, of 5 to 500 ppm of added copper present in an oil-soluble form, from greater than 0.5 to 2.0 wt. % of total sulphur, and a bearing corrosion inhibitor to control oxidation, wear and corrosion and meet at least the quality standard of category SF and/or CD of the API Engine Service Categories.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE

1. Motorschmierstoffzusammensetzung zur Verwendung in Automobilmotoren, die eine größere Menge eines Schmieröls, 5 bis 500 ppm (Gew.-ppm) zugesetztes Kupfer, das in öllöslicher Form vorliegt, eine oder mehrere zugesetzte öllösliche schwefelhaltige Verbindungen, so daß die Zusammensetzung von



mehr als 0,5 bis 2,0 Gew.% Gesamtschwefel umfaßt, und einen Korrosionsinhibitor für Lager umfaßt, wobei die Zusammensetzung weniger als 0,05 Gew.% Phosphor und weniger als 0,01 Gew.% Zink enthält.

2. Zusammensetzung nach Anspruch 1, in der die Menge an zugesetztem Kupfer in der Zusammensetzung 10 bis 400 ppm beträgt.
3. Zusammensetzung nach Anspruch 2, in der die Menge an zugesetztem Kupfer in der Zusammensetzung 10 bis 200 ppm beträgt.
4. Zusammensetzung nach Anspruch 3, in der die Menge an zugesetztem Kupfer in der Zusammensetzung 60 bis 200 ppm beträgt.
5. Zusammensetzung nach einem der vorangehenden Ansprüche, in der Kupfer als das Kupfersalz einer C₁₀ bis C₁₈ Fettsäure, einer ungesättigten Carbonsäure, einer Naphthensäure mit einem Molekulargewicht von 200 bis 500 oder einer alkyl- oder alkenylsubstituierten Dicarbonsäure, als ein öllösliches Kupferdithiocarbamat der allgemeinen Formel (RR'NCSS)_nCu, wobei n 1 oder 2 ist und R und R' die gleichen oder unterschiedliche Kohlenwasserstoffreste mit 1 bis 18 Kohlenstoffatomen sind, ein Kupfersulfonat, ein Kupferphenolat oder ein Kupferacetylacetonat mit dem Öl verschnitten werden kann.
6. Zusammensetzung nach einem der vorangehenden Ansprüche, in der die öllösliche Schwefelverbindung ein Dithiocarbamat der Formel (RR'NCSS)_nM (wobei R, R' und n wie in Anspruch 5 definiert sind und M ein Metall ist) oder ein Mercaptid, eine sulfurierte ungesättigte organische Verbindung, ein Sulfid, ein Thioether, ein Thiophenol, ein Thioxanthogenat, ein sulfurierter Ester, ein Thioester, ein Thioamid, ein Thiazol oder ein Thiadiazol ist.
7. Zusammensetzung nach Anspruch 6, in der die öllösliche Schwefelverbindung ein Dialkyldithiocarbamat mit 2 bis 12 Kohlenstoffatomen ist.
8. Zusammensetzung nach einem der vorangehenden Ansprüche, die von mehr als 0,5 bis 1,0 Gew.% Gesamtschwefel, einschließlich 0,1 bis 0,5 Gew.% S als zugesetzte öllösliche schwefelhaltige Verbindung, enthält.
9. Zusammensetzung nach einem der vorangehenden Ansprüche, die im wesentlichen zinkfrei ist.
10. Zusammensetzung nach Anspruch 6, die 0,5 bis 3 Gew.% sulfurierten Ester enthält.
11. Zusammensetzung nach einem der vorangehenden Ansprüche, in der der Korrosionsinhibitor für Lager einen oder mehrere Boratester der Formel

$$B(OR)_3 \text{ oder } (RO)_2B-O-B(OR)_2, (ROBO)_3 \text{ oder } (RO)_2BO-R'-OB(OR)_2$$

 (wobei R eine substituierte oder nicht substituierte Alkyl-, Aryl- oder Aralkylgruppe ist oder zwei Gruppen R zusammen eine substituierte oder nicht substituierte Alkylengruppe bilden und R' eine substituierte oder nicht substituierte Alkylengruppe ist) und/oder ein Thiadiazolpolysulfid mit 5 bis 50 Kohlenstoffatomen, ein Derivat oder ein Polymer desselben umfaßt.
12. Zusammensetzung nach Anspruch 11, die 0,01 bis 10 Gew.% eines Boratesters enthält.
13. Zusammensetzung nach Anspruch 11 oder Anspruch 12, in der der Boratester ein Tris(ethoxyethyl)-orthoboratester oder ein Diborat von Butan-1,3-diol ist.
14. Zusammensetzung nach Anspruch 11, die 0,01 bis 10 Gew.% 2,5-bis(t-nonyldithio)-1,3,4-thiadiazol enthält.
15. Zusammensetzung nach einem der vorangehenden Ansprüche, die weniger als 0,005 Gew.% Phosphor enthält.



16. Zusammensetzung nach Anspruch 15, die im wesentlichen frei von Phosphor ist.

17. Zusammensetzung nach einem der vorangehenden Ansprüche, die weiterhin

(A) 1 bis 10 Gew.% einer aschefreien Dispersionsmittelverbindung und/oder

(B) 0,3 bis 10 Gew.% eines stickstoff- oder esterhaltigen polymeren Viskositätsindexverbesserer-Dispersionsmittels umfaßt.

18. Zusammensetzung nach einem der vorangehenden Ansprüche, die 2 bis 8 000 ppm Calcium und/oder Magnesium umfaßt.

19. Zusammensetzung nach Anspruch 18, die 500 bis 5 000 ppm Calcium und/oder Magnesium als ein basisches Calcium- und/oder Magnesiumsulfonat umfaßt.

20. Zusammensetzung nach einem der vorangehenden Ansprüche, die weiterhin einen oder mehrere von Rostinhibitoren, Stockpunktsenkern, zusätzlichen Antioxidantien und Viskositätsverbesserern umfaßt.

21. Konzentrat, das eine Öllösung umfaßt, die

(1) weniger als 0,1 Gew.% Phosphor; und weniger als 0,1 Gew.% Zink;

(2) 1 bis 50 Gew.% einer öllöslichen schwefelhaltigen Verbindung;

(3) 0,005 bis 2 Gew.% Kupfer;

(4) 0,1 bis 20 Gew.% eines Korrosionsinhibitors für Lager; und

(5) 0 bis 60 Gew.% eines aschefreien Dispersionsmittels und/oder 0 bis 40 Gew.% eines polymeren Viskositätsindexverbesserer-Dispersionsmittels

enthält.

22. Konzentrat nach Anspruch 21, das weiterhin 0,01 bis 8 Gew.% Calcium und/oder Magnesium umfaßt.

23. Verwendung von öllöslichem Kupfer als Antioxidans in einer zinkfreien und phosphorfreen Schmierstoffzusammensetzung, die eine öllösliche schwefelhaltige Verbindung, so daß die Zusammensetzung von mehr als 0,5 bis 2,0 Gew.% Gesamtschwefel umfaßt, einen Korrosionsinhibitor für Lager, ein aschefreies Dispersionsmittel und/oder ein polymeres Viskositätsindexverbesserer-Dispersionsmittel und ein calcium- und/oder magnesiumhaltiges Detergens umfaßt, wobei das Kupfer in einer solchen Menge verwendet wird, daß die Zusammensetzung 5 bis 500 ppm zugesetztes Kupfer, das in öllöslicher Form vorliegt, enthält.

24. Verwendung in einer Motorschmierstoffzusammensetzung für Automotoren, die weniger als 0,05 Gew.% Phosphor und weniger als 0,01 Gew.% Zink, von 5 bis 500 ppm zugesetztes Kupfer, das in öllöslicher Form vorliegt, von mehr als 0,5 bis 2,0 Gew.% Gesamtschwefel und einen Korrosionsinhibitor für Lager enthält, um Oxidation, Verschleiß und Korrosion zu kontrollieren und mindestens den Qualitätsstandard der Kategorie SF und/oder CD der API Engine Service Categories zu erfüllen.

Patentansprüche für folgenden Vertragsstaat : ES

1. Motorschmierstoffzusammensetzung zur Verwendung in Automotoren, die eine größere Menge eines Schmieröls, 5 bis 500 ppm (Gew.-ppm) zugesetztes Kupfer, das in öllöslicher Form vorliegt, eine oder mehrere zugesetzte öllösliche schwefelhaltige Verbindungen, so daß die Zusammensetzung von mehr als 0,5 bis 2,0 Gew.% Gesamtschwefel umfaßt, und einen Korrosionsinhibitor für Lager umfaßt, wobei die Zusammensetzung weniger als 0,05 Gew.% Phosphor und weniger als 0,01 Gew.% Zink enthält.

2. Zusammensetzung nach Anspruch 1, in der die Menge an zugesetztem Kupfer in der Zusammensetzung 10 bis 400 ppm beträgt.

3. Zusammensetzung nach Anspruch 2, in der die Menge an zugesetztem Kupfer in der Zusammensetzung 10 bis 200 ppm beträgt.

4. Zusammensetzung nach Anspruch 3, in der die Menge an zugesetztem Kupfer in der Zusammensetzung



zung 60 bis 200 ppm beträgt.

5. Zusammensetzung nach einem der vorangehenden Ansprüche, in der Kupfer als das Kupfersalz einer C_{10} bis C_{18} Fettsäure, einer ungesättigten Carbonsäure, einer Naphthensäure mit einem Molekulargewicht von 200 bis 500 oder einer alkyl- oder alkenylsubstituierten Dicarbonsäure, als ein öllösliches Kupferdithiocarbamat der allgemeinen Formel $(RR'NCSS)_nCu$, wobei n 1 oder 2 ist und R und R' die gleichen oder unterschiedliche Kohlenwasserstoffreste mit 1 bis 18 Kohlenstoffatomen sind, ein Kupfersulfonat, ein Kupferphenolat oder ein Kupferacetylacetonat mit dem Öl verschnitten werden kann.
6. Zusammensetzung nach einem der vorangehenden Ansprüche, in der die öllösliche Schwefelverbindung ein Dithiocarbamat der Formel $(RR'NCSS)_nM$ (wobei R , R' und n wie in Anspruch 5 definiert sind und M ein Metall ist) oder ein Mercaptid, eine sulfurierte ungesättigte organische Verbindung, ein Sulfid, ein Thioether, ein Thiophenol, ein Thioxanthogenat, ein sulfurierter Ester, ein Thioester, ein Thioamid, ein Thiazol oder ein Thiadiazol ist.
7. Zusammensetzung nach Anspruch 6, in der die öllösliche Schwefelverbindung ein Dialkyldithiocarbamat mit 2 bis 12 Kohlenstoffatomen ist.
8. Zusammensetzung nach einem der vorangehenden Ansprüche, die von mehr als 0,5 bis 1,0 Gew.% Gesamtschwefel, einschließlich 0,1 bis 0,5 Gew.% S als zugesetzte öllösliche schwefelhaltige Verbindung, enthält.
9. Zusammensetzung nach einem der vorangehenden Ansprüche, die im wesentlichen zinkfrei ist.
10. Zusammensetzung nach Anspruch 6, die 0,5 bis 3 Gew.% sulfurierten Ester enthält.
11. Zusammensetzung nach einem der vorangehenden Ansprüche, in der der Korrosionsinhibitor für Lager einen oder mehrere Boratester der Formel
 $B(OR)_3$ oder $(RO)_2B-O-B(OR)_2$, $(ROBO)_3$ oder $(RO)_2BO-R'-OB(OR)_2$
 (wobei R eine substituierte oder nicht substituierte Alkyl-, Aryl- oder Aralkylgruppe ist oder zwei Gruppen R zusammen eine substituierte oder nicht substituierte Alkylengruppe bilden und R' eine substituierte oder nicht substituierte Alkylengruppe ist) und/oder ein Thiadiazolpolysulfid mit 5 bis 50 Kohlenstoffatomen, ein Derivat oder ein Polymer desselben umfaßt.
12. Zusammensetzung nach Anspruch 11, die 0,01 bis 10 Gew.% eines Boratesters enthält.
13. Zusammensetzung nach Anspruch 11 oder Anspruch 12, in der der Boratester ein Tris(ethoxyethyl)-orthoboratester oder ein Diborat von Butan-1,3-diol ist.
14. Zusammensetzung nach Anspruch 11, die 0,01 bis 10 Gew.% 2,5-bis(t-nonyldithio)-1,3,4-thiadiazol enthält.
15. Zusammensetzung nach einem der vorangehenden Ansprüche, die weniger als 0,005 Gew.% Phosphor enthält.
16. Zusammensetzung nach Anspruch 15, die im wesentlichen frei von Phosphor ist.
17. Zusammensetzung nach einem der vorangehenden Ansprüche, die weiterhin
 (A) 1 bis 10 Gew.% einer aschefreien Dispersionsmittelverbindung und/oder
 (B) 0,3 bis 10 Gew.% eines stickstoff- oder esterhaltigen polymeren Viskositätsindexverbesserer-Dispersionsmittels
 umfaßt.
18. Zusammensetzung nach einem der vorangehenden Ansprüche, die 2 bis 8000 ppm Calcium und/oder Magnesium umfaßt.



19. Zusammensetzung nach Anspruch 18, die 500 bis 5 000 ppm Calcium und/oder Magnesium als ein basisches Calcium- und/oder Magnesiumsulfonat umfaßt.

20. Zusammensetzung nach einem der vorangehenden Ansprüche, die weiterhin einen oder mehrere von Rostinhibitoren, Stockpunktsenkern, zusätzlichen Anti-Oxidantien und Viskositätsverbesserern umfaßt.

21. Konzentrat, das eine Öllösung umfaßt, die

(1) weniger als 0,1 Gew.% Phosphor; und weniger als 0,1 Gew.% Zink;

(2) 1 bis 50 Gew.% einer öllöslichen schwefelhaltigen Verbindung;

(3) 0,005 bis 2 Gew.% Kupfer;

(4) 0,1 bis 20 Gew.% eines Korrosionsinhibitors für Lager; und

(5) 0 bis 60 Gew.% eines aschefreien Dispersionsmittels und/oder 0 bis 40 Gew.% eines polymeren Viskositätsindexverbesserer-Dispersionsmittels

enthält.

22. Konzentrat nach Anspruch 21, das weiterhin 0,01 bis 8 Gew.% Calcium und/oder Magnesium umfaßt.

23. Verfahren zur Herstellung einer Motorschmierstoffzusammensetzung zur Verwendung in Automobilmotoren, das das Vermischen einer größeren Menge eines Schmieröls, zugesetztem Kupfer, so daß die Zusammensetzung 5 bis 500 ppm des Gewichts an zugesetztem Kupfer, das in öllöslicher Form vorliegt, umfaßt, einer oder mehrerer zugesetzter öllöslicher schwefelhaltiger Verbindungen, so daß die Zusammensetzung von mehr als 0,5 bis 2,0 Gew.% Gesamtschwefel umfaßt, und eines Korrosionsinhibitors für Lager umfaßt, wobei die zu mischenden Substanzen so gewählt werden, daß die Zusammensetzung weniger als 0,05 Gew.% Phosphor und weniger als 0,01 Gew.% Zink enthält.

24. Verfahren nach Anspruch 23, bei dem die Menge an zugesetztem Kupfer in der Zusammensetzung 60 bis 200 ppm ist.

25. Verfahren nach Anspruch 23 oder 24, in dem die öllösliche Schwefelverbindung ein Dialkyldithiocarbamat mit 2 bis 12 Kohlenstoffatomen ist.

26. Verfahren nach einem der Ansprüche 23 bis 25, bei dem der Anteil der zugesetzten öllöslichen schwefelhaltigen Verbindung(en) so ist, daß die Zusammensetzung von mehr als 0,5 bis 1,0 Gew.% Gesamtschwefel, einschließlich 0,1 bis 0,5 Gew.% S als zugesetzte öllösliche schwefelhaltige Verbindung, enthält.

27. Verfahren nach einem der Ansprüche 23 bis 26, bei dem die zu mischenden Substanzen so gewählt werden, daß die Zusammensetzung im wesentlichen zinkfrei ist.

28. Verfahren nach einem der Ansprüche 23 bis 27, bei dem der Korrosionsinhibitor für Lager einen oder mehrere Boratester der Formel



(wobei R eine substituierte oder nicht substituierte Alkyl-, Aryl- oder Aralkylgruppe ist oder zwei Gruppen R zusammen eine substituierte oder nicht substituierte Alkylengruppe bilden und R' eine substituierte oder nicht substituierte Alkylengruppe ist) und/oder ein Thiadiazolpolysulfid mit 5 bis 50 Kohlenstoffatomen, ein Derivat oder ein Polymer desselben umfaßt, wobei der Boratester oder das Thiadiazol vorzugsweise in einem Anteil von 0,01 bis 10 Gew.%, bezogen auf die Endzusammensetzung, beigemischt werden.

29. Verfahren nach einem der Ansprüche 23 bis 28, bei dem die zu mischenden Substanzen so gewählt werden, daß die Zusammensetzung im wesentlichen frei von Phosphor ist.

30. Verfahren nach einem der Ansprüche 23 bis 29, bei dem ein oder mehrere von (A), (B), (C) und (D) ebenfalls in die Zusammensetzung eingebracht ist/sind:

(A) 1 bis 10 Gew.% einer aschefreien Dispersionsmittelverbindung;

(B) 0,3 bis 10 Gew.% eines stickstoff- oder esterhaltigen polymeren Viskositätsindexverbesserer-



Dispersionsmittels;

(C) 2 bis 8 000 ppm Calcium und/oder Magnesium; und

(D) einen oder mehrere Rostinhibitoren, Stockpunktsenker, zusätzliche Antioxidantien und Viskositätsindexverbesserer.

31. Verfahren zur Herstellung eines Konzentrats, das das Mischen von einer oder mehreren öllöslichen schwefelhaltigen Verbindungen, einer oder mehreren kupferhaltigen Verbindungen, einem Korrosionsinhibitor für Lager und gegebenenfalls einer oder mehrerer zusätzlicher Substanzen, ausgewählt aus phosphorhaltigen Verbindungen, aschefreien Dispersionsmitteln, Calciumverbindungen und Magnesiumverbindungen mit Öl unter Bildung einer Lösung umfaßt, wobei die Anteile der gemischten Substanzen so sind, daß das Konzentrat

(1) weniger als 0,1 Gew.% Phosphor; und weniger als 0,1 Gew.% Zink;

(2) 1 bis 50 Gew.% einer öllöslichen schwefelhaltigen Verbindung;

(3) 0,005 bis 2 Gew.% Kupfer;

(4) 0,1 bis 20 Gew.% eines Korrosionsinhibitors für Lager;

(5) 0 bis 60 Gew.% eines aschefreien Dispersionsmittels und/oder 0 bis 40 Gew.% eines polymeren Viskositätsindexverbesserer-Dispersionsmittels; und gegebenenfalls

(6) 0,01 bis 8 Gew.% Calcium und/oder Magnesium

enthält.

32. Verwendung von öllöslichem Kupfer als Antioxidans in einer zinkfreien und phosphorfreen Schmierstoffzusammensetzung, die eine öllösliche schwefelhaltige Verbindung, so daß die Zusammensetzung von mehr als 0,5 bis 2,0 Gew.% Gesamtschwefel umfaßt, einen Korrosionsinhibitor für Lager, ein aschefreies Dispersionsmittel und/oder ein polymeres Viskositätsindexverbesserer-Dispersionsmittel und ein calcium- und/oder magnesiumhaltiges Detergens umfaßt, wobei das Kupfer in einer solchen Menge verwendet wird, daß die Zusammensetzung 5 bis 500 ppm zugesetztes Kupfer, das in öllöslicher Form vorliegt, enthält.

33. Verwendung in einer Motorschmierstoffzusammensetzung für Automobilmotoren, die weniger als 0,05 Gew.% Phosphor und weniger als 0,01 Gew.% Zink enthält, von 5 bis 500 ppm zugesetztem Kupfer, das in öllöslicher Form vorliegt, mehr als 0,5 bis 2,0 Gew.% Gesamtschwefel und einen Korrosionsinhibitor für Lager, um Oxidation, Verschleiß und Korrosion zu kontrollieren und mindestens den Qualitätsstandard der Kategorie SF und/oder CD der API Engine Service Categories zu erfüllen.

Revendications

Revendications pour les Etats contractants suivants : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE

1. Composition de lubrifiant pour carter destinée à être utilisée dans des moteurs de véhicules automobiles, comprenant une quantité dominante d'une huile lubrifiante, 5 à 500 parties par million en poids (ppm) de cuivre ajouté présent sous une forme soluble dans l'huile, un ou plusieurs composés ajoutés contenant du soufre, solubles dans l'huile, de manière que la composition renferme plus de 0,5 à 2,0 % en poids de soufre total, et un inhibiteur de corrosion des paliers, la composition contenant moins de 0,05 % en poids de phosphore et moins de 0,01 % en poids de zinc.

2. Composition suivant la revendication 1, dans laquelle la quantité de cuivre ajouté dans la composition est de 10 à 400 ppm.

3. Composition suivant la revendication 2, dans laquelle la quantité de cuivre ajouté dans la composition est de 10 à 200 ppm.

4. Composition suivant la revendication 3, dans laquelle la quantité de cuivre ajouté dans la composition est de 60 à 200 ppm.

5. Composition suivant l'une quelconque des revendications précédentes, dans laquelle du cuivre peut être incorporé dans l'huile sous forme du sel de cuivre d'un acide gras en C₁₀ à C₁₈, d'un acide carboxylique non saturé, d'un acide naphénique de poids moléculaire allant de 200 à 500 ou d'un acide dicarboxylique à substituant alkyle ou alcényle, d'un dithiocarbamate de cuivre soluble dans l'huile de formule générale (RR'NCSS)_nCu dans lequel n a la valeur 1 ou 2 et R et R' sont des radicaux



hydrocarbyle identiques ou différents contenant 1 à 18 atomes de carbone, un sulfonate de cuivre, un phénate de cuivre ou un acétylacétonate de cuivre.

6. Composition suivant l'une quelconque des revendications précédentes, dans laquelle le composé de soufre soluble dans l'huile est un dithiocarbamate de formule $(RR'NCSS)_n$ M (dans laquelle R, R' et n sont tels que définis dans la revendication 5 et M est un métal) ou un mercaptide, un composé organique non saturé sulfuré, un sulfure, un thioéther, un thiophénol, un thioxanthate, un ester sulfuré, un thioester, un thioamide, un thiazole ou un thiadiazole.
7. Composition suivant la revendication 6, dans laquelle le composé de soufre soluble dans l'huile est un dialkyl-dithiocarbamate contenant 2 à 12 atomes de carbone.
8. Composition suivant l'une quelconque des revendications précédentes, qui contient plus de 0,5 à 1,0 % en poids de soufre total, comprenant 0,1 à 0,5 % en poids de soufre sous forme d'un composé ajouté contenant du soufre, soluble dans l'huile.
9. Composition suivant l'une quelconque des revendications précédentes, qui est principalement dépourvue de zinc.
10. Composition suivant la revendication 6, qui contient 0,5 à 3 % en poids d'ester sulfuré.
11. Composition suivant l'une quelconque des revendications précédentes, dans laquelle l'inhibiteur de corrosion des paliers comprend un ou plusieurs esters boriques de formule :
 $B(OR)_3$ ou $(RO)_2B-O-B(OR)_2$, $(ROBO)_3$ ou $(RO)_2BO-R^1-OB(OR)_2$
 (où R est un groupe alkyle, aryle ou aralkyle substitué ou non substitué ou bien deux groupes R forment conjointement un groupe alkylène substitué ou non substitué et R' est un groupe alkylène substitué ou non substitué) et/ou un polysulfure de thiadiazole contenant 5 à 50 atomes de carbone ou un dérivé ou polymère de ce composé.
12. Composition suivant la revendication 11, qui contient 0,01 à 10 % en poids d'un ester d'acide borique.
13. Composition suivant la revendication 11 ou la revendication 12, dans laquelle l'ester d'acide borique est un orthoborate de tris(éthoxyéthyle) ou un bionate de butane-1,3,-diol.
14. Composition suivant la revendication 11, qui contient 0,01 à 10 % en poids de 2,5-bis(tertio-nonyl-dithio)-1,3,4-thiadiazole.
15. Composition suivant l'une quelconque des revendications précédentes, qui contient moins de 0,005 % en poids de phosphore.
16. Composition suivant la revendication 15, qui est principalement dépourvue de phosphore.
17. Composition suivant l'une quelconque des revendications précédentes, qui comprend en outre :
 (A) 1 à 10 % en poids d'un composé dispersant sans cendre et/ou
 (B) 0,3 à 10 % en poids d'un dispersant-agent améliorant l'indice de viscosité polymérique contenant de l'azote ou une fonction ester.
18. Composition suivant l'une quelconque des revendications précédentes, qui comprend 2 à 8000 parties par million de calcium et/ou de magnésium.
19. Composition suivant la revendication 18, qui comprend 500 à 5000 parties par million de calcium et/ou de magnésium sous forme de sulfonate basique de calcium et/ou de magnésium.
20. Composition suivant l'une quelconque des revendications précédentes, qui comprend en outre un ou plusieurs additifs tels que des inhibiteurs de rouille, des agents abaissant le point d'écoulement, d'autres antioxydants et des agents améliorant l'indice de viscosité.



21. Concentré comprenant une solution dans l'huile, contenant :

- (1) moins de 0,1 % en poids de phosphore ; et moins de 0,1 % en poids de zinc ;
- (2) 1 à 50 % en poids d'un composé contenant du soufre soluble dans l'huile ;
- (3) 0,005 à 2 % en poids de cuivre ;
- (4) 0,1 à 20 % en poids d'un inhibiteur de corrosion des paliers ; et
- (5) 0 à 60 % en poids d'un dispersant sans cendre et/ou 0 à 40 % en poids d'un agent polymérique dispersant-améliorant l'indice de viscosité.

22. Concentré suivant la revendication 21, qui comprend en outre 0,01 à 8 % en poids de calcium et/ou de magnésium.

23. Utilisation de cuivre soluble dans l'huile comme antioxydant dans une composition lubrifiante dépourvue de zinc et dépourvue de phosphore, comprenant un composé contenant du soufre soluble dans l'huile de manière que la composition renferme plus de 0,5 à 2,0 % en poids de soufre total, un inhibiteur de corrosion des paliers, un dispersant sans cendre et/ou un agent polymérique dispersant-améliorant l'indice de viscosité, et un détergent contenant du calcium et/ou du magnésium, le cuivre étant utilisé en quantité telle que la composition renferme 5 à 500 ppm de cuivre ajouté, présent sous une forme soluble dans l'huile.

24. Utilisation d'une composition de lubrifiant pour carter, pour moteurs de véhicules automobiles, qui contient moins de 0,05 % en poids de phosphore et moins de 0,01 % en poids de zinc, 5 à 500 ppm de cuivre ajouté présent sous une forme soluble dans l'huile, plus de 0,5 à 2,0 % en poids de soufre total, et un inhibiteur de corrosion des paliers pour limiter l'oxydation, l'usure et la corrosion et pour satisfaire au moins aux normes de qualité de la catégorie SF et/ou CD des Engine Service Categories de l'API.

Revendications pour l'Etat contractant suivant : ES

1. Composition de lubrifiant pour carter destinée à être utilisée dans des moteurs de véhicules automobiles, comprenant une quantité dominante d'une huile lubrifiante, 5 à 500 parties par million en poids (ppm) de cuivre ajouté présent sous une forme soluble dans l'huile, un ou plusieurs composés ajoutés contenant du soufre, solubles dans l'huile, de manière que la composition renferme plus de 0,5 à 2,0 % en poids de soufre total, et un inhibiteur de corrosion des paliers, la composition contenant moins de 0,05 % en poids de phosphore et moins de 0,01 % en poids de zinc.

2. Composition suivant la revendication 1, dans laquelle la quantité de cuivre ajouté dans la composition est de 10 à 400 ppm.

3. Composition suivant la revendication 2, dans laquelle la quantité de cuivre ajouté dans la composition est de 10 à 200 ppm.

4. Composition suivant la revendication 3, dans laquelle la quantité de cuivre ajouté dans la composition est de 60 à 200 ppm.

5. Composition suivant l'une quelconque des revendications précédentes, dans laquelle du cuivre peut être incorporé dans l'huile sous forme du sel de cuivre d'un acide gras en C_{10} à C_{18} , d'un acide carboxylique non saturé, d'un acide naphénique de poids moléculaire allant de 200 à 500 ou d'un acide dicarboxylique à substituant alkyle ou alcényle, d'un dithiocarbamate de cuivre soluble dans l'huile de formule générale $(RR'NCSS)_nCu$ dans lequel n a la valeur 1 ou 2 et R et R' sont des radicaux hydrocarbyle identiques ou différents contenant 1 à 18 atomes de carbone, un sulfonate de cuivre, un phénate de cuivre ou un acétylacétonate de cuivre.

6. Composition suivant l'une quelconque des revendications précédentes, dans laquelle le composé de soufre soluble dans l'huile est un dithiocarbamate de formule $(RR'NCSS)_nM$ (dans laquelle R, R' et n sont tels que définis dans la revendication 5 et M est un métal) ou un mercaptide, un composé organique non saturé sulfuré, un sulfure, un thioéther, un thiophénol, un thioxanthate, un ester sulfuré, un thioester, un thioamide, un thiazole ou un thiadiazole.



7. Composition suivant la revendication 6, dans laquelle le composé de soufre soluble dans l'huile est un dialkyl-dithiocarbamate contenant 2 à 12 atomes de carbone.

8. Composition suivant l'une quelconque des revendications précédentes, qui contient plus de 0,5 à 1,0 % en poids de soufre total, comprenant 0,1 à 0,5 % en poids de soufre sous forme d'un composé ajouté contenant du soufre, soluble dans l'huile.

9. Composition suivant l'une quelconque des revendications précédentes, qui est principalement dépourvue de zinc.

10. Composition suivant la revendication 6, qui contient 0,5 à 3 % en poids d'ester sulfuré.

11. Composition suivant l'une quelconque des revendications précédentes, dans laquelle l'inhibiteur de corrosion des paliers comprend un ou plusieurs esters boriques de formule :



(où R est un groupe alkyle, aryle ou aralkyle substitué ou non substitué ou bien deux groupes R forment conjointement un groupe alkylène substitué ou non substitué et R' est un groupe alkylène substitué ou non substitué) et/ou un polysulfure de thiadiazole contenant 5 à 50 atomes de carbone ou un dérivé ou polymère de ce composé.

12. Composition suivant la revendication 11, qui contient 0,01 à 10 % en poids d'un ester d'acide borique.

13. Composition suivant la revendication 11 ou la revendication 12, dans laquelle l'ester d'acide borique est un orthoborate de tris(éthoxyéthyle) ou un diborate de butane-1,3,-diol.

14. Composition suivant la revendication 11, qui contient 0,01 à 10 % en poids de 2,5-bis(tertio-nonyl-dithio)-1,3,4-thiadiazole.

15. Composition suivant l'une quelconque des revendications précédentes, qui contient moins de 0,005 % en poids de phosphore.

16. Composition suivant la revendication 15, qui est principalement dépourvue de phosphore.

17. Composition suivant l'une quelconque des revendications précédentes, qui comprend en outre :

(A) 1 à 10 % en poids d'un composé dispersant sans cendre et/ou

(B) 0,3 à 10 % en poids d'un dispersant-agent améliorant l'indice de viscosité polymérique contenant de l'azote ou une fonction ester.

18. Composition suivant l'une quelconque des revendications précédentes, qui comprend 2 à 8000 parties par million de calcium et/ou de magnésium.

19. Composition suivant la revendication 18, qui comprend 500 à 5000 parties par million de calcium et/ou de magnésium sous forme de sulfonate basique de calcium et/ou de magnésium.

20. Composition suivant l'une quelconque des revendications précédentes, qui comprend en outre un ou plusieurs additifs tels que des inhibiteurs de rouille, des agents abaissant le point d'écoulement, d'autres antioxydants et des agents améliorant l'indice de viscosité.

21. Concentré comprenant une solution dans l'huile, contenant :

(1) moins de 0,1 % en poids de phosphore ; et moins de 0,1 % en poids de zinc ;

(2) 1 à 50 % en poids d'un composé contenant du soufre soluble dans l'huile ;

(3) 0,005 à 2 % en poids de cuivre ;

(4) 0,1 à 20 % en poids d'un inhibiteur de corrosion des paliers ; et

(5) 0 à 60 % en poids d'un dispersant sans cendre et/ou 0 à 40 % en poids d'un agent polymérique dispersant-améliorant l'indice de viscosité.



22. Concentré suivant la revendication 21, qui comprend en outre 0,01 à 8 % en poids de calcium et/ou de magnésium.

23. Procédé de préparation d'une composition lubrifiante pour carter destinée à être utilisée dans des moteurs de véhicules automobiles, qui consiste à mélanger une quantité dominante d'une huile lubrifiante, du cuivre ajouté de manière que la composition comprenne 5 à 500 parties par million en poids (ppm) de cuivre ajouté présent sous une forme soluble dans l'huile, un ou plusieurs composés sulfurés ajoutés solubles dans l'huile de manière que la composition comprenne plus de 0,5 à 2,0 % en poids de soufre total, et un inhibiteur de corrosion des paliers, les substances à mélanger étant choisies de manière que la composition contienne moins de 0,05 % en poids de phosphore et moins de 0,01 % en poids de zinc.

24. Procédé suivant la revendication 23, dans lequel la quantité de cuivre ajouté dans la composition va de 80 à 200 ppm.

25. Procédé suivant la revendication 23 ou la revendication 24, dans lequel le composé de soufre soluble dans l'huile est un dialkyl-dithiocarbamate contenant 2 à 12 atomes de carbone.

26. Procédé suivant l'une quelconque des revendications 23 à 25, dans lequel la proportion d'un ou plusieurs composés sulfurés ajoutés solubles dans l'huile est choisie de manière que la composition contienne plus de 0,5 à 1,0 % en poids de soufre total, y compris 0,1 à 0,5 % en poids de soufre sous forme de composé sulfuré ajouté soluble dans l'huile.

27. Procédé suivant l'une quelconque des revendications 23 à 26, dans lequel les substances à mélanger sont choisies de manière que la composition soit principalement dépourvue de zinc.

28. Procédé suivant l'une quelconque des revendications 23 à 27, dans lequel l'inhibiteur de corrosion des paliers comprend un ou plusieurs esters d'acide borique de formule :



(où R est un groupe alkyle, aryle ou aralkyle substitué ou non substitué, ou bien deux groupes R forment conjointement un groupe alkylène substitué ou non substitué et R' est un groupe alkylène substitué ou non substitué) et/ou un polysulfure de thiadiazole contenant 5 à 50 atomes de carbone, un dérivé ou polymère de ce composé, l'ester d'acide borique ou le thiadiazole étant de préférence adjoint en une proportion de 0,01 à 10 % en poids sur la base de la composition finale.

29. Procédé suivant l'une quelconque des revendications 23 à 28, dans lequel les substances à mélanger sont choisies de manière que la composition soit principalement dépourvue de phosphore.

30. Procédé suivant l'une quelconque des revendications 23 à 29, dans lequel un ou plusieurs de (A), (B), (C) et (D) sont aussi incorporés dans la composition :

(A) 1 à 10 % en poids d'un composé dispersant sans cendre ;

(B) 0,3 à 10 % en poids d'un agent dispersant-améliorant l'indice de viscosité polymérique contenant de l'azote ou des groupes ester ;

(C) 2 à 8000 parties par million de calcium et/ou de magnésium ; et

(D) un ou plusieurs inhibiteurs de rouille, agents abaissant le point d'écoulement, anti-oxydants additionnels et agents améliorant l'indice de viscosité.

31. Procédé de préparation d'un concentré, qui consiste à mélanger avec l'huile, pour former une solution, un ou plusieurs composés contenant du soufre solubles dans l'huile, un ou plusieurs composés contenant du cuivre, un inhibiteur de corrosion des paliers et, à titre facultatif, une ou plusieurs substances additionnelles choisies entre des composés contenant du phosphore, des dispersants sans cendre, des composés de calcium et des composés de magnésium, les proportions des substances mélangées étant telles que le concentré contient :

(1) moins de 0,1 % en poids de phosphore ; et moins de 0,1 % en poids de zinc ;

(2) 1 à 50 % en poids d'un composé contenant du soufre soluble dans l'huile ;

(3) 0,005 à 2 % en poids de cuivre ;



- (4) 0,1 à 20 % en poids d'un inhibiteur de corrosion des paliers ;
- (5) 0 à 60 % en poids d'un dispersant sans cendre et/ou 0 à 40 % en poids d'un agent polymérique dispersant-améliorant l'indice de viscosité ; et à titre facultatif,
- (6) 0,01 à 8 % en poids de calcium et/ou de magnésium.

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32. Utilisation de cuivre soluble dans l'huile comme antioxydant dans une composition lubrifiante dépourvue de zinc et dépourvue de phosphore, comprenant un composé contenant du soufre soluble dans l'huile de manière que la composition renferme plus de 0,5 à 2,0 % en poids de soufre total, un inhibiteur de corrosion des paliers, un dispersant sans cendre et/ou un agent polymérique dispersant-améliorant l'indice de viscosité, et un détergent contenant du calcium et/ou du magnésium, le cuivre étant utilisé en quantité telle que la composition renferme 5 à 500 ppm de cuivre ajouté, présent sous une forme soluble dans l'huile.

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33. Utilisation d'une composition de lubrifiant pour carter, pour moteurs de véhicules automobiles, qui contient moins de 0,05 % en poids de phosphore et moins de 0,01 % en poids de zinc, 5 à 500 ppm de cuivre ajouté présent sous une forme soluble dans l'huile, plus de 0,5 à 2,0 % en poids de soufre total, et un inhibiteur de corrosion des paliers pour limiter l'oxydation, l'usure et la corrosion et pour satisfaire au moins aux normes de qualité de la catégorie SF et/ou CD des Engine Service Categories de l'API.