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(54) LUBRICATING OIL COMPOSITION INCLUDING COMB POLYMETHACRYLATE AND ETHYLENE-BASED OLEFIN COPOLYMER VISCOSITY MODIFIERS

SCHMIERÖLZUSAMMENSETZUNG MIT POLYMETHACRYLATKAMMPOLYMEREN UND ETHYLEN-OLEFIN COPOLYMEREN ALS VISKOSITÄTSVERBESSERER

COMPOSITIONS D’HUILES LUBRIFIANTES COMPRENANT DES POLYMÈRES À PEIGNE DES POLYMÉTHACRYLATES ET DES COPOLYMÈRES D’ÉTHYLÈNE-OLÉFINE

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Description

FIELD OF THE INVENTION

[0001] The disclosed technology relates to lubricating oils for internal combustion engines, particularly lubricating oils for spark-ignited engines.

BACKGROUND OF THE INVENTION

[0002] Engine oil is blended with various additives to satisfy performance requirements. A challenge in engine oil formulation is to simultaneously achieve wear, deposit, and varnish control while also achieving improved fuel economy.

[0003] One known way to increase fuel economy of a lubricating oil composition is to decrease viscosity (i.e., High Temperature High Shear (HTHS) viscosity). HTHS is a measure of the viscosity of the lubricating oil composition under severe engine conditions. However, this approach is reaching the limits of current equipment capabilities and specifications. At a given viscosity, adding organic or organometallic friction modifiers reduces the surface friction of the lubricating oil composition and allows for better fuel economy. However, these additives often bring detrimental effects such as increased deposit formation, seals impacts, or they out-compete the anti-wear components for limited surface sites, thereby not allowing the formation of an anti-wear film, causing increased wear.

[0004] Viscosity modifiers are also widely used to improve viscosity index (VI) of the lubricating oil composition, thickening the oil as the temperature increases. However, at high temperatures and under high stress conditions, viscosity modifier degradation can occur. As this happens, the viscosity of the lubricating oil composition decreases which may lead to increased engine wear.

[0005] US patent application US2011/166053 discloses a low-viscosity engine lubricating oil composition comprising a non-dispersant polymethacrylate viscosity modifier and an olefin copolymer.

[0006] Therefore, despite the advances in lubricant oil formulation technology, there remains a need for an engine lubricating oil that provides sufficient fuel economy while also providing superior anti-wear performance, particularly a lubricating oil having an SAE 0W-20 viscosity grade or lower.

SUMMARY OF THE INVENTION

[0007] The invention is defined by the appended claims.

[0008] In one aspect, the present disclosure provides a lubricating oil composition having a Kinematic Viscosity at 100° C of less than 9.3 mm^2/s, comprising:

a) a major amount of an oil of lubricating viscosity;
b) 0.4 wt.% to 2.0 wt.% based on the total weight of the lubricating oil composition of a non-dispersant comb polymethacrylate (PMA) having a weight average molecular weight (Mw) of 390,000 to 460,000 g/mol; and
c) 0.08 wt.% to 0.4 wt.% based on the total weight of the lubricating oil composition of a non-dispersant ethylene-based olefin copolymer having a weight average molecular weight (Mw) of 90,000 to 160,000 g/mol.

[0009] Another aspect of the present disclosure provides a method for reducing wear in an internal combustion engine comprising lubricating the engine with a lubricating oil composition having a Kinematic Viscosity at 100° C of less than 9.3 mm^2/s, the lubricating oil composition comprising:

a) a major amount of an oil of lubricating viscosity;
b) 0.4 wt.% to 2.0 wt.% based on the total weight of the lubricating oil composition of a non-dispersant comb polymethacrylate (PMA) having a weight average molecular weight (Mw) of 390,000 to 460,000 g/mol; and
c) 0.08 wt.% to 0.4 wt.% based on the total weight of the lubricating oil composition of a non-dispersant ethylene-based olefin copolymer having a weight average molecular weight (Mw) of 90,000 to 160,000 g/mol.

[0010] In one embodiment, the lubricating oil composition comprises a) a major amount on an oil of lubricating viscosity; b) the non-dispersant comb polymethacrylate (PMA) in an amount of 0.4 wt. % to 1.9 wt. %, based on the total weight of the lubricating oil composition; and c) the non-dispersant ethylene-based olefin copolymer in an amount of from 0.08 wt. % to 0.36 wt. %, based on the total weight of the lubricating oil composition.

Definitions

[0011] In this specification, the following words and expressions, if and when used, have the meanings given below.

[0012] A "major amount" means in excess of 50 wt. % of a composition.

[0013] A "minor amount" means less than 50 wt. % of a composition, expressed in respect of the stated additive and in respect of the total mass of all the additives present in the composition, reckoned as active ingredient of the additive or additives.

[0014] "Active ingredients" or "actives" refers to additive material that is not diluent or solvent.

[0015] All percentages reported are weight percent (wt. %) on an active ingredient basis (i.e., without regard to carrier or diluent oil) unless otherwise stated.

[0016] The abbreviation "ppm" means parts per million by weight, based on the total weight of the lubricating oil composition.

[0017] Kinematic Viscosity (KV) at 100°C is measured in mm^2/s and determined in accordance with ASTM D445.

[0018] High Temperature High Shear (HTHS) viscosity at 150°C is determined in accordance with ASTM D4683.

[0019] Apparent Viscosity at temperatures from -35° C to -5° C is measured by a Cold Cranking Simulator in accordance with ASTM D5293.

[0020] Metal - The term "metal" refers to alkali metals, alkaline earth metals, or mixtures thereof.

[0021] An oil soluble or dispersible material means that an amount of the material needed to provide the desired level of activity or performance can be incorporated by being dissolved, dispersed or suspended in an oil of lubricating viscosity. Usually, this means that at least about 0.001% by weight of the material can be incorporated in a lubricating oil composition. For a further discussion of the terms oil soluble and dispersible, particularly "stably dispersible", see U.S. Pat. No. 4,320,019.

[0022] The term "sulfated ash" as used herein refers to the non-combustible residue resulting from detergents and metallic additives in lubricating oil. Sulfated ash may be determined in accordance with ASTM D874.

[0023] The term "Total Base Number" or "TBN" as used herein refers to the amount of base equivalent to milligrams of KOH in one gram of sample. Thus, higher TBN numbers reflect more alkaline products, and therefore a greater alkalinity. TBN is determined in accordance with ASTM D2896.

[0024] Boron, calcium, magnesium, molybdenum, phosphorus, sulfur, and zinc contents are determined in accordance with ASTM D5185.

[0025] Weight average molecular weight (Mw) and number average molecular weight (Mw) are measured by GPC (Gel Permeation Chromatography) with polystyrene as a reference.

[0026] Shear Stability Index (SSI) is measured in accordance with ASTM D7109.

[0027] All ASTM standards referred to herein are the most current versions as of the filing date of the present application.

[0028] Olefins - The term "olefins" refers to a class of unsaturated aliphatic hydrocarbons having one or more carbon-carbon double bonds, obtained by a number of processes. Those containing one double bond are called mono-alkenes, and those with two double bonds are called dienes, alkyldienes, or diolefins. Alpha olefins are particularly reactive because the double bond is between the first and second carbons. Examples are 1-octene and 1-octadecene, which are used as the starting point for medium-biodegradable surfactants. Linear and branched olefins are also included in the definition of olefins.

[0029] While the disclosure is susceptible to various modifications and alternative forms, specific embodiments thereof are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the disclosure to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the disclosure as defined by the appended claims.

[0030] Note that not all of the activities described in the general description or the examples are required, that a portion of a specific activity may not be required, and that one or more further activities may be performed in addition to those described. Still further, the order in which activities are listed is not necessarily the order in which they are performed.

[0031] Benefits, other advantages, and solutions to problems have been described herein with regard to specific embodiments. However, the benefits, advantages, solutions to problems, and any feature(s) that may cause any benefit, advantage, or solution to occur or become more pronounced are not to be construed as a critical, required, or essential feature of any or all the claims.

[0032] The specification and illustrations of the embodiments described herein are intended to provide a general understanding of the structure of the various embodiments.

[0033] As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having," or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of features is not necessarily limited only to those features but may include other features not expressly listed or other features that are inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive-or and not to an exclusive-or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[0034] The use of "a" or "an" is employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the embodiments of the disclosure. This description should be read to include one or at least one and the singular also includes the plural, or vice versa, unless it is clear that it is meant otherwise.

[0035] The term "averaged," when referring to a value, is intended to mean an average, a geometric mean, or a median value. Group numbers corresponding to columns within the Periodic Table of the elements use the "New Notation" convention as seen in the CRC Handbook of Chemistry and Physics, 81st Edition (2000-2001).

[0036] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. The materials, methods, and examples are illustrative only and not intended to be limiting. To the extent not described herein, many details regarding specific materials and processing acts are conventional and may be found in textbooks and other sources within the lubricants as well as the oil and gas industries.

[0037] The specification and illustrations are not intended to serve as an exhaustive and comprehensive description of all the elements and features of formulations, compositions, apparatus and systems that use the structures or methods described herein. Separate embodiments may also be provided in combination in a single embodiment, and conversely, various features that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination. Further, reference to values stated in ranges includes each and every value within that range. Many other embodiments may be apparent to skilled artisans only after reading this specification. Other embodiments may be used and derived from the disclosure, such that a structural substitution, logical substitution, or another change may be made without departing from the scope of the disclosure. Accordingly, the disclosure is to be regarded as illustrative rather than restrictive.

Oil of Lubricating Viscosity/Base Oil Component

[0038] The oil of lubricating viscosity (sometimes referred to as "base stock" or "base oil") is the primary liquid constituent of the lubricating oil composition, into which additives and possibly other oils are blended, for example to produce the final lubricating oil composition. A base oil is useful for making concentrates as well as for making lubricating oil compositions therefrom, and may be selected from natural and synthetic oils and combinations thereof.

[0039] Natural oils include animal and vegetable oils, liquid petroleum oils and hydrorefined, solvent-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

[0040] Synthetic oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), and poly(1-decenes); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, and di(2-ethylhexyl)benzenes); polyphenols (e.g., biphenyls, terphenyls, and alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogues and homologues thereof.

[0041] Another suitable class of synthetic oils comprises the esters of dicarboxylic acids (e.g., malonic acid, alkyl malonic acids, alkenyl malonic acids, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, fumaric acid, azclaic acid, suberic acid, sebacic acid, adipic acid, linoleic acid dimer, and phthalic acid) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, and propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0042] The base oil may be a renewable or bio-derived engine oil. Examples of such engine oils are disclosed in WO2016061050. According to some embodiments, the renewable or bio-derived base oil includes a biobased hydrocarbon, such as an isoparaffinic hydrocarbon derived from hydrocarbon terpenes, such as myrcene, ocimene, and farnesene.

[0043] Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol.

[0044] The base oil may be derived from Fischer-Tropsch synthesized hydrocarbons. Fischer-Tropsch synthesized hydrocarbons are made from synthesis gas containing H_2 and CO using a Fischer-Tropsch catalyst. Such hydrocarbons typically require further processing in order to be useful as the base oil. For example, the hydrocarbons may be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed; using processes known to those skilled in the art.

[0045] Unrefined, refined and re-refined oils can be used as the base oil in the present lubricating oil composition. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art.

[0046] Hence, the base oil which may be used to make the present lubricating oil composition may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines (API Publication 1509). Such base oil groups are summarized in Table 1 below:

TABLE 1

	Base Oil Properties		
Group[(a)]	Saturates[(b)], wt. %	Sulfur[(c)], wt. %	Viscosity Index[(d)]
Group I	<90 and/or	>0.03	80 to <120
Group II	≥90	≤0.03	80 to <120
Group III	≥90	≤0.03	≥120
Group IV	Polyalphaolefins (PAOs)		
Group V	All other base stocks not included in Groups I, II, III or IV		

(a) Groups I-III are mineral oil base stocks.
(b) Determined in accordance with ASTM D2007.
(c) Determined in accordance with ASTM D2622, ASTM D3120, ASTM D4294 or ASTM D4927.
(d) Determined in accordance with ASTM D2270.

[0047] Base oils suitable for use herein are any of the variety corresponding to API Group II, Group III, Group IV, and Group V oils and combinations thereof, preferably the Group III to Group V oils due to their exceptional volatility, stability, viscometric and cleanliness features.

[0048] The base oil constitutes the major component of the lubricating oil composition and is present is an amount ranging from greater than 50 to 99 wt. % (e.g., 70 to 95 wt. %, or 85 to 95 wt. %).

[0049] The base oil may be selected from any of the synthetic or natural oils typically used as crankcase lubricating oils for spark-ignited internal combustion engines. The base oil typically has a Kinematic Viscosity at 100°C in a range of 1.5 to 6 mm^2/s. In the case where the Kinematic Viscosity at 100°C of the lubricating base oil exceeds 6 mm^2/s, low temperature viscosity properties may be reduced, and sufficient fuel efficiency may not be obtained. At a Kinematic Viscosity of 1.5 mm^2/s or less, formation of an oil film in a lubrication place is insufficient; for this reason, lubrication is inferior, and the evaporation loss of the lubricating oil composition may be increased.

[0050] However, in some embodiments, a base oil having a Kinematic Viscosity exceeding 6 mm^2/s is needed. For example, the overall base oil could include a minor portion of a higher cut base oil, such as a 10 cSt polyalphaolefin.

[0051] Preferably, the base oil has a Viscosity Index of at least 90 (e.g., at least 95, at least 105, at least 110, at least 115, or at least 120). If the Viscosity Index is less than 90, not only viscosity-temperature properties, heat and oxidation stability, and anti-volatilization are reduced, but also the coefficient of friction tends to be increased; and resistance against wear tends to be reduced.

[0052] The lubricating oil composition can be a multi-grade oil having a viscosity grade of SAE 0W-XX, wherein XX is any one of 8, 10, 12, 16, and 20. According to one preferred embodiment, the lubricating oil composition has a viscosity grade of SAE 0W-20.

[0053] The lubricating oil composition has a High Temperature High Shear (HTHS) viscosity at 150°C of 3.0 cP or less (e.g., 1.0 cP to 3.0 cP or 1.3 cP to 3.0 cP), 2.8 cP or less (e.g., 1.0 cP to 2.8 cP or 1.3 cP to 2.8 cP), 2.7 cP or less (e.g., 1.0 cP to 2.7 cP or 1.3 cP to 2.7 cP), 2.6 cP or less (e.g., 1.0 cP to 2.6 cP or 1.3 cP to 2.6 cP), such as 2.5 cP or less (e.g., 1.0 cP to 2.5 cP or 1.3 cP to 2.5 cP) or 2.0 cP or less (e.g., 1.0 cP to 2.0 cP or 1.3 cP to 2.0 cP). According to example embodiments, the lubricating oil composition has a HTHS viscosity at 150°C of 2.5 cP to 2.6 cP, 2.55 cP to less than 2.9 cP, or 2.55 cP to 2.58 cP.

[0054] The lubricating oil composition has a Viscosity Index of at least 135 (e.g., 135 to 400 or 135 to 250), at least 150 (e.g., 150 to 400 or 150 to 250), at least 165 (e.g., 165 to 400 or 165 to 250), at least 190 (e.g., 190 to 400 or 190 to 250), or at least 200 (e.g., 200 to 400 or 200 to 250). If the Viscosity Index of the lubricating oil composition is less than 135, it may be difficult to improve fuel efficiency while maintaining the desired HTHS viscosity at 150°C. If the Viscosity Index of the lubricating oil composition exceeds 400, evaporation properties may be reduced, and deficits due to insufficient solubility of the additives and matching properties with a seal material may be caused. According to example embodiments, the lubricating oil composition has a Viscosity Index of 200 to 240, 203 to 235, 200 to 210, 220 to 225, or 230 to 240.

[0055] The lubricating oil composition has a Kinematic Viscosity at 100°C in a range of 3 mm^2/s to less than 9.3 mm^2/s (e.g., 3 mm^2/s to 9 mm^2/s, 5 mm^2/s to 9 mm^2/s, or 6 mm^2/s to 8 mm^2/s). According to example embodiments, the lubricating oil composition has a Kinematic Viscosity at 100°C in a range of 6.9 mm^2/s to less than 9.3 mm^2/s, 7.4 mm^2/s to 7.8 mm^2/s, 7.45 mm^2/s to 7.76 mm^2/s, 7.4 mm^2/s to 7.5 mm^2/s, 7.5 mm^2/s to 7.6 mm^2/s, 7.6 mm^2/s to 7.7 mm^2/s, or 7.7 mm^2/s to 7.8 mm^2/s.

[0056] The lubricating oil composition has an Apparent Viscosity at temperatures ranging from 35°C to -5°C, measured by a Cold Cranking Simulator (CCS), of 3600 mPa·s to 3900 mPa s. According to example embodiments, the lubricating oil composition has an apparent viscosity of 3600 mPa·s to 3700 mPa·s, 3700 mPa·s to 3800 mPa·s, or 3800 mPa·s to 3900 mPa·s.

[0057] In general, the level of sulfur in the lubricating oil composition is less than or equal to about 0.7 wt. %, based on the total weight of the lubricating oil composition. For example, the lubricating oil composition can have a level of sulfur of about 0.01 wt. % to 0.5 wt.%, 0.01 wt. % to 0.4 wt.%, 0.01 wt. % to 0.3 wt.%, 0.01 wt. % to 0.2 wt.%, or 0.01 wt. % to 0.10 wt. %. In one embodiment, the level of sulfur in the lubricating oil composition is less than or equal to about 0.60 wt. %, less than or equal to about 0.50 wt. %, less than or equal to about 0.40 wt. %, less than or equal to about 0.30 wt. %, less than or equal to about 0.20 wt. %, or less than or equal to about 0.10 wt. %, based on the total weight of the lubricating oil composition.

[0058] In one embodiment, the level of phosphorus in the lubricating oil composition is less than or equal to about 0.08 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.08 wt. %. In one embodiment, the level of phosphorus in the lubricating oil composition is less than or equal to about 0.07 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.07 wt. %. In one embodiment, the level of phosphorus in the lubricating oil composition is less than or equal to about 0.05 wt. %, based on the total weight of the lubricating oil composition, e.g., a level of phosphorus of about 0.01 wt. % to about 0.05 wt. %.

[0059] In one embodiment, the level of sulfated ash produced by the lubricating oil composition is less than or equal to about 1.00 wt. % as determined by ASTM D874, e.g., a level of sulfated ash of from about 0.10 wt. % to about 1.00 wt. % as determined by ASTM D874. In one embodiment, the level of sulfated ash produced by the lubricating oil composition is less than or equal to about 0.80 wt. % as determined by ASTM D874, e.g., a level of sulfated ash of from about 0.10 wt. % to about 0.80 wt. % as determined by ASTM D874. In one embodiment, the level of sulfated ash produced by the lubricating oil composition is less than or equal to about 0.60 wt. % as determined by ASTM D874, e.g., a level of sulfated ash of from about 0.10 wt. % to about 0.60 wt. % as determined by ASTM D874.

[0060] Suitably, the present lubricating oil composition may have a total base number (TBN) of 4 to 15 mg KOH/g (e.g., 5 mg KOH/g to 12 mg KOH/g, 6 mg KOH/g to 12 mg KOH/g, or 8 mg KOH/g to 12 mg KOH/g).

Viscosity Modifiers

[0061] Viscosity modifiers (VM), sometimes referred to as viscosity index improvers (VIIs), are present in the lubricating oil composition to impart high and low temperature operability. The viscosity modifiers increase the viscosity of the lubricating oil composition at elevated temperatures, which increases film thickness, while having limited effect on viscosity at low temperatures.

[0062] Viscosity modifiers may be used to impart that sole function or may be multifunctional. Multifunctional viscosity modifiers can also function as a dispersant.

[0063] Examples of suitable viscosity modifiers are polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Other suitable viscosity modifiers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example).

[0064] The viscosity modifiers can be present in the lubricating oil composition in a total amount of 0.001 wt. % to 10 wt. %, based on the total weight of the lubricating oil composition. In other embodiments, the viscosity modifiers can be present in a total amount of 0.01 wt. % to 8 wt. %, 0.1 wt. % to 5 wt. %, 0.4 wt. % to 4 wt. %, 0.6 wt. % to 3 wt. %, 0.7 wt. % to 2 wt. %, 1 wt. % to 1.5 wt. %, or 1.05 wt. % to 1.44 wt.%, based on the total weight of the lubricating oil composition. In some example embodiments, the viscosity modifiers are present in a total amount of 1.0 wt. % to 1.2 wt. %, 1.3 wt. % to 1.4 wt. %, or 1.4 wt. % to 1.5 wt. %, based on the total weight of the lubricating oil composition.

[0065] Particularly useful in the lubricating oil composition is the combination of non-dispersant comb polymethacrylate (comb PMA) and at least one non-dispersant ethylene based olefin copolymer (OCP).

Non-dispersant Comb Polymethacrylate

[0066] The non-dispersant comb polymethacrylate (comb PMA) is a comb-shaped polymer and thus is a macromolecule in which the main chain has one long branch per repeat unit.

[0067] The non-dispersant comb PMA has a weight average molecular weight (Mw) of 390,000 g/mol to 460,000 g/mol.

[0068] In one embodiment, the non-dispersant comb PMA has a Shear Stability Index (SSI) of 0.1 to 1.0, 0.2 to 0.9, or 0.3 to 0.8.

[0069] The non-dispersant comb PMA of the lubricating oil composition can be described as set forth in US 2017/0298287A1 and JP2019014802.

[0070] The non-dispersant comb PMA can be provided by Viscoplex® Viscosity Index Improver 3-201 and/or 3-162, which are available from Evonik.

[0071] According to one embodiment, the non-dispersant comb PMA is provided by the compound referred to as Viscoplex® 3-201, which includes, as a main resin component, a comb PMA. This non-dispersant comb PMA has a weight average molecular weight (Mw) of 420,000 g/mol, a number average molecular weight (Mn) of 70,946 g/mol, and a Mw/Mn of 5.92. The compound has at least a constituent unit derived from a macromonomer having a Mn of 500 or more. The non-dispersant comb PMA is present in an amount of 19 wt. %, based on the total weight of the compound.

[0072] According to another embodiment, the non-dispersant comb PMA is provided by the compound referred to as Viscoplex® 3-162, which also includes, as a main resin component, a comb PMA. This non-dispersant comb PMA has a weight average molecular weight (Mw) of 399,292 g/mol, a number average molecular weight (Mn) of 205,952 g/mol, a Mw/Mn of 1.94, and a Shear Stability Index (SSI) of 0.6.

[0073] According to another embodiment, the non-dispersant comb PMA is provided by a combination of compounds, for example a combination of the Viscoplex® 3-201 and the Viscoplex® 3-162.

[0074] The non-dispersant combPMA is present in an amount of 0.4 wt. % to 2.0 wt %, 0.5 wt. % to 1.9 wt. %, 0.6 wt. % to 1.8 wt. %, 0.77 wt. % to 1.5 wt. %, or 0.76 wt. % to 1.33 wt. %, based on the total weight of the lubricating oil composition. According to one embodiment, the non-dispersant combPMA is present in an amount of 0.4 wt. % to 1.9 wt. %, based on the total weight of the lubricating oil composition.

Non-Dispersant Ethylene-based Olefin Copolymer

[0075] The lubricating oil composition also includes a non-dispersant ethylene-based olefin copolymer (OCP) as a viscosity modifier. The non-dispersant ethylene-based olefin copolymer has a weight average molecular weight (Mw) of 90,000 g/mol to 160,000 g/mol. For example, the non-dispersant ethylene-based olefin copolymer could have a weight average molecular weight of 95,000 g/mol to 105,000 g/mol, 110,000 g/mol to 115,000 g/mol, or 145,000 g/mol to 150,000 g/mol.

[0076] In one embodiment, the non-dispersant ethylene-based olefin copolymer has a Shear Stability Index (SSI) of 10 to 70, 15 to 65, or 20 to 60.

[0077] The non-dispersant ethylene-based olefin copolymer can be described as follows, and as set forth in US 2013/0203640.

[0078] In one embodiment, the non-dispersant ethylene-based olefin copolymer is an ethylene propylene copolymer.

[0079] In one embodiment, the non-dispersant ethylene-based olefin copolymer has a total ethylene content of 35 wt. % to 70 wt. % or 40 wt. % to 65 wt. %, based on the total weight of the non-dispersant ethylene-based olefin copolymer. In another embodiment, the non-dispersant ethylene-based olefin copolymer has a total ethylene content of 45 wt. % to 60 wt. %, based on the total weight of the non-dispersant ethylene-based olefin copolymer.

[0080] The lubricating oil composition can include more than one non-dispersant ethylene-based olefin copolymer. In one embodiment, the lubricating oil composition includes a combination of a first ethylene-α-olefin copolymer (a) and a second ethylene-α-olefin copolymer (b). In this case, the lubricating oil composition typically contains about 30 wt. % to about 70 wt. % of the first ethylene-α-olefin copolymer (a) and about 70 wt. % to about 30 wt. % of the second ethylene-α-olefin copolymer (b) based upon the total amount of (a) and (b) in the lubricating oil composition. In another embodiment, the lubricating oil composition contains about 40 wt. % to about 60 wt. % of the first ethylene-α-olefin copolymer (a) and about 60 wt. % to about 40 wt. % of the second ethylene-α-olefin copolymer (b) based upon the total amount of (a) and (b) in the composition. In a particular embodiment, the lubricating oil composition contains about 50 wt. % to about 54 wt. % of the first ethylene-α-olefin copolymer (a) and about 46 wt. % to about 50 wt. % of the second ethylene-α-olefin copolymer (b) based upon the total amount of (a) and (b) in the composition.

[0081] The molecular weight distribution of each of the ethylene-α-olefin copolymers is typically less than about 2.5, and more typically about 2.1 to about 2.4. The polymer distribution as determined by GPC is typically unimodal.

[0082] The at least one non-dispersant ethylene-based olefin copolymer is present in an amount of 0.08 wt. % to 0.4 wt. %, 0.1 wt. or 0.15 wt. % to 0.4 wt. %, based on the total weight of the lubricating oil composition. According to one embodiment, the at least one non-dispersant ethylene-based olefin copolymer is present in an amount of 0.08 wt. % to 0,36 wt. %, based on the total weight of the lubricating oil composition.

Additional Additives

[0083] In addition to the non-dispersant comb PMA and the non-dispersant ethylene-based olefin copolymer viscosity modifiers described above, the lubricating oil composition of the present disclosure may contain one or more additional performance additives that can impart or improve any desirable property of the lubricating oil composition. Any additive known to those of skill in the art may be used in the lubricating oil composition disclosed herein. Some suitable additives have been described by R.M. Mortier et al. "Chemistry and Technology of Lubricants," 3rd Edition, Springer (2010) and L.R. Rudnik "Lubricant Additives: Chemistry and Applications," Second Edition, CRC Press (2009).

[0084] For example, the lubricating oil composition may contain antioxidants, anti-wear agent, metal detergents, dispersants, additional friction modifiers, corrosion inhibitors, demulsifiers, additional viscosity modifiers, pour point depressants, foam inhibitors, and others.

[0085] In general, the concentration of each of the additives in the lubricating oil composition, when used, may range from 0.001 wt. % to 10 wt. % (e.g., 0.01 wt. % to 5 wt. % or 0.05 wt. % to 2.5 wt. %), based on the total weight of the lubricating oil composition. Further, the total amount of additives in the lubricating oil composition may range from 0.001 wt. % to 20 wt. % (e.g., 0.01 wt. % to 15 wt. % or 0.1 wt. % to 10 wt. %), based on the total weight of the lubricating oil composition.

Antioxidants

[0086] Antioxidants retard the oxidative degradation of base oils during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in the lubricating oil composition. Useful antioxidants include hindered phenols, aromatic amines, and sulfurized alkylphenols and alkali and alkaline earth metal salts thereof.

[0087] The hindered phenol antioxidant may contain a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 4,4'-bis(2,6-di-tert-butylphenol) and 4,4'-methylenebis(2,6-di-tert-butylphenol). The hindered phenol antioxidant may be an ester or an addition product derived from 2,6-di-tert-butylphenol and an alkyl acrylate, wherein the alkyl group may contain from 1 to 18 carbon atoms.

[0088] Suitable aromatic amine antioxidants include diarylamines such as alkylated diphenylamines (e.g., dioctyl diphenylamine, dinonyl diphenylamine), phenyl-alpha-naphthalene and alkylated phenyl-alpha-naphthalenes.

[0089] According to an example embodiment, the lubricating oil composition includes an aminic antioxidant.

Anti-wear Agents

[0090] Anti-wear agents help to reduce the wear of metal parts lubricated with the lubricating oil composition. Examples of anti-wear agents include phosphorus-containing anti-wear/extreme pressure agents, such as metal thiophosphates, phosphoric acid esters and salts thereof; phosphorus-containing carboxylic acids, esters, ethers, and amides; and phosphites. The anti-wear agent may be zinc dialkyldithiophosphate (ZnDTP). Non-phosphorus-containing anti-wear agents include borate esters (including borated epoxides), dithiocarbamate compounds, molybdenum-containing compounds, and sulfurized olefins.

[0091] According to one example embodiment, the lubricating oil composition includes ZnDTP as an anti-wear agent.

Metal Detergents

[0092] A typical detergent is an anionic material that contains a long chain hydrophobic portion of the molecule and a smaller anionic or oleophobic hydrophilic portion of the molecule. The anionic portion of the detergent is typically derived from an organic acid, such as a sulfur acid, carboxylic acid, phosphorous acid, phenol, or mixtures thereof. The counterion is typically an alkaline earth or alkali metal.

[0093] In some embodiments, the lubricating oil composition provided herein comprises at least a neutral or overbased metal detergent as an additive, or additive components. In certain embodiments, the metal detergent in the lubricating oil composition acts as a neutralizer of acidic products within the lubricating oil composition. In certain embodiments, the metal detergent prevents the formation of deposits on the surface of an engine. Depending on the nature of the acid used, the detergent may have additional functions, for example, antioxidant properties. In certain aspects, the lubricating oil composition contains a metal detergent comprising either an overbased detergent or a mixture of neutral and overbased detergents. The term "overbased" is intended to define additives which contain a metal content in excess of that required by the stoichiometry of the particular metal and the particular organic acid used. The excess metal exists in the form of particles of inorganic base (e.g., a hydroxide or carbonate) surrounded by a sheath of metal salt. The sheath serves to maintain the particles in dispersion in a liquid oleaginous vehicle. The amount of excess metal is commonly expressed as the ratio of total equivalence of excess metal to equivalence of organic acid and is typically in a range of 0.1 to 30.

[0094] Some examples of suitable metal detergents include sulfurized or unsulfurized alkyl or alkenyl phenates, alkyl or alkenyl aromatic sulfonates, borated sulfonates, sulfurized or unsulfurized metal salts of multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates, metal salts of alkanoic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof. Other examples of suitable metal detergents include metal sulfonates, phenates, salicylates, phosphonates, thiophosphonates, and combinations thereof. The metal can be any metal suitable for making sulfonate, phenate, salicylate, or phosphonate detergents. Non-limiting examples of suitable metals include alkali metals, alkaline metals and transition metals. In some embodiments, the metal is Ca, Mg, Ba, K, Na, Li or the like.

[0095] The metal detergent could be an overbased detergent, such as a low overbased (LOB), medium overbased (MOB), or high overbased (HOB) detergent.

[0096] The low overbased detergent could be an overbased salt having a base number (BN) below 100. In one embodiment, the BN of the low overbased salt may be from about 5 to about 50. In another embodiment, the BN of the low overbased salt may be from about 10 to about 30. In yet another embodiment, the BN of the low overbased salt may be from about 15 to about 20. The base numbers of the overbased detergents are measured in the presence of diluent oil, not on an oil free basis

[0097] The medium overbased detergent could be an overbased salt having a BN from about 100 to about 250. In one embodiment, the BN of the medium overbased salt may be from about 100 to about 200. In another embodiment, the BN of the medium overbased salt may be from about 125 to about 175. The base numbers of the overbased detergents are measured in the presence of diluent oil, not on an oil free basis

[0098] The high overbased detergent could be an overbased salt having a BN above 250. In one embodiment, the BN of the high overbased salt may be from about 250 to about 550. The base numbers of the overbased detergents are measured in the presence of diluent oil, not on an oil free basis.

[0099] An exemplary metal detergent which may be employed in the lubricating oil compositions includes overbased calcium phenate. According to another example embodiment, the lubricating oil composition includes LOB Ca sulfonate, HOB Ca salicylate, and MOB Ca salicylate as detergents.

Ashless Dispersants

[0100] A dispersant is an additive whose primary function is to hold solid and liquid contaminations in suspension, thereby passivating them and reducing engine deposits at the same time as reducing sludge depositions. For example, a dispersant maintains in suspension oil-insoluble substances that result from oxidation during use of the lubricating oil composition, thus preventing sludge flocculation and precipitation or deposition on metal parts of the engine.

[0101] Dispersants are usually "ashless," being non-metallic organic materials that form substantially no ash on combustion, in contrast to metal-containing, and hence ash-forming materials. They comprise a long hydrocarbon chain with a polar head, the polarity being derived from inclusion of at least one nitrogen, oxygen or phosphorus atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having, for example, 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric backbone.

[0102] A preferred class of olefin polymers is constituted by polybutylenes, specifically polyisobutylenes (PIB) or poly-n-butylenes, such as may be prepared by polymerization of a C4 refinery stream.

[0103] Dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids, examples being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. A noteworthy group of dispersants is constituted by hydrocarbon-substituted succinimides, made, for example, by reacting the above acids (or derivatives) with a nitrogen-containing compound, advantageously a polyalkylene polyamine, such as a polyethylene polyamine. Typical commercially available polyisobutylene-based succinimide dispersants contain polyisobutylene polymers having a number average molecular weight ranging from 900 to 2500, functionalized by maleic anhydride, and derivatized with polyamines having a molecular weight of from 100 to 350.

[0104] Other suitable dispersants include succinic esters and ester-amides, Mannich bases, polyisobutylene succinic acid (PIBSA), and other related components.

[0105] Succinic esters are formed by the condensation reaction between hydrocarbon-substituted succinic anhydrides and alcohols or polyols. For example, the condensation product of a hydrocarbon-substituted succinic anhydride and pentaerythritol is a useful dispersant.

[0106] Succinic ester-amides are formed by a condensation reaction between hydrocarbon-substituted succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines, such as polyethylene polyamines. One example is propoxylated hexamethylenediamine.

[0107] Mannich bases are made from the reaction of an alkylphenols, formaldehyde, and a polyalkylene polyamines. Molecular weights of the alkylphenol may range from 800 to 2500.

[0108] Nitrogen-containing dispersants may be post-treated by conventional methods to improve their properties by reaction with any of a variety of agents. Among these are boron compounds (e.g., boric acid) and cyclic carbonates (e.g., ethylene carbonate).

[0109] According to one example embodiment, the lubricating oil composition includes borated succinimide and ethylene carbonate (EC) treated succinimide as ashless dispersants.

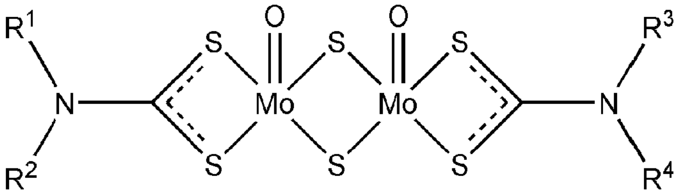
Friction Modifiers

[0110] The lubricating oil composition can include friction modifiers. A friction modifier is any material or materials that can alter the coefficient of friction of a surface lubricated by any lubricant or fluid containing such material(s). Friction modifiers include alkoxylated fatty amines, borated fatty epoxides, fatty phosphites, fatty epoxides, fatty amines, borated alkoxylated fatty amines, metal salts of fatty acids, fatty acid amides, glycerol esters, borated glycerol esters, and fatty imidazolines. As used herein, the term "fatty" means a hydrocarbon chain having 10 to 22 carbon atoms, typically a straight hydrocarbon chain.

[0111] According to example embodiments, the lubricating oil composition includes an organomolybdenum compound, also referred to as a molybdenum containing compound. The organomolybdenum compound contains at least molybdenum, carbon and hydrogen atoms, but may also contain sulfur, phosphorus, nitrogen, and/or oxygen atoms. Suitable organomolybdenum compounds include molybdenum dithiocarbamates, molybdenum dithiophosphates, and various organic molybdenum complexes such as molybdenum carboxylates, molybdenum esters, molybdenum amines, molybdenum amides, which can be obtained by reacting molybdenum oxide or ammonium molybdates with fats, glycerides or fatty acids, or fatty acid derivatives (e.g., esters, amines, and amides). The term "fatty" means a carbon chain having 10 to 22 carbon atoms, typically a straight carbon chain.

[0112] Molybdate esters can be prepared by methods disclosed in US 4,889,647 and US 6,806,241 B2. A commercial example is MOLYVAN® 855 additive, which is manufactured by R. T. Vanderbilt Company, Inc.

[0113] According to an example embodiment, the lubricating oil composition includes molybdenum dithiocarbamate (MoDTC). Molybdenum dithiocarbamate (MoDTC) is an organomolybdenum compound represented by the following structure (1):



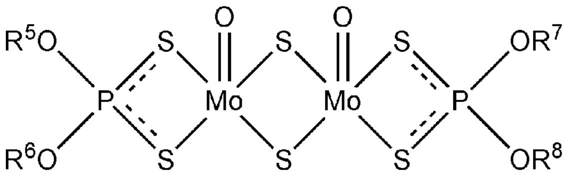
(1)

wherein R^1, R^2, R^3, and R^4 are independently of each other, linear or branched alkyl groups having from 4 to 18 carbon atoms (e.g., 8 to 13 carbon atoms).

[0114] Preparations of these compounds are well known in the literature and U.S. Pat. Nos. 3,356,702 and 4,098,705, which are incorporated herein by reference. Commercial examples include MOLYVAN® 807, MOLYVAN® 822, and MOLYVAN® 2000, which are manufactured by R. T. Vanderbilt Company Inc., SAKURA-LUBE® 165 and SAKURA-LUBE® 515, which are manufactured by ADEKA CORPORATION and Naugalube® MolyFM which is manufactured by Chemtura Corporation.

[0115] Trinuclear molybdenum dialkyldithiocarbamates are also known in the art, as taught by U.S. Pat. Nos. 5,888,945 and 6,010,987. Trinuclear molybdenum compounds preferably have the formulas $Mo_3S_4(dtc)_4$, $Mo_3S_7(dtc)_4$, and mixtures thereof, wherein dtc represents independently selected diorganodithiocarbamate ligands containing independently selected organo groups, and wherein the ligands have a sufficient number of carbon atoms among all the organo groups of the compound's ligands to render the compound soluble or dispersible in the lubricating oil composition.

[0116] According to another embodiment, the lubricating oil composition includes molybdenum dithiophosphate (MoDTP). MoDTP is an organomolybdenum compound represented by the following structure (2):



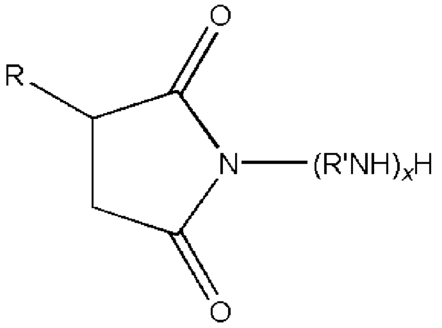
(2)

wherein R^5, R^6, R^7, and R^8 are independently of each other, linear or branched alkyl groups having from 4 to 18 carbon atoms (e.g., 8 to 13 carbon atoms).

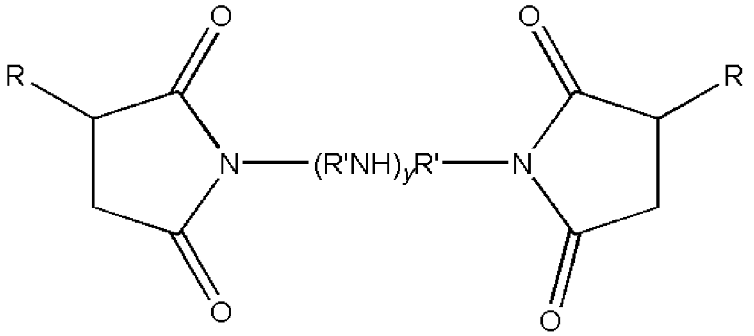
[0117] Molybdenum carboxylates are described in U.S. Pat. RE 38,929, and U.S. Pat. No. 6,174,842, which are incorporated herein by reference. Molybdenum carboxylates can be derived from any oil soluble carboxylic acid. Typical carboxylic acids include naphthenic acid, 2-ethylhexanoic acid, and linolenic acid. Commercial sources of carboxylates produce from these particular acids are MOLYBDENUM NAP-ALL, MOLYBDENUM HEX-CEM, and MOLYBDENUM LIN-ALL respectively. A manufacturer of these products is OMG OM Group.

[0118] Ammonium molybdates are prepared by the reaction of an acidic molybdenum source, such as molybdenum trioxide, molybdic acid, ammonium molybdate, and ammonium thiomolybdates, with oil-soluble amines, optionally in the presence of sulfur sources, such sulfur, inorganic sulfides, polysulfides, and carbons disulfide. The preferred aminic compounds are polyamine dispersants that are commonly used in engine oil compositions. Examples of such dispersants are succinimides and Mannich type dispersants. References to these dispersants are provided in U.S. Pat. Nos. 4,259,194, 4,259,195, 4,265,773, 4,265,843, 4,727,387, 4,283,295, and 4,285,822.

[0119] In one embodiment, the molybdenum amine is a molybdenum-succinimide complex. Suitable molybdenum-succinimide complexes are described, for example, in U.S. Patent No. 8,076,275. These complexes are prepared by a process comprising reacting an acidic molybdenum compound with an alkyl or alkenyl succinimide of a polyamine of structure (3), (4), or mixtures thereof:



(3)



(4)

wherein R is a C_{24} to C_{350} (e.g., C_{70} to C_{128}) alkyl or alkenyl group; R' is a straight or branched-chain alkylene group having 2 to 3 carbon atoms; x is 1 to 11; and *y* is 1 to 10.

[0120] The molybdenum compounds used to prepare the molybdenum-succinimide complex are acidic molybdenum compounds or salts of acidic molybdenum compounds. By "acidic" is meant that the molybdenum compounds will react with a basic nitrogen compound as measured by ASTM D664 or D2896. Generally, the acidic molybdenum compounds are hexavalent. Representative examples of suitable molybdenum compounds include molybdenum trioxide, molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate and other alkaline metal molybdates and other molybdenum salts such as hydrogen salts, (e.g., hydrogen sodium molybdate), $MoOCl_4$, MoO_2Br_2, $Mo_2O_3Cl_6$, and the like.

[0121] The succinimides that can be used to prepare the molybdenum-succinimide complex are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and the related materials encompassed by the term of art "succinimide" are taught in U.S. Patent Nos. 3,172,892; 3,219,666; and 3,272,746. The term "succinimide" is understood in the art to include many of the amide, imide, and amidine species which may also be formed. The predominant product however is a succinimide and this term has been generally accepted as meaning the product of a reaction of an alkyl or alkenyl substituted succinic acid or anhydride with a nitrogen-containing compound. Preferred succinimides are those prepared by reacting a polyisobutenyl succinic anhydride of about 70 to 128 carbon atoms with a polyalkylene polyamine selected from triethylenetetramine, tetraethylenepentamine, and mixtures thereof.

[0122] In one embodiment, the molybdenum containing compound is free of sulfur.

[0123] The molybdenum-succinimide complex may be post-treated with a sulfur source at a suitable pressure and a temperature not to exceed 120°C to provide a sulfurized molybdenum-succinimide complex. The sulfurization step may be carried out for a period of from about 0.5 to 5 hours (e.g., 0.5 to 2 hours). Suitable sources of sulfur include elemental sulfur, hydrogen sulfide, phosphorus pentasulfide, organic polysulfides of formula R_2S_x, where R is hydrocarbyl (e.g., C_1 to C_{10} alkyl) and x is at least 3, C_1 to C_{10} mercaptans, inorganic sulfides and polysulfides, thioacetamide, and thiourea.

[0124] The molybdenum containing compound is used in an amount that provides molybdenum to the lubricating oil composition in an amount of 50 ppm to 1200 ppm, 50 ppm to 1000 ppm, 50 ppm to 800 ppm, 50 ppm to 600 ppm, 50 ppm to 400 ppm, or 50 ppm to 200 ppm.

[0125] In some embodiments, the lubricating oil composition is substantially free of the molybdenum containing compound.

[0126] During use of the lubricating oil composition in an engine, the molybdenum containing compound can promote the formation of a molybdenum containing lubricating film on a metal surface of the engine.

[0127] According to an example embodiment, the lubricating oil composition includes MoDTC in an amount ranging from 0.6 wt. % to 0.8 wt. %, based on the total weight of the lubricating composition.

Corrosion Inhibitors

[0128] Corrosion inhibitors protect lubricated metal surfaces against chemical attack by water or other contaminants. Suitable corrosion inhibitors include polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, thiadiazoles, and anionic alkyl sulfonic acids.

Pour Point Depressants

[0129] Pour point depressants lower the minimum temperature at which a fluid will flow or can be poured. Suitable pour point depressants include C8 to C18 dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates, and the like.

Foam Inhibitors

[0130] Foam inhibitors retard the formation of stable foams. Examples of suitable foam inhibitors include polysiloxanes, polyacrylates, and the like.

Processes of Preparing Lubricating Oil Compositions

[0131] The lubricating oil compositions disclosed herein can be prepared by any method known to a person of ordinary skill in the art for making lubricating oils. The viscosity modifiers and other additives may be added to the base oil individually or simultaneously. In some embodiments, the additives are added to the base oil individually in one or more additions and the additions may be in any order. In other embodiments, the additives are added to the base oil simultaneously, optionally in the form of an additive concentrate. According to another embodiment, some of the additives are added individually and some are added in the form of the additive concentrate. In some embodiments, the solubilizing of the additives in the base oil may be assisted by heating the mixture to a temperature of about 25 °C to about 200 °C, about 50 °C to about 150 °C, or about 75 °C to about 125 °C.

[0132] Any mixing or dispersing equipment known to a person of ordinary skill in the art may be used for blending, mixing, or solubilizing the ingredients used to form the lubricating oil composition. The blending, mixing, or solubilizing may be carried out with a blender, an agitator, a disperser, a mixer (e.g., planetary mixers and double planetary mixers), a homogenizer (e.g., Gaulin homogenizers and Rannie homogenizers), a mill (e.g., colloid mill, ball mill, and sand mill), or any other mixing or dispersing equipment known in the art.

Application of the Lubricating Oil Composition

[0133] The lubricating oil composition disclosed herein may be suitable for use as a motor oil (an engine oil or crankcase oil) in a spark-ignited internal combustion engine. The lubricating oil composition is preferably used in engines or crankcases requiring a viscosity grade of SAE 0W-20, 0W-16, or 0W-12. For example, the lubricating oil composition can be used to lubricate an engine comprising a valve train system which includes roller follower rocker arms.

[0134] The following inventive examples are presented to exemplify embodiments of the invention but are not intended to limit the invention to the specific embodiments set forth. Unless indicated to the contrary, all parts and percentages are by weight. All numerical values are approximate. When numerical ranges are given, it should be understood that embodiments outside the stated ranges may still fall within the scope of the invention. Specific details described in each example should not be construed as necessary features of the invention.

EXAMPLES

[0135] A baseline formulation for all of the invention examples, as well as the comparative examples, was prepared by blending together the following ingredients, provided in wt. %, based on the total weight of the lubricating oil composition:

(a) 1 wt. % borated succinimide,
(b) 3 wt. % ethylene carbonate (EC) treated succinimide,
(c) 0.34 wt. % secondary ZnDTP,
(d) 0.72 wt. % primary ZnDTP,
(e) 0.5 wt. % LOB Ca sulfonate,
(f) 0.77 wt. % HOB Ca salicylate,
(g) 0.5 wt. % MOB Ca salicylate,
(h) 2 wt. % aminic antioxidant,
(i) 0.004 wt. % foam inhibitor, and
(h) diluent oil.

[0136] The wt. % of ingredients (a) - (h) includes any diluent and/or solvent that may be present and thus is not an active basis.

[0137] All the inventive examples and comparative examples were made by top treating the base line formulation with 0.7 wt% molybdenum dithiocarmabate (MoDTC) providing 700 ppm molybdenum, and the viscosity modifier(s) of Tables 2 and 3 (comb PMA and/or OCP) in Yubase 4+, which is a Group III base oil, to obtain a lubricating oil composition having an SAE 0W-20 viscosity grade. The Inventive Example Compositions are provided in Table 2, and the Comparative Example Compositions are provided in Table 3.

TABLE 2. INVENTIVE EXAMPLES

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
[1]PMA	7	6	4	7	6	4	7	6	4
[2]OCP1	1	1.85	3.5	-	-	-	-	-	-
[3]OCP2	-	-	-	1.1	2	3.8	-	-	-
[4]OCP3	-	-	-	-	-	-	0.95	1.85	3.4
KV 100°C	7.45	7.46	7.53	7.50	7.53	7.68	7.50	7.59	7.76
KV 40°C	29.59	30.89	33.47	29.85	31.31	34.16	29.84	31.80	34.44
VI	235	222	203	235	222	204	235	221	206
CCS	3640	3768	3833	3635	3753	3816	3675	3713	3764
HTHS150	2.58	2.56	2.55	2.58	2.57	2.56	2.57	2.57	2.55
HTHS100	4.96	5.02	5.16	4.96	5.03	5.15	4.92	5.01	5.10
HTHS80	7.38	7.55	7.79	7.38	7.51	7.74	7.36	7.50	7.70

TABLE 3. COMPARATIVE EXAMPLES

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
[1]PMA	8.1	-	-	-
[2]OCP1	-	7	-	-
[3]OCP2	-	-	7.5	-
[4]OCP3	-	-	-	6.8

(continued)

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
KV 100°C	7.41	7.90	8.19	8.38
KV 40°C	28.29	39.78	41.42	42.33
VI	248	175	177	179
CCS	3610	4288	4162	4070
HTHS150	2.58	2.58	2.59	2.59
HTHS 100	4.89	5.52	5.02	5.52
HTHS80	7.19	8.28	7.55	8.30

[1] PMA (Viscoplex® 3-201) is a compound containing 19 wt. % non-dispersant comb-shaped polymethacrylate having a Mw of 420,000 g/mol and a Mw/Mn of 5.92.

[2] OCP1 is a concentrate containing 10 wt% of a non-dispersant ethylene-propylene copolymer having an ethylene content of 57 wt. %, Mw of about 100,000, Mn of about 40,000, and a SSI of 24.

[3] OCP 2 is a concentrate containing 8.75 wt% of a non-dispersant ethylene-propylene copolymer having an ethylene content of 57 wt. %, Mw of 112,000, Mn of 49,000, and a SSI of 35.

[4] OCP 3 is a concentrate containing 8.8 wt. % of a non-dispersant ethylene-propylene copolymer having an ethylene content of 49 wt. %, a Mw of 146,000, a Mn of 84,000 Mn, and a SSI of 50.

Fuel Economy Testing in a Toyota 2ZR-FE Motored Engine

[0138] The lubricating oil compositions of Inventive Examples 1-9 as well as Comparative Examples 1-4 were tested for their fuel economy performance in a gasoline motored engine test. The engine was a Toyota 2ZR-FE 1.8L in-line 4-cylinder arrangement. The torque meter was positioned between the motor and the crank shaft of the engine and the percent torque change was measured between a reference and candidate lubricating oil composition. The percent (%) torque change at oil temperatures of 60° C, 80° C, and 100° C, and engine speeds of 400 rpm, 550 rpm, 750 rpm, 1000 rpm, 1500 rpm, and 2000 rpm were measured. Lower percent torque change (i.e., more negative) reflects better fuel economy. The configuration of the motored engine friction torque test and its test conditions are further described in SAE Paper 2013-01-2606. Table 4 provides the average % torque change at the oil temperatures of 60° C, 80° C, and 100° C for the Invention Example Compositions, and Table 5 provides the average % torque change at the oil temperatures of 60° C, 80° C, and 100° C for the Comparative Example Compositions.

TABLE 4. MOTORED ENGINE FRICTION TORQUE - INVENTIVE EXAMPLES

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
60° C	rpm	-2.99	-3.16	-2.77	-2.71	-3.08	-2.75	-2.99	-2.91	-2.61
80° C		-1.93	-1.89	-1.72	-1.29	-1.83	-1.84	-1.45	-1.63	-1.53
100° C		-1.51	-1.72	-1.60	-1.41	-1.73	-1.80	-1.31	-1.59	-1.51
Total		-2.14	-2.26	-2.03	-1.80	-2.21	-2.13	-1.92	-2.04	-1.88

TABLE 5. MOTORED ENGINE FRICTION TORQUE - COMPARATIVE EXAMPLES

		Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
60° C	rpm	-2.95	-2.35	-2.08	-1.69
80° C		-1.51	-1.54	-1.22	-1.10
100° C		-1.41	-1.69	-1.48	-1.39
Total		-1.96	-1.86	-1.59	-1.39

Claims

1. A lubricating oil composition, comprising:

    a) a major amount of an oil of lubricating viscosity;
    b) 0.4 wt. % to 2.0 wt.%, based on the total weight of the lubricating oil composition, of a non-dispersant comb polymethacrylate (PMA) having a weight average molecular weight (Mw) of 390,000 g/mol to 460,000 g/mol; and
    c) 0.08 wt. % to 0.4 wt. %, based on the total weight of the lubricating oil composition, of a non-dispersant ethylene-based olefin copolymer having a weight average molecular weight (Mw) of 90,000 g/mol to 160,000 g/mol,

    the lubricating oil composition having a Kinematic Viscosity at 100° C of less than 9.3 mm^2/s.

2. The lubricating oil composition of claim 1, wherein the non-dispersant comb PMA has a Shear Stability Index (SSI) of 0.3 to 0.8, measured in accordance with ASTM D7109.

3. The lubricating oil composition of claim 1, wherein the non-dispersant ethylene-based olefin copolymer has a Shear Stability Index (SSI) of 10 to 70, measured in accordance with ASTM D7109.

4. The lubricating oil composition of claim 1, wherein the non-dispersant ethylene-based olefin copolymer:

    (i) has a total ethylene content of 45 wt. % to 60 wt. %, based on the total weight of the non-dispersant ethylene-based olefin copolymer, or
    (ii) is an ethylene propylene copolymer.

5. The lubricating oil composition of claim 1, wherein the non-dispersant comb PMA is present in an amount of 0.76 wt. % to 1.33 wt. %, and the non-dispersant ethylene-based olefin copolymer is present in an amount of 0.08 to 0.4 wt. %, based on the total weight of the lubricating oil composition.

6. The lubricating oil composition of claim 1, wherein the non-dispersant comb PMA and the non-dispersant ethylene-based olefin copolymer are present in a total amount of 0.4 wt. % to 4 wt. %, based on the total weight of the lubricating oil composition.

7. The lubricating oil composition of claim 1, wherein the oil of lubricating viscosity is an API Group III base oil.

8. The lubricating oil composition of claim 1, wherein the composition further comprises a molybdenum compound, optionally wherein:

    (i) the molybdenum compound is molybdenum dithiocarbamate (MoDTC), or
    (ii) the molybdenum compound provides the lubricating oil composition with an amount of molybdenum ranging from 50 ppm to 1200 ppm.

9. The lubricating oil composition of claim 1, wherein lubricating oil composition has a viscosity grade of SAE 0W-20, 0W-16, or 0W-12.

10. The lubricating oil composition of claim 1, wherein the lubricating oil composition has a High Temperature High Shear (HTHS) viscosity at 150° C of 2.55 cP to less than 2.9 cP.

11. The lubricating oil composition of claim 1, wherein the lubricating oil composition has a viscosity index of 200 to 240.

12. A method for reducing wear in an internal combustion engine comprising lubricating said engine with a lubricating oil composition having a Kinematic Viscosity at 100° C of less than 9.3 mm^2/s, the lubricating oil composition including:

    a) a major amount of an oil of lubricating viscosity;
    b) 0.4 wt. % to 2.0 wt.%, based on the total weight of the lubricating oil composition, of a non-dispersant comb polymethacrylate (PMA) having a weight average molecular weight (Mw) of 390,000 g/mol to 460,000 g/mol; and
    c) 0.08 wt. % to 0.4 wt. %, based on the total weight of the lubricating oil composition, of a non-dispersant ethylene-based olefin copolymer having a weight average molecular weight (Mw) of 90.000 g/mol to 160.000

g/mol.

13. The lubricating oil composition of claim 1, wherein

the non-dispersant comb polymethacrylate (PMA) is present in an amount of 0.4 wt. % to 1.9 wt.%, based on the total weight of the lubricating oil composition; and
the non-dispersant ethylene-based olefin copolymer is present in an amount of 0.08 wt. % to 0.36 wt. %, based on the total weight of the lubricating oil composition.

14. The method for reducing wear in an internal combustion engine according to claim 12 wherein

the non-dispersant comb polymethacrylate (PMA) is present in an amount of 0.4 wt. % to 1.9 wt.%, based on the total weight of the lubricating oil composition; and
the non-dispersant ethylene-based olefin copolymer is present in an amount of 0.08 wt. % to 0.36 wt. %, based on the total weight of the lubricating oil composition.

15. The method of claim 12 or 14, wherein the engine includes roller follower rocker arms.

Patentansprüche

1. Schmierölzusammensetzung umfassend:

a) eine Hauptmenge an einem Öl mit Schmierviskosität;
b) 0,4 Gew.-% bis 2,0 Gew.-%, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung, an einem nicht dispergierwirksamen Kamm-Polymethacrylat (PMA) mit einem gewichtsgemittelten Molekulargewicht (Mw) von 390.000 g/mol bis 460.000 g/mol; und
c) 0,08 Gew.-% bis 0,4 Gew.-%, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung, an einem nicht dispergierwirksamen Olefincopolymer auf Ethylenbasis mit einem gewichtsgemittelten Molekulargewicht (Mw) von 90.000 g/mol bis 160.000 g/mol, wobei die Schmierölzusammensetzung eine kinematische Viskosität bei 100 °C von weniger als 9,3 mm^2/s aufweist.

2. Schmierölzusammensetzung gemäß Anspruch 1, wobei das nicht dispergierwirksame Kamm-PMA einen Scherstabilitätsindex (SSI) von 0,3 bis 0,8, gemessen gemäß ASTM D7109, aufweist.

3. Schmierölzusammensetzung gemäß Anspruch 1, wobei das nicht dispergierwirksame Olefincopolymer auf Ethylenbasis einen Scherstabilitätsindex (SSI) von 10 bis 70, gemessen gemäß ASTM D7109, aufweist.

4. Schmierölzusammensetzung gemäß Anspruch 1, wobei das nicht dispergierwirksame Olefincopolymer auf Ethylenbasis:

(i) einen Gesamt-Ethylengehalt von 45 Gew.-% bis 60 Gew.-%, bezogen auf das Gesamtgewicht des nicht dispergierwirksamen Olefincopolymers auf Ethylenbasis, aufweist, oder
(ii) ein Ethylen-Propylen-Copolymer ist.

5. Schmierölzusammensetzung gemäß Anspruch 1, wobei das nicht dispergierwirksame Kamm-PMA in einer Menge von 0,76 Gew.-% bis 1,33 Gew.-% vorhanden ist und das nicht dispergierwirksame Olefincopolymer auf Ethylenbasis in einer Menge von 0,08 bis 0,4 Gew.-% vorhanden ist, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung.

6. Schmierölzusammensetzung gemäß Anspruch 1, wobei das nicht dispergierwirksame Kamm-PMA und das nicht dispergierwirksame Olefincopolymer auf Ethylenbasis in einer Gesamtmenge von 0,4 Gew.-% bis 4 Gew.-%, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung, vorhanden sind.

7. Schmierölzusammensetzung gemäß Anspruch 1, wobei das Öl mit Schmierviskosität ein API-Gruppe-III-Grundöl ist.

8. Schmierölzusammensetzung gemäß Anspruch 1, wobei die Zusammensetzung ferner eine Molybdänverbindung umfasst, wobei gegebenenfalls:

(i) die Molybdänverbindung Molybdändithiocarbamat (MoDTC) ist oder
(ii) die Molybdänverbindung der Schmierölzusammensetzung eine Menge an Molybdän in dem Bereich von 50 ppm bis 1200 ppm verleiht.

9. Schmierölzusammensetzung gemäß Anspruch 1, wobei die Schmierölzusammensetzung eine Viskositätsklasse von SAE 0W-20, 0W-16 oder 0W-12 aufweist.

10. Schmierölzusammensetzung gemäß Anspruch 1, wobei die Schmierölzusammensetzung eine Hochtemperatur-Hochscher(HTHS)-Viskosität bei 150 °C von 2,55 cP bis weniger als 2,9 cP aufweist.

11. Schmierölzusammensetzung gemäß Anspruch 1, wobei die Schmierölzusammensetzung einen Viskositätsindex von 200 bis 240 aufweist.

12. Verfahren zum Verringern von Verschleiß in einem Verbrennungsmotor, umfassend Schmieren des Motors mit einer Schmierölzusammensetzung mit einer kinematischen Viskosität bei 100 °C von weniger als 9,3 mm^2/s, wobei die Schmierölzusammensetzung enthält:

a) eine Hauptmenge an einem Öl mit Schmierviskosität;
b) 0,4 Gew.-% bis 2,0 Gew.-%, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung, an einem nicht dispergierwirksamen Kamm-Polymethacrylat (PMA) mit einem gewichtsgemittelten Molekulargewicht (Mw) von 390.000 g/mol bis 460.000 g/mol; und
c) 0,08 Gew.-% bis 0,4 Gew.-%, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung, an einem nicht dispergierwirksamen Olefincopolymer auf Ethylenbasis mit einem gewichtsgemittelten Molekulargewicht (Mw) von 90,000 g/mol bis 160,000 g/mol.

13. Schmierölzusammensetzung gemäß Anspruch 1, wobei

das nicht dispergierwirksame Kamm-Polymethacrylat (PMA) in einer Menge von 0,4 Gew.-% bis 1,9 Gew.-%, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung, vorhanden ist; und
das nicht dispergierwirksame Olefincopolymer auf Ethylenbasis in einer Menge von 0,08 Gew.-% bis 0,36 Gew.-%, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung, vorhanden ist.

14. Verfahren zum Verringern von Verschleiß in einem Verbrennungsmotor gemäß Anspruch 12, wobei

das nicht dispergierwirksame Kamm-Polymethacrylat (PMA) in einer Menge von 0,4 Gew.-% bis 1,9 Gew.-%, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung, vorhanden ist; und
das nicht dispergierwirksame Olefincopolymer auf Ethylenbasis in einer Menge von 0,08 Gew.-% bis 0,36 Gew.-%, bezogen auf das Gesamtgewicht der Schmierölzusammensetzung, vorhanden ist.

15. Verfahren gemäß Anspruch 12 oder 14, wobei der Motor Rollenschlepphebelarme enthält.

Revendications

1. Composition d’huile lubrifiante, comprenant :

a) une quantité majoritaire d’une huile de viscosité lubrifiante ;
b) 0,4 % en poids à 2,0 % en poids, sur la base du poids total de la composition d’huile lubrifiante, d’un polyméthacrylate (PMA) en peigne non dispersant ayant un poids moléculaire moyen en poids (Mw) de 390 000 g/mole à 460 000 g/mole ; et
c) 0,08 % en poids à 0,4 % en poids, sur la base du poids total de la composition d’huile lubrifiante, d’un copolymère d’oléfine à base d’éthylène non dispersant ayant un poids moléculaire moyen en poids (Mw) de 90 000 g/mole à 160 000 g/mole,

la composition d’huile lubrifiante ayant une viscosité cinématique à 100 °C inférieure à 9,3 mm^2/s.

2. Composition d’huile lubrifiante selon la revendication 1, dans laquelle le PMA en peigne non dispersant a un indice de stabilité au cisaillement (SSI) de 0,3 à 0,8, mesuré conformément à la norme ASTM D7109.

3. Composition d'huile lubrifiante selon la revendication 1, dans laquelle le copolymère d'oléfine à base d'éthylène non dispersant a un indice de stabilité au cisaillement (SSI) de 10 à 70, mesuré conformément à la norme ASTM D7109.

4. Composition d'huile lubrifiante selon la revendication 1, dans laquelle le copolymère d'oléfine à base d'éthylène non dispersant :

(i) a une teneur totale en éthylène de 45 % en poids à 60 % en poids, sur la base du poids total du copolymère d'oléfine à base d'éthylène non dispersant, ou
(ii) est un copolymère d'éthylène-propylène.

5. Composition d'huile lubrifiante selon la revendication 1, dans laquelle le PMA en peigne non dispersant est présent en une quantité de 0,76 % en poids à 1,33 % en poids, et le copolymère d'oléfine à base d'éthylène non dispersant est présent en une quantité de 0,08 à 0,4 % en poids, sur la base du poids total de la composition d'huile lubrifiante.

6. Composition d'huile lubrifiante selon la revendication 1, dans laquelle le PMA en peigne non dispersant et le copolymère d'oléfine à base d'éthylène non dispersant sont présents en une quantité totale de 0,4 % en poids à 4 % en poids, sur la base du poids total de la composition d'huile lubrifiante.

7. Composition d'huile lubrifiante selon la revendication 1, dans laquelle l'huile de viscosité lubrifiante est une huile de base du groupe III de l'API.

8. Composition d'huile lubrifiante selon la revendication 1, dans laquelle la composition comprend en outre un composé du molybdène, dans laquelle éventuellement :

(i) le composé du molybdène est le dithiocarbamate de molybdène (MoDTC), ou
(ii) le composé du molybdène fournit à la composition d'huile lubrifiante une quantité de molybdène dans la plage de 50 ppm à 1 200 ppm.

9. Composition d'huile lubrifiante selon la revendication 1, dans laquelle la composition d'huile lubrifiante a un degré de viscosité SAE 0W-20, 0W-16 ou 0W-12.

10. Composition d'huile lubrifiante selon la revendication 1, dans laquelle la composition d'huile lubrifiante a une viscosité à cisaillement élevé à haute température (HTHS) à 150 °C de 2,55 cP à moins de 2,9 cP.

11. Composition d'huile lubrifiante selon la revendication 1, dans laquelle la composition d'huile lubrifiante a un indice de viscosité de 200 à 240.

12. Procédé pour la réduction de l'usure dans un moteur à combustion interne comprenant la lubrification dudit moteur avec une composition d'huile lubrifiante ayant une viscosité cinématique à 100 °C inférieure à 9,3 mm^2/s, la composition d'huile lubrifiante comprenant :

a) une quantité majoritaire d'une huile de viscosité lubrifiante ;
b) 0,4 % en poids à 2,0 % en poids, sur la base du poids total de la composition d'huile lubrifiante, d'un polyméthacrylate (PMA) en peigne non dispersant ayant un poids moléculaire moyen en poids (Mw) de 390 000 g/mole à 460 000 g/mole ; et
c) 0,08 % en poids à 0,4 % en poids, sur la base du poids total de la composition d'huile lubrifiante, d'un copolymère d'oléfine à base d'éthylène non dispersant ayant un poids moléculaire moyen en poids (Mw) de 90,000 g/mole à 160,000 g/mole.

13. Composition d'huile lubrifiante selon la revendication 1, dans laquelle

le polyméthacrylate (PMA) en peigne non dispersant est présent en une quantité de 0,4 % en poids à 1,9 % en poids, sur la base du poids total de la composition d'huile lubrifiante ; et
le copolymère d'oléfine à base d'éthylène non dispersant est présent en une quantité de 0,08 % en poids à 0,36 % en poids, sur la base du poids total de la composition d'huile lubrifiante.

14. Procédé pour la réduction de l'usure dans un moteur à combustion interne selon la revendication 12 dans lequel

le polyméthacrylate (PMA) en peigne non dispersant est présent en une quantité de 0,4 % en poids à 1,9 % en poids, sur la base du poids total de la composition d'huile lubrifiante ; et
le copolymère d'oléfine à base d'éthylène non dispersant est présent en une quantité de 0,08 % en poids à 0,36 % en poids, sur la base du poids total de la composition d'huile lubrifiante.

15. Procédé selon la revendication 12 ou 14, dans lequel le moteur comprend des culbuteurs à galet suiveur.

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