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(54) Title: LUBRICATING COMPOSITION

(57) Abstract: Use of a lubricating composition comprising (i) base oil and (ii) from 0.1 to 6 wt%, by weight of the lubricating composition, of an oil-soluble metal salt of an organic monocarboxylic acid wherein the organic monocarboxylic acid is selected from straight-chain and branched-chain, saturated and unsaturated, aliphatic and alicyclic monocarboxylic acids having from 5 to 24 carbon atoms and wherein the metal is selected from cobalt, sodium, calcium, magnesium, zinc, bismuth, lithium, potassium, aluminium, zirconium, tin, vanadium, barium and boron, and mixtures thereof, for providing improved piston cleanliness.



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LUBRICATING COMPOSITION

Field of the Invention

The present invention relates to a lubricating composition, in particular to a lubricating composition which is suitable for lubricating internal combustion engines and which has improved piston cleanliness properties.

Background of the Invention

Lubricants may be used in machinery to prevent friction between moving parts, such as pistons and cylinders of an engine. As lubricants age due to thermal/oxidative breakdown, deposits are formed on hot surfaces in an engine e.g. piston ring/skirt. In some cases, deposits may form in the lubricants that hinder the movement of engine parts and, therefore, impact the performance of the engine. Lubricants may be configured to reduce the likelihood of such deposits and/or affect the performance of the engine.

Lubricants may include a mixture of oils and other additives. The composition of the lubricant may be selected to define properties which can be used to enhance performance of the machinery. For example, various engines may specify the use of a certain viscosity of lubricant under certain conditions, such as outdoor temperature. In another example, the composition of the lubricant (and/or its additives) may be selected to control the engine's tendency to oxidize and form deposits. Antioxidants can delay the onset of deposit formation and detergents can protect metal surfaces against the accumulation of deposits, keeping these species suspended in the lubricant. Current lubricant

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formulations contain a variety of metal-based detergents which are typically calcium or magnesium salts with phenate, salicylate or sulfonate anions that bear an aromatic ring with alkyl side chain(s).

5 It would be desirable to further boost the performance of lubricant formulations, in particular such that their piston cleanliness properties are improved. Any further additives which are added to the lubricant formulations need to be compatible with existing
10 lubricant components and preferably should provide a synergistic boost in piston cleanliness performance.

 US5932653 relates to the preparation of a complex reaction product of an oil soluble cobalt soap and an oil soluble overbased calcium soap, which chemical complex
15 serves as a "loss of dry" inhibitor, for oil-based paints. The cobalt soaps used in making the chemical complex include cobalt salts derived from organic monocarboxylic acids having from 6 to 24 carbon atoms. Suitable organic carboxylic acids used in making the
20 calcium salts include 2-ethylhexanoic acid, iso-octanoic acid, nonanoic acid and iso-nonanoic acid. Troymax (RTM) Calcium 10% is mentioned as a compound suitable for use in preparing the chemical complex.

 EP1243630 discloses a coating composition comprising
25 Troymax 8% Zinc.

 It has now surprisingly been found by the present inventors that certain metal salts of aliphatic and/or alicyclic monocarboxylic acids can be used to provide improved piston cleanliness properties of a lubricating
30 oil composition for the crankcase of an internal combustion engine.

Summary of the Invention

 According to the present invention, there is

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provided use of a lubricating composition comprising (i) base oil and (ii) from 0.1 to 6 wt%, by weight of the lubricating composition, of an oil-soluble metal salt of an organic monocarboxylic acid wherein the organic
5 monocarboxylic acid is selected from straight-chain and branched-chain, saturated and unsaturated, aliphatic and alicyclic monocarboxylic acids having from 5 to 24 carbon atoms, naphthenic acids, tall oil fatty acids, and mixtures thereof, and wherein the metal is selected from
10 cobalt, sodium, calcium, magnesium, zinc, bismuth, lithium, potassium, aluminium, zirconium, tin, vanadium, barium and boron, and mixtures thereof.

The lubricating compositions herein provide improvements in cleanliness attributes, in particular
15 improvements in piston cleanliness.

The metal carboxylates appear to enhance the cleanliness attributes, particularly the piston cleanliness attributes, when added to existing lubricating compositions, in particular when added as a
20 top-treat to lubricating compositions such as passenger car crankcase lubricating compositions.

According to another aspect of the present invention there is provided a method for improving the piston cleanliness properties of a lubricating oil composition
25 used to lubricate the crankcase of an internal combustion engine comprising adding to the lubricating oil composition an additive amount of an oil-soluble metal salt of an organic monocarboxylic acid wherein the monocarboxylic acid is selected from straight-chain and
30 branched-chain, saturated and unsaturated, aliphatic or alicyclic monocarboxylic acids having from 5 to 24 carbon atoms and wherein the metal is selected from cobalt, sodium, calcium, magnesium, zinc, bismuth, lithium,

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potassium, aluminium, zirconium, tin, vanadium, barium and boron, and mixtures thereof.

According to a further aspect of the present invention there is provided a method for providing improved piston cleanliness of an internal combustion engine wherein the method comprises lubricating the internal combustion engine with a lubricating composition as described herein.

According to a further aspect of the present invention there is provided a lubricating composition comprising (i) base oil and (ii) from 0.1 to 6 wt%, by weight of the lubricating composition, of an oil-soluble metal salt of an organic monocarboxylic acid wherein the organic monocarboxylic acid is selected from straight-chain and branched-chain, saturated and unsaturated, aliphatic and alicyclic monocarboxylic acids having from 5 to 24 carbon atoms, naphthenic acids, tall oil fatty acids, and mixtures thereof, and wherein the metal is selected from cobalt, sodium, calcium, magnesium, zinc, bismuth, lithium, potassium, aluminium, zirconium, tin, vanadium, barium and boron, and mixtures thereof.

Detailed Description of the Invention

As used herein, the term "improved piston cleanliness" means reducing the amount of piston deposits which are found on the pistons of an internal combustion engine during operation of the engine, in particular as measured according to the hot tube deposits test method disclosed in WO2014036110.

In a preferred embodiment, the % improvement in piston cleanliness provided by the lubricating oil compositions herein is at least a 10% improvement in piston cleanliness, more preferably at least a 15% improvement in piston cleanliness, even more preferably

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at least a 20% improvement in piston cleanliness,
compared to the piston cleanliness of an equivalent
lubricating oil composition which does not contain an
oil-soluble metal salt of an organic monocarboxylic acid
as defined herein.

In a preferred embodiment of the present invention,
the piston cleanliness properties of the lubricating oil
composition are measured according to the hot tube
deposits test method disclosed in WO2014036110, which
reference is incorporated herein by reference in its
entirety.

As used herein, the term "oil-soluble" when used in
relation to the metal salt of an organic monocarboxylic
acid means that it is soluble in non-aqueous, organic
solvent.

As a first essential component, the lubricating oil
composition herein comprises one or more oil-soluble
metal salts of an organic monocarboxylic acid, preferably
in an amount of from 0.01 wt% to 10 wt%, more preferably
in an amount of from 0.25 wt% to 7 wt%, and even more
preferably in an amount of from 0.1 wt% to 4 wt%, and
especially in an amount of from 0.1 wt% to 2 wt%, by
weight of the total lubricating oil composition.

Suitable oil-soluble metal salts of an organic
monocarboxylic acid for use herein, including preparation
details thereof, are disclosed for example in US5932653,
US3972825 and US4032354. The relevant disclosures of
these patents and applications are incorporated herein by
reference.

Suitable for use herein is one or more oil-soluble
metal salts of an organic monocarboxylic acid wherein the
organic monocarboxylic acid is selected from straight-
chain and branched-chain, saturated and unsaturated,

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aliphatic and alicyclic monocarboxylic acids having from 5 to 24 carbon atoms and wherein the metal is selected from cobalt, sodium, calcium, magnesium, zinc, bismuth, lithium, potassium, aluminium, zirconium, tin, vanadium, barium and boron, and mixtures thereof.

In one embodiment of the present invention the monocarboxylic acid is selected from straight-chain and branched-chain, saturated and unsaturated, aliphatic and alicyclic monocarboxylic acids having from 6 to 18 carbon atoms.

Current lubricant formulations contain a variety of metal-based detergents which are typically calcium or magnesium salts with phenate, salicylate or sulfonate anions that bear an aromatic ring with alkyl side chain(s). The oil-soluble metal salts of a monocarboxylic acid used in the present invention are structurally different from said metal-based detergents.

Examples of suitable monocarboxylic acids for use herein include, but are not limited to, hexanoic acid, n-octanoic acid, 2-ethylhexanoic (octoic) acid, nonanoic acid, isononanoic acid, decanoic acid, isodecanoic acid, neodecanoic acid, lauric acid, myristic acid, stearic acid, arachidic acid, behenic acid, oleic acid, linoleic acid, erucic acid, monobutyl maleate, naphthenic acid, cyclopentanoic acid, cyclohexanoic acid, cycloheptanoic acid, methylcyclohexanoic acid, tall oil acid, and mixtures thereof.

In a preferred embodiment of the present invention, the organic monocarboxylic acid for use herein is selected from straight-chain and branched chain, saturated and unsaturated, aliphatic monocarboxylic acids having from 8 to 18 carbon atoms and alicyclic monocarboxylic acids having from 6 to 18 carbon atoms,

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and mixtures thereof.

A preferred organic monocarboxylic acid for use herein is selected from 2-ethylhexanoic acid, iso-octanoic acid, neodecanoic acid, naphthenic acid, oleic acid, nonanoic acid and iso-nonanoic acid, and mixtures thereof.

A particularly preferred organic monocarboxylic acid for use herein is 2-ethylhexanoic acid.

Preferably the metal is selected from calcium and zinc and mixtures thereof.

In one preferred embodiment the metal salt of an organic monocarboxylic acid is an overbased calcium salt of 2-ethyl hexanoic acid.

In another preferred embodiment the metal salt of an organic monocarboxylic fatty acid is a zinc salt of 2-ethyl hexanoic acid.

Typically, the oil-soluble metal salt of an organic monocarboxylic acid is provided as a solution in an oil-soluble carrier fluid. Suitable oil-soluble carrier fluids for use herein include any base oil which can solubilise the oil-soluble metal salt such that it is soluble in the lubricating composition herein. Suitable oil-soluble carrier fluids include the base oils described herein below under the term "base oil". Thus the oil-soluble carrier fluid can be any base oil which is also used as the base oil in the lubricating composition herein. Examples of suitable oil-soluble carrier fluids for use herein include petroleum oil, esters, Group I base oils, naphthenic base oils, Fischer-Tropsch derived base oils or other Group III base oils.

Other suitable oil-soluble carrier fluids include organic solvents, especially non-polar solvents, selected from the group consisting of aliphatic or cycloaliphatic

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solvents such as hexane, heptane, octane, isooctane, cyclohexane, and cycloheptane; petroleum distillates such as mineral spirits, gasoline, diesel fuel, and fuel oils; aromatic hydrocarbons such as benzene, toluene, xylene, and ethylbenzene; glycols such as tripropylene glycol, dipropylene glycol mono methyl ether, or combinations of these non-polar organic solvents.

Examples of commercially available oil-soluble metal salts of an organic monocarboxylic acid for use herein include those compounds commercially available from Troy Corporation under the tradenames Troycat (RTM) Lithium 2, Troymax (RTM) Bismuth 24, Troycat (RTM) Potassium 10, Troymax (RTM) Potassium 15, Troymax (RTM) Calcium Octoate 6 (neutral calcium carboxylate solution containing 6% calcium metal), Troychem (RTM) Zinc 8 (zinc carboxylate solution containing 8% of zinc metal, including zinc salt of 2-ethyl hexanoic acid), Troymax (RTM) Calcium 10NA (calcium carboxylate solution containing 6% calcium metal), Troycat (RTM) Zinc 18 (zinc carboxylate solution containing 18% of zinc metal, including zinc salt of 2-ethyl hexanoic acid), Troymax (RTM) Cobalt 6 (a mineral spirits solution of cobalt-2-ethylhexanoate containing 6% cobalt as metal), and Troymax (RTM) Calcium 6 (a mineral spirits solution of calcium 2-ethylhexanoate containing 6% calcium as metal - it is neutral or slightly acidic).

There are no particular limitations regarding the base oil used in the lubricating composition herein, and various conventional mineral oils, synthetic oils as well as naturally derived esters such as vegetable oils may be conveniently used.

The base oil used in the lubricating compositions herein may conveniently comprise mixtures of one or more mineral oils and/or one or more synthetic oils; thus,

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according to the present invention, the term "base oil" may refer to a mixture containing more than one base oil. Mineral oils include liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oil of the paraffinic, naphthenic, or mixed paraffinic/naphthenic type which may be further refined by hydrofinishing processes and/or dewaxing.

Suitable base oils for use in the lubricating oil composition herein are Group I-III mineral base oils, Group IV poly-alpha olefins (PAOs), Group II-III Fischer-Tropsch derived base oils (preferably Group III), Group V ester base oils, and mixtures thereof.

By "Group I", "Group II" "Group III" and "Group IV" and "Group V" base oils as used herein are meant lubricating oil base oils according to the definitions of American Petroleum Institute (API) for categories I, II, III, IV and V. These API categories are defined in API Publication 1509, 15th Edition, Appendix E, April 2002.

Fischer-Tropsch derived base oils are known in the art. By the term "Fischer-Tropsch derived" is meant that a base oil is, or is derived from, a synthesis product of a Fischer-Tropsch process. A Fischer-Tropsch derived base oil may also be referred to as a GTL (Gas-To-Liquids) base oil. Suitable Fischer-Tropsch derived base oils that may be conveniently used as the base oil in the lubricating composition herein are those as for example disclosed in EP0776959, EP0668342, WO9721788, WO0015736, WO0014188, WO0014187, WO0014183, WO0014179, WO0008115, WO9941332, EP1029029, WO0118156 and WO0157166.

Typically, the aromatics content of a Fischer-Tropsch derived base oil, suitably determined by ASTM D 4629, will typically be below 1 wt.%, preferably below 0.5 wt.% and more preferably below 0.1 wt.%. Suitably,

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the base oil has a total paraffin content of at least 80 wt.%, preferably at least 85, more preferably at least 90, yet more preferably at least 95 and most preferably at least 99 wt.%. It suitably has a saturates content (as measured by IP-368) of greater than 98 wt.%. Preferably the saturates content of the base oil is greater than 99 wt.%, more preferably greater than 99.5 wt.%. It further preferably has a maximum n-paraffin content of 0.5 wt.%. The base oil preferably also has a content of naphthenic compounds of from 0 to less than 20 wt.%, more preferably of from 0.5 to 10 wt.%.

Typically, the Fischer-Tropsch derived base oil or base oil blend has a kinematic viscosity at 100°C (as measured by ASTM D 7042) in the range of from 1 to 30 mm²/s (cSt), preferably from 1 to 25 mm²/s (cSt), and more preferably from 2 mm²/s to 12 mm²/s. Preferably, the Fischer-Tropsch derived base oil has a kinematic viscosity at 100°C (as measured by ASTM D 7042) of at least 2.5 mm²/s, more preferably at least 3.0 mm²/s. In one embodiment of the present invention, the Fischer-Tropsch derived base oil has a kinematic viscosity at 100°C of at most 5.0 mm²/s, preferably at most 4.5 mm²/s, more preferably at most 4.2 mm²/s (e.g. "GTL 4"). In another embodiment of the present invention, the Fischer-Tropsch derived base oil has a kinematic viscosity at 100°C of at most 8.5 mm²/s, preferably at most 8 mm²/s (e.g. "GTL 8").

Further, the Fischer-Tropsch derived base oil typically has a kinematic viscosity at 40°C (as measured by ASTM D 7042) of from 10 to 100 mm²/s (cSt), preferably from 15 to 50 mm²/s.

Also, the Fischer-Tropsch derived base oil preferably has a pour point (as measured according to

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ASTM D 5950) of below -30°C , more preferably below -40°C , and most preferably below -45°C .

The flash point (as measured by ASTM D92) of the Fischer-Tropsch derived base oil is preferably greater than 120°C , more preferably even greater than 140°C .

The Fischer-Tropsch derived base oil preferably has a viscosity index (according to ASTM D 2270) in the range of from 100 to 200. Preferably, the Fischer-Tropsch derived base oil has a viscosity index of at least 125, preferably 130. Also it is preferred that the viscosity index is below 180, preferably below 150.

In the event the Fischer-Tropsch derived base oil contains a blend of two or more Fischer-Tropsch derived base oils, the above values apply to the blend of the two or more Fischer-Tropsch derived base oils.

The lubricating oil composition herein preferably comprises 80 wt% or greater of Fischer-Tropsch derived base oil.

Synthetic oils include hydrocarbon oils such as olefin oligomers (including polyalphaolefin base oils; PAOs), dibasic acid esters, polyol esters, polyalkylene glycols (PAGs), alkyl naphthalenes and dewaxed waxy isomerates. Synthetic hydrocarbon base oils sold by the Shell Group under the designation "Shell XHVI" (trade mark) may be conveniently used.

Poly-alpha olefin base oils (PAOs) and their manufacture are well known in the art. Preferred poly-alpha olefin base oils that may be used in the lubricating compositions herein may be derived from linear C_2 to C_{32} , preferably C_6 to C_{16} , alpha olefins. Particularly preferred feedstocks for said poly-alpha olefins are 1-octene, 1-decene, 1-dodecene and 1-tetradecene.

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There is a strong preference for using a Fischer-Tropsch derived base oil over a PAO base oil, in view of the high cost of manufacture of the PAOs. Thus, preferably, the base oil contains more than 50 wt.%, preferably more than 60 wt.%, more preferably more than 70 wt.%, even more preferably more than 80 wt.%. most preferably more than 90 wt.% Fischer-Tropsch derived base oil. In an especially preferred embodiment not more than 5 wt.%, preferably not more than 2 wt.%, of the base oil is not a Fischer-Tropsch derived base oil. It is even more preferred that 100 wt% of the base oil is based on one or more Fischer-Tropsch derived base oils.

The total amount of base oil incorporated in the lubricating composition herein is preferably in the range of from 60 to 99 wt.%, more preferably in the range of from 65 to 90 wt.% and most preferably in the range of from 70 to 85 wt.%, with respect to the total weight of the lubricating composition.

Typically the base oil (or base oil blend) as used in the lubricating composition herein has a kinematic viscosity at 100°C (according to ASTM D445) of above 2.5 cSt and below 5.6 cSt. According to a preferred embodiment of the present invention the base oil has a kinematic viscosity at 100°C (according to ASTM D445) of between 3.5 and 4.5 cSt. In the event the base oil contains a blend of two or more base oils, it is preferred that the blend has a kinematic viscosity at 100°C of between 3.5 and 4.5 cSt.

Typically the lubricating compositions herein would be utilised in, but not necessarily limited to, SAE J300 viscosity grades 0W-20, 0W-30, 0W-40, 5W-20, 5W-30 and 5W-40 as these are the grades which target fuel economy. As new SAE J300 viscosity grades are published, with

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lower viscosities than the current 0W-20, the present invention would also be very much applicable to these new viscosity lower grades. It is conceivable that the present invention could also be used with higher viscosity grades.

The lubricating composition herein preferably has a Noack volatility (according to ASTM D 5800) of below 15 wt.%. Typically, the Noack volatility (according to ASTM D 5800) of the composition is between 1 and 15 wt.%, preferably below 14.6 wt.% and more preferably below 14.0 wt.%.

Preferably, the lubricating oil composition has a kinematic viscosity in the range of from 2 to 80 mm²/s at 100 °C, more preferably of from 3 to 70 mm²/s, most preferably of from 4 to 50 mm²/s.

The total amount of phosphorus in the lubricating oil composition herein is preferably less than or equal to 0.08 wt%, by weight of the lubricating composition.

The lubricating oil composition herein preferably has a sulphated ash content of not greater than 2.0 wt.%, more preferably not greater than 1.0 wt.% and most preferably not greater than 0.8 wt.%, based on the total weight of the lubricating oil composition.

The lubricating oil composition herein preferably has a sulphur content of not greater than 1.2 wt.%, more preferably not greater than 0.8 wt.% and most preferably not greater than 0.2 wt.%, based on the total weight of the lubricating oil composition.

The lubricating composition herein further comprises one or more additives such as anti-oxidants, anti-wear additives, dispersants, detergents, overbased detergents, extreme pressure additives, friction modifiers, viscosity index improvers, pour point depressants, metal

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passivators, corrosion inhibitors, demulsifiers, anti-foam agents, seal compatibility agents and additive diluent base oils, etc.

As the person skilled in the art is familiar with the above and other additives, these are not further discussed here in detail. Specific examples of such additives are described in for example Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, pages 477-526.

Antioxidants that may be conveniently used include those selected from the group of aminic antioxidants and/or phenolic antioxidants. In a preferred embodiment, said antioxidants are present in an amount in the range of from 0.1 to 5.0 wt. %, more preferably in an amount in the range of from 0.3 to 3.0 wt. %, and most preferably in an amount in the range of from 0.5 to 1.5 wt. %, based on the total weight of the lubricating oil composition.

Examples of aminic antioxidants which may be conveniently used include alkylated diphenylamines, phenyl- α -naphthylamines, phenyl- β -naphthylamines and alkylated α -naphthylamines.

Preferred aminic antioxidants include dialkyldiphenylamines such as p,p'-dioctyl-diphenylamine, p,p'-di- α -methylbenzyl-diphenylamine and N-p-butylphenyl-N-p'-octylphenylamine, monoalkyldiphenylamines such as mono-t-butyl-diphenylamine and mono-octyldiphenylamine, bis(dialkylphenyl)amines such as di-(2,4-diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine, alkylphenyl-1-naphthylamines such as octylphenyl-1-naphthylamine and n-t-dodecylphenyl-1-naphthylamine, 1-naphthylamine, aryl-naphthylamines such as phenyl-1-naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine,

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phenylenediamines such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and phenothiazines such as phenothiazine and 3,7-dioctylphenothiazine.

5 Preferred aminic antioxidants include those available under the following trade designations: "Sonoflex OD-3" (ex. Seiko Kagaku Co.), "Irganox L-57" (ex. Ciba Specialty Chemicals Co.) and phenothiazine (ex. Hodogaya Kagaku Co.).

10 Examples of phenolic antioxidants which may be conveniently used include C₇-C₉ branched alkyl esters of 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic acid, 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-butylphenol, 2,4-dimethyl-15 6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone, 2,6-di-t-butyl-4-alkylphenols such as 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol, 2,6-di-t-butyl-4-alkoxyphenols such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol, 3,5-di-t-butyl-4-hydroxybenzylmercaptooctylacetate, alkyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionates such as n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, n-butyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and 2'-25 ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 2,6-di-t-butyl- α -dimethylamino-p-cresol, 2,2'-methylenebis(4-alkyl-6-t-butylphenol) such as 2,2'-methylenebis(4-methyl-6-t-butylphenol, and 2,2'-methylenebis(4-ethyl-6-t-butylphenol), bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol, 4,4'-methylenebis(2,6-di-t-butylphenol), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane, 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidenebis(2,6-t-

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butylphenol), hexamethyleneglycol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], triethyleneglycolbis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate], 2,2'-thio-[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate],
5 3,9-bis{1,1-dimethyl-2-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy]ethyl}2,4,8,10-tetraoxaspiro[5,5]undecane, 4,4'-thiobis(3-methyl-6-t-butylphenol) and 2,2'-thiobis(4,6-di-t-butylresorcinol), polyphenols such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]methane, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, bis-[3,3'-bis(4'-hydroxy-3'-t-butylphenyl)butyric acid]glycol ester, 2-(3',5'-di-t-butyl-4-hydroxyphenyl)methyl-4-(2",4"-di-t-butyl-3"-hydroxyphenyl)methyl-6-t-butylphenol and 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)-4-methylphenol,
10 and p-t-butylphenol - formaldehyde condensates and p-t-butylphenol - acetaldehyde condensates.

Preferred phenolic antioxidants include those
20 available under the following trade designations: "Irganox L-135" (ex. Ciba Specialty Chemicals Co.), "Yoshinox SS" (ex. Yoshitomi Seiyaku Co.), "Antage W-400" (ex. Kawaguchi Kagaku Co.), "Antage W-500" (ex. Kawaguchi Kagaku Co.), "Antage W-300" (ex. Kawaguchi Kagaku Co.), "Irganox L109" (ex. Ciba Speciality Chemicals Co.), "Tominox 917" (ex. Yoshitomi Seiyaku Co.), "Irganox L115" (ex. Ciba Speciality Chemicals Co.), "Sumilizer GA80" (ex. Sumitomo Kagaku), "Antage RC" (ex. Kawaguchi Kagaku Co.), "Irganox L101" (ex. Ciba Speciality Chemicals Co.), "Yoshinox 930" (ex. Yoshitomi Seiyaku Co.).
25
30

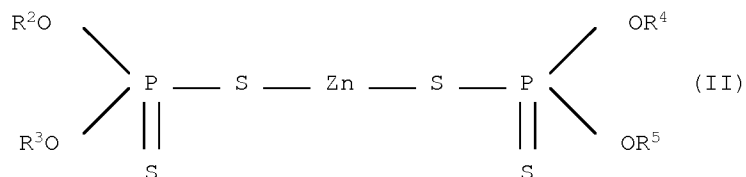
The lubricating oil composition herein may comprise mixtures of one or more phenolic antioxidants with one or more aminic antioxidants.

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Anti-wear additives that may be conveniently used include zinc-containing compounds such as zinc dithiophosphate compounds selected from zinc dialkyl-, diaryl- and/or alkylaryl- dithiophosphates, molybdenum-
 5 containing compounds, boron-containing compounds and ashless anti-wear additives such as substituted or unsubstituted thiophosphoric acids, and salts thereof.

In a preferred embodiment, the lubricating oil composition may comprise a single zinc dithiophosphate or
 10 a combination of two or more zinc dithiophosphates as anti-wear additives, the or each zinc dithiophosphate being selected from zinc dialkyl-, diaryl- or alkylaryl- dithiophosphates.

Zinc dithiophosphate is a well known additive in the
 15 art and may be conveniently represented by general formula II;



wherein R^2 to R^5 may be the same or different and are each a primary alkyl group containing from 1 to 20 carbon atoms preferably from 3 to 12 carbon atoms, a secondary
 20 alkyl group containing from 3 to 20 carbon atoms, preferably from 3 to 12 carbon atoms, an aryl group or an aryl group substituted with an alkyl group, said alkyl substituent containing from 1 to 20 carbon atoms preferably 3 to 18 carbon atoms.

Zinc dithiophosphate compounds in which R^2 to R^5 are all different from each other can be used alone or in admixture with zinc dithiophosphate compounds in which R^2 to R^5 are all the same.

Preferably, the or each zinc dithiophosphate used in

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the present invention is a zinc dialkyl dithiophosphate.

Examples of suitable zinc dithiophosphates which are commercially available include those available ex.

5 Lubrizol Corporation under the trade designations "Lz 1097" and "Lz 1395", those available ex. Chevron Oronite under the trade designations "OLOA 267" and "OLOA 269R", and that available ex. Afton Chemical under the trade designation "HITEC 7197"; zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations "Lz 677A", "Lz 1095" and "Lz 1371", that available ex. Chevron Oronite under the trade designation "OLOA 262" and that available ex. Afton Chemical under the trade designation "HITEC 7169"; and zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations "Lz 1370" and "Lz 1373" and that available ex. Chevron Oronite under the trade designation "OLOA 260".

15 The lubricating oil composition herein may generally comprise in the range of from 0.4 to 1.2 wt.% of zinc dithiophosphate, based on total weight of the lubricating oil composition.

20 Examples of such molybdenum-containing compounds may conveniently include molybdenum dithiocarbamates, trinuclear molybdenum compounds, for example as described in WO9826030, sulphides of molybdenum and molybdenum dithiophosphate.

25 Boron-containing compounds that may be conveniently used include borate esters, borated fatty amines, borated epoxides, alkali metal (or mixed alkali metal or alkaline earth metal) borates and borated overbased metal salts.

30 Typical detergents that may be used in the lubricating composition herein include one or more salicylate and/or phenate and/or sulphonate detergents.

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However, as metal organic and inorganic base salts which are used as detergents can contribute to the sulphated ash content of a lubricating oil composition, in a preferred embodiment of the present invention, the amounts of such additives are minimised.

Furthermore, in order to maintain a low sulphur level, salicylate detergents are preferred.

In order to maintain the total sulphated ash content of the lubricating oil composition herein at a level of preferably not greater than 2.0 wt. %, more preferably at a level of not greater than 1.0 wt. % and most preferably at a level of not greater than 0.8 wt. %, based on the total weight of the lubricating oil composition, said detergents are preferably used in amounts in the range of 0.05 to 20.0 wt. %, more preferably from 1.0 to 10.0 wt. % and most preferably in the range of from 2.0 to 5.0 wt. %, based on the total weight of the lubricating oil composition.

Furthermore, it is preferred that said detergents, independently, have a TBN (total base number) value in the range of from 10 to 500 mg.KOH/g, more preferably in the range of from 30 to 350 mg.KOH/g and most preferably in the range of from 50 to 300 mg.KOH/g, as measured by ISO 3771.

The lubricating oil compositions herein may additionally contain an ash-free dispersant which is preferably admixed in an amount in the range of from 5 to 15 wt. %, based on the total weight of the lubricating oil composition.

Examples of ash-free dispersants which may be used include the polyalkenyl succinimides and polyalkenyl succinic acid esters disclosed in Japanese Patent Nos. JP1367796, JP1667140, JP1302811 and JP1743435. Preferred

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dispersants include borated succinimides.

Examples of viscosity index improvers which may conveniently be used in the lubricating composition herein include the styrene-butadiene stellate copolymers, styrene-isoprene stellate copolymers and the polymethacrylate copolymer and ethylene-propylene copolymers (also known as olefin copolymers) of the crystalline and non-crystalline type. Dispersant-viscosity index improvers may be used in the lubricating composition herein. However, preferably the composition herein contains less than 1.0 wt.%, preferably less than 0.5 wt.%, of a Viscosity Index improver concentrate (i.e. VI improver plus "carrier oil" or "diluent"), based on the total weight of the composition. Most preferably, the composition is free of Viscosity Index improver concentrate. The term "Viscosity Modifier" as used hereafter is meant to be the same as the above-mentioned term "Viscosity Index improver concentrate".

Preferably, the composition contains at least 0.1 wt.% of a pour point depressant. As an example, alkylated naphthalene and phenolic polymers, polymethacrylates, maleate/fumarate copolymer esters may be conveniently used as effective pour point depressants. Preferably not more than 0.3 wt.% of the pour point depressant is used.

Furthermore, compounds such as alkenyl succinic acid or ester moieties thereof, benzotriazole-based compounds and thiodiazole-based compounds may be conveniently used in the lubricating composition herein as corrosion inhibitors.

Compounds such as polysiloxanes, dimethyl polycyclohexane and polyacrylates may be conveniently used in the lubricating composition herein as defoaming agents.

Compounds which may be conveniently used in the

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lubricating composition herein as seal fix or seal compatibility agents include, for example, commercially available aromatic esters.

The above-mentioned additives are typically present in an amount in the range of from 0.01 to 35.0 wt.%, based on the total weight of the lubricating composition, preferably in an amount in the range of from 0.05 to 25.0 wt.%, more preferably from 1.0 to 20.0 wt.%, based on the total weight of the lubricating composition.

Preferably, the composition contains at least 9.0 wt.%, preferably at least 10.0 wt.%, more preferably at least 11.0 wt% of an additive package comprising an anti-wear additive, a metal detergent, an ashless dispersant and an anti-oxidant.

The lubricating compositions herein are preferably engines oils for use in the crankcase of an engine. The engine oil may include a heavy duty diesel engine oil, a passenger car motor engine oil, as well as other types of engine oils, such as motor cycle oils and marine engine oils.

The lubricating compositions herein may be so-called "low SAPS" (SAPS = sulphated ash, phosphorus and sulphur), "mid SAPS" or "regular SAPS" formulations.

For Passenger Car Motor Oil (PCMO) engine oils the above ranges mean:

- a sulphated ash content (according to ASTM D 874) of up to 0.5 wt.%, up to 0.8 wt.% and up to 1.5 wt.%, respectively;
- a phosphorus content (according to ASTM D 5185) of up to 0.05 wt.%, up to 0.08 wt.% and typically up to 0.1 wt.%, respectively; and
- a sulphur content (according to ASTM D 5185) of up to 0.2 wt.%, up to 0.3 wt.% and typically up to 0.5 wt.%,

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respectively.

For Heavy Duty Diesel Engine Oils the above ranges mean:

- a sulphated ash content (according to ASTM D 874) of up to 1 wt.%, up to 1 wt.% and up to 2 wt.%, respectively;
- a phosphorus content (according to ASTM D 5185) of up to 0.08 wt.% (low SAPS) and up to 0.12 wt.% (mid SAPS), respectively; and
- a sulphur content (according to ASTM D 5185) of up to 0.3 wt.% (low SAPS) and up to 0.4 wt.% (mid SAPS), respectively.

The lubricating compositions herein may be conveniently prepared using conventional formulation techniques by admixing base oil with the oil-soluble metal salt of a monocarboxylic acid and other additive components/additive package at a temperature of, for example, around 60°C.

It has surprisingly been found that the lubricating compositions described herein containing the abovementioned oil-soluble metal salt of a monocarboxylic acid provides reduced piston cleanliness, in particular as measured according to the hot tube deposits test method as described in WO2014036110. In the hot tube deposits test method as described in WO2014036110 a cleanliness merit of 10.0 represents completely clean engine pistons. The lubricating compositions described herein comprising a base oil and one or more oil-soluble metal salts of a monocarboxylic acid preferably provide a hot tube cleanliness merit result in the hot tube deposits test method described in WO2014036110 of 8.0 or above.

The present invention is described below with

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reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

Examples

5 Lubricating formulations were prepared by top treating a reference lubricant (reference lubricant A which was a passenger car motor oil (PCMO) meeting GF-5 specification) with 3 wt% of an oil-soluble metal salt of a monocarboxylic acid or a conventional antioxidant
10 compound.

 Comparative Example 1 consisted of reference lubricant A top treated with 3 wt% of a conventional aminic antioxidant (Infineum C9452 commercially available from Infineum).

15 Comparative Example 2 consisted of reference lubricant A top treated with 3 wt% of a conventional phenolic antioxidant (Infineum C9454 commercially available from Infineum).

 Example 1 consisted of the reference lubricant A top
20 treated with 3 wt% of Troymax (RTM) Calcium Octoate 6 (neutral calcium carboxylate solution containing 6% calcium metal) commercially available from Troy Corporation.

 Example 2 consisted of reference lubricant A top
25 treated with 3 wt% of Troychem (RTM) Zinc 8 (metal carboxylate solution containing 8% of zinc metal) commercially available from Troy Corporation.

 Example 3 consisted of reference lubricant A top
30 treated with 3 wt% of Troymax (RTM) Calcium 10NA (calcium carboxylate solution containing 6% calcium metal) commercially available from Troy Corporation.

 Example 4 consisted of reference lubricant A top treated with 3 wt% of Troycat (RTM) Zinc 18 (metal

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carboxylate solution containing 18% of zinc metal)
commercially available from Troy Corporation.

The Examples and Comparative Examples were subjected
to the hot tube deposits test method described in
5 WO2014036110. The results of these experiments are set
out in Table 1 below. A hot tube merit result of 10 means
completely clean. A hot tube merit result over 8
demonstrates excellent piston cleanliness.

Table 1

Description	Hot tube merit
Reference Lubricant A	6.7
Example 1 (Reference Lubricant A + 3 wt% Troymax (RTM) Calcium Octoate 6)	9.3
Example 2 (Reference Lubricant A + 3 wt% Troychem (RTM) Zinc 8)	8.3
Example 3 (Reference Lubricant A + 3 wt% Troymax (RTM) Calcium 10NA)	9.5
Example 4 (Reference Lubricant A + 3 wt% Troycat (RTM) Zinc 18)	9.1
Comparative Example 1 (Reference Lubricant A + 3 wt% Infineum C9452, a conventional aminic antioxidant)	7.5
Comparative Example 2 (Reference Lubricant A + 3 wt% Infineum C9454, a conventional phenolic antioxidant)	6.9

Discussion

As shown in Table 1, Examples 1, 2, 3 and 4 had hot tube merit results of 9.3, 8.3, 9.5 and 9.1, respectively. This compared to hot tube merit results of 7.5 and 6.9 for Comparative Example 1 and Comparative Example 2, respectively. These results demonstrate that lubricating compositions top treated with 3 wt% of an oil-soluble metal salt of a monocarboxylic acid of the type described hereinabove demonstrate improved piston cleanliness compared with comparative compositions top treated with conventional aminic/phenolic antioxidants.

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C L A I M S

1. Use of a lubricating composition comprising (i) base oil and (ii) from 0.1 to 6 wt%, by weight of the lubricating composition, of an oil-soluble metal salt of an organic monocarboxylic acid wherein the organic
5 monocarboxylic acid is selected from straight-chain and branched-chain, saturated and unsaturated, aliphatic and alicyclic monocarboxylic acids having from 5 to 24 carbon atoms and wherein the metal is selected from cobalt, sodium, calcium, magnesium, zinc, bismuth, lithium,
10 potassium, aluminium, zirconium, tin, vanadium, barium and boron, and mixtures thereof, for providing improved piston cleanliness.
2. Use according to Claim 1 wherein the organic monocarboxylic acid is selected from aliphatic
15 monocarboxylic acids having from 8 to 18 carbon atoms and alicyclic monocarboxylic acids having from 6 to 18 carbon atoms, and mixtures thereof.
3. Use according to Claim 1 or 2 wherein the monocarboxylic acid is selected from hexanoic acid, n-
20 octanoic acid, 2-ethylhexanoic acid, nonanoic acid, isononanoic acid, decanoic acid, isodecanoic acid, neodecanoic acid, lauric acid, myristic acid, stearic acid, arachidic acid, behenic acid, oleic acid, linoleic acid, erucic acid, monobutyl maleate, naphthenic acid,
25 cyclopentanoic acid, cyclohexanoic acid, cycloheptanoic acid, methylcyclohexanoic acid, tall oil acid, and mixtures thereof.
4. Use according to Claim 3 wherein the organic monocarboxylic acid is selected from 2-ethylhexanoic
30 acid, iso-octanoic acid, neodecanoic acid, naphthenic

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acid, oleic acid, nonanoic acid and iso-nonanoic acid, and mixtures thereof.

5. Use according to Claims 3 or 4 wherein the organic monocarboxylic acid is 2-ethylhexanoic acid.

5 6. Use according to any of Claims 1 to 5 wherein the metal is selected from calcium and zinc and mixtures thereof.

7. Use according to any of Claims 1 to 6 wherein the metal salt of an organic monocarboxylic acid is an
10 overbased calcium salt of 2-ethylhexanoic acid.

8. Use according to any of Claims 1 to 6 wherein the metal salt of an organic monocarboxylic fatty acid is a zinc salt of 2-ethylhexanoic acid.

9. Method for providing improved piston cleanliness of an internal combustion engine wherein the method comprises lubricating the internal combustion engine with a lubricating composition comprising (i) base oil and (ii) from 0.1 to 6 wt%, by weight of the lubricating composition, of an oil-soluble metal salt of an organic monocarboxylic acid wherein the organic monocarboxylic acid is selected from straight-chain and branched-chain, saturated and unsaturated, aliphatic and alicyclic monocarboxylic acids having from 5 to 24 carbon atoms and wherein the metal is selected from cobalt, sodium, calcium, magnesium, zinc, bismuth, lithium, potassium, aluminium, zirconium, tin, vanadium, barium and boron, and mixtures thereof.

10. A lubricating composition comprising (i) base oil and (ii) from 0.1 to 6 wt%, by weight of the lubricating composition, of an oil-soluble metal salt of an organic monocarboxylic acid wherein the organic monocarboxylic acid is selected from straight-chain and branched-chain, saturated and unsaturated, aliphatic and alicyclic

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monocarboxylic acids having from 5 to 24 carbon atoms, naphthenic acids, tall oil fatty acids, and mixtures thereof, and wherein the metal is selected from cobalt, sodium, calcium, magnesium, zinc, bismuth, lithium, potassium, aluminium, zirconium, tin, vanadium, barium and boron, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/060995

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M129/32 C10M129/40 C10M129/58 C10M129/60 C10M159/20
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M C10N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2004 210908 A (TONEN GENERAL SEKIYU KK; PETROLEUM ENERGY CENTER FOUND) 29 July 2004 (2004-07-29) paragraphs [0001], [0024]; examples 1-3, comp. ex. 1 -----	1-6,8-10
X	EP 1 702 973 A1 (AFTON CHEMICAL CORP [US]) 20 September 2006 (2006-09-20) paragraphs [0001], [0002], [0084], [0080]; table 3 -----	1-4,9,10
X	WO 96/12779 A1 (EXXON RESEARCH ENGINEERING CO [US]) 2 May 1996 (1996-05-02) claims 1, 2 page 6; table 1 ----- -/-	1-4,9,10



Further documents are listed in the continuation of Box C.



See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	page 2, line 1 - line 12 claims 1, 9-12 page 12; examples 9, comp. 3 -----	1-6,8-10
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