



(22) Date de dépôt/Filing Date: 2004/11/02  
(41) Mise à la disp. pub./Open to Public Insp.: 2005/05/04  
(30) Priorité/Priority: 2003/11/04 (10/701,646) US

(51) Cl.Int.<sup>7</sup>/Int.Cl.<sup>7</sup> C10M 137/04  
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(54) Titre : FORMULATIONS D'ADDITIFS EXEMPTES DE CENDRES CONVENANT POUR DES APPLICATIONS  
D'HUILE HYDRAULIQUE

(54) Title: ASHLESS ADDITIVE FORMULATIONS SUITABLE FOR HYDRAULIC OIL APPLICATIONS

(57) **Abrégé/Abstract:**

An ashless additive formulation, particularly suited for hydraulic oil applications, comprising a particular concentration of a monothiophosphate ester and a dithiophosphate ester was found to have improved performance properties and good compatibility with calcium containing packages. Lubricating compositions employing these monothiophosphate and dithiophosphate esters allow for low phosphorous content lubricating oil compositions.



**ABSTRACT**

An ashless additive formulation, particularly suited for hydraulic oil applications, comprising a particular concentration of a monothiophosphate ester and a dithiophosphate ester was found to have improved performance properties and good compatibility with calcium containing packages. Lubricating compositions employing these monothiophosphate and dithiophosphate esters allow for low phosphorous content lubricating oil compositions.

## **ASHLESS ADDITIVE FORMULATIONS SUITABLE FOR HYDRAULIC OIL APPLICATIONS**

### **FIELD OF THE INVENTION**

**[0001]** The present invention is directed in part to a lubricating oil composition for use in industrial oils. The composition comprises metal free low phosphorous content mixtures of monothiophosphate esters and dithiophosphate esters in an oil of lubricating viscosity. Also disclosed is the use of such lubricant compositions in improving the performance properties of lubricants, such as greases, metal-working fluids, gear fluids and hydraulic fluids.

### **BACKGROUND OF THE INVENTION**

**[0002]** Higher performance demands are being placed on today's lubricants which must satisfy a comprehensive list of performance benefits including filterability; compatibility; thermal stability; demulsibility; hydrolytic stability; rust inhibition; water tolerance; corrosion control; oxidation stability; and anti-wear protection; just to name a few.

**[0003]** Zinc dialkyldithiophosphates have been typically employed as additives and are suitable for antiwear and antioxidant purposes. But, on environmental protection grounds, attempts are being made to replace zinc compounds by metal-free compounds. The use of metal-free hydraulic fluids is called for especially in agriculture or generally in mobile hydraulic units, where leakages present a risk of contamination of soil or water with the zinc compounds. Additionally, zinc dialkyldithiophosphates are suspected to accelerate corrosion of copper alloys on some hydraulic pumps and thus are not suitable in many applications. There is therefore a need for metal-free and ashless additives alternatives and for formulations containing these ashless additives.



[0004] Suitable hydraulic fluids need to be compatible upon the inclusion of trace amounts of contaminants often encountered, such as alkaline earth metals such as calcium and for example water. In conventional metal containing hydraulic fluids, the inclusion of water had an adverse effect on the filterability of the oil due to interaction of the water with the metal. Often sludge resulted from the interaction of water with the metal detergents, such as overbased calcium metal salt detergents, giving calcium carbonates, and also from the interaction of the water with the zinc dialkyldithiophosphate liberating zinc oxide and/or zinc hydroxide.

[0005] While the present invention overcomes this immediate drawback since it is a metal free package, based upon service and use of the hydraulic unit, there are often many ways for contaminants to mix with the hydraulic fluid. Thus, hydraulic oil packages must be formulated with compatibility and hydrolytic stability in mind. This is notable, since the filtering properties of the hydraulic fluid can be extremely deteriorated upon exposure to a trace amount of these alkaline earth metals leading to the formation of deposits. This is particularly important for metal free ashless packages which are designed as replacement to more conventional ash formulations. When these hydraulic units are switched over to the new ashless formulations it is possible that some of the residual metal containing components could remain in the unit. Therefore, it is desirable that these new metal free ashless packages demonstrate calcium compatibility and an excellent filtering property when so exposed. In addition, hydraulic fluids must meet the specifications of the leading hydraulic machine manufactures, for example Denison HFO (Denison Hydraulics) or Vickers or Cincinnati Machine and accordingly these fluids should perform in accordance with the specifications of DIN 51524 and Denison HFO, and these formulations should achieve a failure load stage (FLS) of at least 10 in the FZG test.

[0006] Zinc free hydraulic fluids are known. GB 1415964 discloses an antiwear composition combining tricresyl phosphate with an acidic phosphoric ester amine salt or a triaryl phosphate.

[0007] WO 00/11122 describes zinc free hydraulic fluid that comprises an acidic phosphoric ester amine salt, a monothiophosphate ester of the triphenylthiophosphate type and a dithiophosphate ester with a polyamide rust preventing agent.

[0008] U.S Patent No. 6,531,429 in addition to the above added a polyol partial ester, amine or epoxide to the above in an effort to improve water compatibility.



[0009] One disadvantage of the above formulations is their lack of compatibility with calcium containing compositions, water and resulting water acidity due to reaction products of the additive package. Deposit formation due to this compatibility problem leads to increased wear and corrosion and can plug the hydraulic unit filter and/or require additional service. Hydraulic units require very fine filtering and are more susceptible to deposits formed by incompatibility between the components. The filter pore sizes of modern by-pass filtration units have been reduced from the earlier 30  $\mu\text{m}$  to the current 6  $\mu\text{m}$ , therefore it is desirable to minimize compatibility issues. The contamination of hydraulic oil by an alkali metal source and/or water is a frequent occurrence, especially in the case of mobile hydraulic units. The use of certain phosphorus- and sulfur-containing additives gives rise to hydrolytic degradation with the formation of corrosive decomposition products that may attack the metals used in the hydraulic units, e.g. steel and copper alloys, and cause damage to hydraulic pumps. Particularly troublesome is resulting water acidity prevalent with the use of acidic phosphoric ester amine salts, also referred to herein as amine phosphates, typically employed for a FZG boost. In addition, agglomerations of those decomposition products may also block the filters of by-pass filtration units.

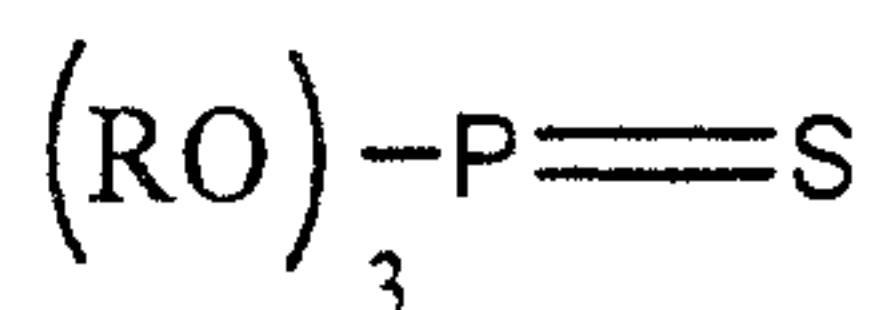
[0010] The problem underlying the present invention is to prepare compositions that have lower phosphorous content while demonstrate improved compatibility with alkaline earth metals, and which demonstrate a significantly lower tendency to form undesired hydrolysis products.

[0011] It has surprisingly been found that lower phosphorous containing compositions comprising monothiophosphate ester(s) combined with dithiophosphate acid ester(s) in a specified range gives compositions that have good calcium compatibility and that can achieve a load carrying capacity in the FZG test of  $> 10$  even when these compositions preferably do not employ an acidic phosphoric ester amine salt. Moreover, these lower phosphorous containing compositions have good water tolerance and when contaminated with water have a significantly lower tendency to form corrosive hydrolysis products.

## SUMMARY OF THE INVENTION

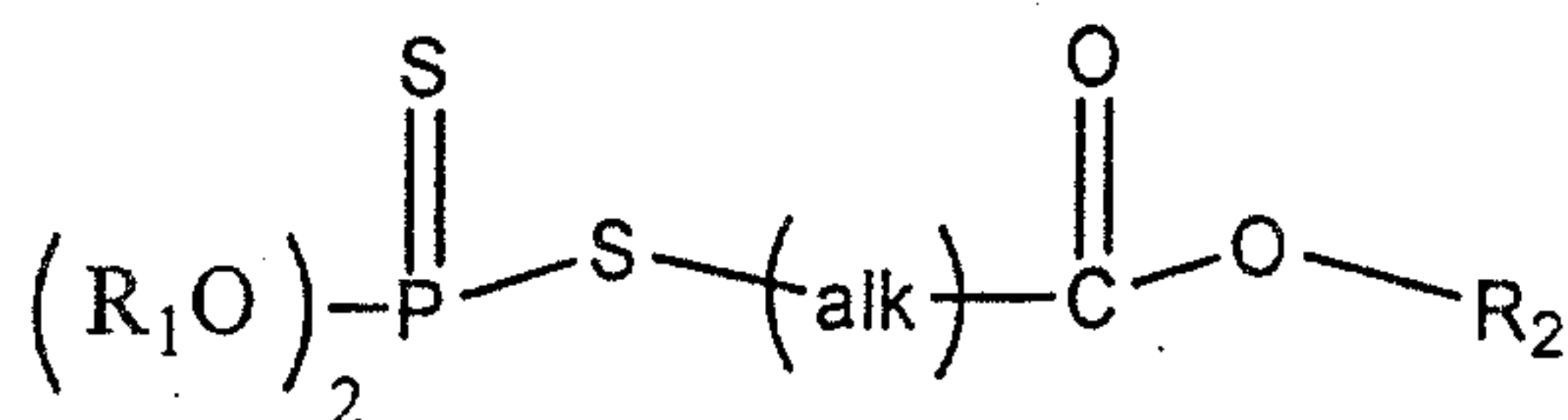
[0012] The present invention is directed in part to a lubricating oil composition for use in industrial oils and is particularly suited for hydraulic fluid applications. The composition comprises metal free low phosphorous content mixture of monothiophosphate esters and dithiophosphate esters in an oil of lubricating viscosity. Accordingly, this inventions is directed to a metal free low phosphorous content lubricating oil composition comprising:

- a) an oil of lubricating viscosity;
- b) a mixture of ashless, sulfur containing organo phosphorous compounds comprising:
  - i) from 0.2 to 0.4 weight percent based upon the total mass of the lubricating oil composition of a monothiophosphate ester of the formula



wherein R is independently selected from phenyl, alkylphenyl, aryl, alkaryl, aralkyl, and alkoxyaryl; and

- ii) from 0.01 to 0.03 weight percent based upon the total mass of the lubricating oil composition of a dithiophosphate ester of the formula



wherein each  $R_1$  is an independently selected hydrocarbyl from 3 to 20 carbon atoms; alk is a straight or branched chain alkylene group of 2 to 6 carbon atoms;  $R_2$  is hydrogen or alkyl from 1 to 4 carbons atoms; wherein the total phosphorous content of the composition is less than 350 parts per million phosphorous.

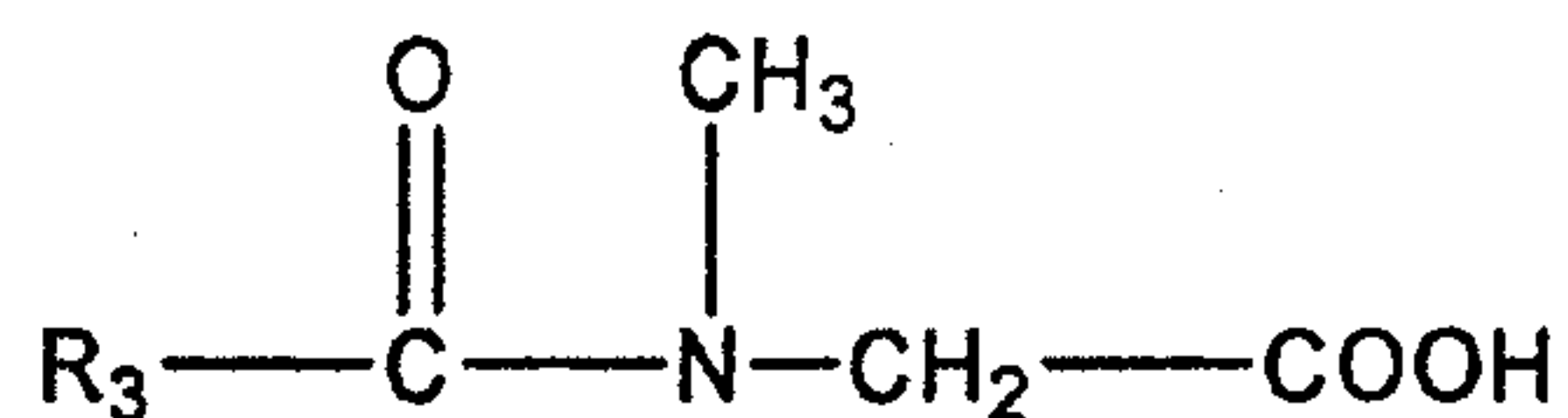


[0013] The monothiophosphate ester is generally not a pure compound but a mixture of various substituents. Thus in formula I, at least one R substituent is selected from alkylphenyl, alkaryl and alkoxyaryl; and more preferably the monothiophosphate ester is derived from aryl or alkaryl substituents. Particularly preferred R groups are selected from phenyl and alkylphenyl of 7 to 18 carbon atoms.

[0014] Particularly good compatibility as measured by filterability upon exposure to calcium was found for low levels of a dithiophosphate ester of formula II and effective compositions are prepared employing less than about 0.015 wt % dithiophosphate ester. Preferred dithiophosphate esters of formula II are selected where R<sub>1</sub> is selected from the group consisting of propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, isopentyl, hexyl, 2-ethylbutyl, 1-methylpentyl, 1,3 dimethylbutyl, and 2 ethylhexyl. Additionally R<sub>2</sub> is preferably hydrogen and -(alk)- is selected from the group consisting of -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>3</sub>)-, -CH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)- and -CH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)-, with the branched chain alkylene groups even more preferable.

[0015] Another embodiment of the invention includes the monothiophosphate ester and dithiophosphate ester as described herein above; but, includes the addition of a rust preventing agent. Specifically, it was unexpectedly discovered that there was an improvement in the hydraulic stability and the thermal stability of the composition when the rust preventing agent was the reaction product of a carboxylic acid having from 4 to 30 carbon atoms and an amino acid. Therefore, a preferred rust preventing agent is N-acyl sarcosine of the formula

(III)



wherein R<sub>3</sub> represents an alkyl or alkenyl group from 8 to 18 carbon atoms.

[0016] A particularly preferred N-acyl sarcosine is selected from the group consisting of lauroyl sarcosine, cocyl sarcosine, oleoyl sarcosine, stearoyl sarcosine and tall oil sarcosine.

[0017] In a further aspect of the invention relates to a method of lubricating hydraulic systems, bearing systems, gear systems, or sliding systems by employing

the lubricating oil composition of the present invention in such said system. Accordingly, the use the lubricating oil composition of the present invention can improve compatibility and filterability and thus increase the service life of the system while being capable of meeting Denison HF-2/HF-0 / DIN 51524 Part 3 / Cincinnati Machine P 68/69/70 performance levels, in parallel with excellent AFNOR 46693 performance.

### DETAILED DESCRIPTION OF THE INVENTION

[0018] The present invention is directed in part to compositions comprising metal free low phosphorous content monothiophosphate esters and dithiophosphate esters in an oil of lubricating viscosity. The lubricating oil composition may be employed in industrial oils such as hydraulic oil, bearing oils, industrial gear oils and sliding surface lubricating oils. The formulation is particularly suited as an ashless hydraulic package, which may be used at low additive concentrations while meeting the Denison HF-2/HF-0 / DIN 51524 Part 3 / Cincinnati Machine P 68/69/70 performance levels. Additionally, the composition demonstrates unexpectedly good compatibility with calcium containing packages. The following terms have are defined.

[0019] The term "alkyl" refers to straight and branched chain saturated aliphatic groups typically having from 1 to 20 carbons atoms, and more preferably 1 to 6 atoms ("lower alkyl"). This term is exemplified by the groups such as methyl, ethyl, propyl butyl, isopropyl, isobutyl, sec-butyl, tert-butyl, and the like.

[0020] The term "alkoxy" refers to the group alkyl-O-. Preferred alkoxy groups are represented by, for example, methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, tert-butoxy, sec-butoxy, n-pentoxy, n-hexoxy, 1,2-dimethylbutoxy, and the like.

[0021] The term "alkylene" as used alone or in combination in any of the formulae herein, refers to an optionally substituted straight or branched chain saturated divalent hydrocarbon group containing from one to ten carbon atoms. Preferably, the alkylene group is a "C<sub>1-6</sub> alkylene" or which refer to such groups containing from one to six carbon atoms, such as methylene, ethylene, n-propylene, isopropylene, n-butylene, isobutylene, sec-butylene, tert-butylene and the like

[0022] The term "aryl" refers to an unsaturated aromatic carbocyclic group from 6 to 20 carbon atoms, preferably 6-10 carbon atoms, having a single ring (e.g. phenyl)



or multiple condensed (fused) rings (e.g., naphthyl or anthryl). Preferred aryls include phenyl, naphthyl and the like.

**[0023]** Unless otherwise constrained by the definition for the aryl substituent, such aryl groups can optionally be substituted with from 1 to 5 substituents, preferably 1 to 3 substituents selected from the group consisting of alkyl, alkoxy, and the like.

**[0024]** The term "hydrocarbyl group" is well known in the art and refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Such groups include hydrocarbon groups, substituted hydrocarbon groups, and heterogroups, as long as they are primarily hydrocarbon in character.

**[0025]** Oil of lubricating viscosity:

**[0026]** Oils of lubricating viscosity contemplated for use in this invention include natural lubricating oils, synthetic lubricating oils and mixtures thereof. Suitable lubricating oils also include basestocks obtained by isomerization of synthetic wax and slack wax, as well as basestocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of crude oil. In general, both the natural and synthetic lubricating oils will each have a kinematic viscosity ranging from about  $1 \times 10^{-6} \text{ m}^2/\text{s}$  to about  $40 \times 10^{-6} \text{ m}^2/\text{s}$  (about 1 to about 40 cSt) at  $100^\circ\text{C}$ , although typical applications will require each oil to have a viscosity ranging from about  $2 \times 10^{-6} \text{ m}^2/\text{s}$  to about  $8 \times 10^{-6} \text{ m}^2/\text{s}$  (about 2 to about 8 cSt) at  $100^\circ\text{C}$ .

**[0027]** Natural base oils include animal oils, vegetable oils (e.g., castor oil and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale. The preferred natural base oil is mineral oil. The mineral oils useful in this invention include all common mineral oil base stocks. This would include oils that are naphthenic or paraffinic in chemical structure. Oils that are refined by conventional methodology using acid, alkali, and clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents such as phenol, sulphur dioxide, furfural, dichlorodiethyl ether, etc. They may be hydrotreated or hydro-refined, dewaxed by chilling or catalytic dewaxing processes, or hydrocracked. The mineral oil may be produced from natural crude sources or be composed of isomerized wax materials or residues of other refining processes.



[0028] Typically the mineral oils will have kinematic viscosities of from  $2 \times 10^{-6} \text{ m}^2/\text{s}$  to  $12 \times 10^{-6} \text{ m}^2/\text{s}$  (2 cSt to 12 cSt) at  $100^\circ\text{C}$ . The preferred mineral oils have kinematic viscosities of from  $3 \times 10^{-6} \text{ m}^2/\text{s}$  to  $10 \times 10^{-6} \text{ m}^2/\text{s}$  (3 to 10 cSt), and most preferred are those mineral oils with viscosities of  $5 \times 10^{-6} \text{ m}^2/\text{s}$  to  $9 \times 10^{-6} \text{ m}^2/\text{s}$  (5 to 9 cSt) at  $100^\circ\text{C}$ .

[0029] Synthetic lubricating oils useful in this invention include hydrocarbon oils and halo-substituted hydrocarbon oils such as oligomerized, polymerized, and interpolymerized olefins [polybutylenes, polypropylenes, propylene, isobutylene copolymers, chlorinated polyacetenes, poly(1-hexenes), poly(1-octenes), and mixtures thereof]; alkylbenzenes [dodecyl-benzenes, tetradecylbenzenes, dinonyl benzenes and di(2-ethylhexyl)benzene]; polyphenyls [biphenyls, terphenyls, alkylated polyphenyls]; and alkylated diphenyl ethers, alkylated diphenyl sulphides, as well as their derivatives, analogs, and homologs thereof, and the like. The preferred synthetic oils are oligomers of  $\alpha$ -olefins, particularly oligomers of 1-decene, also known as polyalpha-olefins or PAO's. Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers, and derivatives thereof where the terminal hydroxyl groups have been modified by esterification or etherification. This class of synthetic oils is exemplified by: polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide; the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polypropylene glycol having a molecular weight of 100-1500); and mono- and poly-carboxylic esters thereof (e.g., the acetic acid esters, mixed fatty acid esters, and oxo acid diester of tetraethylene glycol). Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids and alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoethers and propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, 2,5 di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl isophthalate, didecyl phthalate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of



sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid. A preferred type of oil from this class of synthetic oils is adipates of C<sub>4</sub> to C<sub>12</sub> alcohols.

[0030] Esters useful as synthetic lubricating oils also include those made from C<sub>5</sub> to C<sub>12</sub> monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane pentaerythritol, dipentaerythritol and tripentaerythritol.

[0031] Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. These oils include tetra-ethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxy)-disiloxane, poy(dimethyl)-siloxanes and poly (methylphenyl) siloxanes.

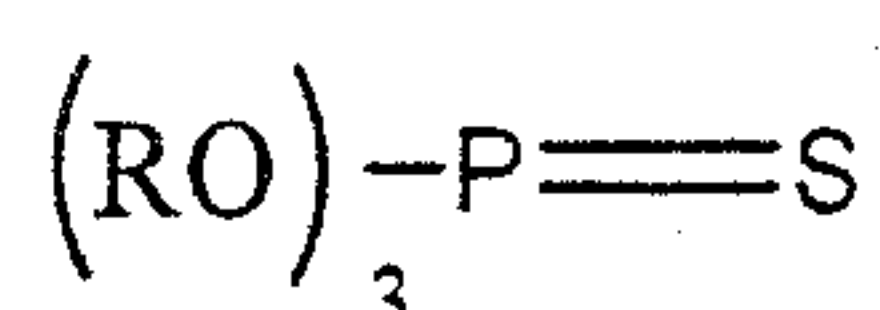
[0032] The lubricating base oils may be derived from refined, re-refined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Re-refined oils are obtained by treating used oils in processes similar to those used to obtain the refined oils. These re-refined oils are also known as reclaimed or reprocessed oils and are often additionally processed by techniques for removal of spent additives and oils breakdown products. White oils, as taught in U.S. Patent No. 5,736,490 may also be used as the base oil, especially for turbine applications.

[0033] In a preferred embodiment of the invention the base oil is a Group I, Group II or Group III base oil. The use of Group I or II base oils are particularly preferred, with a Group I base oil even more preferred. The American Petroleum Institute has categorized these different basestock types as follows: Group I >0.03 wt% sulphur, and/or <90 vol% saturates, viscosity index between 80 and 120;

Group II  $\leq 0.03$  wt% sulphur, and  $\geq 90$  vol% saturates, viscosity index between 80 and 120; Group III  $\leq 0.03$  wt% sulphur, and  $\geq 90$  vol% saturates, viscosity index  $> 120$ ; Group IV, all polyalphaolefins. Hydrotreated basestocks and catalytically dewaxed basestocks, because of their low sulphur and aromatics content, generally fall into the Group II and Group III categories. Polyalphaolefins (Group IV basestocks) are synthetic base oils prepared from various  $\alpha$ -olefins and are substantially free of sulphur and aromatics. The lubricant composition of the present invention may be prepared by simple blending of the various components with the base oil.

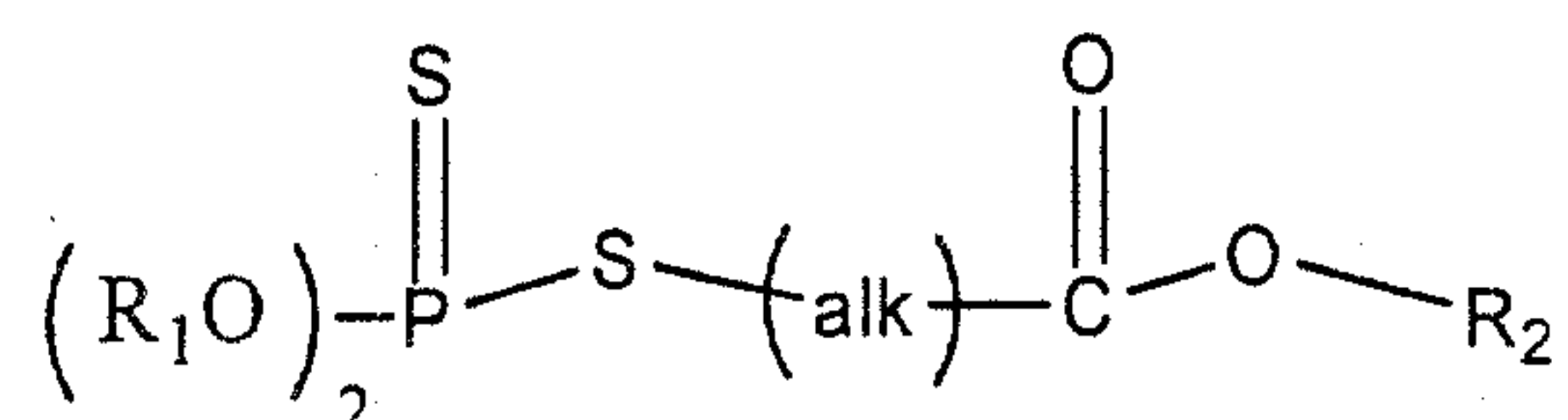
[0034] The mixture of ashless, sulfur containing organo phosphorous compounds comprises:

- i) an antiwear effective amount of a monothiophosphate ester of the formula



wherein R is independently selected from phenyl, alkylphenyl, aryl, alkaryl, aralkyl, and alkoxyaryl; and

- ii) from 0.01 to 0.03 weight percent based upon the total mass of the lubricating composition of a dithiophosphate ester of the formula



wherein each  $\text{R}_1$  is an independently selected hydrocarbyl from 3 to 20 carbon atoms; alk is a straight or branched chain alkylene group of 2 to 6 carbon atoms;  $\text{R}_2$  is hydrogen or alkyl from 1 to 4 carbons atoms;

wherein the total phosphorous content of the composition is less than 350 parts per million phosphorous.

[0035] In formula I, particularly preferred R groups are independently selected from aryl, alkaryl, aralkyl and alkoxyaryl. Particularly preferred aryl groups are phenyl groups and substituted phenyl groups. Even more preferred are alkyphenyl



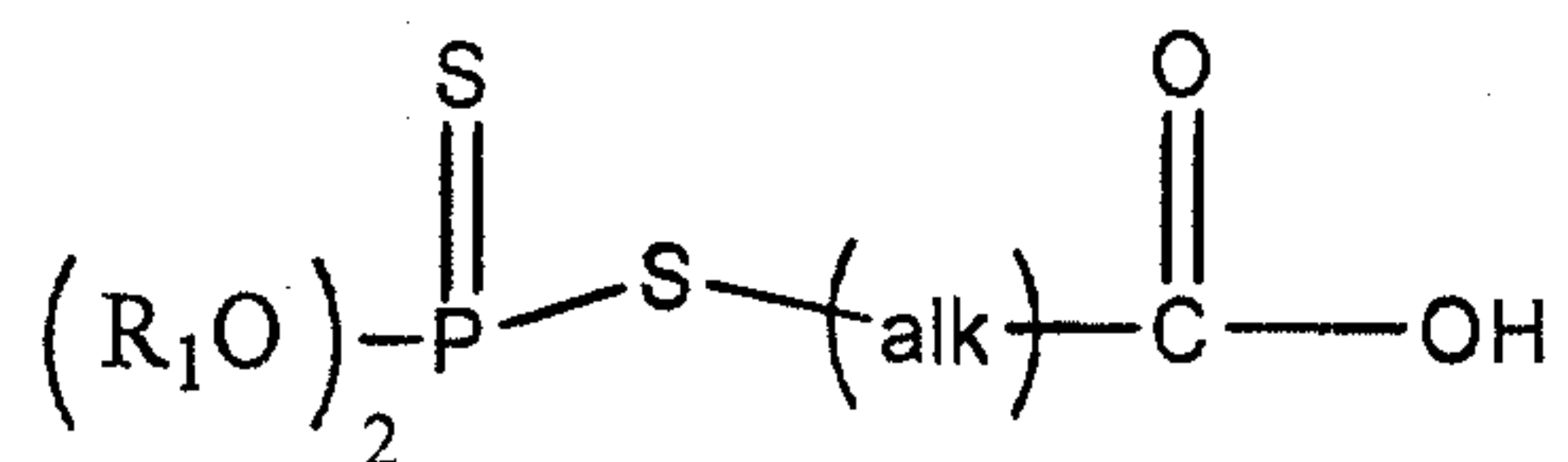
groups having 7 to 18 carbons atoms wherein the phenyl group is substituted for example with one to three C<sub>1-4</sub> alkyl groups, or by one or two C<sub>1-6</sub> alkyl groups or by one C<sub>1-12</sub> alkyl group. Also preferred are alkoxyphenyl groups having 7 to 18 carbons atoms wherein the phenyl group is substituted for example with one to three C<sub>1-4</sub> alkoxy groups, or by one or two C<sub>1-6</sub> alkoxy groups or by one C<sub>1-12</sub> alkoxy group, particularly preferred alkoxy groups are methoxy, and ethoxy groups.

[0036] Particularly preferred phenylalkyl groups are benzyl, phenylethyl and particularly 1-phenyl-1-ethyl. Particularly preferred compounds are triarylthiophosphate mixtures and even more preferred phenyl and alkylphenyl substituted thiophosphates comprising substances such as triphenylthiophosphate, n-decylphenyl-n-nonylphenyl-phenylthiophosphate, o-tert-butylphenyl-o-isopropylphenyl-phenylthiophosphate, or n-hexylphenyl-phenylthiophosphate as well as mixture of the above. Other suitable compounds are for example triphenyl thiophosphate, tricresyl thiophosphate, cresyl diphenyl thiophosphate, dicresyl phenyl thiophosphate, ethylphenyl diphenyl thiophosphate, diethylphenyl phenyl thiophosphate, propylphenyl diphenyl thiophosphate, dipropylphenyl phenyl thiophosphate, triethylphenyl thiophosphate, tripropylphenyl thiophosphate, butylphenyl diphenyl thiophosphate, dibutylphenyl phenyl thiophosphate, and tributylphenyl thiophosphate. Preparation of these alkylated phenyl and triphenyl thiophosphoric acid esters is known and described for example in EP-A-368 803 and commercially available Ciba Specialty Chemicals under the trademark IRGALUBE.

[0037] In formula II, preferably R<sub>1</sub> is hydrocarbyl selected from straight and branched chain alkyl, cycloalkyl, alkylphenyl and substituted alkylphenyl described herein above. Particularly preferred substituents for R<sub>1</sub> are independently selected from alkyl from 3 to 10 carbon atoms, such as propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, isopentyl, hexyl, 2-ethylbutyl, 1-methylpentyl, 1,3 dimethylbutyl, 2 ethylhexyl, and the like. Particularly preferred are mixtures of the above; and even more preferred alkyl groups are selected from isopropyl, isobutyl and 2-ethylhexyl. Particularly preferred -(alk)- groups are selected from the group consisting of ethylene, n-propylene, isopropylene, n-butylene, isobutylene and sec-butylene, and even more preferred is ethylene. Preferably R<sub>2</sub> is hydrogen, methyl, ethyl, propyl and isopropyl. Particularly preferred is hydrogen.



[0038] Thus, particularly preferred dithiophosphate esters are represented by the formula



(II')

where  $R_1$  and  $-(alk)-$  are described above.

[0039] The present invention is directed to overall low phosphorous containing compositions comprising an oil of lubricating composition, particularly a hydraulic oil and component i) and component ii) in relative small amounts. Thus, the lubricating oil composition employs a total of less than 350 parts per million (ppm) phosphorous content, based upon elemental phosphorous in the total mass of the composition. Even more preferred are lower overall phosphorous content compositions having less than 275 ppm phosphorous and preferably less than 250, and even more preferably less than 225 ppm phosphorous content total in the lubricating composition. However, typically the composition requires at least 175 ppm phosphorous content for demonstrated antiwear performance. In a preferred embodiment, the phosphate in the composition is contributed by a mixture comprising a from 0.1 to 0.4 weight percent of monothiophosphate ester of formula I, preferably from 0.2 to 0.4 weight percent; and from 0.01 to 0.03 weight percent of the dithiophosphate ester of formula II, more preferably less than 0.025 wt %, with 0.01 to 0.02 wt % of the dithiophosphate ester of formula II being especially preferred. Even more preferred (employed in the ratios as depicted above) is the dithiophosphate ester represented by formula II'.

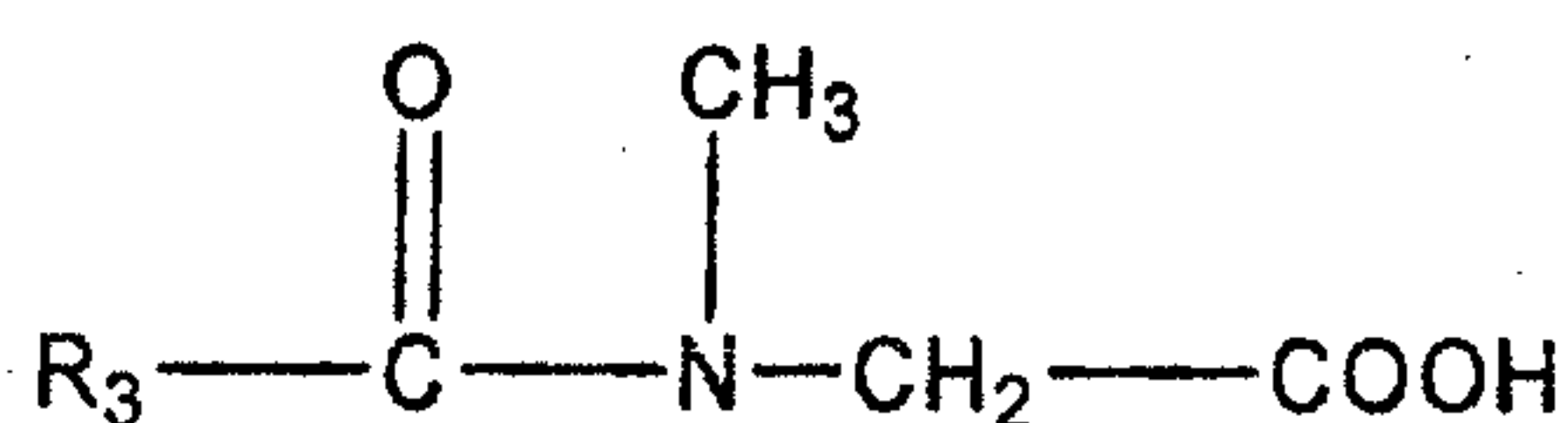
[0040] Preferably the weight ratio of component i) to ii) is from 10:1 to 40:1 and even more preferred form 10:1 to 25:1 with 15:1 to 25:1 being particularly preferred. At this low phosphorous content it was discovered that unexpected benefit when the amount of the dithiophosphate ester of formula II was employed in less than 0.03 weight percent, based upon the total mass of the lubricating composition.

[0041] Amine phosphates are typically added to hydraulic formulations since they are especially good to provide added load carrying capacity (FZG failure load stages greater or equal to 10). If employed in the present invention, preferably they are from 0 to 175 ppm. Preferably when used, amine phosphates are at extremely low concentrations of less than 150 ppm, more preferably less than 75 ppm as measured in



the lubricating composition. Particularly preferred, the lubricating oil compositions have a total phosphorus content less than 350 ppm and comprise an oil of lubricating viscosity and the mixture of ashless, sulfur containing organo phosphorous compounds having from 0.2 to 0.4 wt % of a monothiophosphate of formula I and from 0.01 to 0.03 wt % of the dithiophosphate ester of formula II, with the proviso that the composition does not contain an amine phosphate. Amine phosphate as used above includes ammonium phosphate esters and thus can be depicted as  $(R_aO)_2-P(O)O^- N(R_b)_2$  where  $R_a$  and  $R_b$  are at each occurrence independently selected from hydrocarbyl from 1 to 20 carbon atoms, but preferably lower alkyl groups and additionally  $R_b$  can be hydrogen.

[0042] In a preferred embodiment the lubricating oil compositions further comprise a rust inhibitor. Particularly preferred the rust preventing agents are nitrogen compounds, and more particularly amides prepared as the reaction product of a carboxylic acid having from 4 to 30 carbon atoms and an amino acid. And within this class of compounds particularly preferred are the compounds represented by the N-acyl sarcosine of the formula



(III)

wherein  $R_3$  represents an alkyl or alkenyl group from 8 to 18 carbon atoms.

[0043] With even more preferred N-acyl sarcosine of formula III selected from the group consisting of lauroyl sarcosine, cocyl sarcosine, oleoyl sarcosine, stearoyl sarcosine and tall oil sarcosine.

[0044] Other suitable nitrogen-containing compounds, include tertiary aliphatic or cycloaliphatic amines and amine salts of organic and inorganic acids, e.g. oil-soluble alkylammonium carboxylates, and 1-[N,N-bis(2-hydroxyethyl)amino]-3-(4-nonylphenoxy)propan-2-ol; as well as nitrogen heterocyclic compounds, e.g.: substituted imidazolines and oxazolines, e.g. 2-heptadecenyl-1-(2-hydroxyethyl)imidazoline.

[0045] Similarly other suitable rust inhibitors may include organic acids, their esters, metal salts, amine salts and anhydrides, e.g. alkyl- and alkenyl-succinic acids and their partial esters with alcohols, diols or hydroxycarboxylic acids, partial amides of alkyl- and alkenyl-succinic acids, 4-nonylphenoxyacetic acid, alkoxy- and



alkoxyethoxy-carboxylic acids, such as dodecyloxyacetic acid, dodecyloxy(ethoxy)acetic acid and amine salts thereof, dodecenylsuccinic acid anhydride, 2-(2-carboxyethyl)-1-dodecyl-3-methylglycerol and salts thereof, especially sodium and triethanolamine salts thereof. As well as sulfur-containing compounds, e.g.: barium dinonylnaphthalene sulfonates, calcium petroleum sulfonates, alkylthio-substituted aliphatic carboxylic acids, esters of aliphatic 2-sulfocarboxylic acids and salts thereof.

[0046] In order to further improve the performance or the lubricating oil composition of the invention, various auxiliary additives generally used may be used depending on necessity, in addition to the necessary components. For example, known additives for lubricating oils, such as an antioxidant, a metal deactivator, an extreme-pressure agent, an oiliness agent, a defoaming agent, a viscosity index improving agent, a pour point depressing agent, a detergent dispersant, a rust preventing agent and an anti-emulsification agent.

[0047] Examples of the amine type antioxidant include a dialkyldiphenylamine, such as p,p'-dioctyldiphenylamine (Nonflex OD-3 produced by Seiko chemical Co., Ltd.), p,p'-di-a-methylbenzyldiphenylamine and N-p-butylphenyl-N-p'-octylphenylamine, a monoalkyldiphenylamine, such as mono-t-butylphenylamine and mono-octyldiphenylamine, a bis(dialkylphenyl)amine, such as di(2,4-diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine, an alkylphenyl-1-naphthylamine, such as octylphenyl-1-naphthylamine and N-t-dodecylphenyl-1-naphthylamine, an aryl-naphthylamine, such as 1-naphthylamine, phenyl-1-naphthylamine, phenyl-2 N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine, a phenylenediamine, such as N, N'-diisopropyl-p phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and a phenothiazine, such as phenothiazine (Phenothiazine produced by Hodogaya Chemical Co., Ltd.) and 3,7-dioctylphenothiazine. Other aminic antioxidants include for example: N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di(naphth-2-yl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-



phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfonamido)-diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, e.g. p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylamino-phenol, 4-nonanoylamino-phenol, 4-dodecanoylamino-phenol, 4-octadecanoylamino-phenol, di(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethyl phenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-di[(2-methylphenyl)amino]ethane, 1,2-di(phenylamino)propane, (o-tolyl)biguanide, di[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, mixture of mono- and di-alkylated tert-butyl/tert-octyl-diphenylamines, mixture of mono- and di-alkylated nonyldiphenylamines, mixture of mono- and di-alkylated dodecyldiphenylamines, mixture of mono- and di-alkylated isopropyl/iso-hexyl-diphenylamines, mixtures of mono- and di-alkylated tert-butylidiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, mixture of mono- and di-alkylated tert-butyl/tert-octyl-phenothiazines, mixture of mono- and di-alkylated tert-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine, bis(2,2,6,6-tetramethylpiperidin-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol. Particularly preferred are the alkaryl amines.

**[0048]** Examples of the sulfur type antioxidant include a dialkylsulfide, such as didodecylsulfide and dioctadecylsulfide, a thiodipropionic ester, such as didodecyl thiodipropionate, dioctadecyl thiodipropionate, dimyristyl thiodipropionate and 2-mercaptobenzoimidazole.

**[0049]** Examples of the phenol type antioxidant include 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone (Antage D produced by Kawaguchi Chemical Co. Ltd.), 2,6-di-t-butylphenol, a 2,6-di-t-butyl-4-alkylphenol, such as 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol, a 2,6-di-t-butyl-4-alkoxyphenol, such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol, 3,5-di-t-butyl-4-



hydroxybenzylmercapto octylacetate, an alkyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, such as n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (Yoshinox SS produced by Yoshitomi Pharmaceutical Industries, Ltd.), n-dodecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 2,6 di-t-butyl-a-dimethylamino-p-cresol, a 2,2'-methylenebis (4-alkyl-6-t-butylphenol), such as 2, 2'-methylenebis(4-methyl-6-t-butylphenol) (Antage W-400 produced by Kawaguchi Chemical Co., Ltd.) and 2, 2'-methylenebis(4-ethyl-6-t-butylphenol) (Antage W-500 produced by Kawaguchi Chemical Co., Ltd.), a bisphenol, such as 4,4'-butylidene bis(3-methyl-6-t-butylphenol) (Antage W-300 produced by Kawaguchi Chemical Co., Ltd.), 4,4'-methylenebis(2,6-t-butylphenol) (Ionox 220AH produced by Shell Japan, Inc.), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane, (Bisphenol A produced by Shell Japan, Inc.), 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidene bis(2,6-t-butylphenol), hexamethylene glycol bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (Irganox L109 produced by Ciba Specialty Chemicals, Inc.), triethylene glycol bis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate] (Tominox 917 produced by Yoshitomi Pharmaceutical Industries, Ltd.), 2,2'-thio-[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] (Irganox L115 produced by Ciba Specialty Chemicals, Inc.), 3, 9-bis{1,1-dimethyl-2-[3-(3-t-butyl-4-hydroxy-5-methylphenyl) propionyloxy]-ethyl}-2,4,8,10-tetraoxaspiro[5,5] undecane (Sumilizer GA80 produced by Sumitomo Chemical Industries, Ltd.), 4,4'-thiobis(3-methyl-6-t-butylphenol) (Antage RC produced by Kawaguchi Chemical Co., Ltd.) and 2,2'-thiobis(4,6-di-t-butylresorcin), a polyphenol, such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate]methane (Irganox L101 produced by Ciba Specialty Chemicals, Inc.), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane (Yoshinox 930 produced by Yoshitomi Pharmaceutical Industries, Ltd.), 1,3,5-trimethyl-2,4, 6-tris(3,5-di-t-butyl-4-hydroxybenzyl)-benzene (Ionox 330 produced by Shell Japan, Inc.), bis[3,3'-bis(4'-hydroxy-3'-t-butylphenyl)butyric acid] glycol ester, 2-(3',5'-di-t-butyl-4-hydroxyphenyl)-methyl-4-(2'', 4''-di-t-butyl-3''-hydroxyphenyl)methyl-6-t-butylphenol and 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)-4-methylphenol, a condensation product of p-t-butylphenol and formaldehyde, and a condensation product of p-t-butylphenol and acetaldehyde.



These condensation products of alkylphenols with formaldehydes may also serve as demulsifiers.

[0050] Examples of the phosphorus type antioxidant include a triarylphosphite, such as triphenylphosphite and tricresylphosphite, a trialkylphosphite.

[0051] Examples of a metal deactivator that can be used with the composition of the invention include a benzotriazole derivative, such as benzotriazole, 2-mercaptobenzotriazole, 2,5-dimercaptobenzotriazole, a 4-alkyl-benzotriazole, e.g., 4-menthyl-benzotriazole and 4-ethyl-benzotriazole, a 5-alkyl-benzotriazole, e.g., 5-methyl-benzotriazole and 5-ethyl-benzotriazole, a 1-alkyl-benzotriazole, e.g., 1-dioctylaminomethyl-2,3-benzotriazole, and a 1-alkyl-tolotriazole, e.g., 1-dioctylaminomethyl-2,3-tolotriazole; a benzoimidazole derivative, such as benzoimidazole, a 2-(alkyldithio)-benzoimidazole, e.g., 2-(octyldithio)-benzoimidazole, 2-(decyldithio)-benzoimidazole and 2-(dodecyldithio)-benzoimidazole, and a 2-(alkyldithio)-toluimidazole, e.g., 2-(octyldithio)-toluimidazole, 2-(decyldithio)-toluimidazole and 2-(dodecyldithio)-toluimidazole; an indazole derivative, such as indazole, a 4-alkyl-indazole, a 5-alkyl-indazole; a benzothiazole derivative, such as benzothiazole, a 2-mercaptobenzothiazole (Thiolite E3100 produced by Chiyoda Chemical Industries, Ltd.), a 2-(alkyldithio)benzothiazole, e.g., 2-(hexyldithio)benzothiazole and 2-(octyldithio)benzothiazole, a 2-(alkyl-dithio)toluthiazole, e.g., 2-(hexyldithio)toluthiazole and 2-(octyldithio)toluthiazole, a 2-(N,N-dialkyldithiocarbamyl)benzothiazole, e.g., 2-(N,N-diethyl-dithiocarbamyl)benzothiazole, 2-(N,N-dibutyl-dithiocarbamyl)benzothiazole and 2-(N,N-dihexyldithiocarbamyl)benzothiazole, and a 2-(N,N-di-alkyldithiocarbamyl)toluthiazole, e.g., 2-(N,N-diethyldithiocarbamyl)toluthiazole, 2-(N,N-dibutyldithiocarbamyl)toluthiazole, and a dihexyldithiocarbamyl toluthiazole; a benzoxazole derivative, such as a 2-(alkyldithio)benzoxazole, e.g., 2-(octyldithio)benzoxazole, 2-(decyldithio)benzoxazole and 2-(dodecyldithio)benzoxazole, and a 2-(alkyl-dithio)toluoxazole, e.g., 2-(octyldithio)toluoxazole, 2-(decyldithio)toluoxazole and 2-(dodecyldithio)-toluoxazole; a thiadiazole derivative, such as a 2,5-bis(alkyldithio)-1,3,4-thiadiazole, e.g., 2,5-bis-(heptyldithio)-1,3,4-thiadiazole, 2,5-bis(nonyldithio)-1,3,4-thiadiazole, 2,5-bis(dodecyldithio)-1,3,4-thiadiazole and 2,5-bis(octadecyldithio)-1,3,4-thiadiazole,



a 2,5-bis(N,N-dialkyldithiocarbamyl)-1,3,4-thiadiazole, e.g., 2,5-bis(N,N-diethyldithiocarbamyl)-1,3,4-thiadiazole, 2,5-bis(N,N-dibutyldithiocarbamyl)-1,3,4-thiadiazole and 2,5-bis(N,N-dioctyldithio-carbamyl)-1,3,4-thiadiazole, and a 2-N,N-dialkyl-dithiocarbamyl-5-mercapto-1,3,4-thiadiazole, e.g., 2-N,N-dibutyldithiocarbamyl-5-mercapto-1,3,4-thiadiazole and 2-N,N-dioctyldithiocarbamyl-5-mercapto-1,3,4-thiadiazole; and a triazole derivative, such as a 1-alkyl-2,4-triazole, e.g., 1-dioctylaminomethyl-2,4-triazole. Also useful are Mannich bases of benzotriazole or tolutriazole, such as 1-[di(2-ethylhexyl)aminomethyl]tolutriazole and 1-[di(2-ethylhexyl)aminomethyl]benzotriazole; alkoxyalkylbenzotriazoles, such as 1-(nonyloxymethyl)-benzotriazole, 1-(1-butoxyethyl)-benzotriazole and 1-(1-cyclohexyloxybutyl)-tolutriazole.

[0052] These metal deactivators may be used singly or in combination in an amount of from 0.01 to 0.05 parts by weight per 100 parts by weight of the base oil.

[0053] Examples of the defoaming agent include an organosilicate, such as dimethylpolysiloxane, diethylsilicate and fluorosilicone, and a non-silicone defoaming agent, such as a polyalkylacrylate. The addition amount thereof may be from 0.0001 to 0.1 part by weight of the base oil, and may be used singly or in combination.

[0054] Examples of the viscosity index improving agent include a non-dispersion type viscosity index improving agent, such as a polymethacrylate and an olefin copolymer, e.g., an ethylene-propylene copolymer and a styrene-diene copolymer, and a dispersion type viscosity index improving agent, such as polymers obtained by copolymerizing these polymers with a nitrogen-containing monomer. The addition amount thereof may be from 0.05 to 10 parts by weight per 100 parts by weight of the base oil.

[0055] Examples of the pour point depressing agent include a polymethacrylate type polymer. The addition amount thereof may be from 0.01 to 2 parts by weight per 100 parts by weight of the base oil.

[0056] Examples of the demulsifying agents include alkoxyated phenols and phenol-formaldehyde resins, alkarylsulfonate with polyalkylphenol-formaldehyde resin, and aminoalkylphenolic resins from 0.01 to 0.1 part by weight per 100 parts by weight of the base oil, and they may be used singly or in combination.



[0057] Examples of the extreme-pressure agent and the oiliness agent include a sulfur extreme-pressure agent, such as a dialkylsulfide, dibenzylsulfide, a dialkylpolysulfide, dibenzylsulfide, an alkylmercaptane, dibenzothiophene and 2,2'-dithiobis (benzothiazole), a phosphorus extreme-pressure agent, such as a trialkyl phosphate, a triaryl phosphate, a trialkyl phosphonate, a trialkyl phosphite, a triaryl phosphite, a dialkyl hydrogenphosphite and a trialkyl trithiophosphite, an aliphatic oiliness agent, such as a fatty acid amide and a fatty acid ester, and an amine oiliness agent, such as a primary, secondary or tertiary alkylamine and an alkyleneoxide-added alkylamine. These extreme-pressure agent and oiliness agent may be used singly or in combination in an amount of from 0.1 to 2 parts by weight per 100 parts by weight of the base oil. However, typically sufficient antiwear performance can be obtained by using only the composition of the invention in most cases.

[0058] The metal free low phosphorous containing hydraulic fluid having a mixture of ashless, sulfur containing organo phosphorous compounds comprising a monothiophosphate ester and a dithiophosphate ester of the present invention may be produced by mixing the oil having a viscosity suitable for lubrication and the mixture of ashless, sulfur containing organo phosphorous containing compounds together with the other additives described above optionally present in the oil having a viscosity suitable for lubrication. The constituents of this mixture may interact during the mixing operation, modifying the organo phosphorous compounds and/or the other additives.

[0059] The various preferred conditions indicated above apply both to the lubricating fluids and to the process for the production of a hydraulic fluid and to the uses according to the present invention. The present invention is illustrated in more detail by the following examples which are proposed by way of illustration of the present invention. They are not intended to limit its scope.

## EXAMPLES

[0060] The following examples are given for the purpose of illustrating the invention and are not intended in any way to limit the scope. All percentages and parts are based on weight unless otherwise indicated. The various mixtures were prepared using an ISO VG 46 mineral oil (kinematic viscosity at 40 °C.: 42-50 CSt) and a



baseline of base/additive mixture typically used for hydraulic fluids. The baseline of base/additive mixture is free of metal salts and is a combination of an aromatic amine antioxidant (e.g. Irganox. L 57), a hindered phenol antioxidant (e.g. Ionox 99) and comparatively small amounts of other customary additives, such as pour-point depressants (e.g. Plexol. 156), antifoams (e.g. Mobilad. C<sub>402</sub>), de-emulsification additives (e.g. alkoxyated phenols and phenol-formaldehyde resins), corrosion inhibitors and metal deactivators (e.g. Irgamet 39). To the base additive package was added the monothiophosphate ester of formula I and dithiophosphate ester of formula II. Additionally where indicated was added an antirust compound. These are depicted in wt % in the Table below. The total treat level of all additives in the formulation is listed as dosage %.

[0061] The following tests were carried out: examination of anti-wear properties: four ball test, FZG gear test, filterability test AFNOR NF E 48-693:1996, hydrolytic stability test ASTM D2619, and thermal stability test from Cincinnati Milacron.

[0062] Four ball tester (from Shell according to DIN 51530, IP 239) to determination of the wear characteristics (wear scar diameter, abbreviation WSD) of liquid lubricants according to DIN 51350 T3; revs/min: 1500, load: 40 kg (400 N), duration: 1 hour (h); lower WSD values are indicative of improved performance.

[0063] FZG gear test (description in DIN 51.354, AN8.3/90, IP 334179). In the splash lubrication method, defined gears rotate at a constant speed and fixed initial temperature in the fluid to be tested. The loading of the gears is increased in stages. From load stage 4, the change in the tooth profiles is recorded after each stage by describing and, where appropriate, by photographing, by measuring the roughness, or by contact impression. The limit load stage is one stage below the so-called failure load stage (abbreviation: FLS) at which at least two profiles of the test gear exhibit clear damage (fissures or similar).

[0064] Compatibility Index -the compatibility with calcium is specific to ashless formulations. The objective is to simulate what would happen when an end user replaces an ash-containing oil (ie a calcium containing oil) by an ashless additive package. During change-over it is conceivable that a minor amount of ash-containing oil will remain and will be mixed with the ashless oils. Therefore, it is desirable that there are not compatibility problems such as deposit formulation between these two formulations. The AFNOR NF E 48-693:1996 is a filterability test to evaluate the



compatibility between mixing two fluids and is given as a Compatibility Index "IFc". Although this test compares three ratios it was determined that most severe result was at 90/10 (90% ashless fluid and 10% of Ca containing fluid and thus this is the only result shown). 2.0 liters of the fluid each oil to be tested are first pre-aged at 100 °C for 72 hours. A 330 ml total sample (of the 90/10 ratio) was prepared and manually agitated approximately 30 revolutions in 1 minute. The sample was placed into the filtering apparatus and filtered through a 0.8 µm filter under pressure (1000 mbar) and time is measured at the first drop of filtrate and the time need to collect 50, 100, 200 and 300 ml of filtrate. If the time needed to obtain 50 ml of filtrate is less than 60 seconds, the test is conducted again at a pressure of 500 mbar, alternatively if the time to collect 50 ml of filtrate is greater than 600 seconds, the test is restarted at a pressure of 2000 mbar. The test is complete when all the oil has been filtered or after 2 hours of beginning the test. The result of this test is quoted as the filtration index IFc(x/y) of the mixture made with an x/y ratio of A and B (where A and B are the test fluids). It is calculated as the mean of the 3 samples made iwht the corresponding x/y ratio (herein 90/10 ashless to ash oil).  $IFc = (T_{300} - T_{200})/2 * (T_{100} - T_{50})$ ; where  $T_{300}$  = time, in seconds, required for 300 ml to pass through the filter;  $T_{200}$  = time, in seconds, required for 200 ml to pass through the filter, and so on. Values closer to one indicate good filterability and correspond with good compatibility.

[0065] Hydraulic stability was measured by the ASTM D2619 test. This test measures the propensity of the components to be hydrolysed in the presence of water, heat and active metals, namely a copper coupon. The water acidity in mg KOH from ASTM D2619 is listed below.

[0066] The thermal stability was evaluated according to the standard for purchasing lubricating oils by Cincinnati Milacron, Inc., (10-SP-810160-3). An iron rod and a copper rod as catalysts were immersed in 200 ml of sample which is placed in an oven at 135 °C for 168 hours. The sample is then removed and allowed to cool to ambient room temperature and filtered and 25 milliliters of the filtrate is filtered through a membrane filter having a pore diameter of 8 micrometer, to measure the weight of sludge formed. According to the P-68, P-69 and P-70 Standards as defined by Cincinnati Milacron, Inc. it is required that the amount of sludge is 25 mg of less per 100 ml.

TABLE I

	Base Line	COMPARATIVE RUNS					EXAMPLE RUNS				
		A	B	C	D	E	1	2	3	4	5
Dosage %	0.23	0.40	0.80	0.75	0.65	0.60	0.75	0.65	0.55	0.55	0.55
Component i) <sup>1</sup>				0.40	0.25	0.25	0.40	0.325	0.25	0.25	0.25
Component ii) <sup>2</sup>				0.05	0.10	0.05	0.01	0.03	0.01	0.01	0.015
Component c) <sup>3</sup>									0.02	0.02	0.015
Amine phosphate		0.10	0.50								
Phosphorous content (ppm)	0	82	410	350	290	244	320	290	207	207	211
4-ball test - wear (mm)				0.48		0.49	0.64	0.54	0.58	0.54	0.59
FZG (FLS) <sup>4</sup>				>13		12	12	11	12	9	12
IFC (90/10)				1.53	1.26	1.31*	1.14	1.12	1.15	1.16	1.05
Acidity (mg KOH) ASTM D2619	1.7	5.9	17.4	1.4					1.1	1.1	1.1
Sludge (mg/100 ml) Cincinnati test (limit <25)			40.6		18.1		30.5	18.7	29.5	13.4	15.6

<sup>1</sup> Monothiophosphate ester (butylated triphenyl phosphorothionate, IRGALUBE 232, available from Ciba Specialty Chemicals Inc.)

<sup>2</sup> Dithiophosphate ester (dialkylidithiophosphate derivative, IRGALUBE 353, available from Ciba Specialty Chemicals Inc.)

<sup>3</sup> Rust inhibitor (N-acyl sarcosine, SARKOSYL O, available from Ciba Specialty Chemicals Inc.)

<sup>4</sup> FLS means Failure Load Stage

\* Average of 2 runs

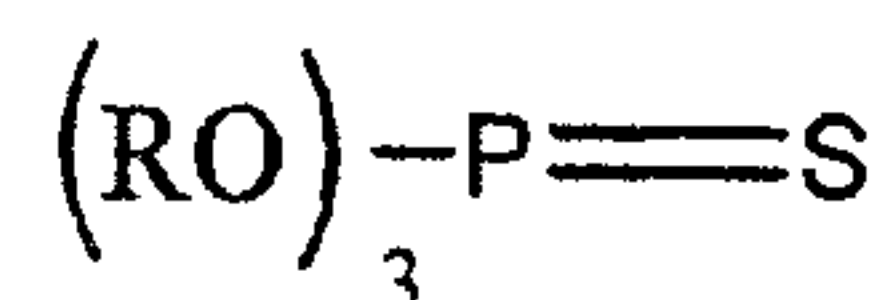


[0067] As demonstrated by Comparative runs A and B, which employed different amine phosphates at differing wt % in the lubricant composition, the addition of this component led to unacceptable acidity values as determined by ASTM D2619 method.

[0068] Quite surprisingly, it was discovered that low phosphorous formulations of a particular mixture of ashless, sulfur containing organo-phosphorous compounds comprising a specified monothiophosphate ester and a specified dithiophosphate ester in the prescribed amounts would yield good wear results and unexpectedly demonstrate good calcium compatibility in the AFNOR NFE 48693 (90/10) filterability index. Additionally, it was discovered that small amount of an antirust agent, more particularly N-acyl sarcosine of the formula III employed in amount from about 0.01 to 0.025 wt % showed improved hydraulic stability and thermal stability in comparison to similar formulations.

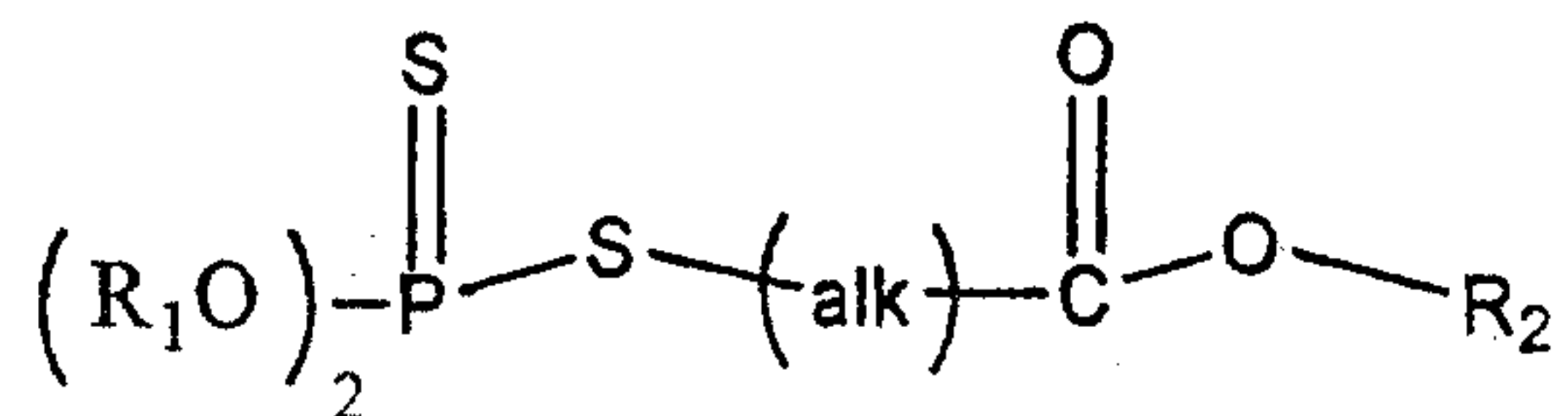
**WHAT IS CLAIMED IS:**

1. A metal free low phosphorous content lubricating oil composition comprising
  - a) an oil of lubricating viscosity;
  - b) a mixture of ashless, sulfur containing organo phosphorous compounds comprising
    - i) from 0.2 to 0.4 weight percent based upon the total mass of the lubricating oil composition of a monothiophosphate ester of the formula



wherein R is independently selected from phenyl, alkylphenyl, aryl, alkaryl, aralkyl, and alkoxyaryl; and

- ii) from 0.01 to 0.03 weight percent based upon the total mass of the lubricating oil composition of a dithiophosphate ester of the formula



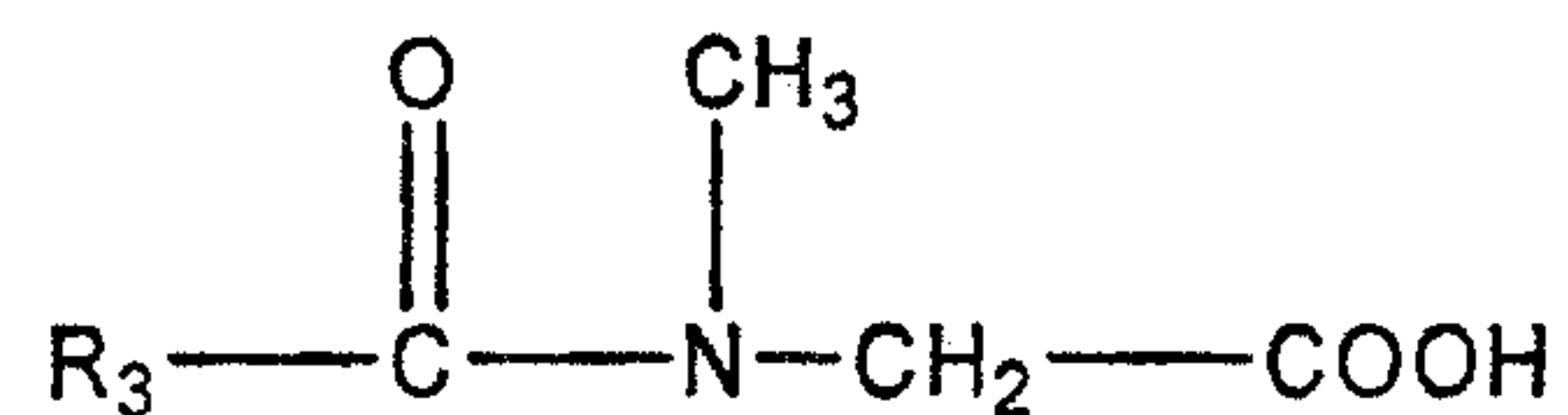
wherein each R<sub>1</sub> is an independently selected hydrocarbyl from 3 to 20 carbon atoms; alk is a straight or branched chain alkylene group of 2 to 6 carbon atoms; R<sub>2</sub> is hydrogen or alkyl from 1 to 4 carbons atoms; wherein the total phosphorous content of the composition is less than 350 parts per million phosphorous.

2. The lubricating oil composition of Claim 1, wherein the oil of lubricating viscosity is a hydraulic fluid.
3. The lubricating oil composition of Claim 1, wherein at least one R substituent of the monothiophosphate ester is selected from alkylphenyl, alkaryl and alkoxyaryl.
4. The lubricating oil composition of Claim 3, wherein R is selected from phenyl and alkylphenyl of 7 to 18 carbon atoms.



5. The lubricating oil composition of Claim 1, wherein the monothiophosphate ester is present at less than about 0.3 weight percent.
6. The lubricating oil composition of Claim 1, wherein  $R_1$  is selected from the group consisting of propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, isopentyl, hexyl, 2-ethylbutyl, 1-methylpentyl, 1,3 dimethylbutyl, and 2 ethylhexyl.
7. The lubricating oil composition of Claim 1, wherein  $R_2$  is hydrogen.
8. The lubricating oil composition of Claim 1, wherein -(alk)- is selected from the group consisting of  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_3)-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)-$  and  $-\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{CH}_3)-$ .
9. The lubricating oil composition of Claim 1, wherein the dithiophosphate ester is present at less than about 0.02 weight percent.
10. The lubricating oil composition of Claim 9, wherein the dithiophosphate ester is present at less than about 0.015 weight percent.
11. The lubricating oil composition of Claim 1, wherein the weight ratio of component i) to component ii) is in the range from 10:1 to 25:1.
12. The lubricating oil composition of Claim 11, wherein the weight ratio of component i) to component ii) is in the range from 15:1 to 25:1.
13. The lubricating oil composition of Claim 1, further comprising a rust preventing agent.
14. The lubricating oil composition of Claim 13, wherein the rust preventing agent is the reaction product of a carboxylic acid having from 4 to 30 carbon atoms and an amino acid.

15. The lubricating oil composition of Claim 14, wherein the rust preventing agent is N-acyl sarcosine of the formula



wherein R<sub>3</sub> represents an alkyl or alkenyl group from 8 to 18 carbon atoms.

16. The lubricating oil composition of Claim 15 wherein the N-acyl sarcosine is selected from the group consisting of lauroyl sarcosine, cocyl sarcosine, oleoyl sarcosine, stearoyl sarcosine and tall oil sarcosine.
17. The lubricating oil composition of Claim 1 further with the proviso that no phosphorous content in the lubricating oil is attributable to an amine phosphate.