(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 134 496 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
10.03.2021 Bulletin 2021/10

(21) Application number: **15719586.8**

(22) Date of filing: **24.04.2015**

(51) Int Cl.:
C10M 169/04 $^{(2006.01)}$ ***C10N 30/02*** $^{(2006.01)}$
C10N 30/04 $^{(2006.01)}$ ***C10N 30/06*** $^{(2006.01)}$
C10N 30/12 $^{(2006.01)}$ ***C10N 40/25*** $^{(2006.01)}$
C10N 20/02 $^{(2006.01)}$ *C10N 20/04* $^{(2006.01)}$
C10N 30/00 $^{(2006.01)}$

(86) International application number:
PCT/US2015/027416

(87) International publication number:
WO 2015/164682 (29.10.2015 Gazette 2015/43)

(54) MULTIGRADE LUBRICATING COMPOSITIONS

MULTIGRADE-SCHMIERMITTELZUSAMMENSETZUNG

COMPOSITIONS LUBRIFIANTES MULTIGRADES

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **25.04.2014 US 201461984232 P**

(43) Date of publication of application:
01.03.2017 Bulletin 2017/09

(73) Proprietor: **The Lubrizol Corporation**
Wickliffe, OH 44092-2298 (US)

(72) Inventors:
- **LOOP, John G.**
  Wickliffe, Ohio 44092-2298 (US)
- **GALIC RAGUZ, Mary**
  Wickliffe, Ohio 44092-2298 (US)

(74) Representative: **D Young & Co LLP**
120 Holborn
London EC1N 2DY (GB)

(56) References cited:

EP-A1- 2 610 333	**EP-A2- 1 418 220**
WO-A1-95/34615	**WO-A1-2007/127661**
WO-A1-2010/115594	**WO-A1-2012/106170**
WO-A2-2011/022266	**US-A1- 2011 077 179**

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] The disclosed technology relates to a lubricating composition for a heavy duty diesel engine that provides for improved fuel economy without reducing durability (i.e. anti-wear) performance of the engine. This may be achieved through the use of high viscosity index base oils in combination with ashless dispersants and overbased metal-containing detergents.

BACKGROUND OF THE INVENTION

[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. 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 15W-40, for example 10W-30.

[0004] Polymeric viscosity index improvers are typically added to lubricating base oils, including highly refined mineral oils, to improve the viscosity-temperature characteristics and/or low-temperature viscosity characteristics of the lubricating compositions. The viscosity index is commonly evaluated as the viscosity-temperature characteristic of lubricating base oils and lubricating compositions, while the properties evaluated for the low-temperature viscosity characteristics are generally the pour point, cloud point and freezing point. Polymeric viscosity index improvers have also been implicated in deposit formation.

[0005] EP 2 610 333 A1 discloses fuel economical lubricating oil compositions for internal combustion engines.

SUMMARY OF THE INVENTION

[0006] The objectives of the invention described herein include providing improved fuel economy while also providing at least one of (i) reduced wear (such as cam wear or lifter wear), (ii) decreased deposit formation, (iii) improved soot handling, (iv) reduced lead or copper corrosion, (v) increased oxidation resistance, and/or (vi) improved seal compatibility in an internal combustion engine. For example, the objectives of the present invention includes providing improved fuel economy while also providing at least one of (i) reduced wear or (ii) decreased deposit formation, especially in compression ignition (i.e. diesel) engines.

[0007] The invention described herein provides a multigrade lubricating , comprising: (a) 80 wt % to 95 wt % of an oil of lubricating viscosity having a viscosity index of at least 130; (b) an ashless dispersant; and (c) an overbased metal detergent; wherein the lubricating composition contains less than 0.01 weight percent of a polymeric viscosity index improver; and the lubricant composition has a SAE viscosity grade of XW-Y, wherein X may be 0, 5, or 10; and Y may be 16, 20, 26, 30, or 40.

[0008] The invention further provides a lubricating composition as described herein wherein the multigrade crankcase lubricant is a SAE 0W-16, 0W-20, 0W-26, 5W-16, 5W-20, 5W-26, 5W-30, 10W-16, 10W-30, or 10W-40 lubricant.

[0009] The invention further provides a lubricating composition as described herein in which the ashless dispersant is derived from a polyolefin having a number average molecular weight of 500 to 5000.

[0010] The invention further provides a lubricating composition as described herein in which the metal-containing overbased detergent includes one or more of a calcium sulfonate, a calcium phenate, a magnesium sulfonate or a magnesium phenate.

[0011] The invention further provides a lubricating composition as described herein in which the metal-containing overbased detergent is present in an amount to deliver at least 4 TBN to the composition.

[0012] The invention further provides a lubricating composition as described herein in which the lubricating composition has a viscosity index of at least 130 or at least 135. In one embodiment, the lubricating composition has a viscosity index of 130 to 230, 135 to 195, or 140 to 175.

[0013] The invention further provides a lubricating composition as described herein in which the oil of lubricating viscosity includes from 0.1 weight percent to 20 weight percent of an oil derived from hydroisomerization of a high wax-containing feed stream.

[0014] The invention further provides a lubricating composition as described herein in which the oil of lubricating viscosity includes from 0.5 weight percent to 5 weight percent of an oil derived from hydroisomerization of a high wax-containing feed stream.

[0015] The invention further provides a use of a lubricant composition for lubricating a compression-ignition internal combustion engine including supplying the engine a lubricant composition as described herein.

[0016] The invention further provides a use of a lubricant composition for improving the fuel economy of a compression-ignition internal combustion engine including supplying to the engine the lubricant composition as described herein, wherein the lubricant is a SAE 0W-16, 0W-20, 0W-26, 5W-16, 5W-20, 5W-30, 10W-16, 10W-30 or 10W-40 lubricant .

DETAILED DESCRIPTION OF THE INVENTION

[0017] Various preferred features and embodiments will be described below by way of non-limiting illustration. As used herein, reference to the amounts of additives present in the lubricating composition disclosed are quoted on an oil free basis, i.e., amount of actives, unless otherwise indicated.

Oil of Lubricating Viscosity

[0018] The oil of lubricating viscosity of the invention may be defined as an API Group II+ base oil. API Group II+ base oils are known and described for example in SAE publication entitled "Design Practice: Passenger Car Automatic Transmissions", fourth Edition, AE-29, published 2012, page 12-9. US 8,216,448 also defines a API Group II+ as a "Group II plus base oil" having a viscosity index greater than or equal to 110 and less than 120.

[0019] The oil of lubricating viscosity of the invention has a viscosity index (VI) of at least 130, or at least 135.

[0020] Examples of an oil of lubricating viscosity of the present invention include base oils sold under the registered trade names of Ultra-S, Nexbase®, Yubase®, Petrocanada, and Chevron neutral oil 110RLV.

[0021] The oil of lubricating viscosity of the invention is present at 80 wt % to 95 wt % of the lubricating composition.

[0022] The oil of lubricating viscosity of the invention may also be blended with a conventional oil of lubricating viscosity (*i.e.,* an oil of lubricating viscosity other than that defined by the present invention) with the proviso that the base oil mixture continues to exhibit a viscosity index as described above. The conventional oil of lubricating viscosity may be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulfur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80-120); Group II (sulfur content ≤0.03 wt %, and ≥90 wt % saturates, viscosity index 80-120); Group III (sulfur content ≤0.03 wt %, and ≥90 wt % saturates, viscosity index ≥120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The oil of lubricating viscosity comprises an API Group I, Group II (other than the oil of lubricating viscosity defined by the present invention), Group III, Group IV, Group V oil or mixtures thereof.

[0023] Often the conventional oil of lubricating viscosity is an API Group I, Group II (other than the oil of lubricating viscosity defined by the present invention), Group III, Group IV oil or mixtures thereof. Alternatively the conventional oil of lubricating viscosity is often an API Group II (other than the oil of lubricating viscosity defined by the present invention), Group III or Group IV oil or mixtures thereof. Groups I, II and III are mineral oil base stocks. The oil of lubricating viscosity can include natural or synthetic oils and mixtures thereof. Mixture of mineral oil and synthetic oils, e.g., polyalphaolefin oils and/or polyester oils, may be used.

[0024] Base oils of API Group II and Group III are subjected to hydrotreating to reduce/remove aromatics and raise viscosity index. Group III base oils are subjected to severe hydrotreating process conditions in order to produce oils with viscosity index of at least 120. In one embodiment, the lubricating composition of the invention comprises a severely hydrotreated base oil with a viscosity index of at least 110, at least 120, at least 130, or even at least 140. In one embodiment the lubricating composition comprises a Group III base oil. Some high viscosity index Group III base oils are produced in part by inclusion of high wax containing feed streams that are subjected to hydroisomerization to produce high viscosity index isoparaffinic base oils.

[0025] Natural oils include animal oils and vegetable oils (e.g. vegetable acid esters) as well as mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid treated mineral lubricating oils of the paraffinic, naphthenic, or mixed paraffinic-naphthenic types. Hydrotreated or hydrocracked oils are also useful oils of lubricating viscosity. Oils of lubricating viscosity derived from coal or shale are also useful.

[0026] Synthetic oils include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymerized olefins and mixtures thereof, alkylbenzenes, polyphenyl, alkylated diphenyl ethers, and alkylated diphenyl sulfides and their derivatives, analogs and homologues thereof. Alkylene oxide polymers and interpolymers and derivatives thereof, and those where terminal hydroxyl groups have been modified by, e.g., esterification or etherification, are other classes of synthetic lubricating oils. Other suitable synthetic lubricating oils comprise esters of dicarboxylic acids and those made from C5 to C12 monocarboxylic acids and polyols or polyol ethers. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, silicon-based oils such as polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils, and silicate oils.

[0027] Other synthetic oils include those produced by Fischer-Tropsch reactions, typically 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.

[0028] In one embodiment, the base oil of lubricating viscosity contains 0.1 weight percent to 20 weight percent of a base oil fraction derived from hydroisomerization of a high wax-containing feed stream and/or base oil derived from hydroisomerization of a Fischer-Tropsch wax feed stream. In one embodiment, the oil of lubricating viscosity contains 0.5 weight percent to 5 weight percent of a base oil fraction derived from hydroisomerization of a high wax-containing feed stream and/or base oil derived from hydroisomerization of a Fischer-Tropsch wax feed stream. In one embodiment, the lubricating composition is free of (or substantially free of) a hydroisomerized wax-derived base oil.

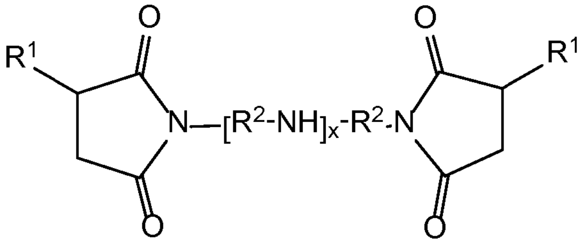
[0029] Unrefined, refined, and rerefined oils, either natural or synthetic (as well as mixtures thereof) of the types disclosed hereinabove can used. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Rerefined oils often are additionally processed to remove spent additives and oil breakdown products.

[0030] 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 performance additives of the present invention.

[0031] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the performance additives of this invention are 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 performance 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.

Ashless Dispersant

[0032] Dispersants, generally, are well known in the field of lubricants and include primarily what is known as ashless dispersants and polymeric dispersants. Ashless dispersants are so-called because, as supplied, they do not contain metal and thus do not normally contribute to sulfated ash when added to a lubricant. However, they may interact with ambient metals once they are added to a lubricant which includes a metal-containing species. Ashless dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides, having a variety of chemical structures, including those represented by Formula (I):



(I)

where each R^1 is independently an alkyl group, frequently a polyisobutylene group with a molecular weight (M_n) of 500-5000 based on the polyisobutylene precursor, and R^2 are alkylene groups, commonly ethylene (C_2H_4) groups.

[0033] Such molecules are commonly derived from reaction of an alkenyl acylating agent with a polyamine, and a wide variety of linkages between the two moieties is possible beside the simple imide structure shown above, including a variety of amides and quaternary ammonium salts. In the above Formula (I), the amine portion is shown as an alkylene polyamine, although other aliphatic and aromatic mono- and polyamines may also be used. Also, a variety of modes of linkage of the R^1 groups onto the imide structure are possible, including various cyclic linkages. The ratio of the carbonyl groups of the acylating agent to the nitrogen atoms of the amine may be 1:0.5 to 1:3, and in other instances 1:1 to 1:2.75 or 1:1.5 to 1:2.5. Succinimide dispersants are more fully described in U.S. Patents 4,234,435 and 3,172,892 and in EP

0355895.

[0034] In certain embodiments, the dispersant is prepared by a process that involves the presence of small amounts of chlorine or other halogen, as described in U.S. Patent 7,615,521 (see, e.g., col. 4, lines 18-60 and preparative example A). Such dispersants typically have some carbocyclic structures in the attachment of the hydrocarbyl substituent to the acidic or amidic "head" group. In other embodiments, the dispersant is prepared by a thermal process involving an "ene" reaction, without the use of any chlorine or other halogen, as described in U.S. Patent 7,615,521; dispersants made in this manner are often derived from high vinylidene (i.e. greater than 50% terminal vinylidene) polyisobutylene(See col. 4, line 61 to col. 5, line 30 and preparative example B). Such dispersants typically do not contain the above-described carbocyclic structures at the point of attachment. In certain embodiments, the dispersant is prepared by free radical catalyzed polymerization of high-vinylidene polyisobutylene with an ethylenically unsaturated acylating agent, as described in United States Patent 8,067,347.

[0035] Dispersants may be derived from, as the polyolefin, high vinylidene polyisobutylene, that is, having greater than 50, 70, or 75% terminal vinylidene groups (α and β isomers). In certain embodiments, the succinimide dispersant may be prepared by the direct alkylation route. In other embodiments it may comprise a mixture of direct alkylation and chlorine-route dispersants.

[0036] Suitable dispersants for use in the compositions of the present invention include succinimide dispersants. In one embodiment, the dispersant may be present as a single dispersant. In one embodiment, the dispersant may be present as a mixture of two or three different dispersants, wherein at least one may be a succinimide dispersant.

[0037] The succinimide dispersant may be a derivative of an aliphatic polyamine, or mixtures thereof. The aliphatic polyamine may be aliphatic polyamine such as an ethylenepolyamine, a propylenepolyamine, a butylenepolyamine, or mixtures thereof. In one embodiment, the aliphatic polyamine may be ethylenepolyamine. In one embodiment the aliphatic polyamine may be selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyamine still bottoms, and mixtures thereof.

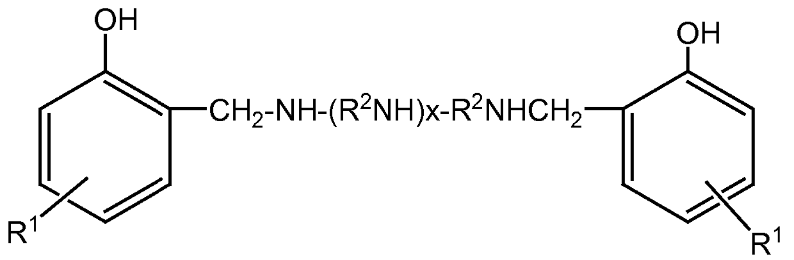
[0038] The succinimide dispersant may be a derivative of an aromatic amine, an aromatic polyamine, or mixtures thereof. The aromatic amine may be 4-aminodiphenylamine (ADPA) (also known as *N*-phenylphenylenediamine), derivatives of ADPA (as described in United States Patent Publications 2011/0306528 and 2010/0298185), a nitroaniline, an aminocarbazole, an amino-indazolinone, an aminopyrimidine, 4-(4-nitrophenylazo)aniline, or combinations thereof. In one embodiment, the dispersant is derivative of an aromatic amine wherein the aromatic amine has at least three non-continuous aromatic rings.

[0039] The succinimide dispersant may be a derivative of a polyether amine or polyether polyamine. Typical polyether amine compounds contain at least one ether unit and will be chain terminated with at least one amine moiety. The polyether polyamines can be based on polymers derived from C_2-C_6 epoxides such as ethylene oxide, propylene oxide, and butylene oxide. Examples of polyether polyamines are sold under the Jeffamine® brand and are commercially available from Hunstman Corporation located in Houston, Texas.

[0040] Another class of ashless dispersant is high molecular weight esters. These materials are similar to the above-described succinimides except that they may be seen as having been prepared by reaction of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Such materials are described in more detail in U.S. Patent 3,381,022. Aromatic succinate esters may also be prepared as described in United States Patent Publication 2010/0286414.

[0041] A succinic-based dispersant (succinimide, succinamide, succinic ester, and mixtures thereof) may be formed by reacting maleic anhydride or a reactive equivalent thereof, such as an acid or ester, with a hydrocarbon chain by any method such as those disclosed above (e.g., chlorine-based process or thermal process). Other acids or equivalents thereof may be used in place of the maleic anhydride. These include fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citaconic anhydride, and cinnamic acid as well as other ethylenically unsaturated acids such as acrylic or methacrylic acid; and their reactive equivalents.

[0042] Another class of ashless dispersant is Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde. Such materials may have the general structure as represented by Formula (II)



(II)

(including a variety of isomers and the like) and are described in more detail in U.S. Patent 3,634,515.

[0043] Another class of ashless dispersants include dispersants comprising a quaternary ammonium salt. Quaternary ammonium salts include the reaction product of: (i) a compound comprising at least one tertiary amino group; and (ii) a quaternizing agent suitable for converting the tertiary amino group of compound (i) to a quaternary nitrogen. Examples of suitable quaternary ammonium salts include (i) imide quaternary ammonium salts, (ii) Mannich quaternary ammonium salts, (iii) polyalkene substituted amine quaternary ammonium salts, (iv) amide quaternary ammonium salts, (v) ester quaternary ammonium salts, (vi) polyester quaternary ammonium salts, or (vii) any combination thereof.

[0044] These various types of quaternary ammonium salts may be prepared in any number of ways but generally are prepared by reacting a non-quaternized nitrogen-containing compound with a quaternizing agent. Each of the different types of quaternary ammonium salts described uses a different non-quaternized nitrogen-containing compound in its preparation, but generally the non-quaternized nitrogen-containing compound contains a tertiary nitrogen capable of being quaternized (or a primary or secondary nitrogen atom that can be alkylated to a tertiary nitrogen that can then be quaternized) and a hydrocarbyl substituent group. The preparation and use of quaternized ammonium dispersants is described in detail in United States Patent 7,951,211 and United States Patent 7,906,470.

[0045] The dispersant may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds, urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds.

[0046] The dispersant may also exhibit basicity, as measured by Total Base Number (TBN). TBN may be determined by ASTM D2896. This will particularly be the case if the dispersant is prepared with an amine, such as a polyamine, and the amine contains one or more amino groups that have not reacted with acidic groups of the dispersant. In some embodiments, the TBN of the dispersant may be 1 to 110, or 5 to 50, or 10 to 40 or 30 to 70. In some embodiments, however, the dispersant may not exhibit basicity (that is, have a TBN of 0 or nearly 0). In one embodiment the dispersant has a TBN of zero as measured by D2896. Such could be the case if no basic nitrogen is present on the dispersant.

[0047] The dispersant may be present at 0.01 wt % to 20 wt %, or 0.1 wt % to 15 wt %, or 0.1 wt % to 10 wt %, or 0.5 wt % to 8 wt % , or 1.0 wt % to 6.5 wt % of the lubricating composition.

Metal Overbased Detergent

[0048] 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 non-sulfur containing phenates, sulfur containing phenates, sulfonates, salicylates, and mixtures thereof.

[0049] The amount of excess metal is commonly expressed in terms of substrate to 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 detergent of the invention may have a metal ratio of 5 to 30, or a metal ratio of 7 to 22, or a metal ratio of at least 11.

[0050] 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/phenate detergent is employed, the hybrid detergent would be considered equivalent to amounts of distinct phenate and sulfonate detergents introducing like amounts of phenate 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 600, or 300 to 500. Overbased detergents are known in the art.

[0051] 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 of the invention 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.

[0052] The overbased metal-containing detergent may be alkali metal or alkaline earth metal salts. In one embodiment, the overbased detergent may be sodium salts, calcium salts, magnesium salts, or mixtures thereof of the phenates, sulfur-containing phenates, sulfonates, salixarates and salicylates. In one embodiment, the overbased detergent is a calcium detergent, a magnesium detergent or mixtures thereof. In one embodiment, the overbased calcium detergent may be present in an amount to deliver at least 500 ppm calcium by weight and no more than 3000 ppm calcium by weight, or at least 1000 ppm calcium by weight, or at least 2000 ppm calcium by weight, or no more than 2500 ppm calcium by weight to the lubricating composition. In one embodiment, the overbased detergent may be present in an amount to deliver no more than 500 ppm by weight of magnesium to the lubricating composition, or no more than 330 ppm by weight, or no more than 125 ppm by weight, or no more than 45 ppm by weight. In one embodiment, the lubricating composition is essentially free of (i.e. contains less than 10 ppm) magnesium resulting from the overbased detergent. In one embodiment, the overbased detergent may be present in an amount to deliver at least 200 ppm by weight of magnesium, or at least 450 ppm by weight magnesium, or at least 700 ppm by weight magnesium to the lubricating composition. In one embodiment, both calcium and magnesium containing detergents may be present in the lubricating composition. Calcium and magnesium detergents may be present such that the weight ratio of calcium to magnesium is 10:1 to 1:10, or 8:3 to 4:5, or 1:1 to 1:3. In one embodiment, the overbased detergent is free of or substantially free of sodium.

[0053] In one embodiment, the sulfonate detergent may be predominantly a linear alkylbenzene sulfonate detergent having a metal ratio of at least 8 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.

[0054] 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. 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 of the invention is a salicylate detergent. In one embodiment, the salicylate detergent of the invention is free of unreacted p-alkylphenol (i.e. contains less than 0.1 weight percent). In one embodiment, the salicylate detergent of the invention is prepared by alkylation of salicylic acid.

[0055] The overbased detergent may be present at 0.2 wt % to 15 wt %, or 0.3 wt % to 10 wt %, or 0.3 wt % to 8 wt %, or 0.4 wt % to 3 wt %. For example, in a heavy duty diesel engine, the detergent may be present at 2 wt % to 3 wt % of the lubricating composition. For a passenger car engine, the detergent may be present at 0.2 wt % to 1 wt % of the lubricating composition.

[0056] Metal-containing overbased detergents often provide TBN to the lubricating composition. In one embodiment, the overbased detergent is present in an amount to deliver at least 4 mg KOH/g of TBN to the lubricating composition, or 4 to 15 mg KOH/g, or 5 to 9 mg KOH/g of TBN to the lubricating composition.

[0057] Metal-containing detergents contribute sulfated ash to a lubricating composition. Sulfated ash may be determined by ASTM D874. In one embodiment, the lubricating composition of the invention comprises a metal-containing detergent in an amount to deliver at least 0.4 weight percent sulfated ash to the total composition. In another embodiment, the metal-containing detergent is present in an amount to deliver at least 0.6 weight percent sulfated ash, or at least 0.75 weight percent sulfated ash, or even at least 0.9 weight percent sulfated ash to the lubricating composition.

[0058] 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 lubricating composition comprises 0.05 weight percent to 1.5 weight percent detergent soap, or 0.1 weight percent to 0.9 weight percent detergent soap. In one embodiment, the lubricating composition contains no more than 0.5 weight percent detergent soap. The overbased detergent may have a weight ratio of ash:soap of 5:1 to 1:2.3, or 3.5:1 to 1:2, or 2.9:1 to 1:1:7.

Other Performance Additives

[0059] The compositions of the invention may optionally comprise one or more additional performance additives. These additional performance additives may include one or more metal deactivators, detergents, friction modifiers, antiwear agents, corrosion inhibitors, soot-dispersing additives, extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents, and any combination or mixture thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives, and often a package of multiple performance additives.

[0060] In one embodiment, the invention provides a lubricating composition further comprising an antiwear agent, a dispersant viscosity modifier, a friction modifier, a viscosity modifier, an antioxidant, an overbased detergent, a dispersant (different from that of the invention), or a combination thereof, where each of the additives listed may be a mixture of two or more of that type of additive. In one embodiment, the invention provides a lubricating composition further comprising an antiwear agent, a dispersant viscosity modifier, a friction modifier, a viscosity modifier (typically an olefin copolymer such as an ethylene-propylene copolymer), an antioxidant (including phenolic and aminic antioxidants), an overbased detergent (including overbased sulfonates and phenates), or a combination thereof, where each of the additives listed may be a mixture of two or more of that type of additive.

[0061] Another additive is an antiwear agent. Examples of anti-wear agents include phosphorus-containing antiwear/extreme pressure agents such as metal thiophosphates, phosphoric acid esters and salts thereof, phosphorus-containing carboxylic acids, esters, ethers, and amides, and phosphites. In certain embodiments a phosphorus antiwear agent may be present in an amount to deliver 0.01 to 0.2 or 0.015 to 0.15 or 0.02 to 0.1 or 0.025 to 0.08 percent phosphorus. Often the antiwear agent is a zinc dialkyldithiophosphate (ZDP).

[0062] 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 compositions of the invention include primary zinc dialkyldithiophosphates. In some embodiments the compositions of the invention include secondary zinc dialkyldithiophosphates. In some embodiments the compositions of the invention 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. In some embodiments component (b) is a mixture of primary and secondary zinc dialkyldithiophosphates that is at least 50 percent by weight primary, or even at least 60, 70, 80, or even 90 percent by weight primary. In some embodiments component (b) is free of primary zinc dialkyldithiophosphates.

[0063] The phosphorus antiwear agent may be present at 0 wt % to 3 wt %, or 0.1 wt % to 1.5 wt %, or 0.5 wt % to 0.9 wt % of the lubricating composition.

[0064] Another class of anti-wear additives includes oil-soluble titanium compounds as disclosed in U.S. Pat. No. 7,727,943 and US20060014651. 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 may be a titanium (IV) alkoxide. The titanium alkoxide may be 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 may be titanium (IV) isopropoxide. In one embodiment, the titanium alkoxide may be 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 may be oleic acid. In one embodiment, the oil soluble titanium compound may be a titanium carboxylate. In one embodiment the titanium (IV) carboxylate may be titanium neodecanoate. In one embodiment the oil soluble titanium compound may be present in the lubricating composition in an amount necessary to provide for 10 ppm to 1500 ppm titanium by weight or 25 ppm to 150 ppm titanium by weight.

[0065] In one embodiment, the invention provides a lubricating composition which further comprises ashless antioxidant. Ashless antioxidants may comprise one or more of arylamines, diarylamines, alkylated arylamines, alkylated diaryl amines, phenols, hindered phenols, sulfurized olefins, or mixtures thereof. In one embodiment the lubricating composition includes an antioxidant, or mixtures thereof. The antioxidant may be present at 0 wt % to 15 wt %, or 0.1 wt % to 10 wt %, or 0.5 wt % to 5 wt %, or 0.5 wt % to 3 wt %, or 0.3 wt % to 1.5 wt % of the lubricating composition.

[0066] The diarylamine or alkylated diarylamine may be a phenyl-α-naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenylnapthylamine, 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 one 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 phenylnapthylamines.

[0067] The diarylamine antioxidant of the invention may be present on a weight basis of the lubrication composition at 0.1% to 10%, 0.35% to 5%, or even 0.5% to 2%.

[0068] The phenolic antioxidant may be a simple alkyl phenol, a hindered phenol, or coupled phenolic compounds.

[0069] 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, 4-dodecyl-2,6-di-tert-butylphenol, or butyl 3-(3,5-ditert-butyl-4-hydroxyphenyl)propanoate. In one embodiment, the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 from Ciba.

[0070] Coupled phenols often contain two alkylphenols coupled with alkylene groups to form bisphenol compounds. Examples of suitable coupled phenol compounds include 4,4'- methylene bis-(2,6-di-tert-butyl phenol), 4-methyl-2,6-di-tert-butylphenol, 2,2'-bis-(6-t-butyl-4-heptylphenol); 4,4'-bis(2,6-di-t-butyl phenol), 2,2'-methylenebis(4-methyl-6-t-butylphenol), and 2,2'-methylene bis(4-ethyl-6-t-butylphenol).

[0071] Phenols of the invention also include polyhydric aromatic compounds and their derivatives. Examples of suitable polyhydric aromatic compounds include esters and amides of gallic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 1,4-dihydroxy-2-naphthoic acid, 3,5-dihydroxynaphthoic acid, 3,7-dihydroxy naphthoic acid, and mixtures thereof.

[0072] In one embodiment, the phenolic antioxidant comprises a hindered phenol. In another embodiment the hindered phenol is derived from 2,6-ditertbutyl phenol.

[0073] In one embodiment the lubricating composition of the invention comprises a phenolic antioxidant in a range of 0.01 wt % to 5 wt %, or 0.1 wt % to 4 wt %, or 0.2 wt % to 3 wt %, or 0.5 wt % to 2 wt % of the lubricating composition.

[0074] Sulfurized olefins are well known commercial materials, and those which are substantially nitrogen-free, that is, not containing nitrogen functionality, are readily available. The olefinic compounds which may be sulfurized are diverse in nature. They contain at least one olefinic double bond, which is defined as a nonaromatic double bond; that is, one connecting two aliphatic carbon atoms. These materials generally have sulfide linkages having 1 to 10 sulfur atoms, for instance, 1 to 4, or 1 or 2.

[0075] Ashless antioxidants may be used separately or in combination. In one embodiment of the invention, two or more different antioxidants are used in combination, such that there is at least 0.1 weight percent of each of the at least two antioxidants and wherein the combined amount of the ashless antioxidants is 0.5 to 5 weight percent. In one embodiment, there may be at least 0.25 to 3 weight percent of each ashless antioxidant.

[0076] In one embodiment, the invention provides a lubricating composition further comprising a molybdenum compound. The molybdenum compound may be selected from the group consisting of molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, amine salts of molybdenum compounds, molybdenum-containing dispersants, and mixtures thereof. Examples of commercially available molybdenum compounds include Sakura-lube™ 525 and Sakura-lube™ 710, both available from Adeka Corporation; and Molyvan® 855 available from Vanderbilt Chemicals, LLC. The molybdenum compound may provide the lubricating composition with 0 to 1000 ppm, or 5 to 1000 ppm, or 10 to 750 ppm, or 5 ppm to 300 ppm, or 20 ppm to 250 ppm of molybdenum. In one embodiment, the molybdenum compound is a molybdenum dithiocarbamate compound present in an amount to provide 300 ppm to 750 ppm molybdenum to the lubricating composition.

[0077] In one embodiment, the lubricating composition of the invention further comprises a soot dispersing additive. The soot dispersing additive may be present at 0 wt % to 5 wt %, or 0 wt % to 4 wt %, or 0.05 wt % to 2 wt % of the lubricating composition.

[0078] Suitable soot dispersing additives include functionalized low molecular weight polyolefins, for example, ethylene-propylene copolymers with a number average molecular weight (Mn) of less than 20,000 that have been functionalized with an acylating agent such as maleic anhydride and an amine, preferably an aromatic amine. Other soot dispersing additives may be prepared from acylated polyisobutylene that has been functionalized with aromatic (poly)amines. More detailed description of soot-dispersing additives are disclosed in U.S. Patents 4,863,623; 5,182,041; 7,790,661; 8,557,753; and 8,637,437. In one embodiment, the soot dispersing additive may include those described in U.S. Patent 7,790,661 or in U.S. Patent 8,557,753.

[0079] In one embodiment, the invention provides a lubricating composition further comprising a friction modifier. Examples of friction modifiers include long chain fatty acid derivatives of amines, fatty esters, or epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty esters, amides, and/or imides of α-hydroxy-carbonyl compounds such as tartaric acid, malic acid, citric acid, glycolic acid, lactic acid and mandelic acid. The term fatty, as used herein, can mean having a C8-22 linear alkyl group.

[0080] Friction modifiers may also encompass materials such as sulfurized fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or monoester of a polyol and an aliphatic carboxylic acid.

[0081] In one embodiment the friction modifier may be selected from the group consisting of long chain fatty acid derivatives of amines, long chain fatty esters, or long chain fatty epoxides; fatty imidazolines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; and fatty alkyl tartramides. The friction modifier may be present at 0 wt % to 6 wt %, or 0.05 wt % to 4 wt %, or 0.1 wt % to 2 wt % of the lubricating composition.

[0082] In one 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 or a diester or a mixture thereof, and in another embodiment the long chain fatty acid ester may be a triglyceride.

[0083] Other performance additives such as corrosion inhibitors include those described in paragraphs 5 to 8 of US Application US05/038319, published as WO2006/047486, octyl octanamide, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. In one embodiment, the corrosion inhibitors include the Synalox® (a registered trademark of The Dow Chemical Company) corrosion inhibitor. The Synalox® corrosion inhibitor may be a homopolymer or copolymer of propylene oxide. The Synalox® corrosion inhibitor is described in more detail in a product brochure with Form No. 118-01453-0702 AMS, published by The Dow Chemical Company. The product brochure is entitled "SYNALOX Lubricants, High-Performance Polyglycols for Demanding Applications."

[0084] The lubricating composition may further include metal deactivators, including derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles; foam inhibitors, including copolymers of ethyl acrylate and 2-ethylhexylacrylate and copolymers of ethyl acrylate and 2-ethylhexylacrylate and vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; and pour point depressants, including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides.

[0085] The lubricating composition may further comprise a polyether compound. The polyether compound may be a polyether, a polyetheramine, a (poly)alkoxylated amine, an ethoxylated alcohol, or mixtures thereof. The polyether can be represented by the formula $RO[CH_2CH(R^1)O]_xH$ where R is a hydrocarbyl group; R^1 is selected from the group consisting of hydrogen, alkyl groups of 1 to 14 carbon atoms, and mixtures thereof; and x is a number from 2 to 50. The hydrocarbyl group R is a univalent hydrocarbon group, has one or more carbon atoms, and includes alkyl and alkylphenyl groups having 7 to 30 total carbon atoms, such as 9 to 25 total carbon atoms, or 11 to 20 total carbon atoms. The repeating oxyalkylene units may be derived from ethylene oxide, propylene oxide, or butylene oxide. The number of oxyalkylene units x may be 10 to 35, or 18 to 27. The polyether of the present invention can be prepared by various well-known methods including condensing one mole of an alcohol or alkylphenol with two or more moles of an alkylene oxide, mixture of alkylene oxides, or with several alkylene oxides in sequential fashion, usually in the presence of a base catalyst. U.S. Pat. No. 5,094,667 provides reaction conditions for preparing a polyether. Suitable polyethers are commercially available from Dow Chemicals, Huntsman, ICI and include the Actaclear® series from Bayer. Suitable ethoxylates include Surfonic® ethoxylates, for example Surfonic L24-5, available from Huntsman International LLC.

[0086] Polymeric viscosity modifiers may be present with the proviso that they are present in an amount less than 0.01 weight percent of the lubricating composition. Suitable viscosity modifiers include ethylene-olefin co-polymers, especially ethylene-propylene; maleic anhydride-styrene alternating copolymers and esters thereof, polymethacrylates (including random, block and star architectures), hydrogenated styrene-butadiene block copolymers, hydrogenated styrene-isoprene radial and/or block copolymers, or mixtures thereof. In one embodiment, the polymeric viscosity modifier includes an ethylene-olefin based copolymer. In some embodiments, the ethylene makes up from 50 weight percent to 90 weight percent or from 65 weight percent to 85 weight percent, on a molar basis of the monomer used to prepare the copolymer of the ethylene-olefin-based copolymer. In another embodiment, the ethylene makes up at least 70 weight percent of the monomer used to prepare the copolymer. In one embodiment, the ethylene-olefin copolymer has a molecular weight from 5,000 to 40,000 Mn.

[0087] Pour point depressants that may be useful in the compositions of the invention further include polyalphaolefins, esters of maleic anhydride-styrene, poly(meth)acrylates, polyacrylates or polyacrylamides.

Industrial Application

[0088] Generally, the lubricant is added to the lubricating system of the internal combustion engine, which then delivers the lubricating composition to the critical parts of the engine, during its operation, that require lubrication.

[0089] The lubricating compositions described above may be utilized in an internal combustion engine. The engine components may have a surface of steel or aluminum (typically a surface of steel), and may also be coated for example with a diamond-like carbon (DLC) coating.

[0090] An aluminum surface may be comprised of an aluminum alloy that may be a eutectic or hyper-eutectic aluminum alloy (such as those derived from aluminum silicates, aluminum oxides, or other ceramic materials). The aluminum surface may be present on a cylinder bore, cylinder block, or piston ring having an aluminum alloy, or aluminum composite.

[0091] The internal combustion engine may be fitted with an emission control system, an oil mist separator or a turbocharger. Examples of the emission control system include diesel particulate filters (DPF), or systems employing selective catalytic reduction (SCR).

[0092] The internal combustion engine is distinct from a gas turbine. In an internal combustion engine, individual combustion events translate from a linear reciprocating force into a rotational torque through the rod and crankshaft. In contrast, in a gas turbine (which may also be referred to as a j et engine) a continuous combustion process generates a rotational torque continuously without translation, and can also develop thrust at the exhaust outlet. These differences in operation conditions of a gas turbine and internal combustion engine result in different operating environments and stresses.

[0093] The lubricant composition for an internal combustion engine may be suitable for any engine lubricant irrespective of the sulfur, phosphorus or sulfated ash (ASTM D-874) content. The sulfur content of the engine oil lubricant may be 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less, or 0.3 wt % or less. In one embodiment, the 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 100 ppm to 1000 ppm, or 200 ppm to 600 ppm. The total sulfated ash content may be 2 wt % or less, or 1.5 wt % or less, or 1.1 wt % or less, or 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less, or 0.4 wt % or less. In one embodiment, the sulfated ash content may be 0.05 wt % to 0.9 wt %, or 0.1 wt % to 0.2 wt % or to 0.45 wt %.

[0094] In one embodiment, the lubricating composition may be an engine oil, wherein the lubricating composition may be characterized as having at least one of (i) a sulfur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, (iii) a sulfated ash content of 1.5 wt % or less, or combinations thereof.

EXAMPLES

[0095] The following examples provide illustrations of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention. Examples:

[0096] A series of 10W-30 diesel lubricating compositions are prepared according to Table 1 below. Compositions are prepared by blending components as shown in Table 1 into a lubricant. The amounts in Table 1 are on an oil-free basis.

TABLE 1 - Lubricating Compositions

Embodiments (wt %)	Inv. Ex1	Comp Ex 1
Group III Base Oil	84.8[1]	76.8[2]
PIBsuccinimide Dispersant[3]	3.1	3.1
Calcium Sulfonate Detergent[4]	1.2	1.2
Calcium Phenate Detergent[5]	0.8	0.8
Soot Dispersing Additive[6]	0.67	0.67
Zinc dialkyldithiophosphate	1.0	1.0
Other Performance Additives[7]	1.44	1.44
E-P Viscosity Index Improver	0	0.7
Pour Point Depressant	0.2	0.2
Dil Oil (from components)	Balance to 100%	

1. Ultra-S (S-Oil) VHVI-8cSt; VI = 131
2. Ultra-S (S-Oil) VHVI-4cSt (29.64%) (VI = 125)/Ultra-S (S-Oil) VHV-8cSt(46.36%) VI = 131
3. PIBsuccinimide
4. Combination of low metal ratio (<3) and high metal ratio (>10) alkylbenzene sulfonate
5. Combination of low metal ratio (<2) and higher metal ratio (>5) sulfur-coupled phenates
6. Ethylene-propylene copolymer (Mn 7000) acylated with maleic anhydride and functionalized with nitroaniline
7. Other additives include metal passivators, surfactant, ashless antioxidants, and foam inhibitor

[0097] The lubricating compositions are evaluated for wear protection in GM 6.5L Roller Follower Wear Test (RFWT) (ASTM D5966). This test measures wear on camshaft roller follower pins to determine the ability of an engine oil to control wear in the presence of soot-laden oil. The results obtained are summarized in Table 2, below.

[0098] In addition, the lubricating compositions were also evaluated in the Volvo D12D fuel economy engine test; this test estimates the fuel economy benefits of the candidate oil versus a baseline oil (HVES 540). The baseline lubricant was a commercial SAE 15W-40 API CJ-4 Heavy-Duty Diesel Engine Oil. The results obtained are summarized in Table 2, below.

TABLE 2 - Wear and Fuel Economy Test Results

	Inv. Ex1	Comp Ex 1
Base Oil Viscosity @100C	5.80	7.11
KV100	10.5	11.5
VI (D2270)	137	159
Calcium (wt %)	0.29	0.29
Phosphorus (wt %)	0.11	0.11
Sulfur (wt %)	0.38	0.38
HTHS (cP) (D4683)	3.3	3.3
RFWT - GM 6.5L		
Average Wear (mils)	0.10	0.24
D12D FE Screen Test		
Ave. FE improvement (%)	0.71	0.47

[0099] The results obtained demonstrate that the lubricating composition disclosed herein provides improved fuel economy performance without sacrificing wear protection. This has been accomplished in a composition free of polymeric viscosity index improver.

[0100] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, byproducts, derivatives, and other such materials which are normally understood to be present in the commercial grade.

[0101] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

[0102] hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

[0103] 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);

[0104] 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.

[0105] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

[0106] As described hereinafter the molecular weight of the materials described above have 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 star polymer Chemistry", Cornell University Press 91953), Chapter VII, pp 266-315; or (ii) "Macromolecules, an Introduction to star polymer

Science", F. A. Bovey and F. H. Winslow, Editors, Academic Press (1979), pp 296-312. As used herein the weight average and number weight average molecular weights of the materials described are obtained by integrating the area under the peak corresponding to the material of interest, excluding peaks associated with diluents, impurities, uncoupled star polymer chains and other additives.

[0107] The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

[0108] As used herein, the transitional term "comprising," which is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of "comprising" herein, it is intended that the term also encompass, as alternative embodiments, the phrases "consisting essentially of' and "consisting of," where "consisting of' excludes any element or step not specified and "consisting essentially of' permits the inclusion of additional un-recited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration.

[0109] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims.

Claims

1. A multigrade lubricant composition, comprising:

(a) 80 wt % to 95 wt % of an oil of lubricating viscosity having a viscosity index of at least 130;
(b) an ashless dispersant; and
(c) an overbased metal detergent;

wherein the lubricating composition contains less than 0.01 weight percent of a polymeric viscosity index improver; and
the lubricant composition has a SAE viscosity grade of XW-Y, wherein X may be 0, 5, or 10; and Y may be 16, 20, 26, 30, or 40.

2. The lubricant composition of claim 1, wherein the multigrade crank-case lubricant is a SAE OW-16, 0W-20, 0W-26, 5W-16, 5W-20, 5W-26, 5W-30, 10W-16, 10W-30, or 10W-40 lubricant.

3. The lubricating composition of claim 1, wherein the metal-containing overbased detergent comprises one or more of a calcium sulfonate, a calcium phenate, a magnesium sulfonate or a magnesium phenate.

4. The lubricating composition of claim 3, where the metal-containing overbased detergent is present in amount to deliver at least 4 TBN to the composition, wherein the TBN is measured using the method in ASTM D2896

5. The lubricating composition of claim 1, wherein the lubricating composition has a viscosity index of at least 135.

6. Use of a lubricant composition according to claim 1 for lubricating a compression-ignition internal combustion engine, wherein the use comprises supplying the composition to said engine.

7. Use of a lubricant composition according to claim 2 for improving the fuel economy of a compression-ignition internal combustion engine.

Patentansprüche

1. Mehrbereichsschmiermittelzusammensetzung, die Folgendes umfasst:

(a) 80 Gew.-% bis 95 Gew.-% eines Öls mit Schmierviskosität, das einen Viskositätsindex von wenigstens 130

aufweist;
(b) ein aschefreies Dispergiermittel; und
(c) ein überbasisches Metalldetergens;

wobei die Schmierzusammensetzung weniger als 0,01 Gew.-% eines polymeren Viskositätsindexverbesserers enthält; und
die Schmiermittelzusammensetzung eine SAE-Viskositätsklasse von XW-Y aufweist, wobei X 0, 5 oder 10 sein kann; und
Y 16, 20, 26, 30 oder 40 sein kann.

2. Schmiermittelzusammensetzung nach Anspruch 1, wobei das Mehrbereichsschmiermittel für ein Kurbelgehäuse ein SAE OW-16-, 0W-20-, OW-26-, 5W-16-, 5W-20-, 5W-26-, 5W-30-, 10W-16-, 10W-30- oder 10W-40-Schmiermittel ist.

3. Schmierzusammensetzung nach Anspruch 1, wobei das metallhaltige, überbasische Detergens ein Calciumsulfonat, ein Calciumphenat, ein Magnesiumsulfonat und/oder ein Magnesiumphenat umfasst.

4. Schmierzusammensetzung nach Anspruch 3, wobei das metallhaltige, überbasische Detergens in einer Menge vorhanden ist, um wenigstens 4 TBN an die Zusammensetzung abzugeben, wobei die TBN unter Verwendung des Verfahrens in ASTM D2896 gemessen wird.

5. Schmierzusammensetzung nach Anspruch 1, wobei die Schmierzusammensetzung einen Viskositätsindex von wenigstens 135 aufweist.

6. Verwendung einer Schmiermittelzusammensetzung nach Anspruch 1 zum Schmieren eines Verbrennungsmotors mit Selbstzündung, wobei die Verwendung das Zuführen der Zusammensetzung zu dem Motor umfasst.

7. Verwendung einer Schmiermittelzusammensetzung nach Anspruch 2 zum Verbessern der Kraftstoffeinsparung eines Verbrennungsmotors mit Selbstzündung.

Revendications

1. Composition lubrifiante multigrade, comprenant :

(a) 80 à 95 % en poids d’une huile de viscosité lubrifiante présentant un indice de viscosité d’au moins 130 ;
(b) un dispersant sans cendre ; et
(c) un détergent métallique surbasique ;

la composition lubrifiante contenant moins de 0,01 % en poids d’un améliorant d’indice de viscosité polymère ; et
la composition lubrifiante présentant un grade de viscosité SAE de XW-Y, X pouvant être 0, 5 ou 10 ; et Y pouvant être 16, 20, 26, 30 ou 40.

2. Composition lubrifiante selon la revendication 1, dans laquelle le lubrifiant de carter de moteur multigrade est un lubrifiant SAE OW-16, 0W-20, OW-26, 5W-16, 5W-20, 5W-26, 5W-30, 10W-16, 10W-30 ou 10W-40.

3. Composition lubrifiante selon la revendication 1, dans laquelle le détergent métallique surbasique comprend un ou plusieurs parmi un sulfonate de calcium, un phénate de calcium, un sulfonate de magnésium ou un phénate de magnésium.

4. Composition lubrifiante selon la revendication 3, dans laquelle le détergent métallique surbasique est présent en quantité suffisante pour délivrer au moins 4 TBN à la composition, le TBN étant mesuré selon le procédé de la norme ASTM D2896.

5. Composition lubrifiante selon la revendication 1, dans laquelle la composition lubrifiante présente un indice de viscosité d’au moins 135.

6. Utilisation d’une composition lubrifiante selon la revendication 1 pour la lubrification d’un moteur à combustion interne à allumage par compression, l'utilisation comprenant la fourniture de la composition audit moteur.

7. Utilisation d'une composition lubrifiante selon la revendication 2 pour améliorer l'économie de carburant d'un moteur à combustion interne à allumage par compression.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- EP 2610333 A1 **[0005]**
- US 8216448 B **[0018]**
- US 4234435 A **[0033]**
- US 3172892 A **[0033]**
- EP 0355895 A **[0033]**
- US 7615521 B **[0034]**
- US 8067347 B **[0034]**
- US 20110306528 A **[0038]**
- US 20100298185 A **[0038]**
- US 3381022 A **[0040]**
- US 20100286414 A **[0040]**
- US 3634515 A **[0042]**
- US 7951211 B **[0044]**
- US 7906470 B **[0044]**
- US 6429178 B **[0050]**
- US 6429179 B **[0050]**
- US 6153565 A **[0050]**
- US 6281179 B **[0050]**
- US 2005065045 A **[0053]**
- US 7407919 B **[0053]**
- US 8399388 B **[0054]**
- US 7009072 B **[0054]**
- US 7727943 B **[0064]**
- US 20060014651 A **[0064]**
- US 4863623 A **[0078]**
- US 5182041 A **[0078]**
- US 7790661 B **[0078]**
- US 8557753 B **[0078]**
- US 8637437 B **[0078]**
- US 05038319 A **[0083]**
- WO 2006047486 A **[0083]**
- US 5094667 A **[0085]**

Non-patent literature cited in the description

- Design Practice: Passenger Car Automatic Transmissions. 2012, 12-9 **[0018]**
- **P.J. FLORY.** Principles of star polymer Chemistry. Cornell University Press, 266-315 **[0106]**
- Macromolecules, an Introduction to star polymer Science. Academic Press, 1979, 296-312 **[0106]**