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(54) Lubricating composition containing ashfree antiwear agent based on hydroxypolycarboxylic acid derivative and a molybdenum compound

(57) The invention provides a lubricating composition containing an oil of lubricating viscosity, an oil soluble molybdenum compound, and an ashless antiwear agent. The invention further provides for a new antioxidant. The lubricating composition is suitable for lubricating an internal combustion engine.

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Description

FIELD OF INVENTION

[0001] The invention provides a lubricating composition containing an oil of lubricating viscosity, an oil soluble molybdenum compound, and an ashless antiwear agent. The invention further provides for a new antioxidant. The lubricating composition is suitable for lubricating an internal combustion engine.

BACKGROUND OF THE INVENTION

[0002] Engine manufacturers have focused on improving engine design in order to improve fuel economy and efficiency (typically, based on Federal Corporate Average Fuel Economy (CAFE) standards). Whilst improvements in engine design and operation have contributed, improved formulation of engine oil lubricant may also improve fuel economy and efficiency. Lubricants function to reduce and disperse engine deposits which accumulate when the engines are running. They also serve to reduce the friction between sliding moving parts (typically metallic or ceramic) that are in contact.

[0003] It is well known for lubricating oils to contain a number of additives (including antiwear agents, antioxidants, dispersants, detergents etc.) used to protect the mechanical devices such as internal combustion engines from wear, oxidation, soot deposits and acidity build up. A common antiwear additive for engine lubricating oils is zinc dialkyldithiophosphate (ZDDP). It is believed that ZDDP antiwear additives protect the engine by forming a protective film on metal surfaces. ZDDP is also believed to have a detrimental impact on fuel economy and efficiency. Consequently, engine lubricants also contain friction modifier to obviate the detrimental impact of ZDDP on fuel economy and efficiency. Both ZDDP and friction modifier function by adsorption on sliding surfaces, and each may interfere with each other's respective functions.

[0004] Further, engine lubricants containing phosphorus compounds and sulphur have been shown to contribute in part to particulate emissions, and emissions of other pollutants. In addition, sulphur and phosphorus tend to poison the catalysts used in catalytic converters, resulting in a reduction in performance of said catalysts.

[0005] With increasing control of emissions (often associated with contributing to NO_x formation, SO_x formation, formation of sulphated ash and reducing the efficiency of after-treatment catalytic converters) there is a desire towards reduced amounts of sulphur, phosphorus and sulphated ash in engine oils. However, reducing the levels of antiwear additives such as ZDDP, is likely to increase wear and result in other detrimental performance of an engine.

[0006] In addition, as technology develops, components of an engine are exposed to more severe operating conditions. Operating conditions may include higher power density engines, use of turbo chargers, use of alternative fuels and the like. Under many severe operating conditions, oxidation of lubricant and components occurs more readily. Thus there is a need to reduce oxidation, that in turn may also increase equipment longevity, or reliability.

[0007] International Publication WO 2005/087904 discloses a lubricant composition containing at least one hydroxy-carboxylic acid ester or hydroxy polycarboxylic acid. The lubricant composition disclosed may also contain zinc dihydrocarbyldithiophosphates, or other phosphorous-containing additives such as trilauryl phosphate or triphenylphosphorothionate. The lubricant composition has anti-wear or anti-fatigue properties.

[0008] International Publication WO 2006/044411 discloses a low-sulphur, low-phosphorus, low-ash lubricant composition suitable for lubricating an internal combustion engine, containing a tartrate ester, or amide having 1 to 150 carbon atoms per ester of amide group.

[0009] US Patent 5,338,470 discloses alkylated citric acid derivatives obtained as a reaction product of citric acid and an alkyl alcohol or amine. The alkylated citric acid derivative is effective as an antiwear agent and friction modifier.

[0010] U.S. Patent 4,237,022 discloses tartrimides useful as additives in lubricants and fuels for effective reduction in squeal and friction as well as improvement in fuel economy.

[0011] U.S. Patent 4,952,328 discloses lubricating oil compositions for internal combustion engines, comprising (A) oil of lubricating viscosity, (B) a carboxylic derivative produced by reacting a succinic acylating agent with certain amines, and (C) a basic alkali metal salt of sulphonic or carboxylic acid.

[0012] U.S. Patent 4,326,972 discloses lubricant compositions for improving fuel economy of internal combustion engines. The composition includes a specific sulphurised composition (based on an ester of a carboxylic acid) and a basic alkali metal sulphonate.

[0013] U.S. Patent Application 60/867534 discloses malonate esters suitable as antiwear agents.

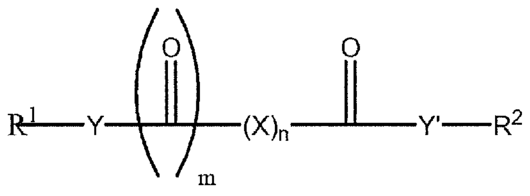
[0014] Canadian Patent CA 1 183 125 discloses lubricants for gasoline engines containing alkyl-ester tartrates, where the sum of carbon atoms on the alkyl groups is at least 8.

[0015] Consequently, it would be desirable to provide a lubricating composition capable of providing at least one of (i) reducing or preventing phosphorus emissions, (ii) reducing or preventing sulphur emissions, (ii) wholly or partially replacing ZDDP in lubricating oils, (iii) improving fuel economy, (iv) fuel economy retention/efficiency, and (v) oxidation control. The present invention provides an antiwear agent capable of achieving at least one of (i), (ii) (iii), (iv), and (v).

In addition it may also be desirable for the antiwear agent to not have a detrimental affect on other components of a mechanical device. It may also be desirable for the antiwear agent to have antioxidant performance.

SUMMARY OF THE INVENTION

[0016] In one embodiment the invention provides a lubricating composition comprising an oil of lubricating viscosity, an oil-soluble molybdenum compound, and an ashless antiwear agent represented by Formula (1):



$$R^1-Y-\left(\overset{O}{\|}\right)_m-(X)_n-\overset{O}{\|}-Y'-R^2$$

Formula (1)

wherein
Y and Y' are independently -O-, >NH, >NR^3, or an imide group formed by taking together both Y and Y' groups and forming a R^1-N< group between two >C=O groups;
X is independently -Z-O-Z'-, >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), >C(CO$_2$R^2)$_2$, >CCH$_2$CO$_2$R^2, or >CHOR^6;
Z and Z' are independently >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), or >CHOR^6;
n is 0 to 10, or 1 to 8, or 1 to 6, or 2 to 6, or 2 to 4, with the proviso that when n=1, X is not >CH$_2$, and when n=2, both X's are not simultaneously >CH$_2$;
m is 0 or 1;
R^1 is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18, or 8 to 10 carbon atoms, with the proviso that when R^1 is hydrogen, m is 0, and n is more than or equal to 1;
R^2 is a hydrocarbyl group, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18, or 8 to 10 carbon atoms;
R^3, R^4 and R^5 are independently hydrocarbyl groups or hydroxy-containing hydrocarbyl groups or carboxyl-containing hydrocarbyl groups; and
R^6 is hydrogen or a hydrocarbyl group, typically containing 1 to 150, or 4 to 30 carbon atoms.

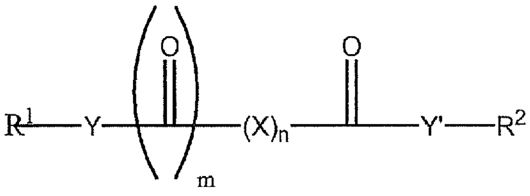
[0017] In one embodiment the lubricating composition is characterised as having at least one of (i) a sulphur content of 0.8 wt % or less, (ii) a phosphorus content of 0.2 wt % or less, or (iii) a sulphated ash content of 2 wt % or less.

[0018] In one embodiment the invention the lubricating composition is characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, and (iii) a sulphated ash content of 1.5 wt % or less.

[0019] In one embodiment the invention provides a method of lubricating an internal combustion engine comprising, supplying to the internal combustion engine a lubricating compositions as disclosed herein.

[0020] In one embodiment the invention provides for the use of a lubricating composition as disclosed herein for providing at least one of (i) reducing or preventing phosphorus emissions, (ii) reducing or preventing sulphur emissions, (ii) wholly or partially replacing ZDDP in lubricating oils, (iii) improving fuel economy, and (iv) fuel economy retention/efficiency.

[0021] In one embodiment the invention provides for the use of a compound of Formula (1) as an antioxidant in a lubricant, wherein the compound of Formula (1) may be represented by:



$$R^1-Y-\left(\overset{O}{\|}\right)_m-(X)_n-\overset{O}{\|}-Y'-R^2$$

wherein
Y and Y' are independently -O-, >NH, >NR^3, or an imide group formed by taking together both Y and Y' groups and forming a R^1-N< group between two >C=O groups;
X is independently -Z-O-Z'-, >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), >C(CO$_2$R^2)$_2$, or >CHOR^6;
Z and Z' are independently >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), or >CHOR^6;

n is 0 to 10, or 1 to 8, or 1 to 6, or 2 to 6, or 2 to 4, with the proviso that when n=1, X is not >CH_2, and when n=2, both X's are not >CH_2;
m is 0 or 1;
R^1 is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18, or 8 to 10 carbon atoms, with the proviso that when R^1 is hydrogen, m is 0, and n is more than or equal to 1;
R^2 is a hydrocarbyl group, typically containing 1 to 150, 4 to 30, or 6 to 20, or 10 to 20, or 11 to 18, or 8 to 10 carbon atoms;
R^3, R^4 and R^5 are independently hydrocarbyl groups; and
R^6 is hydrogen or a hydrocarbyl group, typically containing 1 to 150, or 4 to 30 carbon atoms.

[0022] In one embodiment the invention provides for the use of the compound of Formula (1) as an antioxidant in a lubricant, wherein the compound of Formula (1) is an ester (such as a monoester, a diester or a triester).

[0023] In one embodiment the invention provides for the use of the compound of Formula (1) as an antioxidant in a lubricant, wherein the compound of Formula (1) is not a citrate.

[0024] In one embodiment the invention provides for the use of a tartaric acid derivative (typically a tartrate ester) as an antioxidant in a lubricant.

[0025] In one embodiment the invention provides for the use of the compound of Formula (1) (typically a tartaric acid derivative) as an antioxidant in an internal combustion engine lubricant.

DETAILED DESCRIPTION OF THE INVENTION

[0026] The present invention provides a lubricating composition and a method for lubricating an engine as disclosed above.

Oil-Soluble Molybdenum Compound)

[0027] The oil-soluble molybdenum compound may have the functional performance of an antiwear agent, an antioxidant, a friction modifier, or mixtures thereof. Typically, the oil-soluble molybdenum compound includes molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, amine salts of molybdenum compounds, molybdenum xanthates, molybdenum sulphides, molybdenum carboxylates, molybdenum alkoxides, or mixtures thereof. The molybdenum sulphides include molybdenum disulphide. The molybdenum disulphide may be in the form of stable dispersions. In one embodiment the oil-soluble molybdenum compound may be selected from the group consisting of molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, amine salts of molybdenum compounds, and mixtures thereof. In one embodiment the oil-soluble molybdenum compound is a molybdenum dithiocarbamate.

[0028] Suitable examples of molybdenum dithiocarbamates which may be used as an antioxidant include commercial materials sold under the trade names such as Molyvan 822™ and Molyvan™ A from R. T. Vanderbilt Co., Ltd., and Adeka Sakura-Lube™ S-100, S-165, S-515, and S-600 from Asahi Denka Kogyo K. K and mixtures thereof.

[0029] The oil-soluble molybdenum compound may be present in an amount sufficient to provide 0.5 ppm to 2000 ppm, 1 ppm to 700 ppm, 1 ppm to 550 ppm, 5 ppm to 300 ppm, or 20 ppm to 250 ppm of molybdenum.

Ashless Antiwear Agent

[0030] In one embodiment the compound of Formula (1) is an ashless antiwear agent, and it may also act as an antioxidant.

[0031] In one embodiment the compound of Formula (1) contains an imide group. The imide group is typically formed by taking together the Y and Y' groups and forming a R^1-N< group between two >C=O groups.

[0032] In one embodiment the compound of Formula (1) has m, n, X, and R^1, R^2 and R^6 defined as follows: m is 0 or 1, n is 1 to 2, X is >$CHOR^6$, and R^1, R^2 and R^6 are independently hydrocarbyl groups containing 4 to 30 carbon atoms.

[0033] In one embodiment Y and Y' are both -O-.

[0034] In one embodiment the compound of Formula (1) has m, n, X, Y, Y' and R^1, R^2 and R^6 defined as follows: m is 0 or 1, n is 1 to 2, X is >$CHOR^6$; Y and Y' are both -O-, and R^1, R^2 and R^6 are independently hydrogen or hydrocarbyl groups containing 4 to 30 carbon atoms.

[0035] In one embodiment the ashless antiwear agent includes imides, di-esters, di-amides, di-imides, ester-amides, ester-imides, or imide-amides. In one embodiment the antiwear agent includes imides, di-esters, di-amides, or ester-amides.

[0036] The di-esters, di-amides, ester-amide, ester-imide compounds of Formula (1) may be prepared by reacting a dicarboxylic acid (such as tartaric acid), with an amine or alcohol, optionally in the presence of a known esterification catalyst. In the case of ester-imide compounds it is necessary to have at least three carboxylic acid groups (such as citric acid). In the case of a di-imide, it is necessary to have at least four carboxylic acid groups. The amine or alcohol typically has sufficient carbon atoms to fulfill the requirements of R^1 and/or R^2 as defined in Formula (1).

[0037] In one embodiment R^1 and R^2 are independently linear or branched hydrocarbyl groups. In one embodiment the hydrocarbyl groups are branched. In one embodiment the hydrocarbyl groups are linear. The R^1 and R^2 may be incorporated into Formula (1) by either an amine or an alcohol. The alcohol includes both monohydric alcohol and polyhydric alcohol. The carbon atoms of the alcohol may be linear chains, branched chains, or mixtures thereof.

[0038] Examples of a suitable branched alcohol include 2-ethylhexanol, isotridecanol, Guerbet alcohols, or mixtures thereof.

[0039] Examples of a monohydric alcohol include methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, nonadecanol, eicosanol, or mixtures thereof. In one embodiment the monohydric alcohol contains 5 to 20 carbon atoms.

[0040] The alcohol includes either a monohydric alcohol or a polyhydric alcohol. Examples of a suitable polyhydric alcohol include ethylene glycol, propylene glycol, 1,3-butylene glycol, 2,3-butylene glycol, 1,5-pentane diol, 1,6-hexane diol, glycerol, sorbitol, pentaerythritol, trimethylolpropane, starch, glucose, sucrose, methylglucoside, or mixtures thereof. In one embodiment the polyhydric alcohol is used in a mixture along with a monohydric alcohol. Typically, in such a combination the monohydric alcohol constitutes at least 60 mole percent, or at least 90 mole percent of the mixture.

[0041] In one embodiment ashless antiwear agent is derived from tartaric acid. The tartaric acid used for preparing the tartrates of the invention can be commercially available, and it is likely to exist in one or more isomeric forms such as d-tartaric acid, 1-tartaric acid or mesotartaric acid, often depending on the source (natural) or method of synthesis (from maleic acid). For example a racemic mixture of d-tartaric acid and 1-tartaric acid is obtained from a catalysed oxidation of maleic acid with hydrogen peroxide (with tungstic acid catalyst). These derivatives can also be prepared from functional equivalents to the diacid readily apparent to those skilled in the art, such as esters, acid chlorides, or anhydrides.

[0042] When the compound of Formula (1) is derived from tartaric acid, resultant tartrates may be solid, semi-solid, or oil depending on the particular alcohol used in preparing the tartrate. For use as additives in a lubricating composition the tartrates are advantageously soluble and/or stably dispersible in such oleaginous compositions. For example, compositions intended for use in oils are typically oil-soluble and/or stably dispersible in an oil in which they are to be used. The term "oil-soluble" as used in this specification and appended claims does not necessarily mean that all the compositions in question are miscible or soluble in all proportions in all oils. Rather, it is intended to mean that the composition is soluble in an oil (mineral, synthetic, etc.) in which it is intended to function to an extent which permits the solution to exhibit one or more of the desired properties. Similarly, it is not necessary that such "solutions" be true solutions in the strict physical or chemical sense. They may instead be micro-emulsions or colloidal dispersions which, for the purpose of this invention, exhibit properties sufficiently close to those of true solutions to be, for practical purposes, interchangeable with them within the context of this invention.

[0043] In one embodiment the ashless antiwear agent includes a compound derived from a hydroxycarboxylic acid. In one embodiment the ashless antiwear agent is derived from at least one of hydroxy-polycarboxylic acid di-ester, a hydroxy-polycarboxylic acid di-amide, a hydroxy-polycarboxylic acid di-imide, a hydroxy-polycarboxylic acid ester-amide, a hydroxy-polycarboxylic acid ester-imide, and a hydroxy-polycarboxylic acid imide-amide. In one embodiment the ashless antiwear agent is derived from at least one of the group consisting of a hydroxy-polycarboxylic acid di-ester, a hydroxy-polycarboxylic acid di-amide, and a hydroxy-polycarboxylic acid ester-amide.

[0044] Examples of a suitable a hydroxycarboxylic acid include citric acid, tartaric acid, lactic acid, glycolic acid, hydroxy-propionic acid, hydroxyglutaric acid, or mixtures thereof. In one embodiment ashless antiwear agent is derived from tartaric acid, citric acid, hydroxy-succinic acid, dihydroxy mono-acids, mono-hydroxy diacids, or mixtures thereof. In one embodiment the ashless antiwear agent includes a compound derived from tartaric acid or citric acid. In one embodiment the ashless antiwear agent includes a compound derived from tartaric acid. In one embodiment the compound of Formula (1) is not a citrate.

[0045] US Patent Application 2005/198894 discloses suitable hydroxycarboxylic acid compounds, and methods of preparing the same.

[0046] Canadian Patent 1183125; US Patent Publication numbers 2006/0183647 and US-2006-0079413; US Patent Application number 60/867402; and British Patent 2 105 743 A, all disclose examples of suitable tartaric acid derivatives.

[0047] In one embodiment the di-esters, di-amides, di-imides, ester-amide, ester-imide, imide-amide compounds are derived from a compound of Formula (1). In one embodiment the di-esters, di-amides, ester-amide, compounds are derived from a compound of Formula (1).

[0048] A detailed description of methods for preparing suitable tartrimides (by reacting tartaric acid with a primary amine) is disclosed in US Patent 4,237,022.

[0049] In one embodiment the ashless antiwear agent includes imide, di-esters, di-amides, ester-amide derivatives of tartaric acid.

[0050] Examples of a suitable citric acid derivative include trialkyl citrates or borated trialkyl citrates. Suitable examples include triethyl citrate, tripentyl citrate with ethyl dipentyl citrate, borated triethyl citrate, tributyl citrate, triethyl citrate transesterified with 1,2-propandiol, triethyl O-acetyl citrate, triethyl citrate octadecyl succinate, or mixtures thereof. A more detailed description of suitable citrates is disclosed in WO 2005/087904 and U.S. Patent 5,338,470. Other suitable citrates include 2-ethylhexyl citrate, dodecyl citrate, or mixtures thereof.

[0051] The ashless antiwear agent of the invention, typically a tartrate, may also function as rust and corrosion inhibitors, friction modifiers, antiwear agents and demulsifiers.

[0052] In one embodiment the ashless antiwear agent is not borated.

[0053] The ashless antiwear agent of the may be present at 0.01 wt % to 20 wt %, or 0.05 to 10 wt %, or 0.1 to 5 wt % of the lubricating composition.

Oils of Lubricating Viscosity

[0054] The lubricating composition comprises an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined and re-refined oils and mixtures thereof.

[0055] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0056] 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.

[0057] 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.

[0058] Natural oils useful in making the inventive lubricants include animal oils, vegetable oils (e.g., castor 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.

[0059] Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerized, oligomerised, or interpolymerised olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), trimers or oligomers of 1-decene, e.g., poly(1-decenes),such materials being often referred to as poly α-olefins, and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulphides and the derivatives, analogs and homologs thereof or mixtures thereof.

[0060] Other synthetic lubricating oils include polyol esters (such as Prolube®3970), diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0061] 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 (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The oil of lubricating viscosity comprises an API Group I, Group II, Group III, Group IV, Group V oil or mixtures thereof. Often the oil of lubricating viscosity is an API Group I, Group II, Group III, Group IV oil or mixtures thereof. Alternatively the oil of lubricating viscosity is often an API Group II, Group III or Group IV oil or mixtures thereof.

[0062] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 wt % the sum of the amount of the ashless antiwear agent, the oil-soluble molybdenum compound and the other performance additives.

[0063] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the invention (comprising (i) the ashless antiwear agent and (ii) the oil-soluble molybdenum compound) is in the form of a concentrate (which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the of components of the invention to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight.

Other Performance Additives

[0064] The composition optionally comprises other performance additives. The other performance additives comprise at least one of metal deactivators, viscosity modifiers, detergents, friction modifiers (other than an oil-soluble molybdenum compound or a compound of Formula (1)), antiwear agents (other than the ashless antiwear agent of the invention), corrosion inhibitors, dispersants, dispersant viscosity modifiers, extreme pressure agents, antioxidants (other than an oil-soluble molybdenum compound of the invention), foam inhibitors, demulsifiers, pour point depressants, seal swelling agents and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[0065] In one embodiment the lubricating composition comprises the ashless antiwear agent and further comprises at least one of a viscosity modifier, an antioxidant, an overbased detergent, a succinimide dispersant, or mixtures thereof.

[0066] In one embodiment the lubricating composition comprising the ashless antiwear agent further comprises a phosphorus-containing antiwear agent.

Detergents

[0067] The lubricant composition optionally further comprises other known neutral or overbased detergents. Suitable detergent substrates include phenates, sulphur containing phenates, sulphonates, salixarates, salicylates, carboxylic acid, phosphorus acid, mono- and/or di- thiophosphoric acid, alkyl phenol, sulphur coupled alkyl phenol compounds, or saligenins. Various overbased detergents and their methods of preparation are described in greater detail in numerous patent publications, including WO2004/096957 and references cited therein. The detergent substrate is typically salted with a metal such as calcium, magnesium, potassium, sodium, or mixtures thereof. In one embodiment the lubricating composition further includes an overbased detergent. Typically the overbased detergent includes phenates, sulphur containing phenates, sulphonates, salixarates, salicylates, or mixtures thereof.

[0068] The detergent may be present at 0 wt % to 10 wt %, or 0.1 wt % to 8 wt %, or 1 wt % to 4 wt %, or greater than 4 to 8 wt %.

Dispersants

[0069] Dispersants are often known as ashless-type dispersants because, prior to mixing in a lubricating oil composition, they do not contain ash-forming metals and they do not normally contribute any ash forming metals when added to a lubricant and polymeric dispersants. Ashless type dispersants are characterised by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides. Examples of N-substituted long chain alkenyl succinimides include polyisobutylene succinimide with number average molecular weight of the polyisobutylene substituent in the range 350 to 5000, or 500 to 3000. Succinimide dispersants and their preparation are disclosed, for instance in US Patent 3,172,892 or US Patent 4,234,435 or in EP 0355895. Succinimide dispersants are typically the imide formed from a polyamine, typically a poly(ethyleneamine).

[0070] In one embodiment the invention further comprises at least one polyisobutylene succinimide dispersant derived from polyisobutylene with number average molecular weight in the range 350 to 5000, or 500 to 3000. The polyisobutylene succinimide may be used alone or in combination with other dispersants.

[0071] In one embodiment the invention further comprises at least one dispersant derived from polyisobutylene succinic anhydride, an amine and zinc oxide to form a polyisobutylene succinimide complex with zinc. The polyisobutylene succinimide complex with zinc may be used alone or in combination.

[0072] Another class of ashless dispersant is Mannich bases. Mannich dispersants are the reaction products of alkyl phenols with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). The alkyl group typically contains at least 30 carbon atoms.

[0073] The dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron, urea, thiourea, dimercaptothiadiazoles, carbon disulphide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds.

[0074] The dispersant may be present at 0 wt % to 20 wt %, or 0.1 wt % to 15 wt%, or 0.1 wt % to 10 wt %, or 1 wt % to 6 wt %, or 7 wt % to 12 wt % of the lubricating composition.

Antioxidants

[0075] Antioxidant compounds are known and include for example, sulphurised olefins (typically sulphurised 4-carbobutoxy cyclohexene, or triphenylphosphite equivalents thereof, or olefin sulphide), alkylated diphenylamines (e.g., nonyl diphenylamine, typically di-nonyl diphenylamine, octyl diphenylamine, di-octyl diphenylamine), hindered phenols, or mixtures thereof. Antioxidant compounds may be used alone or in combination. The antioxidant may be present in ranges 0 wt % to 20 wt %, or 0.1 wt % to 10 wt %, or 1 wt % to 5 wt %, of the lubricating composition.

[0076] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group is often further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 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 or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant is an ester and may include, e.g., Irganox™ L-135 from Ciba or as addition product derived from 2,6-di-tert-butylphenol and an alkyl acrylate, wherein the alkyl group may contain 1 to 18, or 2 to 12, or 2 to 8, or 2 to 6, or 4 carbon atoms. A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in US Patent 6,559,105.

[0077] In one embodiment the lubricant does not contain (or contains reduced amounts of) phenolic antioxidant, when the compound of Formula (1) is employed. This embodiment may be useful because the compound of Formula (1) may be used as a partial or whole replacement for phenolic antioxidants. It is believed that during the preparation of tertiary butyl phenols trace amounts of an impurity tris-tert-butyl phenol are formed and retained in the final product. Tris-tert-butyl phenol is known to bioaccumulate and builds up to high concentrations in sediment. Thus employing the compound of Formula (1) as an antioxidant may allow for reduction of bioaccumulants.

Viscosity Modifiers

[0078] Viscosity modifiers include hydrogenated copolymers of styrenebutadiene, ethylene-propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, hydrogenated isoprene polymers, polymethacrylates, polyacrylates, polyalkyl styrenes, hydrogenated alkenyl aryl conjugated diene copolymers, polyolefins, esters of maleic anhydride-styrene copolymers, or esters of (alpha-olefin maleic anhydride) copolymers, or mixtures thereof.

Dispersant Viscosity Modifiers

[0079] Dispersant viscosity modifiers (often referred to as DVM), include functionalised polyolefins, for example, ethylene-propylene copolymers that have been functionalised with the reaction product of an acylating agent (such as maleic anhydride) and an amine; polymethacrylates functionalised with an amine, or esterified maleic anhydride-styrene copolymers reacted with an amine.

[0080] The total amount of viscosity modifier and/or dispersant viscosity modifier may be 0 wt % to 20 wt %, 0.1 wt % to 15 wt %, or 0.1 wt % to 10 wt %, of the lubricating composition.

Antiwear Agents

[0081] The lubricant composition optionally further comprises at least one other antiwear agent other than the ashless antiwear agent of the invention. Examples of suitable antiwear agents include phosphate esters, sulphurised olefins, sulphur-containing anti-wear additives including metal dihydrocarbyldithiophosphates (such as zinc dialkyldithiophosphates), thiocarbamate-containing compounds including, thiocarbamate esters, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulphides.

[0082] The dithiocarbamate-containing compounds may be prepared by reacting a dithiocarbamate acid or salt with an unsaturated compound. The dithiocarbamate containing compounds may also be prepared by simultaneously reacting an amine, carbon disulphide and an unsaturated compound. Generally, the reaction occurs at a temperature of 25 °C to 125 °C. US Patents 4,758,362 and 4,997,969 describe dithiocarbamate compounds and methods of making them.

[0083] Examples of suitable olefins that may be sulphurised to form an the sulphurised olefin include propylene, butylene, isobutylene, pentene, hexane, heptene, octane, nonene, decene, undecene, dodecene, undecyl, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof. In one embodiment, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof and their dimers, trimers and tetramers are especially useful olefins. Alternatively, the olefin may be a Diels-Alder adduct of a diene such as 1,3-butadiene and an unsaturated ester, such as, butylacrylate.

[0084] Another class of sulphurised olefin includes fatty acids and their esters. The fatty acids are often obtained from vegetable oil or animal oil and typically contain 4 to 22 carbon atoms. Examples of suitable fatty acids and their esters include triglycerides, oleic acid, linoleic acid, palmitoleic acid or mixtures thereof. Often, the fatty acids are obtained from lard oil, tall oil, peanut oil, soybean oil, cottonseed oil, sunflower seed oil or mixtures thereof. In one embodiment fatty acids and/or ester are mixed with olefins, such as α-olefins.

[0085] In an alternative embodiment, the ashless antiwear agent (which may also be described as a friction modifier) may 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 ashless antiwear agent mixture include 5 to 95, or in other embodiments 10 to 90, or 20 to 85, or 20 to 80 weight percent of said mixture. The aliphatic carboxylic acids (especially a monocarboxylic acid) which form the esters are those acids typically containing 12 to 24 or 14 to 20 carbon atoms. Examples of carboxylic acids include dodecanoic acid, stearic acid, lauric acid, behenic acid, and oleic acid.

[0086] 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; butanediol; hexanediol; sorbitol; arabitol; mannitol; sucrose; fructose; glucose; cyclohexane diol; erythritol; and pentaerythritols, including di- and tripentaerythritol. Often the polyol is diethylene glycol, triethylene glycol, glycerol, sorbitol, pentaerythritol or dipentaerythritol. The commercial material known as glycerol monooleate 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 the amounts of the commercial grade material.

[0087] The antiwear agent may be present in ranges including 0 wt % to 15 wt %, or 0 wt % to 10 wt %, or 0.05 wt % to 5 wt %, or 0.1 wt % to 3 wt % of the lubricating composition.

[0088] In one embodiment the lubricating composition is free of zinc dihydrocarbyl dithiophosphate. In one embodiment the lubricating composition further includes zinc dihydrocarbyl dithiophosphate.

Extreme Pressure Agents

[0089] Extreme Pressure (EP) agents that are soluble in the oil include sulphur- and chlorosulphur-containing EP agents, chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; organic sulphides and polysulphides such as dibenzyldisulphide, bis-(chlorobenzyl) disulphide, dibutyl tetrasulphide, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, and sulphurised Diels-Alder adducts; phosphosulphurised hydrocarbons such as the reaction product of phosphorus sulphide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenyl phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids, including, for example, the amine salt of the reaction product of a dialkyldithiophosphoric acid with propylene oxide; and mixtures thereof.

Friction Modifiers

[0090] In one embodiment the further comprises a friction modifier, or mixtures thereof. Typically the friction modifier may be present in ranges including 0 wt % to 10 wt %, or 0.05 wt % to 8 wt %, or 0.1 wt % to 4 wt %.

[0091] Examples of suitable friction modifiers include long chain fatty acid derivatives of long chain fatty acid derivatives of amines, esters, or epoxides; fatty imidazolines (that is, long chain fatty amides, long chain fatty esters, long chain fatty epoxide derivatives, and long chain fatty imidazolines); and amine salts of alkylphosphoric acids.

[0092] Friction modifiers may also encompass materials such as sulphurised fatty compounds and olefins, triglycerides (e.g. sunflower oil) or monoester of a polyol and an aliphatic carboxylic acid (all these friction modifiers have been described as antioxidants or antiwear agents).

[0093] In one embodiment the friction modifier is a long chain fatty amide, a long chain fatty ester, a long chain fatty epoxide derivatives, or a long chain fatty imidazoline.

[0094] In one embodiment the friction modifier is a long chain fatty acid ester (previously described above as an ashless antiwear agent). In another embodiment the long chain fatty acid ester is a mono-ester and in another embodiment the long chain fatty acid ester is a (tri)glyceride.

Other Additives

[0095] Other performance additives such as corrosion inhibitors include those described in paragraphs 5 to 8 of US Application US05/038319 (filed on October 25, 2004 McAtee and Boyer as named inventors), octylamine octanoate, and condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. In one embodiment the corrosion inhibitors include the Synalox® corrosion inhibitor. The Synalox® corrosion inhibitor is typically a homopolymer or copolymer of propylene oxide. The Synalox® corrosion inhibitor is described in more detail in a product brochure with Form No. 118-01453-0702 AMS, published by The Dow Chemical Company. The product brochure is entitled "SYNALOX Lubricants, High-Performance Polyglycols for Demanding Applications."

[0096] Metal deactivators including derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazole derivatives, 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.

Industrial Application

[0097] The lubricating composition may be utilised in a range of surfaces typically found in mechanical devices, including aluminum-alloy surfaces. The mechanical devices include an internal combustion engine, a gearbox, an automatic transmission, a hydraulic or a turbine. Typically the lubricating composition may be an engine oil, a gear oil, an automatic transmission oil, a hydraulic fluid, a turbine oil, a metal working fluid or a circulating oil. In one embodiment the mechanical device is an internal combustion engine.

[0098] In one embodiment the internal combustion engine may be a diesel fuelled engine, a gasoline fuelled engine, a natural gas fuelled engine or a mixed gasoline/alcohol fuelled engine. In one embodiment the internal combustion engine may be a diesel fuelled engine and in another embodiment a gasoline fuelled engine.

[0099] The internal combustion engine may be a 2-stroke or 4-stroke engine. Suitable internal combustion engines include marine diesel engines, aviation piston engines, low-load diesel engines, and automobile and truck engines.

[0100] In one embodiment the internal combustion engine contains components of an aluminium-alloy. The aluminium-alloy includes aluminium silicates, aluminium oxides, or other ceramic materials. In one embodiment the aluminium-alloy is an aluminium-silicate surface. As used herein, the term "aluminum alloy" is intended to be synonymous with "aluminium composite" and to describe a component or surface comprising aluminium and another component intermixed or reacted on a microscopic or nearly microscopic level, regardless of the detailed structure thereof. This would include any conventional alloys with metals other than aluminium as well is composite or alloy-like structures with non-metallic elements or compounds such as with ceramic-like materials.

[0101] The lubricant composition for an internal combustion engine may be suitable for any engine lubricant irrespective of the sulphur, phosphorus or sulphated ash (ASTM D-874) content. The sulphur content of the engine oil lubricant may be 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less, or 0.3 wt % or less. In one embodiment the sulphur content may be in the range of 0.001 wt % to 0.5 wt %, or 0.01 wt % to 0.3 wt %. The phosphorus content may be 0.2 wt % or less, or 0.1 wt % or less, or 0.085 wt % or less, or even 0.06 wt % or less, 0.055 wt % or less, or 0.05 wt % or less. In one embodiment the phosphorus content may be 100 ppm to 1000 ppm, or 325 ppm to 700 ppm. The total sulphated ash content may be 2 wt % or less, or 1.5 wt % or less, or 1.1 wt % or less, or 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less. In one embodiment the sulphated ash content may be 0.05 wt % to 0.9 wt %, or 0.1 wt % or 0.2 wt % to 0.45 wt %. In another embodiment the sulphur content is 0.4 wt % or less, the phosphorus content is 0.08 wt % or less, and the sulphated ash is 1 wt % or less. In yet another embodiment the sulphur content is 0.3 wt% or less, the phosphorus content is 0.05 wt % or less, and the sulphated ash is 0.8 wt % or less.

[0102] In one embodiment the lubricating composition is an engine oil, wherein the lubricating composition is characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, and (iii) a sulphated ash content of 1.5 wt % or less.

[0103] In one embodiment the lubricating composition is suitable for a 2-stroke or a 4-stroke marine diesel internal combustion engine. In one embodiment the marine diesel combustion engine is a 2-stroke engine. The ashless antiwear agent of the invention may be added to a marine diesel lubricating composition at 0.01 to 20 wt %, or 0.05 to 10 wt %, or 0.1 to 5 wt %.

[0104] The following examples provide illustrations of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention.

EXAMPLES

[0105] As used herein all of the quantities for dispersants, detergents and viscosity modifiers shown below include conventional amount of diluent oil Typically the diluent oil constitutes 20 wt % to 90 wt % of each component. For antiwear agents, corrosion inhibitors, antioxidants the amounts shown are on an actives basis i.e. excluding diluent oil because the components are typically not carried in diluent oil.

[0106] Example 1 (EX1): A lubricating composition is prepared containing 1 wt % of di-2-ethylhexyl tartrate, 0.6 wt % of other antiwear agents, 7.9 wt % of dispersants, 1.5 wt % of detergents, 3.6 wt % of antioxidants including an effective amount of molybdenum dithiocarbamate, 6.1 wt % of viscosity modifier, 0.1 wt % of corrosion inhibitor, and 0.1 wt % of friction modifier. The lubricating composition has a sulphated ash content of 0.6 wt %, a phosphorus content of about 570 ppm, and a sulphur content of 0.17 wt %.

[0107] Example 2 (EX2): A lubricating composition is prepared containing 1 wt % of a C_{12-14}-alkyl tartrate, 4.1 wt % of dispersants, 1.4 wt % of detergents, 2.5 wt % of antioxidants including 0.7 wt % of molybdenum dithiocarbamate (commercially available as Sakuralube™515, manufactured by Asahi Denka), 0.56 wt % of antiwear agents, 0.1 wt % of corrosion inhibitor, and 0.1 wt % of friction modifier. The lubricating composition has a phosphorus content of about 560 ppm.

[0108] Comparative Example 1 (CE1): is similar to Example 2 except the composition does not contain 0.7 wt % of molybdenum dithiocarbamate, nor 1 wt % of a C_{12-14}-alkyl tartrate.

[0109] Comparative Example 2 (CE2): is similar to Example 2 except the composition does not contain 0.7 wt % of molybdenum dithiocarbamate.

[0110] Comparative Example 3 (CE3): is similar to Example 2 except the composition does not contain 1 wt % of a C_{12-14}-alkyl tartrate.

[0111] 10 g samples of the examples above are each treated with one volume percent of cumene hydroperoxide. The samples (2 ml portions) are then evaluated for wear performance in an isothermal temperature high frequency reciprocating rig (HFRR) available from PCS Instruments. HFRR conditions for the evaluations are 500g load, 75 minute duration, 1000 micrometer stroke, 20 hertz frequency, and at 105 °C. Wear scar in micrometers and film formation as percent film thickness are then measured with lower wear scar values and higher film formation values indicating improved wear performance. The results obtained are:

Tartrate Examples	Wear Scar (μm)	Film Thickness (%)
EX2	169	95
CE1	358	1
CE2	188	88
CE3	189	57

[0112] Overall the results indicate that the lubricating composition of the invention is capable of providing at least one of (i) reducing or preventing phosphorus emissions, (ii) reducing or preventing sulphur emissions, (ii) wholly or partially replacing ZDDP in lubricating oils, (iii) improving fuel economy, and (iv) fuel economy retention/efficiency.

[0113] Example 3 (EX3): A lubricating composition is designed to meet Euro 4 and Euro 5 emission standards and containing 1 wt % of C_{8-10} alkyl tartrate. The lubricating composition has a phosphorus content of 900 ppm or less, 0.3 wt % or less of sulphur, and 0.9 wt % or less of sulphated ash.

[0114] Example 4 (EX4): A lubricating composition is designed to meet Euro 4 and Euro 5 emission standards and containing 1 wt % of C_{8-10} alkyl tartrate. The lubricating composition has a phosphorus content of 500 ppm or less, 0.2 wt % or less of sulphur, and 0.5 wt % or less of sulphated ash.

[0115] Comparative Examples 4 (CE4) and 5 (CE5): are lubricating composition similar to EX3 and EX4 respectively, except the C_{8-10} alkyl tartrate is not included.

[0116] An iron-catalysed bulk oxidation test is carried out on EX3, EX4, CE4 and CE5. The test is run at 170 °C, with an air flow of 10 litres per hour, and in the presence of 360 ppm of iron catalyst. Oxidation is measured by the monitoring the peak area increase of the CO stretch from FT-IR. The results obtained for EX4 and CE5 indicate that the relative peak area increases by 383 units for EX4. In contrast, the relative peak area increases by 428 units for CE5. Thus using a compound within the definition of Formula (1) of the present invention reduces oxidation of a lubricant (especially an internal combustion engine).

[0117] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. The products formed thereby, including the products formed upon employing lubricant composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses lubricant composition prepared by admixing the components described above.

[0118] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." 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. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention may be used together with ranges or amounts for any of the other elements.

[0119] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

(i) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substit-

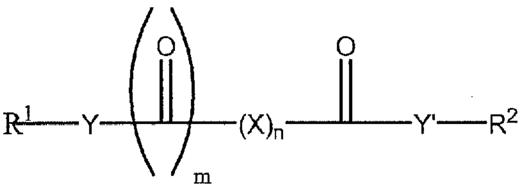
uents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);
(ii) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulphoxy);
(iii) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms.

[0120] Heteroatoms include sulphur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. 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.

[0121] While the invention has been explained in relation to its preferred embodiments, 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.

[0122] The antiwear agent described herein may be an oil-soluble derivative of a molecule containing a first carboxy group and at least one additional -OH,- NHR, or =O moiety separated from the carbon of said first carboxy group by a chain of 2 or 3 atoms, where R is hydrogen or alkyl, e.g, C1-6 alkyl.
Various preferred features and embodiments of the present invention will now be described with reference to the following numbered paragraphs (paras).

1. A lubricating composition comprising an oil of lubricating viscosity, an oil-soluble molybdenum compound, and an ashless antiwear agent represented by Formula (1):



$$R^1\text{—}Y\text{—}\left(\overset{O}{\overset{\|}{C}}\right)_m\text{—}(X)_n\text{—}\overset{O}{\overset{\|}{C}}\text{—}Y'\text{—}R^2$$

Formula (1)

wherein
Y and Y' are independently -O-, >NH, >NR^3, or an imide group formed by taking together both Y and Y' groups and forming a R^1-N< group between two >C=O groups;
X is independently -Z-O-Z'-, >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), >C(CO$_2$R^2)$_2$, >CCH$_2$CO$_2$R^2 or >CHOR^6;
Z and Z' are independently >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), or >CHOR^6;
n is 0 to 10, with the proviso that when n=1, X is not >CH$_2$, and when n=2, both X's are not simultaneously >CH$_2$;
m is 0 or 1;
R^1 is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150 carbon atoms, with the proviso that when R^1 is hydrogen, m is 0, and n is more than or equal to 1;
R^2 is a hydrocarbyl group, typically containing 1 to 150 carbon atoms;
R^3, R^4 and R^5 are independently hydrocarbyl groups or hydroxy-containing hydrocarbyl groups or carboxyl-containing hydrocarbyl groups; and
R^6 is hydrogen or a hydrocarbyl group, typically containing 1 to 150 carbon atoms.
2. The lubricating composition of para 1, wherein the ashless antiwear agent of Formula (1) is derived from at least one hydroxy-polycarboxylic acid.
3. The lubricating composition of para 1 wherein the ashless anti-wear agent comprises a hydroxy-polycarboxylic acid di-ester, a hydroxy-polycarboxylic acid di-amide, a hydroxyl-polycarboxylic acid imide, a hydroxy-polycarboxylic acid di-imide, a hydroxy-polycarboxylic acid ester-amide, a hydroxy-polycarboxylic acid ester-imide, and a hydroxy-polycarboxylic acid imide-amide.
4. The lubricating composition of para 1, wherein the ashless antiwear agent represented by Formula (1) is an imide, a di-ester, or a di-amide..
5. The lubricating composition of para 1, wherein Y and Y' of Formula (1) are both -O-.
6. The lubricating composition of para 1, wherein Formula (1) defines m as 0 or 1, n as 1 to 2, X is >CHOR^6, and

R^1, R^2 and R^6 are independently hydrogen or hydrocarbyl groups containing 4 to 30 carbon atoms.

7. The lubricating composition of para 1 wherein the ashless antiwear agent is derived from tartaric acid or citric acid.

8. The lubricating composition of para 1, wherein the ashless antiwear agent is present at 0.05 to 10 wt %, or 0.1 to 5 wt % of the lubricating composition.

9. The lubricating composition of para 1, wherein the oil-soluble molybdenum compound is selected from at least one member of the group consisitng of molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, amine salts of molybdenum compounds, molybdenum xanthates, molybdenum sulphides, molybdenum carboxylates, and molybdenum alkoxides.

10. The lubricating composition of para 9, wherein the oil-soluble molybdenum compound is selected from at least one member of the group consisting of molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, and amine salts of molybdenum compounds.

11. The lubricating composition of para 10, wherein the oil-soluble molybdenum compound is a molybdenum dithiocarbamate.

12. The lubricating composition of para 1, wherein the oil-soluble molybdenum compound is present in an amount to provide 0.5 ppm to 2000 ppm, 1 ppm to 700 ppm, or 20 ppm to 250 ppm of molybdenum.

13. The lubricating composition of para 1, wherein the lubricating composition is further characterised as having at least one of (i) a sulphur content of 0.8 wt % or less, (ii) a phosphorus content of 0.2 wt % or less, or (iii) a sulphated ash content of 2 wt % or less.

14. The lubricating composition of para 1, wherein the lubricating composition is characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, and (iii) a sulphated ash content of 1.5 wt % or less.

15. The lubricating composition of para 1 further comprises at least one of a friction modifier (other than an oil-soluble molybdenum compound or a compound of Formula (1)), a viscosity modifier, an antioxidant (other than the oil-soluble molybdenum compound), an overbased detergent, a succinimide dispersant, or mixtures thereof.

16. The lubricating composition of para 15, wherein the friction modifier is selected from the group consisting of long chain fatty amides, long chain fatty esters, long chain fatty epoxide derivatives, long chain fatty imidazolines, and amine salts of alkylphosphoric acids.

17. The lubricating composition of para 1 further comprising a phosphorus-containing antiwear agent.

18. The lubricating composition of para 1 further comprising an overbased detergent.

19. The lubricating composition of para 18, wherein the overbased detergent is selected from the group consisting of non-sulphur-containing phenates, sulphur-containing phenates, sulphonates, salixarates, salicylates, and mixtures thereof.

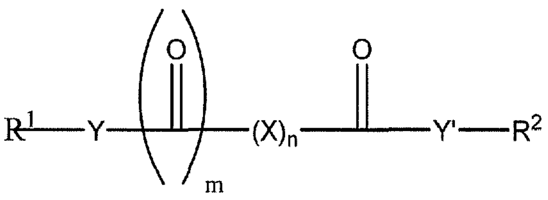
20. A method of lubricating an internal combustion engine comprising, supplying to the internal combustion engine the lubricating composition of para 1.

21. The use of a tartaric acid derivative as an antioxidant in a lubricant.

22. The use of para 21, wherein the tartaric acid derivative is a tartrate ester.

Claims

1. A lubricating composition comprising an oil of lubricating viscosity, an oil-soluble molybdenum compound, and an ashless antiwear agent represented by Formula (1):



$$R^1-Y-\left(\overset{\displaystyle O}{\overset{\|}{C}}\right)_m-(X)_n-\overset{\displaystyle O}{\overset{\|}{C}}-Y'-R^2$$

Formula (1)

wherein

Y and Y' are independently -O-, >NH, >NR^3, or an imide group formed by taking together both Y and Y' groups and forming a R^1-N< group between two >C=O groups;

X is >C(OH)(CO$_2$R^2);

n is 0 to 10, with the proviso that when n=1, X is not >CH$_2$, and when n=2, both X's are not simultaneously >CH$_2$;

m is 1;
R^1 is a hydrocarbyl group, typically containing 6 to 20 carbon atoms; and R^2 is a hydrocarbyl group, typically containing 1 to 150 carbon atoms, wherein the ashless antiwear agent is derived from citric acid,
wherein the oil-soluble molybdenum compound is present in an amount to provide 0.5 ppm to 2000 ppm of molybdenum, and
wherein the ashless antiwear agent is present at 0.1 to 5 wt % of the lubricating composition.

2. The lubricating composition of claim 1, wherein R is a hydrocarbyl group containing 8 to 10 carbon atoms.

3. The lubricating composition of claim 1, wherein Y and Y' of Formula (1) are both -O-.

4. The lubricating composition of claim 1, wherein the oil-soluble molybdenum compound is selected from at least one member of the group consisitng of molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, amine salts of molybdenum compounds, molybdenum xanthates, molybdenum sulphides, molybdenum carboxylates, and molybdenum alkoxides.

5. The lubricating composition of claim 4, wherein the oil-soluble molybdenum compound is selected from at least one member of the group consisting of molybdenum dithiocarbamates, molybdenum dialkyldithiophosphates, and amine salts of molybdenum compounds.

6. The lubricating composition of claim 1, wherein the oil-soluble molybdenum compound is present in an amount to provide 1 ppm to 700 ppm, or 20 ppm to 250 ppm of molybdenum.

7. The lubricating composition of claim 1, wherein the lubricating composition is characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, and (iii) a sulphated ash content of 1.5 wt % or less.

8. The lubricating composition of claim 1 further comprises at least one of a friction modifier (other than an oil-soluble molybdenum compound or a compound of Formula (1)), a viscosity modifier, an antioxidant (other than the oil-soluble molybdenum compound), an overbased detergent, a succinimide dispersant, or mixtures thereof.

9. The lubricating composition of claim 1 further comprising an overbased detergent, wherein the overbased detergent is selected from the group consisting of non-sulphur-containing phenates, sulphur-containing phenates, sulphonates, salixarates, salicylates, and mixtures thereof.

10. A method of lubricating an internal combustion engine comprising, supplying to the internal combustion engine the lubricating composition of claim 1.

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EUROPEAN SEARCH REPORT

Application Number
EP 12 15 8486

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