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(54) **LUBRICATING OIL COMPOSITION**

(57) Provided is a lubricating oil composition for a gas engine comprising: a base oil (A), at least one over-based calcium detergent (B) selected from the group consisting of calcium salicylate (B1) and calcium phenate (B2), alkenyl succinimide (C), and a hindered amine-based antioxidant (D), wherein the content (X) of calcium atoms derived from the component (B) is less than 0.090% by mass based on the total amount of the lubricating oil composition; the content (Y) of calcium car-

bonate contained in the component (B) is 0.060% by mass or more based on the total amount of the lubricating oil composition; the content of boron atoms derived from the component (C) is less than 0.020% by mass based on the total amount of the lubricating oil composition; and the content of the component (D) is more than 0.20% by mass based on the total amount of the lubricating oil composition.

EP 4 317 385 A1

Description

[Technical Field]

5 **[0001]** The present invention relates to a lubricating oil composition, a gas engine to which the lubricating oil composition is applied, and a method for using the lubricating oil composition.

[Background Art]

10 **[0002]** A gas engine heat pump system and a gas engine cogeneration system have been put into practical use for air conditioning of houses and buildings. In these systems, a gas engine using natural gas, liquefied petroleum gas (LPG) or the like as a fuel is generally used.

[0003] Gas engine oils applied to such a gas engine have been variously developed.

15 **[0004]** For example, Patent Literature 1 describes a lubricating oil composition for a gas engine comprising a lubricating oil base oil, an anti-wear agent containing phosphorus as a constituent element and not containing sulfur, an organomolybdenum-based friction modifier, a calcium salicylate-based detergent, and a magnesium salicylate-based detergent, wherein an element content ratio between magnesium and calcium is adjusted in a predetermined range, and a sulfated ash content is set to 0.6% by mass or less, to provide a lubricating oil composition for a gas engine capable of suppressing preignition.

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[Citation List]

[Patent Literature]

25 **[0005]** [Patent Literature 1] JP-A-2018-203952

[Summary of Invention]

[Technical Problem]

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[0006] In recent years, the achievement of high power and high efficiency of a gas engine has been desired, and the temperature inside the gas engine also tends to be extremely high. Along with the use in such an environment, abnormal combustion called preignition in a gas engine is likely to occur.

35 **[0007]** As a factor for preignition, preignition is considered to occur due to the heat generated by an incomplete combustion product deposited with the use of the lubricating oil composition, which is called a "deposit". Such a deposit is considered to be derived from a metal-based detergent such as a calcium detergent, and the reduction of the content of the metal-based detergent is considered to be able to suppress preignition. However, there is a concern that the reduction of the content of the metal-based detergent may cause the deterioration of long drain properties.

40 **[0008]** Under such circumstances, a lubricating oil composition for a gas engine having improved long drain properties while having a preignition suppression effect is desired.

[Solution to Problem]

45 **[0009]** The present invention provides a lubricating oil composition for a gas engine comprising a base oil, at least one overbased calcium detergent selected from the group consisting of calcium salicylate and calcium phenate, alkenyl succinimide that may be modified with boron, and an antioxidant including a hindered amine-based antioxidant, in which the content of the calcium carbonate contained in the overbased calcium detergent, the content of calcium atoms and boron atoms, and the content of the hindered amine-based antioxidant are adjusted in a specific range.

50 **[0010]** That is, one aspect of the present invention provides a lubricating oil composition for a gas engine including a base oil (A), at least one overbased calcium detergent (B) selected from the group consisting of calcium salicylate (B1) and calcium phenate (B2), alkenyl succinimide (C), and a hindered amine-based antioxidant (D), wherein

the content (X) of calcium atoms derived from the component (B) is less than 0.090% by mass based on the total amount of the lubricating oil composition;

55 the content (Y) of calcium carbonate contained in the component (B) is 0.060% by mass or more based on the total amount of the lubricating oil composition;

the content of boron atoms derived from the component (C) is less than 0.020% by mass based on the total amount of the lubricating oil composition; and

the content of the component (D) is more than 0.20% by mass based on the total amount of the lubricating oil composition. Another aspect of the present invention provides a gas engine to which the lubricating oil composition is applied.

- 5 **[0011]** Another aspect of the present invention provides a method for lubricating a gas engine, including applying the lubricating oil composition to the gas engine.

[Advantageous Effects of Invention]

- 10 **[0012]** The lubricating oil composition of one preferred aspect of the present invention is excellent in at least one of various characteristics required for lubrication of a gas engine, and in a more preferred aspect, the lubricating oil composition has improved long drain properties while having a preignition suppression effect, so that it can be suitably used for lubrication of a gas engine.

15 [Description of Embodiments]

- [0013]** In the numerical range described in the present specification, any combination of upper limit and lower limit values is possible. For example, when a description of "preferably 30 to 100, more preferably 40 to 80" is described as a numerical range, ranges such as "30 to 80" and "40 to 100" are included in the numerical range described in the present specification.

[0014] For example, the description of "60 to 100" as the numerical range described in the present specification means a range of "60 or more and 100 or less".

- [0015]** Further, in the definition of the upper limit value and the lower limit value described in the present specification, appropriate selection from each option and any combination thereof is possible in order to define a numerical value range from a lower limit value to an upper limit value.

[0016] In the present specification, a kinematic viscosity and a viscosity index mean values measured and calculated in accordance with JIS K2283: 2000.

[0017] The contents of calcium atoms (Ca), magnesium atoms (Mg), phosphorus atoms (P), zinc atoms (Zn), boron atoms (B), and molybdenum atoms (Mo) mean values measured in accordance with JPI-5S-38-92.

- 30 **[0018]** The content of nitrogen atoms (N) means a value measured in accordance with JIS K2609: 1998.

[Constitution of lubricating oil composition]

- 35 **[0019]** The lubricating oil composition of the present invention contains a base oil (A), at least one overbased calcium detergent (B) selected from the group consisting of calcium salicylate (B1) and calcium phenate (B2), alkenyl succinimide (C) that may be modified with boron, and a hindered amine-based antioxidant (D).

- [0020]** In addition, in the lubricating oil composition of the present invention, the contents of calcium atoms and calcium carbonate derived from the component (B), the content of boron atoms derived from the component (C), and the content of the component (D) are adjusted in specific ranges so that the lubricating oil composition of the present invention is suitably applicable as a lubricating oil composition for a gas engine.

- [0021]** As mentioned above, the development of a lubricating oil composition that can suppress preignition in a gas engine and can be suitably used for a gas engine is desired. To suppress a factor for preignition, that is, the amount generated by an incomplete combustion product deposited, which is called a "deposit", a method for reducing the content of a metal-based detergent such as a calcium detergent is exemplified. However, the reduction of the content of the metal-based detergent may be a factor for causing the deterioration of long drain properties.

- 45 **[0022]** To solve such problems, in the lubricating oil composition of the present invention, the preignition suppression effect is improved by adjusting the content of calcium atoms derived from the component (B) and the content of boron atoms derived from the component (C) in predetermined ranges to suppress the deposition of the above deposit, and further, by setting the content of calcium carbonate contained in the component (B) to a predetermined range.

- 50 **[0023]** For the deterioration of long drain properties along with the reduction of the content of calcium atoms derived from the component (B) and the content of boron atoms derived from the component (C), long drain properties are improved by containing at least one overbased calcium detergent selected from the group consisting of calcium salicylate (B1) and calcium phenate (B2) as the component (B), and setting the content of the component (D) to a predetermined range.

- 55 **[0024]** As a result, the lubricating oil composition of the present invention is considered to be able to be a lubricating oil composition having improved long drain properties while having a preignition suppression effect.

[0025] The lubricating oil composition of one aspect of the present invention preferably further contains zinc dithiophosphate (E).

[0026] The lubricating oil composition of one aspect of the present invention may further contain lubricating oil additives other than the components (B) to (E) if necessary, as long as the effects of the present invention are not impaired.

[0027] In the lubricating oil composition of one aspect of the present invention, the total content of the components (A), (B), (C), and (D) is preferably 60% by mass or more, more preferably 65% by mass or more, further preferably 70% by mass or more, still further more preferably 75% by mass or more, and particularly preferably 80% by mass or more, and may further be 85% by mass or more, 87% by mass or more, 90% by mass or more, or 92% by mass or more, or may be 100% by mass or less, 99.99% by mass or less, 99.90% by mass or less, 99.50% by mass or less, 99.0% by mass or less, 98.0% by mass or less, or 97.0% by mass or less, based on the total amount (100% by mass) of the lubricating oil composition.

[0028] Hereinafter, details of each component contained in the lubricating oil composition of one aspect of the present invention will be described.

<Component (A): base oil>

[0029] In the lubricating oil composition of one aspect of the present invention, one or more selected from mineral oils and synthetic oils can be exemplified as the base oil used as the component (A).

[0030] Examples of the mineral oil include atmospheric residues obtained by subjecting crude oils such as paraffinic crude oil, intermediate base crude oil and naphthenic crude oil, to atmospheric distillation; distillates obtained by subjecting these atmospheric residues to vacuum distillation; and refined oils obtained by subjecting the distillates to one or more of refining treatments such as solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, catalytic dewaxing, and hydrotreating.

[0031] Examples of the synthetic oil include poly α -olefins such as an α -olefin homopolymer, or an α -olefin copolymer (e.g., an α -olefin copolymer having 8 to 14 carbon atoms, such as an ethylene- α -olefin copolymer); isoparaffin; polyalkylene glycol; ester oils such as polyol ester, dibasic acid ester, and phosphoric acid ester; ether oils such as polyphenyl ether; alkylbenzene; alkyl naphthalene; and synthetic oils (GTL) obtained by isomerizing wax (GTL WAX (Gas To Liquids WAX)) produced from natural gas through Fischer-Tropsch process or the like.

[0032] The component (A) used in one aspect of the present invention is preferably one or more selected from mineral oils classified in Group II and Group III of API (American Petroleum Institute) base oil categories, and synthetic oils.

[0033] The kinematic viscosity of the component (A) used in one aspect of the present invention at 40°C is preferably 10 to 130 mm²/s, more preferably 20 to 120 mm²/s, further preferably 30 to 110 mm²/s, and still further more preferably 40 to 100 mm²/s.

[0034] The viscosity index of the component (A) used in one aspect of the present invention is preferably 70 or more, more preferably 80 or more, still more preferably 90 or more, still further more preferably 100 or more, and particularly preferably 105 or more.

[0035] When a mixed oil in which two or more base oils are combined is used as the component (A) in one aspect of the present invention, the kinematic viscosity and the viscosity index of the mixed oil are preferably in the above ranges.

[0036] In the lubricating oil composition of one aspect of the present invention, the content of the component (A) is preferably 50% by mass or more, more preferably 60% by mass or more, further preferably 65% by mass or more, still further more preferably 70% by mass or more, and particularly preferably 75% by mass or more, and may further be 80% by mass or more, 82% by mass or more, 85% by mass or more, 87% by mass or more, or 89% by mass or more, and is preferably 99.5% by mass or less, more preferably 99.0% by mass or less, further preferably 98.0% by mass or less, still further more preferably 97.0% by mass or less, and particularly preferably 96.0% by mass or less, based on the total amount (100% by mass) of the lubricating oil composition.

<Component (B): overbased calcium detergent>

[0037] The lubricating oil composition of one aspect of the present invention contains at least one overbased calcium detergent selected from the group consisting of calcium salicylate (B1) and calcium phenate (B2) as the component (B).

[0038] The component (B) may be used alone or in combination of two or more.

[0039] For the content of the component (B), the lubricating oil composition of the present invention is required to satisfy the following requirements (I) and (II).

Requirement (I): the content (X) of calcium atoms derived from the component (B) is less than 0.090% by mass based on the total amount of the lubricating oil composition.

Requirement (II): the content (Y) of calcium carbonate contained in the component (B) is 0.060% by mass or more based on the total amount of the lubricating oil composition.

[0040] By adjusting the content (X) of calcium atoms derived from the component (B) to satisfy the requirement (I), a

lubricating oil composition that suppresses the deposition of the deposit that may be generated along with the use of the lubricating oil composition and has an improved preignition suppression effect can be obtained. In addition, when it is applied to a gas engine, it may be a lubricating oil composition having good engine efficiency. That is, in a lubricating oil composition which does not satisfy the requirement (I) and in which the content (X) of calcium atoms derived from the component (B) is 0.090% by mass or more, the preignition suppression effect is likely to be insufficient.

[0041] From the above viewpoint, the content (X) of calcium atoms derived from the component (B) is less than 0.090% by mass, preferably less than 0.085% by mass, more preferably less than 0.080% by mass, more preferably less than 0.075% by mass, further preferably less than 0.070% by mass, still further more preferably less than 0.065% by mass, and particularly preferably less than 0.060% by mass, based on the total amount (100% by mass) of the lubricating oil composition.

[0042] From the viewpoint of obtaining a lubricating oil composition having more improved long drain properties, the content (X) of calcium atoms derived from the component (B) is preferably 0.0010% by mass or more, more preferably 0.0030% by mass or more, more preferably 0.0050% by mass or more, further preferably 0.0070% by mass or more, still further more preferably 0.010% by mass or more, and particularly preferably 0.015% by mass or more, and may further be 0.017% by mass or more, 0.020% by mass or more, 0.022% by mass or more, 0.025% by mass or more, 0.030% by mass or more, 0.032% by mass or more, 0.035% by mass or more, 0.037% by mass or more, or 0.040% by mass or more, based on the total amount (100% by mass) of the lubricating oil composition.

[0043] Since the component (B) used in the present invention is an overbased calcium detergent, it is constituted by a soap component and calcium carbonate. The above requirement (II) defines the content (Y) of calcium carbonate contained in the component (B).

[0044] Calcium carbonate contained in the component (B) contributes to further improvement of the preignition suppression effect. Thus, by setting the content (Y) of calcium carbonate contained in the component (B) to 0.060% by mass or more, as defined in the requirement (II), a lubricating oil composition having a further improved preignition suppression effect can be obtained. That is, in a lubricating oil composition which does not satisfy the requirement (II) and in which the content (Y) of calcium carbonate contained in the component (B) is less than 0.060% by mass, the preignition suppression effect is likely to be insufficient.

[0045] From the above viewpoint, the content (Y) of calcium carbonate contained in the component (B) is 0.060% by mass or more, preferably 0.065% by mass or more, more preferably 0.070% by mass or more, more preferably 0.075% by mass or more, further preferably 0.080% by mass or more, further preferably 0.085% by mass or more, still further more preferably 0.090% by mass or more, and particularly preferably 0.095% by mass or more, and may further be 0.10% by mass or more, 0.11% by mass or more, 0.12% by mass or more, or 0.13% by mass or more, based on the total amount (100% by mass) of the lubricating oil composition.

[0046] From the viewpoint of suppressing the amount of deposit deposited that affects the occurrence of preignition, the content (Y) of calcium carbonate contained in the component (B) is preferably 2.00% by mass or less, more preferably 1.80% by mass or less, more preferably 1.50% by mass or less, further preferably 1.20% by mass or less, further preferably 1.00% by mass or less, still further more preferably 0.80% by mass or less, and particularly preferably 0.60% by mass or less, and may further be 0.50% by mass or less, 0.45% by mass or less, 0.40% by mass or less, 0.35% by mass or less, 0.30% by mass or less, 0.25% by mass or less, 0.20% by mass or less, 0.18% by mass or less, 0.17% by mass or less, 0.16% by mass or less, or 0.15% by mass or less, based on the total amount (100% by mass) of the lubricating oil composition.

[0047] In the lubricating oil composition of one aspect of the present invention, a ratio $[(X)/(Y)]$ of the content (X) of calcium atoms derived from the component (B) (unit: % by mass) to the content (Y) of calcium carbonate contained in the component (B) (unit: % by mass) is preferably 0.20 or more, more preferably 0.25 or more, more preferably 0.30 or more, further preferably 0.35 or more, still further more preferably 0.38 or more, and particularly preferably 0.40 or more, and preferably 0.90 or less, more preferably 0.80 or less, more preferably 0.70 or less, further preferably 0.60 or less, further preferably 0.55 or less, still further more preferably 0.52 or less, and particularly preferably 0.50 or less, from the viewpoint of obtaining a lubricating oil composition having a more improved preignition suppression effect.

[0048] The content of the soap component contained in the component (B) used in one aspect of the present invention is preferably 0.050% by mass or more, more preferably 0.060% by mass or more, more preferably 0.070% by mass or more, further preferably 0.080% by mass or more, further preferably 0.090% by mass or more, still further more preferably 0.100% by mass or more, and particularly preferably 0.110% by mass or more, and preferably 3.00% by mass or less, more preferably 2.00% by mass or less, more preferably 1.50% by mass or less, further preferably 1.20% by mass or less, further preferably 1.00% by mass or less, still further more preferably 0.80% by mass or less, and particularly preferably 0.60% by mass or less, and may further be 0.50% by mass or less, 0.45% by mass or less, 0.40% by mass or less, 0.35% by mass or less, 0.30% by mass or less, 0.25% by mass or less, or 0.20% by mass or less, based on the total amount (100% by mass) of the lubricating oil composition.

[0049] The component (B) used in the present invention is at least one overbased calcium detergent selected from the group consisting of calcium salicylate (B1) and calcium phenate (B2).

[0050] By containing at least one selected from the group consisting of the components (B1) and (B2) as the overbased calcium detergent, a lubricating oil composition having improved long drain properties while having a preignition suppression effect can be obtained.

[0051] The "overbased" calcium detergent used in one aspect of the present invention as the component (B) means a calcium detergent having a base number of 100 mgKOH/g or more.

[0052] The base number of the component (B) used in one aspect of the present invention may be 100 mgKOH/g or more, 120 mgKOH/g or more, 150 mgKOH/g or more, 170 mgKOH/g or more, or 200 mgKOH/g or more, and 600 mgKOH/g or less, 550 mgKOH/g or less, 500 mgKOH/g or less, 450 mgKOH/g or less, or 400 mgKOH/g or less.

[0053] The range of the base numbers of the components (B1) and (B2) is the same as the above range.

[0054] In the present specification, the "base number" of the component (B) means a base number measured by the hydrochloric acid method in accordance with JIS K2501 "Petroleum products and lubricants - Determination of neutralization number", 7.

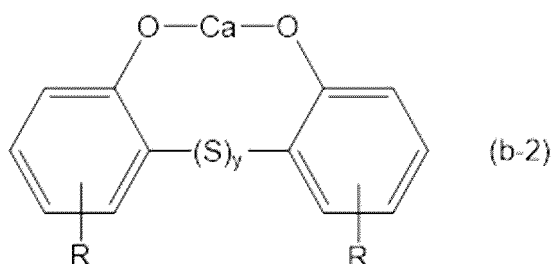
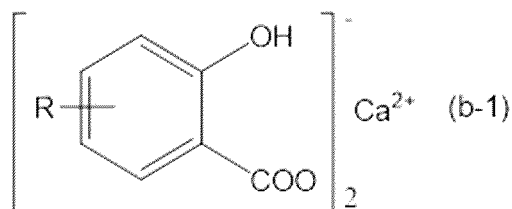
[0055] As the component (B) used in one aspect of the present invention, a calcium detergent mixture having a base number of 100 mgKOH/g or more obtained by mixing a calcium detergent having a base number of 100 mgKOH/g or more with a calcium detergent having a base number of less than 100 mgKOH/g may be used.

[0056] However, when the component (B) used in one aspect of the present invention is a mixture of two or more calcium detergents, the component (B) is preferably a calcium detergent mixture obtained by mixing two or more calcium detergents each having a base number of 100 mgKOH/g or more, from the viewpoint of obtaining a lubricating oil composition having an improved preignition suppression effect and improved long drain properties.

[0057] From the viewpoint of obtaining a lubricating oil composition having improved long drain properties while having a preignition suppression effect, the component (B) used in one aspect of the present invention preferably contains at least calcium salicylate (B1).

[0058] In the lubricating oil composition of one aspect of the present invention, from the above viewpoint, the content of the component (B1) in the component (B) is preferably 30 to 100% by mass, more preferably 50 to 100% by mass, further preferably 70 to 100% by mass, still further more preferably 80 to 100% by mass, and particularly preferably 90 to 100% by mass, based on the total amount (100% by mass) of the component (B) contained in the lubricating oil composition.

[0059] The component (B1) used in one aspect of the present invention is preferably a compound represented by the following general formula (b-1). The component (B2) used in one aspect of the present invention is preferably a compound represented by the following general formula (b-2).



[0060] In the general formulas (b-1) and (b-2), each R is independently a hydrogen atom or a hydrocarbon group having 1 to 18 carbon atoms.

[0061] Examples of the hydrocarbon group capable of being selected as R include an alkyl group having 1 to 18 carbon atoms, an alkenyl group having 1 to 18 carbon atoms, a cycloalkyl group having 3 to 18 ring-forming carbon atoms, an aryl group having 6 to 18 ring-forming carbon atoms, an alkylaryl group having 7 to 18 carbon atoms, and an arylalkyl group having 7 to 18 carbon atoms.

[0062] In the general formula (b-2), y is an integer of 0 or more, and preferably an integer of 0 to 3.

<Metal-based detergent other than component (B)>

[0063] The lubricating oil composition of one aspect of the present invention may contain a metal-based detergent other than the component (B) as long as the effects of the present invention are not impaired.

[0064] The metal-based detergent other than the component (B) is one or more selected from metal salicylate, metal phenate, and metal sulfonate, each of which contains an alkali metal atom or an alkaline earth metal atom other than a calcium atom.

[0065] In the lubricating oil composition of one aspect of the present invention, the content of the metal-based detergent other than the component (B) may be 0 to 50 parts by mass, 0 to 40 parts by mass, 0 to 30 parts by mass, 0 to 20 parts by mass, 0 to 10 parts by mass, 0 to 5.0 parts by mass, 0 to 2.0 parts by mass, 0 to 1.0 part by mass, 0 to 0.1 parts by mass, 0 to 0.01 parts by mass, or 0 to 0.001 parts by mass, based on the total amount (100 parts by mass) of the component (B) contained in the lubricating oil composition, from the viewpoint of obtaining a lubricating oil composition in which both the preignition suppression effect and long drain properties are improved with good balance.

[0066] However, from the viewpoint of obtaining a lubricating oil composition in which both the preignition suppression effect and long drain properties are improved with good balance, the lubricating oil composition of one aspect of the present invention is preferably a lubricating oil composition that satisfies at least one of the following requirements (i) and (ii), and more preferably a lubricating oil composition that satisfies both the following requirements (i) and (ii).

Requirement (i): substantially no metal sulfonate is contained.

Requirement (ii): substantially no magnesium detergent is contained.

[0067] Examples of the metal that constitutes the metal sulfonate described in the above requirement (i) include alkali metals or alkali earth metals. In one aspect of the present invention, the metal sulfonate defined in the requirement (i) is more preferably calcium sulfonate, that is, it is preferable to contain substantially no calcium sulfonate.

[0068] Examples of the magnesium detergent described in the above requirement (i) include magnesium salicylate, magnesium phenate, and magnesium sulfonate.

[0069] For example, the definition of the above (i), "substantially no metal sulfonate is contained" is a definition that denies an aspect in which metal sulfonate is blended and contained for a predetermined purpose, and is not a definition that denies an aspect in which metal sulfonate is unintentionally or inevitably included or present.

[0070] However, in the lubricating oil composition of one aspect of the present invention, even in consideration of the aspect in which metal sulfonate is unintentionally or inevitably included or present, the content of metal sulfonate in this case is usually less than 20 parts by mass, and may be less than 10 parts by mass, less than 5 parts by mass, less than 1 part by mass, less than 0.1 parts by mass, less than 0.01 parts by mass, less than 0.001 parts by mass, or less than 0.0001 parts by mass, based on the total amount (100 parts by mass) of the component (B) contained in the lubricating oil composition.

[0071] The same applies to the definition of the above (ii), and it is interpreted by replacing "metal sulfonate" in the above description with "magnesium detergent".

<Component (C): alkenyl succinimide>

[0072] The lubricating oil composition of the present invention contains alkenyl succinimide (C) as the component (C).

[0073] The component (C) may be used alone or in combination of two or more. The component (C) may be boron-modified alkenyl succinimide that is modified with boron or non-boron-modified alkenyl succinimide that is not modified with boron.

[0074] The component (C) used in one aspect of the present invention is only required to be one or more selected from the group consisting of non-boron-modified alkenyl succinimide (C1) and boron-modified alkenyl succinimide (C2), and preferably contains both the component (C1) and the component (C2).

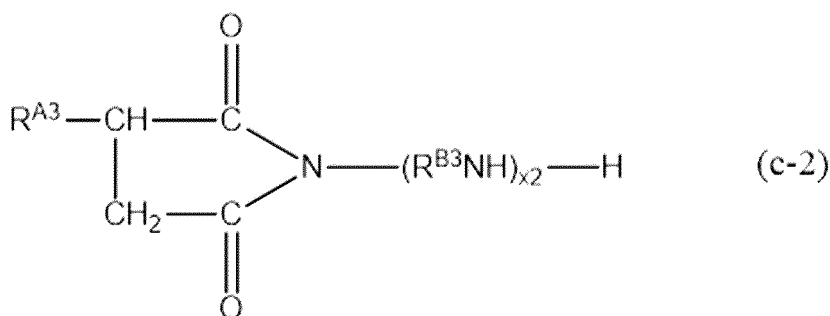
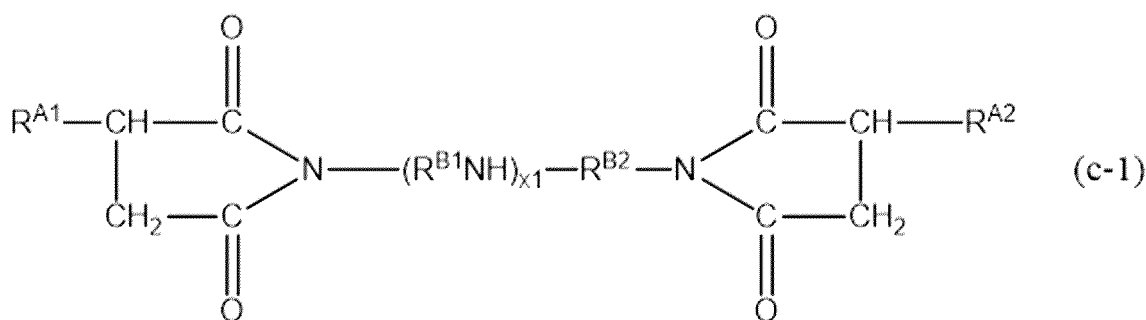
[0075] However, the component (C2) is likely to a factor for the generation of deposit along with a long time use, which is in turn likely to be a factor for the occurrence of preignition. Thus, from the viewpoint of obtaining a lubricating oil composition having an improved preignition suppression effect, the lubricating oil composition of the present invention is required to satisfy the following requirement (III). Requirement (III): the content of boron atoms derived from the component (C) is less than 0.020% by mass based on the total amount of the lubricating oil composition.

[0076] By adjusting the content of boron atoms derived from the component (C) to satisfy the requirement (III), a lubricating oil composition that reduces the amount of deposit deposited which may be generated along with the use of the lubricating oil composition, and may suppress preignition can be obtained. That is, in a lubricating oil composition which does not satisfy the requirement (III) and in which the content of boron atoms derived from the component (C) is 0.020% by mass or more, the preignition suppression effect is likely to be insufficient.

[0077] From the above viewpoint, the content of boron atoms derived from the component (C) is less than 0.020% by

mass, preferably 0.018% by mass or less, more preferably 0.016% by mass or less, more preferably 0.015% by mass or less, further preferably 0.014% by mass or less, further preferably 0.013% by mass or less, still further more preferably 0.012% by mass or less, and particularly preferably 0.011% by mass or less, and may further be 0.010% by mass or less, 0.0080% by mass or less, 0.0070% by mass or less, 0.0060% by mass or less, 0.0050% by mass or less, or 0.0040% by mass or less, and 0.0001% by mass or more, 0.0005% by mass or more, 0.0010% by mass or more, 0.0015% by mass or more, or 0.0020% by mass or more, based on the total amount (100% by mass) of the lubricating oil composition.

[0078] Examples of the component (C1) used in one aspect of the present invention include alkenyl bis-succinimide represented by the following general formula (c-1) and alkenyl monosuccinimide represented by the following general formula (c-2).



[0079] In the general formulas (c-1) and (c-2), R^{A1} , R^{A2} , and R^{A3} are each independently an alkenyl group having a weight average molecular weight (Mw) of 500 to 3000 (preferably 900 to 2500).

[0080] Examples of the alkenyl group capable of being selected as R^{A1} , R^{A2} , and R^{A3} include a polybutenyl group, a polyisobutenyl group, and an ethylene-propylene copolymer, and among these, a polybutenyl group or a polyisobutenyl group is preferable.

[0081] R^{A1} , R^{A2} , and R^{A3} are each independently an alkylene group having 2 to 5 carbon atoms.

[0082] x_1 is an integer of 0 to 10, preferably an integer of 1 to 4, and more preferably 2 or 3.

[0083] x_2 is an integer of 1 to 10, preferably an integer of 2 to 5, and more preferably 3 or 4.

[0084] Examples of the components (C2) used in one aspect of the present invention include a boron-modified product of the alkenyl bis-succinimide represented by the aforesaid general formula (c-1) and a boron-modified product of the alkenyl monosuccinimide represented by the general formula (c-2), and a boron-modified product of the alkenyl monosuccinimide represented by the general formula (c-2) is preferable.

[0085] In one aspect of the present invention, the ratio [B/N] of boron atoms to nitrogen atoms that constitute the component (C2) is preferably 0.1 or more, more preferably 0.2 or more, further preferably 0.3 or more, still further more preferably 0.5 or more, and particularly preferably 0.7 or more.

[0086] In the lubricating oil composition of one aspect of the present invention, the content ratio [N/Ca] of nitrogen atoms derived from the component (C) to calcium atoms derived from the component (B) by mass is preferably 1.20 or less, more preferably 1.17 or less, more preferably 1.15 or less, further preferably 1.10 or less, still further more preferably 1.00 or less, and particularly preferably 0.90 or less, and preferably 0.01 or more, more preferably 0.05 or more, more preferably 0.10 or more, more preferably 0.15 or more, further preferably 0.20 or more, further preferably 0.25 or more, further preferably 0.30 or more, still further more preferably 0.35 or more, and particularly preferably 0.40 or more, from the viewpoint of improving the dispersibility of the component (B), and obtaining a lubricating oil composition having a more improved preignition suppression effect even in a long time use.

[0087] In the lubricating oil composition of one aspect of the present invention, the content ratio [B/N] of boron atoms derived from the component (C2) to nitrogen atoms derived from the component (C) by mass is preferably 0.01 or more, more preferably 0.02 or more, further preferably 0.03 or more, still further more preferably 0.04 or more, and particularly preferably 0.05 or more, and preferably 0.90 or less, more preferably 0.60 or less, more preferably less than 0.30, further preferably 0.28 or less, further preferably 0.25 or less, still further more preferably 0.23 or less, and particularly preferably 0.20 or less.

[0088] In the lubricating oil composition of one aspect of the present invention, the content of the component (C) in terms of nitrogen atoms is preferably 0.005 to 0.15% by mass, more preferably 0.010 to 0.10% by mass, further preferably 0.020 to 0.090% by mass, still further more preferably 0.025 to 0.070% by mass, and particularly preferably 0.030 to 0.060, based on the total amount (100% by mass) of the lubricating oil composition.

[0089] The amount of the component (C) blended (content) is preferably 0.10 to 15.0% by mass, more preferably 0.50 to 12.0% by mass, more preferably 0.7 to 10.0% by mass, further preferably 1.0 to 8.0% by mass, further preferably 1.5 to 7.0% by mass, still further more preferably 2.0 to 6.0% by mass, and particularly preferably 2.5 to 5.0% by mass, based on the total amount (100% by mass) of the lubricating oil composition.

[0090] When the lubricating oil composition of one aspect of the present invention contains the component (C2) as the component (C), the amount of the component (C2) blended (content) is preferably less than 1.05% by mass, more preferably 1.00% by mass or less, more preferably 0.90% by mass or less, further preferably 0.80% by mass or less, further preferably 0.70% by mass or less, still further more preferably 0.60% by mass or less, and particularly preferably 0.50% by mass or less, and preferably 0.01% by mass or more, more preferably 0.03% by mass or more, more preferably 0.05% by mass or more, further preferably 0.07% by mass or more, still further more preferably 0.10% by mass or more, and particularly preferably 0.12% by mass or more, based on the total amount (100% by mass) of the lubricating oil composition, from the viewpoint of obtaining a lubricating oil composition capable of reducing the amount of deposit deposited which may be generated along with the use of the lubricating oil composition, and suppressing preignition.

<Component (D): hindered amine-based antioxidant>

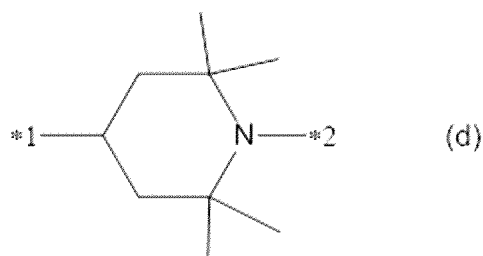
[0091] The lubricating oil composition of the present invention contains a hindered amine-based antioxidant as the component (D). For the content of the component (D), the lubricating oil composition of the present invention is required to satisfy the following requirement (IV). Requirement (IV): the content of the component (D) is more than 0.20% by mass based on the total amount of the lubricating oil composition.

[0092] Since the hindered amine-based antioxidant (D) contains no metal atom, it can contribute to the improvement of the oxidation prevention performance and suppress the oxidation degradation of the lubricating oil composition along with use without increasing the sulfated ash content of the lubricating oil composition and the content of calcium atoms in the component (B).

[0093] In the lubricating oil composition of the present invention, although the preignition suppression effect is improved by reducing the content of calcium atoms derived from the component (B) as described in the above requirement (I), the deterioration of long drain properties is concerned. Thus, by not only containing at least one overbased calcium detergent (B) selected from the group consisting of the component (B1) and the component (B2), but also adjusting the content of the component (D) to satisfy the above requirement (IV), the lubricating oil composition of the present invention can be a lubricating oil composition having improved long drain properties while having a preignition suppression effect. A lubricating oil composition which does not satisfy the requirement (IV) and in which the content of the component (D) is 0.20% by mass or less is difficult to suppress the deterioration of long drain properties along with the reduction of the component (B).

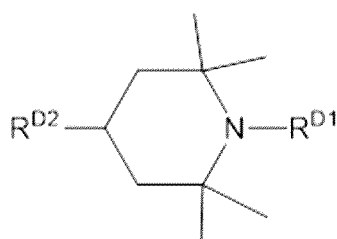
[0094] In the lubricating oil composition of one aspect of the present invention, the content of the component (D) is more than 0.20% by mass, preferably 0.25% by mass or more, more preferably 0.30% by mass or more, further preferably 0.32% by mass or more, still further more preferably 0.35% by mass or more, still further more preferably 0.37% by mass or more, and particularly preferably 0.40% by mass or more, based on the total amount (100% by mass) of the lubricating oil composition, and the upper limit is not particularly limited, but may be 5.0% by mass or less, 4.0% by mass or less, 3.0% by mass or less, 2.0% by mass or less, 1.5% by mass or less, or 1.0% by mass or less, from the viewpoint of obtaining a lubricating oil composition having improved long drain properties.

[0095] In one aspect of the present invention, the hindered amine-based antioxidant used as the component (D) is only required to be an antioxidant containing a structure represented by the following formula (d). The component (D) may be used alone or may be used in combination of two or more.

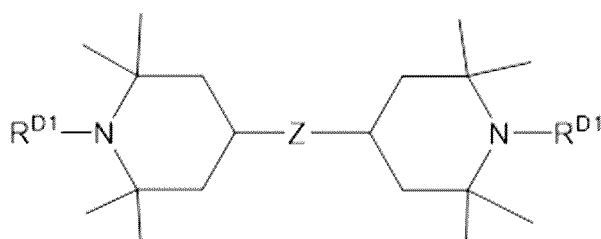


[0096] In the above formula, *1 and *2 each represent a binding position with another atom.

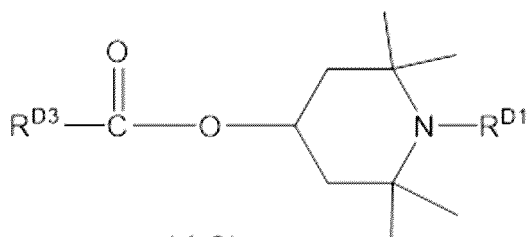
[0097] More specific examples of the component (D) include a compound represented by any one of the following general formulas (d-1) to (d-4).



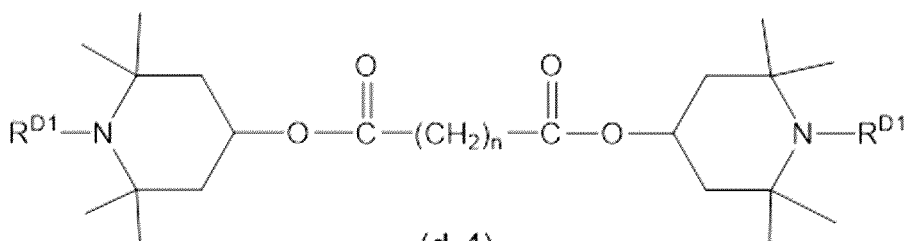
(d-1)



(d-2)



(d-3)



(d-4)

[0098] In the general formulas (d-1) to (d-4), each R^{D1} independently represents a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, and preferably a hydrogen atom or an alkyl group having 1 to 3 carbon atoms.

[0099] In the general formula (d-1), R^{D2} is a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group having 6 to 18 ring-forming carbon atoms, an aryl group having 6 to 18 ring-forming carbon atoms, a hydroxyl group, an amino group, or a group represented by $-O-CO-R^{D3}$ (R^{D3} is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms).

[0100] In the general formula (d-2), Z is an alkylene group having 1 to 20 carbon atoms, a cycloalkylene group having 6 to 18 ring-forming carbon atoms, an arylene group having 6 to 18 ring-forming carbon atoms, an oxygen atom, a sulfur atom, or a group represented by $-O-CO-(CH_2)_n-COO-$ (n is an integer of 1 to 20).

[0101] In the general formula (d-3), R^{D3} is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms.

[0102] In the general formula (d-4), n is an integer of 1 to 20.

<Antioxidants other than hindered amine-based antioxidant (D)>

[0103] The lubricating oil composition of one aspect of the present invention may contain an antioxidant other than the component (D) as other additives.

[0104] Examples of the antioxidant other than the component (D) include amine-based antioxidants other than the component (D), phenol-based antioxidants, sulfur-based antioxidants, and phosphorus-based antioxidants.

[0105] These other antioxidants may be used alone or in combination of two or more.

[0106] Examples of the amine-based antioxidant other than the component (D) include diphenylamine-based antioxidants such as diphenylamine and alkylated diphenylamine including an alkyl group having 3 to 20 carbon atoms; and naphthylamine-based antioxidants such as α -naphthylamine, phenyl- α -naphthylamine, and substituted phenyl- α -naphthylamine including an alkyl group having 3 to 20 carbon atoms.

[0107] Examples of the phenol-based antioxidant include monophenol-based antioxidants such as 2,6-di-*t*-butylphenol, 2,6-di-*t*-butyl-4-methylphenol, 2,6-di-*t*-butyl-4-ethylphenol, isooctyl 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, and octadecyl 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate; and diphenol-based antioxidants such as 4,4'-methylenebis(2,6-di-*t*-butylphenol) and 2,2'-methylenebis(4-ethyl-6-*t*-butylphenol).

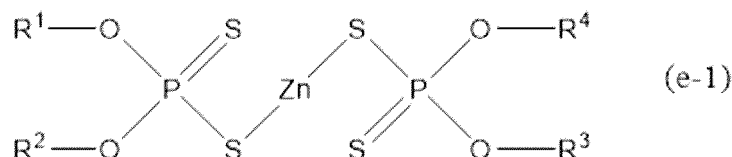
[0108] In the lubricating oil composition of one aspect of the present invention, the content of the antioxidant other than the component (D) may be 0.01% by mass or more, 0.05% by mass or more, 0.10% by mass or more, 0.30% by mass or more, 0.50% by mass or more, 0.70% by mass or more, or 1.00% by mass or more, and may be 10.0% by mass or less, 8.0% by mass or less, 7.0% by mass or less, 6.0% by mass or less, 5.0% by mass or less, 4.5% by mass or less, or 4.0% by mass or less, based on the total amount (100% by mass) of the lubricating oil composition.

[0109] In the lubricating oil composition of one aspect of the present invention, the content of the antioxidant other than the component (D) may be 0 to 1000 parts by mass, 0 to 950 parts by mass, 0 to 900 parts by mass, 0 to 850 parts by mass, 0 to 800 parts by mass, or 0 to 750 parts by mass, based on the total amount (100 parts by mass) of the component (D) contained in the lubricating oil composition.

<Component (E): zinc dithiophosphate>

[0110] The lubricating oil composition of one aspect of the present invention preferably contains zinc dithiophosphate (ZnDTP) (E) as the component (E). The component (E) may be used alone or in combination of two or more. The component (E) has a function as an anti-wear agent.

[0111] The component (E) used in one aspect of the present invention is preferably a compound represented by the following general formula (e-1).



[0112] In the above formula (e-1), R^1 to R^4 each independently represent a hydrocarbon group, and may be the same as one another or may be different from one another.

[0113] The number of carbon atoms of the hydrocarbon groups capable of being selected as R^1 to R^4 is preferably 1 to 20, more preferably 1 to 16, further preferably 3 to 12, and still further more preferably 3 to 10.

[0114] Specific examples of the hydrocarbon groups capable of being selected as R^1 to R^4 include alkyl groups such as a methyl group, an ethyl group, 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 undecyl group, a dodecyl group, a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group and an octadecyl group; alkenyl groups, such as an octenyl group, a nonenyl group, a decenyl group, a undecenyl group, a dodecenyl group, a tridecenyl group, a tetradecenyl group and a pentadecenyl group; cycloalkyl groups such as a cyclohexyl group, a dimethylcyclohexyl group, an ethylcyclohexyl group, a methylcyclohexylmethyl group, a cyclohexylethyl group, a propylcyclohexyl group, a butylcyclohexyl group and a heptylcyclohexyl group; aryl groups such as a phenyl group, a naphthyl group, an anthracenyl group, a biphenyl group and a terphenyl group; alkylaryl groups such as a tolyl group, a dimethylphenyl group, a butylphenyl group, a nonylphenyl group, a methylbenzyl group and a dimethylnaphthyl group; and arylalkyl groups such as a phenylmethyl group, a phenylethyl group and a diphenylmethyl group.

[0115] Among these, alkyl groups are preferable, primary or secondary alkyl groups are more preferable, and secondary alkyl groups are further preferable as the hydrocarbon groups capable of being selected as R^1 to R^4 .

[0116] In the lubricating oil composition of one aspect of the present invention, the content of the component (E) in

terms of zinc atoms is preferably 0.001 to 1.0% by mass, more preferably 0.005 to 0.80% by mass, further preferably 0.01 to 0.60% by mass, still further more preferably 0.02 to 0.50% by mass, and particularly preferably 0.03 to 0.40% by mass, based on the total amount (100% by mass) of the lubricating oil composition.

[0117] The content (amount blended) of the component (E) is only required to be adjusted such that the content in terms of zinc atoms falls within the above range, and is preferably 0.01 to 10.0% by mass, more preferably 0.05 to 5.0% by mass, further preferably 0.10 to 2.0% by mass, and still further more preferably 0.20 to 1.0% by mass, based on the total amount (100% by mass) of the lubricating oil composition.

<Lubricating oil additives>

[0118] The lubricating oil composition of one aspect of the present invention may further contain lubricating oil additives other than the components (B) to (E) if necessary, as long as the effects of the present invention are not impaired.

[0119] Examples of such lubricating oil additives include a pour point depressant, a viscosity index improver, a demulsifier, a friction modifier, a corrosion inhibitor, a metal deactivator, an antistatic agent, and an antifoaming agent.

[0120] These lubricating oil additives may be each used alone or in combination of two or more.

[0121] The contents of these lubricating oil additives can be each appropriately adjusted as long as the effects of the present invention are not impaired, and the contents of the additives are each independently usually 0.001 to 15 mass%, preferably 0.005 to 10 mass%, and more preferably 0.01 to 5 mass%, based on the total amount (100 mass%) of the lubricating oil composition.

<Production method for lubricating oil composition>

[0122] The production method for the lubricating oil composition of one aspect of the present invention is not particularly limited, but from the viewpoint of productivity, a method having a step of blending the aforementioned components (B) to (D), and if necessary, the component (E) and other lubricating oil additives into the base oil (A) is preferable.

[Properties of lubricating oil composition]

[0123] The kinematic viscosity of the lubricating oil composition of one aspect of the present invention at 40°C is preferably 10 to 200 mm²/s, more preferably 30 to 170 mm²/s, further preferably 50 to 150 mm²/s, still further more preferably 60 to 130 mm²/s, and particularly preferably 80 to 120 mm²/s.

[0124] The kinematic viscosity of the lubricating oil composition of one aspect of the present invention at 100°C is preferably 2.5 to 20.0 mm²/s, more preferably 4.0 to 18.0 mm²/s, further preferably 5.5 to 16.0 mm²/s, still further more preferably 7.0 to 15.0 mm²/s, and particularly preferably 8.0 to 14.0 mm²/s.

[0125] The viscosity index of the lubricating oil composition of one aspect of the present invention is preferably 80 or more, more preferably 85 or more, further preferably 90 or more, still further more preferably 95 or more, and particularly preferably 100 or more.

[0126] The acid number of the lubricating oil composition of one aspect of the present invention is preferably 0.10 to 2.00 mgKOH/g, more preferably 0.15 to 1.50 mgKOH/g, further preferably 0.20 to 1.20 mgKOH/g, still further more preferably 0.25 to 1.00 mgKOH/g, and particularly preferably 0.30 to 0.80 mgKOH/g.

[0127] In the present specification, the acid number of the lubricating oil composition means a value measured in accordance with JIS K2501: 2003 (potentiometric titration method).

[0128] The base number of the lubricating oil composition of one aspect of the present invention is preferably 1.0 to 10.0 mgKOH/g, more preferably 1.5 to 8.0 mgKOH/g, further preferably 2.0 to 6.5 mgKOH/g, still further more preferably 2.3 to 5.0 mgKOH/g, and particularly preferably 2.5 to 4.0 mgKOH/g.

[0129] In the present specification, the base number of the lubricating oil composition means a value measured in accordance with JIS K2501: 2003 (hydrochloric acid method).

[0130] The sulfated ash content of the lubricating oil composition of one aspect of the present invention is preferably less than 0.50% by mass, more preferably less than 0.40% by mass, further preferably less than 0.30% by mass, and still further more preferably less than 0.27% by mass.

[0131] In the present specification, the sulfated ash content means a value measured in accordance with JIS K2272: 1998.

[0132] In the lubricating oil composition of one aspect of the present invention, the content of phosphorus atoms is preferably 0.01 to 0.15% by mass, more preferably 0.015 to 0.12% by mass, further preferably 0.02 to 0.10% by mass, and still further more preferably 0.025 to 0.08% by mass, based on the total amount (100% by mass) of the lubricating oil composition.

[0133] In the lubricating oil composition of one aspect of the present invention, the content of nitrogen atoms is preferably 0.01 to 1.00% by mass, more preferably 0.02 to 0.80% by mass, further preferably 0.03 to 0.50% by mass,

still further more preferably 0.05 to 0.30% by mass, and particularly preferably 0.07 to 0.20% by mass, based on the total amount (100% by mass) of the lubricating oil composition.

[0134] In the lubricating oil composition of one aspect of the present invention, the content of magnesium atoms is preferably less than 0.04% by mass, more preferably less than 0.02% by mass, further preferably less than 0.01% by mass, still further more preferably less than 0.001% by mass, and particularly preferably less than 0.0005% by mass, based on the total amount of the lubricating oil composition, from the viewpoint of reducing the causative substance of the deposit and obtaining a lubricating oil composition having a more improved preignition suppression effect.

[0135] In the lubricating oil composition of one aspect of the present invention, the content of molybdenum atoms is preferably less than 0.01% by mass, more preferably less than 0.005% by mass, further preferably less than 0.001% by mass, and still further more preferably less than 0.0005% by mass, based on the total amount (100% by mass) of the lubricating oil composition, from the viewpoint of obtaining a lubricating oil composition having a more improved preignition suppression effect even in a long time use.

[0136] The temperature of the lubricating oil composition of one aspect of the present invention is increased from 50°C to 600°C at a temperature rising rate of 10°C/min in a high-pressure oxygen atmosphere of 3 MPa using a differential scanning calorimeter (manufactured by METTLER TOLEDO, high-pressure DSC) based on the method described in Examples described below, thereby measuring the maximum value of the calorific value (maximum calorific value), which is preferably 25.0 mW or less, more preferably 20.0 mW or less, more preferably 18.0 mW or less, further preferably 16.0 mW or less, still further more preferably 12.0 mW or less, and particularly preferably 8.0 mW or less.

[0137] In the above temperature rising process, the heat-generation start temperature, which is the temperature when the calorific value reaches 0.5 mW, is preferably 220°C or more, more preferably 255°C or more, more preferably 270°C or more, further preferably 280°C or more, still further more preferably 300°C or more, and particularly preferably 320°C or more.

[0138] The lubricating oil composition can be said to have a higher preignition suppression effect, as the maximum calorific value is lower and the heat-generation start temperature is higher.

[0139] A mixed gas obtained by mixing air (flow rate: 150 mL/min) with a gas in which nitrogen monoxide (NO) is diluted with nitrogen (NO concentration: 2,000 vol. ppm, flow rate: 50 mL/min) is introduced to the lubricating oil composition of one aspect of the present invention based on the method described in Examples described below, and the base number of the lubricating oil composition (hydrochloric acid method) is measured in the process of degradation by NO_x. The "NO_x-ISOT lifetime", which is the time until the base number decreases to 1.0 mgKOH/g, is preferably 100 hours or more, more preferably 105 hours or more, further preferably 110 hours or more, and still further more preferably 115 hours or more. The lubricating oil composition can be said to be more excellent in long drain properties as the NO_x-ISOT lifetime is longer.

[Application of lubricating oil composition]

[0140] The lubricating oil composition of one aspect of the present invention is excellent in characteristics such as the preignition suppression effect and long drain properties.

[0141] Thus, the lubricating oil composition of one aspect of the present invention can be applied to various apparatuses capable of exhibiting the above characteristics, but it is preferably applied to the lubrication of a gas engine.

[0142] In consideration of the aforementioned characteristics of the lubricating oil composition of one aspect of the present invention, the present invention can also provide the following [I] and [II].

[I] A gas engine to which the aforementioned lubricating oil composition of one aspect of the present invention is applied.

[II] A method for lubricating a gas engine, including applying the aforementioned lubricating oil composition of one aspect of the present invention to the gas engine.

[0143] The present invention provides the following aspects [1] to [11].

[1] A lubricating oil composition for a gas engine, comprising: a base oil (A), at least one overbased calcium detergent (B) selected from the group consisting of calcium salicylate (B1) and calcium phenate (B2), alkenyl succinimide (C), and a hindered amine-based antioxidant (D), wherein

a content (X) of calcium atoms derived from the component (B) is less than 0.090% by mass based on a total amount of the lubricating oil composition;

a content (Y) of calcium carbonate contained in the component (B) is 0.060% by mass or more based on the total amount of the lubricating oil composition;

a content of boron atoms derived from the component (C) is less than 0.020% by mass based on the total

amount of the lubricating oil composition; and

a content of the component (D) is more than 0.20% by mass based on the total amount of the lubricating oil composition.

[2] The lubricating oil composition according to the above [1], wherein a ratio [(X)/(Y)] of the content (X) of calcium atoms derived from the component (B) (unit: % by mass) to the content (Y) of calcium carbonate contained in the component (B) (unit: % by mass) is 0.20 to 0.90.

[3] The lubricating oil composition according to the above [1] or [2], wherein the content (X) of calcium atoms derived from the component (B) is less than 0.080% by mass based on the total amount of the lubricating oil composition.

[4] The lubricating oil composition according to any one of the above [1] to [3], wherein the component (B) comprises at least calcium salicylate (B1).

[5] The lubricating oil composition according to any one of claims [1] to [4], comprising substantially no metal sulfonate.

[6] The lubricating oil composition according to any one of the above [1] to [5], wherein the component (C) comprises both non-boron-modified alkenyl succinimide (C1) and boron-modified alkenyl succinimide (C2).

[7] The lubricating oil composition according to any one of the above [1] to [6], wherein a content ratio [N/Ca] of nitrogen atoms derived from the component (C) to calcium atoms derived from the component (B) is 1.20 or less.

[8] The lubricating oil composition according to any one of the above [1] to [7], further comprising zinc dithiophosphate (E).

[9] The lubricating oil composition according to any one of the above [1] to [8], having a sulfated ash content of less than 0.50% by mass based on the total amount of the lubricating oil composition.

[10] A gas engine to which the lubricating oil composition according to any one of the above [1] to [9] is applied.

[11] A method for lubricating a gas engine, including applying the lubricating oil composition according to any one of the above [1] to [9] to the gas engine.

[Examples]

[0144] Next, the present invention will be described in further more detail with reference to Examples, but the present invention is in no way limited to these Examples. Measuring methods for various properties are as follows.

(1) Kinematic viscosity, viscosity index

[0145] The kinematic viscosity and viscosity index were measured and calculated in accordance with JIS K2283: 2000.

(2) Contents of Ca, Mg, Mo, P, Zn, B

[0146] The contents were measured in accordance with JPI-5S-38-92.

(3) Content of nitrogen atoms (N)

[0147] The content was measured in accordance with JIS K2609: 1998.

(4) Acid number

[0148] The acid number was measured in accordance with JIS K2501: 2003 (potentiometric titration method).

(5) Base number (hydrochloric acid method)

[0149] The base number was measured in accordance with JIS K2501: 2003 (hydrochloric acid method).

(6) Sulfated ash content

[0150] The sulfated ash content was measured in accordance with JIS K2272: 1998.

(7) Weight-average molecular weight (Mw)

[0151] Using a gel permeation chromatograph apparatus (manufactured by Agilent Technologies, Inc., "1260 model HPLC"), the weight-average molecular weight was measured under the following conditions, and a value measured in terms of standard polystyrene was used.

(Measurement conditions)

[0152]

5 Column: sequentially connected two of "Shodex LF404".
 Column temperature: 35°C
 Developing solvent: chloroform
 Flow rate: 0.3 mL/min

10 Examples 1 to 7 and Comparative Examples 1 to 8

[0153] A base oil and various additives were added and mixed in amounts blended as shown in Table 1 and Table 2, thereby preparing each lubricating oil composition. The amount of the calcium-based detergent and the additive mixture blended as shown in Table 1 and Table 2 are amounts blended including a diluent oil.

15 **[0154]** Details of each component used in the preparation of the lubricating oil composition are as follows.

<Base oil>

20 **[0155]** "Paraffinic mineral oil": paraffinic mineral oil classified in Group II, 40°C kinematic viscosity = 90.51 mm²/s, viscosity index = 107, corresponding to the component (A).

<Calcium detergent>

25 **[0156]** "Ca salicylate (b1-i)": base number = 316 mgKOH/g (hydrochloric acid method), Ca atom content = 12.1% by mass calcium salicylate, corresponding to the component (B).

[0157] "Ca salicylate (b1-ii)": base number = 219 mgKOH/g (hydrochloric acid method), Ca atom content = 8.0% by mass calcium salicylate, corresponding to the component (B).

[0158] "Ca salicylate (b1-iii)": base number = 223 mgKOH/g (hydrochloric acid method), Ca atom content = 7.94% by mass calcium salicylate, corresponding to the component (B).

30 **[0159]** "Ca salicylate (b1-iv)": base number = 59.8 mgKOH/g (hydrochloric acid method), Ca atom content = 2.3% by mass calcium salicylate, corresponding to the component (B).

[0160] "Ca phenate (b2-i)": base number = 218 mgKOH/g (hydrochloric acid method), Ca atom content = 9.25% by mass calcium phenate, corresponding to the component (B).

35 **[0161]** "Ca sulfonate (1)": base number = 304 mgKOH/g (hydrochloric acid method), Ca atom content = 11.6% by mass calcium sulfonate.

[0162] "Ca sulfonate (2)": base number = 11.3 mgKOH/g (hydrochloric acid method), Ca atom content = 2.15% by mass calcium sulfonate.

<Alkenyl succinimide>

40 **[0163]** "Non-boron-modified succinimide": polybutenyl bis-succinimide having a polybutenyl group of Mw = 2200, content of nitrogen atoms (N) = 1.2% by mass, corresponding to the component (C).

[0164] "Boron-modified succinimide": boron-modified product of polybutenyl monosuccinimide having a polybutenyl group of Mw = 950, content of boron atoms (B) = 1.9% by mass, content of nitrogen atoms (N) = 2.3% by mass, B/N = 0.83, corresponding to the component (C).

<Hindered amine-based antioxidant>

50 **[0165]** "Hindered amine-based AO": hindered amine-based antioxidant in which R^{D1} in the general formula (d-3) is a hydrogen atom and R^{D3} is -C₁₁H₂₃, nitrogen content = 4.2% by mass, corresponding to the component (D).

<Zinc dithiophosphate>

55 **[0166]** "ZnDTP": primary zinc dialkyldithiophosphate, phosphorus atom content = 7.4 mass%, zinc atom content = 8.9 mass%, corresponding to the component (E).

<Other additives>

[0167] Additive mixture: additive mixture of amine-based antioxidant that is not hindered amine, phenol-based antioxidant, pour point depressant, demulsifier, metal deactivator, and defoaming agent.

[0168] Regarding the lubricating oil compositions prepared, the kinematic viscosity, viscosity index, acid number, base number, sulfated ash content, and each atom content were measured or calculated, and the test of the preignition suppression effect and evaluation test of long drain properties below were carried out. The results of them are shown in Table 1 and Table 2.

(1) Test of preignition suppression effect

[0169] The temperature of the lubricating oil compositions prepared was increased from 50°C to 600°C at a temperature rising rate of 10°C/min in a high-pressure oxygen atmosphere of 3 MPa using a differential scanning calorimeter (manufactured by METTLER TOLEDO, high pressure DSC), thereby measuring the calorific value of the lubricating oil compositions. Then, the maximum value of the calorific value (unit: mW) was taken as the "maximum calorific value", and the temperature at which the calorific value reached 0.5 mW was taken as "heat-generation start temperature". The lubricating oil composition can be said to have a higher preignition suppression effect, as the "maximum calorific value" is lower and the "heat-generation start temperature" is higher.

(2) Evaluation test of long drain properties

[0170] The oil temperature of 250 g of the lubricating oil compositions prepared was increased to 150°C, and a mixed gas obtained by mixing air (flow rate: 150 mL/min) with a gas in which nitrogen monoxide (NO) is diluted with nitrogen (NO concentration: 2,000 vol. ppm, flow rate: 50 mL/min) was introduced thereto, thereby degrading the lubricating oil compositions by NOx. The base number (hydrochloric acid method) of the lubricating oil compositions was measured in the process of degradation by NOx, and the time until the base number decreases to 1.0 mgKOH/g was measured as the "NOx-ISOT lifetime" (unit: time). The lubricating oil composition can be said to be more excellent in long drain properties as the "NOx-ISOT lifetime" is longer.

[Table 1]

			Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	
Composition	Base oil	Component (A): paraffinic mineral oil	% by mass	90.83	90.73	90.50	90.28	90.05	90.05	90.15
		Component (B): Ca salicylate (b1-i)	% by mass	0.45	0.45		0.45			
	Calcium detergent	Component (B): Ca salicylate (b1-ii)	% by mass			0.68		0.68		
		Component (B): Ca salicylate (b1-iii)	% by mass						0.68	
		Component (B): Ca salicylate (b1-iv)	% by mass							
		Component (B) Ca phenate (b2-i)	% by mass							0.58
		Ca sulfonate (1)	% by mass							
		Ca sulfonate (2)	% by mass							
		Alkenyl succinimide	Component (C): non-boron-modified succinimide	% by mass	3.50	3.50	3.50	3.50	3.50	3.50
	Component (C): boron-modified succinimide		% by mass	0.15	0.15	0.15	0.70	0.70	0.70	0.70
	Hindered amine-based antioxidant	Component (D): hindered amine-based AO	% by mass	0.40	0.50	0.50	0.40	0.40	0.40	0.40
		Zinc dithiophosphate	% by mass	0.42	0.42	0.42	0.42	0.42	0.42	0.42
	Other additives	Additive mixture	% by mass	4.25	4.25	4.25	4.25	4.25	4.25	4.25
	Total			% by mass	100.00	100.00	100.00	100.00	100.00	100.00
Content (Y) of calcium carbonate contained in calcium detergent based on total amount (100% by mass) of composition			% by mass	0.13	0.13	0.13	0.10	0.136	0.133	
Content of soap component contained in calcium detergent based on total amount (100% by mass) of composition			% by mass	0.13	0.13	0.13	0.33	0.224	0.197	

(continued)

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
	Content of Ca atoms derived from component (B) based on total amount (100% by mass) of composition	% by mass	0.054	0.054	0.054	0.054	0.054	0.054
	(X)/(Y)	-	0.42	0.54	0.42	0.54	0.40	0.40
	Content of B atoms derived from component (C) based on total amount (100% by mass) of composition	% by mass	0.003	0.003	0.013	0.013	0.013	0.013
	Content of N atoms derived from component (C) based on total amount (100% by mass) of composition	% by mass	0.045	0.045	0.058	0.058	0.058	0.058
	Content ratio [B/N] of B atoms to N atoms derived from component (C)	-	0.063	0.063	0.229	0.229	0.229	0.229
	Content ratio [N/Ca] of N atoms derived from component (C) to Ca atoms derived from component (B)	-	0.83	0.84	1.07	1.07	108	108
Various properties	Kinematic viscosity at 40°C	mm ² /s	105.2	105.5	106.1	107.3	111.9	109.3
	Kinematic viscosity at 100°C	mm ² /s	12.40	12.49	12.54	12.61	13.00	12.78
	Viscosity index	-	110	111	111	110	111	110
	Acid number	mgKOH/g	0.43	0.43	0.51	0.40	0.52	0.34
	Base number (hydrochloric acid method)	mgKOH/g	2.97	3.13	3.11	2.72	2.90	2.53
	Sulfated ash content	% by mass	0.25	0.25	0.25	0.26	0.25	0.25
	Mg	mass ppm	2	2	3	2>	2>	3
	Mo	mass ppm	2>	2>	2>	2>	2>	2>
Content of each atom	P	mass ppm	306	297	305	305	303	304
	Zn	mass ppm	366	361	364	364	370	365
	N	mass ppm	920	930	930	980	980	930

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(continued)

Evaluation item	Test of preignition suppression effect	Maximum calorific value	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
			mW	4.63	1032	16.40	18.19	19.13	1966
		Heat-generation start temperature	°C	328	315	286	236	279	274
	Evaluation test of long drain properties	NOx-ISOT lifetime	Hours	142	133	123	136	134	118

[Table 2]

Composition			Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
		% by mass								
	Base oil	Component (A): paraffinic mineral oil	9103	90.73	90.48	89.93	90.25	88.37	9026	88.63
	Calcium detergent	Component (B): Ca salicylate (b1-i)	0.45	0.45	0.45	0.45				
		Component (B): Ca salicylate (b1-ii)					0.68			
		Component (B): Ca salicylate (b1-iii)								
		Component (B): Ca salicylate (b1-iv)						2.36		
		Component (B): Ca phenate (b2-i)								
		Ca sulfonate (1)							0.47	
		Ca sulfonate (2)								2.65
	Alkenyl succinimide	Component (C): non-boron-modified succinimide	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50
		Component (C): boron-modified succinimide	0.15	0.45	0.70	1.05	0.70	0.70	0.70	0.15
	Zinc dithiophosphate	Component (D): hindered amine-based AO	0.20	0.20	0.20	0.40	0.20	0.40	0.40	0.40
	Zinc dithiophosphate	Component (E): ZnDTP	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42
	Other additives	Additive mixture	425	4.25	425	425	425	4.25	425	4.25
	Total		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

(continued)

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Content (Y) of calcium carbonate contained in calcium detergent based on total amount (100% by mass) of composition	0.13	0.13	0.13	0.13	0.10	0.05	0.127	none
Content of soap component contained in calcium detergent based on total amount (100% by mass) of composition	0.13	0.13	0.13	0.13	0.33	0.71	0.13	1.38
Content of Ca atoms derived from component (B) based on total amount (100% by mass) of composition	0.054	0.054	0.054	0.054	0.054	0.054	-	-
(X)/(Y)	0.42	0.42	0.42	0.42	0.54	109	-	-
Content of B atoms derived from component (C) based on total amount (100% by mass) of composition	0.003	0.009	0.013	0.020	0.013	0.013	0.013	0.003
Content of N atoms derived from component (C) based on total amount (100% by mass) of composition	0.045	0.052	0.058	0.066	0.058	0.058	0.058	0.045
Content ratio [B/N] of B atoms to N atoms derived from component (C)	0.063	0.163	0.229	0.302	0.229	0.229	0.229	0.063
Content ratio [N/Ca] of N atoms derived from component (C) to Ca atoms derived from component (B)	0.83	0.96	1.07	1.21	1.07	1.07	-	-

(continued)

Evaluation item	Test of preignition suppression effect	Maximum calorific value	Heat-generation start temperature	NOx-ISOT lifetime	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
					mm ² /s	mm ² /s	mm ² /s	mm ² /s	mm ² /s	mm ² /s	mm ² /s	mm ² /s
Various properties	Kinematic viscosity at 40°C				107.0	108.1	107.1	107.5	111.9	110.3	109.2	111.5
	Kinematic viscosity at 100°C				12.57	12.67	12.58	12.68	13.00	12.88	12.76	12.90
	Viscosity index				110	110	110	111	111	111	110	110
	Acid number				0.39	0.38	0.47	0.32	0.52	0.76	0.36	1.33
	Base number (hydrochloric acid method)				2.76	2.72	2.71	2.97	2.90	2.85	2.61	1.56
	Sulfated ash content				0.25	0.26	0.26	0.27	0.25	0.25	0.25	0.26
	Mg				2	2	3	3	2>	2>	2>	2>
	Mo				2>	2>	2>	2>	2>	2>	2>	2>
	P				308	302	305	302	303	302	306	327
	Zn				370	369	362	360	370	360	360	393
Evaluation item	N				820	880	940	1100	960	980	980	860
	Test of preignition suppression effect				3.72	18.92	19.43	29.31	18.19	25.05	55.17	43.63
	Heat-generation start temperature				348	266	308	203	236	129	144	167
	NOx-ISOT lifetime				89	91	98	124	83	117	120	71

[0171] As shown in Table 1, each of the lubricating oil compositions prepared in Examples 1 to 7 resulted in having a high preignition suppression effect and further having excellent long drain properties, since having a low maximum calorific value and a high heat-generation start temperature. On the other hand, each of the lubricating oil compositions prepared in Comparative Examples 1 to 8 resulted in that at least one of the preignition suppression effect and the long drain properties was poor.

Claims

1. A lubricating oil composition for a gas engine, comprising: a base oil (A), at least one overbased calcium detergent (B) selected from the group consisting of calcium salicylate (B1) and calcium phenate (B2), alkenyl succinimide (C), and a hindered amine-based antioxidant (D), wherein
 - a content (X) of calcium atoms derived from the component (B) is less than 0.090% by mass based on a total amount of the lubricating oil composition;
 - a content (Y) of calcium carbonate contained in the component (B) is 0.060% by mass or more based on the total amount of the lubricating oil composition;
 - a content of boron atoms derived from the component (C) is less than 0.020% by mass based on the total amount of the lubricating oil composition; and
 - a content of the component (D) is more than 0.20% by mass based on the total amount of the lubricating oil composition.
2. The lubricating oil composition according to claim 1, wherein a ratio $[(X)/(Y)]$ of the content (X) of calcium atoms derived from the component (B) (unit: % by mass) to the content (Y) of calcium carbonate contained in the component (B) (unit: % by mass) is 0.20 to 0.90.
3. The lubricating oil composition according to claim 1 or 2, wherein the content (X) of calcium atoms derived from the component (B) is less than 0.080% by mass based on the total amount of the lubricating oil composition.
4. The lubricating oil composition according to any one of claims 1 to 3, wherein the component (B) comprises at least calcium salicylate (B1).
5. The lubricating oil composition according to any one of claims 1 to 4, comprising substantially no metal sulfonate.
6. The lubricating oil composition according to any one of claims 1 to 5, wherein the component (C) comprises both non-boron-modified alkenyl succinimide (C1) and boron-modified alkenyl succinimide (C2).
7. The lubricating oil composition according to any one of claims 1 to 6, wherein a content ratio $[N/Ca]$ of nitrogen atoms derived from the component (C) to calcium atoms derived from the component (B) is 1.20 or less.
8. The lubricating oil composition according to any one of claims 1 to 7, further comprising zinc dithiophosphate (E).
9. The lubricating oil composition according to any one of claims 1 to 8, having a sulfated ash content of less than 0.50% by mass based on the total amount of the lubricating oil composition.
10. A gas engine to which the lubricating oil composition according to any one of claims 1 to 9 is applied.
11. A method for lubricating a gas engine, comprising applying the lubricating oil composition according to any one of claims 1 to 9 to the gas engine.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/008757

A. CLASSIFICATION OF SUBJECT MATTER

C10N 10/04(2006.01)n; *C10N 30/00*(2006.01)n; *C10N 30/04*(2006.01)n; *C10N 30/10*(2006.01)n; *C10N 40/12*(2006.01)n;
C10M 133/12(2006.01)n; *C10M 133/16*(2006.01)n; *C10M 133/56*(2006.01)n; *C10M 137/10*(2006.01)n;
C10M 139/00(2006.01)n; *C10M 159/22*(2006.01)n; ***C10M 163/00***(2006.01)i
 FI: C10M163/00; C10M159/22; C10M133/16; C10M133/12; C10M133/56; C10M137/10 A; C10M139/00 A; C10N40:12;
 C10N10:04; C10N30:04; C10N30:10; C10N30:00 Z

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)

C10N10/04; C10N30/00; C10N30/04; C10N30/10; C10N40/12; C10M133/12; C10M133/16; C10M133/56; C10M137/10;
 C10M139/00; C10M159/22; C10M163/00

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2022
 Registered utility model specifications of Japan 1996-2022
 Published registered utility model applications of Japan 1994-2022

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A		9
Y	WO 2020/203525 A1 (IDEMITSU KOSAN CO) 08 October 2020 (2020-10-08) claims 1-12, paragraphs [0001]-[0005], [0008]-[0014], [0032]-[0050], examples 1-6, comparative examples 1-3	1-8, 10-11
A		9
A	JP 2020-164747 A (IDEMITSU KOSAN CO) 08 October 2020 (2020-10-08) claims 1-8	1-11
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☒ 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

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/008757

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	JP 10-219266 A (TONEN CORP) 18 August 1998 (1998-08-18) claims 1-2	1-11

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2022/008757

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Form PCT/ISA/210 (patent family annex) (January 2015)

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