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(54) **LUBRICATING OIL COMPOSITION WITH
ANTIWEAR PERFORMANCE**

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(57) **ABSTRACT**

The present invention relates to a lubricating oil composition containing: (1) an antiwear package comprising: (a) a hydrocarbyl phosphate and amine salt thereof; and (b) an alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound; (2) an antioxidant package comprising: (a) a hydrocarbyl diphenylamine; and (b) a sterically hindered phenol; (3) a metal deactivator; and (4) an oil of lubricating viscosity. The invention further relates to the process to make the lubricating oil composition and its use in industrial fluids especially hydraulic fluids.

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LUBRICATING OIL COMPOSITION WITH ANTIWEAR PERFORMANCE

FIELD OF THE INVENTION

[0001] The present invention relates to a lubricating composition comprising: (1) an antiwear package comprising: (a) a hydrocarbyl phosphate and amine salt thereof; and (b) an alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound; (2) an antioxidant package comprising: (a) a hydrocarbyl diphenylamine; and (b) a sterically hindered phenol; (3) a metal deactivator; and (4) an oil of lubricating viscosity. The invention further relates to the process to make the lubricating oil composition and its use in industrial fluids.

BACKGROUND OF THE INVENTION

[0002] Protecting a lubricating oil composition against oxidation degradation by selecting the proper balance of oxidation inhibitor components can significantly improve the life of a lubricant. Oxidation occurs when oxygen attacks a petroleum fluid, which leads to increased viscosity and deposit formation in the fluid. The oxidation process contributes to the formation of sludge in oils and the breakdown of viscosity characteristics of the lubricant.

[0003] Protecting a metal surface against wear degradation by selecting the proper balance of antiwear agents in a lubricating composition can significantly increase the life of the metal surface. Antiwear agents form a thin film on metal surfaces which prevents metal to metal contact, resulting in a decrease in the amount of wear. Known antiwear agents are typically derived from ash containing compounds such as zinc dialkyldithiophosphate (ZDDP). However, many industrial processes use high temperatures and/or high pressures which decompose ash containing compounds in a lubricating oil composition. Furthermore, as ash containing compounds decompose and release divalent metals such as zinc, these divalent metals are capable of reacting with other performance additives present such as alkenyl succinic anhydrides and alkenyl succinimides creating sludge and other particulate matter that can cause filter plugging. Likewise filter plugging may occur if industrial fluids contain other divalent metals from contaminants or other performance additives such as calcium or magnesium detergents.

[0004] In an attempt to overcome filter plugging issues associated with ash containing industrial fluids, ash free alternatives in lubricating compositions have been developed. However, known ash free compositions often are highly acidic and hydrolytically unstable.

[0005] U.S. Patent Application 2002/0010103 A1 discloses a lubricating oil composition having a major amount of a base oil and a minor amount of (a) at least one compound containing phosphorus selected from phosphoric acid ester, a thiophosphoric acid ester and amine salts thereof; (b) a phosphorus acid ester and amine salts thereof; and (c) at least one compound selected from alkenyl succinimide, an alkenyl succinic acid ester, benzylamine and

derivatives thereof. The composition contains alkenyl succinic anhydrides or derivatives thereof which are capable of reacting with contaminant amounts of divalent metals to form sludge that can cause filter plugging.

[0006] International publication WO 02/053687 A2 discloses a lubricating oil composition containing (a) triaryl phosphate; (b) β -dithiophosphorylated propionic acid, and (c) a base oil. The lubricating oil composition provides antiwear properties and minimal amounts of ash. GB Patent Number 1,415,964 discloses lubricating oils with a hydrocarbon oil-soluble triester of phosphorothionic acid and (b) at least one of (i) triaryl phosphate and mono- or di-esters of phosphoric acid amine salts. However, lubricating oils containing triaryl phosphate antiwear agents are known to have high activation temperatures and as a result they are less effective at lower temperature and/or low loads.

[0007] U.S. Pat. No. 5,531,911 discloses a metal free hydraulic fluid containing phosphorus antiwear agents and a corrosion inhibitor prepared by the reaction of an amine and a sulphonic acid. However, a corrosion inhibitor prepared by the reaction of an amine and a sulphonic acid increases the stability of an emulsion formed when hydraulic fluid mixes with water.

[0008] It would be desirable to have a lubricating oil composition containing metal free performance additives capable of imparting good levels of antiwear and/or oxidation inhibition. The present invention provides a lubricating oil composition containing metal free performance additives capable of imparting good levels of antiwear and/or oxidation inhibition.

[0009] It would be desirable to have a lubricating oil composition that prevents the formation of unwanted deposits that increase the viscosity of industrial fluids. The present invention provides an ash free lubricating oil composition that prevents the formation of unwanted deposits and/or sludge that increases the viscosity of industrial fluids.

[0010] It would be desirable to have a lubricating oil composition that prevents filter plugging and sludge formation. The present invention provides a lubricating oil composition that prevents filter plugging and sludge formation.

[0011] It would be desirable to have a lubricating oil composition capable of operating at a wide range of temperatures and/or loads. The present invention provides a lubricating oil composition capable of operating at a wide range of temperatures and/or loads.

[0012] It would be desirable to have a lubricating oil composition that is hydrolytically stable. The present invention provides a lubricating oil composition that has hydrolytic stability.

SUMMARY OF THE INVENTION

[0013] The present invention provides a lubricating oil composition comprising:

[0014] (1) an antiwear package comprising:

[0015] (a) a hydrocarbyl phosphate and amine salt thereof; and

[0016] (b) an alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound;

[0017] (2) an antioxidant package comprising:

[0018] (a) a hydrocarbyl diphenylamine; and

[0019] (b) a sterically hindered phenol;

[0020] (3) a metal deactivator; and

[0021] (4) an oil of lubricating viscosity.

[0022] In one embodiment the invention provides a lubricating oil composition described above that is substantially free of to free of metal cations, in particular divalent metal cations. In one embodiment the invention provides a lubricating oil composition described above that is substantially free of to free of rust inhibitors that are prepared by the reaction of an amine and sulphonic acid.

[0023] The invention further provides a process for the preparation of a lubricating oil composition, comprising mixing and/or dissolving a metal deactivator, an antioxidant package, an antiwear package, and optionally at least one additive selected from the group consisting of a foam inhibitor, a demulsifier, a viscosity modifier, a rust inhibitor, a pour point depressant and combinations thereof in a base oil and/or diluent oil.

[0024] The lubricating oil composition of the invention imparts good levels of antiwear and/or oxidation inhibition. The lubricating oil composition of the invention decreases the formation of filter plugging deposits and sludge. The lubricating oil composition of the invention has hydrolytic stability.

DETAILED DESCRIPTION OF THE INVENTION

[0025] The present invention provides a lubricating oil composition comprising:

[0026] (1) an antiwear package comprising:

[0027] (a) a hydrocarbyl phosphate and amine salt thereof; and

[0028] (b) an alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound;

[0029] (2) an antioxidant package comprising:

[0030] (a) a hydrocarbyl diphenylamine; and

[0031] (b) a sterically hindered phenol;

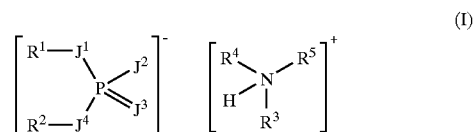
[0032] (3) a metal deactivator; and

[0033] (4) an oil of lubricating viscosity.

[0034] In one embodiment the invention provides a lubricating oil composition described above that is substantially free of to free of metal cations, in particular divalent metal cations for example calcium, magnesium or mixtures thereof. In one embodiment the invention provides a lubricating oil composition described above that is substantially free of to free of rust inhibitors prepared by the reaction of an amine and sulphonic acid.

[0035] Antiwear Package

[0036] The antiwear package contains a hydrocarbyl phosphate and amine salt thereof that can be represented by the formula:



[0037] wherein J^1, J^2, J^3, J^4 are independently oxygen or sulphur, preferably at least 1, more preferably at least 2, even more preferably at least 3 and most preferably all of J^1, J^2, J^3, J^4 are oxygen. In one embodiment J^1, J^2 and J^3 are all oxygen and J^4 is sulphur. In one embodiment J^1, J^2, J^3 and J^4 are all oxygen.

[0038] R^1 and R^2 are independently hydrogen or a hydrocarbyl group, preferably the hydrocarbyl group is alkyl, cycloalkyl, aryl or mixtures thereof. In one embodiment the hydrocarbyl group is alkyl or mixtures thereof. When the hydrocarbyl group is alkyl, alkyl chains can be branched or linear, although linear is preferred. R^1 and R^2 contain about 4 to about 30, preferably about 8 to about 25, more preferably about 10 to about 20, and most preferably about 13 to about 19 carbon atoms. In one embodiment R^1 is hydrogen and R^2 is hydrocarbyl, and in another embodiment R^1 and R^2 are both hydrocarbyl groups.

[0039] Examples of suitable R^1 and R^2 include but are not limited to lauryl, myristyl, palmityl stearyl, cetyl, oleyl and mixtures thereof. In one embodiment R^1 and R^2 are both cetyl and in another embodiment R^1 and R^2 are both oleyl. In one embodiment R^1 and R^2 are mixtures of cetyl and oleyl.

[0040] R^3, R^4 and R^5 are independently hydrogen or alkyl and can be linear or branched, branched is preferred. The alkyl groups contain about 1 to about 30, preferably about 4 to about 24, even more preferably about 6 to about 20, and most preferably about 8 to about 16 carbon atoms. In one embodiment R^3, R^4 and R^5 are all alkyl. In one embodiment R^3 and R^4 are alkyl and R^5 is hydrogen. In one embodiment R^3 and R^4 are hydrogen and R^5 is alkyl.

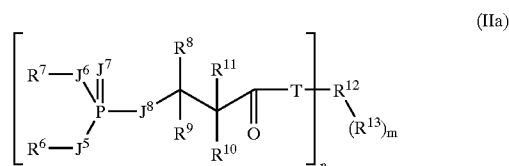
[0041] Examples of alkyl groups suitable for R^3, R^4 and R^5 include but are not limited to butyl, sec-butyl, isobutyl, tert-butyl, pentyl, n-hexyl, sec-hexyl, n-octyl, 2-ethylhexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, octadecenyl, nonodecyl, eicosyl, iso-nonyl, iso-decyl, iso-undecyl, iso-dodecyl, iso-tridecyl, iso-tetradecyl, iso-pentadecyl, iso-hexadecyl, iso-heptadecyl, iso-octadecyl, iso-octadecenyl, iso-nonodecyl, iso-eicosyl or mixtures thereof. Preferably groups suitable for R^3, R^4 and R^5 include but are not limited to n-octyl, 2-ethylhexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, iso-nonyl, iso-decyl, iso-undecyl, iso-dodecyl, iso-tridecyl, iso-tetradecyl, iso-pentadecyl, iso-hexadecyl and mixtures thereof.

[0042] In one embodiment the hydrocarbyl phosphate and amine salts thereof is formed by the reaction of (a) a C_{14} to C_{18} alkylated phosphoric acid and (b) a nonyl primary amine.

[0043] In one embodiment the hydrocarbyl phosphate and amine salts thereof is the reaction product of a C₁₄ to C₁₈ alkylated phosphoric acid salted with Primene 81R (produced and sold by Rohm & Haas) which is a mixture of C₁₁ to C₁₄ tertiary alkyl primary amines.

[0044] The hydrocarbyl phosphate and amine salts thereof are present in the range from about 0.01 to about 5, preferably from about 0.1 to about 1.5, even more preferably about 0.2 to about 1 and most preferably from about 0.25 to about 0.75 weight percent of the lubricating oil composition.

[0045] The antiwear package further contains an alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound that can be represented by the formula:



[0046] wherein J⁵, J⁶, J⁷, J⁸ are independently sulphur or oxygen, provided at least one, preferably at least two are sulphur. In one embodiment J⁵, J⁶ are both oxygen, and J⁷ and J⁸ are both sulphur.

[0047] R⁶ and R⁷ are independently hydrogen or a hydrocarbyl group, preferably the hydrocarbyl group is alkyl, cycloalkyl, aryl or mixtures thereof; and most preferably alkyl. When the hydrocarbyl group is alkyl, alkyl chains can be branched or linear, although branched is preferred. R⁶ and R⁷ can contain about 4 to about 30, preferably about 5 to about 25, more preferably about 5 to about 20, and most preferably about 6 to about 19 carbon atoms. In one embodiment R⁶ is hydrogen and R⁷ is a hydrocarbyl group. In another embodiment R⁶ and R⁷ are both hydrocarbyl groups.

[0048] Suitable examples R⁶ and R⁷ include but are not limited to butyl, pentyl, hexyl, heptyl, octyl, isooctyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl and mixtures thereof. Preferably R⁶ decyl, and R⁷ include but are not limited to heptyl, octyl, isooctyl, nonyl, decyl and mixtures thereof. In one embodiment R⁶ is hydrogen and R⁷ is isooctyl. In one embodiment R⁶ is isooctyl and R⁷ is hydrogen. In another embodiment R⁶ and R⁷ are both isooctyl.

[0049] R⁸ and R⁹ are independently hydrogen or a hydrocarbyl group, preferably the hydrocarbyl group is alkyl typically containing 1 to about 30, preferably 1 to about 20, more preferably 1 to about 10 and most preferably 1 to about 5 carbon atoms. In one embodiment R⁸ and R⁹ are both hydrogen, in another embodiment both are hydrocarbyl and in another embodiment R⁸ and R⁹ are mixtures of hydrogen and hydrocarbyl groups.

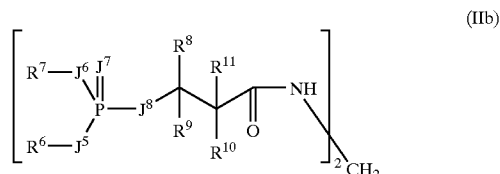
[0050] R¹⁰ and R¹¹ can be independently hydrogen or an alkyl group. The alkyl group can contain 1 to about 5, preferably, 1 to about 3 and most preferably 1 to 2 carbon atoms. In one embodiment, R¹⁰ is hydrogen. In one embodiment R¹⁰ is methyl. In one embodiment R¹⁰ is a mixture of hydrogen and methyl. In one embodiment R¹¹ is hydrogen.

[0051] R¹² can be hydrogen, hydrocarbylene or an oxygen containing hydrocarbylene group optionally containing ether linkages. The hydrocarbylene group contains 1 to about 30, preferably 1 to about 20, more preferably 1 to about 10 and most preferably 1 to about 5 carbon atoms. In one embodiment R¹² is methylene. In one embodiment R¹² is hydrogen.

[0052] When present R¹³ can be hydrogen or a hydrocarbyl group, preferably a hydrocarbyl group. n can be 1 or 2 provided that m+n=2, except when R¹² is hydrogen. Preferably n is 2 and m is 0. m can be 0 or 1 provided that m+n=2, except when R¹² is hydrogen.

[0053] T can be —S—, —O—, or NR¹⁴. R¹⁴ can be hydrogen or a hydrocarbyl group. The hydrocarbyl group can be alkyl, containing 1 to about 25, preferably 1 to about 18, more preferably 1 to about 12 and most preferably 1 to about 6 carbon atoms. Suitable examples of R¹⁴ can include but are not limited to methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl and mixtures thereof. In one embodiment R¹⁴ is hydrogen.

[0054] In an especially useful embodiment, T is NR¹⁴ in formula (IIa) forming a compound that can be represented by the formula (IIb):



[0055] wherein J⁵, J⁶, J⁷, J⁸, R⁶, R⁷, R⁸, R⁹, R¹⁰ and R¹¹ are defined as described above.

[0056] In one embodiment the α,β -unsaturated carbonyl containing compound is selected from the group consisting of methylene-bis-acrylamide, methylene-bis-methacrylamide, acrylamide, methacrylamide, acrylic acid, methacrylic acid, acrylate esters, methacrylate esters and mixtures thereof.

[0057] In one embodiment the α,β -unsaturated carbonyl containing compound is free of acrylate esters, methacrylate esters and mixtures thereof; and can be selected from the group consisting of methylene-bis-acrylamide, methylene-bis-methacrylamide, acrylamide, methacrylamide, acrylic acid, methacrylic acid, and mixtures thereof.

[0058] In one embodiment the α,β -unsaturated carbonyl containing compound is selected from the group consisting of methylene-bis-acrylamide, methylene-bis-methacrylamide and mixtures thereof. Preferably the α,β -unsaturated carbonyl containing compound is methylene-bis-acrylamide or mixtures thereof. The α,β -unsaturated carbonyl containing compound can be used alone or in combination.

[0059] Suitable examples of an alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound include but are not limited to methylene coupled adduct of di-isooctyldithiophosphoric acid and acrylamide, methylene coupled

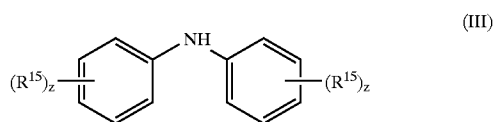
adduct of di-isooctyldithiophosphoric acid and methacrylamide, methylene coupled adduct of di-isooctyldithiophosphoric acid and ethyl acrylate, methylene coupled adduct of di-isooctyldithiophosphoric acid and ethyl methacrylate, di-nonyldithiophosphoric acid and acrylamide, di-nonyldithiophosphoric acid and methacrylamide, methylene coupled adduct of di-nonyldithiophosphoric acid and ethyl acrylate, methylene coupled adduct of di-nonyldithiophosphoric acid and ethyl methacrylate and mixtures thereof. In one embodiment the alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound is a methylene coupled adduct of di-isooctyldithiophosphoric acid and acrylamide.

[0060] Suitable examples of alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound include but are not limited to an adduct of di-isooctyldithiophosphoric acid and methylene-bis-acrylamide, an adduct of di-isooctyldithiophosphoric acid and methylene-bis-methacrylamide, an adduct of di-isooctyldithiophosphoric acid and ethyl acrylate, an adduct of di-isooctyldithiophosphoric acid and ethyl methacrylate, di-nonyldithiophosphoric acid and methylene-bis-acrylamide, di-nonyldithiophosphoric acid and methylene-bis-methacrylamide, an adduct of di-nonyldithiophosphoric acid and ethyl acrylate, an adduct of di-nonyldithiophosphoric acid and ethyl methacrylate and mixtures thereof. In one embodiment the alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound is an adduct of di-isooctyldithiophosphoric acid and methylene-bis-acrylamide.

[0061] The alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound is present in the range from about 0.01 to about 5, preferably from about 0.02 to about 1.5, even more preferably about 0.03 to about 1 and most preferably from about 0.04 to about 0.5 weight percent of the lubricating oil composition.

[0062] Antioxidant Package

[0063] The antioxidant package contains a hydrocarbyl diphenylamine that can be represented by the following formula:

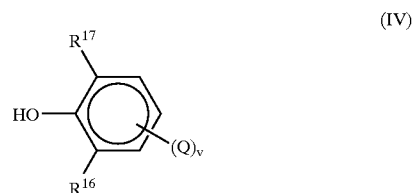


[0064] wherein R^{15} can be the same or different and is independently hydrogen or a hydrocarbyl group, preferably arylalkyl or alkyl groups or mixtures thereof. The arylalkyl groups contain about 5 to about 20, preferably about 6 to about 10 carbon atoms. The alkyl groups can be linear or branched, preferably branched; the alkyl group contains about 1 to about 24, preferably about 2 to about 18 and most preferably about 4 to about 12 carbon atoms; and z is independently 0, 1, 2, or 3, provided that at least one

aromatic ring contains a hydrocarbyl group. Suitable examples of a hydrocarbyl diphenylamine include but are not limited to bis-nonylated diphenylamine, nonyl diphenylamine, octyl diphenylamine, bis-octylated diphenylamine, bis-decylated diphenylamine, decyl diphenylamine and mixtures thereof. In one embodiment the hydrocarbyl diphenylamine is bis-nonylated diphenylamine. The hydrocarbyl diphenylamine can be used alone or in combination.

[0065] The hydrocarbyl diphenylamine is present in the range from about 0.01 to about 5, preferably from about 0.03 to about 1.5, even more preferably about 0.05 to about 1 and most preferably from about 0.1 to about 0.5 weight percent of the lubricating oil composition.

[0066] The oxidation package further contains a sterically hindered phenol that can be represented by the formula:



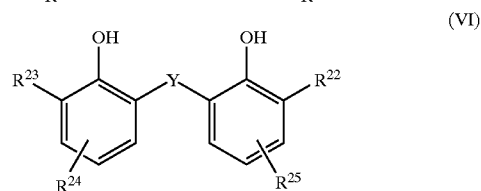
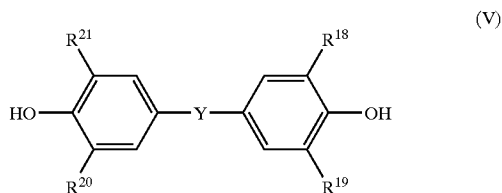
[0067] wherein R^{16} and R^{17} are independently branched or linear alkyl groups containing about 1 to about 24, preferably about 4 to about 18, and most preferably about 4 to about 12 carbon atoms.

[0068] R^{16} and R^{17} can be either straight or branched chain; branched is preferred. Preferably the phenol is butyl substituted containing two t-butyl groups. Q is hydrogen or a hydrocarbyl group, and can be meta or para to the OH group, although para is preferred. v can be 1, 2 or 3, preferably 1 or 2, even more preferably 1. Examples of suitable hydrocarbyl groups include but are not limited to 2-ethylhexyl, n-butyl, dodecyl and mixtures thereof. In one embodiment R^{16} and R^{17} are both t-butyl.

[0069] Suitable examples of sterically hindered phenols derived from formula (IV) include but are not limited to 2,6-di-tert-butylphenol, 4-Methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol, 4-butyl-2,6-di-tert-butylphenol, 2,6-di-tert-butylphenol, 4-pentyl-2,6-di-tert-butylphenol, 4-hexyl-2,6-di-tert-butylphenol, 4-heptyl-2,6-di-tert-butylphenol, 4-(2-ethylhexyl)-2,6-di-tert-butylphenol, 4-octyl-2,6-di-tert-butylphenol, 4-nonyl-2,6-di-tert-butylphenol, 4-decyl-2,6-di-tert-butylphenol, 4-undecyl-2,6-di-tert-butylphenol, 4-dodecyl-2,6-di-tert-butylphenol, 4-tridecyl-2,6-di-tert-butylphenol, 4-tetradecyl-2,6-di-tert-butylphenol and mixtures thereof.

[0070] In one embodiment the sterically hindered phenol is 2,6-di-tert-butylphenol and mixtures thereof. In one embodiment the sterically hindered phenol is 4-(2-ethylhexyl)-2,6-di-tert-butylphenol and mixtures thereof. In one embodiment the sterically hindered phenol is 4-dodecyl-2,6-di-tert-butylphenol and mixtures thereof.

[0071] Other optional sterically hindered phenols suitable for the invention include but are not limited to those represented by the formulae:

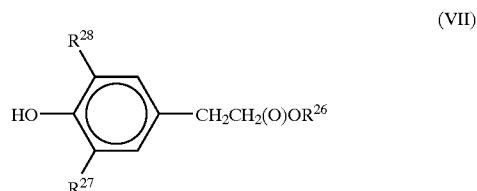


[0072] or

[0073] wherein R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} are either straight or branched chain and contain about 4 to about 18, preferably about 4 to about 12 carbon atoms. Preferably the phenol is butyl substituted. R^{24} and R^{25} are independently hydrogen or hydrocarbyl; preferably R^{24} and R^{25} are independently arylalkyl, alkyl or mixtures thereof. The alkyl groups can be linear or branched, linear being preferred. R^{24} and R^{25} are typically in the para position to the —OH group. The arylalkyl or alkyl groups typically contain 1 to about 15, preferably 1 to about 10, and more preferably 1 to about 5 carbon atoms. The bridging group Y include but are not limited to —CH₂— (methylene bridge) or —CH₂OCH₂— (ether bridge) and mixtures thereof.

[0074] Examples of methylene-bridged sterically hindered phenols include but are not limited to 4,4'-methylenebis(6-tert-butyl-o-cresol), 4,4'-methylenebis(2-tert-amyl-o-cresol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-methylene-bis(2,6-di-tertbutylphenol) and mixtures thereof.

[0075] In one embodiment the sterically hindered phenol antioxidant can be represented by the formula:



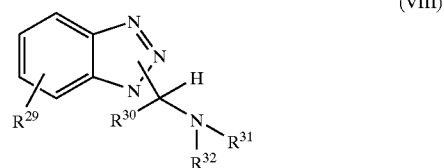
[0076] wherein R^{26} , R^{27} and R^{28} can be the same or different and are straight or branched alkyl groups containing about 2 to about 22, preferably about 2 to about 18, more preferably about 4 to about 8 carbon atoms. Specific examples of alkyl groups include but are not limited to 2-ethylhexyl, n-butyl, dodecyl and mixtures thereof. In one embodiment R^{27} and R^{28} are tertiary butyl and R^{26} is n-butyl.

[0077] The sterically hindered phenol of the invention can be used alone or in combination. The sterically hindered phenol of the invention is present in the range from about 0.01 to about 5, preferably from about 0.03 to about 1.5, even more preferably about 0.05 to about 1 and most preferably from about 0.1 to about 0.5 weight percent of the lubricating oil composition.

[0078] Metal Deactivator

[0079] The invention further includes a metal deactivator that can be used to neutralise the catalytic effect of metal for promoting oxidation in lubricating oil. Examples of metal deactivators include but are not limited to derivatives of benzotriazoles, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, 2-alkyldithiobenzothiazoles, 2-(N, N-dialkyldithiocarbamoyl)benzothiazoles, 2,5-bis(alkyldithio)-1,3,4-thiadiazoles, 2,5-bis(N, N-dialkyldithiocarbamoyl)-1,3,4-thiadiazoles, 2-alkyldithio-5-mercapto thiadiazoles and mixtures thereof. In one embodiment the metal deactivator is a derivative of benzotriazole. In one embodiment the metal deactivator is a 2,5-bis(alkyl-dithio)-i,3,4-thiadiazole. The metal deactivator may be used alone or in combination with other metal deactivators.

[0080] Hydrocarbyl derivatives of benzotriazole contain hydrocarbyl substitutions at one or more of the following ring positions: 1- or 2- or 4- or 5- or 6- or 7-. The hydrocarbyl groups contain 1 to about 30, preferably 1 to about 15, more preferably 1 to about 7 carbon atoms. In one embodiment the metal deactivator is tolyltriazole. In one embodiment hydrocarbyl benzotriazoles substituted at positions 4- or 5- or 6- or 7-can be further reacted with an aldehyde and a secondary amine and can be represented by the formula:



[0081] wherein the reaction product can form a carbon-nitrogen bond at ring position 1- or 2-. In one embodiment the carbon-nitrogen bond is at ring position 1-. R^{29} can be hydrogen or a hydrocarbyl group or mixtures thereof, containing about 1 to about 30, preferably about 1 to about 15, more preferably about 1 to about 7 carbon atoms. In one embodiment R^{29} is hydrogen. In one embodiment R^{29} is methyl.

[0082] R^{30} is derived from the aldehyde of the reaction and can be hydrogen or a hydrocarbyl group, typically containing 1 to about 7, more preferably 1 to about 4 and most preferably 1 to about 2 carbon atoms. In one embodiment R^{30} is hydrogen. Examples of suitable aldehydes include but are not limited to formaldehyde, acetaldehyde, propionaldehyde and mixtures thereof. In one embodiment the aldehyde is formaldehyde, which can be monomeric, polymeric (paraformaldehyde) or in aqueous solution; preferably the formaldehyde is in aqueous solution.

[0083] R^{31} and R^{32} are derived from the amine of the reaction and are independently hydrogen or a hydrocarbyl group, preferably R^{31} and R^{32} are both hydrocarbyl groups. The hydrocarbyl group contains 1 to about 22, more preferably about 2 to about 18, more preferably about 4 to about 16 and most preferably about 6 to about 14 carbon atoms. Suitable examples of amines include but are not limited to dimethylamine, diethylamine, dipropylamine, dipropenylamine, diisobutylamine, diisobutenylamine, dipentylamine, dipentenylamine, dibenzylamine, dinaphthylamine, di-2-ethylhexylamine and mixtures thereof. In one embodiment the amine is di-2-ethylhexylamine. The amine can be used alone or in combination with other amines.

[0084] Examples of compounds derived from formula (VIII) suitable as a metal deactivator include but are not limited to N,N-bis(heptyl)-ar-methyl-1H-Benzotriazole-1-methanamine, N,N-bis(nonyl)-ar-methyl-1H-Benzotriazole-1-methanamine, N,N-bis(decyl)-ar-methyl-1H-Benzotriazole-1-methanamine, N,N-bis(undecyl)-ar-methyl-1H-Benzotriazole-1-methanamine, N,N-bis(dodecyl)-ar-methyl-1H-Benzotriazole-1-methanamine, N,N-bis(2-ethylhexyl)-ar-methyl-1H-Benzotriazole-1-methanamine and mixtures thereof. In one embodiment the metal deactivator is N,N-bis(2-ethylhexyl)-ar-methyl-1H-Benzotriazole-1-methanamine.

[0085] In one embodiment, the metal deactivator is a 2,5-bis(alkyl-dithio)-1,3,4-thiadiazole. The alkyl groups of 2,5-bis(alkyl-dithio)-1,3,4-thiadiazole contain 1 to about 30, preferably about 2 to about 25, more preferably 4 to about 20 and most preferably about 6 to about 16 carbon atoms. Examples of suitable 2,5-bis(alkyl-dithio)-1,3,4-thiadiazoles include but are not limited to 2,5-bis(tert-octyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-nonyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-decyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-undecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-dodecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-tridecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-tetradecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-pentadecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-hexadecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-heptadecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-octadecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-nonadecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-eicosyldithio)-1,3,4-thiadiazole and mixtures thereof. Preferably the is 2,5-bis(tert-nonyldithio)-1,3,4-thiadiazole and mixtures thereof.

[0086] The metal deactivator is present in the range from about 0.0001 to about 5, preferably from about 0.0003 to about 1.5, even more preferably about 0.0005 to about 0.5 and most preferably from about 0.001 to about 0.2 weight percent of the lubricating oil composition.

[0087] Oil of Lubricating Viscosity

[0088] The lubricating oil compositions of the present invention include but are not limited to natural oil, synthetic oil, hybrids of natural oil and synthetic oil of lubricating viscosity, oil derived from hydrocracking, hydrogenation, hydrofinishing, unrefined, refined and re-refined oils and mixtures thereof.

[0089] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0090] Refined oils are similar to the unrefined oils except they have been further treated in one or more purification

steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

[0091] Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0092] Natural oils include but are not limited to animal oils, vegetable oils (e.g., castor oil, lard oil), mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types and oils derived from coal or shale and mixtures thereof.

[0093] Synthetic lubricating oils include but are not limited to hydrocarbon oils such as polymerised and interpolymerised olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulphides and the derivatives, analogs and homologs thereof and mixtures thereof.

[0094] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methylhexyl)silicate, tetra-(p-tert-butylphenyl) silicate, hexyl-(4-methyl-2-pentoxy)disiloxane, poly(methyl) siloxanes, and poly-(methylphenyl)siloxanes). In one embodiment the oil of lubricating viscosity is free of silicon.

[0095] Other synthetic lubricating oils include but are not limited to liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), and polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes.

[0096] Oils of lubricating viscosity can also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I sulphur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80-120; Group II sulphur content ≤ 0.03 wt %, and ≥ 90 wt % saturates, viscosity index 80-120; Group III sulphur content ≤ 0.03 wt %, and ≥ 90 wt % saturates, viscosity index ≥ 120 ; Group IV all polyalphaolefins (PAO's); and Group V all others not included in Groups I, II, III, or IV. In one embodiment the oil of lubricating viscosity comprises an API Group I, II, III, IV, V oil or mixtures thereof, and preferably API Group I, II, III oil or mixtures thereof.

[0097] The oil of lubricating viscosity is present in the range from about 34 to about 99.96, preferably from about 74.8 to about 99.8, even more preferably about 80.6 to about 99.5 and most preferably from about 84.7 to about 99.2 wt % of the lubricating oil composition. The oil of lubricating viscosity may be used alone or mixtures thereof. In one

embodiment the oil of lubricating viscosity is present at about 98.9 wt % of the lubricating oil composition.

[0098] Performance Additives

[0099] Optionally the composition can include at least one performance additive selected from the group consisting of rust inhibitors, foam inhibitors, demulsifiers, friction modifiers, viscosity modifiers, pour point depressants and mixtures thereof.

[0100] Rust Inhibitors

[0101] Rust inhibitors are known and include but are not limited to amine salts of carboxylic acids such as octylamine octanoate, condensation products of dodecyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine, e.g. a polyalkylene polyamine such as triethylenetetramine, and half esters of alkenyl succinic acids in which the alkenyl radical contains about 8 to about 24 carbon atoms with alcohols such as polyglycols. The rust inhibitors can be used alone or in combination.

[0102] Another class of rust inhibitor is the reaction product of an amine and a compound containing a sulphonic acid group. The amine can be selected from monoamines, polyamines and mixtures thereof. The amines can be saturated, unsaturated, acyclic, cyclic, aromatic, linear, branched and mixtures thereof. Typical classes of amine can include but are not limited to alkylenemonoamines, heterocyclic monoamines, alkylenepolyamines, heterocyclic polyamines and mixtures thereof.

[0103] A particularly useful class of amines are alkylenepolyamines, preferably ethylenepolyamines. Examples of suitable ethylenepolyamines include but are not limited to ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, polyamine still bottoms and mixtures thereof.

[0104] The compound containing a sulphonic acid group suitable for the invention can be saturated, unsaturated, acyclic, cyclic, aromatic, linear, branched and mixtures thereof. Suitable examples of a compound containing a sulphonic acid group include but are not limited to monoeicosanyl-substituted naphthalene sulphonic acids, dodecylbenzene sulphonic acids, didodecylbenzene sulphonic acids, dinonylbenzene sulphonic acids, cetylchlorobenzene sulphonic acids, dilauryl beta-naphthalene sulphonic acids and mixtures thereof.

[0105] Another suitable type of compound containing a sulphonic acid can be prepared by the treatment of polybutene having a number average molecular weight (Mn) in the range of about 500 to about 5000, preferably about 800 to about 3000, more preferably about 1000 to about 2000 with chlorosulphonic acid, nitronaphthalene sulphonic acid, paraffin wax sulphonic acid, cetyl-cyclopentane sulphonic acid, lauryl-cyclohexane sulphonic acids, and mixtures thereof.

[0106] Another suitable type of compound containing a sulphonic acid can be prepared by treatment of polyethylene having a number average molecular weight (Mn) in the range of about 300 to about 1500, preferably about 400 to about 1000 and most preferably about 500 to about 900 with chlorosulphonic acid, nitronaphthalene sulphonic acid, paraffin wax sulphonic acid, cetyl-cyclopentane sulphonic acid, lauryl-cyclohexane sulphonic acids, and mixtures thereof.

[0107] In one embodiment the composition of the invention is substantially free to free of a rust inhibitor prepared by the reaction of an amine and a compound containing a sulphonic acid group. In another embodiment, the composition of the invention is substantially free to free of rust inhibitor.

[0108] The rust inhibitors are present in the range from 0 to about 5, preferably from about 0.001 to about 1.5, even more preferably about 0.002 to about 1 and most preferably from about 0.0025 to about 0.75 weight percent of the lubricating oil composition.

[0109] Foam Inhibitors

[0110] Foam inhibitors are known and include but are not limited to organic silicones such as dimethyl silicone or polysiloxanes, polyacetates, polyacrylates or mixtures thereof. Foam inhibitors can be used alone or in combination.

[0111] Examples of foam inhibitors include but are not limited to poly(ethyl acrylate), poly(2-ethylhexylacrylate), poly(vinyl acetate), copolymer of 2-ethylhexylacrylate and ethyl acrylate and mixtures thereof. In one embodiment the foam inhibitor is a copolymer of 2-ethylhexylacrylate and ethyl acrylate.

[0112] The foam inhibitors are present in the range from about 0 to about 5, preferably from about 0.005 to about 0.1, even more preferably about 0.007 to about 0.05 and most preferably from about 0.01 to about 0.03 weight percent of the lubricating oil composition.

[0113] Demulsifiers

[0114] Demulsifiers are known and include but are not limited to derivatives of propylene oxide, ethylene oxide, polyoxyalkylene alcohols, alkyl amines, amino alcohols, diamines or polyamines reacted sequentially with ethylene oxide or substituted ethylene oxides and mixtures thereof. Demulsifiers can be used alone or in combination.

[0115] Examples of demulsifiers include but are not limited to trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides, (ethylene oxide-propylene oxide) copolymers and mixtures thereof. In one embodiment the demulsifier is ethylene oxide-propylene oxide copolymer.

[0116] The demulsifiers are present in the range from about 0 to about 5, preferably from about 0.0005 to about 0.05, even more preferably about 0.0007 to about 0.01 and most preferably from about 0.001 to about 0.005 weight percent of the lubricating oil composition.

[0117] Pour Point Depressants

[0118] Pour point depressants are known and include but are not limited to esters of maleic anhydride-styrene copolymers, polymethacrylates, polyacrylates, polyacrylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids, ethylene-vinyl acetate copolymers, alkyl phenol formaldehyde condensation resins, alkyl vinyl ethers and mixtures thereof. Preferred pour point depressants include but are not limited to esters of maleic anhydride-styrene copolymers, polymethacrylates, Viscoplex® 1-153, polyacrylates and mixtures thereof. Pour point depressants can be used alone or in combination.

[0119] The pour point depressants are present in the range from about 0 to about 5, preferably from about 0.005 to about 0.5, even more preferably about 0.007 to about 0.1 and most preferably from about 0.01 to about 0.05 weight percent of the lubricating oil composition.

[0120] Friction Modifiers

[0121] The lubricant may additionally contain a friction modifier. Useful friction modifiers include but are not limited to fatty amines, esters, especially glycerol esters such as glycerol monooleate, borated glycerol esters, fatty phosphites, fatty acid amides, fatty epoxides, borated fatty epoxides, alkoxyated fatty amines, borated alkoxyated fatty amines, metal salts of fatty acids, sulphurised olefins, fatty imidazolines, condensation products of carboxylic acids and polyalkylene-polyamines, amine salts of alkylphosphoric acids, and molybdenum-containing friction modifiers such as molybdenum dithiocarbamates and mixtures thereof. Preferred friction modifiers include fatty amines, esters, especially glycerol esters, sulphurised olefins, fatty imidazolines, condensation products of carboxylic acids and polyalkylene-polyamines and mixtures thereof. Friction modifiers can be used alone or in combination.

[0122] The friction modifiers are present in the range from about 0 to about 6, preferably from about 0.05 to about 1, even more preferably about 0.1 to about 0.75 and most preferably from about 0.2 to about 0.5 weight percent of the lubricating oil composition.

[0123] Viscosity Modifiers

[0124] Viscosity modifiers are known and include but are not limited to copolymers of styrene-butadiene rubbers, ethylene-propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, hydrogenated radical isoprene polymers, polymethacrylate acid esters, polyacrylate acid esters, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins, polyalkylmethacrylates, esters of maleic anhydride-styrene copolymers and mixtures thereof. Preferred viscosity modifiers include polyacrylate acid esters, polyalkylmethacrylates, esters of maleic anhydride-styrene copolymers and mixtures thereof. Viscosity modifiers can be used alone or in combination.

[0125] The viscosity modifiers are present in the range from about 0 to about 20, preferably from about 0.03 to about 16, even more preferably about 0.1 to about 14 and most preferably from about 0.2 to about 12 weight percent of the lubricating oil composition.

[0126] Process

[0127] The invention further provides a process for preparing a lubricating oil composition comprising the steps of first mixing at least one metal deactivator or mixtures thereof, in a hydrocarbyl phosphate and amine salt thereof until the metal deactivator is substantially or wholly dissolved at elevated temperatures. The temperatures are in the range of about 40° C. to about 110° C., preferably about 50° C. to 95° C. and most preferably about 55° C. to about 85° C. The mixture is held at a temperature for a period of time in the range of about 30 seconds to about 24 hours, preferably about 2 minutes to about 8 hours, and most preferably about 5 minutes to about 4 hours. The pressures are in the range of about 93.3 kPa to about 266.7 kPa (about 700 mm of Hg to about 2000 mm of Hg), preferably about 1000 kPa

to about 133.3 kPa (about 750 mm of Hg to about 1000 mm of Hg), and most preferably about 103 kPa to about 120 kPa (about 775 mm of Hg to about 900 mm of Hg).

[0128] Substantially all of the mixture of first step is added to an alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound, and the antioxidant package selected from the group comprising a hydrocarbyl diphenylamine, a sterically hindered phenol or mixtures thereof to form a mixture. The compounds of the resultant mixture are added sequentially, separately or combinations thereof. The mixture is processed at temperatures of about 20° C. to about 140° C., preferably about 25° C. to 85° C. and most preferably about 30° C. to about 65° C. The mixture is processed at pressures in the range of about 93.3 kPa to about 266.7 kPa (about 700 mm of Hg to about 2000 mm of Hg), preferably about 94.6 kPa to about 133.3 kPa (about 710 mm of Hg to about 1000 mm of Hg), and most preferably about 96 kPa to about 120 kPa (about 720 mm of Hg to about 900 mm of Hg). The mixture is held for a period of time in the range of about 1 minute to about 3 days, preferably about 5 minutes to about 8 hours, and most preferably about 10 minutes to about 4 hours.

[0129] Substantially all of the mixture of the second step is added and mixed into the oil of lubricating viscosity, base oil, diluent oil or mixtures thereof by any known method to form a lubricating oil composition.

[0130] The process optionally includes adding to the mixture of step (2), step (3) or combinations thereof, performance additives selected from the group of a rust inhibitor, a foam inhibitor, a demulsifier, a viscosity modifier, a pour point depressant, and mixtures thereof.

[0131] In one embodiment the present invention is in the form of a concentrate, wherein the antiwear package, the antioxidant package, the metal deactivator and optionally performance additives are added to all of or substantially all of or a portion of lubricating oil, base oil, diluent oil or mixtures thereof, and when ready to use is combined with the remaining substantial amount of lubricating oil, base oil, diluent oil or mixtures thereof resulting in a finished fluid. A process to prepare a concentrate of a lubricating oil composition comprising the steps of:

[0132] (1) mixing at least one metal deactivator, in a hydrocarbyl phosphate and amine salt thereof; and

[0133] (2) adding and mixing substantially all of the product of step (1) to an alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound, and substantially all of the antioxidant package selected from the group comprising a hydrocarbyl diphenylamine, a sterically hindered phenol and mixtures thereof sequentially, separately or combinations thereof to form a mixture; and

[0134] (3) adding with mixing to the resultant mixture of step (2) a sufficient portion of the lubricating oil, base oil, diluent oil or mixtures thereof to form a concentrate of the lubricating oil composition.

[0135] If the present invention is in the form of a concentrate the amount of diluent oil is less than about 50, preferably less than about 30, more preferably less than

about 15 and most preferably less than about 10 wt % of a concentrate of the lubricating oil composition. In one embodiment the diluent oil is present at about 5.5 wt % of a concentrate of the lubricating oil composition.

[0136] Industrial Application

[0137] The lubricating oil composition of the invention is used in industrial fluids, hydraulic fluids, turbine oils, circulating oils and combinations thereof.

[0138] In one embodiment of the invention the lubricating oil composition may be used in turbine oils. The use of the lubricating oil composition decreases the formation of filter plugging deposits and sludge in turbines. The lubricating oil composition further provides good levels of antiwear and/or oxidation inhibition. The lubricating oil composition has good hydrolytic stability.

[0139] The following examples provide an illustration of the invention. It should however be noted that these examples are non exhaustive and not intended to limit the scope of the invention.

[0140] Specific Embodiment

EXAMPLES

Example 1

[0141] A hydraulic fluid is prepared by mixing into about 100 g of base oil containing about 35 wt % of Group I base oil, of $11.90 \text{ mm}^2\text{s}^{-1}$ (cSt) at 100°C . and about 65 wt % a Group I base oil, $5.2 \text{ mm}^2\text{s}^{-1}$ (cSt) at 100°C . with (a) about 0.53 wt % of the reaction product of a C_{14} to C_{18} alkylated phosphoric acid with Primene 81R; (b) about 0.1 wt % of a methylene coupled adduct of di-isooctyldithiophosphoric acid and acrylamide; (c) about 0.196 wt % of a bis-nonylated diphenylamine; (d) about 0.196 wt % of 2,6-di-tert-butylphenol; (e) about 0.005 wt % of tolyltriazole; (f) about 0.02 wt % of a copolymer of 2-ethylhexylacrylate and ethyl acrylate; and (g) about 0.049 wt % of a diluent oil.

Example 2

[0142] The hydraulic fluid is the same as example 1 except the base oil contains about 40 wt % of Group II base oil, of $5.8 \text{ mm}^2\text{s}^{-1}$ (cSt) at 100°C . and about 60 wt % a Group II base oil, $11.5 \text{ mm}^2\text{s}^{-1}$ (cSt) at 100°C . and about 0.02 wt % of Viscoplex® 1-153 has been added.

Example 3

[0143] The hydraulic fluid is the same as example 1 except the base oil contains about 90 wt % of Group I base oil, of $5.3 \text{ mm}^2\text{s}^{-1}$ (cSt) at 100°C . and about 10 wt % a Group I base oil, $12.1 \text{ mm}^2\text{s}^{-1}$ (cSt) at 100°C . and the metal deactivator tolyltriazole is present at about 0.002 wt %.

Example 4

[0144] The hydraulic fluid is the same as example 1 except the metal deactivator is 2,5-bis(tert-nonylthio)-1,3,4-thiadiazole and present at about 0.005 wt %.

Example 5

[0145] The hydraulic fluid is the same as example 1 except the metal deactivator is N,N-bis(2-ethylhexyl)-ar-methyl-1H-Benzotriazole-1-methanamine and present at about 0.01 wt %.

[0146] Test 1: ASTM D665

[0147] The ASTM D665 test measures the rust preventing characteristics of oil in the presence of water. A steel pin about 12.7 mm in diameter and about 68 mm across exclusive of the threaded portion is screwed to a plastic holder. The steel pin is immersed in a beaker of about 30 ml of distilled water and about 300 ml of oil. The beaker is placed in an oil bath held at about 60°C . and the contents of the beaker are stirred for about 24 hours. The amount of corrosion/rust is measured. The procedure is repeated using synthetic seawater and a new steel pin.

[0148] All Examples pass the D665 test. Examples 1-5 have lubricating oil compositions with sufficient protection from a metal deactivator, antioxidant package and antiwear package to pass the distilled water and synthetic seawater pin rating.

[0149] Test 2: ASTM D2619

[0150] The ASTM D2619 test measures hydrolytic stability of hydraulic fluids in the presence of water. A mixture of about 75 g oil and about 25 g of water is placed in a pressure-type beverage bottle along with a clean copper sample about 13 mm by about 51 mm, weighed to within about $\pm 0.2 \text{ mg}$. The bottle is placed in an oven and rotated at about 5 rpm whilst being heated to about 93°C . and held for about 48 hours. The bottle is cooled and the contents excluding the copper sample are placed into a 100 ml cone shaped centrifuge tube and centrifuged for about 10 minutes at 1500 rpm. The sample is decanted to separate water and emulsion layers and filtered through a membrane. The sample is washed with about 25 ml of distilled water. The sample wash is repeated until washings are neutral to litmus paper. The change in weight of the copper sample is recorded and the total acid number of the oil is determined in accordance with ASTM D974. The Denison Hydraulics Limits HF-0 requirements for a good hydraulic fluid have a total acidity in the aqueous phase of less than about 4 mg KOH. The maximum decrease in weight of the copper sample is about 0.20 mg/cm^2 . The results obtained are for the decrease in weight of the copper sample and the total acidity are:

TABLE 1

ASTM D2619 Results		
Example	Decrease in weight of copper sample (mg/cm^2)	Total Acid Number (mg KOH)
1	0.15	1.68
2	0.03	2.24
3	0.02	2.24
4	0	1.68
5	0.04	2.53

[0151] All of the samples pass the D2619 test. Overall the tests indicate the lubricating oil compositions have sufficient properties from the metal deactivator, antioxidant package and the antiwear package to provide protection against wear and oxidation and to have a total acidity below 4 mg KOH.

[0152] While the invention has been explained, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention

disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

What is claimed is:

1. A lubricating oil composition comprising:

(1) an antiwear package comprising:

- (a) a hydrocarbyl phosphate and amine salt thereof; and
- (b) an alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound;

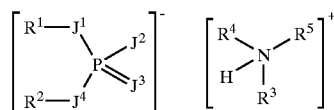
(2) an antioxidant package comprising:

- (a) a hydrocarbyl diphenylamine; and
- (b) a sterically hindered phenol;

(3) a metal deactivator; and

(4) an oil of lubricating viscosity.

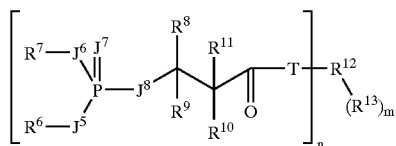
2. The composition of claim 1 wherein the hydrocarbyl phosphate and amine salts thereof is represented by the formula:



(I)

wherein J^1, J^2, J^3, J^4 are independently oxygen or sulphur; R^1 and R^2 are independently hydrogen or a hydrocarbyl group; and R^3, R^4 and R^5 are independently hydrogen or alkyl.

3. The composition of claim 1 wherein the alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound is represented by the formula:



(IIa)

wherein:

J^5, J^6, J^7, J^8 are independently sulphur or oxygen, provided at least one of J^5, J^6, J^7, J^8 is sulphur;

n is 1 or 2 provided that $m+n=2$, except when R^{12} is hydrogen;

m is 0 or 1 provided that $m+n=2$, except when R^{12} is hydrogen;

R^6, R^7, R^8 and R^9 are independently hydrogen or a hydrocarbyl group;

R^{10} and R^{11} are independently hydrogen or an alkyl group;

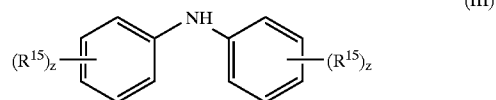
R^{12} is hydrogen, hydrocarbylene or an oxygen containing hydrocarbylene group optionally containing ether linkages;

R^{13} is hydrogen or a hydrocarbyl group; and

T is $-S-$, $-O-$, or $-NR^{14}$, wherein R^{14} is hydrogen or a hydrocarbyl group.

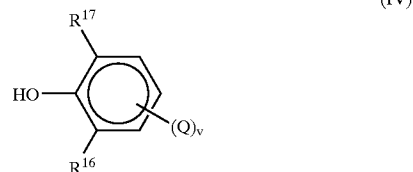
4. The composition of claim 3, wherein the α,β -unsaturated carbonyl containing compound is selected from the group consisting of methylene-bis-acrylamide, methylene-bis-methacrylamide, acrylamide, methacrylamide, acrylic acid, methacrylic acid, acrylate esters, methacrylate esters and mixtures thereof.

5. The composition of claim 1 wherein the hydrocarbyl diphenylamine is represented by the following formula:



wherein R^{15} can be the same or different and is independently hydrogen or a hydrocarbyl group; and z is independently 0, 1, 2, or 3, provided that at least one aromatic ring contains a hydrocarbyl group.

6. The composition of claim 1 wherein a sterically hindered phenol that can be represented by the formula:



wherein: R^{16} and R^{17} are independently alkyl groups; Q is hydrogen or a hydrocarbyl group; and v is 1, 2 or 3.

7. The composition of claim 1 wherein the metal deactivator is a derivative of benzotriazole containing hydrocarbyl substitutions which include at least one of the following ring positions 1- or 2- or 4- or 5- or 6- or 7-.

8. The composition of claim 1 wherein the metal deactivator is a 2,5-bis(alkyl-dithio)-1,3,4-thiadiazole.

9. The composition of claim 1 wherein the oil of lubricating viscosity is an API Group I, II, III oil or mixtures thereof.

10. The composition of claim 1 further comprising at least one performance additive selected from the group consisting of rust inhibitors, foam inhibitors, demulsifiers, friction modifiers, viscosity modifiers, pour point depressants and mixtures thereof.

11. The composition of claim 1 wherein the hydrocarbyl phosphate and amine salts thereof is present in the range from about 0.01 to about 5 weight percent of the lubricating oil composition;

alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound is present in the range from about 0.01 to about 5 weight percent of the lubricating oil

composition; wherein the hydrocarbyl diphenylamine is present in the range from about 0.01 to about 5 weight percent of the lubricating oil composition; wherein the sterically hindered phenol is present in the range from about 0.01 to about 5 weight percent of the lubricating oil composition; wherein the metal deactivator is present in the range from about 0.0001 to about 5 weight percent of the lubricating oil composition; and wherein the oil of lubricating viscosity is present in the range from about 34 to about 99.96 weight percent of the lubricating oil composition.

12. The composition of claim 11 further comprising performance additives wherein the rust inhibitors are present in the range from 0 to about 5 weight percent of the lubricating oil composition wherein foam inhibitors are present in the range from about 0 to about 5 weight percent of the lubricating oil composition; wherein the demulsifiers are present in the range from about 0 to about 5 weight percent of the lubricating oil composition; wherein the pour point depressants are present in the range from about 0 to about 5 weight percent of the lubricating oil composition; wherein the friction modifiers are present in the range from about 0 to about 6 weight percent of the lubricating oil composition; and wherein the viscosity modifiers are present in the range from about 0 to about 20 weight percent of the lubricating oil composition.

13. A process for preparing a lubricating oil composition comprising the steps of:

- (1) mixing at least one metal deactivator, in a hydrocarbyl phosphate and amine salt thereof; and
- (2) adding and mixing substantially all of the product of step (1) to an alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound, and substantially all of the antioxidant package selected from the group comprising a hydrocarbyl diphenylamine, a sterically hindered phenol and mixtures thereof sequentially, separately or combinations thereof to form a mixture; and
- (3) adding and mixing the resultant mixture of step (2) into the oil of lubricating viscosity or mixtures thereof.

14. The process of claim 13 further comprising adding to the mixture of step (2), step (3) or combinations thereof,

performance additives selected from the group of a rust inhibitor, a foam inhibitor, a demulsifier, a viscosity modifier, a pour point depressant and mixtures thereof.

15. A process to prepare a concentrate of a lubricating oil composition comprising the steps of:

- (1) mixing at least one metal deactivator, in a hydrocarbyl phosphate and amine salt thereof; and
- (2) adding and mixing substantially all of the product of step (1) to an alkylene coupled adduct of a hydrocarbyl substituted dithiophosphoric acid and a α,β -unsaturated carbonyl containing compound, and substantially all of the antioxidant package selected from the group comprising a hydrocarbyl diphenylamine, a sterically hindered phenol and mixtures thereof sequentially, separately or combinations thereof to form a mixture; and
- (3) adding with mixing to the resultant mixture of step (2) a sufficient portion of the lubricating oil, base oil, diluent oil or mixtures thereof to form a concentrate of the lubricating oil composition.

16. The process of claim 15 further comprising adding to the mixture of step (2), step (3) or combinations thereof, performance additives selected from the group of a rust inhibitor, a foam inhibitor, a demulsifier, a viscosity modifier, a pour point depressant and mixtures thereof.

17. The process of claim 15, further comprising adding the concentrate to the final portion of lubricating oil, base oil, diluent oil or mixtures thereof resulting in a finished fluid.

18. A lubricating oil composition for use as industrial fluids, hydraulic fluids, turbine oils, circulating oils and combinations thereof, comprising the lubricating oil composition of claim 1.

19. A lubricant composition for hydraulic fluids comprising the composition of claim 1.

20. A lubricant composition for the hydraulic fluid according to claim 19, wherein the hydraulic fluid has at least one property selected from the group consisting of decreased formation of filter plugging deposits and sludge, good levels of antiwear, good levels of oxidation inhibition, good hydrolytic stability.

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