



(11) **EP 1 702 049 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
21.02.2018 Bulletin 2018/08

(51) Int Cl.:
C10M 163/00 (2006.01) C10M 159/22 (2006.01)

(21) Application number: **04814892.8**

(86) International application number:
PCT/US2004/042758

(22) Date of filing: **17.12.2004**

(87) International publication number:
WO 2005/068590 (28.07.2005 Gazette 2005/30)

(54) **LUBRICATING COMPOSITION SUBSTANTIALLY FREE OF ZDDP**

WEITGEHEND ZDDP-FREIE SCHMIERMITTELZUSAMMENSETZUNG

COMPOSITION LUBRIFIANTE PRATIQUEMENT EXEMPTÉ DE ZDDP

(84) Designated Contracting States:
DE FR GB

(30) Priority: **05.01.2004 US 751809**

(43) Date of publication of application:
20.09.2006 Bulletin 2006/38

(73) Proprietor: **The Lubrizol Corporation**
Wickliffe, Ohio 44092 (US)

(72) Inventors:
• **FRIEND, Christopher L.**
Bobber's Mill Nottingham NG7 5NR (GB)
• **MCATEE, Rodney J.**
Belper Derbyshire DE56 1TE (GB)
• **SUTTON, Michael**
Matlock Derbyshire DE4 5FL (GB)
• **CRESSEY, David**
Belper Derbyshire DE56 1NJ (GB)

(74) Representative: **dompatent von Kreisler Selting**
Werner -
Partnerschaft von Patent- und Rechtsanwälten
mbB
Deichmannhaus am Dom
Bahnhofsvorplatz 1
50667 Köln (DE)

(56) References cited:
EP-A- 0 708 171 EP-A- 1 167 497
WO-A-2004/048503 WO-A-2004/096957
WO-A-2005/026299 US-A1- 2003 158 048
US-B1- 6 200 936

Remarks:

The file contains technical information submitted after
the application was filed and not included in this
specification

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 1 702 049 B1

DescriptionFIELD OF INVENTION

[0001] The present invention relates to a lubricating oil composition containing a metal salixarate and other performance additives. The lubricating oil composition has antiwear and detergency performance in the absence of a metal hydrocarbyl dithiophosphate.

BACKGROUND OF THE INVENTION

[0002] It is well known for lubricating oils to contain a number of additives used to protect the engine from wear, the accumulation of sludge and filter plugging. Common additives for engine lubricating oils are zinc dialkyldithiophosphate (ZDDP) as an antiwear additive, and overbased calcium sulphonate detergents. It is believed that ZDDP antiwear additives protect the engine by forming a protective film on metal surfaces. Typical treatment quantities of ZDDP range from 1 to 2 weight percent based on the total weight of the lubricant. Detergents such as overbased calcium sulphonate help keep the engine parts clean of soot and other deposits, and offer an alkalinity reserve. Typical treatment quantities of detergents range from 0.05 to 10 weight percent based on the total weight of the lubricant.

[0003] In recent years phosphates and sulphonates derived from engine lubricants have been shown to contribute in part to particulate emissions. Further, sulphur and phosphorus tend to poison the NO_x catalysts used in catalytic converters, resulting in a reduction in performance of said catalysts. Any reduction in the performance of catalytic converters tends to result in increased amounts of greenhouse gases such as nitric oxide and/or sulphur oxides. However, reducing the amount of ZDDP will increase the amount of wear in an engine. Also reducing the amount of detergent will decrease engine cleanliness and result in increased soot deposits.

[0004] International Publication WO03/18728 (Cressey et al.) discloses additives for lubricants containing linear compounds containing phenolic and salicylic units in the form of oligomers or polymers. The linear compounds can be salted with calcium and optionally cosalted with boric acid. The additives have detergency and/or antiwear properties. Lubricant examples contain an ashless dispersant and a zinc dithiophosphate.

[0005] US Patent Number 6,200,936 (Moreton) discloses compounds containing phenolic units and salicylic units in a lubricating composition. The compounds can be salted with calcium. The examples of lubricating compositions contain phenolic units with a dodecyl alkyl group. The compounds of the invention can be used as a detergent in gasoline or diesel fuel. They also stabilise gasoline or diesel compositions against thermal decomposition.

[0006] International Publication WO99/25793 (Taylor) discloses a fuel composition containing kerosene and compounds containing phenolic units and salicylic units. The compounds can be salted with calcium. The examples of lubricating compositions contain phenolic units with a dodecyl alkyl group.

[0007] International Publication WO01/56968 (Taylor et al.) discloses a cyclic compound containing phenolic units and salicylic units. The salicylic units can be salted with a metal or an ammonium cation.

[0008] European Patent Application 1 262 538 A2 (Locke et al.) discloses a metal detergent derived from an aromatic carboxylic acid, a metal detergent derived from phenol capable of imparting oxidation resistance in a lubricating oil composition. In a preferred embodiment the aromatic carboxylic acid is a salicylic acid substituted with an alkyl group.

[0009] US-A-2003/158048 discloses lubricants for internal combustion engines having low SASH ash, low P content derived from ZnDTP.

[0010] EP-A-1167497 refers to low P, low ash lubricants compositions for diesel engines using conventional detergents alone with other additives.

[0011] It has now been found that the composition of the present invention provides detergency and antiwear performance to an oil of lubricating viscosity often used in an engine oil and said composition is substantially free of a metal hydrocarbyl dithiophosphate.

SUMMARY OF THE INVENTION

[0012] The present invention provides a composition comprising:

- (a) a metal salixarate;
- (b) 0.01 to 6 weight percent of the composition on an oil-free basis, of a dispersant viscosity modifier selected from the group consisting of (a) an olefin copolymer grafted with an unsaturated dicarboxylic acid anhydride or derivatives thereof and an amine; (b) a polymethacrylate functionalised with an amine; (c) an esterified copolymer comprising (i) styrene, (ii) an unsaturated dicarboxylic acid anhydride or derivatives thereof, optionally functionalised with an amine; and mixtures thereof;
- (c) an oil of lubricating viscosity,

wherein the composition contains 400 ppm or less of phosphorus derived from a metal hydrocarbyl dithiophosphate; and wherein the total sulphated ash content is below 1.5 weight percent.

[0013] The invention further provides method for lubricating an internal combustion engine comprising supplying thereto a lubricant comprising the composition mentioned above.

Preferred embodiments of the invention are apparent from the dependent claims.

[0014] The use of the composition of the invention imparts one or more of improved engine cleanliness, decreased wear, decreased NO_x emissions and decreased particulate emissions.

DETAILED DESCRIPTION OF THE INVENTION

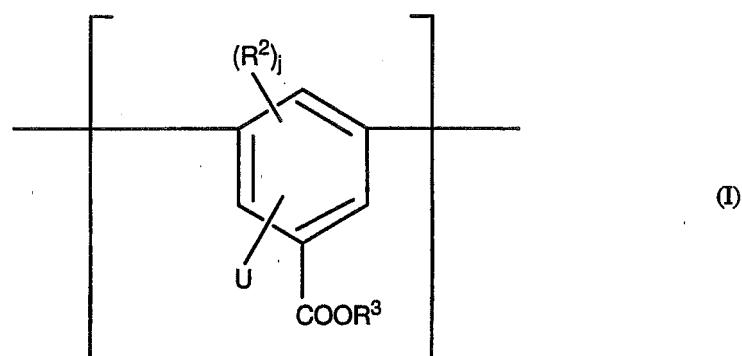
[0015] The present invention provides a composition as described above. Often the composition has a total sulphur content below 0.5 wt %, preferably below 0.3 wt %, more preferably 0.1 wt % and most preferably near 0 wt %. Often the major source of sulphur in the composition of the invention is derived from diluent oil. Usually the diluent oil is used in the manufacturing processes used for preparing many of the component additives mentioned below. Excluding the diluent oil, the composition of the invention often have a sulphur content of 700 ppm or less, preferably 600 ppm or less, more preferably 300 ppm or less, even more preferably 100 ppm or less and most preferably 50 ppm or less such as less than 30 ppm, 25 ppm or less, 20 ppm or less and 15 ppm or less. When sulphur from the diluent oil is included, the sulphur content of the composition is often increased by up to 800 ppm, preferably up to 600 ppm and most preferably up to 400 ppm, for instance 200 ppm or 300 ppm.

[0016] Often the composition has a total phosphorus content below 0.1 wt %, preferably equal to or less than 0.085 wt %, more preferably equal to or less than 0.07 wt %, even more preferably equal to or less than 0.055 wt % and most preferably equal to or less than 0.05 wt % of the composition, such as 200 ppm or less, preferably 100 ppm or less, more preferably 50 ppm or less and most preferably 10 ppm or less. In one embodiment the phosphorus is present from 1 ppm or 10 ppm to 50 ppm or 200 ppm.

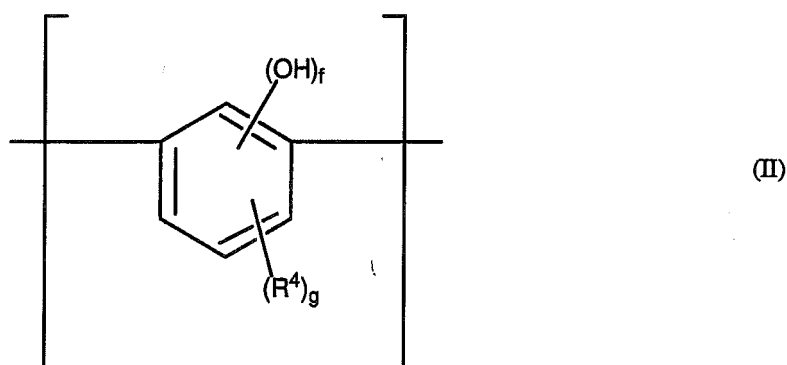
[0017] The composition has a total ash content as determined by ASTM D-874 of below 1.5 wt %, preferably equal to or less than 1.1 wt %, more preferably equal to or less than 1.0 wt %, even more preferably equal to or less than 0.8 wt % and most preferably equal to or less than 0.5 wt % of the composition. In one embodiment the total ash content is present from 0.1 wt % or 0.2 wt % to 0.6 wt % or 0.7 wt %.

Salixarate Salt Detergent

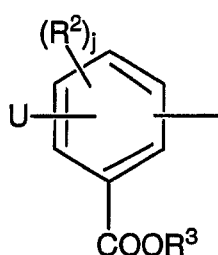
[0018] The substrate of the metal salixarate of the invention is often represented by one or a mixture of substantially linear compounds comprising at least one unit of the formulae (I) or (II):



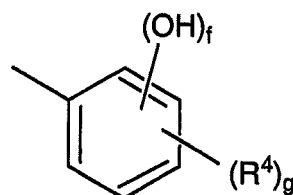
or



each end of the compound having a terminal group of formulae (III) or (IV):



(III)



(IV)

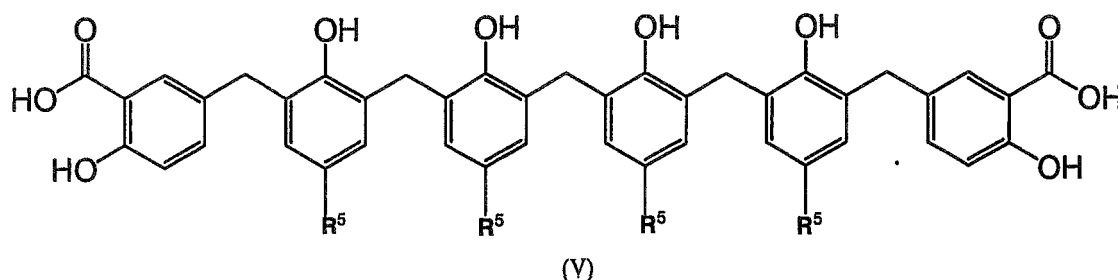
such groups being linked by divalent bridging groups, which may be the same or different for each linkage; wherein in formulas (I)-(IV) f is 1, 2 or 3, preferably 1 or 2; U is $-OH$, $-NH_2$, $-NHR^1$, $-N(R^1)_2$ or mixtures thereof, R^1 is a hydrocarbyl group containing 1 to 5 carbon atoms; R^2 is hydroxyl or a hydrocarbyl group and j is 0, 1, or 2; R^3 is hydrogen or a hydrocarbyl group; R^4 is a hydrocarbyl group or a substituted hydrocarbyl group; g is 1, 2 or 3, provided at least one R^4 group contains 8 or more carbon atoms; and wherein the molecules on average contain at least one of unit (I) or (III) and at least one of unit (II) or (IV) and the ratio of the total number of units (I) and (III) to the total number of units of (II) and (IV) in the composition overall is 0.1:1 to 2:1, although individual molecules within the composition may fall outside this range.

[0019] The U group in formulae (i) and (iii) may be located in one or more positions ortho, meta, or para to the $-COOR^3$ group. Preferably the U group is located ortho to the $-COOR^3$ group. When the U group is a $-OH$ group, formulae (i) and (iii) are derived from 2-hydroxybenzoic acid (often called salicylic acid), 3-hydroxybenzoic acid, 4-hydroxybenzoic acid or mixtures thereof. When U is a $-NH_2$ group, formulae (i) and (iii) are derived from 2-aminobenzoic acid (often called anthranilic acid), 3-aminobenzoic acid, 4-aminobenzoic acid or mixtures thereof.

[0020] The divalent bridging group, which may be the same or different in each occurrence, includes $-CH_2-$ (methylene bridge) and $-CH_2OCH_2-$ (ether bridge), either of which may be derived from an aldehyde such as formaldehyde or a formaldehyde equivalent (e.g., paraform, formalin), ethanal or propanal.

[0021] The metal of the metal salixarate is often mono-valent, di-valent or mixtures thereof. Preferably the metal is selected from an alkali metal or alkaline earth metal such as magnesium, calcium, potassium or sodium, although magnesium, calcium, potassium or mixtures thereof are most preferred.

[0022] It is believed that a significant fraction of salixarate molecules (prior to neutralisation) may be represented on average by the following formula:



wherein each R^5 can be the same or different, and are hydrogen or an alkyl group, provided at least one R^5 is alkyl. In a preferred embodiment, R^5 is a polyisobutene group (especially of molecular weight 200 to 1,000, or about 550). Significant amounts of di- or trinuclear species may also be present containing one salicylic end group of formula (III). The salixarate detergent may be used alone or with other detergents.

15 **[0023]** Salixarate derivatives and methods of their preparation are described in greater detail in U.S. -A-6,200,936 and PCT Publications WO-A-01/56968 and

[0024] WO-A-03/18728. It is believed that the salixarate derivatives have a predominantly linear, rather than macrocyclic, structure, although both structures are intended to be encompassed by the term "salixarate." Additionally "Linear" does not exclude branching or other structures in the substituent R groups.

20 **[0025]** The metal salixarate is often present on an oil free basis at 0.01 to 20, preferably 0.1 to 10, more preferably 0.2 to 8 and most preferably 0.5 to 5 weight percent of the composition.

Additives

25 **[0026]** Further additives are selected from the group consisting of (1) an antioxidant; (2) a friction modifier; (3) a dispersant; (4) a viscosity modifier; and (5) an antiwear agent other than a metal hydrocarbyl dithiophosphate. Often 2 or more and most preferably 3 or more of additives (1)-(5) are present in the invention.

[0027] Often the amount of each of the additives (1)-(5) are present on an oil free basis at 0 to 25, preferably 0.1 to 20, more preferably 0.3 to 15 and most preferably 1 to 10 weight percent of the composition, with the proviso that at

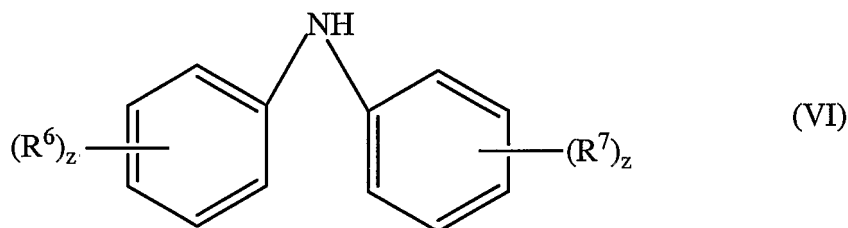
Antioxidant

35 **[0028]** When present in the invention the antioxidant often includes a diphenylamine antioxidant, a hindered phenol antioxidant, or mixtures thereof.

[0029] Other antioxidant additives such as a molybdenum dithiocarbamate or a sulphurised olefin may also be added to the composition of the invention, although preferably the composition is substantially free of a molybdenum dithiocarbamate or a sulphurised olefin. As used herein the term "substantially free of a molybdenum dithiocarbamate or a sulphurised olefin" means the composition will contain a molybdenum dithiocarbamate or a sulphurised olefin present

40 at less than 100 ppm, preferably less than 20ppm and most preferably 1 ppm or less.

[0030] When present, the diphenylamine suitable for the invention is often represented by the formula:

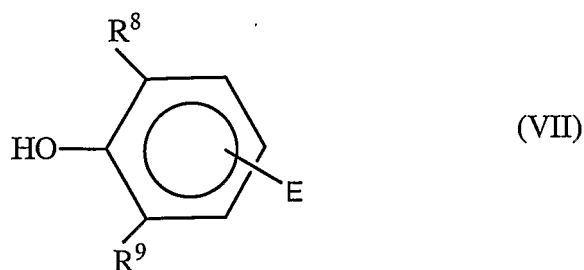


wherein are independently a hydrocarbyl group; and z is zero or higher, provided that on at least one ring, z is non-zero. Often the hydrocarbyl group contains 1 to 24, preferably 2 to 18 and most preferably 4 to 12 carbon atoms.

55 **[0031]** Examples of suitable diphenylamine antioxidants include octyl diphenylamine, nonyl diphenylamine, bis-octyl diphenylamine, bis-nonyl diphenylamine or mixtures thereof.

[0032] When present, the diphenylamine is often present on an oil free basis at 0.01 to 20, preferably 0.05 to 10, more preferably 0.1 to 5 and most preferably 0.2 to 3 weight percent of the composition.

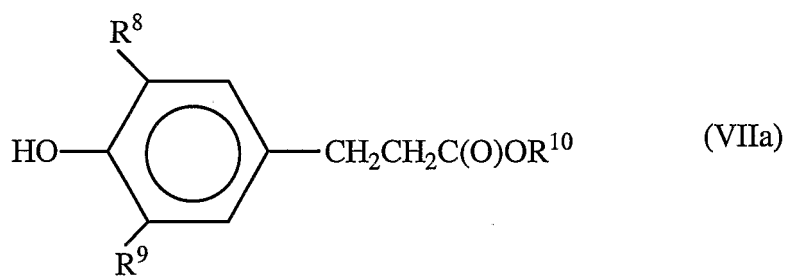
[0033] When present, the hindered phenol suitable for the invention is often represented by the formula:



15 wherein R⁸ and R⁹ are independently branched or linear alkyl groups containing 1 to 24, preferably 4 to 18, and most preferably 4 to 12 carbon atoms; and E is hydrogen, a hydrocarbonyl group, a bridging group linking to a second aromatic group, an ester-containing group, or mixtures thereof.

[0034] R⁸ and R⁹ may be either straight or branched chain; branched is preferred. Suitable examples of R⁸ and R⁹ include secondary butyl and tertiary butyl.

20 **[0035]** In one embodiment, the hindered phenol of formula (VII) suitable for the invention are esters or acids represented by the formula:

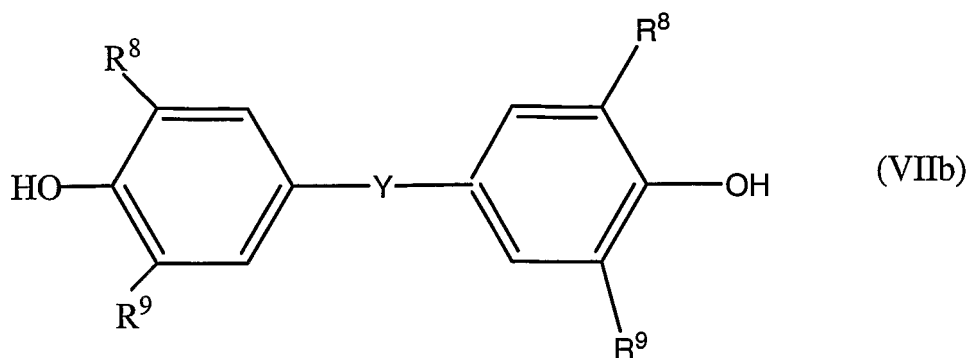


wherein R⁸ and R⁹ are as defined above and R¹⁰ is hydrogen, a hydrocarbonyl group or mixtures thereof.

[0036] When R¹⁰ is a hydrocarbonyl group, R¹⁰ is preferably selected from the group consisting of butyl, sec-butyl, isobutyl, tert-butyl, pentyl, n-hexyl, sechexyl, n-octyl, 2-ethylhexyl, nonyl, decyl, undecyl, dodecyl and mixtures thereof.

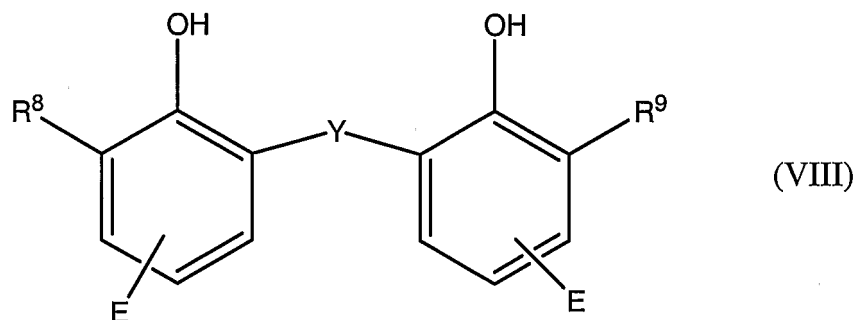
35 **[0037]** In one embodiment, the hindered phenol of formula (VII) suitable for the invention contains a bridging group. Examples of suitable bridging groups include an alkylene bridge or an ether bridge, often containing 1 to 8, preferably 1 to 6, more preferably 1 to 4 and most preferably 1 to 2 carbon atoms. Examples of a suitable bridge group include -CH₂-, -CH₂CH₂-, -CH₂OCH₂- and -CH₂CH₂OCH₂CH₂-.

[0038] When present, the hindered phenol with a bridging group is often represented by the formula:



55 wherein R¹¹ and R¹² are defined above and Y is a bridging group. Examples of a methylene-bridged hindered phenol include 4,4'-methylene-bis-(6-tert-butyl-o-cresol), 4,4'-methylene-bis-(2-tert-amyl-o-cresol) and 4,4'-methylene-bis-(2,6-di-tertbutylphenol).

[0039] The hindered phenol of the invention also includes compounds represented by the formula:



wherein R^8 , E and Y are defined above. Examples of a suitable methylene-bridged hindered phenol of formula (VIII) include 2,2-methylene-bis-(4-methyl-6-tert-butylphenol), and 2,2-methylene-bis-(4-ethyl-6-tert-butylphenol), 2,2-methylene-bis-(4-propyl-6-tert-butylphenol).

[0040] When present, the hindered phenol is often present on an oil free basis at 0.01 to 25, preferably 0.1 to 20, more preferably 0.5 to 15 and most preferably 1 to 10 weight percent of the composition.

Dispersant

[0041] When present, the invention further includes a dispersant often derived from N-substituted long chain alkenyl succinimide or mixtures thereof. The dispersants can be used alone or in combination with other dispersants.

[0042] The N-substituted long chain alkenyl succinimides have a variety of chemical structures and include a mono-succinimide and/or a di-succinimide. Often the long chain alkenyl group will have number average molecular weight of 350 to 10,000, preferably 400 to 7000, more preferably 500 to 5000 and most preferably 500 to 4000. In one embodiment the long chain alkenyl group is a polyisobutylene group, which has a number average molecular weight from 800 to 1600 and in another embodiment from 1600 to 3000. The succinimide is often prepared by the condensation of a hydrocarbyl-substituted acylating agent (e.g., hydrocarbyl-substituted succinic anhydride) with a polyamine or an amino alcohol, often a polyalkylene polyamine or poly(ethyleneamine) such as triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine or, in one embodiment, polyamine still bottoms.

[0043] N-substituted long chain alkenyl succinimides dispersant additives and their preparation are disclosed, for instance, in US -A- 3,361,673, 3,401,118 and 4,234,435.

[0044] Another class of suitable dispersants include Mannich bases, which are the reaction products of alkyl phenols in which the alkyl group typically contains at least 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines) and are described in more detail in U.S. -A- 3,634,515.

[0045] Another class of ashless dispersant is high molecular weight esters. These materials are similar to the above-described succinimides except that they may be seen as having been prepared by reaction of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Such materials are described in more detail in U.S. -A- 3,381,022.

[0046] Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer.

[0047] Dispersants may also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds. References detailing such treatment are listed in U.S. -A- 4,654,403.

[0048] When present, the dispersant is often present on an oil free basis at 0.01 to 20, preferably 0.1 to 15, more preferably 0.2 to 10 and most preferably 0.5 to 6 weight percent of the composition.

Friction Modifiers

[0049] When present in the invention, the friction modifier can be a monoester of a polyol and an aliphatic carboxylic acid, often an acid containing 12 to 24 carbon atoms. Often the monoester of a polyol and an aliphatic carboxylic acid is in the form of a mixture with a sunflower oil or the like, which may be present in the friction modifier mixture from 5 to 95, preferably 10 to 90, more preferably 20 to 85 and most preferably 20 to 80 weight percent of said mixture.

[0050] Polyols include diols, triols, and alcohols with higher numbers of alcoholic OH groups. Polyhydric alcohols include ethylene glycols, including di-, tri- and tetraethylene glycols; propylene glycols, including di-, tri- and tetrapropylene glycols; glycerol; butane diol; hexane diol; sorbitol; arabitol; mannitol; sucrose; fructose; glucose; cyclohexane diol;

erythritol; and pentaerythritols, including di- and tripentaerythritol; preferably, diethylene glycol, triethylene glycol, glycerol, sorbitol, pentaerythritol and dipentaerythritol.

[0051] The aliphatic carboxylic acids which form the esters are those acids containing 12 to 24 carbon atoms. Acids containing straight chain hydrocarbyl groups containing 12 to 24 carbon atoms are preferred, for instance, 14 to 20 or 16 to 18 carbon atoms. Such acids can be used in combination with acids with more or fewer carbon atoms as well.

[0052] Generally the acid is a monocarboxylic acid. Examples of carboxylic acids include dodecanoic acid, stearic acid, lauric acid, behenic acid, and oleic acid.

[0053] The esters used in the present invention are in particular the monoesters of such polyols and such carboxylic acids. A preferred ester is glycerol monooleate. It is to be understood that glycerol monooleate, as is the case with other such materials, in its commercially available grade, is a mixture which includes such materials as glycerol, oleic acid, other long chain acids, glycerol dioleate, and glycerol trioleate. The commercial material is believed to include about 60 ± 5 percent by weight of the chemical species "glycerol monooleate," along with 35 ± 5 percent glycerol dioleate, and less than about 5 percent trioleate and oleic acid. The amounts of the monoesters, described below, are calculated based on the actual, corrected, amount of polyol monoester present in any such mixture.

[0054] Other friction modifiers that are suitable for the invention include fatty amines, fatty phosphites, fatty acid amides, fatty epoxides, alkoxylated fatty amines, metal salts of fatty acids, sulfurised olefins, fatty imidazolines, condensation products of carboxylic acids and polyalkylene-polyamines, amine salts of alkylphosphoric acids. Preferably the friction modifier is free of sulphur and/or phosphorus.

[0055] When present, the friction modifier is often present on an oil free basis at 0.01 to 20, preferably 0.05 to 10, more preferably 0.1 to 5 and most preferably 0.2 to 3 such as 0.5 to 2 weight percent of the composition.

Viscosity Modifiers

[0056] When present in the invention the viscosity modifier is often an olefin copolymer. The olefin copolymer backbone often contains two to four, preferably two to three and most preferably two different olefin monomers. The olefin monomers often contain 2 to 20, preferably 2 to 10, more preferably 2 to 6 and most preferably 2 to 4 carbon atoms.

[0057] When present, the viscosity modifiers are often present on an oil free basis at of 0.01 to 15, preferably 0.05 to 10, more preferably 0.1 to 5 and most preferably 0.2 to 3 weight percent of the composition.

[0058] The olefin copolymer preferably contains an ethylene monomer and at least one other comonomer derived from an alpha-olefin having the formula $H_2C=CHR^{10}$, wherein R^{10} is a hydrocarbyl group, preferably an alkyl radical containing 1 to 18, preferably 1 to 10, more preferably 1 to 6 and most preferably 1 to 3 carbon atoms. The hydrocarbyl group includes an alkyl radical that has a straight chain, a branched chain or mixtures thereof.

[0059] Examples of suitable comonomers include propylene, 1-butene, 1-hexene, 1-octene, 4-methylpentene-1, 1-decene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene or mixtures thereof. Preferably the comonomer is 1-butene, propylene or mixtures thereof. Example of olefin copolymers include ethylenepropylene copolymers or ethylene-butene-1 copolymers.

[0060] Other viscosity modifiers suitable for the invention include polymeric materials including hydrogenated styrene-butadiene rubbers, hydrogenated styrene-isoprene polymers, hydrogenated radical isoprene polymers, polymethacrylate acid esters, polyacrylate acid esters, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyalkylmethacrylates, esters of maleic anhydride-styrene copolymers or mixtures thereof.

[0061] Optionally the olefin copolymer of the invention is further grafted with an unsaturated dicarboxylic acid anhydride or derivatives thereof and an amine to form a dispersant viscosity modifier (often referred to as DVM), thus named because they also exhibit dispersant properties. DVM additives and their preparation are disclosed, for instance, in US - A - 6,107,258 and 6,107,257.

[0062] Examples of olefin copolymer DVM's include those commercially available from DSM as PA1250™, PA1260™ and PA1274™ as well as Hitec 5777™ (commercially available from Ethyl Corporation).

[0063] The dispersant viscosity modifier is selected from the group consisting of (a) an olefin copolymer grafted with an unsaturated dicarboxylic acid anhydride or derivatives thereof and an amine; (b) a polymethacrylate functionalised with an amine; (c) an esterified copolymer comprising (i) styrene, (ii) an unsaturated dicarboxylic acid anhydride or derivatives thereof, optionally functionalised with an amine; and mixtures thereof. Often DVM's derived from a polymethacrylate and/or a styrene copolymer are prepared by reacting with an amine as described in US - A - 6,107,258 and 6,107,257. The DVM can be used alone or in combination with other DVM's.

[0064] According to the invention, the dispersant viscosity modifier is present on an oil free basis at 0.01 to 6, preferably 0.05 to 6, more preferably 0.08 to 4 and most preferably 0.1 to 2 weight percent of the composition.

Antiwear Agents

[0065] The composition of the invention may additionally contain an antiwear agent other than a metal hydrocarbyl

dithiophosphate. Suitable antiwear agents include phosphoric acid esters or salt thereof; phosphites; and phosphorus-containing carboxylic esters, ethers, and amides or mixtures thereof. Preferably the composition of the invention is substantially free of phosphorus- and/or sulphur-containing antiwear agents. In one embodiment of the invention the composition is free of antiwear agents.

[0066] As used herein the term "substantially free of antiwear agents containing sulphur and/or phosphorus" means the composition will contain antiwear agents present at less than 50 ppm, preferably less than 10 ppm and most preferably 1 ppm or less. In one embodiment of the invention no antiwear agents containing sulphur and/or phosphorus are present. In one embodiment of the invention 1 ppm to 15 ppm of antiwear agents containing sulphur and/or phosphorus are present.

Oils of Lubricating Viscosity

[0067] The lubricating oil composition of the present invention may be added to an oil of lubricating viscosity. The oil includes natural and synthetic oils, oil derived from hydrocracking, hydrogenation, hydrofinishing, unrefined, refined and re-refined oils, or mixtures thereof.

[0068] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0069] 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.

[0070] 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.

[0071] Natural oils useful in making the inventive lubricants include 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 or mixtures thereof.

[0072] Synthetic lubricating oils are useful and include 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; alkyl-benzenes (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 or mixtures thereof. Preferably the synthetic lubricating oils are free of alkylated diphenyl sulphides.

[0073] Other synthetic lubricating oils include but are not limited to polyol esters, 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. Preferably the synthetic lubricating oils are free of phosphorus-containing esters.

[0074] Oils of lubricating viscosity may 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). The oil of lubricating viscosity is selected from the group consisting of an API Group I, II, III, IV, V oil and mixtures thereof; preferably an API Group II, III, IV or V oil and mixtures thereof; and most preferably an API Group III, IV or V oil and mixtures thereof. If the oil of lubricating viscosity is an API Group II, III, IV or V oil there may be up to a maximum of 20 wt %, preferably up to a maximum of 10 wt %, more preferably up to a maximum of 5 wt % and most preferably up to a maximum of 1.5 wt % of the lubricating oil an API Group I oil.

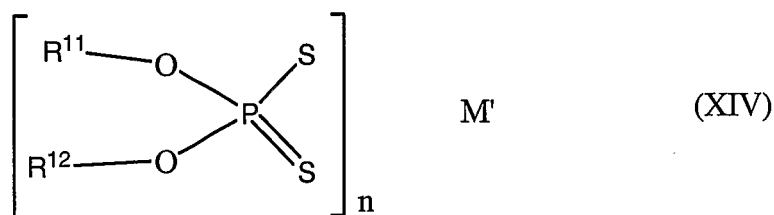
[0075] Examples of suitable API Group III oils include Nexbase™ 3050, Nexbase™ 3043, Yubase™ 4, Yubase™ 6, and Shell™ XHVI 5.2.

[0076] The oil of lubricating viscosity is often present at up to 99.98, preferably up to 99.8, more preferably up to 99.65 and most preferably up to 99.3 weight percent of the composition.

[0077] If the present invention is in the form of a concentrate (which can be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of each of the above-mentioned dispersant, as well as other components, to diluent oil is often 80:20 to 10:90 by weight.

Metal Hydrocarbyl Dithiophosphate

[0078] The invention is substantially free of to free of a metal hydrocarbyl dithiophosphate often represented by the formula:



wherein R¹¹ and R¹² are independently hydrogen, hydrocarbyl groups or mixtures thereof, provided that at least one of R¹¹ and R¹² is a hydrocarbyl group, preferably alkyl or cycloalkyl with 1 to 30, preferably 2 to 20 and most preferably 2 to 15 carbon atoms.

[0079] The term "substantially free of" means that the composition contains 400 ppm or less of phosphorus, preferably 300 ppm or less of phosphorus, more preferably 200 ppm or less of phosphorus, even more preferably 100 ppm or less of phosphorus and most preferably 100 ppm or less of phosphorus such as 50 ppm, 20 ppm or 1 ppm or less, derived from a metal hydrocarbyl dithiophosphate. In one embodiment of the invention the composition contains 0.5 ppm or 10ppm to 50 ppm of phosphorus derived from a metal hydrocarbyl dithiophosphate. In one embodiment of the invention the composition is free of a metal hydrocarbyl dithiophosphate.

[0080] M' is a metal, and n is an integer equal to the available valence of M'. M' is mono- or di- or tri- valent, preferably divalent, more preferably a divalent transition metal. In one embodiment M' is zinc. In one embodiment M' is calcium. In one embodiment M' is barium. Examples of a metal hydrocarbyl dithiophosphate include zinc dihydrocarbyl dithiophosphates (often referred to as ZDDP, ZDP or ZDTP).

Other Performance Additives

[0081] The composition of the invention optionally further includes other performance additives. The other performance additives selected from the group consisting of detergents other than those of component (a) of the invention, corrosion inhibitors, antiscuffing agents, foam inhibitors, demulsifiers, pour point depressants seal swelling agents and mixtures thereof.

[0082] The total combined amount of the other performance additives present on an oil free basis is often from 0 to 20, preferably 0.01 to 15, more preferably 0.05 to 10 and most preferably 0.1 to 5 weight percent of the composition. Although one or more of the other performance additives may be present, it is common for the other performance additives to be present in different amounts relative to each other.

[0083] Detergents other than those of component (a) of the invention are known and include neutral or overbased, Newtonian or non-Newtonian, basic salts of alkali, alkaline earth and transition metals with one or more of a phenate, a sulphonate, a carboxylic acid, a phosphorus acid, a mono- and/or a dithiophosphoric acid, a saligenins, an alkylsalicylate or mixtures thereof. Commonly used metals include sodium, potassium, calcium, magnesium lithium or mixtures thereof. Most commonly used metals include sodium, magnesium and calcium. Preferably the composition of the invention is free of detergents containing sulphur and/or phosphorus.

[0084] Other performance additives such as corrosion inhibitors including octylamine octanoate, condensation products of dodeceny succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine; metal deactivators including derivatives of benzotriazoles, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles or 2-alkyldithiobenzothiazoles; foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides; and seal swell agents including Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil (FN 3200); may also be used in the composition of the invention.

Process

[0085] In a process for the preparation of a composition as described above, the components (a)-(c) are often mixed sequentially, separately for the composition of the invention. The mixing conditions are often 15°C to 130°C, preferably 20°C to 120°C and most preferably 25°C to 110°C; and for a period of time in the range 30 seconds to 48 hours, preferably 2 minutes to 24 hours, more preferably 5 minutes to 16 hours and most preferably 10 minutes to 5 hours; and at pressures in the range 86 kPa to 266 kPa (650 mm Hg to 2000 mm Hg), preferably 91 kPa to 200 kPa (690 mm Hg to 1500 mm Hg), and most preferably 95 kPa to 133 kPa (715 mm Hg to 1000 mm Hg).

[0086] The process optionally includes mixing other optional performance additives as described above. The optional performance additives are often added sequentially, separately or as a concentrate.

Industrial Application

[0087] The composition of the present invention is useful in an internal combustion engines, for example diesel fuelled engines, gasoline fuelled engines, natural gas fuelled engines or a mixed gasoline/alcohol fuelled engines.

[0088] In one embodiment of the invention provides a method for lubricating an internal combustion engine, comprising supplying thereto a lubricant comprising the composition as described herein. The use of the composition of the invention is capable of imparting one or more of the group selected from improved engine cleanliness, decreased wear, decreased NO_x emissions and decreased particulate emissions.

[0089] The following examples provide an illustration of the invention.

EXAMPLESPreparative Example 1: Preparation of Salixarate Substrate - Salixarene

[0090] A sample of a salixarene substrate is prepared using a flange flask approximately 2 litres in volume, a flange and clip, overhead stirrer with paddle and polytetrafluoroethylene (PTFE) stirrer gland, Dean Stark trap and double surface condenser, an electric mantle/thermocouple/Eurotherm™ temperature controller system, the glassware from just above the mantle to just below the condenser being covered with glass wool. The flask is filled with 475g polyisobutenyl phenol derived from high vinylidene polyisobutylene with a number average molecular weight of 550 (GLISSOPAL®550 commercially available from BASF) and 330g of mineral oil (SN 150) and heated to 30°C via a pressure equalizing dropping funnel 3.4g of 50% aqueous KOH is added. The contents of the flask are heated to 75°C and the temperature is kept constant for 30 minutes while 81.6g of 37% aqueous formaldehyde (formalin) is added. The reaction is charged with 51.6g of salicylic acid and heated to 140°C while controlling reflux. Water is removed using Dean Stark trap. The product is vacuum stripped at 140°C/13kPa (equivalent to 100mm Hg) for 30 minutes. A more detailed description of the reaction process is given in Examples 1 and 5 of International Publication WO03/018728, pages 22 and 23.

Preparative Example 2: Calcium Salixarate

[0091] A vessel is charged with 1200g of the salixarene from Preparative Example 1, 25g of ethylene glycol, 130g of calcium hydroxide and 410g of 2-ethylhexanol. The vessel and contents are heated to 95°C and stirred under vacuum (64 kPa, which is equivalent to 480mm Hg). The vessel and contents are then subject to vacuum at 6.7 kPa (equivalent to 50mm Hg) for 15 minutes and heated to 130°C. The vessel is then charged with an additional 120g of ethylene glycol added dropwise over 10 minutes before carbon dioxide is added via a dip tube under a slight negative pressure at 1.0 g/minute or less until 48g are added. Upon completion of carbon dioxide addition, the dip tube is removed and the temperature is increased to 200°C under a vacuum of 6.7 kPa (equivalent to 50mm Hg) to remove solvents. The residue is vacuum filtered through a 12mm diatomaceous earth pad in a sintered funnel yielding a viscous brown liquid.

Preparative Example 3: Magnesium Salixarate

[0092] A vessel is charged with 560.5g of the salixarene from Preparative Example 1 with 433g of xylene. The vessel and contents are heated to 35°C under a nitrogen atmosphere where 53g of magnesium oxide is added. The vessel is then charged with 20.2g of glacial acetic acid and then a mixture of methanol (42g) and water (30g) is added. The vessel and contents are heated to 61°C and carbonated. The vessel and contents are held at 61°C for a further 2 hours and a further mixture of methanol (36g) and water (26.2g) is added. The vessel heated to 150°C and held for 1 hour. The product is vacuum stripped.

Preparative Example 4: Potassium Salixarate

[0093] A vessel is charged with 313g of the salixarene from Preparative Example 1, and heated under a nitrogen atmosphere to 80°C where 12.1g of potassium hydroxide in 7g of water is added dropwise followed by the addition of 85g of a diluent oil. The vessel and contents are heated to 110°C for 10 minutes, then heated to 120°C for 90 minutes and heated to 140°C for 3 hours. A dark brown product is formed.

Reference Example 1

[0094] A composition is prepared by mixing (a) 42.5g of Nexbase™ 3050 oil, (b) 34.4g of Nexbase™ 3043 oil, (c) on an oil free basis 0.4g of an amine dispersant viscosity modifier, (d) on an oil free basis 2.8g of polyisobutylene succinimide dispersants, (e) 5g of antioxidants including a diphenylamine and a hindered phenol, (f) 0.7g of an olefin

copolymer viscosity modifier and (g) a glycerol monooleate friction modifier. The composition contains 0 wt % of calcium, 0 wt % of phosphorus, 190 ppm of sulphur and 0 wt % of zinc. The composition has a KV100 of 13.11 mm²/s (cSt) and a sulphated ash content of 0 wt %.

Reference Example 2: Top Tier European Passenger Car Oil Formulation

[0095] Reference Example 2 is a successful European top tier passenger car oil formulation containing zinc dithiophosphate. The elemental analysis of the oil formulation indicates a calcium content of 3307ppm, a phosphorus content of 889ppm, a sulphur content of 2645ppm and a zinc content of 889ppm. The oil formulation has a KV100 of 11.3 mm²/s (cSt) and sulphated ash content of 1.26 wt %.

Example 1

[0096] Example 1 has the same composition as Reference Example 1 except 2.5g (on an oil free basis) of the product of Preparative Example 2 is also added. The phosphorus content is 0 wt % and the sulphur content is 190 ppm (all derived from diluent oil).

Example 2

[0097] Example 2 has the same composition as Reference Example 1 except 2.5g (on an oil free basis) of the product of Preparative Example 3 is also added. The phosphorus content is 0 wt % and the sulphur content is 190 ppm (all derived from diluent oil).

Example 3

[0098] Example 3 has the same composition as Reference Example 1 except 2.5g (on an oil free basis) of the product of Preparative Example 4 is also added. The phosphorus content is 0 wt % and the sulphur content is 190 ppm (all derived from diluent oil).

[0099] A number of lubricating oil compositions are formed using Reference Example 1 and adding examples 1-3 at 2.5g on a oil free basis to the oil thus forming "Lubricating Oil Composition with Example 1", Example 2 is titled "Lubricating Oil Composition with Example 2" and "Lubricating Oil Composition with Example 3." Reference example 1 and the corresponding Lubricating Oil Composition with examples 1-3 have a KV100 of 13.11 mm²/s (or cSt).

Test 1: HFRR of Examples 1-3 and Reference Examples 1-2

[0100] Lubricating Oil Composition with Example 1-3 are and Reference Example 1-2 are evaluated for wear performance in a programmed temperature high frequency reciprocating rig (HFRR) available from PCS Instruments. HFRR conditions for the evaluations are 200g load, 75 minute duration, 1000 micrometer stroke, 20 hertz frequency, and temperature profile of 15 minutes at 40°C followed by an increase in temperature to 160°C at a rate of 2°C per minute. Wear scar in micrometers and film formation as percent film thickness are measured with lower wear scar values and higher film formation values indicating improved wear performance.

[0101] The percent film thickness is based on the measurement of electrical potential between an upper and a lower metal test plate in the HFRR. When the film thickness is 100%, there is a high electrical potential for the full length of the 1000 micrometre stroke, suggesting no metal to metal contact. Conversely for a film thickness of 0% there is no electrical potential suggesting continual metal to metal contact between the plates. For intermediate film thicknesses, there is an electrical potential suggesting the upper and lower metal test plate have a degree of metal to metal contact as well as other areas with no metal to metal contact. The wear scar and film formation results obtained are presented in Table 1:

Table 1: HFRR Wear Scar and Film Formation Data

Example	Wear Scar	Film Formation
Lubricating Oil Composition Example 1	128	70
Lubricating Oil Composition Example 2	174	19
Lubricating Oil Composition Example 3	169	30
Reference Example 1	189	12

(continued)

Example	Wear Scar	Film Formation
Reference Example 2	126	88

Test 2: Cameron Plint of Example 1 and Reference Examples 1-2

[0102] The Cameron Plint TE-77™ is a reciprocating wear tester. In this test a steel ball upper specimen is reciprocated against a steel flat lower specimen. The Cameron Plint is charged with 10ml of sample and heated to 50°C and held for 1 minute. The sample is then subject to a load of 100N over two minutes while at the same time the reciprocation is started at 10 Hz over 15mm stroke length. The sample is then heated to 250°C at 3°C per minute. At the end of the test the average diameter of the wear scar (in micrometers) on the ball (measured in the X and Y directions) is measured using a calibrated microscope. The results obtained are:

Table 2: Cameron Plint Wear Scar Data

Example	Wear Scar
Lubricating Oil Composition Example 1	396
Reference Example 1	753
Reference Example 2	517

Test 3: 4 Ball Wear Test Using ASTM D4172

[0103] The "Lubricating Oil Composition Example 4" and "Lubricating Oil Composition Example 5" used in this test are the same as the "Lubricating Oil Composition Example 1" except "Example 4" contains 2g on a oil free basis of the product of Preparative Example 2 and delivering about 1900 ppm of calcium and a TBN of about 146; and "Example 5" contains 1.2g on a oil free basis of the product of preparative Example 2 and delivering about 1300 ppm of calcium and a TBN of about 146. Reference Example 3 has the same oil composition as Reference Example 1, except a calcium alkylsalicylate (commercially available from AC60C™ range of products from Infineum) is added in sufficient quantity to deliver about 1300 ppm of calcium and a TBN of about 146. Reference Example 4 has the same oil composition as Reference Example 1, except a magnesium saligenin (commercially available from The Lubrizol Corporation) is added in sufficient quantity to deliver about 1300 ppm of magnesium and a TBN of about 146.

[0104] The ASTM D4172 test is run on a number of examples using the modified B conditions indicated on page Section 8 of ASTM D 4172 - 94 (reapproved 1999). The wear scar is measured in micrometers. The results obtained are:

Table 2: ASTM D4172 Wear Scar Data

Example	Wear Scar
Lubricating Oil Composition Example 4	416
Lubricating Oil Composition Example 5	433
Reference Example 1	583
Reference Example 4	483
Reference Example 5	482

[0105] Overall the analysis of the data from Test 1 and Test 2 shows the compositions of the invention produce good antiwear and film formation results compared with reference example 1. The analysis also indicates that the lubricating oil composition example 1 has antiwear and film formation results comparable with a successful European top tier passenger car oil formulation containing zinc dithiophosphate.

[0106] In this specification the terms "hydrocarbyl substituent" or "hydrocarbyl group," as used herein are used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group primarily composed of carbon and hydrogen atoms and is attached to the remainder of the molecule through a carbon atom and does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the molecule having a predominantly hydrocarbon character. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon

substituents in the hydrocarbyl group. A more detailed definition of the terms "hydrocarbyl substituent" or "hydrocarbyl group," is described in US -A- 6, 583,092.

[0107] Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated.

Claims

1. A composition comprising:

- (a) a metal salixarate;
- (b) 0.01 to 6 weight percent of the composition on an oil-free basis, of a dispersant viscosity modifier selected from the group consisting of (a) an olefin copolymer grafted with an unsaturated dicarboxylic acid anhydride or derivatives thereof and an amine; (b) a polymethacrylate functionalised with an amine; (c) an esterified copolymer comprising (i) styrene, (ii) an unsaturated dicarboxylic acid anhydride or derivatives thereof, optionally functionalised with an amine; and mixtures thereof;
- (c) an oil of lubricating viscosity,

wherein the composition contains 400 ppm or less of phosphorus derived from a metal hydrocarbyl dithiophosphate; and wherein the total sulphated ash content is below 1.5 weight percent.

2. The composition of claim 1, wherein the metal of the metal salixarate is an alkali metal or alkaline earth metal.

3. The composition of claim 1, wherein the metal salixarate is present on an oil free basis at 0.01 to 20 weight percent of the composition.

4. The composition of claims 1 to 3, wherein the total sulphur content is below 0.5 weight percent and the total phosphorus content is below 0.07 weight percent.

5. A method for lubricating an internal combustion engine, comprising supplying thereto a lubricant comprising the composition of any one of claims 1 to 4.

6. The use of the composition of any one of claims 1 to 4 for imparting one or more of the group selected from improved engine cleanliness, decreased wear, decreased NO_x emissions and decreased particulate emissions.

Patentansprüche

1. Zusammensetzung, umfassend:

- (a) ein Metallsalixarat;
- (b) 0,01 bis 6 Gew.-% der Zusammensetzung, auf einer ölfreien Basis, eines Dispergiermittelviskositätsmodifikators, der aus der Gruppe ausgewählt ist, die aus (a) einem Olefincopolymer, das mit einem ungesättigten Dicarbonsäureanhydrid oder Derivaten davon und einem Amin gepropft ist, (b) einem Polymethacrylat, das mit einem Amin funktionalisiert ist, (c) einem veresterten Copolymer, das (i) Styrol und (ii) ein ungesättigtes Dicarbonsäureanhydrid oder Derivate davon umfasst und gegebenenfalls mit einem Amin funktionalisiert ist, und Gemischen davon besteht;
- (c) ein Öl mit Schmierviskosität;

wobei die Zusammensetzung 400 ppm oder weniger Phosphor, der aus einem Metallhydrocarbyldithiophosphat stammt, enthält und wobei der Gesamtgehalt an sulfatierter Asche unter 1,5 Gew.-% liegt.

2. Zusammensetzung gemäß Anspruch 1, wobei das Metall des Metallsalixarats ein Alkalimetall oder ein Erdalkalimetall ist.

3. Zusammensetzung gemäß Anspruch 1, wobei das Metallsalixarat auf ölfreier Basis in einer Menge von 0,01 bis 20 Gew.-% der Zusammensetzung vorhanden ist.
4. Zusammensetzung gemäß Anspruch 1 bis 3, wobei der Gesamtschwefelgehalt unter 0,5 Gew.-% liegt und der Gesamtposphorgehalt unter 0,07 Gew.-% liegt.
5. Verfahren zum Schmieren eines Verbrennungsmotors, umfassend das Zuführen eines Schmierstoffs, der die Zusammensetzung gemäß einem der Ansprüche 1 bis 4 umfasst.
6. Verwendung der Zusammensetzung gemäß einem der Ansprüche 1 bis 4 zum Erreichen von einem oder mehreren der Gruppe, die aus einer verbesserten Motorsauberkeit, reduziertem Verschleiß, reduzierten NO_x-Emissionen und reduzierten Partikelemissionen besteht.

Revendications

1. Composition comprenant:

- (a) un salixarate métallique;
- (b) 0,01 à 6 pour-cent en poids de la composition sur une base sans huile, d'un modificateur de viscosité dispersant choisi dans le groupe consistant en (a) un copolymère d'oléfines greffé avec un anhydride d'acide dicarboxylique insaturé ou des dérivés de celui-ci et une amine; (b) un polyméthacrylate fonctionnalisé avec une amine; (c) un copolymère estérifié comprenant (i) du styrène, (ii) un anhydride d'acide dicarboxylique insaturé ou des dérivés de celui-ci, éventuellement fonctionnalisé avec une amine; et leurs mélanges;
- (c) une huile de viscosité lubrifiante,

où la composition contient 400 ppm ou moins de phosphore dérivé d'un hydrocarbyle dithiophosphate métallique; et où la teneur en cendres sulfatées totale est inférieure à 1,5 pour-cent en poids.

2. Composition selon la revendication 1, où le métal du salixarate métallique est un métal alcalin ou un métal alcalino-terreux.
3. Composition selon la revendication 1, où le salixarate métallique est présent sur une base sans huile à raison de 0,01 à 20 pour-cent en poids de la composition.
4. Composition selon les revendications 1 à 3, où la teneur en soufre totale est inférieure à 0,5 pour-cent en poids et la teneur en phosphore totale est inférieure à 0,07 pour-cent en poids.
5. Procédé pour lubrifier un moteur à combustion interne, comprenant la fourniture à celui-ci d'un lubrifiant comprenant la composition selon l'une quelconque des revendications 1 à 4.
6. Utilisation de la composition selon l'une quelconque des revendications 1 à 4 pour conférer une ou plusieurs du groupe choisi parmi une propreté de moteur améliorée, une usure diminuée, des émissions de NO_x diminuées et des émissions de particules diminuées.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 0318728 A, Cressey [0004] [0024]
- US 6200936 B, Moreton [0005]
- WO 9925793 A, Taylor [0006]
- WO 0156968 A, Taylor [0007] [0023]
- EP 1262538 A2, Locke [0008]
- US 2003158048 A [0009]
- EP 1167497 A [0010]
- US 6200936 A [0023]
- US 3361673 A [0043]
- US 3401118 A [0043]
- US 4234435 A [0043]
- US 3634515 A [0044]
- US 3381022 A [0045]
- US 4654403 A [0047]
- US 6107258 A [0061] [0063]
- US 6107257 A [0061] [0063]
- WO 03018728 A [0090]
- US 6583092 A [0106]