

TITLE

Method of Lubricating an Internal Combustion Engine

FIELD OF INVENTION

The invention provides a method of lubricating an internal combustion engine in the presence of a contaminant amount of water. The invention further relates to the use of a derivative of a hydroxy-carboxylic acid as a rust inhibitor.

BACKGROUND OF THE INVENTION

[0001] Many modern lubricating oil formulations require the addition of rust inhibitors to prevent or inhibit rust formation, most often caused by water contacting a ferro-metallic based surface. The water is believed to originate as a fuel combustion by-product. The water is believed to ingress through equipment seals or engine blow-by during operation. Some of the contaminant water may then reside in the crankcase, thereby contaminating the lubricant. In most instances the amount of water may be up to 50 ppm or less (typically less than 25 ppm). In order to overcome the rust formation, detergents and other ash-containing additives have been employed. However, recent trends towards reducing the sulphur, sulphated ash and phosphorus levels of lubricants may result in increased occurrences of rust formation.

[0002] The problem highlighted above is believed to be increased for mechanical devices (typically internal combustion engines) where there may be significant amounts of water contacting the ferro-metallic based surface. This example may be exacerbated in salt water e.g., sea water. For example, internal combustion engines used in recreational modes of transport like power boats, snowmobiles, jet-skis, or all-terrain vehicles may be susceptible. Internal combustion engines may be outboards, inboards or stern drive engines.

[0003] 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. The tartrates are disclosed as antiwear agents.

[0004] International Publication WO 2006/044411, and US Patent Applications US 60/939949 (filed May 24, 2007) and US 60/939952 (filed May

24, 2007) all disclose lubricating compositions containing tartrates and/or tartrimides in lubricants for internal combustion engines requiring reduced amounts of sulphur, sulphated ash, and phosphorus. The lubricant composition has anti-wear or anti-fatigue properties. The lubricating compositions are suitable for road vehicles.

[0005] 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.

[0006] US Patent 5,338,470 and International Publication WO 2005/087904 disclose lubricants containing at least one hydroxycarboxylic acid ester or hydroxy polycarboxylic acid (in particular citrates). The lubricant composition has anti-wear or anti-fatigue properties.

[0007] U.S. Patent Application 60/867534 discloses malonate esters suitable as antiwear agents.

[0008] None of the references disclosed above have contemplated reduction or prevention of iron corrosion (may also be referred to as rust inhibition).

SUMMARY OF THE INVENTION

[0009] The inventors of the present invention have discovered that a lubricating composition containing an amide, ester or imide derivative of a hydroxy-carboxylic acid, a method and use as disclosed herein is capable of providing rust inhibition, in particular in the internal combustion engines disclosed herein.

[0010] In one embodiment the invention provides a method for lubricating an internal combustion engine using a lubricating composition comprising:

- (a) an oil of lubricating viscosity;
- (b) either:
 - (i) an amide, ester or imide derivative of a hydroxy-carboxylic acid, or
 - (ii) a monoester of a polyol and an aliphatic carboxylic acid; and
- (c) a contaminant amount of water, wherein the water is present at 500 ppm or more.

[0011] The amide, ester or imide derivative of a hydroxy-carboxylic acid, the monoester of a polyol and an aliphatic carboxylic acid, or mixtures thereof may be present in the lubricating composition at 0.01 wt % to 2 wt %, or 0.1 wt % to 1 wt %, or 0.2 wt % to 0.6 wt % of the lubricating composition.

[0012] In one embodiment the invention provides a method of lubricating an internal combustion engine with an engine capacity of six litres or less comprising supplying to said engine a lubricating composition comprising:

(a) an oil of lubricating viscosity;

(b) either:

(i) an amide, ester or imide derivative of a hydroxy-carboxylic acid, or

(ii) a monoester of a polyol and an aliphatic carboxylic acid; and

(c) a contaminant amount of water, wherein the water is present at 500 ppm or more.

[0013] In one embodiment the invention provides for the use of an amide, ester or imide derivative of a hydroxy-carboxylic acid as a rust inhibitor in a water-contaminated lubricant for an internal combustion engine with an engine capacity of six litres or less.

[0014] In one embodiment the invention provides for the use of monoester of a polyol and an aliphatic carboxylic acid as a rust inhibitor in a water-contaminated lubricant for an internal combustion engine with an engine capacity of six litres or less.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The present invention provides a method and use as disclosed above.

Contaminant Water

[0016] The contaminant water may be present in the lubricating composition at 550 ppm or more, 600 ppm or more, or 750 ppm or more. In one embodiment the amount of contaminant water in the lubricating composition may be at least 0.09 wt % to 3 wt %, or 0.1 wt % to 0.5 wt % water. The water may be fresh water or salt water, or sea water. The sea water contains various salts of magnesium, sodium, potassium, and calcium. Examples include magnesium, sodium, potassium, and calcium chlorides, carbonates and bromides. A person

skilled in the art will appreciate that the contaminant water is typically incorporated into the lubricating composition during normal use of the internal combustion engine with an engine capacity of six litres or less.

Amide, Ester or Imide Derivative of a Hydroxy-Carboxylic Acid

[0017] The amide, ester or imide derivative of a hydroxy-carboxylic acid (typically a hydroxy-polycarboxylic acid), or mixtures thereof may be employed in the present invention as rust inhibitors (i.e., reduce or prevent corrosion of iron).

[0018] In one embodiment the amide, ester or imide derivative of a hydroxy-carboxylic acid may be at least one of a 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 amide, ester or imide derivative of a hydroxy-polycarboxylic acid may be 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.

[0019] Examples of a suitable hydroxycarboxylic acid include mandelic acid, malic acid, citric acid, tartaric acid, lactic acid, glycolic acid, hydroxypropionic acid, hydroxyglutaric acid, or mixtures thereof. In one embodiment the amide, ester or imide derivative of a hydroxy-carboxylic acid may be derived from tartaric acid, citric acid, hydroxy-succinic acid, dihydroxy monoacids, mono-hydroxy diacids, or mixtures thereof. In one embodiment the amide, ester or imide derivative of a hydroxy-carboxylic acid include a compound derived from tartaric acid or citric acid. In one embodiment the amide, ester or imide derivative of a hydroxy-carboxylic acid may include a compound derived from tartaric acid.

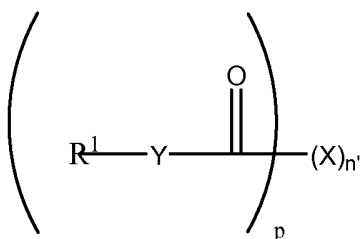
[0020] In one embodiment the derivative of a hydroxy-carboxylic acid is either an ester or imide. The ester derivative of a hydroxy-carboxylic acid may be a tartrate. The imide derivative of a hydroxy-carboxylic acid may be a tartramide, that is, a tartarimide..

[0021] In one embodiment the rust inhibitor is provided by an imide derivative of a hydroxy-carboxylic acid.

[0022] US Patent Applications US 60/939949 (filed May 24, 2007), now WO2008/147704, and US 60/939952 (filed May 24, 2007), now WO2008/147700, disclose suitable hydroxycarboxylic acid compounds, and methods of preparing the same.

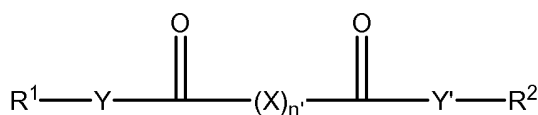
[0023] Canadian Patent 1 183 125; US Patent Publication numbers 2006/0183647 and US-2006-0079413; US Patent Application number 60/867402 now WO2008/067259; and British Patent 2 105 743 A, all disclose examples of suitable tartaric acid derivatives.

[0024] In one embodiment the amide, ester or imide derivative of a hydroxy-carboxylic acid may be represented by Formula (1) (that is, 1a or 1b):



Formula (1a)

or



Formula (1b)

wherein

n' is 0 to 10 for Formula (1b), and 1 to 10 for Formula (1a);

p is 1 to 5;

Y and Y' are independently $-\text{O}-$, $>\text{NH}$, $>\text{NR}^3$, or an imide group formed by taking together both Y and Y' groups in (1b) or two Y groups in (1a) and forming a $\text{R}^1-\text{N}<$ group between two $>\text{C}=\text{O}$ groups;

X is independently $-\text{CH}_2-$, $>\text{CHR}^4$ or $>\text{CR}^4\text{R}^5$, $>\text{CHOR}^6$, or $>\text{C}(\text{CO}_2\text{R}^6)_2$, or $>\text{C}(\text{OR}^6)\text{CO}_2\text{R}^6$, or $-\text{CH}_3$, $-\text{CH}_2\text{R}^4$ or CHR^4R^5 , $-\text{CH}_2\text{OR}^6$, or $-\text{CH}(\text{CO}_2\text{R}^6)_2$, $\equiv\text{C}-\text{R}^6$ (where $\equiv$ equals three valences, and may only apply to Formula (1a)) or mixtures thereof to fulfill the valence of Formula (1a) and/or (1b) (typically the

compound of Formula (1a) or (1b) has at least one X that is hydroxyl-containing (i.e., $>\text{CHOR}^6$, wherein R^6 is hydrogen));

R^1 and R^2 are independently hydrocarbyl groups, typically containing 1 to 150, or 4 to 30, or 8 to 15 carbon atoms;

R^3 is a hydrocarbyl group;

R^4 and R^5 are independently keto-containing groups (such as acyl groups), ester groups or hydrocarbyl groups; and

R^6 is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150, or 4 to 30, or 8 to 15 carbon atoms.

[0025] 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 $\text{R}^1\text{-N}<$ group between two $>\text{C}=\text{O}$ groups.

[0026] 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 $>\text{CHOR}^6$, and R^1 , R^2 and R^6 are independently hydrocarbyl groups containing 4 to 30 carbon atoms.

[0027] In one embodiment Y and Y' are both -O-.

[0028] 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 $>\text{CHOR}^6$; 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.

[0029] 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 catalyst. In the case of ester-imide compounds it is necessary to have at least three carboxylic acid groups (such as citric acid). 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).

[0030] 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.

[0031] Examples of a suitable branched alcohol include 2-ethylhexanol, isotridecanol, Guerbet alcohols, or mixtures thereof.

[0032] 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.

[0033] 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-pentanediol, 1,6-hexanediol, 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.

[0034] The tartaric acid used for preparing the tartrates of the invention is commercially available, and it is likely to exist in one or more isomeric forms such as d-tartaric acid, l-tartaric acid, d,l-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 l-tartaric acid is obtained from a catalysed oxidation of maleic acid with hydrogen peroxide (with tungstic acid catalyst). These derivatives may also be prepared from functional equivalents to the diacid readily apparent to those skilled in the art, such as esters, acid chlorides, or anhydrides.

[0035] 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.

Monoester of a Polyol and an Aliphatic Carboxylic Acid

[0036] In one embodiment the lubricating composition includes the monoester of a polyol and an aliphatic carboxylic acid, or mixtures thereof. The monoester of a polyol and an aliphatic carboxylic acid may be an acid containing 12 to 24 carbon atoms. Often the monoester of a polyol and an aliphatic carboxylic acid may be in the form of a mixture with a sunflower oil or the like, which may be present in 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.

[0037] 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. The polyol may be diethylene glycol, triethylene glycol, glycerol, sorbitol, pentaerythritol or dipentaerythritol.

[0038] The commercially available monoester known as “glycerol monooleate” is believed to include 60 ± 5 percent by weight of the chemical species glycerol monooleate, along with 35 ± 5 percent glycerol dioleate, and less than 5 percent trioleate and oleic acid. The amounts of the monoesters, described above, are calculated based on the actual, corrected, amount of polyol monoester present in any such mixture.

[0039] In one embodiment both the amide, ester or imide derivative of a hydroxy-carboxylic acid and the monoester of a polyol and an aliphatic carboxylic acid may have hydroxy groups attached to adjacent carbon atoms (i.e., said compounds may be described as being derived from a vicinal diol).

Oils of Lubricating Viscosity

[0040] 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.

[0041] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0042] 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.

[0043] 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.

[0044] 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.

[0045] Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerised and interpolymers olefins (typically hydrogenated) (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkylbenzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulphides and the derivatives, analogs and homologs thereof or mixtures thereof.

[0046] Other synthetic lubricating oils include polyol esters (such as Priolube®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.

[0047] 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 includes 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.

[0048] 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 compound of the invention and the other performance additives.

[0049] 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 the additives disclosed herein above 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 these additives to the oil of lubricating viscosity and/or to diluent oil in the concentrate or the lubricant include the ranges of 1:99 to 99:1 by weight, or 10:90 to 80:20 by weight.

Other Performance Additives

[0050] The composition optionally includes other performance additives. The other performance additives comprise at least one of metal deactivators, viscosity modifiers, detergents, friction modifiers, antiwear agents, corrosion inhibitors, dispersants, dispersant viscosity modifiers, extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, emulsifiers, pour point depressants, seal swelling agents and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[0051] In one embodiment the lubricating composition of the invention further includes at least one of a friction modifier, a viscosity modifier, an antioxidant, an overbased detergent, a succinimide dispersant, or mixtures thereof.

[0052] In one embodiment the lubricating composition of the invention further includes at least one of a viscosity modifier, an antioxidant, an overbased detergent, a succinimide dispersant, or mixtures thereof.

Detergents

[0053] In one embodiment the lubricating composition further includes one or more neutral or overbased detergents. Suitable known detergents or detergent substrates include phenates, sulphur containing phenates, sulphonates, salixarates, salicylates, carboxylic acid, phosphorus acid, mono- and/or di- thiophosphoric acids, alkyl phenols, 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 may be salted with a metal such as calcium, magnesium, potassium, sodium, or mixtures thereof.

[0054] In one embodiment the overbased detergent is selected from the group consisting of phenates, sulphur containing phenates, sulphonates, salixarates, salicylates, and mixtures thereof. Typically the selected overbased detergent includes calcium or magnesium phenates, sulphur containing phenates, sulphonates, salixarates, saliginens, salicylates, or mixtures thereof.

[0055] In one embodiment the detergent may be a calcium salicylate. In one embodiment the detergent may be a calcium sulphonate. In one embodiment the invention the detergent may be a mixture of a calcium sulphonate and a calcium salicylate.

[0056] In one embodiment the detergent may be a calcium phenate. In one embodiment the detergent may be a calcium sulphonate. In one embodiment the invention the detergent may be a mixture of a calcium sulphonate and a calcium phenate.

[0057] The detergent may be present at 0 wt % to 10 wt %, or 0.1 wt % to 8 wt %, or 1 wt % to 4 wt % (on an oil free basis i.e., an actives basis) of the lubricating composition.

Dispersants

[0058] 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. 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. Succinimide dispersants are typically the imide formed from a polyamine, typically a poly(ethyleneamine).

[0059] In one embodiment the invention further includes at least one dispersant which is a polyisobutylene succinimide derived from a 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.

[0060] In one embodiment the invention further includes 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.

[0061] Another class of ashless dispersant includes 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.

[0062] 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, dimercapthiadiazoles, carbon disulphide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds.

[0063] The dispersant may be present (on an oil free basis i.e., an actives basis) 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 % of the lubricating composition.

Antioxidants

[0064] Antioxidant compounds are known and include for example, sulphurised olefins, alkylated diphenylamines (typically di-nonyl diphenylamine, octyl diphenylamine, di-octyl diphenylamine), hindered phenols, molybdenum compounds (such as molybdenum dithiocarbamates), or mixtures thereof. Antioxidant compounds may be used alone or in combination. The antioxidant may be present in ranges (on an oil free basis i.e., an actives basis) of 0 wt % to 20 wt %, or 0.1 wt % to 10 wt %, or 1 wt % to 5 wt %, of the lubricating composition.

[0065] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group (typically linear or branched alkyl) 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 may be an ester and may include, e.g., Irganox™ L-135 from Ciba. A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in US Patent 6,559,105.

[0066] In one embodiment the lubricating composition further includes a molybdenum compound.

[0067] The molybdenum compound is selected from the group consisting of molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, amine salts of molybdenum compounds, and mixtures thereof.

[0068] 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.

[0069] When present, the molybdenum compound may provide 5 ppm to 300 ppm, or 20 ppm to 250 ppm of molybdenum to the lubricating composition.

Viscosity Modifiers

[0070] Viscosity modifiers include hydrogenated copolymers of styrene-butadiene, ethylene-propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, hydrogenated isoprene polymers, polymethacrylates, polyacrylates, polyalkyl styrenes, hydrogenated alkenyl arene conjugated diene copolymers, polyolefins, esters of maleic anhydride-styrene copolymers.

Dispersant Viscosity Modifiers

[0071] Dispersant viscosity modifiers (often referred to as DVM), include functionalised polyolefins, for example, ethylene-propylene copolymers that have been functionalized with an acylating agent such as maleic anhydride and an amine; polymethacrylates functionalised with an amine, or styrene-maleic anhydride copolymers reacted with an amine.

Antiwear Agents

[0072] In one embodiment the lubricating composition further includes an antiwear agent.

[0073] The additional antiwear agent may be either ashless or ash-forming. Typically ashless antiwear agents do not contain metal, whereas ash-forming do contain metal.

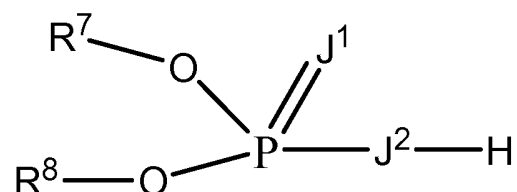
[0074] The antiwear agent may be present (on an oil free basis i.e., an actives basis) in ranges including 0 wt % to 15 wt %, or 0 wt % to 10 wt %, or 0.05 wt % to 5 wt %, or 0.1 wt % to 3 wt % of the lubricating composition.

[0075] In one embodiment the lubricating composition further includes a phosphorus-containing antiwear agent. Typically the phosphorus-containing antiwear agent may be present in an amount to deliver the ranges of phosphorus described below in the subject matter under the sub-heading "Industrial Application".

[0076] Examples of suitable antiwear agents include phosphate esters, sulphurised olefins, sulphur-containing anti-wear additives including metal dihydrocarbyldithiophosphates (such as primary or secondary zinc dialkyldithiophosphates, or molybdenum dialkyldithiophosphates), molybdenum thiocarbamate-containing compounds including thiocarbamate esters, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulphides.

[0077] Examples of suitable zinc dialkyldithiophosphates include those disclosed in PCT Application US07/073428 (entitled "Method of Lubricating an Internal Combustion Engine and Improving the Efficiency of the Emissions Control System of the Engine") or in PCT Application US07/073426 (entitled "Lubricating Oil Composition and Method of Improving Efficiency of

Emissions Control System”). Both applications claim priority from July 17, 2006. The zinc dialkyldithiophosphates or dialkylphosphates in one embodiment may be defined as a zinc salt of a mixture of phosphorus-containing compounds represented by the formula:



wherein in formula, J^1 and J^2 are independently S or O, and R^7 and R^8 may be independently hydrocarbyl groups, the average total number of carbon atoms in R^7 plus R^8 for the mixture of phosphorus-containing compounds being at least 9.5; wherein R^7 and R^8 are characterised in that (i) 4 to 70 mole percent of such groups contain 2 to 4 carbon atoms and (ii) 30 to 96 mole percent such groups contain 5 to 12 carbon atoms; and wherein, in less than 8 mole percent of the molecules of the formula in the mixture of phosphorus-containing compounds, each of R^7 and R^8 contain 2 to 4 carbon atoms and in greater than 11 mole percent of the molecules of the formula in said mixture R^7 has 2 to 4 carbon atoms and R^8 has 5 to 12 carbon atoms; and wherein, within the formula, the average total number of hydrogen atoms in R^7 and R^8 on carbon atoms located beta to the O atoms is at least 7.25.

[0078] 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.

[0079] Examples of suitable olefins that may be sulphurised to form an 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.

[0080] 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.

Extreme Pressure Agents

[0081] 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 dibenzyl disulphide, 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, dioleoyl phosphite, di-2-ethylhexyl phosphite, didodecylphosphite, di-C₁₂₋₁₄alkyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol 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

[0082] In one embodiment the further includes a friction modifier, or mixtures thereof. Typically the friction modifier may be present (on an oil free basis i.e., an actives basis) in ranges including 0 wt % to 10 wt %, or 0.05 wt % to 8 wt %, or 0.1 wt % to 4 wt %.

[0083] Examples of suitable friction modifiers include long chain fatty acid derivatives of amines, esters, or epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; or fatty alkyl tartramides. A more detailed description of the tartrates and tartrimides are disclosed above. The tartrimides and tartrates in addition to performing as a rust inhibitor as described above, may also perform as a friction modifier.

[0084] Friction modifiers may also encompass materials such as sulphurised fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or monoester of a polyol and an aliphatic carboxylic acid (all these friction modifiers have been described as antioxidants or antiwear agents).

[0085] In one embodiment the friction modifier friction modifier is selected from the group consisting of long chain fatty acid derivatives of amines, esters, or epoxides; fatty alkyl tartrates; fatty alkyl tartrimides; and fatty alkyl tartramides.

[0086] In one embodiment the friction modifier may be a long chain fatty acid ester (previously described above as an ashless antiwear agent). In one embodiment the long chain fatty acid ester may be a mono-ester e.g. glycerol monooleate and in one embodiment the long chain fatty acid ester may be a (tri)glyceride.

Other Additives

[0087] 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, 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.”

[0088] Metal deactivators including derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazone 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 may be useful. Foam inhibitors that may be useful in the compositions of the invention include 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.

[0089] Pour point depressants that may be useful in the compositions of the invention include polyalphaolefins, esters of maleic anhydride-styrene, poly(meth)acrylates, polyacrylates or polyacrylamides.

Industrial Application

[0090] In one embodiment the internal combustion engine may be a diesel fueled engine, a gasoline fueled engine, a natural gas fueled engine or a mixed gasoline/alcohol fueled engine. In one embodiment the internal combustion engine may be a diesel fueled engine and in one embodiment a gasoline fueled engine.

[0091] In one embodiment the internal combustion engine capacity may be six litres or less, or three litres or less, one litre or less, 0.5 litres or less, or 0.2 to 0.45 litres. The engine capacity may be described as engine displacement. Engine displacement is defined as the total volume of air/fuel mixture an engine draws during one complete cycle. Engine displacement may also be described as the

total volume swept as the piston or pistons move from top dead centre to bottom dead centre.

[0092] In one embodiment the internal combustion engine may be an outboard engine, inboard engine or stern drive engine.

[0093] An outboard engine is described in the National Marine Manufacturers Association October 1 2004/ (revised 5 April 2005 Certification Procedure Manual for understanding of engines).

[0094] In one embodiment the internal combustion engine may be a gasoline 4-cycle engine.

[0095] In one embodiment the internal combustion engine may be a gasoline 4-cycle outboard engine.

[0096] As used herein the components of the internal combustion engine include all of the parts of the engine derived from metal lubricated by an engine lubricant. This includes for example, cylinder liners, camshafts, piston heads etc.

[0097] In one embodiment the internal combustion engine contains ferric components. The ferric components include metallic iron, steel, FeO, Fe₃O₄ or other materials containing iron.

[0098] 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.

[0099] The lubricating 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 200 ppm to 600 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 % to 0.2 wt % to 0.45 wt %.

[0100] In one embodiment the lubricating composition may be an engine oil, wherein the lubricating composition may be characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.07 wt % or less, and (iii) a sulphated ash content of 1.5 wt % or less.

[0101] In one embodiment the lubricating composition may be characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.12 wt % or less, and (iii) a sulphated ash content of 1 wt % or less.

[0102] 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

[0103] Comparative Example 1 (CE1): is a passenger car lubricant containing 800 ppm of phosphorus (phosphorus from zinc dialkylthiophosphate), glycerol monooleate and molybdenum dithiocarbamate. The lubricant contains at most 25 ppm (and ideally no) water.

[0104] Comparative Example 2 (CE2): is a passenger car lubricant containing 800 ppm of phosphorus (phosphorus from zinc dialkylthiophosphate) and a tartrate ester. The lubricant contains at most 25 ppm (and ideally no) water.

Testing

[0105] CE1 and CE2 are evaluated for copper and lead corrosion by ASTM methods D6594 and D130. The lubricants are evaluated in Sequence VIII test.

[0106] The results obtained for CE1 and CE2 are:

Tests	CE1	CE2
ASTM D6594		
Change in lead mass (mg)	217	13
Change in copper mass (mg)	11	4
Copper rating (ASTM D130)	4C	1B
Sequence VIII Test		
Final Bearing Weight Loss (mg) (pass limit max. 26 mg)	34.1	6.6

[0107] Overall the results obtained when comparing CE2 to CE1 indicate that lubricants containing tartrates are useful for reducing copper and lead corrosion in a passenger car lubricant.

[0108] Comparative Example 3 (CE3): is a commercially available outboard engine lubricant. The lubricant is expected to be exposed to contaminant amounts of water during operation.

[0109] Comparative Example 4 (CE4): is another commercially available outboard engine lubricant. The lubricant contains an overbased detergent known to be capable of reducing rust formation. The lubricant is expected to be exposed to contaminant amounts of water during operation.

[0110] Example 1 (EX1): is an outboard engine lubricant containing 800 ppm of phosphorus (phosphorus from zinc dialkylthiophosphate) and a C₁₂₋₁₄ alkyl tartrate ester. The lubricant is expected to be exposed to contaminant amounts of water during operation.

[0111] Example 2 (EX2): is an outboard engine lubricant containing 800 ppm of phosphorus (phosphorus from zinc dialkylthiophosphate) and a C₁₈ alkyl tartramide. The lubricant is expected to be exposed to contaminant amounts of water during operation.

[0112] Example 3 (EX3): is an outboard engine lubricant containing 800 ppm of phosphorus (phosphorus from zinc dialkylthiophosphate) and glycerol monooleate. The lubricant is expected to be exposed to contaminant amounts of water during operation.

Testing

[0113] CE3, CE4, EX1, EX2 and EX3 are evaluated for copper and lead corrosion by ASTM methods D6594. The results obtained are:

ASTM D6594	CE3	CE4	EX1	EX2	EX3
Change in copper mass (mg)	15	6	18	46	12
Change in lead mass (mg)	2	3	3	22	19

[0114] The results show that although tartrates, tartrides and glycerol monooleate are useful for solving copper and lead corrosion in many lubricant formulations, they do not appear to be as effective in outboard formulations for reducing copper and lead corrosion.

[0115] CE3, CE4, EX1, EX2 and EX3 are then evaluated for rust inhibition in a humidity cabinet (ASTM method D1748-02) to determine the tendency to corrode various metals, specifically iron. The steel strips of the test are suspended in the humidity cabinet at 49 °C for 100 hours. The steel strips are rated on a scale of 0 to 100 %. Typically lower percent ratings indicate reduced surface rust formation. The results obtained are:

Humidity Cabinet	CE3	CE4	EX1	EX2	EX3
Rating (% surface with rust)	40-50	5-10	2-5	0	0

[0116] CE4, EX1 and EX2 are evaluated in 4-cycle watercraft test entitled Corrosion Salt Fog Test. The test is described in the National Marine Manufacturers Association October 1 2004/ (revised 5 April 2005 Certification Procedure Manual for understanding of engines) pages 7 to 13. Each sample is evaluated by comparing the rating to a standard reference run concurrently in the same cabinet. The average percent rust of the candidate is calculated from 4 individual runs. Typically, passing candidates have a percent rust less than that obtained for a reference oil calculated in the same manner. The results obtained from the test are:

Salt Fog Test		CE3	CE4	EX1	EX2	EX3
Percent Rust	Candidate	50	46	14	2	2
Percent Rust	Reference	30	35	35	25	25

[0117] Overall the results obtained for EX1, EX2 and EX3 indicate that lubricants containing tartrates, tartrimides or glycerol monooleate reduce rust formation in outboard engines.

[0118] 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 lubricating 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 lubricating composition prepared by admixing the components described above.

[0119] 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. Multiple groups represented by the same symbol in the formulae described above, may be the same or different.

[0120] 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) substituents, 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 sulphony);

(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, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl; and

(iv) heteroatoms, including sulphur, oxygen, and nitrogen. 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.

What is claimed is:

1. A method of lubricating an internal combustion engine with an engine capacity of six litres or less comprising supplying to said engine a lubricating composition comprising:

(a) an oil of lubricating viscosity;

(b) an amide, ester or imide derivative of a hydroxy-carboxylic acid; and

(c) a contaminant amount of water, wherein the water is present at 500 ppm or more.

2. The method of claim 1, wherein the engine capacity is three litres or less

3. The method of claim 1, wherein the engine capacity is one litre or less.

4. The method of any one of claims 1 to 3, wherein the internal combustion engine is an outboard engine, inboard engine or stern drive engine.

5. The method of any one of claims 1 to 4, wherein the internal combustion engine is gasoline 4-cycle outboard engine.

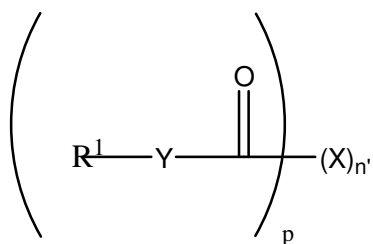
6. The method of any one of claims 1 to 5, wherein the lubricating composition contains at least 0.09 wt % to 3 wt % water.

7. The method of any one of claims 1 to 5, wherein the lubricating composition contains at least 0.1 wt % to 0.5 wt % water.

8. The method of any one of claims 1 to 7, wherein the lubricating composition is characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.12 wt % or less, and (iii) a sulphated ash content of 1 wt % or less.

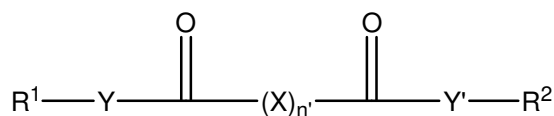
9. The method of any one of claims 1 to 8, wherein the derivative of a hydroxy-carboxylic acid is selected from the group consisting of a hydroxy-polycarboxylic acid di-ester, a hydroxy-polycarboxylic acid di-amide, a hydroxyl-polycarboxylic acid imide, a hydroxy-polycarboxylic acid di-imide, a hydroxy-polycarboxylic acid ester-amide, a hydroxy-polycarboxylic acid ester-imide, and a hydroxy-polycarboxylic acid imide-amide.

10. The method of any one of claims 1 to 9, wherein the derivative of a hydroxy-carboxylic acid is



Formula (1a)

or



Formula (1b)

wherein

n' is 0 to 10 for Formula (1b), and 1 to 10 for Formula (1a);

p is 1 to 5;

Y and Y' are independently $-\text{O}-$, $>\text{NH}$, $>\text{NR}^3$, or an imide group formed by taking together both Y and Y' groups in (1b) or two Y groups in (1a) and forming a $\text{R}^1-\text{N}<$ group between two $>\text{C}=\text{O}$ groups;

X is independently $-\text{CH}_2-$, $>\text{CHR}^4$ or $>\text{CR}^4\text{R}^5$, $>\text{CHOR}^6$, or $>\text{C}(\text{CO}_2\text{R}^6)_2$, or $>\text{C}(\text{OR}^6)\text{CO}_2\text{R}^6$, or $-\text{CH}_3$, $-\text{CH}_2\text{R}^4$ or CHR^4R^5 , $-\text{CH}_2\text{OR}^6$, or $-\text{CH}(\text{CO}_2\text{R}^6)_2$, $\equiv\text{C}-\text{R}^6$ (where $\equiv$ equals three valences, and may only apply to Formula (1a)) or mixtures thereof to fulfill the valence of Formula (1a) and/or (1b);

R^1 and R^2 are independently hydrocarbyl groups;

R^3 is a hydrocarbyl group;

R^4 and R^5 are independently keto-containing groups, ester groups or hydrocarbyl groups; and

R^6 is independently hydrogen or a hydrocarbyl group.

11. Use of an amide, ester or imide derivative of a hydroxy-carboxylic acid as a rust inhibitor in a water-contaminated lubricant for an internal combustion engine with an engine capacity of six litres or less, wherein water contaminant is present at 500ppm or more.

12. The use of claim 11, wherein the rust inhibitor is provided by an imide derivative of a hydroxy-carboxylic acid.

13. The use of claim 12, wherein the imide derivative of a hydroxy-carboxylic acid is a tartramide.

14. The use of claim 11, wherein the rust inhibitor is provided by an ester derivative of a hydroxy-carboxylic acid.
15. The use of claim 14, wherein the ester derivative of a hydroxy-carboxylic acid is a tartrate.
16. The use of any one of claims 11 to 15, wherein the internal combustion engine is an outboard engine, inboard engine or stern drive engine.
17. The use of any one of claims 11 to 16, wherein the internal combustion engine is gasoline 4-cycle outboard engine.