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(54) **USE OF GLYCERIDES OF HYDROXY POLYCARBOXYLIC ACIDS AS ANTI-CAMSHAFT-WEAR ADDITIVES IN LUBRICANTS AND FUELS**

VERWENDUNG VON GLYCERIDEN VON HYDROXYPOLYCARBONSÄUREN ALS
NOCKENWELLENVERSCHLEISSSCHUTZADDITIVEN IN SCHMIERMITTELN UND
BRENNSTOFFEN

UTILISATION DES GLYCÉRIDES D'ACIDES HYDROXYPOLYCARBOXYLIQUES À TITRE
D'ADDITIFS ANTI-USURE D'ARBRES À CAMES DANS LES LUBRIFIANTS ET LES CARBURANTS

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WO-A1-2011/161406 WO-A1-2013/004811
WO-A1-2013/171319 GB-A- 635 708

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Description

[0001] This invention relates to anti-camshaft-wear additives and their use in lubricant compositions and fuel compositions.

[0002] It is known to use anti-wear additives and/or friction modifiers in lubricant compositions. It is also known to use anti-wear additives and/or friction modifiers in fuel compositions for internal combustion engines.

[0003] The ingress of fuel and fuel additives into the crankcase lubricant of an internal combustion engine is known, for example from paragraph 2 of the abstract of SAE paper 2001-01-1962 by C. Y. Thiel et al. "The Fuel Additive/lubricant Interactions:..."

[0004] Zinc dihydrocarbyl dithiophosphates (ZDDP) have been used as anti-wear additives in lubricant compositions for many years. A disadvantage of these additives is that, when used to lubricate internal combustion engines, they give rise to ash which contributes to particulate matter in the exhaust emissions from the internal combustion engines. It is therefore desirable to reduce the amount of ash-forming additives used for lubricating internal combustion engines. It is also desirable to reduce the amount of zinc and/or phosphorus and/or sulphur in the exhaust emissions from internal combustion engines. A range of anti-wear additives and/or friction modifiers which contain neither zinc nor phosphorus, or at least contain them in reduced amounts, have therefore been produced.

[0005] Various methods have been developed for testing the effectiveness of wear reducing additives, including both ash-forming and ashless additives. A particularly widely used test is the Sequence IVA test, and a number of organic, ashless anti-wear components are known to improve performance in these tests. However, whilst the Sequence IVA test is the key wear test in the API test sequences, it is not applicable for European ACEA specifications. The key engine wear test for ACEA specifications is the diesel OM646LA test. Generally, organic, ashless anti-wear additives, for example oleamide, that are known to improve performance in the Sequence IVA test do not give similar benefits in the OM646LA test. The OM646LA test particularly measures camshaft wear, and it would therefore be useful to identify ashless, anti-wear additives that function as anti-camshaft-wear additives in lubricant compositions, or in fuel compositions when the fuels are used to lubricate internal combustion engines and at least a portion of the additives ingress into the lubricating composition during operation of said engine; for example additives which enable compositions containing the additives to pass the OM646LA engine test.

[0006] International patent application publication WO 2008/124191 relates to the use of one or more oil-soluble fatty acid esters of a polyol in a lubricating oil composition having a base oil comprising a major amount of a gas-to-liquid (GTL) derived base oil. Polyols are said to include diols, triols and the like. It is stated therein that the esters of the polyols are those of carboxylic acids having 12 to 24 carbon atoms. According to WO 2008/124191, preferably the fatty acid ester is a fatty acid ester of glycerol, more preferably, a monoester of glycerol and most preferably, the ester is glycerol mono-octadecanoate. WO 2008/124191 does not describe the use of glycerides of hydroxy polycarboxylic acids.

[0007] International patent application publication WO 2011/161406 relates to the use of an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, as an anti-wear additive and/or friction modifier in a non-aqueous lubricant composition and/or in a fuel composition. According to WO 2011/161406, lubricant compositions comprising the oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, may be used to lubricate internal combustion engines. It is stated that in one embodiment, the hydroxy polycarboxylic acid has at least one hydroxy group which is in an alpha position with respect to a carboxylic moiety. Particularly desirable results are said to have been obtained with additives in which the glyceride is a glyceride of citric acid and oleic acid, a glyceride of citric acid and linoleic acid, or a mixture thereof. WO 2011/161406 does not describe the use of oil-soluble mono-, di-, or tri-glycerides of at least one hydroxy polycarboxylic acid, or derivatives thereof, as anti-camshaft-wear additives.

[0008] There remains a need for alternative compositions exhibiting anti-camshaft-wear properties, for example for use in non-aqueous lubricant compositions and/or for use in internal combustion engine fuel compositions.

[0009] Thus, according to the present invention there is provided the use of an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, as an anti-camshaft-wear additive in a non-aqueous lubricant composition and/or in a fuel composition, wherein the non-aqueous lubricant composition and/or fuel composition is used in a compression-ignition internal combustion engine.

[0010] The present invention solves the technical problem defined above by the use as an anti-camshaft-wear additive of an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof in a compression-ignition internal combustion engine.

[0011] In at least some examples, the use of an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, as an anti-camshaft-wear additive in a non-aqueous lubricant composition and/or in a fuel composition reduces camshaft wear as measured in the OM646LA engine test.

[0012] Uses of the non-aqueous lubricant composition incorporating an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, as an anti-camshaft-wear additive include all conventional lubricant purposes, for example to lubricate internal combustion engines. In at least some examples, the lubricating oil

composition may initially be free of oil-soluble mono-, di-, or tri-glycerides of hydroxy polycarboxylic acids, or derivatives thereof, or contain only very low amounts thereof, the oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, instead being provided in liquid fuel composition used to operate a compression-ignition internal combustion engine, and at least a portion of said glyceride ingressing into the lubricating oil composition to act as an anti-camshaft-wear additive during the operation of said engine.

[0013] The amount of oil-soluble mono-, di- or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, used as an anti-camshaft-wear additive in a non-aqueous lubricant composition in accordance with the present invention includes any amount suitable to reduce camshaft wear, for example an amount sufficient for the composition to pass the OM646LA engine test, for example from 0.1 to 5% by weight, from 0.2 to 2.5% by weight or from 0.5 to 1% by weight.

[0014] In at least some examples, the numerical percentages referenced in this application may be preceded by the word "about."

[0015] The amount of oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, used as an anti-camshaft-wear additive in a fuel composition in accordance with the present invention includes any amount suitable to cause a lubricating oil composition used to provide lubrication to a compression-ignition internal combustion engine fuelled by the liquid fuel composition to have anti-camshaft-wear properties following the ingress of the oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, into lubricating oil composition during operation of said engine, for example sufficient to provide amounts as discussed above.

[0016] In at least some examples, the hydroxy polycarboxylic acid of the oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy carboxylic acid, or a derivative thereof, used as an anti-camshaft-wear additive has at least one hydroxy group or derivative (for example ether or ester) thereof, which is in an alpha position with respect to a carboxylic moiety.

[0017] In at least some examples, each hydroxy polycarboxylic acid independently has from 4 to 22 carbon atoms, for example 4 to 15 carbon atoms. In at least some examples, the oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or derivative thereof, has from 16 to 80 carbon atoms. The number of carbon atoms in the glyceride may affect its solubility in oil of lubricating viscosity and/or in liquid fuel.

[0018] By oil-soluble is meant that the glyceride is soluble in an oil of lubricating viscosity and/or a liquid fuel, suitably in an anti-camshaft-wear improving amount, for example in an amount by weight of at least 200 ppm in an oil of lubricating viscosity and/or in an amount by weight of at least 10 ppm in a liquid fuel. In at least some examples, the solubility is determined at ambient temperature, for example at 20 °C. Methods of determining the solubility include those for determining solubility at atmospheric pressure.

[0019] Suitable hydroxy polycarboxylic acids include:

- citric acid (also sometimes called 3-carboxy-3-hydroxy pentanedioic acid; 2-hydroxypropane-1,2,3- tricarboxylic acid; or 3-hydroxypentanedioic acid-3-carboxylic acid);
- tartaric acid (also sometimes called 2,3-dihydroxybutanedioic acid; or 2,3-dihydroxysuccinic acid);
- malic acid (also sometimes called hydroxybutanedioic acid);
- monohydroxy trimesic acid; and
- hydrogenated monohydroxy trimesic acid (sometimes also called 1,3,5 tricarboxy, 2-hydroxy cyclohexane).

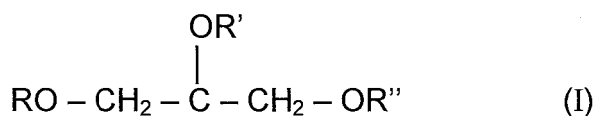
[0020] Examples of the oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, include a di-, or tri-glyceride which is a glyceride of at least one hydroxy polycarboxylic acid and at least one second carboxylic acid which is a saturated, mono-unsaturated or poly-unsaturated, branched or linear, monocarboxylic or polycarboxylic acid having 4 to 22 carbon atoms, or a derivative thereof.

[0021] In at least some examples, the second carboxylic acid is saturated, mono-unsaturated or poly-unsaturated. Suitably, the second carboxylic acid is unsaturated. In at least some examples, the second carboxylic acid is branched or linear. In at least some examples, the second carboxylic acid is a monocarboxylic or polycarboxylic acid. If the second carboxylic acid is a polycarboxylic acid, the derivative of the glyceride includes those in which the glyceride is an ester of the second carboxylic acid group.

[0022] Suitable saturated second carboxylic acids include caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid and arachidic acid. Suitable unsaturated second carboxylic acids include oleic acid, linoleic acid, linolenic acid, myristoleic acid, palmitoleic acid, sapienic acid, erucic acid (also known as *cis*-13-docosenoic acid) and brassidic acid.

[0023] In at least some examples, the glyceride is a glyceride of citric acid and oleic acid, a glyceride of citric acid and linoleic acid or a mixture thereof.

[0024] In at least some examples, the mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid or derivative thereof is represented by the general formula (I):



wherein RO, OR' and OR'' independently represent:

-OH;

a saturated, mono-unsaturated or poly-unsaturated, branched or linear, monocarboxylic or polycarboxylic group having from 4 to 22 carbon atoms or an ether or an ester thereof; or

a hydroxy polycarboxylic acid moiety or an ether and/or ester thereof, provided that at least one of RO, OR' and OR'' is a hydroxy polycarboxylic acid moiety or an ether and/or ester thereof.

[0025] In at least some examples, in formula (I) at least one of RO, OR' and OR'' is a hydroxy polycarboxylic acid moiety or an ether and/or ester thereof and at least one of RO, OR' and OR'' is a saturated, mono-unsaturated or poly-unsaturated, branched or linear, monocarboxylic or polycarboxylic group having from 4 to 22 carbon atoms or an ester thereof.

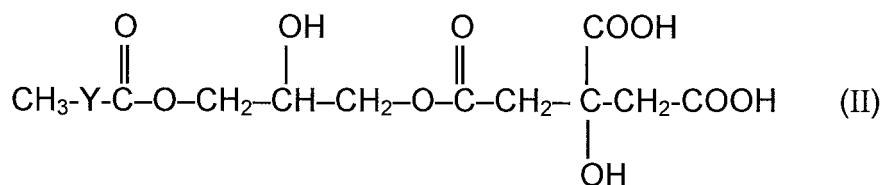
[0026] In at least some examples, in formula (I) the hydroxy polycarboxylic moiety acid has at least one hydroxy group or derivative (for example ether or ester) thereof which is in an alpha position with respect to a carboxylic moiety.

[0027] In at least some examples, in formula (I) each hydroxy polycarboxylic moiety independently has from 4 to 22 carbon atoms. In formula (I) the hydroxy polycarboxylic moiety, in at least some examples, is derivable from acids including, for example, citric acid, tartaric acid, malic acid, monohydroxy trimesic acid and hydrogenated monohydroxy trimesic acid.

[0028] In at least some examples, in formula (I), when present, each saturated, branched or linear, monocarboxylic or polycarboxylic group having from 4 to 22 carbon atoms or an ester thereof, is derivable from saturated carboxylic acids or their halide equivalents. Suitable saturated carboxylic acids include, for example, caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid and arachidic acid. In formula (I) when present, each mono-unsaturated or poly-unsaturated, branched or linear, monocarboxylic or polycarboxylic group having from 4 to 22 carbon atoms or an ester thereof may be derivable from unsaturated carboxylic acids or their halide equivalents. Suitable mono-unsaturated acids include, for example, oleic acid, myristoleic acid, palmitoleic acid, sapienic acid, erucic acid and brassidic acid. Suitable polyunsaturated acids include, for example, linoleic acid and linolenic acid.

[0029] In at least some examples, the glyceride is a glyceride of at least one hydroxy polycarboxylic acid and a saturated C₄ to C₂₂ polycarboxylic acid, or a derivative thereof. Suitable polycarboxylic acids include branched and linear acids. In at least some examples, the glyceride is a glyceride of at least one hydroxy polycarboxylic acid and a mono-unsaturated or polyunsaturated C₄ to C₂₂ polycarboxylic acid, or a derivative thereof. Suitable polycarboxylic acids include branched or linear acids. In at least some examples, the glyceride is a glyceride of at least one hydroxy polycarboxylic acid and a saturated C₄ to C₂₂ monocarboxylic acid, or a derivative thereof. Suitable monocarboxylic acids include branched and linear acids. Suitable saturated C₁₆ monocarboxylic acids include palmitic acid. Suitable saturated C₁₈ monocarboxylic acids include stearic acid. In at least some examples, the glyceride is a glyceride of at least one hydroxy polycarboxylic acid and a mono-unsaturated or polyunsaturated C₄ to C₂₂ monocarboxylic acid, or a derivative thereof. Suitable unsaturated monocarboxylic acids include branched and linear acids. In at least some examples, the glyceride is a glyceride of at least one hydroxy polycarboxylic acid and an unsaturated C₁₈ monocarboxylic acid, or a derivative thereof. Suitable monocarboxylic acids include branched or linear acid. Suitable hydroxy polycarboxylic acids include citric acid. The glyceride additive may be a glyceride of citric acid and an unsaturated C₁₈ monocarboxylic acid, or a derivative thereof. Suitable unsaturated C₁₈ monocarboxylic acids include oleic acid and linoleic acid.

[0030] In at least some examples, the glyceride is a citric acid ester of a mono-glyceride of a saturated, mono-unsaturated or polyunsaturated, branched or linear, monocarboxylic or polycarboxylic C₄ to C₂₂ carboxylic acid, for example a C₁₆ or C₁₈ carboxylic acid, for example palmitic acid, stearic acid, oleic acid or linoleic acid. Suitable glycerides include citric acid esters of mono-glyceride made from vegetable oil, for example sunflower and/or palm oil. Suitable glycerides include citric acid esters of mono-glyceride made from edible, refined sunflower and palm based oil. Suitably, the glyceride is a glyceride of citric acid and oleic acid, a glyceride of citric acid and linoleic acid or a mixture thereof. A suitable source of glycerides of citric acid with oleic acid and/or linoleic acid is GRINSTED CITREM SP70 (Trade Mark) which is available from Danisco. GRINSTED CITREM SP70 is believed to be a citric acid ester of mono-glyceride made from edible, refined sunflower and palm based oil. GRINSTED CITREM SP70 is also believed to comprise at least one diglyceride having the structural formula (II):



wherein -Y- represents a C₁₆ hydrocarbyl moiety which is mono- or di-unsaturated.

[0031] Thus, diglycerides having structural formula (II) include a glyceride of citric acid and oleic acid and a glyceride of citric acid and linoleic acid. This corresponds to a structure of formula (I) in which (i) RO represents a carboxyl group having 18 carbon atoms, which may be derivable from oleic acid and/or linoleic acid, (ii) OR' represents a hydroxy moiety, and (iii) OR'' represents a hydroxy polycarboxylic acid moiety, which may be derivable from citric acid.

[0032] GRINSTED® CITREM N 12 VEG from Danisco is believed to be a neutralised citric acid ester of mono-glyceride made from edible, fully hydrogenated palm based oil. It was found to be unsuitable because it was not oil soluble.

[0033] The use of GRINSTED® CITREM 2-IN-1 from Danisco as a carboxylic acid anionic surfactant is described in paragraphs [0167] to [0171] of US patent application publication US 2008/0176778. US 2008/0176778 relates to conveyor lubricants including emulsion of a lipophilic compound and an emulsifier and/or an anionic surfactant (title). The lipophilic compound is said to include water insoluble organic compounds including two or more ester linkages and in one embodiment is said to be a water insoluble organic compound including three or more oxygen atoms. It is stated that in one embodiment, the lipophilic compound is an ester including a di-, tri-, or poly-hydric alcohol, such as glycerol, with 2 or more of the hydroxy groups each being coupled to a carboxylic acid as an ester group (paragraph [0033]). In the example at paragraphs [0167] to [0171], two triglyceride lubricant compositions were tested. Lubricant A was said to contain an emulsion of 10 wt% of a caprylate, caprate, cocoate triglyceride in water to which was added the anionic surfactant 1.5 wt% lecithin (sold under the trade name Terradrill V408, Cognis) and the emulsifier 1.5 wt% 20 mol ethoxysorbitan monostearate (sold under the trade name Tween 60V, ICI). Lubricant B was said to contain 1.5 wt% citrate ester, said to be a carboxylic acid anionic surfactant sold under the name GRINSTED® CITREM 2-IN-1, Danisco in place of the Terradrill V408. According to paragraph [0171], Triglyceride lubricants including anionic surfactant worked well as dry conveyor lubricants and effectively lubricated after water was applied to the conveyor. According to paragraph [0061] of US 2008/0176778, the composition therein can include any variety of anionic surfactants that are effective to increase the ability of the lipophilic emulsion to withstand application of water to the conveyor. Examples are given in paragraphs [0065] to [0075] of ten classes of anionic surfactant.

[0034] According to paragraph [0029] of US patent application publication US 2009/0152502, hydrophilic emulsifier CITREM is a composition of matter containing citric esters of mono- and diglycerides of edible fatty acids. It is also stated therein that edible fatty acids have, in particular, 6 to 24 carbon atoms.

[0035] The glyceride may be an ester of citric acid with a partial glyceride, for example mono- or di- glyceride or mixtures thereof, which have free hydroxy groups. Suitable partial glycerides include those derived from fatty acids with 12 to 18 carbon atoms, including for example those derived from coconut oil fatty acids and palm oil fatty acids. Examples include Lamegin® ZE 306, Lamegin® ZE 609 and Lamegin® ZE 618 (Cognis Deutschland GmbH & Co. KG). Thus, suitable glycerides include a citric acid ester of the monoglyceride of hydrogenated tallow fatty acid, for example Lamegin® ZE 309, or an ester of diacetyl tartaric acid with monoglyceride of hydrogenated tallow fatty acid, for example Lamegin® DW 8000, or citric acid ester based on sunflower oil fatty acid monoglyceride, for example Lamegin® ZE 609 FL. Such esters are described, for example, in US 5770185 and US 2010/0087319.

[0036] In at least some examples, the derivative of the glyceride is an ester of the at least one hydroxy polycarboxylic acid moiety. Suitable esters include esters of a carboxylic acid moiety of the hydroxy polycarboxylic acid. In at least some examples, each carboxylic acid moiety of the hydroxy polycarboxylic acid is independently derivatisable as an ester. Suitable ester derivatives include hydrocarbyl esters, in which the hydrocarbyl moiety has, for example, from 4 to 22 carbon atoms. In at least some examples, the hydrocarbyl moieties include alkyl moieties which have, for example, from 4 to 22 carbon atoms. In at least some examples, the hydrocarbyl moiety comprises one or more hetero atoms, for example nitrogen and/or oxygen.

[0037] In at least some examples, the derivative of the glyceride is an ether or an ester of the hydroxy moiety of the hydroxy polycarboxylic acid. In at least some examples, if more than one hydroxy moiety is present in the mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, each hydroxy moiety is, for example, independently derivatisable as an ether or an ester. Suitable ethers include hydrocarbyl ethers. In at least some examples, the hydrocarbyl moiety of each ether independently has from 1 to 22 carbon atoms, for example, from 1 to 18 carbon atoms. In at least some examples, the hydrocarbyl moiety of each ether is independently an alkyl moiety. Suitable alkyl moieties of each ether independently include alkyl moieties containing from 1 to 22 carbon atoms, for example, from 1 to 18 carbon atoms. In at least some examples, the hydrocarbyl moiety of each ether independently comprises one or more hetero atoms, for example nitrogen and/or oxygen. In at least some examples, each ester is independently a hydrocarbyl ester. In at

least some examples, the hydrocarbyl moiety of each ester has from 4 to 22 carbon atoms. Suitable hydrocarbyl moieties of each ester independently include alkyl moieties. In at least some examples, the alkyl moiety of each ester may independently have from 4 to 22 carbon atoms. The hydrocarbyl moiety of each ester independently comprises one or more hetero atoms, for example nitrogen and/or oxygen.

[0038] If the saturated, mono-unsaturated or polyunsaturated, branched or linear carboxylic acid having 4 to 22 carbon atoms is a polycarboxylic acid, the derivative of the glyceride, in at least some examples, is an ester of a carboxylic acid moiety of one or more of the at least one saturated, mono-unsaturated or poly-unsaturated, branched or linear, polycarboxylic acid containing from 4 to 22 carbon atoms, if present. In at least some examples, each ester independently is a hydrocarbyl ester. Suitable hydrocarbyl moieties of each ester independently include those containing from 4 to 22 carbon atoms. In at least some examples, the hydrocarbyl moiety is an alkyl moiety. Suitable alkyl moieties of each ester independently include those containing from 4 to 22 carbon atoms. In at least some examples, the hydrocarbyl moiety of each ester independently comprises one or more hetero atoms, for example nitrogen and/or oxygen.

[0039] The oil-soluble mono-, di-, or tri-glycerides of at least one hydroxy polycarboxylic acid and derivatives thereof may be made by methods known in the art. Suitable methods for the preparation of the di- and tri-glycerides include the partial hydrolysis of a fat to produce a mono-glyceride followed by esterification with a hydroxy polycarboxylic acid. Suitable methods for the preparation of the mono-glycerides include esterification of glycerol with a hydroxy polycarboxylic acid. In at least some examples, the hydrocarbyl ether derivatives are made from corresponding hydrocarbyl halides.

[0040] The oil-soluble mono-, di-, or tri-glycerides of at least one hydroxy polycarboxylic acid and derivatives thereof do not contain zinc or molybdenum, that is, they are molybdenum-free and zinc-free. They also are sulphur-free and phosphorus-free.

[0041] GRINSTED CITREM SP70 (Trade Mark) has low volatility and has low toxicity.

Lubricant Compositions

[0042] In at least some examples, the oil-soluble mono-, di-, or tri-glycerides of at least one hydroxy polycarboxylic acid, or derivatives thereof, are used as anti-camshaft-wear additives in any suitable lubricant compositions. Similarly, in at least some examples, the oil-soluble mono-, di-, or tri-glycerides of at least one hydroxy polycarboxylic acid, or derivatives thereof, are used to improve the camshaft wear properties of any conventional lubricant composition. Further details of suitable lubricant compositions are set out herein.

[0043] In at least some examples, the lubricant composition comprises a major amount of oil of lubricating viscosity and a minor amount of at least one additive. Major amount means greater than 50% and minor amount means less than 50 % by weight.

[0044] In at least some examples, the lubricant composition and the oil of lubricating viscosity may comprise base oil. Base oil comprises at least one base stock. In at least some examples, the lubricant composition comprises one or more additives other than the mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid. In at least some examples, the lubricant composition and/or the oil of lubricating viscosity comprises base oil in an amount of from greater than 50 % to about 99.5 % by weight, for example from about 85% to about 95% by weight.

[0045] The base stocks may be defined as Group I, II, III, IV and V base stocks according to API standard 1509, "ENGINE OIL LICENSING AND CERTIFICATION SYSTEM", April 2007 version 16th edition Appendix E, as set out in Table 1.

[0046] Group I, Group II and Group III base stocks may be derived from mineral oils. Group I base stocks are typically manufactured by known processes comprising solvent extraction and solvent dewaxing, or solvent extraction and catalytic dewaxing. Group II and Group III base stocks are typically manufactured by known processes comprising catalytic hydrogenation and/or catalytic hydrocracking, and catalytic hydroisomerisation. A suitable Group I base stock is AP/E core 150, for example, available from ExxonMobil. Suitable Group II basestocks include EHC 50 and EHC 110, for example, available from ExxonMobil. Suitable group III base stocks include Yubase 4 and Yubase 6 available, for example, from SK Lubricants. Suitable Group V base stocks include ester base stocks, for example Priolube 3970, available from Croda International plc. Suitable Group IV base stocks include hydrogenated oligomers of alpha olefins. Suitably, the oligomers may be made by free radical processes, Zeigler catalysis or by cationic Friedel-Crafts catalysis. Polyalpha olefin base stocks may be derived from C8, C10, C12, C14 olefins and mixtures of one or more thereof.

Table 1

Group	Saturated hydrocarbon content (% by weight) ASTM D2007		Sulphur content (% by weight) ASTM D2622 or D4294 or D4927 or D3120		Viscosity Index ASTM D2270
I	< 90	and/or	> 0.03	and	≥ 80 and < 120

(continued)

Group	Saturated hydrocarbon content (% by weight) ASTM D2007		Sulphur content (% by weight) ASTM D2622 or D4294 or D4927 or D3120		Viscosity Index ASTM D2270
II	≥ 90	and	≤ 0.03	and	≥ 80 and < 120
III	≥ 90	and	≤ 0.03	and	≥ 120
IV	polyalpha olefins				
V	all base stocks not in Groups I, II, III or IV				

[0047] In at least some examples, the lubricant composition and the oil of lubricating viscosity comprise one or more base oil and/or base stock which is/are natural oil, mineral oil (sometimes called petroleum-derived oil or petroleum-derived mineral oil), non-mineral oil and mixtures thereof. Natural oils include animal oils, fish oils, and vegetable oils. Mineral oils include paraffinic oils, naphthenic oils and paraffinic-naphthenic oils. Mineral oils may also include oils derived from coal or shale.

[0048] Suitable base oils and base stocks may be derived from processes such as chemical combination of simpler or smaller molecules into larger or more complex molecules (for example polymerisation, oligomerisation, condensation, alkylation, acylation).

[0049] Suitable base stocks and base oils may be derived from gas-to-liquids materials, coal-to-liquids materials, biomass-to-liquids materials and combinations thereof.

[0050] Suitable gas-to-liquids (sometimes also referred to as GTL materials) include these obtained by one or more process steps of synthesis, combination, transformation, rearrangement, degradation and combinations of two or more thereof applied to gaseous carbon-containing compounds. Suitable GTL derived base stocks and base oils include those obtained from the Fischer-Tropsch synthesis process in which synthesis gas comprising a mixture of hydrogen and carbon monoxide is catalytically converted to hydrocarbons, usually waxy hydrocarbons that are generally converted to lower-boiling materials hydroisomerisation and/or dewaxing (see, for example, WO 2008/124191).

[0051] Suitable biomass-to-liquids (sometimes also referred to as BTL) materials include those manufactured from compounds of plant origin, for example by hydrogenation of carboxylic acids or triglycerides to produce linear paraffins, followed by hydroisomerisation to produced branched paraffins (see, for example, WO-2007-068799-A).

[0052] Suitable coal-to-liquids materials include those made by gasifying coal to make synthesis gas which is then converted to hydrocarbons.

[0053] In at least some examples, the base oil and/or oil of lubricating viscosity have a kinematic viscosity at 100 °C in the range of 2 to 100 cSt, for example in the range of 3 to 50 cSt or in the range 3.5 to 25 cSt.

[0054] In at least some examples, the lubricant composition is a multi-grade lubricating oil composition according to the API classification xW-y where x is 0, 5, 10, 15 or 20 and y is 20, 30, 40, 50 or 60 as defined by SAE J300 2004, for example 5W-20, 5W-30, or 0W-20. In at least some examples, the lubricant composition has a High Temperature High Shear rate (HTHS) viscosity at 150 °C of at least 2.6 cP, for example as measured according to ASTM D4683, CEC L-36-A-90 or ASTM D5481.

[0055] In at least some examples, the lubricant composition has an HTHS viscosity at 150 °C according to ASTM D4683 of from 1 to < 2.6 cP, for example about 1.8 cP.

[0056] Methods of preparing the lubricant compositions include admixing an oil of lubricating viscosity with an effective amount of at least one additive which is an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, optionally together with one or more other lubricant additive.

[0057] Uses and methods of improving the anti-camshaft-wear properties of an oil of lubricating viscosity according to the present invention, include admixing an oil of lubricating viscosity with an effective amount of at least one additive which is an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof.

[0058] In at least some examples, the oil of lubricating viscosity is admixed with at least one additive in one or more steps by methods known in the art. In at least some examples, the additives are admixed as one or more additive concentrates or part additive package concentrates, optionally comprising solvent or diluent. In at least some examples, the oil of lubricating viscosity is prepared by admixing in one or more steps by methods known in the art, one or more base oils and/or base stocks, optionally with one or more additives and/or part additive package concentrates. In at least some examples, the additives, additive concentrates and/or part additive package concentrates are admixed with oil of lubricating viscosity or components thereof in one or more steps by methods known in the art.

Other Anti-wear Additives

[0059] In at least some examples, the lubricant composition further comprises at least one anti-wear additive other than the additive which is an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof. Such other anti-wear additives include ash-producing additives and ashless additives. Examples of such other anti-wear additives include non-phosphorus containing additives, for example sulphurised olefins. Examples of such other anti-wear additives also include phosphorus-containing anti-wear additives. Examples of suitable ashless phosphorus-containing anti-wear additives include triauryl phosphite and triphenylphosphorothionate and those disclosed in paragraph [0036] of US 2005/0198894. Examples of suitable ash-forming, phosphorus-containing anti-wear additives include dihydrocarbyl dithiophosphate metal salts. Examples of suitable metals of the dihydrocarbyl dithiophosphate metal salts include alkali and alkaline earth metals, aluminium, lead, tin, molybdenum, manganese, nickel, copper and zinc. Suitable dihydrocarbyl dithiophosphate metal salts include zinc dihydrocarbyl dithiophosphates (ZDDP). Suitable ZDDP's include those comprising hydrocarbyl groups independently having 1 to 18 carbon atoms, for example 2 to 13 carbon atoms or 3 to 18 carbon atoms, or for example 2 to 12 carbon atoms or 3 to 13 carbon atoms, for example 3 to 8 carbon atoms. Examples of suitable hydrocarbyl groups include alkyl, cycloalkyl and alkaryl groups, examples of which include those comprising ether or ester linkages, and also those that comprise substituent groups, for example halogen or nitro groups. Suitable hydrocarbyl groups include alkyl groups including, for example, linear and/or branched alkyl groups including, for example, those containing from 3 to 8 carbon atoms. Suitable ZDDP's include those comprising hydrocarbyl groups which are a mixture of secondary alkyl groups and primary alkyl groups, for example 90 mol. % secondary alkyl groups and 10 mol. % primary alkyl groups.

[0060] The oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, additive may reduce the amount of phosphorus- and/or zinc-containing anti-wear additive which might be required to achieve a desired amount of anti-wear properties for the lubricant composition.

[0061] In at least some examples, phosphorus-containing anti-wear additives are present in the lubricating oil composition at a concentration of 10 to 6000 ppm by weight of phosphorus, for example 10 to 1000 ppm by weight of phosphorus, or 200 to 1400 ppm by weight of phosphorus, or 200 to 800 ppm by weight of phosphorus or 200 to 600 ppm by weight of phosphorus.

[0062] It has been found that the presence in the lubricant composition of at least one oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, may assist in the performance of anti-wear additives, such as for example, zinc dihydrocarbyl dithiophosphate additives. This may reduce the amount of metals, for example zinc, present in the lubricant composition.

[0063] This may also reduce the amount of phosphorus-containing anti-wear additives in the lubricant composition, which in turn may reduce the amount of phosphorus in the exhaust emissions when the lubricant is used to lubricate an internal combustion engine. The reduction in the amount of phosphorus in the exhaust emissions may have benefits for any exhaust after treatment system.

[0064] This may also reduce the amount of sulphur-containing anti-wear additives in the lubricant composition, which in turn may reduce the amount of sulphur in exhaust emissions when the lubricant is used to lubricate an internal combustion engine. The reduction in the amount of sulphur in exhaust emissions may have benefits for any exhaust after treatment system.

Other Friction Modifiers.

[0065] In at least some examples, the lubricant composition comprises at least one friction modifier other than the additive which is an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof. Such other friction modifiers may be ash-producing additives or ashless additives. Examples of such other friction modifiers include fatty acid derivatives including, for example, fatty acid esters, amides, amines, and ethoxylated amines. Examples of ester friction modifiers include esters of glycerol, for example mono-, di-, and tri-oleates, mono-palmitates and mono-myristates, for example glycerol monooleate. Examples of such other friction modifiers also include molybdenum compounds, for example organo molybdenum compounds, molybdenum dialkyldithiocarbamates, molybdenum dialkylthiophosphates, molybdenum disulphide, tri-molybdenum cluster dialkyldithiocarbamates, non-sulphur molybdenum compounds and the like. Suitable molybdenum-containing compounds are described, for example, in EP-1533362-A1, for example, in paragraphs [0101] to [0117].

[0066] Examples of friction modifiers other than the additive which is an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, also include a combination of an alkoxylated hydrocarbyl amine and a polyol partial ester of a saturated or unsaturated fatty acid or a mixture of such esters, for example as described in WO 93/21288.

[0067] In at least some examples, the oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, is used as an alternative to other friction modifiers and/or to reduce the amount of such

other friction modifiers that might be required to achieve a desired friction property for the lubricant composition. This may reduce the amount of metals, for example molybdenum, present in the lubricant composition.

[0068] In at least some examples, friction modifiers other than the additive which is an oil-soluble mono-, di-, or triglyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, which are fatty acid derivative friction modifiers are present in the lubricating oil composition at a concentration of 0.01 to 5 % by weight actives, for example in the range of 0.01 to 1.5 % by weight actives.

[0069] In at least some examples, molybdenum containing friction modifiers are present in the lubricating oil composition at a concentration of 10 to 1000 ppm by weight molybdenum, for example in the range of 400 to 600 ppm by weight.

Other Additives.

[0070] In at least some examples, the lubricant composition also comprises other additives. Examples of such other additives include dispersants (metallic and non-metallic), dispersant viscosity modifiers, detergents (metallic and non-metallic), viscosity index improvers, viscosity modifiers, pour point depressants, rust inhibitors, corrosion inhibitors, antioxidants (sometimes also called oxidation inhibitors), anti-foams (sometimes also called anti-foaming agents), seal swell agents (sometimes also called seal compatibility agents), extreme pressure additives (metallic, non-metallic, phosphorus containing, non-phosphorus containing, sulphur containing and non-sulphur containing), surfactants, demulsifiers, anti-seizure agents, wax modifiers, lubricity agents, anti-staining agents, chromophoric agents and metal deactivators.

Dispersants

[0071] Dispersants (also called dispersant additives) help hold solid and liquid contaminants, for example resulting from oxidation of the lubricant composition during use, in suspension and thus reduce sludge flocculation, precipitation and/or deposition for example on lubricated surfaces. They generally comprise long-chain hydrocarbons, to promote oil-solubility, and a polar head capable of associating with material to be dispersed. Examples of suitable dispersants include oil soluble polymeric hydrocarbyl backbones each having one or more functional groups which are capable of associating with particles to be dispersed. The functional groups may be amine, alcohol, amine-alcohol, amide or ester groups. In at least some examples, the functional groups are attached to the hydrocarbyl backbone through bridging groups. In at least some examples, more than one dispersant is present in the lubricant composition.

[0072] Examples of suitable ashless dispersants include oil soluble salts, esters, amino-esters, amides, imides and oxazolines of long chain hydrocarbon-substituted mono- and polycarboxylic acids or anhydrides thereof; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having polyamine moieties attached directly thereto; Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine; Koch reaction products and the like. Examples of suitable dispersants include derivatives of long chain hydrocarbyl-substituted carboxylic acids, for example in which the hydrocarbyl group has a number average molecular weight of up to 20000, for example 300 to 20000, 500 to 10000, 700 to 5000 or less than 15000. Examples of suitable dispersants include hydrocarbyl-substituted succinic acid compounds, for example succinimide, succinate esters or succinate ester amides and in particular, polyisobutenyl succinimide dispersants. Suitable dispersants include those that are borated or non-borated. A suitable non-borated dispersant is ADX 222.

Dispersant Viscosity Modifiers.

[0073] Additionally or alternatively, in at least some examples, dispersancy is provided by polymeric compounds capable of providing viscosity index improving properties and dispersancy. Such compounds are generally known as dispersant viscosity improver additives or multifunctional viscosity improvers. Methods of preparing such suitable dispersant viscosity modifiers include chemically attaching functional moieties (for example, amines, alcohols and amides) to polymers which tend to have number average molecular weights of at least 15000, for example in the range 20000 to 600000 (for example, as determined by gel permeation chromatography or light scattering methods). Examples of suitable dispersant viscosity modifiers and methods of making them are described in WO99/21902, WO2003/099890 and WO2006/099250. In at least some examples, more than one dispersant viscosity modifier is present in the lubricant composition.

Detergents

[0074] Detergents (also called detergent additives) may help reduce high temperature deposit formation, for example on pistons in internal combustion engines, including, for example, high-temperature varnish and lacquer deposits, by helping to keep finely divided solids in suspension in the lubricant composition. Detergents may also have acid-neutralising

properties. In at least some examples, ashless (that is non-metal containing) detergents are present. Metal-containing detergent comprises at least one metal salt of at least one organic acid, which is called soap or surfactant. Detergents may be overbased, in which the detergent comprises an excess of metal in relation to the stoichiometric amount required to neutralise the organic acid. The excess metal is usually in the form of a colloidal dispersion of metal carbonate and/or hydroxide. Examples of suitable metals include Group 1 and Group 2 metals, for example calcium, magnesium and combinations thereof. In at least some examples, more than one metal is present.

[0075] Examples of suitable organic acids include sulphonic acids, phenols (sulphurised or sulphurised and including, for example, phenols with more than one hydroxy group, phenols with fused aromatic rings, phenols which have been modified, for example alkylene bridged phenols, and Mannich base-condensed phenols and saligenin-type phenols, produced, for example, by reaction of phenol and an aldehyde under basic conditions) and sulphurised derivatives thereof, and carboxylic acids including, for example, aromatic carboxylic acids (for example, hydrocarbyl-substituted salicylic acids and sulphurised derivatives thereof, for example hydrocarbyl substituted salicylic acid and derivatives thereof). In at least some examples, more than one type of organic acid is present.

[0076] In at least some examples, additionally or alternatively, non-metallic detergents are present. Suitable non-metallic detergents are described for example in US7622431.

[0077] In at least some examples, more than one detergent is present in the lubricant composition and/or additive concentrate.

Viscosity Index Improvers/Viscosity Modifiers

[0078] Viscosity index improvers (also called viscosity modifiers, viscosity improvers or VI improvers) impart high and low temperature operability to a lubricant composition and facilitate it remaining shear stable at elevated temperatures whilst also exhibiting acceptable viscosity and fluidity at low temperatures.

[0079] Examples of suitable viscosity modifiers include high molecular weight hydrocarbon polymers (for example, polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins); polyesters (for example, polymethacrylates); hydrogenated poly(styrene-co-butadiene or isoprene) polymers and modifications (for example, star polymers); and esterified poly(styrene-co-maleic anhydride) polymers. Oil-soluble viscosity modifying polymers generally have number average molecular weights of at least 15,000 to 1,000,000, preferably 20,000 to 600,000, as determined by gel permeation chromatography or light scattering methods.

[0080] Viscosity modifiers may have additional functions as multifunction viscosity modifiers. In at least some examples, more than one viscosity index improver is present.

Pour Point Depressants

[0081] Pour point depressants (also called lube oil improvers or lube oil flow improvers), lower the minimum temperature at which the lubricant will flow and can be poured. Examples of suitable pour point depressants include C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers, methacrylates, polyacrylates, polyarylamides, polymethacrylates, polyalkyl methacrylates, vinyl fumarates, styrene esters, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers, wax naphthalene and the like.

[0082] In at least some examples, more than one pour point depressant is present.

Rust inhibitors

[0083] Rust inhibitors generally protect lubricated metal surfaces against chemical attack by water or other contaminants. Examples of suitable rust inhibitors include non-ionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, polyoxyalkylene polyols, anionic alkyl sulphonic acids, zinc dithiophosphates, metal phenolates, basic metal sulphonates, fatty acids and amines.

[0084] In at least some examples, more than one rust inhibitor is present.

Corrosion Inhibitors

[0085] Corrosion inhibitors (also called anti-corrosive agents) reduce the degradation of metallic parts contacted with the lubricant composition. Examples of corrosion inhibitors include phosphosulphurised hydrocarbons and the products obtained by the reaction of phosphosulphurised hydrocarbon with an alkaline earth metal oxide or hydroxide, non-ionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, thiadiazoles, triazoles and anionic alkyl sulphonic acids. Examples of suitable epoxidised ester corrosion inhibitors are described in US2006/0090393.

[0086] In at least some examples, more than one corrosion inhibitor is present.

Antioxidants

[0087] Antioxidants (sometimes also called oxidation inhibitors) reduce the tendency of oils to deteriorate in use. Evidence of such deterioration might include, for example, the production of varnish-like deposits on metal surfaces, the formation of sludge and viscosity increase. ZDDP's exhibit some antioxidant properties.

[0088] Examples of suitable antioxidants other than ZDDP's include alkylated diphenylamines, N-alkylated phenylenediamines, phenyl- α -naphthylamine, alkylated phenyl- α -naphthylamines, dimethylquinolines, trimethyldihydroquinolines and oligomeric compositions derived therefrom, hindered phenolics (including ashless (metal-free) phenolic compounds and neutral and basic metal salts of certain phenolic compounds), aromatic amines (including alkylated and non-alkylated aromatic amines), sulphurised alkyl phenols and alkali and alkaline earth metal salts thereof, alkylated hydroquinones, hydroxylated thiodiphenyl ethers, alkylidenebisphenols, thiopropionates, metallic dithiocarbamates, 1,3,4-dimercaptothiadiazole and derivatives, oil soluble copper compounds (for example, copper dihydrocarbyl thio- or thio-phosphate, copper salts of a synthetic or natural carboxylic acid, for example a C₈ to C₁₈ fatty acid, an unsaturated acid or a branched carboxylic acid, for example basic, neutral or acidic Cu^I and/or Cu^{II} salts derived from alkenyl succinic acids or anhydrides), alkaline earth metal salts of alkylphenolthioesters, for example containing C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulphide, barium *t*-octylphenyl sulphide, dioctylphenylamine, phosphosulphurised or sulphurised hydrocarbons, oil soluble phenates, oil soluble sulphurised phenates, calcium dodecylphenol sulphide, phosphosulphurised hydrocarbons, sulphurised hydrocarbons, phosphorus esters, low sulphur peroxide decomposers and the like.

[0089] In at least some examples, more than one anti-oxidant is present. In at least some examples, more than one type of anti-oxidant is present.

Antifoams

[0090] Anti-foams (sometimes also called anti-foaming agents) retard the formation of stable foams. Examples of suitable anti-foam agents include silicones, organic polymers, siloxanes (including poly siloxanes and (poly) dimethyl siloxanes, phenyl methyl siloxanes), acrylates and the like.

[0091] In at least some examples, more than one anti-foam is present.

Seal Swell Agents

[0092] Seal swell agents (sometimes also called seal compatibility agents or elastomer compatibility aids) help to swell elastomeric seals, for example by causing a reaction in the fluid or a physical change in the elastomer. Examples of suitable seal swell agents include long chain organic acids, organic phosphates, aromatic esters, aromatic hydrocarbons, esters (for example butylbenzyl phthalate) and polybutenyl succinic anhydride.

[0093] In at least some examples, more than one seal swell agent is present.

Other Additives

[0094] In at least some examples, other additives are present in the lubricant composition and these include, for example, extreme pressure additives (including metallic, non-metallic, phosphorus containing, non-phosphorus containing, sulphur containing and non-sulphur containing extreme pressure additives), surfactants, demulsifiers, anti-seizure agents, wax modifiers, lubricity agents, anti-staining agents, chromophoric agents and metal deactivators.

[0095] Some additives may exhibit more than one function.

[0096] The amount of demulsifier, if present, might be higher than in conventional lubricants to off-set any emulsifying effect of the mono-, di-, or tri-glyceride additive.

Solvent

[0097] The additive concentrate for a lubricant composition may comprise solvent. Examples of suitable solvents include highly aromatic, low viscosity base stocks, for example 100N, 60N and 100SP base stocks.

[0098] The representative suitable and more suitable independent amounts of additives (if present) in the lubricant composition are given in Table 2. The concentrations expressed in Table 2 are by weight of active additive compounds, that is, independent of any solvent or diluent.

[0099] In at least some examples, more than one of each type of additive is present. Within each type of additive, in at least some examples, more than one class of that type of additive is present. In at least some examples, more than one additive of each class of additive is present. In at least some examples, additives are supplied by manufacturers and suppliers in solvents or diluents.

Table 2

		Lubricant Composition	
ADDITIVE TYPE		Suitable amount (actives), if present (by weight)	More suitable amount (actives), if present (by weight)
Oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof		0.02 to 5%	0.1 to 2.5%
Phosphorus-containing anti-wear additives		corresponding to 10 to 6000 ppm P	corresponding to 10 to 1000 ppm P
Molybdenum-containing anti-wear additives		corresponding to 10 to 1000 ppm Mo	corresponding to 40 to 600 ppm Mo
Boron-containing anti-wear additives		corresponding to 10 to 250 ppm B	corresponding to 50 to 100 ppm B
Friction modifiers other than the mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof		0.01 to 5 %	0.01 to 1.5 %
Molybdenum-containing friction modifiers		corresponding to 10 to 1000 ppm Mo	corresponding to 400 to 600 ppm Mo
Dispersants		0.1 to 20 %	0.1 to 8 %
Detergents		0.01 to 6 %	0.01 to 4 %
Viscosity index improvers		0.01 to 20%	0.01 to 15%
Pour point depressants		0.01 to 5 %	0.01 to 1.5 %
Corrosion and/or rust inhibitors		0.01 to 5 %	0.01 to 1.5%
Anti -oxidants		0.1 to 10 %	0.5 to 5 %
Antifoams containing silicon		corresponding to 1 to 20 ppm Si	corresponding to 1 to 10 ppm Si

Lubricant Applications.

[0100] According to the invention, the mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, is used as an anti-camshaft-wear additive in a non-aqueous lubricant composition and/or in a fuel composition.

[0101] In at least some examples, the mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, is used as an anti-camshaft-wear additive in a non-aqueous lubricant composition and/or in a fuel composition used to lubricate a solid surface, including for example metallic surfaces and non-metallic surfaces. Suitable metallic surfaces include surfaces of ferrous based materials, for example cast iron and steels; surfaces of aluminium-based solids, for example aluminium-silicon alloys; surfaces of metal matrix compositions; surfaces of copper and copper alloys; surfaces of lead and lead alloys; surfaces of zinc and zinc alloys; and surfaces of chromium-plated materials. Suitable non-metallic surfaces include surfaces of ceramic materials; surfaces of polymer materials; surfaces of carbon-based materials; and surfaces of glass. Other surfaces which may be lubricated include surfaces of coated materials, for example surfaces of hybrid materials for example metallic materials coated with non-metallic materials and non-metallic materials coated with metallic materials; surfaces of diamond-like carbon coated materials and SUMEBore™ materials for example, as described in Sulzer technical review 4/2009 pages 11-13.

[0102] In at least some examples, the oil-soluble, mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, is used in a non-aqueous lubricant composition and/or in a fuel composition to lubricate a surface at any typical temperature which might be encountered in a lubricating environment, for example at a temperature such as may be encountered in an internal combustion engine, for example a temperature in the range of ambient to 250°C, e.g. 90 to 120°C. Typical ambient temperature is 20°C, but in at least some examples, is less than 20°C, for example 0°C or lower.

Internal Combustion Engine Lubrication.

[0103] According to the invention, the oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, is used as an anti-camshaft-wear additive in a lubricant composition which is used to lubricate a compression-ignition internal combustion engine, for example as a crankcase lubricant. Suitable internal combustion engines include two-stroke compression-ignition engines and, in at least the examples, the oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, is used as an anti-camshaft-wear additive in a system oil lubricant composition used to lubricate the engine. In at least some examples, the two-stroke compression-ignition engine is used in marine applications.

[0104] In at least some examples, additionally, or alternatively the mono-, di- or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, is present in the fuel for a compression-ignition internal combustion engine. In use, the oil-soluble, mono-, di- or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, passes with or without fuel into a lubricant composition used to lubricate the engine, for example as a crankcase lubricant, and thereby provides anti-camshaft-wear benefits to the engine.

[0105] Typically, the rate of ingress of fuel into crankcase lubricant is higher for spark-ignition internal combustion engines than for compression-ignition engines. However, the rate at which fuel ingresses into the crankcase lubricant for compression-ignition engines may depend and may increase depending upon the use of post-injection strategies for operation of the engine.

Fuels

[0106] In at least some examples, the oil-soluble mono-, di- or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, is used as anti-camshaft-wear additives in any suitable fuel compositions.

[0107] Suitable liquid fuels for compression-ignition internal combustion engines, include hydrocarbon fuels, oxygenate fuels and combinations thereof. Hydrocarbon fuels may be derived from mineral sources and/or from renewable sources such as biomass (e.g. biomass-to-liquid sources) and/or from gas-to-liquid sources and/or from coal-to-liquid sources. Suitable sources of biomass include sugar (e.g. sugar to diesel fuel) and algae. Suitable oxygenate fuels include alcohols, for example straight and/or branched chain alkyl alcohols having from 1 to 6 carbon atoms, esters, for example fatty acid alkyl esters and ethers, for example methyl tert butyl ether. Suitable fuels may also include LPG-diesel fuels (LPG being liquefied petroleum gas). In at least some examples, the fuel composition is an emulsion. In at least some examples, the fuel composition is not an emulsion.

[0108] Suitable fatty acid alkyl esters include methyl, ethyl, propyl, butyl and hexyl esters. In at least some examples, the fatty acid alkyl ester is a fatty acid methyl ester. In at least some examples, the fatty acid alkyl ester has 8 to 25 carbon atoms, for example 12 to 25 carbon atoms, for example 16 to 18 carbon atoms. In at least some examples, the fatty acid is saturated. In at least some examples, the fatty acid is unsaturated. In at least some examples, the fatty acid alkyl ester is acyclic. Methods of preparing such fatty acid alkyl esters include esterification of one or more fatty acids and/or by transesterification of one or more triglycerides of fatty acids. In at least some examples, the triglycerides is obtained from vegetable oils, for example castor oil, soyabean oil, cottonseed oil, sunflower oil, rapeseed oil (which is sometimes called canola oil), Jatropa oil or palm oil, or obtained from tallow (for example, sheep and/or beef tallow), fish oil or used cooking oil. Suitable fatty acid alkyl esters include rapeseed oil methyl ester (RME), soya methyl ester or combinations thereof.

[0109] In at least some examples, the fuel compositions are prepared by admixing in one or more steps a hydrocarbon fuel, an oxygenate fuel, or a combination thereof, with an effective amount of at least one additive which is a mono-, di- or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, and optionally at least one other fuel additive.

[0110] In at least some examples, the use and the method of improving the anti-camshaft-wear properties of a liquid fuel of the present invention comprises admixing in one or more steps said liquid fuel (which may be, for example, a hydrocarbon fuel, an oxygenate fuel or a combination thereof) with an effective amount of at least one additive which is a mono-, di- or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, and optionally at least one other fuel additive.

[0111] In at least some examples, the fuel is admixed with at least one additive in one or more steps by methods known in the art. In at least some examples, the additives are admixed as one or more additive concentrates or part additive package concentrates, optionally comprising solvent or diluent. In at least some examples, the hydrocarbon fuel, oxygenate fuel or combination thereof is prepared by admixing in one or more steps by methods known in the art, one or more base fuels and components therefor, optionally with one or more additives and/or part additive package concentrates. In at least some examples, the additives, additive concentrates and/or part additive package concentrates is admixed with the fuel or components therefor in one or more steps by methods known in the art.

Fuels For Compression-ignition Engines.

[0112] According to the invention, the fuel composition comprising an oil-soluble, mono-, di- or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, as an anti-camshaft-wear additive is suitable for use in an internal combustion engine which is a compression-ignition internal combustion engine, suitably a direct injection diesel engine, for example of the rotary pump, in-line pump, unit pump, electronic unit injector or common rail type, or in an indirect injection diesel engine. In at least some examples, the fuel composition is suitable for use in heavy and/or light duty diesel engines.

[0113] In at least some examples, the fuel composition for compression-ignition internal combustion engines has a sulphur content of up to 500 ppm by weight, for example up to 15 ppm by weight or up to 10 ppm by weight. In at least some examples, the fuel composition for compression-ignition internal combustion engines meets the requirements of the EN590 standard, for example as set out in BS EN 590:2009.

[0114] In at least some examples, oxygenate components in the fuel composition for compression-ignition internal combustion engines include fatty acid alkyl esters, for example fatty acid methyl esters. In at least some examples, the fuel comprises one or more fatty acid methyl esters complying with EN 14214 at a concentration of up to 7 % by volume. In at least some examples, oxidation stability enhancers are present in the fuel composition, comprising one or more fatty acid alkyl or methyl esters, for example at a concentration providing an action similar to that obtained with 1000 mg/kg of 3,5-di-tert-butyl-4-hydroxy-toluol (also called butylated hydroxy-toluene or BHT). In at least some examples, dyes and/or markers are present in the fuel composition for compression-ignition internal combustion engines.

[0115] In at least some examples, the fuel composition for compression-ignition internal combustion engines have one or more of the following, for example, as defined according to BS EN 590:2009 :- a minimum cetane number of 51.0, a minimum cetane index of 46.0, a density at 15 °C of 820.0 to 845.0 kg/m³, a maximum polycyclic aromatic content of 8.0% by weight, a flash point above 55°C, a maximum carbon residue (on 10% distillation) of 0.30 % by weight, a maximum water content of 200 mg/kg, a maximum contamination of 24 mg/kg, a class 1 copper strip corrosion (3 h at 50 °C), a minimum oxidation stability limit of 20 h according to EN 15751 and a maximum oxidation stability limit of 25 g/m³ according to EN ISO 12205, a maximum limit for lubricity corrected wear scar diameter at 60 °C of 460µm, a minimum viscosity at 40°C of 2.00 mm²/s and a maximum viscosity at 40°C of 4.50 mm²/s, < 65% by volume distillation recovery at 250°C, a minimum distillation recovery at 350°C of 85% by volume and a maximum of 95 % by volume recovery at 360°C.

[0116] In at least some examples, the fuel composition suitable for use in a compression-ignition internal combustion engine further comprises at least one friction modifier other than the additive which is a mono-, di- or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof. Such other friction modifiers include compounds described herein as friction modifiers for lubricant compositions and additive concentrates for lubricant compositions.

[0117] In at least some examples, the fuel composition suitable for use with a compression-ignition internal combustion engine further comprises at least one lubricity additive. Suitable lubricity additives include tall oil fatty acids, mono- and di-basic acids and esters.

[0118] In at least some examples, the fuel composition suitable for use in a compression-ignition internal combustion engine further comprises independently one or more cetane improver, one or more detergent, one or more anti-oxidant, one or more anti-foam, one or more demulsifier, one or more cold flow improver, one or more pour point depressant, one or more biocide, one or more odorant, one or more colorant (sometimes called dyes), one or more marker, one or more spark aiders and/or combinations of one or more thereof. In at least some examples, other suitable additives are present, including one or more thermal stabilizers, metal deactivators, corrosion inhibitors, antistatic additives, drag reducing agents, emulsifiers, dehazers, anti-icing additives, antiknock additives, anti-valve-seat recession additives, surfactants and combustion improvers, for example as described in EP-2107102-A.

[0119] In at least some examples, the additive concentrate for a fuel composition for a compression-ignition internal combustion engine comprises one or more solvents, for example carrier oils (for example. mineral oils), polyethers (which may be capped or uncapped), non-polar solvents (for example. toluene, xylene, white spirits and those sold by Shell companies under the trade mark "SHELLSOL"), and polar solvents (for example esters and alcohols e.g. hexanol, 2-ethylhexanol, decanol, isotridecanol and alcohol mixtures, for example those sold by Shell companies under the trade mark "LINEVOL", e.g. LINEVOL 79 alcohol which is a mixture of C₇₋₉ primary alcohols, or a C₁₂₋₁₄ alcohol mixture which is commercially available.

[0120] Suitable cetane improvers include 2-ethyl hexyl nitrate, cyclohexyl nitrate and di-tert-butyl peroxide. Suitable antifoams include siloxanes. Suitable detergents include polyolefin substituted succinimides and succinimides of polyamines, for example polyisobutylene succinimides, polyisobutylene amine succinimides, aliphatic amines, Mannich bases and amines and polyolefin (e.g. polyisobutylene) maleic anhydride. Suitable antioxidants include phenolic antioxidants (for example 2,6-di-tert-butylphenol) and aminic antioxidants (for example N,N'-di-sec-butyl-p-phenylenediamine). Suitable anti-foaming agents include polyether-modified polysiloxanes.

[0121] The representative suitable and more suitable independent amounts of additives (if present) in the fuel com-

position suitable for a compression-ignition engine are given in Table 3. The concentrations expressed in Table 3 are by weight of active additive compounds that is, independent of any solvent or diluent.

[0122] In at least some examples, the additives in the fuel composition suitable for use in compression-ignition internal combustion engines are suitably present in a total amount in the range of 100 to 1500 ppm by weight.

Table 3

Fuel composition for compression-ignition internal combustion engine	
Additive type	Suitable amount (actives), if present (ppm by weight) More suitable amount (actives), if present (ppm by weight)
Oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof	20 to 500 20 to 200
Lubricity additives	1 to 200 50 to 200
Cetane improvers	50 to 2000 100 to 1200
Detergents	20 to 300 50 to 200
Anti-oxidants	1 to 100 2 to 50
Anti foams	1 to 50 5 to 20
Demulsifiers	1 to 50 5 to 25
Cold flow improvers	10 to 500 50 to 100

Fuels For Spark-ignition Engines. (not according to the invention)

[0123] A fuel composition comprising an oil-soluble, mono-, di- or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, as an anti-camshaft-wear additive may be suitable for use in an internal combustion engine which is a spark-ignition internal combustion engine. The use of said compound in a spark-ignition internal combustion engine is not covered by the claims.

[0124] In at least some examples, the fuel composition for spark-ignition internal combustion engines has a sulphur content of up to 50.0 ppm by weight, for example up to 10.0 ppm by weight.

[0125] In at least some examples, the fuel composition for spark-ignition internal combustion engines is leaded or unleaded.

[0126] In at least some examples, the fuel composition for spark-ignition internal combustion engines meets the requirements of EN 228, for example as set out in BS EN 228:2008. In at least some examples, the fuel composition for spark-ignition internal combustion engines meets the requirements of ASTM D 4814-09b.

[0127] In at least some examples, the fuel composition for spark-ignition internal combustion engines has one or more of the following, for example, as defined according to BS EN 228:2008 :- a minimum research octane number of 95.0, a minimum motor octane number of 85.0 a maximum lead content of 5.0 mg/l, a density of 720.0 to 775.0 kg/m³, an oxidation stability of at least 360 minutes, a maximum existent gum content (solvent washed) of 5 mg/100 ml, a class 1 copper strip corrosion (3 h at 50 °C), clear and bright appearance, a maximum olefin content of 18.0 % by weight, a maximum aromatics content of 35.0 % by weight, and a maximum benzene content of 1.00 % by volume.

[0128] In at least some examples, oxygenate components in the fuel composition for spark-ignition internal combustion engines include straight and/or branched chain alkyl alcohols having from 1 to 6 carbon atoms, for example methanol, ethanol, n-propanol, n-butanol, isobutanol, tert-butanol. In at least some examples, oxygenate components in the fuel composition for spark-ignition internal combustion engines include ethers, for example having 5 or more carbon atoms. In at least some examples, the fuel composition has a maximum oxygen content of 2.7% by mass. In at least some examples, the fuel composition has maximum amounts of oxygenates, as specified in EN 228, for example methanol: 3.0% by volume, ethanol: 5.0% by volume, iso-propanol: 10.0 % by volume, iso-butyl alcohol: 10.0% by volume, tert-butanol: 7.0% by volume, ethers (C₅ or higher): 10% by volume and other oxygenates (subject to suitable final boiling point): 10.0% by volume. In at least some examples, the fuel composition comprises ethanol complying with EN 15376 at a concentration of up to 5.0% by volume.

[0129] In at least some examples, the fuel composition suitable for use in a spark-ignition internal combustion engine further comprises at least one friction modifier other than the additive which is a mono-, di- or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof. In at least some examples, such other friction modifiers include

compounds described herein as friction modifiers for lubricant compositions and additive concentrates for lubricant compositions.

[0130] In at least some examples, the fuel composition suitable for use in a spark-ignition internal combustion engine further comprises independently one or more detergent, one or more octane improver, one or more friction modifier, one or more anti-oxidant, one or more valve seat recession additive, one or more corrosion inhibitor, one or more anti-static agent, one or more odorant, one or more colorant, one or more marker and/or combinations of one or more thereof.

[0131] In at least some examples, the additive concentrate for a fuel composition for a spark-ignition internal combustion engine comprises one or more solvents, for example polyethers and aromatic and/or aliphatic hydrocarbons, for example heavy naphtha e.g. Solvesso (Trade mark), xylenes and kerosine.

[0132] Suitable detergents include poly isobutylene amines (PIB amines) and polyether amines.

[0133] Suitable octane improvers include N-methyl aniline, methyl cyclopentadienyl manganese tricarbonyl (MMT) (for example present at a concentration of up to 120 ppm by weight), ferrocene (for example present at a concentration of up to 16 ppm by weight) and tetra ethyl lead (for example present at a concentration of up to 0.7 g/l, e.g. up to 0.15 g/l).

[0134] Suitable anti-oxidants include phenolic anti-oxidants (for example 2,4-di-tert-butylphenol and 3,5-di-tert-butyl-4-hydroxyphenylpropionic acid) and aminic anti-oxidants (for example para-phenylenediamine, dicyclohexylamine and derivatives thereof).

[0135] Suitable corrosion inhibitors include ammonium salts of organic carboxylic acids, amines and heterocyclic aromatics, for example alkylamines, imidazolines and tolyltriazoles.

[0136] In at least some examples, valve seat recession additives are present at a concentration of up to 15000 ppm by weight, for example up to 7500 ppm by weight.

[0137] The representative suitable and more suitable independent amounts of additives (if present) in the fuel composition suitable for a spark-ignition engine are given in Table 4. The concentrations expressed in Table 4 are by weight of active additive compounds that is, independent of any solvent or diluent.

[0138] In at least some examples, the additives in the fuel composition suitable for use in spark-ignition internal combustion engines are present in a total amount in the range of 20 to 25000 ppm by weight.

Table 4

Additive type	Fuel composition for spark-ignition internal combustion engine	
	Suitable amount (actives), if present (ppm by weight)	More suitable amount (actives), if present (ppm by weight)
Oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof	20 to 500	20 to 200
Friction modifiers other than mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof	10 to 500	25 to 150
Detergents	10 to 2000	50 to 300
Octane improvers	50 to 20000	
Anti -oxidants	1 to 100	10 to 50
Anti-static agents	0.1 to 5	0.5 to 2

[0139] The invention will now be described by way of example only with reference to the following experiments and examples in which examples according to the present invention are labeled numerically as Example 1, Example 2, etc. and experiments not according to the present invention are labeled alphabetically as Experiment A, Experiment B, etc.

Preparation of Lubricant Compositions.

[0140] A lubricant composition (Lubricant A) was prepared to model a typical lubricant composition suitable for passenger cars with either compression-ignition or spark-ignition internal combustion engines. The lubricant composition was made by admixing additives as in a commercially available additive package containing dispersant, calcium sulphate and calcium phenate detergents, antioxidant, antifoam and ZDDP with Group III base oil, a pour point depressant and a viscosity modifier.

[0141] A lubricant composition (Lubricant B) was prepared in the same way as Lubricant A, but with the addition of

0.2% by weight of oleamide.

[0142] A lubricant composition (Lubricant 1) according to the invention was prepared in the same way as Lubricant A, but with the addition of 0.5 % Citrem SP 70 (Trade Mark) (a diglyceride of citric acid and oleic/linoleic acid).

[0143] A lubricant composition (Lubricant C) was prepared to model a typical lubricant composition suitable for passenger cars with either compression-ignition or spark-ignition internal combustion engines. The lubricant composition was made by admixing additives as in a commercially available additive package containing dispersant, calcium sulphonate and calcium phenate detergents, antioxidant, antifoam and ZDDP with Group I and III base oils, a pour point depressant and a viscosity modifier.

[0144] A lubricant composition (Lubricant D) was prepared in the same way as Lubricant C, but with the addition of 0.2% by weight of oleamide.

[0145] A lubricant composition (Lubricant 2) according to the invention was prepared in the same way as Lubricant C, but with the addition of 0.5 % Citrem SP 70 (Trade Mark) (a diglyceride of citric acid and oleic/linoleic acid).

[0146] Lubricants A to D are not according to the present invention because the lubricant compositions do not contain an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, in particular a diglyceride of citric acid and an unsaturated C₁₈ carboxylic acid (e.g. oleic and/or linoleic acid), for example Citrem SP70 (Trade Mark). Lubricants 1 and 2 are according to the present invention.

Anti-Wear Testing of Lubricant Compositions.

1. Sequence IVA Engine Test (not according to the invention)

[0147] Sequence IVA engine tests according to ASTM test method ASTM D6891 were undertaken for Lubricants A and B, as well as for Lubricant 1. The Sequence IVA test is an industry standard test used to evaluate the camshaft wear protection of internal combustion engine lubricant compositions. This test method is designed to simulate extended engine idling vehicle operation. The primary result is camshaft lobe wear (measured at seven locations around each of the twelve lobes) and the pass/fail criteria for the test include a maximum average seven-location cam lobe wear of 90 microns (μm).

[0148] The results for the tests are shown in Table 5. Experiments A and B are not according to the present invention because the lubricant compositions do not contain an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, in particular a diglyceride of citric acid and an unsaturated C₁₈ carboxylic acid (e.g. oleic and/or linoleic acid), for example Citrem SP70 (Trade Mark). Example 1 is according to the present invention.

[0149] The results in Table 5 show that both oleamide and an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, in particular a diglyceride of citric acid and an unsaturated C₁₈ carboxylic acid (e.g. oleic and/or linoleic acid), for example Citrem SP70 (Trade Mark), significantly reduce cam lobe wear and are thus effective as anti-camshaft-wear additives in the Sequence IVA test.

Table 5

	Lubricant	Anti-camshaft - wear additive	Treat rate of anti-wear additive (wt.%)	Average cam lobe wear (micron, μm)
Expt. A	A	-	-	42.56
Expt. B	B	Oleamide	0.2%	24.38
Example 1	1	Citrem SP70	0.5%	22.17

2. OM646LA Engine Test (inventive)

[0150] OM646LA (CEC L-99-08) engine tests were undertaken for Lubricants C and D, as well as for Lubricant 2. This 300 hour cyclic test uses a 4 cylinder 2.2L diesel OM646 DE 22 LA engine to evaluate engine lubricant performance with respect to engine wear and overall cleanliness, as well as piston cleanliness and ring sticking, under severe operating conditions. The primary result is cam wear, although bore polish, cylinder wear and tappet wear may also be measured.

[0151] The results for the tests are shown in Table 6. Experiments C and D are not according to the present invention because the lubricant compositions do not contain an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, in particular a diglyceride of citric acid and an unsaturated C₁₈ carboxylic acid (e.g. oleic and/or linoleic acid), for example Citrem SP70 (Trade Mark). Example 2 is according to the present invention.

[0152] The results in Table 6 show that there is moderately high camshaft wear in the OM646LA test in respect of Lubricant C, which contains no anti-camshaft-wear additive (Experiment C). No appreciable reduction in camshaft wear is observed as a result of the presence of oleamide additive in Lubricant D (Experiment D). In contrast, a significant reduction in camshaft wear is observed for Lubricant 2, containing Citrem SP70 (trade mark) (Example 2). Thus, the results demonstrate that an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, in particular a diglyceride of citric acid and an unsaturated C₁₈ carboxylic acid (e.g. oleic and/or linoleic acid), for example Citrem SP70 (Trade Mark), is effective as an anti-camshaft-wear additive in the OM646LA test.

Table 6

	Experiment C	Experiment D	Example 2
Lubricant	C	D	2
Anti -Camshaft - Wear Additive	-	Oleamide	Citrem SP70
Treat rate of Anti-Camshaft-Wear Additive (wt.%)	-	0.2%	0.9%
Avg. Inlet camshaft (mm)	60.06	63.7	39.1
Avg. Outlet camshaft (mm)	111.4	105	35.7

[0153] In contrast to known anti-wear additives, such as oleamide, an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, in particular a diglyceride of citric acid and an unsaturated C₁₈ carboxylic acid (e.g. oleic and/or linoleic acid), for example Citrem SP70 (Trade Mark), is surprisingly effective as an anti-camshaft-wear additive in both Sequence IVA and OM646LA wear tests.

Claims

1. The use of an oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, as an anti-camshaft-wear additive in a non-aqueous lubricant composition and/or in a fuel composition, wherein the non-aqueous lubricant composition and/or fuel composition is used in a compression-ignition internal combustion engine.
2. The use as claimed in claim 1, wherein the oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, reduces camshaft wear as measured in the OM646LA engine test.
3. The use as claimed in claim 1 or claim 2, wherein the oil-soluble mono-, di-, or tri-glyceride of at least one hydroxy polycarboxylic acid, or a derivative thereof, is provided in a liquid fuel composition used to operate the internal combustion engine, and a portion at least, of said glyceride ingresses into the lubricating oil composition during operation of said engine.
4. The use as claimed in any one of the preceding claims, wherein the hydroxy polycarboxylic acid has at least one hydroxy group which is in an alpha position with respect to a carboxylic moiety, and is preferably citric acid.
5. The use as claimed in any one of claims 1 to 4, wherein the glyceride is a glyceride of at least one hydroxy polycarboxylic acid and at least one second carboxylic acid which is a saturated, mono-unsaturated or poly-unsaturated, branched or linear, monocarboxylic or polycarboxylic acid having 4 to 22 carbon atoms, or a derivative thereof.
6. The use as claimed in any one of claims 1 to 4, wherein the glyceride is a glyceride of at least one hydroxy polycarboxylic acid and a mono-unsaturated C₄ to C₂₂ monocarboxylic acid, or a derivative thereof.
7. The use as claimed in any one of claims 1 to 4, wherein the glyceride is a glyceride of at least one hydroxy polycarboxylic acid and a polyunsaturated C₄ to C₂₂ monocarboxylic acid, or a derivative thereof.
8. The use as claimed in claim 6 or claim 7, wherein the glyceride is a glyceride of at least one hydroxy polycarboxylic acid and a mono-unsaturated or polyunsaturated C₁₈ monocarboxylic acid, or a derivative thereof.
9. The use as claimed in claim 8, wherein the glyceride is a glyceride of citric acid and a mono-unsaturated or poly-

unsaturated C₁₈ monocarboxylic acid, or a derivative thereof.

10. The use as claimed in any one of claims 6 to 9, wherein the mono-unsaturated or polyunsaturated C₄ to C₂₂ carboxylic acid is linear.
11. The use as claimed in any one of claims 1 to 4, wherein the glyceride is a glyceride of citric acid and oleic acid, a glyceride of citric acid and linoleic acid or a mixture thereof.
12. The use as claimed in claim 5, wherein the carboxylic acid having 4 to 22 carbon atoms is a polycarboxylic acid and the derivative is an ester of a carboxylic acid moiety of said polycarboxylic acid.
13. The use as claimed in any one of the preceding claims, wherein the derivative of the glyceride is an ether of the hydroxy moiety of the hydroxy polycarboxylic acid.
14. The use as claimed in any one of claims 1 to 12, wherein the derivative of the glyceride is an ester of the hydroxy moiety of the hydroxy polycarboxylic acid.
15. The use as claimed in any one of the preceding claims, wherein the derivative of the glyceride is an ester of a carboxylic acid moiety of the hydroxy polycarboxylic acid.

Patentansprüche

1. Verwendung eines öllöslichen Mono-, Di- oder Triglycerids mindestens einer Hydroxypolycarbonsäure oder eines Derivats davon als Nockenwellen-Antiverschleißzusatz in einer nichtwässrigen Schmiermittelzusammensetzung und/oder in einer Kraftstoffzusammensetzung, wobei die nichtwässrige Schmiermittelzusammensetzung und/oder Kraftstoffzusammensetzung in einem kompressionsgezündeten Verbrennungsmotor verwendet wird.
2. Verwendung nach Anspruch 1, wobei das öllösliche Mono-, Di- oder Triglycerid mindestens einer Hydroxypolycarbonsäure oder eines Derivats davon Nockenwellenverschleiß, gemessen im OM646LA-Motortest, reduziert.
3. Verwendung nach Anspruch 1 oder Anspruch 2, wobei das öllösliche Mono-, Di- oder Triglycerid mindestens einer Hydroxypolycarbonsäure oder eines Derivats davon in einer flüssigen Kraftstoffzusammensetzung bereitgestellt wird, die zum Betreiben des Verbrennungsmotors verwendet wird, und mindestens ein Teil des genannten Glycerids während des Betriebs des genannten Motors in die Schmierölzusammensetzung eindringt.
4. Verwendung nach einem der vorherigen Ansprüche, wobei die Hydroxypolycarbonsäure mindestens eine Hydroxygruppe aufweist, die sich in Bezug auf einen Carboxylanteil in Alpha-Position befindet, und vorzugsweise Zitronensäure ist.
5. Verwendung nach einem der Ansprüche 1 bis 4, wobei das Glycerid ein Glycerid mindestens einer Hydroxypolycarbonsäure und mindestens einer zweiten Carbonsäure, die eine gesättigte, einfach ungesättigte oder mehrfach ungesättigte, verzweigte oder lineare Mono- oder Polycarbonsäure mit 4 bis 22 Kohlenstoffatomen ist, oder eines Derivats davon ist.
6. Verwendung nach einem der Ansprüche 1 bis 4, wobei das Glycerid ein Glycerid mindestens einer Hydroxypolycarbonsäure und einer einfach ungesättigten C₄-C₂₂-Monocarbonsäure oder eines Derivats davon ist.
7. Verwendung nach einem der Ansprüche 1 bis 4, wobei das Glycerid ein Glycerid mindestens einer Hydroxypolycarbonsäure und einer mehrfach ungesättigten C₄-C₂₂-Monocarbonsäure oder eines Derivats davon ist.
8. Verwendung nach Anspruch 6 oder Anspruch 7, wobei das Glycerid ein Glycerid mindestens einer Hydroxypolycarbonsäure und einer einfach oder mehrfach ungesättigten C₁₈-Monocarbonsäure oder eines Derivats davon ist.
9. Verwendung nach Anspruch 8, wobei das Glycerid ein Glycerid von Zitronensäure und einer einfach oder mehrfach ungesättigten C₁₈-Monocarbonsäure oder eines Derivats davon ist.
10. Verwendung nach einem der Ansprüche 6 bis 9, wobei die einfach ungesättigte oder mehrfach ungesättigte

C₄-C₂₂-Carbonsäure linear ist.

11. Verwendung nach einem der Ansprüche 1 bis 4, wobei das Glycerid ein Glycerid von Zitronensäure und Ölsäure, ein Glycerid von Zitronensäure und Linolsäure oder eine Mischung davon ist.
12. Verwendung nach Anspruch 5, wobei die Carbonsäure mit 4 bis 22 Kohlenstoffatomen eine Polycarbonsäure ist und das Derivat ein Ester eines Carbonsäureanteils der genannten Polycarbonsäure ist.
13. Verwendung nach einem der vorherigen Ansprüche, wobei das Derivat des Glycerids ein Ether des Hydroxyanteils der Hydroxypolycarbonsäure ist.
14. Verwendung nach einem der Ansprüche 1 bis 12, wobei das Derivat des Glycerids ein Ester des Hydroxyanteils der Hydroxypolycarbonsäure ist.
15. Verwendung nach einem der vorherigen Ansprüche, wobei das Derivat des Glycerids ein Ester eines Carbonsäureanteils der Hydroxypolycarbonsäure ist.

Revendications

1. Utilisation d'un monoglycéride, diglycéride ou triglycéride liposoluble d'au moins un acide hydroxypolycarboxylique, ou d'un dérivé de celui-ci, comme additif anti-usure pour arbre à cames dans une composition lubrifiante non aqueuse et/ou dans une composition de carburant, la composition lubrifiante non aqueuse et/ou la composition de carburant étant utilisée dans un moteur à combustion interne à allumage par compression.
2. Utilisation selon la revendication 1, dans laquelle le monoglycéride, diglycéride ou triglycéride liposoluble d'au moins un acide hydroxypolycarboxylique, ou un dérivé de celui-ci, réduit l'usure de l'arbre à cames telle que mesurée dans l'essai de moteur OM646LA.
3. Utilisation selon la revendication 1 ou la revendication 2, dans laquelle le monoglycéride, diglycéride ou triglycéride liposoluble d'au moins un acide hydroxypolycarboxylique, ou un dérivé de celui-ci, est présent dans une composition de carburant liquide utilisée pour faire fonctionner le moteur à combustion interne, et une partie au moins dudit glycéride pénètre dans la composition d'huile lubrifiante durant le fonctionnement dudit moteur.
4. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle l'acide hydroxypolycarboxylique comporte au moins un groupe hydroxy qui est dans une position alpha par rapport à une fraction carboxylique, et est préférentiellement l'acide citrique.
5. Utilisation selon l'une quelconque des revendications 1 à 4, dans laquelle le glycéride est un glycéride d'au moins un acide hydroxypolycarboxylique et d'au moins un deuxième acide carboxylique qui est un acide monocarboxylique ou polycarboxylique saturé, monoinsaturé ou polyinsaturé, ramifié ou linéaire, comportant 4 à 22 atomes de carbone, ou un dérivé de celui-ci.
6. Utilisation selon l'une quelconque des revendications 1 à 4, dans laquelle le glycéride est un glycéride d'au moins un acide hydroxypolycarboxylique et d'un acide monocarboxylique monoinsaturé C₄ à C₂₂, ou un dérivé de celui-ci.
7. Utilisation selon l'une quelconque des revendications 1 à 4, dans laquelle le glycéride est un glycéride d'au moins un acide hydroxypolycarboxylique et d'un acide monocarboxylique polyinsaturé C₄ à C₂₂, ou un dérivé de celui-ci.
8. Utilisation selon la revendication 6 ou la revendication 7, dans laquelle le glycéride est un glycéride d'au moins un acide hydroxypolycarboxylique et d'un acide monocarboxylique monoinsaturé ou polyinsaturé C₁₈, ou un dérivé de celui-ci.
9. Utilisation selon la revendication 8, dans laquelle le glycéride est un glycéride d'acide citrique et d'un acide monocarboxylique monoinsaturé ou polyinsaturé C₁₈, ou un dérivé de celui-ci.
10. Utilisation selon l'une quelconque des revendications 6 à 9, dans laquelle l'acide carboxylique monoinsaturé ou polyinsaturé C₄ à C₂₂ est linéaire.

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11. Utilisation selon l'une quelconque des revendications 1 à 4, dans laquelle le glycéride est un glycéride d'acide citrique et d'acide oléique, un glycéride d'acide citrique et d'acide linoléique, ou un mélange de ceux-ci.
12. Utilisation selon la revendication 5, dans laquelle l'acide carboxylique comportant 4 à 22 atomes de carbone est un acide polycarboxylique et le dérivé est un ester d'une fraction acide carboxylique dudit acide polycarboxylique.
13. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le dérivé du glycéride est un éther de la fraction hydroxy de l'acide hydroxypolycarboxylique.
14. Utilisation selon l'une quelconque des revendications 1 à 12, dans laquelle le dérivé du glycéride est un ester de la fraction hydroxy de l'acide hydroxypolycarboxylique.
15. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le dérivé du glycéride est un ester d'une fraction acide carboxylique de l'acide hydroxypolycarboxylique.

REFERENCES CITED IN THE DESCRIPTION

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