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(54) **FUEL-EFFICIENT ENGINE OIL COMPOSITION**

(57) The present invention provides an engine oil composition with excellent fuel saving properties, which comprises a lubricating base oil with a saturate content of 70 percent by mass or more and a viscosity index of 90 or greater and a star polymer as a viscosity index improver in an amount of at least 4 percent by mass or

more on the basis of the total mass of the engine oil composition, the ratio (B/A) of (B) the high temperature high shear viscosity at 1×10^7 /s shear rate and 100°C to (A) the high temperature high shear viscosity at 1×10^6 /s shear rate and 100°C being 0.85 or less.

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Description

Technical Field

5 [0001] The present invention relates to an engine oil composition with excellent fuel saving properties.

Background Art

10 [0002] Recently, an engine oil has also been demanded to be effective in reducing fuel economy in order to deal with environmental issues such as global warming. Examples of techniques to improve the fuel saving properties with an engine oil include a reduction of the viscosity thereof to reduce friction at hydrodynamic lubrication regions and blend of friction modifiers to reduce friction at boundary lubrication regions.

15 [0003] However, if an engine oil is excessively reduced in viscosity not only in a gasoline engine but also particularly in a diesel engine, it would cause harmful effects on the durability of the engines due to lack of oil film thickness and increase in friction at boundary lubrication regions, and thus would cause a problem that such a mere viscosity reduction would degrade significantly the fuel saving effect.

Furthermore, friction reduction at boundary lubrication regions with friction modifiers would be deteriorated in the effect thereof due to contamination with soots that is a combustion products generated in a diesel engine.

20 Citation List

Patent Literature

[0004]

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Patent Literature 1: Japanese Patent Application Laid-Open Publication No. 2010-095662

Patent Literature 2: Japanese Patent Application Laid-Open Publication No. 2010-095663

Patent Literature 3: Japanese Patent Application Laid-Open Publication No. 2010-095664

30 Summary of Invention

Technical Problem

35 [0005] The present invention has an object to provides a highly fuel efficient engine oil composition.

Solution to Problem

40 [0006] As the result of the extensive studies of the above problems, the present invention has been accomplished on the basis of the finding that an engine oil composition comprising a lubricating base oil with specific properties blended with a star polymer as a viscosity index improver in an amount of at least 4 percent by mass or more on the basis of the total mass of the engine oil composition so as to adjust the ratio of the high temperature high shear viscosity at a shear velocity of $1 \times 10^7/\text{s}$ and 100°C to the high temperature high shear viscosity at $1 \times 10^6/\text{s}$ shear rate and 100°C can exhibit an excellent fuel saving effect while maintaining oil film thickness.

45 [0007] That is, the present invention relates to an engine oil composition comprising a lubricating base oil with a saturate content of 70 percent by mass or more and a viscosity index of 90 or greater and a star polymer as a viscosity index improver in an amount of at least 4 percent by mass or more on the basis of the total mass of the engine oil composition, the ratio (B/A) of (B) the high temperature high shear viscosity at $1 \times 10^7/\text{s}$ shear rate and 100°C to (A) the high temperature high shear viscosity at $1 \times 10^6/\text{s}$ shear rate and 100°C being 0.85 or less.

50 [0008] The present invention also relates to the foregoing engine oil composition wherein the high temperature high shear viscosity at $1 \times 10^6/\text{s}$ shear rate and 150°C is $2.6 \text{ mPa}\cdot\text{s}$ or higher.

[0009] The present invention also relates to the foregoing engine oil composition wherein the base oil has a 100°C kinematic viscosity of 3.5 to $5.0 \text{ mm}^2/\text{s}$.

[0010] Furthermore, the present invention relates to the foregoing engine oil composition for a diesel engine.

55 Advantageous Effect of Invention

[0011] The present invention provides an engine oil composition with excellent fuel saving properties.

Description of Embodiments

[0012] The present invention will be described in detail below.

[0013] The engine oil composition of the present invention is characterized in that the ratio (B/A) of (B) the high temperature high shear viscosity at $1 \times 10^6/s$ shear rate and 100°C to (A) the high temperature high shear viscosity at $1 \times 10^6/s$ shear rate and 100°C is 0.85 or less.

[0014] The present invention provides a highly fuel efficient engine oil composition by adjusting the B/A ratio to 0.85 or less. The B/A ratio is preferably 0.82 or less, more preferably 0.80 or less. Whilst, no particular limitation is imposed on the lower limit, which is, however, preferably 0.60 or greater, more preferably 0.70 or greater. A B/A ratio of greater than 0.85 is not preferable because fuel economy deteriorates.

[0015] In the engine oil composition of the present invention, (A) the high temperature high shear viscosity at $1 \times 10^6/s$ shear rate and 100°C is generally from 6.0 to 6.8 mPa·s, preferably 6.3 to 6.6 mPa·s.

[0016] The high temperature high shear viscosity at $1 \times 10^6/s$ shear rate and 150°C is the value measured in accordance with ASTM D4683-10.

[0017] In the engine oil composition of the present invention, (B) the high temperature high shear viscosity at of $1 \times 10^6/s$ shear rate and 100°C is generally from 4.7 to 5.3 mPa·s, preferably 4.8 to 5.2 mPa·s.

[0018] The high temperature high shear viscosity at $1 \times 10^6/s$ shear rate and 100°C is the value measured with a USV viscometer manufactured by PCS Instruments.

[0019] In the engine oil composition of the present invention, the high temperature high shear viscosity at $1 \times 10^6/s$ shear rate and 150°C is preferably 2.6 mPa·s or higher, more preferably 2.7 mPa·s or higher, more preferably 2.9 mPa·s or higher. If the high temperature high shear viscosity at $1 \times 10^6/s$ shear rate and 150°C is lower than 2.6 mPa·s, friction would be increased due to insufficient oil film formation, possibly resulting in a deterioration in fuel saving properties.

[0020] The base oil of the engine oil composition of the present invention is a lubricating base oil having a saturate content of 70 percent by mass or more and a viscosity index of 90 or greater.

[0021] The saturate content is preferably 80 percent by mass or more, more preferably 90 percent by mass or more, more preferably 95 percent by mass or more, most preferably 99 percent by mass or more. If the saturate content is less than 70 percent by mass, the resulting engine oil composition would not be sufficient in oxidation stability to be used under high temperature high shear lubrication conditions and would be poor in viscosity-temperature characteristics, resulting in a failure to exhibit the properties intended by the present invention.

[0022] The saturate content referred herein is the value (unit: percent by mass) measured in accordance with ASTM D 2007-11.

[0023] In the present invention, the $\%C_P$ of the base oil is preferably 60 or greater, more preferably 70 or greater. The $\%C_P$ referred herein denotes the value measured in accordance with ASTM D3238.

[0024] The viscosity index of the lubricating base oil is preferably 90 or greater, more preferably 100 or greater, more preferably 120 or greater. Whilst, the viscosity index is preferably 160 or less. If the viscosity index is less than 90, the resulting engine oil composition would not only be deteriorated in viscosity-temperature characteristics, thermal/oxidation stability and anti-evaporation properties but also likely to be increased in friction coefficient and degraded in anti-wear properties. If the viscosity index exceeds 160, the resulting engine oil composition would be likely to be degraded in low temperature viscosity characteristics.

[0025] The viscosity index referred herein denotes the viscosity index measured in accordance with JIS K 2283-1993.

[0026] Examples of the base oil of the engine oil composition of the present invention include mineral base oils and synthetic base oils. The oils may be used alone or in combination.

[0027] Examples of the mineral base oil include: paraffinic mineral base oils which can be produced by subjecting a lubricating oil fraction produced by atmospheric- and/or vacuum-distillation of a crude oil, to any one of or any combination of refining processes selected from solvent deasphalting, solvent extraction, hydrocracking, hydroisomerizing, solvent dewaxing, catalytic dewaxing, hydrotreating, sulfuric acid treatment, and clay treatment; n-paraffin base oils; and iso-paraffin base oils.

[0028] The mineral base oil used in the present invention is particularly preferably a hydrocracked base oil produced by hydrocracking an atmospheric distillation bottom oil or a lubricating oil fraction recovered from a vacuum distillation unit and subjecting the resulting product or a lubricating oil fraction recovered therefrom by distillation, to a dewaxing treatment such as solvent or catalytic dewaxing, optionally followed by distillation. The base oil is more preferably a mineral oil subjected to catalytic dewaxing.

[0029] The mineral base oil has a pour point of preferably -15°C or lower, more preferably -17.5°C or lower, more preferably -20°C or lower. The mineral base oils has a pour point of preferably higher than -35°C , more preferably -30°C or higher, more preferably -25°C or higher. This is because the resulting engine oil composition would be degraded in properties at low temperatures if the pour point is higher than -15°C and could not obtain sufficient viscosity index if the pour point is -35°C or lower. The pour point referred herein denotes the pour point measured in accordance with JIS K 2269-1987.

[0030] The mineral base oil has a NOACK value of preferably 15 percent by mass or less. The NOACK evaporation loss referred herein denotes the evaporation loss amount measured in accordance with ASTM D 5800-95.

[0031] No particular limitation is imposed on the sulfur content of the mineral base oil, which is, however, preferably 100 ppm by mass or less, more preferably 50 ppm by mass or less, more preferably 10 ppm by mass or less, particularly preferably 5 ppm by mass or less with the objective of further enhancing the thermal/oxidation stability and reducing the sulfur content. The sulfur content referred herein denotes the value measured in accordance with JIS 5S-38-2003.

[0032] No particular limitation is imposed on the aromatic content of the mineral base oil, which is, however, preferably 30 percent by mass or less, more preferably 10 percent by mass or less, more preferably 2 percent by mass or less, particularly preferably 0.5 percent by mass or less with the objective of further enhancing the thermal/oxidation stability and reducing the sulfur content.

[0033] If the aromatic content exceeds 30 percent by mass, the resulting engine oil composition would not be sufficient in oxidation stability to be used under high temperature high shear lubrication conditions and would be poor in viscosity-temperature characteristics, resulting in a failure to exhibit the properties intended by the present invention.

[0034] Examples of synthetic base oils include: poly- α -olefins and hydrogenated compounds thereof; isobutene oligomers and hydrogenated compounds thereof; isoparaffins; alkylbenzenes; alkylnaphthalenes; diesters such as ditiodecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate and di-2-ethylhexyl sebacate; polyol esters such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol 2-ethylhexanoate and pentaerythritol pelargonate; polyoxyalkylene glycols; dialkyldiphenyl ethers; and polyphenyl ethers. Preferred synthetic lubricating base oils are poly- α -olefins. Typical examples of poly- α -olefins include oligomers or cooligomers of α -olefins having 2 to 32, preferably 6 to 16 carbon atoms, such as 1-octene oligomer, decene oligomer, ethylene-propylene cooligomer, and hydrogenated compounds thereof.

[0035] The lubricating base oil has a 100°C kinematic viscosity of preferably 1 mm²/s or higher, more preferably 2 mm²/s or higher, more preferably 3 mm²/s or higher, particularly preferably 3.5 mm²/s or higher. Whilst, the lubricating base oil has a 100°C kinematic viscosity of preferably 10 mm²/s or lower, more preferably 5 mm²/s or lower. If the 100°C kinematic viscosity exceeds 10 mm²/s, the resulting engine oil composition would be degraded in low temperature viscosity characteristics and thus would not obtain sufficient fuel saving properties. If the 100°C kinematic viscosity is lower than 1 mm²/s, the resulting engine oil composition would be poor in lubricity due to insufficient oil film formation at lubricating sites and large in evaporation loss.

[0036] The 100°C kinematic viscosity referred herein denotes the 100°C kinematic viscosity defined with ASTM D-445.

[0037] The lubricating base oil has a 40°C kinematic viscosity of preferably 8 mm²/s or higher, more preferably 10 mm²/s or higher, more preferably 12 mm²/s or higher. Whilst, the lubricating base oil has a 40°C kinematic viscosity of preferably 45 mm²/s or lower, more preferably 40 mm²/s or lower, more preferably 36 mm²/s or lower. If the 40°C kinematic viscosity is lower than 8 mm²/s, the resulting engine oil composition would be degraded in low temperature viscosity characteristics and thus would not obtain sufficient fuel saving properties. If the 40°C kinematic viscosity exceeds 45 mm²/s, the resulting engine oil composition would be degraded in low temperature viscosity characteristics and thus would not obtain sufficient fuel saving properties.

[0038] The 40°C kinematic viscosity referred herein denotes the 40°C kinematic viscosity defined with ASTM D-445.

[0039] The engine oil composition of the present invention necessarily contains a star polymer as a viscosity index improver in an amount of at least 4 percent by mass or more on the basis of the total mass of the engine oil composition.

[0040] The star polymer is a compound that is well-known in the field of engine oil compositions. Such a compound and methods for preparing the compound are described in many literatures and patents (for example, U.S. Patent Nos. 4116917, 4141847, 4346193 and 4409120).

[0041] The star polymer used as a suitable viscosity index improver blended in the engine oil composition of the present invention is preferably a star polymer containing a polyalkenyl compound in its core and at least 4 or more arms containing a hydrogenated polymerized diene. More preferred are those having 5 or more arms, and more preferred are those having 6 or more arms. The star polymer contains preferably 15 or fewer arms, more preferably 10 or fewer arms.

[0042] If the number of the arm is fewer than 4, the resulting engine oil composition would be insufficient in shear stability and not be able to retain intrinsically necessary viscosity because the viscosity reduces with time during which the composition is used. If the number of the arm exceeds 15, the resulting engine oil composition would not be insufficiently reduced in viscosity when subjected to high shear and thus would not retain the fuel saving properties intended by the present invention.

[0043] The polyalkenyl compound making up the core of the star polymer is preferably divinylbenzene or a polyvinyl aliphatic compound, more preferably divinylbenzene. The diene making up the polymer arms is preferably butadiene or isoprene, and more preferably has a styrene structure at its terminal of the arms. The styrene content is preferably 2 mol% or more, more preferably 3 mol% or more. The styrene content is preferably 10 mol% or less, more preferably 7 mol% or less. If the styrene content is 2 mol% or less, the resulting engine oil composition would not obtain sufficient high temperature shear viscosity reduction. If the styrene content is more than 10 mol%, the star polymer would not be able to obtain sufficient solubility in the base oil.

[0044] The molecular weight of the star polymer is necessarily selected considering the shear stability. Specifically, the star polymer has a weight-average molecular weight of preferably from 10,000 to 1,000,000, more preferably 100,000 to 800,000, more preferably 300,000 to 600,000.

[0045] The star polymer has a PSSI (permanent shear stability index) of preferably 45 or less, more preferably 40 or less. If the PSSI exceeds 45, the resulting composition would be degraded in shear stability and thus needed to be enhanced in initial kinematic viscosity, possibly resulting in degraded fuel saving properties. If the PSSI is less than 1, the viscosity index improver would be less effective in viscosity index enhancement when it is dissolved in a lubricating base oil and thus the resulting composition would not only be poor fuel saving properties and low temperature viscosity characteristics but also increased in production cost.

[0046] The content of the star polymer in the engine oil composition of the present invention is necessarily at least 4 percent by mass or more, preferably 5 percent by mass or more on the basis of the total mass of the engine oil composition. Whilst, the content is preferably 20 percent by mass or less, more preferably 15 percent by mass or less, more preferably 10 percent by mass or less. If the content is less than 4 percent by mass, the resulting engine oil composition would not be able to reduce the high temperature high shear viscosity at 100°C and 10⁷/s shear rate while keeping the high temperature high shear viscosity at 100°C and 10⁶/s shear rate higher. If the content exceeds 20 percent by mass, the resulting engine oil composition would be degraded in shear stability.

[0047] In the present invention, the content of the star polymer is adjusted depending on the characteristics of the lubricating base oil and the characteristics of the viscosity index improver, i.e., star polymer thereby easily preparing an engine oil composition wherein the ratio (B/A) of (B) the high temperature high shear viscosity at 1 x 10⁷/s shear rate and 100°C to (A) the high temperature high shear viscosity at 1 x 10⁶/s shear rate and 100°C is 0.85 or less.

[0048] Alternatively, the engine oil composition of the present invention may contain a conventional viscosity index improver together with the star polymer used as a viscosity index improver.

[0049] Specific examples of the viscosity index improver include non-dispersant type viscosity index improvers such as copolymers of one or more monomers selected from various methacrylic acid esters or hydrogenated compounds thereof; dispersant type viscosity index improvers such as copolymers of various methacrylic acid esters further containing nitrogen compounds; and non-dispersant type or dispersant type ethylene- α -olefin copolymers (of which α -olefin may be propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene or 1-dodecene) or hydrogenated compounds thereof; polyisobutylenes or hydrogenated compounds thereof; hydrogenated compounds of styrene-diene copolymers (the diene may be butadiene or isoprene); styrene-maleic anhydride ester copolymers; and polyalkylstyrenes.

[0050] Among these viscosity index improvers, preferred are ethylene- α -olefin copolymers and hydrogenated compounds thereof in view of shear stability.

[0051] When a conventional viscosity index improver together with a star polymer is blended with the engine oil composition of the present invention, the content of the conventional viscosity index improver is preferably 10 percent by mass or less, more preferably 5 percent by mass or less, more preferably 3 percent by mass or less on the basis of the total mass of the engine oil composition.

[0052] Preferably, the engine oil composition of the present invention contains a metallic detergent.

[0053] Examples of the metallic detergent include normal or basic alkali metal/alkaline earth metal sulfonates, normal or basic alkali metal/alkaline earth metal phenates, and normal or basic alkali metal/alkaline earth metal salicylates. Examples of the alkali metal include sodium and potassium. Examples of the alkaline earth metal include magnesium, calcium and barium. Preferred are magnesium and calcium. Particularly preferred is calcium.

[0054] Although the base number of the alkaline earth metal detergent is arbitrary, it is usually from 0 to 500 mgKOH/g, preferably 150 to 450 mgKOH/g.

[0055] The term "total base number" used herein denotes the base number measured by the perchloric acid potentiometric titration method in accordance with section 7 of JIS K2501 "Petroleum products and lubricants-Determination of neutralization number".

[0056] Examples of the alkali metal or alkaline earth metal sulfonates include alkali metal or alkaline earth metal salts of alkyl aromatic sulfonic acids, produced by sulfonating an alkyl aromatic compound having a molecular weight of 100 to 1,500, preferably 200 to 700. Specific examples of the alkyl aromatic sulfonic acids include petroleum sulfonic acids and synthetic sulfonic acids.

[0057] The engine oil composition of the present invention contain a basic (low basic) sulfonate having a base number of preferably 50 mgKOH/g or less, more preferably 30 mgKOH/g or less, more preferably 20 mgKOH/g or less or preferably 5 mgKOH/g or greater, more preferably 10 mgKOH/g or greater in an amount by base number of preferably 0.01 mgKOH/g or greater, more preferably 0.02 mgKOH/g or greater, or preferably 2 mgKOH/g or less, more preferably 1 mgKOH/g or less, more preferably 0.5 mgKOH/g or less. If the base number is less than 0.01 mgKOH/g, detergency for crankcase required for the engine oil composition of the present invention would be insufficient. If the base number exceeds 2 mgKOH/g, the effect would not be enhanced.

[0058] Examples of the alkali metal/alkaline earth metal phenates include an alkali metal/alkaline earth metal salt of an alkylphenol having at least one straight-chain or branched alkyl group having 4 to 30, preferably 6 to 18 carbon atoms,

an alkylphenolsulfide produced by reacting the alkylphenol with sulfur or a Mannich reaction product of an alkylphenol produced by reacting the alkylphenol with formaldehyde.

[0059] The engine oil composition of the present invention contain an overbased phenate having a base number of preferably 150 mgKOH/g or greater, more preferably 200 mgKOH/g or greater, more preferably 250 mgKOH/g or greater, or preferably 350 mgKOH/g or less in an amount by base number of preferably 0.3 mgKOH/g or greater, more preferably 0.7 mgKOH/g or greater, more preferably 1 mgKOH/g or greater, or preferably 5 mgKOH/g or less, more preferably 3 mgKOH/g or less, more preferably 2 mgKOH/g or less. If the base number is less than 0.3 mgKOH/g, the resulting engine oil composition would be insufficient in oxidation stability required for the engine oil composition of the present invention. If the base number exceeds 5 mgKOH/g, the effect would not be enhanced.

[0060] Specific examples of the alkali metal/alkaline earth metal salicylates include alkali metal/alkaline earth metal salts of alkyl salicylic acids having at least one straight chain or branched alkyl group having 4 to 30, preferably 6 to 18 carbon atoms.

[0061] The engine oil composition of the present invention contains an overbased salicylate having a base number of preferably 150 mgKOH/g or greater, more preferably 200 mgKOH/g or greater, more preferably 250 mgKOH/g or greater, most preferably 300 mgKOH/g or greater, or preferably 350 mgKOH/g or less in an amount by base number of preferably 2 mgKOH/g or greater, more preferably 3 mgKOH/g or greater, or preferably 10 mgKOH/g or less, more preferably 7 mgKOH/g or less, more preferably 5 mgKOH/g or less. If the base number is less than 2 mgKOH/g, the engine oil composition would be insufficient in oxidation stability required for the engine oil composition of the present invention. If the base number exceeds 10 mgKOH/g, the ash content would be too much, resulting in the increased amount of combustion chamber deposits.

[0062] The above-mentioned alkali metal/alkaline earth metal sulfonate, alkali metal/alkaline earth metal phenate and alkali metal/alkaline earth metal salicylate include not only neutral salts (normal salts) but also basic salts and overbased salts (ultrabasic salts).

[0063] In the present invention, the above-described overbased basic sulfonate, overbased salicylate and basic (low basic) sulfonate are preferably used in combination with the above described ranges of base number. Most preferably, the above-described three types of metallic detergents are used in combination within the above-described ranges. Whereby, the resulting engine oil composition can achieve detergency required for an engine oil and fuel saving properties in a well-balanced manner.

[0064] When the engine oil composition of the present invention contains the metallic detergent, the content thereof is preferably 500 ppm by mass or more, more preferably 800 ppm by mass or more, more preferably 1000 ppm by mass or more on the metal basis based on the total mass of the composition. The content is preferably, 3500 ppm by mass or less, more preferably 3000 ppm by mass or less, more preferably 2600 ppm by mass or less. If the content is less than 500 ppm by mass, the resulting engine oil composition would not be able to exhibit base number retainability or high temperature detergency sufficiently. Whilst, if the content exceeds 2600 ppm by mass, the resulting engine oil composition would be increased in the sulfated ash content and facilitate the filter of an exhaust gas after-treatment devices to be clogged.

[0065] The engine oil composition of the present invention contains preferably an ashless dispersant.

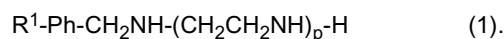
[0066] Examples of the ashless dispersant include nitrogen-containing compounds having per molecule at least one straight-chain or branched alkyl or alkenyl group having 40 to 400 carbon atoms or derivatives thereof and modified products of alkenylsuccinimides. Any one or more type selected from these ashless dispersants may be blended in the engine oil composition of the present invention.

[0067] The carbon number of the alkyl or alkenyl group of the ashless dispersant is preferably 40 to 400, more preferably 60 to 350. If the carbon number of the alkyl or alkenyl group is fewer than 40, the ashless dispersant would tend to be degraded in solubility in the lubricating base oil. Whereas, if the carbon number of the alkyl or alkenyl group is more than 400, the resulting engine oil composition would be degraded in low-temperature fluidity. The alkyl or alkenyl group may be straight-chain or branched but is preferably a branched alkyl or alkenyl group derived from oligomers of olefins such as propylene, 1-butene or isobutylene or a co-oligomer of ethylene and propylene.

[0068] The succinimide includes a mono-type succinimide wherein a succinic anhydride is added to one end of a polyamine and a bis-type succinimide wherein a succinic anhydride is added to the both ends of a polyamine.

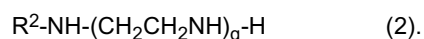
[0069] The lubricating oil composition of the present invention may contain either one or both of the mono-type and bis-type succinimides.

[0070] The ashless dispersant may be a benzylamine. Preferred examples of the benzylamine include compounds represented by formula (1):



In formula (1), R^1 is an alkyl or alkenyl group having 40 to 400 carbon atoms, preferably an alkyl or alkenyl group having 60 to 350 carbon atoms, Ph is a phenylene group, and p is an integer of 1 to 5, preferably 2 to 4.

[0071] Specific examples of the aforementioned polyamine include compounds represented by formula (2) :



In formula (2), R² is an alkyl or alkenyl group having 40 to 400 carbon atoms, preferably an alkyl or alkenyl group having 60 to 350 carbon atoms, and q is an integer of 1 to 5, preferably 2 to 4.

[0072] Specific examples of the other derivative include an organic acid-modified compound produced by allowing any of the above-described nitrogen-containing compounds to react with a monocarboxylic acid (fatty acids or the like) having 1 to 30 carbon atoms, a polycarboxylic acid having 2 to 30 carbon atoms, such as oxalic acid, phthalic acid, trimellitic acid, and pyromellitic acid or an oxygen-containing compound such as hydroxy(poly)alkylene carbonate, so as to neutralize or amidize the whole or part of the remaining amino and/or imino groups; and a sulfur modified-compound produced by allowing any of the above-described nitrogen-containing compounds to react with a sulfur compound. Alternatively, a boron-modified compound may also be used.

[0073] The boron-modified ashless dispersant is produced by boronating any ashless dispersant used for lubricating oil. Boronation is generally carried out by allowing the above-described nitrogen-containing compound to react with boric acid to neutralize the whole or part of the remaining amino and/or imino groups.

[0074] Examples of a method of producing a boronated succinimide are those disclosed in Japanese Patent Publication Nos. 42-8013 and 42-8014 and Japanese Laid-Open Patent Publication Nos. 51-52381 and 51-130408. More specifically, a boronated succinimide may be produced by mixing polyamine and polybutenylsuccinic acid (anhydride) with a boron compound such as boric acid, a boric acid ester, or a borate in a solvent including alcohols, organic solvent such as hexane or xylene, or a light fraction lubricating base oil and by heating the mixture under appropriate conditions. The boron content of the boron-modified succinimide produced in this manner is generally from 0.1 to 4.0 percent by mass.

[0075] When the lubricating oil composition of the present invention contains the ashless dispersant, the content thereof is preferably from 0.1 to 20 percent by mass, more preferably from 1 to 10 percent by mass based on the total mass of the lubricating oil composition. If the ashless dispersant content is less than 0.1 percent by mass, the resulting composition would be insufficient in friction-reduction enhancing effect. Whilst, if the content exceeds 20 percent by mass, the resulting lubricating oil composition would be extremely degraded in low temperature fluidity.

[0076] In the case of using a boron-containing ashless dispersant such as the above-described boron-containing succinimide, the boron content thereof is 0.01 percent by mass or more, preferably 0.02 percent by mass or more, more preferably 0.025 percent by mass and 0.15 percent by mass or less, preferably 0.1 percent by mass or less, particularly preferably 0.05 percent by mass or less on the basis of the total mass of the composition.

[0077] The engine oil composition of the present invention contains preferably a boron-containing succinimide and a boron-free succinimide as ashless dispersants. The ratio of the boronated succinimide to the non-boronated succinimide is preferably 0.1 or greater, more preferably 0.2 or greater, more preferably 0.3 or greater. The ratio is preferably 0.6 or less, more preferably 0.5 or less, more preferably 0.4 or less. If the ratio is less than 0.1, the heat resistance and anti-wear properties of the boronated succinimide would be insufficient. If the ratio exceed 0.6, the detergency would be insufficient.

[0078] The engine oil composition of the present invention contains preferably an antioxidant.

[0079] The anti-oxidant may be any of antioxidants that are generally used in lubricating oil such as ashless antioxidants for example phenol-based antioxidants and amine-based antioxidants and organic metal-based antioxidants. Addition of an ashless antioxidant can further enhance the antioxidation properties of the lubricating oil composition of the present invention and also can enhance the suppression properties in respect of deposit generation, anti-corrosion or anti-wear properties for lead-containing metals, and base number retainability of the lubricating oil composition of the present invention.

[0080] Examples of phenol-based antioxidants include 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-nonylphenol), 2,2'-isobutylidenebis(4,6-dimethylphenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert- α -dimethylamino-p-cresol, 2,6-di-tert-butyl-4(N,N'-dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 4,4'-thiobis(3-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)sulfide, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, 2,2'-thio-diethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], tridecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, pentaerythrityl-tetraakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], octyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, and 3-methyl-5-tert-butyl-4-hydroxyphenyl-substituted fatty acid esters. Two or more of these compounds may be used.

[0081] Examples of the amine-based antioxidant include aromatic amine-based antioxidants such as phenyl- α -naphthylamines, alkylphenyl- α -naphthylamines and dialkyldiphenylamines. A mixture of two or more these compounds may

also be used.

[0082] The above-described phenol-based antioxidant or amine-based antioxidant may be used alone but preferably is used in combination. The ratio is preferably 0.1 or greater, more preferably 0.2 or greater, more preferably 0.4 or greater of amine-based antioxidant of the total mass of the phenol-based antioxidant and amine-based antioxidant. The ratio is also preferably 0.4 or less, more preferably 0.8 or less, more preferably 0.6 or less.

[0083] If necessary, the engine oil composition of the present invention may be blended with various additives other than the above-described additives such as friction modifiers, antiwear agents (or extreme pressure additive), corrosion inhibitors, rust inhibitors, demulsifiers, metal deactivators, pour point depressants, rubber swelling agents, anti foamer and colorants alone or in combination in order to further enhance various properties of the composition.

[0084] Examples of the friction modifiers include organic molybdenum compounds and ashless friction modifiers.

[0085] Examples of the organic molybdenum compound include sulfur-containing organic molybdenum compounds such as molybdenum dithiocarbamate and molybdenum dithiophosphate, complexes of molybdenum compound and sulfur-containing organic compounds, and complexes of sulfur-containing molybdenum compound such as sulfurized molybdenum and sulfurized molybdenum acid and alkenylsuccinimide.

[0086] The organic molybdenum compound may be an organic molybdenum compound containing no sulfur as a constituent. Specific examples of the organic molybdenum compound containing no sulfur as a constituent include complexes of molybdenum compounds such as molybdenum-amine complexes and molybdenum-succinimides and sulfur-free organic compounds, molybdenum salts of organic acids, and molybdenum salts of alcohols.

[0087] When an organic molybdenum compound is used, no particular limitation is imposed on the content thereof, which is, however, preferably 50 ppm by mass or more, more preferably 100 ppm by mass or more, particularly preferably 300 ppm by mass or more on the molybdenum basis based on the total mass of the composition. Whilst, the content is preferably 2000 ppm by mass or less, more preferably 1000 ppm by mass or less, particularly preferably 800 ppm by mass or less. If the content is less than 50 ppm by mass, the resulting lubricating oil composition tends to be insufficient in thermal/oxidation stability and in particular fail to maintain detergency for a long period of time. If the content exceeds 2000 ppm by mass, the resulting composition would fail to exhibit its advantageous effects as balanced with the content and poor in storage stability.

[0088] The ashless friction modifier may be any compound that is usually used as a friction modifier for lubricating oil. Examples of the ashless friction modifier include ashless friction modifiers such as amine compounds, fatty acid esters, fatty acid amides, fatty acids, aliphatic alcohols, and aliphatic ethers, each having at least one alkyl or alkenyl group having 6 to 30 carbon atoms, in particular straight-chain alkyl or alkenyl group having 6 to 30 carbon atoms per molecule. Alternative examples include various ashless friction modifiers as exemplified in International Publication No. 2005/037967 Pamphlet.

[0089] When the ashless friction modifier is used, no particular limitation is imposed on the content thereof, which is, however, preferably 0.01 percent by mass or more, more preferably 0.1 percent by mass or more, particularly preferably 0.3 percent by mass or more on the basis of the total mass of the composition. Whilst, the content is preferably 3 percent by mass or less, more preferably 2 percent by mass or less, particularly preferably 1 percent by mass or less. If the content is less than 0.01 percent by mass, the resulting engine oil composition would be insufficient in friction reducing effect by addition of the ashless friction modifier. If the content exceeds 3 percent by mass, the effects of additives would likely be inhibited and the solubility of additives would likely be degraded.

[0090] The antiwear agent (or extreme pressure additive) may be any antiwear agents or extreme pressure additives that are used for lubricating oil. For example, sulfuric-, phosphoric- and sulfuric-phosphoric extreme pressure additives may be used.

[0091] In the present invention, a zinc alkyldithiophosphate is effective. The alkyl may be those having 3 to 12 carbon atoms. In the present invention, a zinc alkyldithiophosphate having a primary alkyl group and a secondary alkyl group is preferable with the objective of keeping the balance of extreme pressure properties and oxidation stability. The ratio of the primary to the secondary is preferably 0.3 or greater, more preferably 0.5 or greater, more preferably 0.55 or greater. The ratio is preferably 0.8 or less, more preferably 0.7 or less. If the ratio is less than 0.3, the resulting engine composition would possibly lack oxidation stability. If the ratio exceeds 0.8, the resulting engine oil composition would possibly lack extreme pressure properties. The use of the primary and secondary alkyl groups in combination may be in the same zinc alkyldithiophosphate or mixed in different zinc alkyldithiophosphates.

[0092] The content of the zinc alkyldithiophosphate is preferably 0.02 percent by mass or more, more preferably 0.05 percent by mass or more, more preferably 0.08 percent by mass or more on the phosphorus basis based on the total mass of the engine oil composition. The content is preferably 0.2 percent by mass or less, more preferably 0.15 percent by mass or less, more preferably 0.12 percent by mass or less. If the content is less than 0.02 percent by mass, sufficient extreme pressure properties would not be obtained. If the content exceeds 0.2 percent by mass, an exhaust gas post treatment device would be adversely affected.

[0093] Examples of the corrosion inhibitors include benzotriazole-, tolyltriazole-, thiadiazole-, and imidazole-types compounds.

[0094] Examples of the rust inhibitor include petroleum sulfonates, alkylbenzene sulfonates, dinonylnaphthalene sulfonates, alkenyl succinic acid esters, and polyhydric alcohol esters.

[0095] Examples of the demulsifier include polyalkylene glycol-based non-ionic surfactants such as polyoxyethylene-alkyl ethers, polyoxyethylenealkylphenyl ethers, and polyoxyethylenealkylnaphthyl ethers.

[0096] Examples of the metal deactivator include imidazolines, pyrimidine derivatives, alkylthiadiazoles, mercapto-benzothiazoles, benzotriazoles and derivatives thereof, 1,3,4-thiadiazolepolysulfide, 1,3,4-thiadiazolyl-2,5-bisdi-alkyldithiocarbamate, 2-(alkyldithio)benzimidazole, and β -(o-carboxybenzylthio)propionitrile.

[0097] Examples of the antifoamer include silicone oil with a 25°C kinematic viscosity of 1000 to 100,000 mm²/s, alkenylsuccinic acid derivatives, esters of polyhydroxy aliphatic alcohols and long-chain fatty acids, aromatic amine salts of methylsalicylate and o-hydroxybenzyl alcohol.

[0098] When these additives are contained in the lubricating oil composition, the content of the antifoamer is preferably from 0.0001 to 0.01 percent by mass and the content of the other additives is preferably from 0.01 to 10 percent by mass on the basis of the total mass of the engine oil composition.

[0099] The engine oil composition of the present invention has a viscosity index of preferably 140 or greater, more preferably 150 or greater, more preferably 160 or greater. If the viscosity index is less than 140, the resulting engine oil composition would not be able to exhibit sufficient fuel saving properties at low temperatures.

[0100] The engine oil composition of the present invention has a 100°C kinematic viscosity of preferably 5.6 mm²/s or higher, more preferably 9.3 mm²/s or higher and preferably 12.5 mm²/s or lower, more preferably 11.5 mm²/s or lower. If the 100°C kinematic viscosity exceeds 12.5 mm²/s, no fuel saving effect cannot be obtained. If the 100°C kinematic viscosity is less than 5.6 mm²/s, the hydraulic pressure of an engine would not reach a predetermined pressure and the supply of the engine oil composition would lack, possibly causing seizure.

[0101] The engine oil composition of the present invention can be applied to various engines and thus has no particular limitation but is preferably used in a diesel engine.

Examples

[0102] Hereinafter, the present invention will be described in more detail by way of the following examples and comparative examples, which should not be construed as limiting the scope of the invention.

(Evaluation method)

[0103] A motoring test was carried out using a 2 L class engine to evaluate friction reducing effects at an oil temperature of 65°C and a revolution number of 2520 rpm or 3020 rpm.

(Examples 1 and 2, Comparative Examples 1 to 3)

[0104] Various engine oil compositions were prepared using a base oil having properties set forth in Table 1 by blending thereto viscosity index improvers and other additives in the amounts set forth in Table 2. The properties of the other additives are set forth in Table 3.

[0105] Table 2 sets forth the composition and properties of each engine oil and the results of the evaluation.

[0106] As apparent from the results set forth in Table 2, the engine oils of Examples 1 and 2 wherein the B/A ratios are 0.78 and 0.79, respectively can be expected to be excellent in fuel saving properties as the torque reduction rate compared with 5W-30 evaluated by the motoring test was from 3.0 to 3.6 percent. Whilst, the engine oils of Comparative Examples 1 to 3 wherein the B/A ratios were from 0.88 to 0.94 were from 1.9 to 2.3 percent in the torque reduction rate compared with 5W-30 evaluated by the motoring test and thus could not obtain excellent torque reduction effect as those obtained by Examples 1 and 2.

[Table 1]

Kinematic viscosity	40°C	mm ² /s	20.30
	100°C	mm ² /s	4.316
Viscosity index			121
Sulfur content		ppm	<1
Nitrogen content		ppm	<1
Basic nitrogen content		ppm	<1

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(continued)

n-d-M ring analysis	MW		392
	%CA		0.0
	%CN		22.8
	%CP		77.2
	RA		0.00
	RN		1.10
Column chromatography analysis	Saturate content	mass%	99.8
	Aromatic content	mass%	0.2
	Resin content	mass%	<0.01
NOACK		mass%	14.2
Pour point		°C	-20.0

[Table 2]

			Example 1	Example 2	Comparative Example 1	Comparative Example 2	Comparative Example 3
Base oil	mass%		79.9	80.5	78.3	81.6	72.6
VM-A	in mass%		7.7	5.3			
VM-B				1.8			
VM-C					9.3		
VM-D						6	
VM-E	in mass%						15
Other additives			12.4	12.4	12.4	12.4	12.4
Kinematic viscosity	40°C	mm ² /s	58.37	54.77	38.43	39.32	40.47
	100°C	mm ² /s	10.70	10.11	9.273	10.43	9.445
Viscosity index			176	175	237	269	228
HTHS viscosity	100°C (A)	mPa·s	6.45	6.39	6.18	6.16	5.60
	10 ⁶ /s	150°C mPa·s	3.01	2.98	3.09	3.06	3.00
HTHS viscosity	100°C (B)	mPa·s	5.01	5.03	5.66	5.41	5.28
	10 ⁷ /s	150°C mPa·s	2.38	2.43	2.66	2.57	2.49
B/A			0.78	0.79	0.92	0.88	0.94
2ZR M/T	65°C, 2520 rpm	%	3.6	3.4	2.1	2.3	2.1

(continued)

			Example 1	Example 2	Comparative Example 1	Comparative Example 2	Comparative Example 3
5	(vs 5W-30)	65°C, 3020 rpm	3.5	3.0	2.2	2.3	1.9
10	Base oil base oil produced through a hydrocracking process including a catalytic dewaxing process (see Table 1 regarding the properties) VM-A star polymer containing divinyl benzene as the core arms made of isoprene, having its terminal a styrene structure the styrene content based on the polymer is 5 mol%. the styrene content was measured through ¹⁴ C NMR. effective concentration is 15%, weight-average molecular weight: 430,000 PSSI=25 VM-B mixture of OCPs of PSSI=25, PSSI=35 VM-C non-dispersant type polymethacrylate, weight average molecular weight: 450,000, PSSI: 5 VM-D non-dispersant type polymethacrylate, weight average molecular weight: 430,000, PSSI: 5 VM-E non-dispersant type polymethacrylate, weight average molecular weight: 380,000, PSSI: 25 Other additives See Table 3						

[Table 3]

Other additives	Amount
	(mass%)
Overbased Ca salicylate	1.3
(Ca content=11.4%, base number=320 mgKOH/g)	
Overbased Ca phenate	0.4
(Ca content= 10.3%, base number=280 mgKOH/g)	
Low basic Ca sulfonate	0.2
(Ca content=2.4%, base number=17 mgKOH/g)	
Non-boronated succinimide, N 0.9% 0.052% as N (N content=0.9 mass%, Mn=6580, Mw=11700)	5.8
B-based dispersant B 0.5% N 1.3% 0.026% as N	2
(N content=1.3 mass%, B content=0.5%, Mn=2700, Mw=3900)	
Hindered phenol	0.5
Zinc dialkyldithiophosphate (P: 7.1 mass%)	1.6
(primary/secondary ratio=0.6)	
Diluting oil and others	0.63

Claims

1. An engine oil composition comprising a lubricating base oil with a saturate content of 70 percent by mass or more and a viscosity index of 90 or greater and a star polymer as a viscosity index improver in an amount of at least 4 percent by mass or more on the basis of the total mass of the engine oil composition, the ratio (B/A) of (B) the high temperature high shear viscosity at $1 \times 10^7/\text{s}$ shear rate and 100°C to (A) the high temperature high shear viscosity at $1 \times 10^6/\text{s}$ shear rate and 100°C being 0.85 or less.
2. The engine oil composition according to claim 1 wherein the high temperature high shear viscosity at $1 \times 10^6/\text{s}$ shear rate and 150°C is 2.6 mPa·s or higher.

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3. The engine oil composition according to claim 1 or 2 wherein the base oil has a 100°C kinematic viscosity of 3.5 to 5.0 mm²/s.
4. The engine oil composition according to any one of claims 1 to 3, wherein it is used for a diesel engine.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/052494

A. CLASSIFICATION OF SUBJECT MATTER

C10M169/04(2006.01)i, C10M101/02(2006.01)n, C10M143/12(2006.01)n,
C10N20/02(2006.01)n, C10N30/00(2006.01)n, C10N40/25(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10M169/04, C10M101/02, C10M143/12, C10N20/02, C10N30/00, C10N40/25

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2014
Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-197399 A (JX Nippon Oil & Energy Corp.), 18 October 2012 (18.10.2012), & WO 2012/128350 A1	1-4
A	JP 2011-132340 A (JX Nippon Oil & Energy Corp.), 07 July 2011 (07.07.2011), & US 2012/0258898 A1 & EP 2518135 A1 & WO 2011/077811 A1 & CN 102686712 A & KR 10-2012-0123374 A	1-4
A	JP 6-184580 A (Showa Shell Sekiyu Kabushiki Kaisha), 05 July 1994 (05.07.1994), (Family: none)	1-4

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search
11 April, 2014 (11.04.14)

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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2011-219632 A (Cosmo Oil Lubricants Co., Ltd.), 04 November 2011 (04.11.2011), (Family: none)	1-4
A	JP 2010-095665 A (Cosmo Oil Lubricants Co., Ltd.), 30 April 2010 (30.04.2010), (Family: none)	1-4
E, A	JP 2014-051572 A (Cosmo Oil Lubricants Co., Ltd.), 20 March 2014 (20.03.2014), (Family: none)	1-4

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2010095662 A [0004]
- JP 2010095663 A [0004]
- JP 2010095664 A [0004]
- US 4116917 A [0040]
- US 4141847 A [0040]
- US 4346193 A [0040]
- US 4409120 A [0040]
- JP 428013 A [0074]
- JP 428014 A [0074]
- JP 51052381 A [0074]
- JP 51130408 A [0074]
- WO 2005037967 A [0088]