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(54) **LUBRICANT OIL COMPOSITION FOR SPARK IGNITION TYPE INTERNAL COMBUSTION ENGINE, METHOD FOR PRODUCING LUBRICANT OIL COMPOSITION, SPARK IGNITION TYPE INTERNAL COMBUSTION ENGINE USING LUBRICANT OIL COMPOSITION, AND METHOD FOR LUBRICATING INTERNAL COMBUSTION ENGINE**

(57) Provided are a lubricating oil composition for internal combustion engine capable of preventing a deterioration of the combustion state of a spark-ignition internal combustion engine, specifically, a lubricating oil composition to be used for a spark-ignition internal combustion engine in which a total tension per piston of tensions applied to the piston ring is 100 N or less, the lubricating oil composition being a lubricating oil composition includ-

ing a base oil, (A) a calcium-based detergent, at least one selected from (B1) a sodium-based additive and (B2) a magnesium-based additive, and (C) an ash-free sulfur-based additive in predetermined contents; a method for producing the lubricating oil composition; a spark-ignition internal combustion engine using the lubricating oil composition; and a method for lubricating the internal combustion engine.

EP 3 275 980 A1

Description

Technical Field

5 **[0001]** The present invention relates to a lubricating oil composition for spark-ignition internal combustion engine, a method for producing the lubricating oil composition, a spark-ignition internal combustion engine using the lubricating oil composition, and a method for lubricating the internal combustion engine.

Background Art

10 **[0002]** In view of increasing awareness of environmental issues, an improvement of fuel consumption performance of automobiles having an internal combustion engine, or the like is being demanded. As an example of the improvement of fuel consumption performance, there is known a method of reducing a friction loss to be caused due to friction between a piston ring and a cylinder inner wall of an internal combustion engine (see PTL 1). According to this method, the friction

15 loss is reduced by reducing a tension applied to the piston ring.
[0003] Meanwhile, the fuel consumption performance may also be improved by setting a viscosity of a lubricating oil composition to be used for an internal combustion engine low.

Citation List

20 Patent Literature

[0004] PTL 1: JP 2012-215238A

25 Brief Description of Drawing

[0005] FIG. 1 is a constitutional view explaining a spark-ignition internal combustion engine 1 according to an embodiment of the present invention.

30 Summary of Invention

Technical Problem

35 **[0006]** However, if the piston ring tension is excessively reduced, so-called oil loss through piston, in which the lubricating oil composition invades into a combustion chamber, is liable to be generated. In addition, even in the case of using a low-viscosity lubricating oil composition, similarly in view of the facts that a flow resistance is small and that a permeation amount in an oil ring increases, oil loss through piston is liable to be generated.

[0007] The lubricating oil composition which has invaded into the combustion chamber due to the oil loss through piston is exposed to high heat, a base oil evaporates, and a metal-based additive blended in the lubricating oil composition is concentrated. In order to improve detergency of the lubricating oil composition, for example, a calcium-based detergent

40 is added as the metal-based additive. However, it may be considered that if this metal-based additive is concentrated, a deterioration of the combustion state is caused, resulting in causing knocking.
[0008] Then, even in a spark-ignition internal combustion engine in which oil loss through piston is liable to be generated, upon determining an additive and an amount thereof for a good combustion state, and its addition amount, an object of the present invention is to provide a lubricating oil composition for spark-ignition internal combustion engine, which has excellent detergency, a method for producing the lubricating oil composition, a spark-ignition internal combustion engine

Solution to Problem

50 **[0009]** The present inventors have found that according to a lubricating oil composition having the following constitution, even if the oil loss through piston is generated, not only the combustion state is made favorable, but also excellent detergency is obtained.

[0010] The present invention provides the following.

55 [1] A lubricating oil composition for spark-ignition internal combustion engine that is a lubricating oil composition to be used for a spark-ignition internal combustion engine in which a total tension per piston of tensions applied to the piston ring is 100 N or less, the lubricating oil composition being a lubricating oil composition including a base oil,

(A) a calcium-based detergent, at least one selected from (B1) a sodium-based additive and (B2) a magnesium-based additive, and (C) an ash-free sulfur-based additive, wherein the content of the component (A) as expressed in terms of a calcium atom is 0.15% by mass or less on a basis of the total amount of the lubricating oil composition; a sum total of the content of the component (B1) as expressed in terms of a sodium atom and the content of the component (B2) as expressed in terms of a magnesium atom is 0.2% by mass or less on a basis of the total amount of the lubricating oil composition; and the content of the component (C) as expressed in terms of a sulfur atom is 0.01% by mass or more on a basis of the total amount of the lubricating oil composition.

[2] A method for producing a lubricating oil composition for spark-ignition internal combustion engine that is a lubricating oil composition to be used for a spark-ignition internal combustion engine in which a total tension per piston of tensions applied to the piston ring is 100 N or less, the method including blending a base oil with (A) a calcium-based detergent, at least one selected from (B1) a sodium-based additive and (B2) a magnesium-based additive, and (C) an ash-free sulfur-based additive in such a manner that the content of the component (A) as expressed in terms of a calcium atom is 0.15% by mass or less on a basis of the total amount of the lubricating oil composition; a sum total of the content of the component (B1) as expressed in terms of a sodium atom and the content of the component (B2) as expressed in terms of a magnesium atom is 0.2% by mass or less on a basis of the total amount of the lubricating oil composition; and the content of the component (C) as expressed in terms of a sulfur atom is 0.01% by mass or more on a basis of the total amount of the lubricating oil composition.

[3] A spark-ignition internal combustion engine in which a total tension per piston of tensions applied to the piston ring is 100 N or less, the spark-ignition internal combustion engine including using a lubricating oil composition including a base oil, (A) a calcium-based detergent, at least one selected from (B1) a sodium-based additive and (B2) a magnesium-based additive, and (C) an ash-free sulfur-based additive, wherein the content of the component (A) as expressed in terms of a calcium atom is 0.15% by mass or less on a basis of the total amount of the lubricating oil composition; a sum total of the content of the component (B1) as expressed in terms of a sodium atom and the content of the component (B2) as expressed in terms of a magnesium atom is 0.2% by mass or less on a basis of the total amount of the lubricating oil composition; and the content of the component (C) as expressed in terms of a sulfur atom is 0.01% by mass or more on a basis of the total amount of the lubricating oil composition.

[4] A method for lubricating a spark-ignition internal combustion engine in which a total tension per piston of tensions applied to the piston ring is 100 N or less, the method including undergoing lubrication using a lubricating oil composition including a base oil, (A) a calcium-based detergent, at least one selected from (B1) a sodium-based additive and (B2) a magnesium-based additive, and (C) an ash-free sulfur-based additive, wherein the content of the component (A) as expressed in terms of a calcium atom is 0.15% by mass or less on a basis of the total amount of the lubricating oil composition; a sum total of the content of the component (B1) as expressed in terms of a sodium atom and the content of the component (B2) as expressed in terms of a magnesium atom is 0.2% by mass or less on a basis of the total amount of the lubricating oil composition; and the content of the component (C) as expressed in terms of a sulfur atom is 0.01% by mass or more on a basis of the total amount of the lubricating oil composition.

Advantageous Effects of Invention

[0011] In accordance with the present invention, it is possible to provide a lubricating oil composition for internal combustion engine, in which even if the oil loss through piston is generated, not only the combustion state is made favorable, but also excellent detergency is revealed, a method for producing the lubricating oil composition, a spark-ignition internal combustion engine using the lubricating oil composition, and a method for lubricating the internal combustion engine.

Description of Embodiments

[0012] The present invention is hereunder described in more detail. [Lubricating Oil Composition for Spark-Ignition Internal Combustion Engine]

[0013] The lubricating oil composition for spark-ignition internal combustion engine according to an embodiment of the present invention is a lubricating oil composition including a base oil, (A) a calcium-based detergent, at least one selected from (B1) a sodium-based additive and (B2) a magnesium-based additive, and (C) an ash-free sulfur-based additive, wherein the content of the component (A) as expressed in terms of a calcium atom is 0.15% by mass or less on a basis of the total amount of the lubricating oil composition; a sum total of the content of the component (B1) as expressed in terms of a sodium atom and the content of the component (B2) as expressed in terms of a magnesium atom is 0.2% by mass or less on a basis of the total amount of the lubricating oil composition; and the content of the component (C) as expressed in terms of a sulfur atom is 0.01% by mass or more on a basis of the total amount of the lubricating oil composition.

<Base Oil>

[0014] As the base oil which is used in the lubricating oil composition according to an embodiment of the present invention, an arbitrary material may be properly selected and used among mineral oils and synthetic oils which have been conventionally used as the base oil of lubricating oil for internal combustion engine.

[0015] Examples of the mineral oil may include distillates obtained through atmospheric distillation of paraffin-base crude oil, intermediate-base crude oil, or naphthene-base crude oil, or distillates obtained through vacuum distillation of a residual oil of atmospheric distillation, or refined oils obtained through refining of such a distillate according to a conventional method, for example, solvent refined oil, hydrogenated refined oil, dewaxing treated oil, white clay treated oil, etc.

[0016] Examples of the synthetic oil include poly- α -olefins (PAO), such as polybutene, homopolymers or copolymers of an α -olefin (for example, homopolymers or copolymers of an α -olefin having 8 to 14 carbon atoms, e.g., an ethylene- α -olefin copolymer, etc.), etc.; various esters, such as polyol esters, dibasic acid esters, phosphate esters, etc.; various ethers, such as polyphenyl ether, etc.; polyglycols; alkylbenzenes; alkylnaphthalenes; synthetic oils obtained through isomerization of a wax (GTL wax) produced by the Fischer-Tropsch process, etc.; and the like.

[0017] In the present invention, as the base oil, a single kind of each of the aforementioned mineral oils and synthetic oils may be used, or a combination of two or more kinds thereof may be used. In addition, a mixture of the mineral oil and the synthetic oil may also be used.

[0018] Although a viscosity of the base oil may be properly determined according to an application of the lubricating oil composition, the kinematic viscosity at 100°C is generally 2 mm²/s or more and 30 mm²/s or less, preferably 2 mm²/s or more and 15 mm²/s or less, and more preferably 2 mm²/s or more and 10 mm²/s or less. When the kinematic viscosity at 100°C is 2 mm²/s or more, an evaporation loss is small; whereas when it is 30 mm²/s or less, a power loss to be caused due to viscous resistance is not so large, and hence, a fuel consumption improving effect is obtained.

[0019] As for the base oil, its viscosity index is generally 80 or more, preferably 100 or more, and more preferably 120 or more. The base oil having a viscosity index of 80 or more is small in a change of viscosity to be caused due to a change of temperature, and hence, it is preferred.

[0020] In the case of using, as the base oil, a mixture of mineral oils, a mixture of synthetic oils, or a mixture of a mineral oil and a synthetic oil, the viscosity after mixing has only to fall within the aforementioned range. As an example, the base oil containing a mineral oil having a viscosity index of 120 or more which is corresponding to Group 3 of the API classification and/or a poly- α -olefin (PAO) may be used.

[0021] It is to be noted that the content of the base oil on a basis of the total amount of the lubricating oil composition for spark-ignition internal combustion engine is preferably 60% by mass or more, more preferably 70% by mass or more, and still more preferably 80% by mass or more. In addition, an upper limit of the content is preferably 99% by mass, and more preferably 95% by mass or less.

<(A) Calcium-Based Detergent>

[0022] Examples of the calcium-based detergent (A) which is used in the lubricating oil composition according to an embodiment of the present invention include calcium salts of a sulfonate, a phenate, and a salicylate. These may be used alone or in combination of plural kinds thereof. From the viewpoint of detergency, a calcium salt of salicylate (calcium salicylate) is preferred.

[0023] The calcium salt of sulfonate has a molecular weight of preferably 300 to 1,500, and more preferably 400 to 700. Calcium salts of an alkyl aromatic sulfonic acid obtained through sulfonation of an alkyl aromatic compound are preferably used.

[0024] As the phenate, calcium salts of an alkylphenol, an alkylphenol sulfide, or a Mannich reaction product of an alkylphenol are preferably used.

[0025] As the salicylate, calcium salts of an alkylsalicylic acid are preferably used.

[0026] The alkyl group constituting the calcium-based detergent is an alkyl group having preferably 4 to 30 carbon atoms, and more preferably 6 to 18 carbon atoms, and the alkyl group may be either linear or branched. The alkyl group may be a primary alkyl group, a secondary alkyl group, or a tertiary alkyl group.

[0027] Examples of the calcium salts of a sulfonate, a phenate, and a salicylate include not only a neutral calcium-based detergent, such as a neutral calcium sulfonate, a neutral calcium phenate, and a neutral calcium salicylate, each of which is obtained by allowing the aforementioned alkyl aromatic sulfonic acid, alkylphenol, alkylphenol sulfide, Mannich reaction product of an alkylphenol, or alkylsalicylic acid, or the like to react directly with a calcium salt base, such as an oxide or hydroxide, etc., of calcium, or once forming into an alkali metal salt, such as a sodium salt, a potassium salt, etc., and then substituting with a calcium salt, or other means; but also a basic calcium-based detergent, such as a basic calcium sulfonate, a basic calcium phenate, and a basic calcium salicylate, each of which is obtained by heating a neutral calcium-based detergent and an excess of a calcium salt or a calcium base in the presence of water, etc., as well as an

overbased calcium-based detergent, such as an overbased calcium sulfonate, an overbased calcium phenate, and an overbased calcium salicylate, each of which is obtained by allowing a neutral calcium sulfonate, a neutral calcium phenate, or a neutral calcium salicylate to react with a carbonate or borate of calcium in the presence of a carbon dioxide gas, etc.

[0028] As for a metal ratio of the calcium-based detergent, a material having a metal ratio of generally 20 or less may be used alone or in admixture of two or more thereof.

[0029] It is to be noted that the metal ratio as referred to herein is expressed by (valence of metal element) x (metal element content (mol%))/(soap group content (mol%)) in the metal-based detergent (in this case, the calcium-based detergent); the metal element as referred to herein means calcium; and the soap group as referred to herein means a sulfonic acid group, a phenol group, a salicylic acid group, or the like.

[0030] From the viewpoint of detergency, the content of the calcium atom contained in the calcium-based detergent is preferably 1 to 20% by mass, more preferably 2 to 15% by mass, and still more preferably 3 to 10% by mass.

[0031] From the viewpoints of detergency and acid neutralization performance, a base number of the calcium-based detergent is preferably 10 to 600 mgKOH/g, more preferably 50 to 300 mgKOH/g, and still more preferably 100 to 250 mgKOH/g.

[0032] It is to be noted that the base number as referred to herein means a base number as measured by the hydrochloric acid method in conformity with JIS K2501, the 7th section of "Petroleum products and lubricating oils-neutralization number test method".

[0033] The content of the calcium-based detergent (A) as expressed in terms of a calcium atom is 0.15% by mass or less on a basis of the total amount of the lubricating oil composition. When the content of the component (A) is 0.15% by mass or less, even if the oil loss through piston is generated, the combustion state may be made favorable. From the same viewpoint and also taking into consideration detergency and fuel consumption performance, the content of the component (A) is preferably 0.05 to 0.15% by mass, more preferably 0.06 to 0.15% by mass, and still more preferably 0.08 to 0.15% by mass.

[0034] <(B1) Sodium-Based Additive>

[0035] The lubricating oil composition according to an embodiment of the present invention contains at least one selected from (B1) a sodium-based additive and (B2) a magnesium-based additive.

[0036] As the sodium-based additive (B1) which is used in the present invention, for example, a sodium-based detergent is preferably exemplified. Examples of the sodium-based detergent include sodium salts of a sulfonate, a phenate, and a salicylate. These may be used alone or in combination of plural kinds thereof. From the viewpoint of detergency, a sodium salt of sulfonate (sodium sulfonate) is preferred.

[0037] With respect to the aforementioned sodium-based detergent, the sulfonate, phenate, and salicylate are the same as in the explanation of the sulfonate, phenate, and salicylate for the aforementioned calcium-based detergent. In addition, the matter that a basic sodium-based detergent and an overbased sodium-based detergent may be adopted is the same as in the explanation for the calcium-based detergent.

[0038] From the viewpoint of detergency, the content of the sodium atom contained in the sodium-based detergent is preferably 1 to 25% by mass, more preferably 5 to 25% by mass, and still more preferably 10 to 20% by mass.

[0039] From the viewpoints of detergency and acid neutralization performance, a base number of the sodium-based detergent is preferably 10 to 650 mgKOH/g, more preferably 100 to 600 mgKOH/g, and still more preferably 300 to 550 mgKOH/g.

<(B2) Magnesium-Based Additive>

[0040] As the magnesium-based additive (B2) which is used in the lubricating oil composition according to an embodiment of the present invention, for example, a magnesium-based detergent is preferably exemplified. Examples of the magnesium-based detergent include magnesium salts of a sulfonate, a phenate, and a salicylate. These may be used alone or in combination of plural kinds thereof. From the viewpoint of detergency, a magnesium salt of salicylate (magnesium salicylate) is preferred.

[0041] With respect to the aforementioned magnesium-based detergent, the sulfonate, phenate, and salicylate are the same as in the explanation of the sulfonate, phenate, and salicylate for the aforementioned calcium-based detergent. In addition, the matter that a basic magnesium-based detergent and an overbased magnesium-based detergent may be adopted is the same as in the explanation for the calcium-based detergent.

[0042] From the viewpoint of detergency, the content of the magnesium atom contained in the magnesium-based detergent is preferably 1 to 25% by mass, more preferably 2 to 20% by mass, and still more preferably 5 to 20% by mass.

[0043] From the viewpoints of detergency and acid neutralization performance, a base number of the magnesium-based detergent is preferably 10 to 650 mgKOH/g, more preferably 100 to 600 mgKOH/g, and still more preferably 200 to 550 mgKOH/g.

<Contents of Components (A), (B1), and (B2)>

[0044] The lubricating oil composition according to an embodiment of the present invention contains at least one selected from (B1) a sodium-based additive and (B2) a magnesium-based additive in the content of a sum total of the content as expressed in terms of a sodium atom and the content as expressed in terms of a magnesium atom of 0.2% by mass or less on a basis of the total amount of the lubricating oil composition. When the content falls within the aforementioned range, excellent detergency is obtained, and the combustion state may be made favorable. From the same viewpoints, the content of a sum total of the content as expressed in terms of a sodium atom and the content as expressed in terms of a magnesium atom is preferably 0.005 to 0.20% by mass, more preferably 0.01 to 0.15% by mass, and still more preferably 0.01 to 0.10% by mass.

[0045] As for the relation of the calcium-based detergent (A) with the sodium-based additive (B1) and the magnesium-based additive (B2), a mass ratio of the magnesium atom (Mg) contained in the magnesium-based additive and/or the sodium atom (Na) contained in the sodium-based additive to the calcium atom (Ca) [(Mg and/or Na)/Ca] is preferably 0.03 to 3.5. When the content of the calcium-based detergent (A) and the contents of the sodium-based additive (B1) and the magnesium-based additive (B2) satisfy the aforementioned relation, excellent detergency is obtained, and the combustion state may be made favorable. From the same viewpoints, the mass ratio of the magnesium atom (Mg) and/or the sodium atom (Na) to the calcium atom (Ca) [(Mg and/or Na)/Ca] is preferably 0.05 to 2.5, more preferably 0.05 to 1, and still more preferably 0.06 to 0.8.

<(C) Ash-free Sulfur-Based Additive>

[0046] The lubricating oil composition according to an embodiment of the present invention contains (C) an ash-free sulfur-based additive.

[0047] The ash-free sulfur-based additive (C) is not particularly limited so long as it is an additive containing sulfur but not containing a metal atom. Examples thereof include sulfur-containing amine-based additives, such as a thiazine, a dithiazine, an imidazoletione, an imidazoledithione, a thiazole, a dithiazole, a thiadiazole, a dithiadiazole, a dithiocarbamate, etc.; aromatic mercaptan-based additives, such as a thiocresol, a dithiocresol, a thiophenol, a dithiophenol, etc.; thiopropionate-based additives, such as a thiopropionate, a dithiopropionate, a thiodipropionate, a dithiodipropionate, etc.; and those known as an antioxidant, an oxygen scavenger, an anti-wear agent, an extreme pressure agent, or the like, such as a sulfurized fat and oil, a sulfide, a disulfide, a sulfonic acid, a sulfur-containing phenol, etc. These may be used alone or in combination of plural kinds thereof.

[0048] As other ash-free sulfur-based additives than those described above, there are also preferably exemplified additives chiefly used as an anti-wear agent, having a structure in which a heterocyclic ring containing sulfur, for example, a sulfur-containing heterocyclic ring, such as a benzothiophene ring, a naphthothiophene ring, a dibenzothiophene ring, a thienothiophene ring, a dithienobenzene ring, a thiophene ring, a naphthothiazole ring, an isothiazole ring, a naphthoisothiazole ring, a phenothiazine ring, a phenoxathine ring, a dithianaphthalene ring, a thianthrene ring, a thioxanthene ring, a bithiophene ring, etc., is included, and at least one sulfur atom is bonded to the carbon atom of the heterocyclic ring.

[0049] Among these, dithiocarbamates, such as dialkyl dithiocarbamates having a linear or branched alkyl group having 1 to 20 carbon atoms, etc.; thiopropionates, such as dialkyl thiopropionates having a linear or branched alkyl group having 1 to 20 carbon atoms, for example, didodecyl thiopropionate, dioctadecyl thiopropionate, dimyristyl thiopropionate, dodecyl octadecyl thiopropionate, etc., etc.; thiodipropionates, such as dialkyl thiodipropionates corresponding to the foregoing thiopropionates, etc.; thiazoles, such as alkyl thiazoles, aminoalkyl thiazoles, alkyl benzothiazoles, and alkyl mercaptothiazoles, each having a linear or branched alkyl group having 1 to 20 carbon atoms, aminothiazole, benzothiazole, etc.; sulfides, such as benzyl sulfides, for example, bis(3-methyl-4-hydroxy-5-t-butylbenzyl)sulfide, etc., hydroxybenzyl sulfides, for example, tetraphthaloyl-di(2,6-dimethyl-4-t-butyl-3-hydroxybenzyl)sulfide), etc., dialkyl sulfides having a linear or branched alkyl group having 1 to 20 carbon atoms, for example, didodecyl sulfide, dioctadecyl sulfide, etc., etc.; disulfides corresponding to the aforementioned sulfides; and sulfur-containing phenols having a phenol group which may be substituted with at least a linear or branched alkyl group having 1 to 20 carbon atoms and which may have, together with the foregoing phenol group, a nitrogen-containing organic group or nitrogen-containing heterocyclic group, such as an amino group, an imino group, an amide group, an imide group, a pyridyl group, a pyrazine group, a triazine group, a benzimidazole group, etc., or a linear or branched alkyl group having 1 to 20 carbon atoms, such groups being optionally connected with each other via a divalent organic group, such as an alkylene group, a cycloalkylene group, an alkenylene group, an arylene group, etc., -NH-, -O-, -S-, -COO-, etc., for example, 2,2'-thiobis-(6-t-butyl-4-methylphenol), 4,4'-[thiobis(ethyleneoxycarbonyl ethylene)]bis(2,6-di-t-butylphenol), tridecyl-3,5-di-t-butyl-4-hydroxybenzyl thioacetate, 2,6-di-t-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino)phenol, 2-octylthio-4,6-di(3,5-di-t-butyl-4-hydroxyphenoxy)-s-triazine, etc., are preferred. As described above, the ash-free sulfur-based additive which is used in the present invention may or may not have a cyclic structure in a molecule thereof and may or may not have a hetero ring containing sulfur.

[0050] Though the content of the sulfur atom contained in the ash-free sulfur-based additive varies with the additive to be used, it is generally 1 to 40% by mass, and preferably 3 to 35% by mass. In addition, with respect to the thiopropionate-based additive, the sulfide, or the disulfide, the content of the sulfur atom is more preferably 3 to 15% by mass. When the content of the sulfur atom falls within the aforementioned range, not only the combustion state may be made favorable, but also excellent detergency and fuel consumption performance are obtained.

[0051] The content of the ash-free sulfur-containing additive (C) as expressed in terms of a sulfur atom is 0.01% by mass or more on a basis of the total amount of the lubricating oil composition. When the content of the component (C) is less than 0.01% by mass, the detergency is not obtained, and the combustion state may not be made favorable. From the same viewpoints, the content of the component (C) as expressed in terms of a sulfur atom is preferably 0.01 to 3% by mass, more preferably 0.03 to 1% by mass, and still more preferably 0.03 to 0.5% by mass.

<(D) Organic Molybdenum-Based Additive>

[0052] The lubricating oil composition according to an embodiment of the present invention may contain (D) an organic molybdenum-based additive. As the organic molybdenum-based additive, for example, a molybdenum-based friction modifier and a molybdenum-based antioxidant may be used.

[0053] As the molybdenum-based friction modifier, all of arbitrary compounds which are generally used as a friction modifier of lubricating oil for internal combustion engine may be used. For example, there is exemplified at least one selected from a molybdenum amine complex and/or oxymolybdenum dithiocarbamate sulfide, a trinuclear molybdenum-sulfur compound, and molybdenum dithiophosphate. More specifically, at least one selected from molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate (MoDTP), and an amine salt of molybdic acid may be used.

[0054] As the molybdenum-based antioxidant, there is preferably exemplified a molybdenum amine complex. As the molybdenum amine complex, hexavalent molybdenum compounds, specifically those obtained through a reaction of molybdenum trioxide and/or molybdic acid with an amine compound, for example, compounds obtained by the production method described in JP 2003-252887A, may be used.

[0055] As for a reaction ratio of the hexavalent molybdenum compound to the amine compound, a molar ratio of the Mo atom of the molybdenum compound is preferably 0.7 to 5, more preferably 0.8 to 4, and still more preferably 1 to 2.5 relative to one mole of the amine compound. As for a reaction method, a conventionally known method, for example, a method described in JP 2003-252887A, may be adopted.

[0056] In the present invention, as the molybdenum-based antioxidant, besides the aforementioned molybdenum amine complex, a sulfur-containing molybdenum complex of succinimide, as described in JP 3-22438B, JP 2004-2866A, etc., may also be used.

[0057] In the present invention, from the viewpoint of fuel consumption performance, the component (D) is preferably a molybdenum-based friction modifier. Above all, at least one selected from molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate (MoDTP), and an amine salt of molybdic acid is preferred, and molybdenum dithiocarbamate (MoDTC) is especially preferred.

[0058] The content of the component (D) is preferably 0.05 to 5% by mass, more preferably 0.1 to 3% by mass, and still more preferably 0.3 to 1.5% by mass on a basis of the total amount of the lubricating oil composition. In addition, the content of the component (D) as expressed in terms of a molybdenum atom is preferably 0.005 to 0.20% by mass on a basis of the total amount of the lubricating oil composition. From the viewpoint of maintaining the wear resistant properties, the content of the component (D) is more preferably 0.01 to 0.15% by mass, and still more preferably 0.03 to 0.15% by mass.

<Additives>

[0059] In the lubricating oil composition according to the embodiment of the present invention, it is preferred to further contain at least one additive selected from a viscosity index improver, a dispersant, an extreme pressure agent, a non-sulfur-based antioxidant, and a defoaming agent.

(Viscosity Index Improver)

[0060] Examples of the viscosity index improver include a poly(meth)acrylate (a dispersion type and a non-dispersion type), an olefin-based copolymer (for example, an ethylene-propylene copolymer, etc.), a dispersion type olefin-based copolymer, a styrene-based copolymer (for example, a styrene-diene copolymer, a styrene-isoprene copolymer, etc.), and the like. Above all, a poly(meth)acrylate is preferred.

[0061] A weight average molecular weight (M_w) of such a viscosity index improver is preferably 10,000 to 1,000,000, more preferably 30,000 to 600,000, and still more preferably 100,000 to 600,000. When the molecular weight falls within the aforementioned range, an excellent fuel consumption performance is obtained. Here, the weight average molecular

weight is a value as measured by means of GPC and obtained while making polystyrene as a calibration curve, and in detail, it is measured under the following condition.

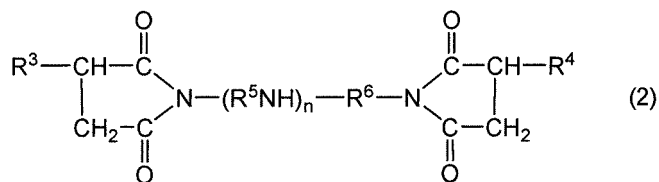
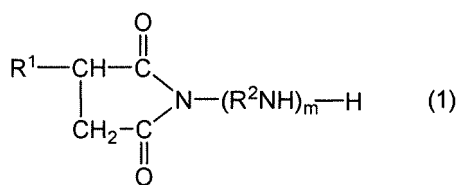
Column: Two of TSK gel GMH6
 Measurement temperature: 40°C
 Sample solution: 0.5% by mass THF solution
 Detection device: Refractive index detector
 Standard: Polystyrene

[0062] A blending amount of such a viscosity index improver may be properly determined according to a desired viscosity (for example, HTHS viscosity at 150°C), and from the standpoint of a blending effect, it is preferably 0.01 to 10.00% by mass, more preferably 0.05 to 5.00% by mass, and still more preferably 0.05 to 2.00% by mass on a basis of the lubricating oil composition.

[0063] Here, the content of the poly(meth)acrylate means the content of only the resin component composed of a poly(meth)acrylate and is the content on a basis of the solid component in which a mass of, for example, a diluent oil, etc. contained together with the poly(meth)acrylate is not included.

(Dispersant)

[0064] As the dispersant, a non-boronated imide-based dispersant may be used. The non-boronated imide-based dispersant is one generally called an imide-based dispersant. As such an imide-based dispersant, it is suitable to use a succinimide. Examples of the succinimide include compounds of a mono-type represented by the following general formula (1) and a bis-type represented by the following general formula (2).



[0065] In the aforementioned general formulae (1) and (2), R¹, R³, and R⁴ are each an alkenyl group or alkyl group having a number average molecular weight of 500 to 4,000, and R³ and R⁴ may be the same as or different from each other. The number average molecular weight of each of R¹, R³, and R⁴ is preferably 1,000 to 4,000.

[0066] When the number average molecular weight of each of R¹, R³, and R⁴ is 500 or more, the solubility in the base oil is favorable, and when it is 4,000 or less, favorable dispersibility is obtained, and excellent detergency is obtained.

[0067] R², R⁵, and R⁶ are each an alkylene group having 2 to 5 carbon atoms, and R⁵ and R⁶ may be the same as or different from each other.

[0068] m is an integer of 1 to 10, preferably an integer of 2 to 5, and more preferably 3 or 4. When m is 1 or more, the dispersibility is favorable, and when it is 10 or less, the solubility in the base oil is favorable, and excellent detergency is obtained. In addition, n is an integer of 0 to 10, preferably an integer of 1 to 4, and more preferably 2 or 3. When n falls within the aforementioned range, such is preferred from the standpoints of dispersibility and solubility in the base oil, and excellent detergency is obtained.

[0069] In general, the succinimide may be produced by allowing an alkenylsuccinic anhydride obtained through a reaction of a polyolefin with maleic anhydride, or an alkylsuccinic anhydride obtained through hydrogenation of the alkenylsuccinic anhydride, to react with a polyamine. In addition, the succinimide compound of a mono-type and the succinimide compound of a bis-type may be produced by altering a reaction ratio of the alkenylsuccinic anhydride or alkylsuccinic anhydride to the polyamine,

[0070] Examples of the polyamine may include single diamines, such as ethylenediamine, propylenediamine, butylenediamine, etc.; polyalkylenepolyamines, such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, di(methylethylene)triamine, dibutylenetriamine, tributylene tetramine, etc.; and piperazine de-

rivatives, such as aminoethylpiperazine, etc.

[0071] Taking into consideration the detergency, the content of the succinimide is preferably 0.1 to 10% by mass, more preferably 0.3 to 8% by mass, and still more preferably 0.5 to 5% by mass on a basis of the total amount of the lubricating oil composition; and the content of the succinimide as expressed in terms of a nitrogen atom is preferably 0.005 to 0.3% by mass, and more preferably 0.01 to 0.1% by mass on a basis of the total amount of the lubricating oil composition.

[0072] A boronated succinimide may be, for example, produced by allowing the aforementioned alkenylsuccinic anhydride obtained through a reaction of a polyolefin with maleic anhydride, or the alkylsuccinic anhydride, to react with the aforementioned polyamine and a boron compound.

[0073] Examples of the boron compound include boron oxide, a boron halide, boric acid, boric anhydride, a boric acid ester, an ammonium salt of boric acid, and the like.

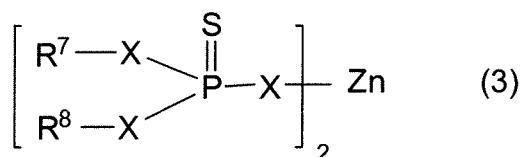
[0074] It is to be noted that a mass ratio of the boron content B to the nitrogen content N (B/N) in the boronated succinimide is generally 0.1 to 3, and preferably 0.2 to 1.

[0075] Taking into consideration the detergency, the content of the boronated succinimide is preferably 0.1 to 10% by mass, more preferably 0.3 to 8% by mass, and still more preferably 0.5 to 5% by mass on a basis of the total amount of the lubricating oil composition; and the content of the boronated succinimide as expressed in terms of a boron atom is preferably 0.005 to 0.3% by mass, and more preferably 0.01 to 0.1% by mass on a basis of the total amount of the lubricating oil composition.

[0076] In the lubricating oil composition of the present invention, a modified polybutenyl succinimide obtained by allowing the aforementioned succinimide to react with an alcohol, an aldehyde, a ketone, an alkylphenol, a cyclic carbonate, an epoxy compound, an organic acid, or the like may also be used.

(Anti-Wear Agent)

[0077] As the anti-wear agent, for example, a zinc dithiophosphate represented by the following general formula (3), such as a zinc dialkyldithiophosphate, a zinc dialkyldioxyphosphate, etc., is preferably exemplified.



[0078] In the aforementioned general formula (3), Xs are each independently an oxygen atom or a sulfur atom, and at least two of them are the same atom; and R⁷ and R⁸ are each independently a primary or secondary alkyl group having 3 to 22 carbon atoms or an alkylaryl group substituted with an alkyl group having 3 to 18 carbon atoms.

[0079] Here, examples of the primary or secondary alkyl group having 3 to 22 carbon atoms include a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, a dodecyl group, a tetradecyl group, a hexadecyl group, an octadecyl group, and an eicosyl group, each of which is primary or secondary, and the like. In addition, examples of the alkylaryl group substituted with an alkyl group having 3 to 18 carbon atoms include a propylphenyl group, a pentylphenyl group, an octylphenyl group, a nonylphenyl group, a dodecylphenyl group, and the like.

[0080] In the present invention, the aforementioned zinc dithiophosphate may be used alone or in combination of plural kinds thereof; however, from the viewpoint of enhancing the wear resistant properties, it is especially preferred to use a zinc dithiophosphate of a secondary alkyl group.

[0081] As the anti-wear agent, other anti-war agent than the aforementioned dithiophosphoric acid, such as an ash-free friction modifier, e.g., an aliphatic amine, a fatty acid ester, a fatty acid amide, a fatty acid, an aliphatic alcohol, an aliphatic ether, etc., etc., may also be used.

[0082] The content of the anti-wear agent is preferably 0.1 to 10% by mass, and more preferably 0.3 to 5% by mass on a basis of the total amount of the lubricating oil composition. In addition, in the case of using a zinc dithiophosphate as the anti-wear agent, the content of the zinc dithiophosphate as expressed in terms of a phosphorus atom is preferably 0.005 to 0.2% by mass, and more preferably 0.01 to 0.15% by mass on a basis of the total amount of the composition.

(Extreme Pressure Agent)

[0083] Examples of the extreme pressure agent include thiophosphoric acid ester-based extreme pressure agents, such as a trialkyl trithiophosphate, a triaryl trithiophosphate, a triaralkyl trithiophosphate, etc.; phosphorus-based extreme

pressure agents, such as phosphoric acid esters or phosphorous acid esters, e.g., a trialkyl phosphate, a triaryl phosphate, a trialkyl phosphonate, a trialkyl phosphite, a triaryl phosphite, a dialkyl hydrogenphosphite, etc., or amine salts thereof, etc.; organic metal-based extreme pressure agents, such as alkali metal salts or alkaline earth metal salts of a carboxylic acid or dicarboxylic acid having 3 to 60 carbon atoms; and the like. These may be used alone or in combination of plural kinds thereof.

[0084] From the viewpoints of lubricity and stability, the content of the extreme pressure agent is preferably 0.001 to 5% by mass, and more preferably 0.005 to 3% by mass on a basis of the total amount of the lubricating oil composition.

(Non-Sulfur-Based Antioxidant)

[0085] As the non-sulfur-based antioxidant, a molybdenum-based antioxidant, a phenol-based antioxidant, an amine-based antioxidant, and so on may be suitably used.

[0086] Examples of the molybdenum-based antioxidant include molybdenum amine complexes obtained through a reaction of molybdenum trioxide and/or molybdic acid with an amine compound; and the like.

[0087] As the phenol-based antioxidant, an arbitrary material may be properly selected and used among known phenol-based antioxidants which have been conventionally used as the antioxidant of lubricating oil for internal combustion engine. Examples thereof include monophenol-based antioxidants, such as alkylphenol-based antioxidants, e.g., 2,6-di-*t*-butyl-4-methylphenol, 2,6-di-*t*-butyl-4-ethylphenol, octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, etc., etc.; diphenol-based antioxidants, e.g., 4,4'-methylenebis(2,6-di-*t*-butylphenol), 2,2'-methylenebis(4-ethyl-6-*t*-butylphenol), etc.; hindered phenol-based antioxidants; and the like.

[0088] As the amine-based antioxidant, an arbitrary material may be properly selected and used among known amine-based antioxidants which have been conventionally used as the antioxidant of lubricating oil for internal combustion engine. Examples thereof include diphenylamine-based antioxidants, such as diphenylamine, an alkylated diphenylamine having an alkyl group having 3 to 20 carbon atoms, etc.; naphthylamine-based antioxidants, such as α -naphthylamine, a phenyl- α -naphthylamine substituted with an alkyl group having 3 to 20 carbon atoms, etc.; and the like.

[0089] The non-sulfur-based antioxidant may be used alone or in combination of plural kinds among those described above.

[0090] From the standpoints of a balance between effects and economy, and the like, the content of the non-sulfur-based antioxidant is preferably 0.05 to 7% by mass, and more preferably 0.05 to 5% by mass on a basis of the total amount of the lubricating oil composition.

(Defoaming Agent)

[0091] Examples of the defoaming agent include a silicone-based defoaming agent, a fluorosilicone-based defoaming agent, a fluoroalkyl ether-based defoaming agent, and the like. These may be used alone or in combination of plural kinds thereof.

[0092] From the standpoints of a balance between effects and economy, and the like, the content of the defoaming agent is preferably 0.005 to 2% by mass, and more preferably 0.01 to 1% by mass on a basis of the total amount of the lubricating oil composition.

(Other Additives)

[0093] In the lubricating oil composition for spark-ignition internal combustion engine of the present invention, other additive(s) may be further blended within the range where the purpose of the present invention is not impaired, as the need arises.

[0094] Examples of the other additive may include a rust inhibitor, such as a petroleum sulfonate, an alkylbenzene sulfonate, dinonylnaphthalene sulfonate, an alkenyl succinate ester, a polyhydric alcohol ester" etc.; an anticorrosive agent; a surfactant, such as a polyalkylene glycol-based nonionic surfactant, e.g., a polyoxyethylene alkyl ether, a polyoxyethylene alkylphenyl ether, a polyoxyethylene alkylphenyl ether, etc., etc.; a metal deactivator, such as a benzotriazole-based compound, a tolyltriazole-based compound, a thiadiazole-based compound, an imidazole-based compound, etc.; a pour point depressant, such as an ethylene-vinyl acetate copolymer, a condensate of a chlorinated paraffin and naphthalene, a condensate of a chlorinated paraffin and phenol, a polymethacrylate, a polyalkylstyrene, etc.; an oxygen scavenger, such as an aliphatic unsaturated compound, e.g., an olefin of every sort, a diene, a triene, etc., a terpene having a double bond, etc.; and the like.

[0095] The aforementioned other additive(s) may be properly blended in an amount falling within the range where the purpose of the present invention is not impaired.

<Properties of Lubricating Oil Composition for Spark-Ignition Internal Combustion Engine>

[0096] A NOACK volatile loss of the lubricating oil composition according to the embodiment of the present invention is preferably 10% by mass or more, and more preferably 10 to 15% by mass. When the NOACK volatile loss is 10% by mass or more, a low viscosity sufficient for contributing to the low fuel consumption performance is obtained; and when it is 15% by mass or less, excessive oil loss through piston may be inhibited, and an excellent effect for preventing the deterioration of the combustion state of the spark-ignition internal combustion engine is obtained. Here, the NOACK volatile loss is a value as measured in conformity with JPI-5S-41-2004.

[0097] A kinematic viscosity at 100°C of the lubricating oil composition according to the embodiment of the present invention is preferably 10 mm²/s or less, and more preferably 3 to 10 mm²/s. When the kinematic viscosity is 10 mm²/s or less, a sufficient low fuel consumption performance is obtained; and when it is 3 mm²/s or more, excessive oil loss through piston may be inhibited, and an excellent effect for preventing the deterioration of the combustion state of the spark-ignition internal combustion engine is obtained. Here, the kinematic viscosity at 100°C is a value as measured in conformity with "Testing methods for kinematic viscosity of petroleum products" as prescribed in JIS K2283.

[0098] From the viewpoints that a sufficient low fuel consumption performance is obtained and that an excellent effect for preventing the deterioration of the combustion state of the spark-ignition internal combustion engine is obtained, a sulfated ash content of the lubricating oil composition according to the embodiment of the present invention is preferably 1.0% by mass or less, more preferably 0.4 to 1.0% by mass, and still more preferably 0.5 to 1.0% by mass on a basis of the total amount of the composition. Here, the sulfated ash content is a value as measured by the method as prescribed in JIS K2272, the 5th section of "Determination of sulfated ash" of and refers to an ash content obtained by adding sulfuric acid to a carbonized residue caused by combustion of a sample and heating so that the residue has a constant mass. The sulfated ash content is generally used to know a rough amount of metal-based additives contained in the lubricating oil composition.

[0099] An HTHS viscosity at 150°C of the lubricating oil composition according to the embodiment of the present invention is preferably 1.0 to 5 mPa·s, more preferably 1.0 to 4 mPa·s, and still more preferably 1.5 to 3 mPa·s.

[0100] When the HTHS viscosity at 150°C is 1.0 mPa·s or more, the lubricating performance may be made favorable; and when it is 5 mPa·s or less, not only excellent viscosity properties at low temperatures are obtained, but also excellent fuel consumption properties are obtained. The HTHS viscosity at 150°C may also be assumed as a viscosity in a high-temperature region at the time of high-speed operation of an engine. When the HTHS viscosity at 150°C falls with the aforementioned range, it may be said that the foregoing lubricating oil composition is favorable in various properties, such as viscosity in a high-temperature region assuming the time of high-speed operation of an engine, etc.

[0101] The HTHS viscosity at 150°C is a value of high temperature high shear viscosity at 150°C as measured in conformity with ASTM D4741, and specifically, it is a value obtained by the measurement method as described in the Examples.

<Production Method of Lubricating Oil Composition for Spark-Ignition Internal Combustion Engine>

[0102] The production method of a lubricating oil composition according to the embodiment of the present invention is concerned with a method for producing a lubricating oil composition for spark-ignition internal combustion engine that is a lubricating oil composition to be used for a spark-ignition internal combustion engine including a piston having a piston ring, in which a total tension per piston of tensions applied to the piston ring is 100 N or less, the method including blending a base oil with (A) a calcium-based detergent, at least one selected from (B1) a sodium-based additive, and (B2) a magnesium-based additive, and (C) an ash-free sulfur-based additive in such a manner that the content of the component (A) as expressed in terms of a calcium atom is 0.15% by mass or less on a basis of the total amount of the lubricating oil composition; a sum total of the content of the component (B1) as expressed in terms of a sodium atom and the content of the component (B2) as expressed in terms of a magnesium atom is 0.2% by mass or less on a basis of the total amount of the lubricating oil composition; and the content of the component (C) as expressed in terms of a sulfur atom is 0.01% by mass or more on a basis of the total amount of the lubricating oil composition.

[0103] In producing the lubricating oil composition for spark-ignition internal combustion engine, at least the aforementioned component (A), component (B1), component (B2), and component (C) have only to be blended within the aforementioned content ranges. The organic molybdenum-based additive (D) and at least one selected from a viscosity index improver, a dispersant, an anti-wear agent, an extreme pressure agent, a non-sulfur-based antioxidant, and a defoaming agent as well as other additive(s) and the like may further be blended within the range where the effects of the present invention are not impaired. After separately mixing the component (A), the component (B1), the component (B2), and the component (C), and optionally, the component (D) and other additive(s), the resulting mixture may be introduced into the base oil, or the respective components may be added to and mixed with the base oil one after another. It is to be noted that the addition order does not matter.

<Spark-Ignition Internal Combustion Engine and Lubricating Method of the Spark-Ignition Internal Combustion Engine>

[0104] A spark-ignition internal combustion engine 1 according to the present embodiment is described by reference to FIG. 1.

[0105] The spark-ignition internal combustion engine 1 in the present embodiment includes a gasoline engine. Examples of a fuel which is used for the spark-ignition internal combustion engine include, in addition to a fuel oil classified into Class I petroleum, petroleum, biomass ethanol, an alcohol fuel, a liquefied petroleum gas, a natural gas, a synthetic gas, a hydrogen fuel, a bi-fuel, and the like.

[0106] The spark-ignition internal combustion engine 1 includes a cylinder block 11, a piston crank mechanism 12 installed in the cylinder block 11, and a valve mechanism 13 undergoing intake of an air-fuel mixture into the cylinder block 11 and exhaust of a combustion gas.

[0107] The cylinder block 11 is provided with a cylinder 21 and a crank case 22. The spark-ignition internal combustion engine 1 includes a spark plug F in an upper portion of the cylinder 21. In addition, the piston crank mechanism 12 includes a piston 23 and a crank shaft 24. In the piston 23, a piston ring 30 is disposed. The piston ring 30 is constituted of a top ring 31, a second ring 32, and an oil ring 33. In the spark-ignition internal combustion engine 1, a total tension per piston of tensions applied to the piston ring 30 is set to 100 N or less.

[0108] The total tension per piston of tensions applied to the piston ring 30 is a sum total of tensions applied to each of the plural rings. For example, in the spark-ignition internal combustion engine 1 shown in FIG. 1, the total tension is a sum total of tensions (n) applied to the each piston ring of the top ring 31, the second ring 32, and the oil ring 33. Here, the tension applied to the piston ring is a value as measured in conformity with "Measurement method of tangent tension" of JIS B8032-2.

[0109] The spark-ignition internal combustion engine 1 has a lubricating oil composition L. The lubricating oil composition L is stored in an oil pan 41 within the crank case 22 or an oil tank (not shown), and following the operation of the spark-ignition internal combustion engine 1, the lubricating oil composition L is circulated in the piston crank mechanism 12, the valve mechanism 13, and the like and lubricates and cools each of these parts. In the spark-ignition internal combustion engine 1, the aforementioned lubricating oil composition for spark-ignition internal combustion engine according to the embodiment of the present invention is applied as the lubricating oil composition L.

[0110] That is, the method for lubricating the spark-ignition internal combustion engine 1, in which a total tension per piston of tensions applied to the piston ring 30 is 100 N or less, with the aforementioned lubricating oil composition for spark-ignition internal combustion engine is included in the present invention.

[0111] As mentioned above, in the spark-ignition internal combustion engine in the present embodiment, the total tension per piston of tensions applied to the piston ring 30 is 100 N or less. In such a low-tension internal combustion engine, the oil loss through piston from the crank case 22 into a combustion chamber C is liable to be generated. On the other hand, in the lubricating oil composition for spark-ignition internal combustion engine according to the present embodiment, even if the oil loss through piston is generated, the generation timing of a cool flame may be delayed. In addition, so long as the total tension per piston of tensions applied to the piston ring of the spark-ignition internal combustion engine can be lowered, in the case where the spark-ignition internal combustion engine is mounted in an automobile, it is possible to contemplate to improve the fuel consumption performance of the automobile. For this reason, the lubricating oil composition for spark-ignition internal combustion engine may be preferably used for a low-tension spark-ignition internal combustion engine, in which a total tension per piston of tensions applied to the piston ring 30 is 95 N or less, and moreover 90 N or less.

[0112] Meanwhile, though a lower limit value of the total tension per piston of tensions applied to the piston ring 30 is not particularly limited, it is preferably 5 N or more, more preferably 10 N or more, and still more preferably 15 N or more. When the lower limit value is 5 N or more, the oil loss through piston is hardly generated.

Examples

[0113] Next, the present invention is specifically described by reference to Examples, but it should be construed that the present invention is by no means limited by these Examples at all. In the following Examples and so on, measurement of properties and performance evaluation of lubricating oil compositions were carried out in the following manners.

[Evaluation Methods]

<Properties of Lubricating Oil Composition>

[0114] Respective properties of a base oil, an additive, and a lubricating oil composition were measured in the following methods.

EP 3 275 980 A1

(1) Noack Volatile Loss of Lubricating Oil Composition:

The measurement was conducted in conformity with JPI-5S-41-2004.

(2) Kinematic Viscosity:

The kinematic viscosity at each of 40°C and 100°C was measured in conformity with "Testing methods for kinematic viscosity of petroleum products" as prescribed in JIS K2283-2000.

(3) HTHS Viscosity at 150°C (High Temperature High Shear Viscosity):

With respect to the objective lubricating oil composition, the viscosity after shearing at 150°C and a shear rate of $10^6/s$ was measured in conformity with ASTM D4741.

(4) Base Number:

The measurement was conducted by the hydrochloric acid method in conformity with JIS K2501, "Petroleum products and lubricating oils-neutralization value test method".

(5) Amounts of Calcium Atom, Sodium Atom, Magnesium Atom, Sulfur Atom, Phosphorus Atom, Boron Atom, and Molybdenum Atom:

The measurement was conducted in conformity with JPI-5S-38-92.

(6) Content of Nitrogen Atom:

The measurement was conducted in conformity with JIS K2609.

<Combustibility Test>

[0115] The specification and operating condition of a spark-ignition internal combustion engine used in the combustibility test are shown below.

- (1) Bore diameter: 85 mm
- (2) Stroke length: 70 mm
- (3) Displacement: 397 cm³
- (4) Compression ratio: 8/1
- (5) Number of revolution of engine: 1,400 rpm
- (6) Air-fuel ratio: Theoretical air-fuel ratio
- (7) Ignition timing: -5° aTDC

[0116] In the aforementioned engine, a small-sized quartz window was provided in a cylinder head, and a light from a xenon light source was transmitted through a right end portion of a combustion chamber, thereby carrying out light absorption measurement in the end portion. The xenon light having been transmitted through the combustion chamber was introduced into a spectroscope by optical fibers and spectrally separated in a wavelength of 293.1 nm. This wavelength is a wavelength at which strong absorption occurs in formaldehyde. The formaldehyde is an important chemical species such that it is produced at the time of generation of a cool flame and abruptly reduced with the movement into a blue flame and the generation of a hot flame. The spectrally separated light was converted into an electric signal by a photomultiplier tube, and by using a transmission light intensity E0 in a state where no reaction takes place and a transmission light intensity E1 at an arbitrary crank angle, an absorbance was defined as $(E0 - E1)/E0$ and calculated. A timing at which an increase of this absorbance started was defined as a generation timing of a cool flame, and a timing at which the absorbance abruptly decreased was defined as an autoignition timing. In addition, a pressure sensor was provided within the combustion chamber, and an amplitude of pressure vibration generated at the time of knocking was measured and defined as an index of the knock intensity.

[0117] In an internal combustion engine provided with a reciprocating piston, a mixed gas composed of a fuel and an oxidizing agent is compressed by the piston in a cylinder interior, whereby the temperature and pressure increase. At this time, before original ignition accompanied by definite heat generation is generated, the mixed gas ignites itself due to the compression, thereby causing combustion. This is called low-temperature autoignition. The low-temperature

autoignition includes a stage at which a low-temperature flame called a cool flame or a blue flame reveals, and an active chemical species is produced, leading to generation and propagation of a hot flame accompanied by abrupt heat generation.

[0118] In a spark-ignition internal combustion engine, an active chemical species is forcedly provided by an ignition source, such as an electric spark, etc., leading to generation and propagation of a hot flame. For this reason, in the case where the progress of a low-temperature autoignition reaction is faster than the generation and propagation of a hot flame originated from the ignition, a deterioration of the combustion state or abrupt pressure vibration is generated. In view of the fact that this abrupt pressure vibration becomes a cause of knocking, as described above, an amplitude of pressure vibration generated at the time of knocking was measured and defined as an index of the knock intensity.

[0119] After the aforementioned engine was subjected to a warming up operation to set a spark plug washer temperature to 440 to 480K, a sample prepared by blending in each of sample compositions of Test Examples 1 to 13 shown in Tables 1 to 3 was forcedly introduced into the combustion chamber through a fuel injector, and a fuel oil was replaced in the sample and combusted. Since a lubricant base oil is high in viscosity as compared with the fuel oil, it is difficult to spray a lubricating oil composition by a fuel injector. Thus, an additive was mixed in PRF50 that is a fuel oil having an octane number of 50 in place of the lubricant base oil, thereby preparing the sample prepared by blending in each of sample compositions of Test Examples 1 to 13 shown in Tables 1 to 3.

[0120] An amount of the lubricating oil composition which invades into the combustion chamber from a crank chamber due to oil loss through piston is not constant but is largely dominated by the probability. On the occasion when a large amount of the lubricating oil composition accidentally invades into the combustion chamber, and droplets of the lubricating oil composition itself are scattered into the interior of the combustion chamber, the influence which the lubricating oil composition gives to the combustion becomes maximum. For that reason, by forcedly scattering the droplets having specified properties into the interior of the combustion chamber to analyze the combustion state, the maximum influence which the composition may give can be evaluated. Then, in the present combustibility test, assuming the case where in a low-tension spark-ignition internal combustion engine, in which a total tension per cylinder of tensions applied to the piston ring is 100 N or less, and the oil loss through piston is liable to be generated, a large amount of the lubricating oil composition accidentally invaded into the combustion chamber, as described above, the sample was forcedly introduced into the combustion chamber.

[0121] It is to be noted that in the spark-ignition internal combustion engine used for the combustibility test, a general lubricating oil composition is filled in the crank chamber and the like; however, since the invasion of the lubricating oil composition from the crank chamber into the combustion chamber is restricted, it is not necessary to consider the influence against the results of the present test.

[0122] In view of the fact that both the lubricant base oil and the fuel oil are a hydrocarbon, it may be considered that a difference in reactivity with the additive is small and that the influence which droplets of a fuel oil containing a certain concentration of an organic metal-based additive give to the combustion is close to that in the case where droplets of a lubricant base oil containing the foregoing additive are scattered within the combustion chamber. For that reason, as a result of the test, so far as the fuel oil containing a predetermined additive does not influence the combustion, even in the case where the lubricating oil composition similarly containing the foregoing predetermined additive invaded into the combustion chamber, it may be judged that the combustion is not influenced. Conversely, so far as the combustion is influenced, when the lubricating oil composition invades into the combustion chamber in the actual equipment, it may be judged that there is a possibility that the combustion is influenced.

[0123] The comprehensive evaluation was made according to the following criteria. In the case where the evaluation is A or B, the generation timing of a cool flame is equal or close to the timing of usual spark discharge, and the value of pressure vibration is low, and hence, it may be said that the deterioration of the combustion state was inhibited, and the knocking was inhibited. On the other hand, in the case where the evaluation is C, the generation timing of a flame is faster than the timing of usual spark discharge, and the value of pressure vibration is high, and hence, it may be said that the combustion state was deteriorated, and the knocking was promoted.

<Criteria of Comprehensive Evaluation>

[0124]

A: As compared with a standard sample, the generation timing of a cool flame is not accelerated, and an increase of the pressure vibration is 0.04 or less in terms of a ratio to the standard.

B: As compared with a standard sample, the generation timing of a cool flame is accelerated, but an increase of the pressure vibration is 0.04 or less in terms of a ratio to the standard.

C: As compared with a standard sample, the generation timing of a cool flame is accelerated, and an increase of the pressure vibration is more than 0.04 in terms of a ratio to the standard.

EP 3 275 980 A1

Table 1

			Test Example				
			1	2	3	4	5
Sample composition	Fuel oil	-	Whole amount	Remainder	Remainder	Remainder	Remainder
	Component (A)	% by volume	-	-	-	-	-
	Component (B1)	% by volume	-	0.70	0.35	0.18	0.04
	Component (B2)	% by volume	-	-	-	-	-
Characteristic values	Component (A)	% by mass (Ca)	-	-	-	-	-
	Component (B1)	% by mass (Na)	-	0.21	0.11	0.05	0.01
	Component (B2)	% by mass (Mg)	-	-	-	-	-
Measurement results	Acceleration of generation timing of cool flame		Standard	No	No	No	No
	Pressure vibration [MPa]		0.016	0.014	0.027	0.013	0.009
Comprehensive evaluation			A	A	A	A	A

Table 2

			Test Example				
			6	7	8	9	10
Sample composition	Fuel oil	-	Whole amount	Remainder	Remainder	Remainder	Remainder
	Component (A)	% by volume	-	-	-	-	-
	Component (B1)	% by volume	-	-	-	-	-
	Component (B2)	% by volume	-	2.25	1.50	0.33	0.08
Characteristic values	Component (A)	% by mass (Ca)	-	-	-	-	-
	Component (B1)	% by mass (Na)	-	-	-	-	-
	Component (B2)	% by mass (Mg)	-	0.33	0.22	0.06	0.01

EP 3 275 980 A1

(continued)

		Test Example				
		6	7	8	9	10
Measurement results	Acceleration of generation timing of cool flame	Standard	Yes	Yes	No	No
	Pressure vibration [MPa]	0.022	0.183	0.114	0.055	0.024
Comprehensive evaluation		A	C	C	A	A

Table 3

			Test Example		
			11	12	13
Sample composition	Fuel oil	-	Whole amount	Remainder	Remainder
	Component (A)	% by volume	-	2.0	1.0
	Component (B1)	% by volume	-	-	-
	Component (B2)	% by volume	-	-	-
Characteristic values	Component (A)	% by mass (Ca)	-	0.22	0.11
	Component (B1)	% by mass (Na)	-	-	-
	Component (B2)	% by mass (Mg)	-	-	-
Measurement results	Acceleration of generation timing of cool flame		Standard	Yes	Yes
	Pressure vibration [MPa]		0.017	0.061	0.024
Comprehensive evaluation			A	C	B

[0125] It is to be noted that the various additives used are as follows.

- Fuel oil:

Mixture of equal parts of normal-heptane and isooctane (PRF50)

- Component (A):

Calcium-based detergent: Ca salicylate (Ca content: 7.8% by mass, base number: 225 mgKOH/g)

- Component (B1):

Sodium-based detergent: Na sulfonate (Na content: 16.3% by mass, base number: 460 mgKOH/g)

- Component (B2):

Magnesium-based detergent: Mg salicylate (Mg content: 6.9% by mass, base number: 300 mgKOH/g)

[0126] From the results of Table 1, it is understood that in the sodium-based additive (B1), when its content as expressed in terms of a sodium atom is 0.21% by mass or less, the generation timing of the cool flame is not accelerated, and the increase of the pressure vibration is suppressed. From the results of Table 2, it is understood that in the magnesium-based additive (B2), when its content as expressed in terms of a magnesium atom is less than 0.22% by mass, the generation timing of the cool flame is not accelerated, and the increase of the pressure vibration is suppressed. In addition, from the results of Table 3, it is understood that in the calcium-based detergent (A), when its content as

EP 3 275 980 A1

expressed in terms of a calcium atom is less than 0.22% by mass, though the generation timing of the cool flame is accelerated, the increase of the pressure vibration is suppressed. From these results, it is understood that when the contents of the component (A), the component (B1), and the component (B2) in the lubricating oil composition are set to the aforementioned ranges, respectively, the deterioration of the combustion state of the spark-ignition internal combustion engine may be prevented.

(Hot Tube Test (at 280°C))

[0127] The hot tube test was carried out by setting a test temperature to 280°C and a test time to 16 hours and making other conditions in conformity with those of JPI-5S-55-99. Conforming to JPI-5S-55-99, a lacquer attached to a test tube after the test was evaluated between Point 0 (black) and Point 10 (colorless) and evaluated at every 0.5 point. It is meant that as the numerical value is large, a deposit is less, and the detergency is favorable. As for the grade point, though Points 7 or more are evaluated to be acceptable.

Table 4

			Example								Comparative Example	
			1	2	3	4	5	6	7	8	1	2
Composition	Base oil	-	Remainder	Remainder	Remainder	Remainder	Remainder	Remainder	Remainder	Remainder	Remainder	Remainder
	Component (A)	% by mass	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
	Component (B1)	% by mass	0.3	-	-	-	-	-	-	-	-	-
	Component (B2)	% by mass	-	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	-
	Component 1 (C)	% by mass	0.5	0.5	0.2	-	-	-	-	-	-	-
	Component 2 (C)	% by mass	-	-	-	0.9	-	-	-	-	-	0.9
	Component 3 (C)	% by mass	-	-	-	-	0.5	-	-	-	-	-
	Component 4 (C)	% by mass	-	-	-	-	-	0.8	-	-	-	-
	Component 5 (C)	% by mass	-	-	-	-	-	-	0.6	1.7	-	-
	Component (D)	% by mass	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
	Dispersant 1	% by mass	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
	Dispersant 2	% by mass	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	Anti-wear agent	% by mass	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
	Viscosity index improver	% by mass	Adjusted*2	Adjusted*2	Adjusted*2	Adjusted*2	Adjusted*2	Adjusted*2	Adjusted*2	Adjusted*2	Adjusted*2	Adjusted*2

(continued)

		Example										Comparative Example	
		1	2	3	4	5	6	7	8	1	2		
	Other additives	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0		
	Component (A)	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14		
	Component (B1)	0.05	-	-	-	-	-	-	-	-	-		
	Component (B2)	-	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	-		
	Component (C)	0.15	0.15	0.05	0.05	0.05	0.05	0.05	0.15	-	0.05		
	(Mg + Na)/Ca *1	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36		
	HTHS viscosity at 150°C (mPa·s)	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3		
	Kinematic viscosity at 100°C (mm ² /s)	7.2	7.3	7.2	7.3	7.3	7.3	7.2	7.2	7.2	7.1		
	Kinematic viscosity at 40°C (mm ² /s)	30.2	30.8	30.5	30.6	31.1	31.2	30.6	31.1	30.5	29.9		
	Sulfated ash content (% by mass)	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.7		
	NOACK volatile loss (%)	14	14	14	14	14	14	14	14	14	14		
	Hot tube test (point)	10	8	7.5	7	7	7	7	8	6	6.5		

EP 3 275 980 A1

[0128] In the table, the terms "% by mass (Ca)", "% by mass (Na)", "% by mass (Mg)", and "% by mass (S)" are the contents as expressed in terms of a calcium (Ca) atom, a sodium (Na) atom, a magnesium (Mg) atom, and a sulfur (S) atom, respectively on a basis of the total amount of the lubricating oil composition.

*1: A mass ratio of the magnesium atom (Mg) and/or the sodium atom (Na) to the calcium atom (Ca) [(Mg and/or Na)/Ca]

*2: Adjusted to the amount at which the HTHS viscosity at 150°C was 2.3 mPa·s

[0129] The various additives used are as follows.

- Base oil:

Paraffin-based mineral oil (kinematic viscosity at 100°C: 4.1 mm²/s, kinematic viscosity at 40°C: 17.8 mm²/s, viscosity index: 134)

- Component (A):

Calcium-based detergent: Ca salicylate (Ca content: 7.8% by mass, base number: 225 mgKOH/g)

- Component (B1):

Sodium-based detergent: Na sulfonate (Na content: 16.3% by mass, base number: 460 mgKOH/g)

- Compound (B2):

Magnesium-based detergent: Mg salicylate (Mg content: 6.9% by mass, base number: 320 mgKOH/g)

- Component 1 (C):

Dialkyl dithiocarbamate (sulfur content: 30.3% by mass, nitrogen content: 6.6% by mass)

- Component 2 (C):

Dialkyl thiodipropionate (sulfur content: 5.6% by mass)

- Component 3 (C):

Sulfur-containing phenol (sulfur content: 11.0% by mass)

- Component 4 (C):

Hydroxybenzyl sulfide (sulfur content: 6.8% by mass)

- Component 5 (C):

Benzothiazole (sulfur content: 8.9% by mass, nitrogen content: 4.7% by mass)

- Component (D):

Molybdenum dithiocarbamate (MoDTC, Mo content: 10% by mass)

- Dispersant 1:

Polymeric alkenyl succinimide (base number: 24 mgKOH/g, nitrogen content: 1% by mass)

- Dispersant 2:

Boronated alkenyl succinimide (base number: 25 mgKOH/g, boron content: 1.3% by mass)

- Anti-wear agent:

Zinc dithiophosphate (zinc content: 8.9% by mass, phosphorus content: 7.4% by mass, sulfur content: 15.0% by mass)

- Viscosity index improver:

Polymethacrylate (PMA, Mw = 510,000, resin concentration: 19% by mass)

- Other additives:

Diphenylamine, alkylphenol, copper deactivator, silicone-based defoaming agent, and polymethacrylate-based pour point depressant

[0130] From the aforementioned Tables 1 to 3, it was confirmed that even if the oil loss through piston is generated, even at the highest estimate, even in the case where the additives are contained in the quantities shown in Tables 1 to 3 in the combustion chamber of the cylinder, the deterioration of the combustion state does not take place. In view of this fact, the lubricating oil compositions shown in Table 4 were prepared as the composition in which the deterioration of the combustion state does not take place.

[0131] According to the lubricating oil compositions of Examples 1 to 8 as shown in Table 4, it was confirmed that the lubricating oil compositions in which the calcium-based detergent (A), the sodium additive (B1) and/or the magnesium additive (B2), and the various ash-free sulfur-based additives (C) are blended in the predetermined blending ratios have excellent detergency, and that from the results of Tables 1 to 3, they have an excellent effect for preventing the deterioration of the combustion state of the spark-ignition internal combustion engine.

[0132] On the other hand, it was confirmed that the lubricating oil composition of Comparative Example 1 not containing the ash-free sulfur-based additive (C) and the lubricating oil composition of Comparative Example 2 containing the ash-free sulfur-based additive (C) but not containing the sodium additive (B1) and the magnesium additive (B2) were inferior in detergency. In addition, from comparison of the Examples with Comparative Example 1 (in particular, comparison of Example 2 with Comparative Example 1), an effect that by using a combination of the ash-free sulfur-based additive (C) with the calcium-based detergent and the sodium additive (B1) and/or the magnesium additive (B2), the detergency is more improved was confirmed.

Reference Signs List

[0133]

- 1: Spark-ignition internal combustion engine
- 11: Cylinder block
- 12: Piston crank mechanism
- 13: Valve mechanism
- 21: Cylinder
- 22: Crank case
- 23: Piston
- 24: Crank shaft
- 30: Piston ring
- 31: Top ring
- 32: Second ring
- 33: Oil ring
- 41: Oil pan
- C: Combustion chamber
- F: Spark plug
- L: Lubricating oil composition

Claims

1. A lubricating oil composition for spark-ignition internal combustion engine that is a lubricating oil composition to be used for a spark-ignition internal combustion engine in which a total tension per piston of tensions applied to the

piston ring is 100 N or less, the lubricating oil composition being a lubricating oil composition comprising a base oil,

(A) a calcium-based detergent,

at least one selected from (B1) a sodium-based additive and (B2) a magnesium-based additive, and (C) an ash-free sulfur-based additive, wherein

the content of the component (A) as expressed in terms of a calcium atom is 0.15% by mass or less on a basis of the total amount of the lubricating oil composition;

a sum total of the content of the component (B1) as expressed in terms of a sodium atom and the content of the component (B2) as expressed in terms of a magnesium atom is 0.2% by mass or less on a basis of the total amount of the lubricating oil composition; and

the content of the component (C) as expressed in terms of a sulfur atom is 0.01% by mass or more on a basis of the total amount of the lubricating oil composition.

2. The lubricating oil composition for spark-ignition internal combustion engine according to claim 1, wherein a NOACK volatile loss of the lubricating oil composition is 10% by mass or more.

3. The lubricating oil composition for spark-ignition internal combustion engine according to claim 1 or 2, wherein the calcium-based detergent (A) is a calcium-based detergent having a base number of 10 to 600 mgKOH/g.

4. The lubricating oil composition for spark-ignition internal combustion engine according to any one of claims 1 to 3, wherein the sodium-based additive (B1) is a sodium-based detergent having a base number of 10 to 600 mgKOH/g.

5. The lubricating oil composition for spark-ignition internal combustion engine according to any one of claims 1 to 4, wherein the magnesium-based additive (B2) is a magnesium-based detergent having a base number of 10 to 600 mgKOH/g.

6. The lubricating oil composition for spark-ignition internal combustion engine according to any one of claims 1 to 5, further comprising (D) an organic molybdenum-based additive, the content of the component (D) being 0.005 to 0.20% by mass as expressed in terms of a molybdenum atom on a basis of the total amount of the lubricating oil composition.

7. The lubricating oil composition for spark-ignition internal combustion engine according to any one of claims 1 to 6, which has a sulfated ash content of 1.0% by mass or less on a basis of the total amount of the composition.

8. The lubricating oil composition for spark-ignition internal combustion engine according to any one of claims 1 to 7, wherein the content of the component (A) as expressed in terms of a calcium atom is from 0.05 to 0.15% by mass on a basis of the total amount of the lubricating oil composition, and a mass ratio of the magnesium atom (Mg) and/or the sodium atom (Na) to the calcium atom (Ca) [(Mg and/or Na)/Ca] is from 0.03 to 3.5.

9. The lubricating oil composition for spark-ignition internal combustion engine according to any one of claims 1 to 8, further comprising at least one additive for lubricating oil selected from a viscosity index improver, a dispersant, an anti-wear agent, an extreme pressure agent, a non-sulfur-based antioxidant, and a defoaming agent.

10. The lubricating oil composition for spark-ignition internal combustion engine according to any one of claims 1 to 9, wherein the spark-ignition internal combustion engine is a gasoline engine.

11. A method for producing a lubricating oil composition for spark-ignition internal combustion engine that is a lubricating oil composition to be used for a spark-ignition internal combustion engine in which a total tension per piston of tensions applied to the piston ring is 100 N or less, the method comprising:

blending a base oil with

(A) a calcium-based detergent,

at least one selected from (B1) a sodium-based additive and (B2) a magnesium-based additive, and

(C) an ash-free sulfur-based additive in such a manner that

the content of the component (A) as expressed in terms of a calcium atom is 0.15% by mass or less on a basis of the total amount of the lubricating oil composition;

a sum total of the content of the component (B1) as expressed in terms of a sodium atom and the content of

the component (B2) as expressed in terms of a magnesium atom is 0.2% by mass or less on a basis of the total amount of the lubricating oil composition; and
the content of the component (C) as expressed in terms of a sulfur atom is 0.01% by mass or more on a basis of the total amount of the lubricating oil composition.

- 5
12. A spark-ignition internal combustion engine in which a total tension per piston of tensions applied to the piston ring is 100 N or less, the spark-ignition internal combustion engine comprising using a lubricating oil composition comprising:

10 a base oil,

(A) a calcium-based detergent,
at least one selected from (B1) a sodium-based additive and (B2) a magnesium-based additive, and
(C) an ash-free sulfur-based additive, wherein

15 the content of the component (A) as expressed in terms of a calcium atom is 0.15% by mass or less on a basis of the total amount of the lubricating oil composition;
a sum total of the content of the component (B1) as expressed in terms of a sodium atom and the content of the component (B2) as expressed in terms of a magnesium atom is 0.2% by mass or less on a basis of the total
20 amount of the lubricating oil composition; and
the content of the component (C) as expressed in terms of a sulfur atom is 0.01% by mass or more on a basis of the total amount of the lubricating oil composition.

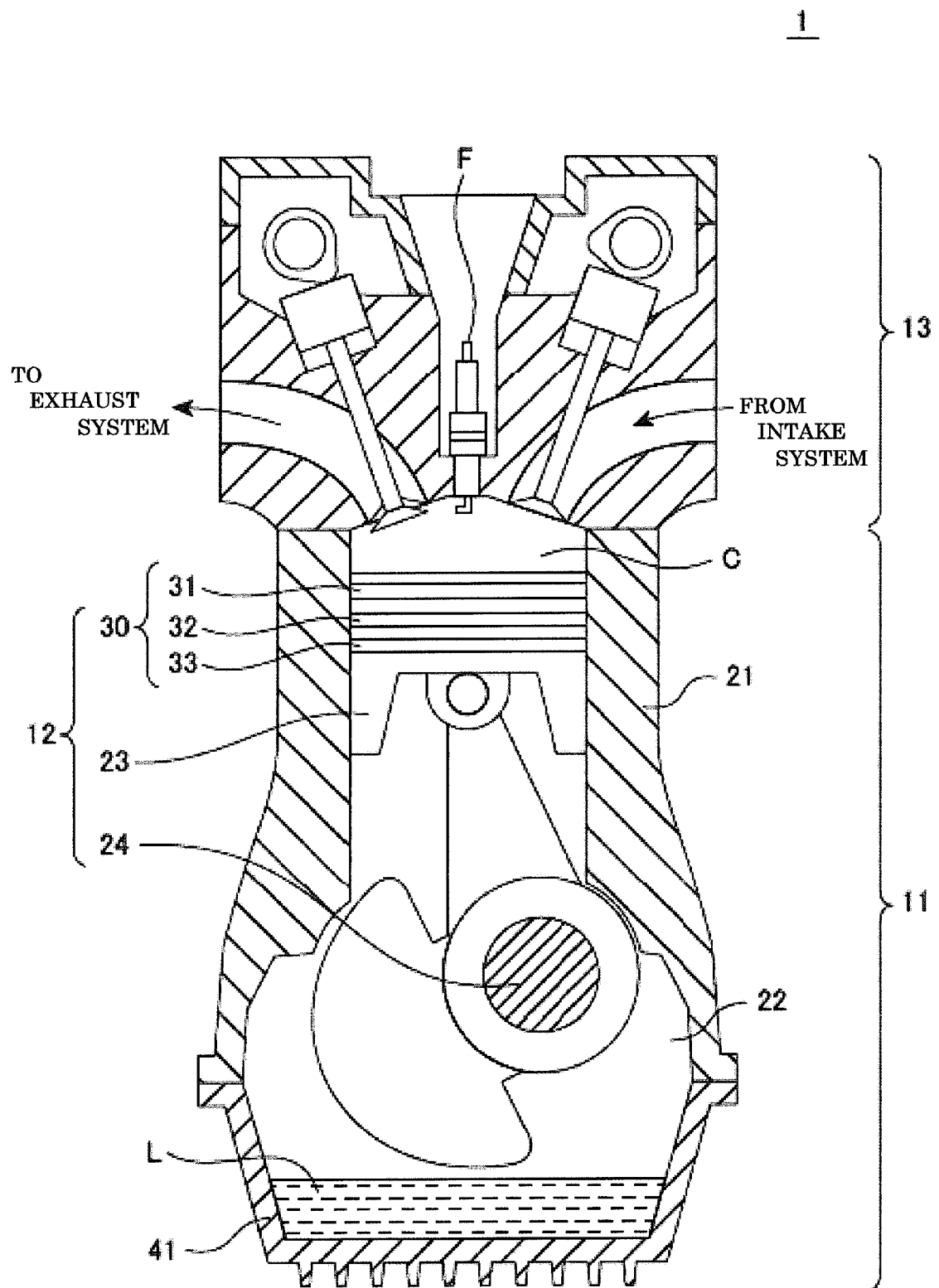
- 25 13. A method for lubricating a spark-ignition internal combustion engine in which a total tension per piston of tensions applied to the piston ring is 100 N or less, the method comprising undergoing lubrication using a lubricating oil composition comprising:

a base oil,

30 (A) a calcium-based detergent,
at least one selected from (B1) a sodium-based additive and (B2) a magnesium-based additive, and
(C) an ash-free sulfur-based additive, wherein

35 the content of the component (A) as expressed in terms of a calcium atom is 0.15% by mass or less on a basis of the total amount of the lubricating oil composition;
a sum total of the content of the component (B1) as expressed in terms of a sodium atom and the content of the component (B2) as expressed in terms of a magnesium atom is 0.2% by mass or less on a basis of the total amount of the lubricating oil composition; and
40 the content of the component (C) as expressed in terms of a sulfur atom is 0.01% by mass or more on a basis of the total amount of the lubricating oil composition.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/059450

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet.

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, C10M135/00, C10M139/00, C10N10/02, C10N10/04, C10N10/12, C10N20/00, C10N30/02, C10N30/04, C10N30/06, C10N30/10, C10N30/18, 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 1996-2016
Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2011/112372 A1 (LUBRIZOL CORP.), 15 September 2011 (15.09.2011), 0052, 0056, 0074 to 0081, 0087; examples; claims & JP 2013-522392 A & US 2013/0150273 A1 examples & EP 2545148 A1 & CA 2792665 A & CN 102884163 A	1-13

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
10 June 2016 (10.06.16)Date of mailing of the international search report
21 June 2016 (21.06.16)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/059450

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 4-261495 A (The Lubrizol Corp.), 17 September 1992 (17.09.1992), claims; 0287; examples & US 5422022 A examples & EP 462319 A1 & DE 69014866 C & NO 905227 A & AU 6702390 A & ES 2067640 T & FI 910751 A & CA 2030481 A & AT 115176 T & BR 9100628 A	1-13
Y	JP 2012-215238 A (Nippon Piston Ring Co., Ltd.), 08 November 2012 (08.11.2012), claims; 0002 to 0007 (Family: none)	1-13
A	JP 2011-42800 A (Afton Chemical Corp.), 03 March 2011 (03.03.2011), claims; examples & US 2007/0111907 A1 examples & EP 1788067 A1	1-13
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Form PCT/ISA/210 (continuation of second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/059450

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 2000-290675 A (Ethyl Corp.), 17 October 2000 (17.10.2000), claims; examples & US 6174842 B1 examples & EP 1041134 A2 & AU 2072600 A & CA 2299229 A & CN 1268556 A & SG 76648 A	1-13
P, A	JP 2015-163673 A (Tonen General Sekiyu Kabushiki Kaisha), 10 September 2015 (10.09.2015), claims; examples & WO 2015/114920 A1	1-13
P, A	WO 2015/111746 A1 (Idemitsu Kosan Co., Ltd.), 30 July 2015 (30.07.2015), examples; claims & JP 2015-140354 A	1-13

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/059450

Continuation of A. CLASSIFICATION OF SUBJECT MATTER

(International Patent Classification (IPC))

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REFERENCES CITED IN THE DESCRIPTION

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