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(54) **DIESEL ENGINE LUBRICATING COMPOSITIONS AND METHODS OF USE THEREOF**

DIESELMOTORSCHMIERZUSAMMENSETZUNGEN UND VERFAHREN ZUR VERWENDUNG DAVON

COMPOSITIONS LUBRIFIANTES DE MOTEUR DIESEL ET LEURS PROCÉDÉS D'UTILISATION

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DescriptionFIELD

5 **[0001]** The instant disclosure provides for diesel engine lubricating compositions and methods of lubricating a diesel engine by supplying the engine with a lubricating composition as disclosed herein. The lubricating compositions disclosed herein may be used in diesels engines including, in particular, heavy-duty diesel engines to improve one or more of fuel economy and wear protection.

10 BACKGROUND

[0002] Lubricating oil compositions are used for the smooth operation of internal combustion engines. The engine oils for internal combustion engines in particular serve to (i) lubricate various sliding interfaces between the piston ring and cylinder liner, in bearings of the crank shaft and the connecting rod, and in the valve driving mechanism including cams and valve lifters, (ii) cool the engine, (iii) clean and disperse the combustion products and (iv) prevent corrosion and consequent rust formation. The stringent requirements for high performance engines in recent years has meant greater demand from lubricants used in such engines.

[0003] There is increasing interest in improving the fuel efficiency of internal combustion engines. Vehicle manufacturers have improved fuel economy through engine design, improvements which take advantage of advances in lubricating oils which provide better oxidative stability, wear protection, and reduced friction. Operators of heavy-duty diesel vehicles have been reluctant to adopt low viscosity grade engine oils to improve fuel economy; durability, i.e., the ability to maintain vehicles on the road for extended periods of time and mileage, has been and remains the primary concern. Thus, the most widely used viscosity grades for on-highway heavy duty diesel vehicles has been SAE 15W-40, 10W-30, and 5W-30. In recent years, there is a growing push to improve the fuel efficiency of heavy-duty diesel vehicles. Consequently, there is a need to improve the fuel economy of diesel engines without compromising the durability of the engines or otherwise negatively impacting the lubricant performance, including deposit and soot control and oxidation and corrosion resistance. This is particularly relevant for viscosity grades lighter than that of SAE 5W-30, especially those of 0W-20, 0W-16, and 0W12.

[0004] US 2011/245120 A1 discloses lubricating oil composition providing good anti-wear and cleanliness performance, i.a. for heavy duty diesel engines.

[0005] There is interest, therefore, in developing a lubricating composition that may be used in diesel engines that may operate under severe conditions and loads while reducing the impact of soot and soot-related wear as well as cleanliness, deposits and better fuel economy.

35 SUMMARY

[0006] The present invention is disclosed in and by the appended claims.

[0007] The present disclosure relates to diesel engine lubricating compositions for an internal combustion engine (typically a compression ignited engine) to have at least one of reduced soot, improved fuel economy, reduced deposit formation, reduced wear and improved cleanliness.

[0008] The lubricating compositions include an oil of lubricating viscosity having greater than 50 weight percent (sometimes referred to as "wt. %") of a Group III base oil, Group IV base oil, Group V base oil, or mixtures thereof. The compositions further include a first PIB succinimide dispersant derived from an 1800 to 2100 Mn PIB and a second PIB succinimide dispersant derived from a PIB with an Mn up to 1600, provided that at least one of the first PIB succinimide dispersant and the second PIB succinimide dispersant is boron-free; an alkaline earth metal salicylate, such as a calcium salicylate, detergent; an alkaline earth metal sulfonate, where the alkaline earth metal sulfonate is present to deliver from 0.1 wt % to 1.5 wt % of alkaline earth metal soap to the composition; a phosphorus antiwear agent present in an amount to deliver 300 to 900 ppm phosphorus to the lubricating composition.

[0009] The lubricating compositions have a sulfated ash of between 0.3 to 0.9 wt %; a kinematic viscosity at 100°C of less than 8.3 cSt; a total alkaline earth metal soap of from 0.6 wt % to 2.1 wt %; and a HTHS measured according to ASTM D4683 of less than 2.7 mPa s.

DETAILED DESCRIPTION

55 **[0010]** The present disclosure provides for diesel engine lubricating compositions and methods for using the same. The lubricating composition includes an oil of lubricating viscosity having greater than 50 weight percent of a Group III base oil, a Group IV base oil, a Group V base oil, or mixtures thereof; a first PIB succinimide dispersant derived from an 1800 to 2500 Mn PIB; a second PIB succinimide dispersant derived from a PIB with an Mn less than 1600, where at

least one of the first PIB succinimide dispersant and the second PIB succinimide dispersant is boron-free; an alkaline earth metal salicylate detergent; an alkaline earth metal sulfonate detergent present in an amount to deliver 0.1 wt % to 1.2 wt % of alkaline earth metal soap to the lubricating composition; and a phosphorus antiwear agent present in an amount to deliver 300 to 900 ppm phosphorous to the lubricating composition. The lubricating compositions disclosed herein further include a total sulfated ash of between 0.3 to 0.9 wt % or 0.3 to 1.1 wt. %, a total alkaline earth metal soap content of from 0.6 wt % to 2.1 wt %, and an HTHS as measured according to ASTM D4683 of less than 2.7 mPa.s.

Oils of Lubricating Viscosity

[0011] The lubricating compositions disclosed herein comprise an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof. A more detailed description of unrefined, refined and re-refined oils is provided in International Publication WO2008/147704, paragraphs [0054] to [0056] (a similar disclosure is provided in US Patent Application 2010/197536, see [0072] to [0073]). A more detailed description of natural and synthetic lubricating oils is described in paragraphs [0058] to [0059] respectively of WO2008/147704 (a similar disclosure is provided in US Patent Application 2010/197536, see [0075] to [0076]). Synthetic oils may also be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment, oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0012] Oils of lubricating viscosity may also be defined as specified in April 2008 version of "Appendix E - API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils", section 1.3 Sub-heading 1.3. "Base Stock Categories". The API Guidelines are also summarized in US Patent US 7,285,516 (see column 11, line 64 to column 12, line 10).

[0013] Group IV base oils (also known as polyalphaolefins or PAO) are known in the art and are prepared by oligomerization or polymerization of linear alpha olefins. PAOs are characteristically water white oils with superior low temperature viscosity properties (as measured, as well as high viscosity index. Typical PAOs suitable for use in internal combustion engines include polyalphaolefins with a kinematic viscosity of 3 to 10 m²/s, such as PAO-4 and PAO-6, i.e. approximately 4 m²/s and 6 m²/s respectively.

[0014] In addition to traditional Group III and Group IV base oils, low levels of some Group V base oils may be present, especially Group V ester base oils. Ester base fluids include esters of monocarboxylic acids with monohydric alcohols; di-esters of diols with monocarboxylic acids and di-esters of dicarboxylic acids with monohydric alcohols; polyol esters of monocarboxylic acids and polyesters of monohydric alcohols with polycarboxylic acids; and mixtures thereof. Esters may be broadly grouped into two categories: synthetic and natural.

[0015] Synthetic esters may comprise esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, and alkenyl malonic acids) with any of variety of monohydric 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. Other synthetic esters include those made from C5 to C12 monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol. Esters can also be monoesters of mono-carboxylic acids and monohydric alcohols.

[0016] Natural (or bio-derived) esters refer to materials derived from a renewable biological resource, organism, or entity, distinct from materials derived from petroleum or equivalent raw materials. Natural esters include fatty acid triglycerides, hydrolyzed or partially hydrolyzed triglycerides, or transesterified triglyceride esters, such as fatty acid methyl ester (or FAME). Suitable triglycerides include, but are not limited to, palm oil, soybean oil, sunflower oil, rapeseed oil, olive oil, linseed oil, and related materials. Other sources of triglycerides include, but are not limited to, algae, animal tallow, and zooplankton. Methods for producing biolubricants from natural triglycerides are described in, e.g., United States Patent Publication 2011/0009300A1.

[0017] In one embodiment, the lubricant composition of the disclosure contains 0.1 to 10 weight percent of an ester base fluid, or 0.25 to 5 weight percent, or 0.1 to 2 weight percent of an ester base fluid. In one embodiment, the lubricating composition comprises no more than 5 weight percent of an ester base fluid, no more than 2.5 weight percent or no more than 1 weight percent of an ester base fluid. In one embodiment, the lubricant composition is free of or substantially free of, that is contains less than 0.2 weight percent, intentionally added ester base fluid.

[0018] In one embodiment the oil of lubricating viscosity may be a base oil including API Group I to IV oil, an ester or a synthetic oil, or mixtures thereof. In one embodiment the oil of lubricating viscosity may be an API Group II, Group III, Group IV oil, an ester or a synthetic oil, or mixtures thereof. In some embodiments, the oil of lubricating viscosity comprises

at least 50 wt %, or at least 60 wt %, or at least 70 wt %, or at least 80 wt %, or at least 90 wt %, or at least 95 wt %, or at least 100 wt % of a Group III or a Group IV base oil, or a mixture of a Group III and Group IV base oil.

[0019] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 wt % the sum of the amount of the additives of the disclosed compositions and the other performance additives.

[0020] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating compositions described herein (comprising the additives disclosed herein) is in the form of a concentrate which may be combined with additional oil to form, in whole or in part, a finished lubricant, the ratio of the of these additives to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight. Typically, the lubricating composition described herein include at least 50 wt %, or at least 60 wt %, or at least 70 wt %, or at least 80 wt % of an oil of lubricating viscosity.

[0021] In some embodiments, the oil of lubricating viscosity can include a base oil having a kinematic viscosity measured at 100 °C of 2.4 m²/s to 6.4 m²/s. In some embodiments, the kinematic viscosity is from 3.8 m²/s to 5.0 m²/s or from 5.2 m²/s to 5.8 m²/s or from 6.0 m²/s to 6.5 m²/s. In other embodiments, the kinematic viscosity of the base oil is 4.5 m²/s or 4.3 m²/s or 4.2 m²/s.

Polyisobutenyl (PIB) succinimide Dispersant(s)

[0022] The lubricating compositions of the instant disclosure further include a first polyisobutenyl succinimide dispersant and a second polyisobutenyl succinimide dispersant. The reference herein to a polyisobutylene succinimide dispersant refers to both the first polyisobutenyl succinimide dispersant as well as the second polyisobutenyl succinimide dispersant. The difference being that that first polyisobutenyl succinimide dispersant is derived from a polyisobutenyl moiety having a larger number average molecular weight (Mn) than the PIB of the second polyisobutenyl succinimide dispersant.

[0023] The first polyisobutenyl succinimide and/or the second polyisobutenyl succinimide dispersants can each be prepared (or, as used herein "derived") from a polyisobutylene ("PIB") succinimide dispersant that is either a "conventional" PIB or a high vinylidene PIB. The difference between a conventional polyolefin and a high vinylidene polyolefin can be illustrated by reference to the production of PIB. In a process for producing conventional PIB, isobutylene is polymerized in the presence of AlCl₃ to produce a mixture of polymers comprising predominantly trisubstituted olefin (III) and tetrasubstituted olefin (IV) end groups, with only a very small amount (for instance, less than 20 percent) of chains containing a terminal vinylidene group (I). In an alternative process, isobutylene is polymerized in the presence of BF₃ catalyst to produce a mixture of polymers comprising predominantly (for instance, at least 70 percent) terminal vinylidene groups, with smaller amounts of tetrasubstituted end groups and other structures. The materials produced in the alternative method, sometimes referred to as "high vinylidene PIB," are also described in U.S. Patent 6,165,235,

[0024] In one embodiment, the polyisobutylene-derived dispersant is a conventional polyisobutylene-derived dispersant. In another embodiment, the polyisobutylene-derived dispersant is a high or mid vinylidene succinimide dispersant. The polyisobutylene-derived dispersant used herein is generally known in the art.

[0025] The polyisobutylene-derived acylating agent may be prepared/obtained/obtainable from reaction with maleic anhydride by an "ene" or "thermal" reaction, also referred to as direct alkylation. The "ene" reaction mechanism and general reaction conditions are summarized in "Maleic Anhydride", pages, 147-149, Edited by B. C. Trivedi and B. C. Culbertson and Published by Plenum Press in 1982. The polyisobutylene-derived dispersant prepared by a process that includes an "ene" reaction includes a dispersant having a carbocyclic ring present on less than 50 mole %, or 0 to less than 30 mole %, or 0 to less than 20 mole %, or 0 mole % of the dispersant molecules. The "ene" reaction may have a reaction temperature of 180° C. to less than 300° C., or 200° C. to 250° C., or 200° C. to 220° C.

[0026] The polyisobutylene-derived acylating agent may also be obtained/obtainable from a chlorine-assisted process, often involving Diels-Alder chemistry, leading to formation of carbocyclic linkages. The process is known to a person skilled in the art. The chlorine-assisted process may produce an acylating agent having a carbocyclic ring present on 50 mol % or more, or 60 to 100 mol % of the molecules. Both the thermal and chlorine-assisted processes are described in greater detail in U.S. Pat. No. 7,615,521, columns 4-5 and preparative examples A and B.

[0027] The polyisobutylene-derived acylating agent may also be prepared/obtained/obtainable from a free radical process, wherein the acylating agent is reacted with polyisobutylene in the presence of a free radical initiator. Free radical processes of this sort are well known in the art and may be carried out in the presence of an additional alpha-olefin.

[0028] The polyisobutylene-derived acylating agent can be obtained from reacting polyisobutylene with an acylating agent, i.e., an ethylenically unsaturated carbonyl compound, to form an acylated polyisobutylene which may be further functionalized with an amine or alcohol to form a suitable dispersant. Suitable acylating agents include maleic anhydride or a reactive equivalent thereof (such as an acid or ester), i.e., succinic acid, and their reactive equivalents. In one embodiment, polyisobutylene may be reacted with maleic anhydride to form acylated product with a conversion between 1 and 2. In one embodiment, the monosuccin is reacted with an amine so that the intended product comprises a mixture wherein all of the anhydride present in the acylating agent has been converted to imide.

[0029] The polyisobutylene-derived dispersant may have a carbonyl to nitrogen ratio (CO:N ratio) of 5:1 to 1:10, 2:1

to 1:10, or 2:1 to 1:5, or 2:1 to 1:2. In one embodiment the dispersant may have a CO:N ratio of 2:1 to 1:10, or 2:1 to 1:5, or 2:1 to 1:2, or 1:1.4 to 1:0.6.

[0030] Polyisobutylene succinimide dispersants of the instant disclosure may be prepared by reaction of the acylated PIB with a suitable amine compound. Suitable amines include one or more hydrocarbylamines, aminoalcohols, polyetheramines, or combinations thereof.

[0031] In one embodiment, the hydrocarbyl amine component may comprise at least one aliphatic amine containing at least one amino group capable of condensing with said acyl group to provide a pendant group and at least one additional group comprising at least one nitrogen, oxygen, or sulfur atom. Suitable aliphatic amines include polyethylene polyamines (such as tetraethylene pentamine (TEPA), triethylene tetra amine (TETA), pentaethylene hexamine (PEHA), and polyamine bottoms), N,N-dimethylaminopropylamine (DMAPA), N-(aminopropyl)morpholine, N,N-dilsostearylaminopropylamine, ethanolamine, and combinations thereof.

[0032] In one embodiment, the hydrocarbyl amine component may comprise at least one aromatic amine containing at least one amino group capable of condensing with said acyl group to provide a pendant group and at least one additional group comprising at least one nitrogen, oxygen, or sulfur atom, wherein said aromatic amine is selected from the group consisting of (i) a nitro-substituted aniline, (ii) an amine comprising two aromatic moieties linked by a C(O)NR-group, a -C(O)O- group, an -O- group, an N=N- group, or an -SO₂- group where R is hydrogen or hydrocarbyl, one of said aromatic moieties bearing said condensable amino group, (iii) an aminoquinoline, (iv) an aminobenzimidazole, (v) an N,N- dialkylphenylenediamine, (vi), an aminodiphenylamine (also N,N-phenyldiamine), and (vii) a ring-substituted benzylamine.

[0033] In one embodiment, the polyetheramine compound may comprise an amine-terminated polyether compound. Amine terminated polyether compounds may comprise units derived from ethylene oxides, propylene oxides, butylene oxides, or some combination thereof. Suitable polyether compounds include Jeffamine® line of polyether amines available from Huntsman.

[0034] In one embodiment, the first polyisobutylene succinimide dispersant may be prepared by a thermal direct alkylation process described herein. In another embodiment, the second polyisobutylene succinimide dispersant may be prepared by a thermal direct alkylation process described herein.

[0035] The polyisobutylene-derived dispersant as described herein can further be described as having a TBN. In one embodiment, the first polyisobutylene succinimide dispersant has a TBN of from 15 to 25. In another embodiment, the first polyisobutylene succinimide dispersant has a TBN of from 15 to 20. In one embodiment, the second polyisobutylene succinimide dispersant has a TBN of from 20 to 35. In another embodiment, the second polyisobutylene succinimide dispersant has a TBN of from 25 to 30. In one embodiment, the second polyisobutylene succinimide dispersant has a TBN of from 27 to 28.

[0036] According to the invention, the first polyisobutylene succinimide dispersant is derived from a PIB having a number average molecular weight ranging from 1800 to 2100. In one embodiment, the first polyisobutylene succinimide dispersant is derived from a PIB having a number average molecular weight ranging from 1850 to 2150.

[0037] According to the invention, the second polyisobutylene succinimide dispersant is derived from a PIB having a number average molecular weight of up to 1600, preferably ranging from 750 to 1600. In another embodiment, the second polyisobutylene succinimide dispersant is derived from a PIB having a number average molecular weight ranging from 1000 to 1600. In one embodiment, the second polyisobutylene succinimide dispersant is derived from a PIB having a number average molecular weight ranging from 1200 to 1600. In one embodiment, the second polyisobutylene succinimide dispersant is derived from a PIB having a number average molecular weight ranging from 800 to 1150. In another embodiment, the second polyisobutylene succinimide dispersant is derived from a PIB having a number average molecular weight ranging from 900 to 1100.

[0038] According to the invention, the first polyisobutylene succinimide dispersant is present in the lubricating composition in an amount of from 0.8 wt % to 6 wt %. In one embodiment, the first polyisobutylene succinimide dispersant may be present in the lubricating composition in an amount of from 1 wt % to 5 wt %. In one embodiment, the first polyisobutylene succinimide dispersant may be present in the lubricating composition in an amount of from 1.1 wt % to 2.2 wt %.

[0039] In one embodiment, the second polyisobutylene succinimide dispersant is present in the lubricating composition in an amount of from 1 wt % to 5 wt %. In another embodiment, the second polyisobutylene succinimide dispersant is present in the lubricating composition in an amount of from 1.5 wt % to 4.8 wt %. In another embodiment, the second polyisobutylene succinimide dispersant is present in the lubricating composition in an amount of from 1.8 wt % to 4.6 wt %. In another embodiment, the second polyisobutylene succinimide dispersant is present in the lubricating composition in an amount of from 1.9 wt % to 3.3 wt %.

[0040] In one embodiment, the first polyisobutylene succinimide dispersant may include a mixture of two or more dispersants where each of the two or more dispersants falls within the scope, including, without limitation, the PIB Mn, TBN, and treat rates of the first polyisobutylene succinimide dispersant as disclosed herein. In another embodiment, the first polyisobutylene succinimide dispersant may include a mixture of two dispersants where each of the two dispersants

falls within the scope, including, without limitation, the PIB Mn, TBN, and treat rates of the first polyisobutylene succinimide dispersant as disclosed herein.

[0041] In some embodiments, the second polyisobutylene succinimide dispersant may include a mixture of two or more dispersants where each of the two or more dispersants falls within the scope, including, without limitation, the PIB Mn, TBN, and treat rates of the second polyisobutylene succinimide dispersant as disclosed herein. In another embodiment, the second polyisobutylene succinimide dispersant includes from 1 wt % to 5 wt % of a PIB succinimide dispersant derived from a PIB having an Mn of 900 to 1100 and from 1 wt % to 5 wt % of a PIB succinimide dispersant derived from a PIB having an Mn of from 1200 to 1600.

[0042] The lubricating compositions of the invention further provide that at least one of the first polyisobutylene succinimide dispersant and the second polyisobutylene succinimide dispersant are boron free. In one embodiment, the first polyisobutylene succinimide dispersant is boron free and the second polyisobutylene succinimide dispersant is borated. In another embodiment, the first polyisobutylene succinimide dispersant is borated and the second polyisobutylene succinimide dispersant is boron free.

[0043] In preparing the boron-containing polyisobutylene succinimide dispersant, the first polyisobutylene-derived succinimide dispersant or the second polyisobutylene-derived succinimide dispersant as described herein may be post-treated by conventional methods including a reaction with boron compounds to generate the boron-containing polyisobutylene succinimide dispersant. Suitable boron compounds that may be used to borate the polyisobutylene-derived dispersant include one or more of a variety of agents selected from the group consisting of the various forms of boric acid (including metaboric acid, HBO_2 , orthoboric acid, H_3BO_3 , and tetraboric acid, $\text{H}_2\text{B}_4\text{O}_7$), boric oxide, boron trioxide, and alkyl borates. In one embodiment the borating agent is boric acid which may be used alone or in combination with other borating agents. Methods of preparing borated dispersants are known in the art. The borated dispersant may be prepared in such a way that they contain 0.1 weight % to 2.5 weight% boron, or 0.1 weight % to 2.0 weight % boron or 0.2 to 1.5 weight % boron or 0.3 to 1.0 weight % boron.

[0044] In some embodiments, either the borated first polyisobutylene succinimide dispersant or the borated second polyisobutylene succinimide dispersant is present in an amount to deliver at least 25 ppm, or at least 50 ppm, or at least 75 ppm boron to the lubricating composition. In another embodiment, either the borated first polyisobutylene succinimide dispersant or the borated second polyisobutylene succinimide dispersant is present in an amount to deliver from 25 ppm to 400 ppm boron to the lubricating composition. In another embodiment, either the borated first polyisobutylene succinimide dispersant or the borated second polyisobutylene succinimide dispersant is present in an amount to deliver from 25 ppm to 400 ppm, or 50 ppm to 200 ppm, or 75 ppm to 150 ppm, or 78 ppm to 100 ppm boron to the lubricating composition.

Detergents

[0045] The lubricating composition of the invention includes an alkaline earth metal salicylate detergent and at least one alkaline earth metal sulfonate detergent as described herein. Metal-containing detergents are well known in the art. They are generally made up of metal salts, especially alkali metals and alkaline earth metals, of acidic organic substrates. Metal-containing detergents may be neutral, i.e. a stoichiometric salt of the metal and substrate also referred to as neutral soap or soap, or overbased.

[0046] Metal overbased detergents, otherwise referred to as overbased detergents, metal-containing overbased detergents or superbased salts, are characterized by a metal content in excess of that which would be necessary for neutralization according to the stoichiometry of the metal and the particular acidic organic compound, i.e. the substrate, reacted with the metal. The overbased detergent may comprise one or more of sulfonates, salicylates, non-sulfur containing phenates, sulfur containing phenates, and mixtures thereof.

[0047] The amount of excess metal to substrate is commonly expressed in terms of metal ratio. The terminology "metal ratio" is used in the prior art and herein to define the ratio of the total chemical equivalents of the metal in the overbased salt to the chemical equivalents of the metal in the salt which would be expected to result from the reaction between the hydrocarbyl substituted organic acid; the hydrocarbyl-substituted phenol or mixtures thereof to be overbased, and the basic metal compound according to the known chemical reactivity and the stoichiometry of the two reactants. Thus, in a normal or neutral salt (i.e., soap) the metal ratio is one and, in an overbased salt, the metal ratio is greater than one, especially greater than 1.3. The overbased metal detergent may have a metal ratio of 5 to 30, or a metal ratio of 7 to 22, or a metal ratio of 11 to 18, or a metal ratio of at least 11.

[0048] The metal-containing detergent may also include "hybrid" detergents formed with mixed surfactant systems including phenate and/or sulfonate components, e.g., phenate-salicylates, sulfonate-phenates, sulfonate-salicylates, sulfonates-phenates-salicylates, as described, for example, in US Patents 6,429,178; 6,429,179; 6,153,565; and 6,281,179. Where, for example, a hybrid sulfonate/salicylate detergent is employed, the hybrid detergent would be considered equivalent to amounts of distinct salicylate and sulfonate detergents introducing like amounts of salicylate and sulfonate soaps, respectively. Overbased phenates and salicylates typically have a total base number of 180 to 450

TBN. Overbased sulfonates typically have a total base number of 250 to 800, or 300 to 600. Overbased detergents are known in the art.

[0049] Alkylphenols are often used as constituents in and/or building blocks for overbased detergents. Alkylphenols may be used to prepare phenate, salicylate, salixarate, or saligenin detergents or mixtures thereof. Suitable alkylphenols may include para-substituted hydrocarbyl phenols. The hydrocarbyl group may be linear or branched aliphatic groups of 1 to 60 carbon atoms, 8 to 40 carbon atoms, 10 to 24 carbon atoms, 12 to 20 carbon atoms, or 16 to 24 carbon atoms. In one embodiment, the alkylphenol overbased detergent is prepared from an alkylphenol or mixture thereof that is free of or substantially free of (i.e., contains less than 0.1 weight percent) p-dodecylphenol. In one embodiment, the lubricating composition contains less than 0.3 weight percent of alkylphenol, less than 0.1 weight percent of alkylphenol, or less than 0.05 weight percent of alkylphenol. In one embodiment, the alkylphenol detergent is a salicylate.

Alkaline Earth Metal Salicylate

[0050] Salicylate detergents and overbased salicylate detergents may be prepared in at least two different manners. Carbonylation (also referred to as carboxylation) of a p-alkylphenol is described in many references including US Patent 8,399,388. Carbonylation may be followed by overbasing to form overbased salicylate detergent. Suitable p-alkylphenols include those with linear and/or branched hydrocarbyl groups of 1 to 60 carbon atoms, 4 to 34 carbon atoms, 14 to 24 carbon atoms, and combinations thereof. Salicylate detergents may also be prepared by alkylation of salicylic acid, followed by overbasing, as described in US Patent 7,009,072. Salicylate detergents prepared in this manner, may be prepared from linear and/or branched alkylating agents (usually 1-olefins) containing 6 to 50 carbon atoms, 10 to 30 carbon atoms, or 14 to 24 carbon atoms. In one embodiment, the overbased detergent is a salicylate detergent. In one embodiment, the salicylate detergent is free of unreacted p-alkylphenol (i.e., contains less than 0.1 weight percent). In one embodiment, the salicylate detergent is prepared by alkylation of salicylic acid.

[0051] In one embodiment, the alkaline earth metal salicylate detergent has a TBN (KOH/g) of from 200 to 575 or 200 to 500. In another embodiment, the alkaline earth metal salicylate detergent has a TBN (KOH/g) of from 250 to 350. In one embodiment, the alkaline earth metal salicylate detergent has a metal ratio of from 2 to 7, or from 2 to 4, or from 2.5 to 3.5. In one embodiment, the alkaline earth metal salicylate detergent is present in the lubricating composition in an amount of from 0.1 to 5 wt %. In another embodiment, the alkaline earth metal salicylate detergent is present in the lubricating composition in an amount of from 0.2 to 3 wt %. In one embodiment, the alkaline earth metal salicylate detergent is present in the lubricating composition in an amount of from 0.5 to 3 wt %. In one embodiment, the alkaline earth metal salicylate detergent is present in the lubricating composition in an amount of from 0.8 to 2.5 wt %. In one embodiment, the calcium alkaline earth metal detergent is present in the lubricating composition in an amount of from 0.9 to 2.3 wt %.

[0052] In one embodiment, the alkaline earth metal salicylate detergent may be a calcium salicylate, a magnesium salicylate or combinations thereof. In one embodiment, the alkaline earth metal salicylate is a calcium salicylate. In one embodiment, the alkaline earth metal salicylate is a magnesium salicylate. The calcium salicylate may be present in an amount to deliver 150 to 1500 ppm calcium to the lubricant composition, or 250 to 1100 ppm calcium to the composition. The magnesium salicylate may be present in an amount to deliver 100 to 2000 ppm of magnesium to the lubricant composition, or 250 to 1750 ppm magnesium, or 300 to 1550 ppm to the lubricant composition.

Alkaline Earth Metal Sulfonate Detergent

[0053] The alkaline earth metal sulfonate may be a neutral sulfonate salt (metal ratio less than 1.3), a low overbased detergent (metal ratio of 1.5 to 6), or a high overbased detergent (metal ratio of at least 8), or any combination therein, such that at least 0.1 weight percent of alkaline earth metal soap is present in the lubricant composition.

[0054] Alkaline earth metal sulfonate detergents may be linear alkylbenzene sulfonate detergent as is described in paragraphs [0026] to [0037] of US Patent Publication 2005/065045 (and granted as US 7,407,919). The linear alkylbenzene sulfonate detergent may be particularly useful for assisting in improving fuel economy. The linear alkyl group may be attached to the benzene ring anywhere along the linear chain of the alkyl group, but often in the 2, 3 or 4 position of the linear chain, and in some instances, predominantly in the 2 position, resulting in the linear alkylbenzene sulfonate detergent.

[0055] In one embodiment, the alkaline earth metal sulfonate detergent of the instant disclosure is selected from a calcium sulfonate detergent and a magnesium sulfonate detergent. In another embodiment, the alkaline earth metal sulfonate detergent is a calcium sulfonate detergent. In one embodiment, the calcium sulfonate detergent has a TBN of less than 250 on an oil free basis. In another embodiment, the calcium sulfonate detergent has a TBN of less than 200, or less than 150, or less than 80. In one embodiment, the calcium sulfonate detergent has a TBN of from 50 to 90. In one embodiment, the calcium sulfonate has a TBN from 120 to 250 mg KOH/g and a metal ratio of 1.5 to 5.

[0056] In one embodiment, the alkaline earth metal sulfonate detergent is a calcium sulfonate detergent present in

the lubricating composition in an amount of from 0.1 wt % to 2.0 wt %. In another embodiment, the calcium sulfonate detergent is present in the lubricating composition in an amount of from 0.3 wt % to 1.5 wt %.

[0057] In one embodiment, the alkaline earth metal sulfonate detergent is a magnesium sulfonate detergent. The magnesium sulfonate may have a TBN (mg KOH/g) of from 300 to 800 on an oil-free basis. In some embodiments, magnesium sulfonate may have a TBN (mg KOH/g) of from 400 to 750. In other embodiments, the magnesium sulfonate may have a TBN (mg KOH/g) of from 250 to 350. In other embodiments, the magnesium sulfonate may have a TBN (mg KOH/g) of from 350 to 375. In one embodiment, the magnesium sulfonate may have a metal ratio of 8 to 30, 10 to 25, or 12 to 18.

[0058] In one embodiment, the magnesium sulfonate detergent is present in the lubricating composition in an amount of from 0.05 wt % to 0.5 wt % or 0.05 to 0.2. In another embodiment, the magnesium sulfonate detergent is present in the lubricating composition in an amount of from 0.06 to 0.1 wt % or 0.06 wt % to 0.2 wt %.

[0059] In one embodiment, the alkaline earth metal sulfonate may be a combination of at least one neutral or low overbased alkaline earth metal sulfonate (i.e., metal ratio less than 6) and at least one high overbased alkaline earth metal sulfonate (metal ratio of at least 8).

[0060] The alkaline earth metal detergent used herein may be sodium salts, calcium salts, magnesium salts, or mixtures thereof of sulfonates. In one embodiment, the alkaline earth metal sulfonate detergent is a calcium sulfonate detergent, a magnesium sulfonate detergent or mixtures thereof. In one embodiment, one or more of the calcium sulfonate detergent and the magnesium sulfonate detergent are overbased. In one embodiment, the alkaline earth metal detergent is an overbased calcium sulfonate detergent. In another embodiment, the alkaline earth metal detergent is an overbased magnesium sulfonate detergent. In yet another embodiment, the alkaline earth metal detergent is mixture of an overbased calcium sulfonate detergent and an overbased magnesium sulfonate detergent. In one embodiment, the alkaline earth metal sulfonate detergent is a mixture of 0.6 wt % to 1.5 wt % of a calcium sulfonate detergent having a TBN (mg KOH/g) of from 50 to 200 and 0.04 wt % to 0.1 wt % of an overbased magnesium sulfonate detergent having a TBN (mg KOH/g) of from 400 to 800.

[0061] The detergents of the disclosed lubricating compositions may include alkaline earth metals contributed from the detergents. In one embodiment, the calcium salicylate detergent is present in an amount to deliver 150 to 1500 ppm, or 250 to 1100 ppm, or 300 to 800 ppm of calcium to the lubricating composition. In embodiments where the alkaline earth metal detergent includes a calcium sulfonate detergent the calcium sulfonate detergent may be present in an amount to deliver 100 to 1000 ppm, 150 to 800 ppm, or 250 to 650 ppm calcium to the lubricating compositions. In embodiments where the alkaline earth metal detergent includes a magnesium sulfonate detergent, the magnesium sulfonate detergent may be present in an amount to deliver 50 to 500, 100 to 425, or 150 to 350 ppm magnesium to the lubricating composition. In some embodiments, the alkaline earth metal detergent includes a calcium sulfonate detergent and the total amount of calcium delivered to the lubricating composition from the calcium salicylate detergent and the calcium sulfonate detergent is 800 to 2500, 900 to 1800, 950 to 1450 ppm calcium to the lubricating composition.

[0062] Metal-containing detergents contribute sulfated ash to a lubricating composition. Sulfated ash may be determined by ASTM D874. In one embodiment, the total sulfated ash delivered to the lubricating composition from the alkaline earth metal salicylate detergent and the alkaline earth metal detergent is from 0.25 to 0.95 weight percent. In other embodiments, the alkaline earth salicylate detergent is present in an amount to deliver 0.05 to 0.5 weight percent, or 0.1 to 0.35 weight percent sulfated ash to the lubricating compositions. In another embodiment, the alkaline earth metal detergent is present in an amount to deliver 0.05 to 0.75, or 0.1 to 0.6 weight percent sulfated ash to the lubricating composition.

[0063] In addition to ash and TBN, overbased detergents contribute detergent soap, also referred to as neutral detergent salt, to the lubricating composition. Soap, being a metal salt of the substrate, may act as a surfactant in the lubricating composition. In one embodiment, the alkaline earth metal sulfonate detergents are present in an amount to deliver 0.1 wt % to 1.5 wt %, or 0.15 to 1.2 wt %, or 0.2 wt % to 0.9 wt % sulfonate soap to the lubricant composition. In one embodiment, the alkaline earth metal salicylate detergents are present in an amount to deliver 0.3 wt % to 1.4 wt %, or 0.35 wt % to 1.2 wt %, or 0.4 wt % to 1.0 wt % salicylate soap to the lubricant composition. In one embodiment, the alkaline earth metal soap may be calcium, magnesium, or any mixture thereof. In one embodiment, alkaline earth metal sulfonate soap is present in an amount 0.2 wt % to 0.8 wt % of the lubricant composition, and the alkaline earth metal salicylate soap is present in an amount 0.3 wt % to 1.0 wt % of the lubricant composition. The total of all alkaline earth metal detergent soap may be present in an amount 0.6 wt % to 2.1 wt %, or 0.7 wt % to 1.4 wt % of the lubricant composition.

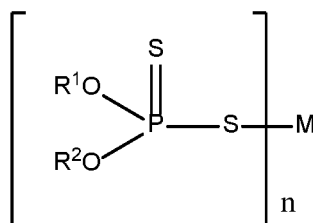
Antiwear Agent

[0064] The lubricating composition of the invention includes one or more phosphorus-containing antiwear agents.

[0065] Phosphorus-containing anti-wear agents are well known to one skilled in the art and include metal di-alkyl(dithio)phosphate salts, hydrocarbyl phosphites, hydrocarbyl phosphines, hydrocarbyl phosphonates, alkylphosphate esters, amine or ammonium (alkyl)phosphate salts, and combinations thereof.

[0066] In one embodiment, the phosphorus-containing anti-wear agent may be a metal dialkyldithiophosphate, which may include a zinc dialkyldithio-phosphate. Such zinc salts are often referred to as zinc dialkyldithiophosphates (ZDDP) or simply zinc dithiophosphates (ZDP). They are well known and readily available to those skilled in the art of lubricant formulation. Further zinc dialkyldithiophosphates may be described as primary zinc dialkyldithiophosphates or as secondary zinc dialkyldithiophosphates, depending on the structure of the alcohol used in its preparation. In some embodiments the instant compositions may include primary zinc dialkyldithiophosphates. In some embodiments, the compositions include secondary zinc dialkyldithiophosphates. In some embodiments, the compositions include a mixture of primary and secondary zinc dialkyldithiophosphates. In some embodiments component (b) is a mixture of primary and secondary zinc dialkyldithiophosphates where the ratio of primary zinc dialkyldithiophosphates to secondary zinc dialkyldithiophosphates (one a weight basis) is at least 1:1, or even at least 1:1.2, or even at least 1:1.5 or 1:2, or 1:10.

[0067] Examples of suitable metal dialkyldithiophosphate include metal salts of the formula:



where R¹ and R² are independently hydrocarbyl groups containing 3 to 24 carbon atoms, or 3 to 12 carbon atoms, or 3 to 8 carbon atoms; M is a metal having a valence n and generally includes zinc, copper, iron, cobalt, antimony, manganese, and combinations thereof. In one embodiment, R¹ and R² are secondary aliphatic hydrocarbyl groups containing 3 to 8 carbon atoms, and M is zinc.

[0068] In one embodiment, the phosphorus-containing anti-wear agent may be a zinc free phosphorus compound. The zinc-free phosphorus anti-wear agent may contain sulfur or may be sulfur-free. Sulfur-free phosphorus-containing antiwear agents include hydrocarbyl phosphites, hydrocarbyl phosphines, hydrocarbyl phosphonates, alkylphosphate esters, amine or ammonium phosphate salts, or mixtures thereof.

[0069] According to the invention, the phosphorus-containing antiwear agent is present in the lubricating composition in an amount to deliver from 300 ppm to 900 ppm phosphorus to the lubricating composition. In one embodiment, the antiwear agent is ZDDP and is present in the composition in an amount to deliver 400 ppm to 850 ppm, or 450 ppm to 800 ppm, or 500 ppm to 800 ppm, or 550 ppm to 780 ppm, or 650 ppm to 780 ppm phosphorus to the lubricating composition.

[0070] In one embodiment, the phosphorus-containing anti-wear agent is present in an amount 0.2 to 2 wt %, or 0.3 to 1.3 wt %, or 0.5 to 0.95 wt % of the lubricant composition.

Other Performance Additives

[0071] A lubricating composition may be prepared by blending the oil of lubricating viscosity, the first PIB succinimide dispersant, the second succinimide dispersant, the calcium salicylate detergent, the alkaline earth metal detergent, the phosphorous antiwear agent and, optionally one or more performance additives (as described herein below).

[0072] The other performance additives include at least one of metal deactivators, viscosity modifiers, friction modifiers, antiwear agents, corrosion inhibitors, extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents and mixtures thereof. Typically, fully formulated lubricating oil will contain one or more of these performance additives.

[0073] The lubricating composition in a further embodiment comprises an antioxidant, wherein the antioxidant comprises a phenolic or an aminic antioxidant or mixtures thereof. The antioxidants include diarylamines, alkylated diarylamines, hindered phenols, or mixtures thereof. When present the individual antioxidants are independently present at 0.1 wt % to 3 wt %, or 0.5 wt % to 2.75 wt %, or 1 wt % to 2.5 wt % of the lubricating composition.

[0074] The diarylamine or alkylated diarylamine may be a phenyl- α -naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenyl-naphthylamine, or mixtures thereof. The alkylated diphenylamine may include di-nonylated diphenylamine, nonyl diphenylamine, octyl diphenylamine, di-octylated diphenylamine, di-decylated diphenylamine, decyl diphenylamine and mixtures thereof. In one embodiment the diphenylamine may include nonyl diphenylamine, dinonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine, or mixtures thereof. In another embodiment the alkylated diphenylamine may include nonyl diphenylamine, or dinonyl diphenylamine. The alkylated diarylamine may include octyl, di-octyl, nonyl, di-nonyl, decyl or di-decyl phenyl-naphthylamines.

[0075] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically

hindering group. The phenol group may be further substituted with a hydrocarbyl group (typically linear or branched alkyl) and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment, the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 from Ciba. Suitable hindered phenol esters include hydrocarbyl esters of 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoic acid, such as hydrocarbyl esters containing 3 to 18 carbon atoms, or 4 to 12 carbon atoms, or 6 to 10 carbon atoms. A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in US Patent 6,559,105.

[0076] In one embodiment, the lubricating composition contains a friction modifier. The friction modifier may be chosen from long chain fatty acid derivatives of amines, long chain fatty esters, or derivatives of long chain fatty epoxides; fatty imidazolines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrides; fatty alkyl tartramides; fatty glycolates; fatty glycolamides; and combinations thereof.

[0077] As used herein, the term "fatty alkyl" or "fatty" in relation to friction modifiers means a carbon chain having 10 to 24 carbon atoms, typically a straight carbon chain, which may be saturated or unsaturated.

[0078] Examples of suitable friction modifiers include long chain fatty acid derivatives of amines, fatty esters, or fatty epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrides; fatty alkyl tartramides; fatty phosphonates; fatty phosphites; borated phospholipids, borated fatty epoxides; glycerol esters; borated glycerol esters; fatty amines; alkoxylated fatty amines; borated alkoxylated fatty amines; hydroxyl and polyhydroxy fatty amines including tertiary hydroxy fatty amines; hydroxy alkyl amides; metal salts of fatty acids; metal salts of alkyl salicylates; fatty oxazolines; fatty ethoxylated alcohols; condensation products of carboxylic acids and polyalkylene polyamines; or reaction products from fatty carboxylic acids with guanidine, aminoguanidine, urea, or thiourea and salts thereof.

[0079] Friction modifiers may also encompass materials such as sulfurized fatty compounds and olefins, molybdenum compounds such as molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, amine salted molybdenum acid compounds, and molybdenum post-treated succinimide dispersants. Molybdenum dithiocarbamates may be mono-nuclear, di-nuclear, or even tri-nuclear complexes. Suitable molybdenum compounds may be present as Mo(IV) complexes, or Mo(V) complexes, or Mo(VI) complexes, or combinations thereof and include commercial materials such as Sakura-lube 525 from Adeka Co. Ltd and Molyvan® 855 from Vanderbilt Chemicals LLC.

[0080] In another embodiment, the friction modifier may be a long chain fatty acid ester. In another embodiment, the long chain fatty acid ester may be a mono-ester and in another embodiment the long chain fatty acid ester may be a triglyceride. Suitable triglycerides include vegetable oils, such as soybean oil or sunflower oil.

[0081] The ashless friction modifier may be present in the lubricating composition in an amount of from 0.01 to 2.5 wt %, or 0.1 to 0.5 wt %, or 0.3 to 2.0 wt %, or 0.5 to 0.9 wt %.

[0082] The lubricating composition optionally further includes at least one antiwear agent other than the phosphorus-containing antiwear agent described above. Examples of suitable antiwear agents include titanium compounds, tartaric acid esters, tartrides, thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulphides. The antiwear agent may in one embodiment include a tartrate, or tartride as disclosed in International Publication WO 2006/044411 or Canadian Patent CA 1 183 125. The tartrate or tartride may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups is at least 8. The antiwear agent may in one embodiment include a citrate as is disclosed in US Patent Application 20050198894.

[0083] Another class of additives includes oil-soluble titanium compounds as disclosed in US 7,727,943 and US2006/0014651. The oil-soluble titanium compounds may function as antiwear agents, friction modifiers, antioxidants, deposit control additives, or more than one of these functions. In one embodiment, the oil soluble titanium compound is a titanium (IV) alkoxide. The titanium alkoxide is formed from a monohydric alcohol, a polyol or mixtures thereof. The monohydric alkoxides may have 2 to 16, or 3 to 10 carbon atoms. In one embodiment, the titanium alkoxide is titanium (IV) isopropoxide. In one embodiment, the titanium alkoxide is titanium (IV) 2-ethylhexoxide. In one embodiment, the titanium compound comprises the alkoxide of a vicinal 1,2-diol or polyol. In one embodiment, the 1,2-vicinal diol comprises a fatty acid mono-ester of glycerol, often the fatty acid is oleic acid.

[0084] In one embodiment, the oil soluble titanium compound is a titanium carboxylate. In a further embodiment the titanium (IV) carboxylate is titanium neodecanoate.

[0085] Extreme Pressure (EP) agents that are soluble in the oil include sulfur- and chlorosulfur-containing EP agents, dimercaptothiadiazole or CS₂ derivatives of dispersants (typically succinimide dispersants), derivative of chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; sulfurized olefins (such as sulfurized isobutylene), a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof, organic sulphides and polysulphides such as dibenzyl disulphide, bis-(chlorobenzyl) disulphide, dibutyl tetrasulphide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, sulfurized terpene, and sulfurized Diels-Alder adducts; phosphosulfurized hydrocarbons such as the reaction product of phosphorus sulphide with turpentine or

methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates such as zinc diocetylthiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids or derivatives including, for example, the amine salt of a reaction product of a dialkyldithiophosphoric acid with propylene oxide and subsequently followed by a further reaction with P_2O_5 ; and mixtures thereof (as described in US 3,197,405).

[0086] Foam inhibitors that may be useful in the instant compositions and include polysiloxanes, copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including fluorinated polysiloxanes, trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxidepropylene oxide) polymers.

[0087] Polymeric viscosity index improvers, also referred to as viscosity modifiers (VM) or dispersant viscosity modifiers (DVM, may be useful in the compositions disclosed herein. The dispersant viscosity modifier may be generally understood to be a functionalized, i.e. derivatized, form of a polymer similar to that of the polymeric viscosity modifier. The polymeric viscosity modifier may be an olefin (co)polymer, a poly(meth)acrylate (PMA), or mixtures thereof. In one embodiment, the polymeric viscosity modifier is an olefin (co)polymer or dispersant viscosity modifier derived therefrom.

[0088] The olefin polymer may be derived from isobutylene or isoprene. In one embodiment, the olefin polymer is prepared from ethylene and a higher olefin within the range of C3-C10 alpha-mono-olefins, for example, the olefin polymer may be prepared from ethylene and propylene.

[0089] Useful olefin polymers, in particular, ethylene-a-olefin copolymers have a number average molecular weight ranging from 4500 to 500,000, for example, 5000 to 100,000, or 7500 to 60,000, or 8000 to 45,000.

[0090] The formation of functionalized ethylene-a-olefin copolymer is well known in the art, for instance those described in U.S. Patent US 7,790,661 column 2, line 48 to column 10, line 38. Additional detailed descriptions of similar functionalized ethylene-a-olefin copolymers are found in International Publication WO2006/015130 or U.S. Patents 4,863,623; 6,107,257; 6,107,258; 6,117,825; and US 7,790,661. In one embodiment, the functionalized ethylene-a-olefin copolymer may include those described in U.S. Patent 4,863,623 (see column 2, line 15 to column 3, line 52) or in International Publication WO2006/015130 (see page 2, paragraph [0008] and preparative examples are described paragraphs [0065] to [0073]).

[0091] In one embodiment, the lubricating composition comprises a dispersant viscosity modifier (DVM). The DVM may comprise an olefin polymer that has been modified by the addition of a polar moiety.

[0092] The olefin polymers are functionalized by modifying the polymer by the addition of a polar moiety. In one useful embodiment, the functionalized copolymer is the reaction product of an olefin polymer grafted with an acylating agent. In one embodiment, the acylating agent may be an ethylenically unsaturated acylating agent. Useful acylating agents are typically α,β -unsaturated compounds having at least one ethylenic bond (prior to reaction) and at least one, for example two, carboxylic acid (or its anhydride) groups or a polar group which is convertible into said carboxyl groups by oxidation or hydrolysis. The acylating agent grafts onto the olefin polymer to give two carboxylic acid functionalities. Examples of useful acylating agents include maleic anhydride, chlormaleic anhydride, itaconic anhydride, or the reactive equivalents thereof, for example, the corresponding dicarboxylic acids, such as maleic acid, fumaric acid, cinnamic acid, (meth)acrylic acid, the esters of these compounds and the acid chlorides of these compounds.

[0093] In one embodiment, the functionalized ethylene-a-olefin copolymer comprises an olefin copolymer grafted with the acyl group, which is further functionalized with a hydrocarbyl amine, a hydrocarbyl alcohol group, amino- or hydroxy-terminated polyether compounds, and mixtures thereof.

[0094] In one embodiment, the hydrocarbyl amine may be selected from aromatic amines, aliphatic amines, and mixtures thereof. In one embodiment, the hydrocarbyl amine component may comprise at least one aromatic amine containing at least one amino group capable of condensing with said acyl group to provide a pendant group and at least one additional group comprising at least one nitrogen, oxygen, or sulfur atom, wherein said aromatic amine is selected from the group consisting of (i) a nitro-substituted aniline, (ii) an amine comprising two aromatic moieties linked by a C(O)NR- group, a -C(O)O- group, an -O- group, an N=N- group, or an -802- group where R is hydrogen or hydrocarbyl, one of said aromatic moieties bearing said condensable amino group, (iii) an aminoquinoline, (iv) an aminobenzimidazole, (v) an N,N- dialkylphenylenediamine, (vi), an aminodiphenyl amine (also N-phenylphenylenediamine), (vii) a ring-substituted benzylamine, and (viii) a methylene-coupled dimer of aminodiphenyl amine.

[0095] In one embodiment, lubricating composition may comprise a poly(meth)acrylate polymeric viscosity modifier. As used herein, the term "(meth)acrylate" and its cognates means either methacrylate or acrylate, as will be readily understood.

[0096] In one embodiment, the poly(meth)acrylate polymer is prepared from a monomer mixture comprising (meth)acrylate monomers having alkyl groups of varying length. The (meth)acrylate monomers may contain alkyl groups that are straight chain or branched chain groups. The alkyl groups may contain 1 to 24 carbon atoms, for example, 1 to 20 carbon atoms.

[0097] In one embodiment, the poly(meth)acrylate polymer comprises a dispersant monomer; dispersant monomers

include those monomers which may copolymerize with (meth)acrylate monomers and contain one or more heteroatoms in addition to the carbonyl group of the (meth)acrylate. The dispersant monomer may contain a nitrogen-containing group, an oxygen-containing group, or mixtures thereof.

[0098] Dispersant monomers may be present in an amount up to 5 mol percent of the monomer composition of the (meth)acrylate polymer. In one embodiment, the poly(meth)acrylate is present in an amount 0 to 5 mol percent, 0.5 to 4 mol percent, or 0.8 to 3 mol percent of the polymer composition. In one embodiment, the poly(meth)acrylate is free of or substantially free of dispersant monomers.

[0099] In one embodiment, the poly(meth)acrylate polymer (P) is a block or tapered block copolymer that comprises at least one polymer block (B₁) that is insoluble or substantially insoluble in the base oil and a second polymer block (B₂) that is soluble or substantially soluble in the base oil.

[0100] In one embodiment, the poly(meth)acrylate polymers may have an architecture selected from linear, branched, hyper-branched, cross-linked, star (also referred to as "radial"), or combinations thereof. Star or radial refers to multi-armed polymers. Such polymers include (meth)acrylate-containing polymers comprising 3 or more arms or branches, which, in some embodiments, contain at least about 20, or at least 50 or 100 or 200 or 350 or 500 or 1000 carbon atoms. The arms are generally attached to a multivalent organic moiety which acts as a "core" or "coupling agent." The multi-armed polymer may be referred to as a radial or star polymer, or even a "comb" polymer, or a polymer otherwise having multiple arms or branches as described herein.

[0101] Linear poly(meth)acrylates, random, block or otherwise, may have weight average molecular weight (M_w) of 1000 to 400,000 Daltons, 1000 to 150,000 Daltons, or 15,000 to 100,000 Daltons. In one embodiment, the poly(meth)acrylate may be a linear block copolymer with a M_w of 5,000 to 40,000 Daltons, or 10,000 to 30,000 Daltons. Radial, cross-linked or star copolymers may be derived from linear random or di-block copolymers with molecular weights as described above. A star polymer may have a weight average molecular weight of 10,000 to 1,500,000 Daltons, or 40,000 to 1,000,000 Daltons, or 300,000 to 850,000 Daltons.

[0102] Another class of polymeric viscosity modifiers is styrene-diene (SD) copolymers, such as styrene isoprene (SI) and styrene butadiene (SBR). Styrene-diene copolymers may be linear or radial (star-shaped), and generally contain one or more distinct blocks of styrene attached to one or more distinct blocks of hydrogenated diene.

[0103] The lubricating compositions may comprise 0.05 weight % to 2 weight %, or 0.08 weight % to 1.2 weight %, or 0.1 to 0.8 weight % of the one or more polymeric viscosity modifiers and/or dispersant viscosity modifiers.

[0104] Pour point depressants that may be useful in the compositions disclosed herein include polyalphaolefins, esters of maleic anhydride-styrene copolymers, poly(meth)acrylates, polyacrylates or polyacrylamides.

[0105] Demulsifiers include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, or mixtures thereof.

[0106] Metal deactivators include derivatives of benzotriazoles (typically tolyltriazole), 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles or 2-alkyldithiobenzothiazoles. The metal deactivators may also be described as corrosion inhibitors.

[0107] Seal swell agents include sulfolene derivatives Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

[0108] The lubricating composition may further include one or more dispersants different from that of the first PIB succinimide dispersant and the second PIB succinimide dispersant of the compositions disclosed herein. Such dispersants include succinimide dispersants different from that of described compositions, Mannich dispersants, polyolefin succinic acid esters, amides, or ester-amides, or mixtures thereof.

[0109] The additional dispersant may be a PIBsuccinimide similar to the dispersants of the described compositions, derived from polyisobutylene with a number average molecular weight of 800 Daltons to 2600 Daltons. Additional dispersants may be present to provide a boost to soot handling or as sources of ashless TBN. Soot dispersants may be functionalized with an aromatic (poly)amine. Dispersants used as TBN boosters typically have high TBN, such as greater than 80 mg KOH/g, greater than 95 mg KOH/g, or even greater than 110 mg KOH/g.

[0110] The additional dispersant may be present in an amount 0.05 to 2 wt %, or 0.1 to 1.1 wt %, or 0.2 to 0.8 wt % of the lubricant composition.

Industrial Application

[0111] The lubricating compositions disclosed herein are suitable for use in diesel engines. Diesel engines are classified by their Gross Vehicle Weight Rating (GVWR). The GVWR includes the maximum rated weight of the vehicle and cargo, including passengers. The GVWR is applied to trucks or trailers, but not the two combined, which is a separate rating referred to as the Gross Combined Weight Rating (GCWR). The GVWR's for various classes of diesel engines are set forth in the table below:

Class	GVWR (lbs)
Class 1	0-6,000 lbs
Class 2	6,001-10,000 lbs (divided into 2 classes Class 2A & 2B, see below)
Class 2A	6,001-8,500 lbs
Class 2B	8,501-10,000 lbs
Class 3	10,001-14,000 lbs
Class 4	14,001-16,000 lbs
Class 5	16,001-19,500 lbs
Class 6	19,5001-26,000 lbs
Class 7	26,001-33,000 lbs
Class 8	Over 33,000 lbs

[0112] Light duty vehicles are classified as those falling in Class 1 to 3. Class 2A vehicles are typically called "light duty" and class 2B vehicles are often called "light heavy duty" vehicles.

[0113] Medium duty vehicles refer to those falling into Classes 4 to 6. Heavy-Duty vehicles are those classified in Class 7 and Class 8.

[0114] There is a distinct difference between the class of vehicles as they relate to operating conditions. The difference in size means that higher classified vehicles have engines that will experience significantly different operating conditions such as load, oil temperatures, duty cycle and engine speeds. Heavy-duty diesel engines are designed to maximize torque for hauling payloads at maximum fuel economy while passenger car (lower class vehicles) are designed for commuting people and acceleration at maximum fuel economy. The designed purpose of the engine hauling versus commuting results in different hardware designs and resulting stresses imparted to lubricant designed to protect and lubricate the engine. Another distinct design difference is the operating revolution per minute (RPM) that each engine operates at to haul versus commute. A heavy-duty diesel engine such as a typical 12-13 liter truck engine would typically not exceed 2200 rpm while a passenger car engine can go up to 4500 rpm.

[0115] In one embodiment, the internal combustion engine is a heavy-duty diesel compression ignited (or spark assisted compression ignited) internal combustion engine.

[0116] The sulfur content of the lubricating composition may be 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less, or 0.3 wt % or less. In one embodiment, the sulfur content may be in the range of 0.001 wt % to 0.5 wt %, or 0.01 wt % to 0.3 wt %. The phosphorus content may be 0.2 wt % or less, or 0.12 wt % or less, or 0.1 wt % or less, or 0.085 wt % or less, or 0.08 wt % or less, or even 0.06 wt % or less, 0.055 wt % or less, or 0.05 wt % or less. In one embodiment, the phosphorus content may be 0.04 wt % to 0.12 wt %. In one embodiment, the phosphorus content may be 100 ppm to 1000 ppm, or 200 ppm to 600 ppm. The total sulfated ash content is 0.3 wt % to 0.9 wt %, or 0.5 wt % to 0.9 wt % of the lubricating composition.

[0117] The lubricating compositions of the invention have a sulfated ash content of from 0.3 to 0.9 wt %, or 0.4 to 0.8 wt %.

[0118] As used herein, TBN values are (total base number) measured by the methodology described in ASTM D4739 (buffer).

[0119] The lubricating composition may be characterized as having a total base number (TBN) content of at least 3, or at least 4, or at least 5 mg KOH/g.

[0120] The lubricating composition may be characterized as having a total base number (TBN) content of 5 to 10 mg KOH/g, or 5 to 8.5 mg KOH/g.

[0121] The lubricating compositions of the invention have a kinematic viscosity as measured by ASTM D-445 at 100°C of from 2.5 to 8.3, or 3.5 to 6.5 cSt (mm²/s) and a kinematic viscosity at 40°C of from 15 to 30 cSt (mm²/s). In another embodiment, the lubricating composition has a kinematic viscosity at 100°C of from 2.5 to 6.5 or 3 to 5.5 cSt (mm²/s) and a kinematic viscosity at 40°C of from 15 to 25 cSt (mm²/s).

[0122] The lubricating composition of the invention have a high temperature, high shear viscosity (HTHS) as measured by ASTM D4683 at 150° C of less than 2.6 mPa-s, or less than 2.5 mPa-s, or less than 2.3 mPa-s, or less than 2.1 mPa-s. In another embodiment, the HTHS of the lubricating composition is from 1.4 to 2.5 mPa-s, or from 1.6 to 2.1 mPa-s, or from 1.8 to 2.1 mPa-s, or from 1.9 to 2.0 mPa-s.

[0123] The lubricating composition may have a SAE viscosity grade of 0W-Y, wherein Y may be 12, 16, or 20. In one embodiment, the lubricating composition has an SAE viscosity grade of 0W-12.

[0124] The internal combustion engine disclosed herein may have a steel surface on a cylinder bore, cylinder block, or piston ring.

[0125] The internal combustion engine may have a surface of steel, or an aluminum alloy, or an aluminum composite.

[0126] Typically, the compression-ignition internal combustion engine has a maximum laden mass over 3,500 kg.

[0127] The instant disclosure is further directed to a method of lubricating a diesel engine by supplying to the diesel engine any one of the lubricating compositions disclosed herein. In one embodiment, the method includes lubricating a diesel engine by supplying to said engine a lubricating composition having an oil of lubricating viscosity having greater than 50 weight percent of a Group III base oil, a Group IV base oil, or mixtures thereof; a first PIB succinimide dispersant derived from an 1800 to 2100 Mn PIB; a second PIB succinimide dispersant derived from a PIB with an Mn up to 1600, where at least one of the first PIB succinimide dispersant and the second PIB succinimide dispersant is boron-free; a calcium salicylate detergent; an alkaline earth metal sulfonate detergent present in an amount to deliver 0.3 wt % to 1.5 wt % of alkaline earth metal soap to the lubricating composition; and a phosphorus antiwear agent present in an amount to deliver 300 to 900 ppm phosphorous to the lubricating composition, wherein the lubricating compositions further include a total sulfated ash of between 0.3 to 0.9 wt. % and an HTHS as measured according to ASTM D4683 of less than 2.7 mPa s.

[0128] Another embodiment provides for the use of any one of the lubricating compositions disclosed herein to improve at least one of wear protection and fuel economy in a compression ignited internal combustion engine (typically a heavy-duty diesel internal combustion engine).

[0129] In different embodiments, the lubricating composition disclosed herein may have a composition as described in the following table:

Additive	Embodiments (wt %)		
	A	B	C
PIB succinimide Dispersant 1	0.5 to 10	0.8 to 5	1.1 to 2.2
PIB succinimide Dispersant 2	0.5 to 8	1 to 5	1.4 to 2.6
Alkaline Earth Salicylate Detergent(s)	0.2 to 3	0.3 to 2	0.4 to 1.2
Alkaline Earth Metal Sulfonate Detergent(s)	0.1 to 2	0.3 to 1.2	0.4 to 0.8
Phosphorous Antiwear Agent	0.2 to 2	0.3 to 1.3	0.5 to 0.95
Ashless Antioxidants	0 to 6	1.2 to 5	1.8 to 4.2
Friction Modifier	0 to 2	0.05 to 1.2	0.1 to 0.85
Additional Dispersant	0 to 2	0.1 to 1.1	0 or 0.2 to 0.8
Additional Detergent	0 to 1	0.05 to 0.7	0 or 0.1 to 0.5
Polymeric VM or DVM	0 to 5	0.05 to 1.8	0.1 to 0.6
Any Other Performance Additive	0 to 1	0.01 to 0.5	0 or 0.1 to 0.3
Group III and/or Group IV Base Oil	50 to 98	75 to 95	80 to 90
Other oil of lubricating viscosity	Balance to 100 %		

[0130] The following examples provide illustrations of the described compositions. These examples are non-exhaustive and are not intended to limit the scope of the invention.

EXAMPLES

[0131] A series of 0W-12 engine lubricants in Group III base oil of lubricating viscosity are prepared containing the additives described above as well as conventional additives including polymeric viscosity modifiers, corrosion inhibitors, pourpoint depressants, as well as other performance additives as follows (Table 1). Elementals are included to demonstrate relative equivalence of compositions.

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Table 1 - Lubricating compositions¹ (EX5 is a comparative example and EX8 is a reference example)

		EX1	EX2	EX3	EX4	EX5	EX6	EX7	EX8
5		0W-12	0W-12	0W-12	0W-12	0W-12	0W-12	0W-12	5W-30
	4.2 cSt Group III Oil	86.3	82.6	87.5	85.8	85.2	86.4	86.4	38
	6.3 cSt Group III Oil	0	0	0	0	0	0	0	36
10	Conventional PIBsuccinimide ²	0	0	0	0	0	0	0	2.0
	Borated Dispersant ³	0	0	0	0	0	0	0	1.0
	Soot Dispersant ⁴	0	0	0	0	0	0	0	0.73
	succinimide from 2000 Mn PIB ⁵	1.22	1.83	1.16	1.16	0.67	1.04	1.16	0
15	PIB Succinimide from 980 Mn PIB ⁵	1.68	2.52	0	0	0	0	0	0
	PIB succinimide from 1550 Mn PIB ⁵	0	0	1.49	1.49	1.42	1.42	1.49	0
	Ashless TBN Booster	0	0	0	0	0	0	0	0.13
20	Overbased Calcium sulfonate ⁸	0	0	0	0	0	0	0	0.22
	S-free Magnesium phenate	0	0	0	0	0	0	0	0.37
	Calcium Salicylate ⁹	0.56	0.84	0.67	0.84	0.84	1.12	0.56	0
25	Low TBN Calcium Sulfonate ¹⁰	0.4	0.6	0.5	0.55	0.55	0.15	0.50	0
	Overbased Magnesium Sulfonate	0.04	0.06	0.12	0.18	0.18	0.18	0.06	0.38
	C3/6 mixed ZDDP	0	0	0	0	0	0	0	0.78
	C6 Secondary ZDDP	0.82	0.82	0.82	0.82	0.82	0.82	0.82	0
30	Ashless Antioxidant ¹¹	3.2	3.2	3.2	4.2	4.2	4.2	4.2	3.5
	DVM ¹²	0.3	0.35	0.13	0.13	0.13	0.13	0.13	0.6
	Styrene diene VI Improver	0	0	0	0	0	0	0	0.4
35	Oleyl glycolamide	0.5	0.5						
	GMO				0.25			0.50	
	Oleyl amide			0.1	0.1				
	Tartrimide Additive ¹³					1.8			
40	Molybdenum Additive ¹⁴						0.16		
	Other Additives ¹⁵	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24
	Diluent Oil	Balance to 100%							
45									
	Calcium (ppm)	1000	1500	1220	1450	1450	1370	1090	1290
	Magnesium (ppm)	70	100	190	280	280	280	90	720
50	Phosphorus (ppm)	760	790	760	760	730	740	720	760
	Zinc (ppm)	820	900	820	870	820	820	800	820
	Sulfur (ppm)	2100	2400	2200	2400	2200	2200	2100	2700
	Boron (ppm)	0	0	0	0	80	0	0	100
55	Molybdenum (ppm)	0	0	0	0	0	310	0	0

(continued)

	EX1	EX2	EX3	EX4	EX5	EX6	EX7	EX8
	0W-12	0W-12	0W-12	0W-12	0W-12	0W-12	0W-12	5W-30
Sulfated Ash (wt%)	0.5	0.7	0.6	0.8	0.8	0.8	0.5	1.0
<p>1. All treat rates presented are oil free, unless otherwise noted</p> <p>2. Polyisobutenyl succinimide dispersant prepared from 2300 Mn low vinylidene PIB via chlorine Diels-Alder process (TBN 54 mg KOH/g)</p> <p>3. Borated analog of above dispersant (1% boron by weight)</p> <p>4. PIBsuccinimide aromatic amine soot dispersant</p> <p>5. Polyisobutenyl succinimide dispersant prepared from high vinylidene 2000 Mn PIB via thermal ene alkylation (TBN 26 mg KOH/g)</p> <p>6. Polyisobutenyl succinimide dispersant prepared from 980 Mn PIB (TBN 25 mg KOH/g)</p> <p>7. Polyisobutenyl succinimide dispersant prepared from high vinylidene 1550 Mn PIB via thermal ene alkylation (TBN 17 mg KOH/g)</p> <p>8. Overbased calcium alkylbenzene sulfonate (TBN 520 mg KOH/g; 48% substrate)</p> <p>9. Calcium overbased alkylsalicylate detergent (TBN 300 mg KOH/g; metal ratio 2.8)</p> <p>10. Low TBN calcium alkylbenzene sulfonate detergent (TBN 170 mg KOH/g; 84% substrate; metal ratio 2.7)</p> <p>11. Combination of diarylamine, hindered phenol, and sulfurized olefin.</p> <p>12. Combination of low Mn (10 kDa) and high Mn (60 kDa) substituted ethylene-propylene copolymers, functionalized with aromatic amines</p> <p>13. Pre-mixture of oleyl tartramide (44 wt%), borating agent, basic nitrogen, and compatibilizer (0.46 wt % Boron; TBN 17 mg KOH/g)</p> <p>14. Sulfur-bridged Molybdenum (V) dimer, dithiocarbamate complex (commercially available as Sakuralube 525 from Adeka)</p> <p>15. Other Additives include pourpoint depressant, foam inhibitor, and low levels of corrosion inhibitors and compatibilizers.</p>								

[0132] Lubricating examples of Table 1 are evaluated for fuel economy improvement and ability to prevent/reduce wear. Results are summarized, along with other chemical and physical properties related to performance (Table 2). Fuel economy improvement is measured according to the Volvo D13TC fuel economy test. In this test, improvement is determined relative to a pre-selected reference oil; in these data, Example 8 (EX8) was selected as the reference oil.

[0133] Resistance to wear (also called durability) was determined on a high frequency reciprocating rig (HFRR) available from PCS Instruments. HFRR conditions for the evaluations were 500 g load, 75minute duration, 1000 micrometer stroke, 20 Hertz frequency, and at a temperature of 105 °C. The wear and contact potential are then measured.

Table 2

	EX1	EX2	EX3	EX4	EX5	EX6	EX7	EX8
Alkaline earth metal soap	0.8	1.2	1.0	1.2	1.2	1.1	0.9	1.3
Alkaline earth metal sulfonate soap	0.35	0.53	0.47	0.54	0.54	0.20	0.44	1.0
Alkaline earth metal salicylate soap	0.44	0.66	0.53	0.66	0.66	0.88	0.44	0
Kinematic Viscosity at 100°C (D445) (m ² /s)	5.7	6.3	5.7	5.7	5.6	5.6	5.7	9.9
HTHS (D4683) (mPa·s)	2.05	2.24	2.06	2.08	2.06	2.04	2.06	3.08
Base Oil viscosity at 100°C (D445)	4.2	4.2	4.2	4.2	4.2	4.2	4.2	5.2
% Fuel Economy Improvement Volvo D13TC	1.41	0.78	1.11	1.11	1.46	1.41	1.08	REF
HFRR Wear Scar (μm)	166	212	230	220	261	215	218	257

[0134] The results obtained indicate that the lubricant compositions EX1-EX4, EX6, EX7 according to the invention are capable of providing improved fuel economy, while maintaining and even improving wear control.

[0135] Lubricant compositions of the described herein also provide cleanliness, deposit control, and oxidation control in suitable bench tests. Deposit performance can be measured according to the Thermo-Oxidation Engine Oil Simulation Test (TEOST 33) as presented in ASTM D6335. The results of the TEOST 33 test show the milligrams of deposit after an engine oil is run at elevated temperatures. Lower TEOST 33 results are indicative of improved resistance to deposit formation. The lubricating compositions can be tested for deposit control in a Panel Coker heated to 325° C., with a sump temperature of 105° C., and a splash/bake cycle of 120 s/45 s. The airflow is 350 ml/min, with a spindle speed of 1000 rpm and the test lasts for 4 hours. The oil is splashed onto an aluminum panel which is then optically rated by computer. Performance ranges from 0% (black panel) to 100% (clean panel).

[0136] Fuel economy of the disclosed lubricating compositions can be tested and may have improvements pursuant to any one of the M111 Fuel Economy Test (CEC L-54-96), Daimler OM501LA Fuel Economy Test, NEDC MB Fuel Economy Tests, and ILSAC Sequence VI Engine Test. Friction performance may also be evaluated in any of several high frequency reciprocating rig (HFRR) bench test, e.g., ASTM D6079.

[0137] Unless otherwise stated herein, reference to treat rates or amounts of components present in the lubricating compositions disclosed herein are quoted on an oil free basis, i.e., amount of active.

[0138] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character including one or more double bonds. Examples of hydrocarbyl groups include: hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclicsubstituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring); substituted hydrocarbon substituents, that is, substituents containing non- hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy); hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. Heteroatoms include sulfur, oxygen, and nitrogen. In general, no more than two, or no more than one, non- hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; alternatively, there may be no non-hydrocarbon substituents in the hydrocarbyl group.

[0139] The present disclosure is not to be limited in terms of the particular embodiments described in this application, which are intended as illustrations of various aspects. Functionally equivalent methods and components within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds, or compositions, which can, of course, vary.

[0140] As used in this document, the singular forms "a," "an," and "the" include plural references unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Nothing in this disclosure is to be construed as an admission that the embodiments described in this disclosure are not entitled to antedate such disclosure by virtue of prior invention. As used in this document, the term "comprising" means "including, but not limited to."

[0141] While various compositions, methods, and devices are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions, methods, and devices can also "consist essentially of" or "consist of" the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[0142] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0143] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as "up to," "at least," and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 wt. % refers to groups having 1, 2, or 3 wt.%. Similarly, a group having 1-5 wt. % refers to groups having 1, 2, 3, 4, or 5 wt. %, and so forth, including all points therebetween.

[0144] Moreover, where a recited range for a treat rate is provided, it is contemplated that such range shall include

treat rates for individual components and/or a mixture of components. Thus, for example, a range of 1 to 3 wt % contemplates that a given component may be present in a range of 1 to 3 wt % or that a mixture of similar components can be present in a range from 1 to 3 wt %.

[0145] As used herein, the term "about" means that a value of a given quantity is within $\pm 20\%$ of the stated value. In other embodiments, the value is within $\pm 15\%$ of the stated value. In other embodiments, the value is within $\pm 10\%$ of the stated value. In other embodiments, the value is within $\pm 5\%$ of the stated value. In other embodiments, the value is within $\pm 2.5\%$ of the stated value. In other embodiments, the value is within $\pm 1\%$ of the stated value.

[0146] Unless otherwise stated, "wt %" as used herein shall refer to the weight percent based on the total weight of the composition on an oil-free basis.

[0147] As described hereinafter the number average molecular weight of the dispersant viscosity modifier and viscosity modifier has been determined using known methods, such as GPC analysis using polystyrene standards. Methods for determining molecular weights of polymers are well known. The methods are described for instance: (i) P.J. Flory, "Principles of Polymer Chemistry", Cornell University Press 91953), Chapter VII, pp 266-315; or (ii) "Macromolecules, an Introduction to Polymer Science", F. A. Bovey and F. H. Winslow, Editors, Academic Press (1979), pp 296-312.

[0148] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Claims

1. A diesel engine lubricating composition comprising:

an oil of lubricating viscosity having greater than 50 weight percent of a Group III base oil, a Group IV base oil, a Group V base oil, or mixtures thereof;
a first polyisobutylene (PIB) succinimide dispersant prepared from a PIB having a number average molecular weight of 1800 to 2100 present in the lubricating composition in an amount of from 0.8 wt% to 6 wt%;
a second polyisobutylene (PIB) succinimide dispersant prepared from a PIB with a number average molecular weight of up to 1600, where at least one of the first PIB succinimide dispersant and the second PIB succinimide dispersant is boron-free;
an alkaline earth metal salicylate detergent;
an alkaline earth metal sulfonate detergent present in an amount to deliver 0.1 wt % to 1.5 wt % of alkaline earth metal soap to the lubricating composition; and
a phosphorus antiwear agent present in an amount to deliver 300 to 900 ppm phosphorous to the lubricating composition,

the lubricating composition having a total sulfated ash measured according to ASTM D784 of between 0.3 to 0.9 wt. %; a kinematic viscosity measured according to ASTM D-445 at 100°C of less than 8.3 cSt; a total alkaline earth metal soap of from 0.6 wt % to 2.1 wt %, and a HTHS measured according to ASTM D4683 of less than 2.7 mPa·s.

2. The composition of claim 1, wherein the first PIB succinimide dispersant has a TBN (KOH/g) of from 15 to 25 or 15 to 20 measured according to ASTM D4739.

3. The composition of any one of the preceding claims, wherein the second PIB succinimide dispersant is prepared from a PIB having a number average molecular weight of from 750 to 1600 or 1000 to 1600 or 1200 to 1600 or is prepared from a PIB having a number average molecular weight of from 800 to 1150 or 900 to 1100.

4. The composition any one of the preceding claims, wherein the second PIB succinimide dispersant is present in the lubricating composition in an amount of from 1 to 5 wt %, or from 1.5 to 4.8 wt %, or from 1.8 to 4.6 wt %, or from 1.9 to 4.6 wt%.

5. The composition of claim 1, wherein the second PIB succinimide dispersant comprises from 1 to 5 wt % of a PIB succinimide dispersant prepared from a PIB having a number average molecular weight of from 900 to 1100 and from 1 to 5 wt % of a PIB succinimide dispersant prepared from a PIB having a number average molecular weight of from 1200 to 1600.

6. The composition of any one of the preceding claims, wherein the second PIB succinimide dispersant has a TBN

(KOH/g) of 20 to 35 or 25 to 30 or 27 to 28 measured according to ASTM D4739.

7. The composition of any one of the preceding claims, wherein the first PIB succinimide dispersant or the second PIB succinimide dispersant is borated.
8. The composition of claim 7, wherein the first borated dispersant or second borated dispersant is present in an amount to deliver independently 25 to 400 or 50 to 200 ppm boron by weight to the lubricating composition.
9. The composition of any one of the preceding claims, wherein the alkaline earth metal salicylate detergent has a TBN (KOH/g) of from 200 to 575 or 200 to 500 measured according to ASTM D4739 or a metal ratio of from 2 to 7, or 2 to 4, or 2.5 to 3.5.
10. The composition of any one of the preceding claims, wherein the alkaline earth metal salicylate is a calcium salicylate detergent having a TBN (KOH/g) of from 250 to 350 measured according to ASTM D4739.
11. The composition of any one of the preceding claims, wherein the alkaline earth metal sulfonate detergent is selected from a calcium sulfonate detergent and a magnesium sulfonate detergent.
12. The composition of any one of the preceding claims, wherein the alkaline earth metal sulfonate detergent is a calcium sulfonate detergent having a TBN (KOH/g) of less than 200 or less than 150, or less than 100, or less than 80 or from 50 to 90 measured according to ASTM D4739.
13. The composition of any one of claims 1 to 11, wherein the alkaline earth metal sulfonate detergent is an overbased magnesium sulfonate detergent having a TBN (KOH/g) of 200 to 500, or 250 to 400, or 250 to 350, or 350 to 375 measured according to ASTM D4739.
14. The composition of any one of claims 1 to 11, wherein the alkaline earth metal sulfonate comprises a mixture of 0.6 wt% to 1.5 wt % of a calcium sulfonate detergent having a TBN (KOH/g) of from 50 to 100 measured according to ASTM D4739 and 0.05 wt% to 0.1 wt % of an overbased magnesium sulfonate detergent having a TBN (KOH/g) of from 250 to 350 measured according to ASTM D4739.
15. The composition of any one of the preceding claims, wherein the total alkaline earth metal soap of the lubricating composition is from 0.6 wt % to 1.5 wt % or 0.7 wt % to 1.4.
16. The composition of any one of the preceding claims, wherein the phosphorus antiwear agent is a zinc dialkyldithiophosphate in an amount to deliver from 400 ppm to 850 ppm, or 450 ppm to 800 ppm, or 500 ppm to 800 ppm, or 550 ppm to 780 ppm, or 650 ppm to 780 ppm to the lubricating composition.
17. The composition of any one of the preceding claims, wherein the HTHS is less than 2.5, or less than 2.3, or less than 2.1 or wherein the HTHS is from 1.4 to 2.5, or 1.6 to 2.1, or 1.8 to 2.1, or 1.9 to 2.0.
18. A method of lubricating a diesel engine comprising supplying to the engine a lubricant composition according to any one of the preceding claims.
19. Use of the lubricating composition according to any one of claims 1 to 17 for improving one or more of fuel economy in a diesel engine and wear protection in a diesel engine.

Patentansprüche

1. Dieselmotorschmierzusammensetzung, umfassend:

ein Öl mit Schmierviskosität, das zu 50 Gew.-% ein Grundöl der Gruppe III, ein Grundöl der Gruppe IV, ein Grundöl der Gruppe V oder Mischungen davon aufweist;
 ein erstes Polyisobutylen- (PIB-) Succinimid-Dispergiermittel, das aus einem PIB mit einem zahlengemittelten Molekulargewicht von 1800 bis 2100 hergestellt ist und in der Schmierzusammensetzung in einer Menge von 0,8 Gew.-% bis 6 Gew.-% vorhanden ist;
 ein zweites Polyisobutylen- (PIB-) Succinimid-Dispergiermittel, das aus einem PIB mit einem zahlengemittelten

Molekulargewicht von bis zu 1600 hergestellt ist, wobei mindestens eines des ersten PIB-Succinimid-Dispergiemittels und des zweiten PIB-Succinimid-Dispergiemittels borfrei ist;
 ein Erdalkalimetallsalicylat-Detergens;
 ein Erdalkalimetallsulfonat-Detergens, das in einer Menge vorhanden ist, um 0,1 Gew.-% bis 1,5 Gew.-% Erdalkalimetallseife an die Schmierzusammensetzung abzugeben; und
 ein Phosphor-Antiverschleißmittel in einer Menge, um 300 bis 900 ppm Phosphor an die Schmierzusammensetzung abzugeben,
 wobei die Schmierzusammensetzung einen Gesamtsulfataschegehalt, gemessen gemäß ASTM D784, zwischen 0,3 und 0,9 Gew.-% aufweist; eine kinematische Viskosität, gemessen gemäß ASTM D-445 bei 100 °C, von weniger als 8,3 cSt; eine Gesamtmenge an Erdalkalimetallseife von 0,6 Gew.-% bis 2,1 Gew.-% und eine HTHS, gemessen gemäß ASTM D4683, von weniger als 2,7 mPa·s.

2. Zusammensetzung nach Anspruch 1, wobei das erste PIB-Succinimid-Dispergiemittel eine TBN (KOH/g) von 15 bis 25 oder 15 bis 20 aufweist, gemessen gemäß ASTM D4739.
3. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das zweite PIB-Succinimid-Dispergiemittel aus einem PIB mit einem zahlengemittelten Molekulargewicht von 750 bis 1600 oder 1000 bis 1600 oder 1200 bis 1600 hergestellt ist oder aus einem PIB mit einem zahlengemittelten Molekulargewicht von 800 bis 1150 oder 900 bis 1100 hergestellt ist.
4. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das zweite PIB-Succinimid-Dispergiemittel in der Schmierzusammensetzung in einer Menge von 1 bis 5 Gew.-% oder von 1,5 bis 4,8 Gew.-% oder von 1,8 bis 4,6 Gew.-% oder von 1,9 bis 4,6 Gew.-% vorhanden ist.
5. Zusammensetzung nach Anspruch 1, wobei das zweite PIB-Succinimid-Dispergiemittel von 1 bis 5 Gew.-% ein PIB-Succinimid-Dispergiemittel, das aus einem PIB mit einem zahlengemittelten Molekulargewicht von 900 bis 1100 hergestellt ist, und von 1 bis 5 Gew.-% ein PIB-Succinimid-Dispergiemittel, das aus einem PIB mit einem zahlengemittelten Molekulargewicht von 1200 bis 1600 hergestellt ist, umfasst.
6. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das zweite PIB-Succinimid-Dispergiemittel eine TBN (KOH/g) von 20 bis 35 oder 25 bis 30 oder 27 bis 28 aufweist, gemessen gemäß ASTM D4739.
7. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das erste PIB-Succinimid-Dispergiemittel oder das zweite PIB-Succinimid-Dispergiemittel boriert sind.
8. Zusammensetzung nach Anspruch 7, wobei das erste borierte Dispergiemittel oder das zweite borierte Dispergiemittel in einer Menge vorhanden sind, um unabhängig 25 bis 400 oder 50 bis 200 ppm Bor, bezogen auf das Gewicht, an die Schmierzusammensetzung abzugeben.
9. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das Erdalkalimetallsalicylat-Detergens eine TBN (KOH/g) von 200 bis 575 oder 200 bis 500, gemessen gemäß ASTM D4739, oder ein Metallverhältnis von 2 bis 7 oder 2 bis 4 oder 2,5 bis 3,5 aufweist.
10. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das Erdalkalimetallsalicylat ein Calciumsalicylat-Detergens mit einer TBN (KOH/g) von 250 bis 350 ist, gemessen gemäß ASTM D4739.
11. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das Erdalkalimetallsulfonat-Detergens aus der Gruppe ausgewählt ist, bestehend aus Calciumsulfonat-Detergens und Magnesiumsulfonat-Detergens.
12. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das Erdalkalimetallsulfonat-Detergens ein Calciumsulfonat-Detergens mit einer TBN (KOH/g) von weniger als 200 oder weniger als 150 oder weniger als 100 oder weniger als 80 oder von 50 bis 90, gemessen gemäß ASTM D4739, ist.
13. Zusammensetzung nach einem der Ansprüche 1 bis 11, wobei das Erdalkalimetallsulfonat-Detergens ein überbasisches Magnesiumsulfonat-Detergens mit einer TBN (KOH/g) von 200 bis 500 oder 250 bis 400 oder 250 bis 350 oder 350 bis 375, gemessen gemäß ASTM D4739, ist.
14. Zusammensetzung nach einem der Ansprüche 1 bis 11, wobei das Erdalkalimetallsulfonat eine Mischung von 0,6

Gew.-% bis 1,5 Gew.-% eines Calciumsulfonat-Detergens mit einer TBN (KOH/g) von 50 bis 100, gemessen gemäß ASTM D4739, und 0,05 Gew.-% bis 0,1 Gew.-% eines überbasischen Magnesiumsulfonat-Detergens mit einer TBN (KOH/g) von 250 bis 350, gemessen gemäß ASTM D4739, umfasst.

- 5 15. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei der Gesamtanteil der Erdalkalimetallseife in der Schmierzusammensetzung 0,6 Gew.-% bis 1,5 Gew.-% oder 0,7 Gew.-% bis 1,4 Gew.-% beträgt.
16. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das Phosphor-Antiverschleißmittel ein Zinkdialkyldithiophosphat in einer Menge ist, um 400 ppm bis 850 ppm oder 450 ppm bis 800 ppm oder 500 ppm bis 800 ppm oder 550 ppm bis 780 ppm oder 650 ppm bis 780 ppm an die Schmierzusammensetzung abzugeben.
17. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei HTHS weniger als 2,5 oder weniger als 2,3 oder weniger als 2,1 beträgt oder wobei HTHS 1,4 bis 2,5 oder 1,6 bis 2,1 oder 1,8 bis 2,1 oder 1,9 bis 2,0 beträgt.
- 15 18. Verfahren zum Schmieren eines Dieselmotors, umfassend ein Zuführen einer Schmierzusammensetzung nach einem der vorstehenden Ansprüche zu dem Motor.
19. Verwendung der Schmierzusammensetzung nach einem der Ansprüche 1 bis 17 zum Verbessern der Kraftstoffeffizienz in einem Dieselmotor und des Verschleißschutzes in einem Dieselmotor.

Revendications

- 25 1. Composition lubrifiante pour moteur diesel comprenant :
 - une huile de viscosité lubrifiante ayant plus de 50 pour cent en poids choisie d'une huile de base du groupe II, d'une huile de base du groupe III, d'une huile de base du groupe IV, d'une huile de base du groupe V, ou de mélanges de celles-ci ;
 - un premier dispersant succinimide de polyisobutylène (PIB) préparé à partir d'un PIB ayant une masse moléculaire moyenne en nombre de 1800 à 2100 présent dans la composition lubrifiante en une quantité allant de 0,8 % en poids à 6 % en poids ;
 - un second dispersant succinimide de polyisobutylène (PIB) préparé à partir d'un PIB avec une masse moléculaire moyenne en nombre allant jusqu'à 1600, où au moins l'un du premier dispersant succinimide de PIB et du second dispersant succinimide de PIB est exempt de bore ;
 - un détergent salicylate de métal alcalino-terreux ;
 - un détergent sulfonate de métal alcalino-terreux présent en quantité suffisante pour fournir 0,1 % en poids à 1,5 % en poids de savon de métal alcalino-terreux à la composition lubrifiante ; et
 - un agent anti-usure au phosphore présent en quantité suffisante pour fournir 300 à 900 ppm de phosphore à la composition lubrifiante,
 - la composition lubrifiante ayant une teneur totale en cendres sulfatées mesurée selon la norme ASTM D784 comprise entre 0,3 et 0,9 % en poids ; une viscosité cinématique mesurée selon la norme ASTM D-445 à 100 °C inférieure à 8,3 cSt ; une teneur totale en savon alcalino-terreux total allant de 0,6 % en poids à 2,1 % en poids, et une HTHS mesurée selon la norme ASTM D4683 inférieure à 2,7 mPa.s.
- 45 2. Composition selon la revendication 1, dans laquelle le premier dispersant succinimide de PIB a un TBN (KOH/g) allant de 15 à 25 ou de 15 à 20 mesuré selon la norme ASTM D4739.
3. Composition selon l'une quelconque des revendications précédentes, dans laquelle le second dispersant succinimide de PIB est préparé à partir d'un PIB ayant une masse moléculaire moyenne en nombre allant de 750 à 1600 ou de 1000 à 1600 ou de 1200 à 1600 ou est préparé à partir d'un PIB ayant une masse moléculaire moyenne en nombre allant de 800 à 1150 ou de 900 à 1100.
- 50 4. Composition selon l'une quelconque des revendications précédentes, dans laquelle le second dispersant succinimide de PIB est présent dans la composition lubrifiante en une quantité allant de 1 à 5 % en poids, ou de 1,5 à 4,8 % en poids, ou de 1,8 à 4,6 % en poids, ou de 1,9 à 4,6 % en poids.
- 55 5. Composition selon la revendication 1, dans laquelle le second dispersant succinimide de PIB comprend de 1 à 5 % en poids d'un dispersant succinimide de PIB préparé à partir d'un PIB ayant une masse moléculaire moyenne

en nombre allant de 900 à 1100 et de 1 à 5 % en poids d'un dispersant succinimide de PIB préparé à partir d'un PIB ayant une masse moléculaire moyenne en nombre allant de 1200 à 1600.

- 5 6. Composition selon l'une quelconque des revendications précédentes, dans laquelle le second dispersant succinimide de PIB a un TBN (KOH/g) de 20 à 35 ou de 25 à 30 ou de 27 à 28 mesuré selon la norme ASTM D4739.
7. Composition selon l'une quelconque des revendications précédentes, dans laquelle le premier dispersant succinimide de PIB ou le second dispersant succinimide de PIB est boraté.
- 10 8. Composition selon la revendication 7, dans laquelle le premier dispersant boraté ou le second dispersant boraté est présent en une quantité suffisante pour fournir indépendamment 25 à 400 ou 50 à 200 ppm de bore en poids à la composition lubrifiante.
- 15 9. Composition selon l'une quelconque des revendications précédentes, dans laquelle le détergent salicylate de métal alcalino-terreux a un TBN (KOH/g) allant de 200 à 575 ou de 200 à 500 mesuré selon la norme ASTM D4739 ou un rapport de métaux allant de 2 à 7, ou de 2 à 4, ou de 2,5 à 3,5.
- 20 10. Composition selon l'une quelconque des revendications précédentes, dans laquelle le salicylate de métal alcalino-terreux est un détergent salicylate de calcium ayant un TBN (KOH/g) allant de 250 à 350 mesuré selon la norme ASTM D4739.
- 25 11. Composition lubrifiante selon l'une quelconque des revendications précédentes, dans laquelle le détergent sulfonate de métal alcalino-terreux est choisi parmi un détergent sulfonate de calcium et un détergent sulfonate de magnésium.
- 30 12. Composition selon l'une quelconque des revendications précédentes, dans laquelle le détergent sulfonate de métal alcalino-terreux est un détergent sulfonate de calcium ayant un TBN (KOH/g) inférieur à 200 ou inférieur à 150, ou inférieur à 100, ou inférieur à 80 ou allant de 50 à 90, mesuré selon la norme ASTM D4739.
- 35 13. Composition selon l'une quelconque des revendications 1 à 11, dans laquelle le détergent sulfonate de métal alcalino-terreux est un détergent sulfonate de magnésium surbasé ayant un TBN (KOH/g) de 200 à 500, ou de 250 à 400, ou de 250 à 350, ou de 350 à 375, mesuré selon la norme ASTM D4739.
- 40 14. Composition selon l'une quelconque des revendications 1 à 11, dans laquelle le sulfonate de métal alcalino-terreux comprend un mélange de 0,6 % en poids à 1,5 % en poids d'un détergent sulfonate de calcium ayant un TBN (KOH/g) allant de 50 à 100 mesuré selon la norme ASTM D4739 et de 0,05 % en poids à 0,1 % en poids d'un détergent sulfonate de magnésium surbasé ayant un TBN (KOH/g) allant de 250 à 350 mesuré selon la norme ASTM D4739.
- 45 15. Composition selon l'une quelconque des revendications précédentes, dans laquelle le savon de métal alcalino-terreux total de la composition lubrifiante représente de 0,6 % en poids à 1,5 % en poids ou de 0,7 % en poids à 1,4 % en poids.
- 50 16. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'agent anti-usure au phosphore est un dialkyldithiophosphate de zinc en une quantité permettant de fournir de 400 ppm à 850 ppm, ou de 450 ppm à 800 ppm, ou de 500 ppm à 800 ppm, ou de 550 ppm à 780 ppm, ou de 650 ppm à 780 ppm à la composition lubrifiante.
- 55 17. Composition selon l'une quelconque des revendications précédentes, dans laquelle la HTHS est inférieure à 2,5, ou inférieure à 2,3, ou inférieure à 2,1, ou dans laquelle la HTHS va de 1,4 à 2,5, ou de 1,6 à 2,1, ou de 1,8 à 2,1, ou de 1,9 à 2,0.
18. Procédé de lubrification d'un moteur diesel comprenant la fourniture au moteur d'une composition lubrifiante selon l'une quelconque des revendications précédentes.
19. Utilisation de la composition lubrifiante selon l'une quelconque des revendications 1 à 17 permettant d'améliorer un ou plusieurs parmi l'économie de carburant d'un moteur diesel et la protection contre l'usure d'un moteur diesel.

REFERENCES CITED IN THE DESCRIPTION

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