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(54) LUBRICATING OIL COMPOSITION

(57) Provided is a lubricating oil composition for a gas engine, comprising a base oil (A), a calcium-based detergent (B), and an alkenyl succinimide (C), wherein a content of calcium atoms is 0.09 to 0.17 mass% based on the total amount of the lubricating oil composition, the

component (C) comprises a non-boron-modified alkenyl bis-succinimide (C1), and a content of boron atoms derived from the component (C) is less than 0.02 mass% based on the total amount of the lubricating oil composition.

Description

Technical Field

5 [0001] The present invention relates to a 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 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 prescribed range, and a sulfated ash content is set to 0.6 mass% or less.

Citation List

20 Patent Literature

[0005] Patent Literature 1: Japanese Patent Laid-Open No. 2018-203952

25 Summary of Invention

Technical Problem

30 [0006] Under such circumstances, a lubricating oil composition preferably employable for a novel gas engine that is favorable in various performance has been desired.

Solution to Problem

35 [0007] The present invention provides a lubricating oil composition for a gas engine, comprising a base oil, a calcium-based detergent, and an alkenyl succinimide comprising a non-boron-modified alkenyl bis-succinimide, wherein contents of calcium atoms and boron atoms are adjusted to specific ranges.

[0008] The present invention provides, for example, a lubricating oil composition, a gas engine, and use of a lubricating oil composition according to the following embodiments [1] to [12].

40 [1] A lubricating oil composition for a gas engine, comprising a base oil (A), a calcium-based detergent (B), and an alkenyl succinimide (C), wherein

a content of the component (B) in terms of calcium atoms is 0.09 to 0.17 mass% based on the total amount of the lubricating oil composition,
45 the component (C) comprises a non-boron-modified alkenyl bis-succinimide (C1), and
a content of boron atoms derived from the component (C) is less than 0.02 mass% based on the total amount of the lubricating oil composition.

50 [2] The lubricating oil composition according to the above [1], wherein a content ratio [N/Ca] by mass of nitrogen atoms derived from the component (C) to calcium atoms derived from the component (B) is 0.90 or less.

[3] The lubricating oil composition according to the above [1] or [2], wherein the component (B) comprises calcium salicylate (B1).

[4] The lubricating oil composition according to any one of the above [1] to [3], wherein the component (C1) is a non-boron-modified alkenyl bis-succinimide at least having a polybutenyl group or a polyisobutylene group having a weight-average molecular weight of 500 to 3000.

[5] The lubricating oil composition according to any one of the above [1] to [4], wherein the component (C) further comprises a boron-modified alkenyl succinimide (C2) together with the component (C1).

[6] The lubricating oil composition according to the above [5], wherein a content ratio [B/N] by mass of boron atoms

derived from the component (C2) to nitrogen atoms derived from the component (C) is 0.01 to 0.35.

[7] The lubricating oil composition according to any one of the above [1] to [6], wherein a content of the component (C) in terms of nitrogen atoms is 0.005 to 0.15 mass% based on the total amount of the lubricating oil composition.

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

[9] The lubricating oil composition according to any one of the above [1] to [8], wherein a content of magnesium atoms is less than 0.04 mass% based on the total amount of the lubricating oil composition.

[10] The lubricating oil composition according to any one of the above [1] to [9], wherein a content of molybdenum atoms is less than 0.01 mass% based on the total amount of the lubricating oil composition.

[11] A gas engine using the lubricating oil composition according to any one of the above [1] to [10].

[12] Use of a lubricating oil composition, wherein the lubricating oil composition according to any one of the above [1] to [10] is applied to a gas engine.

Advantageous Effects of Invention

[0009] The lubricating oil composition of one preferred embodiment 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 embodiment, the lubricating oil composition is excellent in preignition suppression effect even when it is used for a long time. These lubricating oil compositions having such characteristics can be preferably used for lubrication of a gas engine.

Description of Embodiments

[0010] In the present specification, a kinematic viscosity and a viscosity index mean values measured and calculated in accordance with JIS K2283:2000.

[0011] The contents of calcium atoms, phosphorus atoms, boron atoms, zinc atoms, and molybdenum atoms mean values measured in accordance with JP1-5S-38-92.

[0012] The content of nitrogen atoms means a value measured in accordance with JIS K2609:1998.

[Constitution of lubricating oil composition]

[0013] The lubricating oil composition of the present invention is a lubricating oil composition for a gas engine, comprising a base oil (A), a calcium-based detergent (B), and an alkenyl succinimide (C), wherein

a content of the component (B) in terms of calcium atoms is 0.09 to 0.17 mass% based on the total amount of the lubricating oil composition,

the component (C) comprises a non-boron-modified alkenyl bis-succinimide (C1), and

a content of boron atoms derived from the component (C) is adjusted so as to be less than 0.02 mass% based on the total amount of the lubricating oil composition.

[0014] In recent years, achievement of high power and high efficiency of a gas engine has been desired, and along with this, the continuous operation time of a gas engine exceeds 1500 hours, and the temperature inside the gas engine also tends to extremely increase. Along with the use in such environment, abnormal combustion called preignition in a gas engine tends to occur. On that account, development of a lubricating oil composition that can suppress preignition and can be preferably used for a gas engine has been desired.

[0015] By the way, it is usually carried out to judge the occurrence frequency of preignition of a lubricating oil composition from a peak calorific value by subjecting the lubricating oil composition that is a new oil to high-pressure DSC measurement (differential scanning colorimetry).

[0016] However, even for a lubricating oil composition that has been judged to hardly bring about preignition by the evaluation based on a peak calorific value of a new oil through such high-pressure DSC measurement, the occurrence frequency of preignition sometimes increases when the lubricating oil composition is used for a long time.

[0017] In order to specify a factor therefor, various studies have been made, and as a result, it has been found that an incomplete combustion product deposited with the use of the lubricating oil composition, that is called a "deposit", generates heat, and thereby, preignition is sometimes brought about. That is to say, suppression of preignition attributable to heat generation of a deposit is also desired.

[0018] Then, in order to suppress heat generation of a "deposit" produced with the use of a lubricating oil composition for a long time, further studies have been made, and as a result, it has been proved that heat generation of a deposit can be effectively suppressed by the lubricating oil composition of the present invention.

[0019] That is to say, a lubricating oil composition in which a non-boron-modified alkenyl bis-succinimide (C1) was

used as the alkenyl succinimide (C) and the content of the calcium-based detergent (B) in terms of calcium atoms and the content of boron atoms derived from the component (C) were adjusted in prescribed ranges was prepared, and when high-pressure DSC measurement of an ash content of the lubricating oil composition was carried out, the result was that the peak calorific value was suppressed, and it has been shown that the occurrence frequency of preignition is decreased.

[0020] That is to say, it is thought that the lubricating oil composition of the present invention can effectively suppress occurrence of preignition even when it is used for a long time.

[0021] The lubricating oil composition of one embodiment of the present invention preferably further contains zinc dithiophosphate (D).

[0022] The lubricating oil composition of one embodiment of the present invention may further contain lubricating oil additives other than the components (B) to (D) when needed as long as the effects of the present invention are not impaired.

[0023] In the lubricating oil composition of one embodiment of the present invention, the total content of the components (A), (B) and (C) is preferably 60 mass% or more, more preferably 65 mass% or more, still more preferably 70 mass% or more, still much more preferably 75 mass% or more, and particularly preferably 80 mass% or more, based on the total amount (100 mass%) of the lubricating oil composition.

[0024] Hereinafter, details of each component contained in the lubricating oil composition of one embodiment of the present invention will be described.

20 <Base oil (A)>

[0025] As the base oil (A) used in one embodiment of the present invention, one or more selected from mineral oils and synthetic oils can be mentioned.

[0026] Examples of the mineral oils 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 hydrorefining.

[0027] Examples of the synthetic oils include poly- α -olefins, such as an α -olefin homopolymer and an α -olefin copolymer (for example, an α -olefin copolymer having 8 to 14 carbon atoms such as an ethylene- α -olefin copolymer); iso-paraffin; polyalkylene glycol; ester oils, such as polyol ester, dibasic acid ester, and phosphoric acid ester; ether oils, such as polyphenyl ether; alkylbenzene; alkylnaphthalene; and synthetic oil (GTL) obtained by isomerizing wax (GTL WAX (Gas To Liquids WAX)) produced from natural gas through Fischer-Tropsch process or the like.

[0028] The base oil (A) used in one embodiment 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.

[0029] The kinematic viscosity of the base oil (A) used in one embodiment of the present invention at 40°C is preferably 10 to 130 mm²/s, more preferably 20 to 120 mm²/s, still more preferably 30 to 110 mm²/s, and still much more preferably 40 to 100 mm²/s.

[0030] The viscosity index of the base oil (A) used in one embodiment of the present invention is preferably 70 or more, more preferably 80 or more, still more preferably 90 or more, still much more preferably 100 or more, and particularly preferably 105 or more.

[0031] When a mixed oil that is a combination of two or more base oils is used as the base oil (A) in one embodiment of the present invention, the kinematic viscosity and the viscosity index of the mixed oil are preferably in the above ranges.

[0032] In the lubricating oil composition of one embodiment of the present invention, the content of the component (A) is preferably 50 to 99.5 mass%, more preferably 60 to 99.0 mass%, still more preferably 65 to 97.0 mass%, and still much more preferably 70 to 95.0 mass%, based on the total amount (100 mass%) of the lubricating oil composition.

<Calcium-based detergent (B)>

[0033] The lubricating oil composition of the present invention contains a calcium-based detergent (B).

[0034] Since the calcium-based detergent (B) is contained, a lubricating oil composition capable of effectively suppressing occurrence of preignition even when it is used for a long time can be obtained. Moreover, this component contributes to extension of a life of the lubricating oil composition, such as suppression of occurrence of sludge that is produced when the lubricating oil composition is used in a high-temperature high-load environment in a gas engine.

[0035] The component (B) may be used singly, or may be used in combination of two or more.

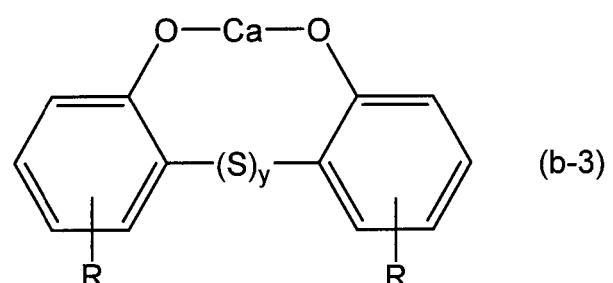
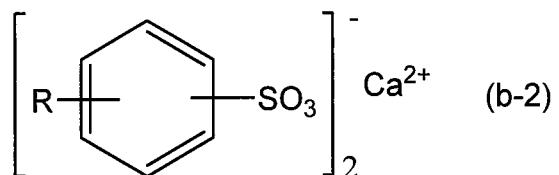
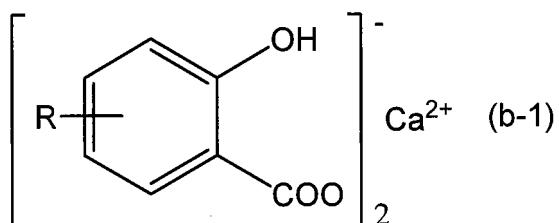
[0036] From the viewpoint of obtaining a lubricating oil composition that is excellent in preignition suppression effect even when it is used for a long time, the content of the component (B) in terms of calcium atoms in the lubricating oil composition of the present invention is 0.09 to 0.17 mass% based on the total amount (100 mass%) of the lubricating

oil composition, but it is preferably 0.10 to 0.16 mass%, more preferably 0.11 to 0.15 mass%, still more preferably 0.115 to 0.14 mass%, and still much more preferably 0.118 to 0.135 mass%.

[0037] From the above viewpoint, the calcium-based detergent (B) used in one embodiment of the present invention is preferably one or more selected from calcium salicylate (B1), calcium sulfonate (B2), and calcium phenate (B3), and more preferably, it contains at least calcium salicylate (B1).

[0038] In one embodiment of the present invention, the content ratio of the calcium salicylate (B1) in the component (B) is preferably 50 to 100 mass%, more preferably 60 to 100 mass%, still more preferably 70 to 100 mass%, still much more preferably 80 to 100 mass%, and particularly preferably 90 to 100 mass%, based on the total amount (100 mass%) of the component (B).

[0039] The calcium salicylate (B1) is preferably a compound represented by the following general formula (b-1), the calcium sulfonate (B2) is preferably a compound represented by the following general formula (b-2), and the calcium phenate (B3) is preferably a compound represented by the following general formula (b-3).



[0040] In the general formulae (b-1) to (b-3), R is a hydrogen atom or a hydrocarbon group having 1 to 18 carbon atoms.

[0041] Examples of the hydrocarbon groups 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.

[0042] In the general formula (b-3), Y is an integer of 0 or more, and preferably an integer of 0 to 3.

[0043] The base number of the component (B) used in one embodiment of the present invention is preferably 0 to 600 mgKOH/g.

[0044] In the lubricating oil composition of one embodiment of the present invention, however, it is more preferable that the component (B) contain an overbased calcium-based detergent having a base number of 100 mgKOH/g or more.

[0045] The base number of the overbased calcium-based detergent is 100 mgKOH/g or more, but it is preferably 150 to 500 mgKOH/g, and more preferably 200 to 400 mgKOH/g.

[0046] In the present specification, the "base number" of the component (B) means a base number measured by hydrochloric acid method in accordance with JIS K2501 "Petroleum products and lubricants - Determination of neutralization number", 7.

[0047] In the lubricating oil composition of one embodiment of the present invention, the compounding amount (content) of the component (B) is appropriately adjusted in such a manner that the content of calcium atoms in the lubricating oil composition is in the aforesaid range, but it is preferably 0.10 to 10.0 mass%, more preferably 0.20 to 7.5 mass%, still more preferably 0.30 to 5.0 mass%, and still much more preferably 0.50 to 2.5 mass%, based on the total amount (100

mass%) of the lubricating oil composition.

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

5 [0048] The lubricating oil composition of one embodiment 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.

10 [0049] The metal-based detergent other than the component (B) is one or more selected from a metal salicylate, a metal phenate, and a metal sulfonate each of which contains an alkali metal atom or an alkaline earth metal atom other than a calcium atom. However, from the viewpoint of decreasing a causative substance of a deposit, the content of a magnesium-based detergent is preferably smaller.

[0050] The above metal salicylate, metal phenate and metal sulfonate are preferably those having structures represented by the aforesaid general formulae (b-1), (b-2) and (b-3), respectively.

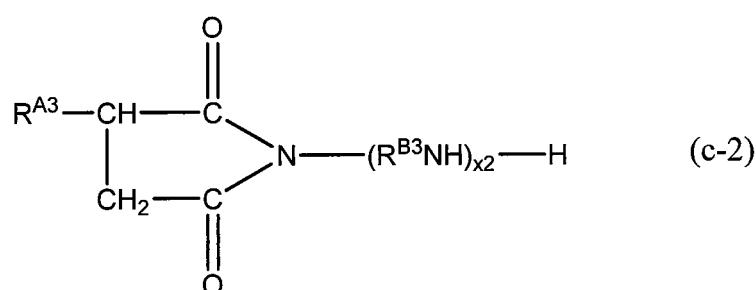
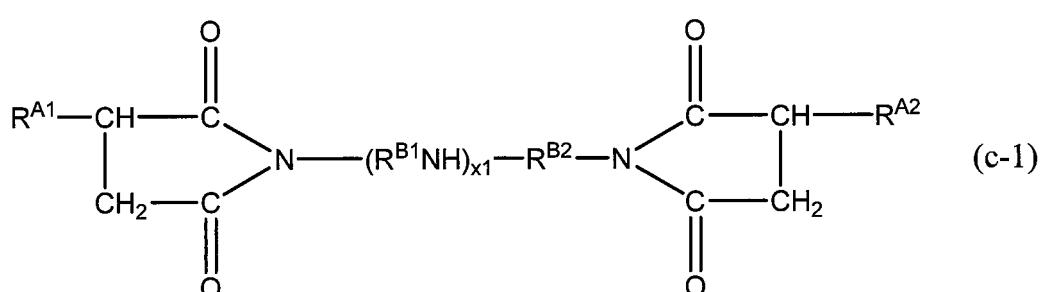
<Alkenyl succinimide (C)>

15 [0051] The lubricating oil composition of the present invention contains an alkenyl succinimide (C).
 [0052] The component (C) may be used singly, or may be used in combination of two or more.
 [0053] The component (C) has a function of homogenously dispersing additives including the component (B).
 20 [0054] In the lubricating oil composition of the present invention, a modified alkenyl succinimide may be used as the alkenyl succinimide (C).
 [0055] For example, a boron-modified alkenyl succinimide that is a boron-modified product is excellent in that it homogeneously disperses an additive such as the component (B) to allow the additive to effectively exhibit its function. However, if the boron-modified alkenyl succinimide is contained in a deposit that has occurred with long time use, it tends to become a factor for the occurrence of preignition.

25 [0056] On that account, in the lubricating oil composition of the present invention, the content of boron atoms derived from the component (C) is less than 0.02 mass% based on the total amount (100 mass%) of the lubricating oil composition.

30 [0057] From the above viewpoint, the content of boron atoms derived from the component (C) in the lubricating oil composition of one embodiment of the present invention is preferably 0.018 mass% or less, more preferably 0.015 mass% or less, still more preferably 0.012 mass% or less, and still much more preferably 0.011 mass% or less, based on the total amount (100 mass%) of the lubricating oil composition.

[0058] Examples of the components (C) used in one embodiment of the present invention include an alkenyl bis-succinimide represented by the following general formula (c-1) and an alkenyl monosuccinimide represented by the following general formula (c-2).



[0059] In the general formulae (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).

[0060] Examples of the alkenyl groups capable of being selected as R^{A1} , R^{A2} and R^{A3} include a polybutenyl group, a polyisobutetyl group and an ethylene-propylene copolymer, and among these, a polybutenyl group or a polyisobutetyl group is preferable.

[0061] R^{B1} , R^{B2} and R^{B3} are each independently an alkylene group having 2 to 5 carbon atoms.

x1 is an integer of 0 to 10, preferably an integer of 1 to 4, and more preferably 2 or 3.

x2 is an integer of 1 to 10, preferably an integer of 2 to 5, and more preferably 3 or 4.

[0062] In the component (C), a modified alkenyl succinimide obtained by reacting a compound represented by the aforesaid general formula (c-1) or (c-2) with one or more selected from a boron compound, an alcohol, an aldehyde, a ketone, an alkylphenol, a cyclic carbonate, an epoxy compound and an organic acid is also contained.

[0063] Here, in the lubricating oil composition of the present invention, the component (C) contains a non-boron-modified alkenyl bis-succinimide (C1). The component (C1) is presumed to have a high effect of homogeneously dispersing the component (B), and it is thought that the component (C) can sustain the preignition suppression effect possessed by the component (B) even in long time use.

[0064] On that account, the lubricating oil composition containing a non-boron-modified alkenyl bis-succinimide (C1) as the component (C) together with the component (B) can effectively suppress occurrence of preignition even when it is used for a long time.

[0065] The component (C1) is a non-boron-modified alkenyl bis-succinimide, but is preferably a non-modified alkenyl bis-succinimide.

[0066] In the studies, it has been proved that the above effect is seen when the non-boron-modified alkenyl bis-succinimide (C1) is used, but on the other hand, the effect is hardly exhibited sufficiently in the case of such an alkenyl monosuccinimide as represented by the aforesaid general formula (c-2).

[0067] From the above viewpoint, the content of the component (C1) in terms of nitrogen atoms in the lubricating oil composition of one embodiment of the present invention is preferably 0.001 to 0.15 mass%, more preferably 0.005 to 0.10 mass%, still more preferably 0.01 to 0.09 mass%, and still much more preferably 0.03 to 0.07 mass%, based on the total amount (100 mass%) of the lubricating oil composition.

[0068] In one embodiment of the present invention, the content ratio of the non-boron-modified alkenyl bis-succinimide (C1) in the component (C) is preferably 30 mass% or more, more preferably 50 mass% or more, still more preferably 60 mass% or more, still much more preferably 70 mass% or more, and particularly preferably 80 mass% or more, based on the total amount (100 mass%) of the component (C).

[0069] From the viewpoint of improving dispersibility of the component (B) and thereby preparing a lubricating oil composition capable of effectively suppressing occurrence of preignition even when it is used for a long time, the component (C1) is preferably an alkenyl bis-succinimide represented by the aforesaid general formula (c-1), and is more preferably a non-boron-modified alkenyl bis-succinimide at least having a polybutenyl group or a polyisobutetyl group having a weight-average molecular weight of 500 to 3000 (preferably 900 to 2500).

[0070] In one embodiment of the present invention, the component (C) can also further contain a boron-modified alkenyl succinimide (C2) together with the component (C1).

[0071] Since the component (C2) is contained, an effect of further improving dispersibility of the component (B) can be expected.

[0072] However, there is also an aspect that the boron-modified alkenyl succinimide (C2) in the component (C) tends to be a factor for the occurrence of preignition if it is contained in a deposit occurring with long time use, as previously described. On that account, the content of the component (C2) needs to be adjusted in such a manner that the content of boron atoms in the lubricating oil composition is in the aforesaid range.

[0073] Examples of the components (C2) 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 aforesaid general formula (c-2), but preferable is a boron-modified product of the alkenyl monosuccinimide represented by the aforesaid general formula (c-2).

[0074] The boron-modified alkenyl succinimide (C2) can be produced by, for example, reacting an alkenyl succinic anhydride obtained by the reaction of a polyolefin with maleic anhydride with a polyamine and a boron compound.

[0075] Examples of the polyolefins include polymers obtained by polymerizing one or two or more selected from α -olefins having 2 to 8 carbon atoms, but preferable is a copolymer of isobutene and 1-butene.

[0076] Examples of the polyamines include single diamines, such as ethylenediamine, propylenediamine, butylenediamine and pentylenediamine, polyalkylene polyamines, such as diethylenetriamine, triethylenetetramine, tetraethyl-eneptenamine, pentaethylhexamine, di(methylethylene)triamine, dibutylenetriamine, tributylenetetramine and pentapentylenehexamine; and piperazine derivatives, such as aminoethylpiperazine.

[0077] Examples of the boron compounds include boron oxide, boron halide, boric acid, boric anhydride, boric acid ester, and ammonium salt of boric acid.

[0078] In one embodiment of the present invention, the ratio [B/N] of boron atoms to nitrogen atoms, both the atoms constituting the component (C2), is preferably 0.1 or more, more preferably 0.2 or more, still more preferably 0.3 or more, and still much more preferably 0.5 or more.

[0079] From the viewpoint of improving dispersibility of the component (B) and thereby preparing a lubricating oil composition capable of effectively suppressing occurrence of preignition even when it is used for a long time, the content ratio [N/Ca] by mass of nitrogen atoms derived from the component (C) to calcium atoms derived from the component (B) in the lubricating oil composition of one embodiment of the present invention is preferably 0.90 or less, more preferably 0.80 or less, still more preferably 0.70 or less, still much more preferably 0.60 or less, particularly preferably 0.55 or less, and is preferably 0.01 or more, more preferably 0.05 or more, still more preferably 0.10 or more, still much more preferably 0.15 or more, particularly preferably 0.20 or more.

[0080] In the lubricating oil composition of one embodiment of the present invention, the content ratio [B/N] by mass of boron atoms derived from the component (C2) to nitrogen atoms derived from the component (C) is preferably 0.01 to 0.35, more preferably 0.03 to 0.25, still more preferably 0.05 to 0.22, still much more preferably 0.10 to 0.20, and particularly preferably 0.12 to 0.18.

[0081] In the lubricating oil composition of one embodiment of the present invention, the content of the component (C) in terms of nitrogen atoms is preferably 0.005 to 0.15 mass%, more preferably 0.01 to 0.10 mass%, still more preferably 0.02 to 0.09 mass%, and still much more preferably 0.04 to 0.07 mass%, based on the total amount (100 mass%) of the lubricating oil composition.

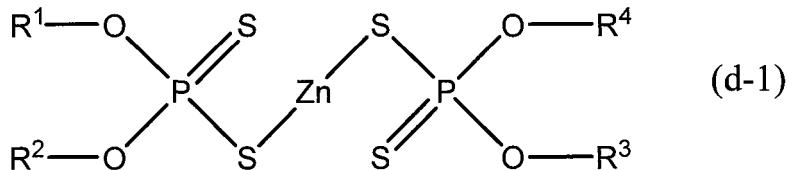
[0082] The compounding amount (content) of the component (C) is appropriately adjusted in such a manner that the content of nitrogen atoms derived from the component (C) is in the aforesaid range, but it is preferably 0.10 to 15.0 mass%, more preferably 0.50 to 12.0 mass%, still more preferably 1.0 to 10.0 mass%, and still much more preferably 2.5 to 8.0 mass%, based on the total amount (100 mass%) of the lubricating oil composition.

<Zinc dithiophosphate (D)>

[0083] The lubricating oil composition of one embodiment of the present invention preferably further contains zinc dithiophosphate (ZnDTP) (D) as an anti-wear agent.

[0084] The component (D) may be used singly, or may be used in combination of two or more.

[0085] The zinc dithiophosphate (D) used in one embodiment of the present invention is preferably a compound represented by the following general formula (d-1).



[0086] In the formula (d-1), R¹ to R⁴ each independently represent a hydrocarbon group, and may be the same as one another or may be different from one another.

[0087] The number of carbon atoms of the hydrocarbon group capable of being selected as R¹ to R⁴ is preferably 1 to 20, more preferably 1 to 16, still more preferably 3 to 12, and still much more preferably 3 to 10.

[0088] Specific examples of the hydrocarbon groups capable of being selected as R¹ to R⁴ 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.

[0089] Among these, preferable are alkyl groups, more preferable are primary or secondary alkyl groups, and still more preferable are secondary alkyl groups, as the hydrocarbon groups capable of being selected as R¹ to R⁴.

[0090] In the lubricating oil composition of one embodiment of the present invention, the content of the component

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

[0091] The content (compounding amount) of the component (D) may be adjusted in such a manner that the content in terms of zinc atoms is in the above range, but it is preferably 0.01 to 15.0 mass%, more preferably 0.05 to 10.0 mass%, still more preferably 0.10 to 8.0 mass%, still much more preferably 0.20 to 5.0 mass%, or may be 1.00 mass% or less, 0.90 mass% or less, 0.85 mass% or less, or 0.80 mass% or less, based on the total amount (100 mass%) of the lubricating oil composition.

10 <Lubricating oil additives>

[0092] The lubricating oil composition of one embodiment of the present invention may further contain lubricating oil additives other than the components (B) to (D) when needed as long as the effects of the present invention are not impaired.

[0093] Examples of such lubricating oil additives include an antioxidant, a pour point depressant, a viscosity index improver, a demulsifier, a friction modifier, a corrosion inhibitor, a metal deactivator, an antistatic agent, and an anti-foaming agent.

[0094] These lubricating oil additives may be each used singly, or may be each used in combination of two or more.

[0095] The contents of these lubricating oil additives can be each appropriately adjusted as long as the effects of the present invention are not impaired, but 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>

[0096] The production method for the lubricating oil composition of one embodiment of the present invention is not particularly limited, but from the viewpoint of productivity, preferable is a method having a step of compounding the aforesaid components (B) and (C), and if necessary, the component (D) and other lubricating oil additives with the base oil (A).

[0097] Here, the compounding amounts of the components (A), (B), (C) and (D), and the lubricating oil additives are as previously described.

[Properties of lubricating oil composition]

[0098] The kinematic viscosity of the lubricating oil composition of one embodiment of the present invention at 40°C is preferably 10 to 130 mm²/s, more preferably 20 to 115 mm²/s, still more preferably 30 to 100 mm²/s, and still much more preferably 40 to 90 mm²/s.

[0099] The kinematic viscosity of the lubricating oil composition of one embodiment of the present invention at 100°C is preferably 2.5 to 20.0 mm²/s, more preferably 4.0 to 16.0 mm²/s, still more preferably 5.5 to 14.0 mm²/s, and still much more preferably 7.0 to 12.0 mm²/s.

[0100] The viscosity index of the lubricating oil composition of one embodiment of the present invention is preferably 90 or more, more preferably 100 or more, still more preferably 110 or more, and still much more preferably 130 or more.

[0101] The acid value of the lubricating oil composition of one embodiment of the present invention is preferably 0.30 to 2.00 mgKOH/g, more preferably 0.35 to 1.70 mgKOH/g, still more preferably 0.40 to 1.30 mgKOH/g, and still much more preferably 0.45 to 1.00 mgKOH/g.

[0102] In the present specification, the acid value of the lubricating oil composition means a value measured in accordance with JIS K2501:2003 (indicator method).

[0103] The base number of the lubricating oil composition of one embodiment of the present invention is preferably 2.0 to 10.0 mgKOH/g, more preferably 2.5 to 8.0 mgKOH/g, still more preferably 3.0 to 6.5 mgKOH/g, and still much more preferably 3.5 to 5.0 mgKOH/g.

[0104] 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).

[0105] In the lubricating oil composition of one embodiment of the present invention, the content of phosphorus atoms is preferably 0.01 to 0.15 mass%, more preferably 0.015 to 0.12 mass%, still more preferably 0.02 to 0.10 mass%, and still much more preferably 0.025 to 0.08 mass%, based on the total amount (100 mass%) of the lubricating oil composition.

[0106] In the lubricating oil composition of one embodiment of the present invention, the content of nitrogen atoms is preferably 0.01 to 0.50 mass%, more preferably 0.02 to 0.30 mass%, still more preferably 0.03 to 0.20 mass%, still much more preferably 0.04 to 0.15 mass%, and particularly preferably 0.045 to 0.10 mass%, based on the total amount (100

mass%) of the lubricating oil composition.

[0107] In the lubricating oil composition of one embodiment of the present invention, the content of magnesium atoms is preferably less than 0.04 mass%, more preferably less than 0.02 mass%, still more preferably less than 0.01 mass%, and still much more preferably less than 0.001 mass%, based on the total amount of the lubricating oil composition, from the viewpoint of decreasing a causative substance of a deposit.

[0108] In the lubricating oil composition of one embodiment of the present invention, the content of molybdenum atoms is preferably less than 0.01 mass%, more preferably less than 0.005 mass%, and still more preferably less than 0.001 mass%, based on the total amount (100 mass%) of the lubricating oil composition, from the viewpoint of preparing a lubricating oil composition capable of effectively suppressing occurrence of preignition even when it is used for a long time.

[Use application of lubricating oil composition]

[0109] The lubricating oil composition of one preferred embodiment of the present invention is excellent in preignition suppression effect even in the case where it is used for a long time.

[0110] On that account, the lubricating oil composition of one embodiment of the present invention can be applied to various apparatuses in which it can exhibit the above characteristics, but it is preferably applied to lubrication of gas engines.

[0111] When the aforesaid characteristics of the lubricating oil composition of one embodiment of the present invention are taken into consideration, the present invention can also provide the following [1] and [2].

[1] A gas engine using the aforesaid lubricating oil composition of one embodiment of the present invention.

[2] Use of a lubricating oil composition, in which the aforesaid lubricating oil composition of one embodiment of the present invention is applied to a gas engine.

25 Examples

[0112] Next, the present invention will be described in much 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.

30 (1) Kinematic viscosity, viscosity index

[0113] The kinematic viscosity and viscosity index were measured and calculated in accordance with JIS K2283:2000.

35 (2) Contents of calcium atoms, phosphorus atoms, boron atoms, zinc atoms and molybdenum atoms

[0114] The contents were measured in accordance with JPI-5S-38-92.

40 (3) Content of nitrogen atoms

[0115] The content was measured in accordance with JIS K2609:1998.

45 (4) Acid value

[0116] The acid value was measured in accordance with JIS K2501:2003 (indicator method).

50 (5) Base number (hydrochloric acid method)

[0117] The base number was measured in accordance with JIS K2501:2003 (hydrochloric acid method).

55 (6) Weight-average molecular weight (Mw)

[0118] 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)

[0119]

Column: sequentially connected two of "Shodex LF404".

Column temperature: 35°C

Developing solvent: chloroform

Flow rate: 0.3 mL/min

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Examples 1 to 6, Comparative Examples 1 to 5

[0120] A base oil and various additives of types shown in Table 1 and Table 2 were added and mixed in compounding amounts shown in Table 1 and Table 2, thereby preparing each lubricating oil composition.

10 [0121] Details of each component used in the preparation of the lubricating oil composition are as follows.

<Base oil>

15 [0122] "Base oil (a-i)": paraffinic mineral oil classified in Group II, 40°C kinematic viscosity = 90.5 mm²/s, viscosity index = 107.

[0123] "Base oil (a-ii)": paraffinic mineral oil classified in Group III, 40°C kinematic viscosity = 44.7 mm²/s, viscosity index = 140.

<Calcium-based detergent>

20 [0124] "Ca salicylate (b-i)": base number = 214 mgKOH/g (hydrochloric acid method), Ca atom content = 8.0 mass%.

<Imide compound>

25 [0125] "Non-modified bis-succinimide (c1-i)": polybutenyl bis-succinimide having a polybutenyl group of Mw=950, content of nitrogen atoms = 1.1 mass%.

[0126] "Non-modified bis-succinimide (c1-ii)": polybutenyl bis-succinimide having a polybutenyl group of Mw=2300, content of nitrogen atoms = 1.0 mass%.

30 [0127] "Boron-modified monosuccinimide (c2-i)": borylation product of polybutenyl monosuccinimide having a polybutenyl group, content of boron atoms (B) = 0.49 mass%, content of nitrogen atoms (N) = 1.50 mass%, B/N = 0.33.

[0128] "Boron-modified monosuccinimide (c2-ii)": borylation product of polybutenyl monosuccinimide having a polybutenyl group, content of boron atoms (B) = 1.30 mass%, content of nitrogen atoms (N) = 1.23 mass%, B/N = 1.06.

35 [0129] "Non-modified monosuccinimide (c3)": polybutenyl monosuccinimide having a polybutenyl group of Mw=950, content of nitrogen atoms = 2.10 mass%.

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<Zinc dithiophosphate>

[0130] "Pri-ZnDTP": primary zinc dialkyldithiophosphate, phosphorus atom content = 7.4 mass%, zinc atom content = 8.9 mass%.

40 [0131] "Sec-ZnDTP": secondary zinc dialkyldithiophosphate, phosphorus atom content = 8.2 mass%, zinc atom content = 9.0 mass%.

<Other additives>

45 [0132] Antioxidant: mixture of amine-based antioxidant and phenol-based antioxidant.

[0133] Regarding the lubricating oil compositions prepared, the kinematic viscosity, viscosity index, acid value and base number were measured or calculated, and the following test of preignition suppression effect was carried out. The results of them are set forth in Table 1 and Table 2.

50 [Test of preignition suppression effect]

[0134] In a crucible, the lubricating oil composition prepared was placed as a 25 mL sample and subjected to complete combustion over a period of 30 minutes. The temperature of the ash content after combustion was increased up to 600°C from 50°C at a temperature-increasing rate of 10°C/min in an atmosphere of oxygen at high pressure of 3 MPa using a differential scanning calorimeter (manufactured by METTLER TOLEDO, high-pressure DSC), and a peak calorific value (unit: mW) of the ash content was measured.

[0135] The peak calorific value of the ash content is preferably 22.0 mW or less, more preferably 20.0 mW or less, still more preferably 18.5 mW or less, still much more preferably 15.0 mW or less, and particularly preferably 11.0 mW

or less.

[0136] The lubricating oil compositions prepared in Example 1 and Comparative Example 1 were each subjected to the same operation as above as a new oil, and a peak calorific value (unit: mW) of the new oil was measured.

[0137] The results of them are as shown in Table 1 and Table 2.

5 **[0138]** [Table 1]

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Table 1

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Base oil	Base oil (a-i)	mass%	14.31	13.00	13.00	13.00	13.00
Base oil	Base oil (a-ii)	mass%	75.82	78.16	78.37	77.27	78.20
Ca-based detergent	Ca salicylate (b-i)	mass%	1.58	1.58	1.58	1.58	1.58
Non-modified bis-succinimide (c1-i)	mass%	4.30					
Non-modified bis-succinimide (c1-ii)	mass%	6.00		3.90	3.90	6.00	4.00
Imide compound	Boron-modified monosuccinimide (c2-i)	mass%		1.30			
	Boron-modified monosuccinimide (c2-ii)	mass%	0.49		0.49	0.49	0.56
	Non-modified monosuccinimide (c3)	mass%			1.00		1.00
Zinc dithiophosphate	Pri ZnDTP	mass%	0.50				
Other additives	Sec-ZnDTP	mass%		0.36	0.36	0.36	0.36
	Antioxidant	mass%	1.30	1.30	1.30	1.30	1.30
	Total	mass%	100.00	100.00	100.00	100.00	100.00
Content of N derived from non-modified bis-succinimide		N content (derived from imide compound)	mass%	0.063	0.065	0.045	0.065
Content of each atom derived from imide compound		B content (derived from imide compound)	mass%	0.008	0.008	0.008	0.008
		B/N (derived from imide compound)	-	0.13	0.12	0.18	0.12
		N (derived from imide compound)/Ca	-	0.49	0.50	0.35	0.51
						0.49	0.14

(continued)

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		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Content of each atom based on total amount (100 mass%) of lubricating oil composition	Ca content	mass %	0.129	0.127	0.129	0.128	0.129
	P content	mass %	0.036	0.029	0.029	0.029	0.029
	N content	mass %	0.100	0.074	0.075	0.054	0.074
	Mo content	mass %	<0.001	<0.001	<0.001	<0.001	<0.001
Various properties of lubricating oil composition	Kinematic viscosity 40°C	mm ² /s	63.65	55.83	61.20	58.91	64.05
	Kinematic viscosity 100°C	mm ² /s	9.89	8.86	9.57	9.31	9.93
	Viscosity index	-	140	136	139	139	140
	Acid value	mgKOH/g	0.87	0.57	0.63	0.73	0.67
	Base number (hydrochloric acid method)	mgKOH/g	4.07	4.21	4.13	3.99	3.91
Test of preignition suppression effect	Peak calorific value of ash content	mW	13.3	2.3	10.4	7.1	5.6
	Peak calorific value of new oil	mW	192	-	-	-	-

[Table 2] Table 2

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Base oil	Base oil (a-i) Base oil (a-ii)	mass% 13.00	14.57	13.00	13.00	14.41
Ca-based detergent	Ca salicylate (b-i)	mass% 75.45	75.82	75.12	64.94	76.92
	Non-modified bis-succinimide (c1-i)	mass% 1.65	1.58	1.58	0.37	0.38
	Non-modified bis-succinimide (c1-ii)	mass% 5.50	4.63		18.40	6.00
	Boron-modified monosuccinimide (c2-i)	mass% 5.90		1.60		
Imide compound	Boron-modified monosuccinimide (c2-ii)	mass% 1.60	1.60		0.49	0.49
	Non-modified monosuccinimide (c3)	mass% 1.00			1.00	
Zinc dithiophosphate	Pri-ZnDTP Sec-ZnDTP	mass% 0.50	0.50	0.50	0.50	0.50
Other additives	Antioxidant	mass% 1.30	1.30	1.30	1.30	1.30
	Total	mass% 100.00	100.00	100.00	100.00	100.00
Content of N derived from non-modified bis-succinimide	mass% 0.055	0.046	0.076	0.184	0.060	

(continued)

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Content of each atom derived from imide compound	N content (derived from imide compound)	mass% 0.094	0.063	0.083	0.250	0.063
	B content (derived from imide compound)	mass% 0.023	0.022	0.023	0.008	0.008
	B/N (derived from imide compound)	- 0.24	0.36	0.27	0.32	0.13
	N (derived from imide compound) /Ca	- 0.69	0.49	0.64	8.12	2.09
	Ca content	mass% 0.137	0.129	0.129	0.031	0.031
	P content	mass% 0.036	0.037	0.036	0.036	0.036
	N content	mass% 0.013	0.010	0.012	0.029	0.100
	Mo content	mass% <0.001	<0.001	<0.001	<0.001	<0.001
	Kinematic viscosity 40°C	mm ² /s 68.99	62.36	58.01	96.73	62.70
	Kinematic viscosity 100°C	mm ² /s 10.52	9.74	9.13	13.92	9.78
Various properties of lubricating oil composition	Viscosity index	- 140	139	137	146	139
	Acid value	mgKOH/g 0.93	0.98	0.86	0.91	0.69
	Base number (hydrochloric acid method)	mgKOH/g 4.65	4.06	4.72	1.54	3.55
	Peak calorific value of ash content	mW 50.0	23.6	44.1	143.2	32.3
Test of preignition suppression effect	Peak calorific value of new oil	mW 190	-	-	-	-

[0139] From Table 1 and Table 2, the peak calorific values of the ash contents of the lubricating oil compositions prepared in Examples 1 to 6 proved to be low as compared with Comparative Examples 1 to 4. On that account, it can be said that the lubricating oil compositions prepared in Examples 1 to 6 have a high effect of suppressing preignition attributable to heat generation of a deposit.

5 [0140] As shown in Table 1 and Table 2, the peak calorific values of new oils of Example 1 and Comparative Example 1 are almost the same, but on the other hand, the results of the peak calorific values of the ash contents were different, and from this, it can be seen that preignition attributable to heat generation of a deposit can occur.

10 **Claims**

1. A lubricating oil composition for a gas engine, comprising a base oil (A), a calcium-based detergent (B), and an alkenyl succinimide (C), wherein

15 a content of the component (B) in terms of calcium atoms is 0.09 to 0.17 mass% based on the total amount of the lubricating oil composition,
the component (C) comprises a non-boron-modified alkenyl bis-succinimide (C1), and
a content of boron atoms derived from the component (C) is less than 0.02 mass% based on the total amount of the lubricating oil composition.

20 2. The lubricating oil composition according to claim 1, wherein a content ratio [N/Ca] by mass of nitrogen atoms derived from the component (C) to calcium atoms derived from the component (B) is 0.90 or less.

25 3. The lubricating oil composition according to claim 1 or 2, wherein the component (B) comprises calcium salicylate (B1).

4. The lubricating oil composition according to any one of claims 1 to 3, wherein the component (C1) is a non-boron-modified alkenyl bis-succinimide at least having a polybutenyl group or a polyisobutyl group having a weight-average molecular weight of 500 to 3000.

30 5. The lubricating oil composition according to any one of claims 1 to 4, wherein the component (C) further comprises a boron-modified alkenyl succinimide (C2) together with the component (C1).

35 6. The lubricating oil composition according to claim 5, wherein a content ratio [B/N] by mass of boron atoms derived from the component (C2) to nitrogen atoms derived from the component (C) is 0.01 to 0.35.

7. The lubricating oil composition according to any one of claims 1 to 6, wherein a content of the component (C) in terms of nitrogen atoms is 0.005 to 0.15 mass% based on the total amount of the lubricating oil composition.

40 8. The lubricating oil composition according to any one of claims 1 to 7, further comprising zinc dithiophosphate (D).

9. The lubricating oil composition according to any one of claims 1 to 8, wherein a content of magnesium atoms is less than 0.04 mass% based on the total amount of the lubricating oil composition.

45 10. The lubricating oil composition according to any one of claims 1 to 9, wherein a content of molybdenum atoms is less than 0.01 mass% based on the total amount of the lubricating oil composition.

11. A gas engine using the lubricating oil composition according to any one of claims 1 to 10.

50 12. Use of a lubricating oil composition, wherein the lubricating oil composition according to any one of claims 1 to 10 is applied to a gas engine.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/013227

5	A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. C10N10/04(2006.01)n, C10N20/04(2006.01)n, C10N30/04(2006.01)n, C10N40/12(2006.01)n, C10N40/25(2006.01)n, C10M133/56(2006.01)i, C10M137/10(2006.01)i, C10M139/00(2006.01)i, C10M159/22(2006.01)i FI: C10M133/56, C10M139/00 A, C10M159/22, C10M137/10 A, C10N20:04, C10N10:04, C10N40:12, C10N30:04, C10N40:25																	
10	According to International Patent Classification (IPC) or to both national classification and IPC																	
15	B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int. Cl. C10N10/04, C10N20/04, C10N30/04, C10N40/12, C10N40/25, C10M133/56, C10M137/10, C10M139/00, C10M159/22																	
20	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 1971-2020 Registered utility model specifications of Japan 1996-2020 Published registered utility model applications of Japan 1994-2020																	
25	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)																	
30	C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left; padding: 2px;">Category*</th> <th style="text-align: left; padding: 2px;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="text-align: left; padding: 2px;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; padding: 2px;">X</td> <td style="padding: 2px;">JP 2004-107556 A (OSAKA GAS CO., LTD.) 08 April 2004, claims, examples, reference examples, paragraph [0021]</td> <td style="text-align: center; padding: 2px;">1-4, 7-12</td> </tr> <tr> <td style="text-align: center; padding: 2px;">A</td> <td style="padding: 2px;">JP 09-071795 A (NIPPON OIL CO., LTD.) 18 March 1997, example 6</td> <td style="text-align: center; padding: 2px;">5-6</td> </tr> <tr> <td style="text-align: center; padding: 2px;">A</td> <td style="padding: 2px;">JP 2019-147864 A (IDEMITSU KOSAN CO., LTD.) 05 September 2019, claims, examples</td> <td style="text-align: center; padding: 2px;">1-12</td> </tr> <tr> <td style="text-align: center; padding: 2px;">P, A</td> <td style="padding: 2px;"></td> <td style="text-align: center; padding: 2px;">1-12</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	JP 2004-107556 A (OSAKA GAS CO., LTD.) 08 April 2004, claims, examples, reference examples, paragraph [0021]	1-4, 7-12	A	JP 09-071795 A (NIPPON OIL CO., LTD.) 18 March 1997, example 6	5-6	A	JP 2019-147864 A (IDEMITSU KOSAN CO., LTD.) 05 September 2019, claims, examples	1-12	P, A		1-12
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																
X	JP 2004-107556 A (OSAKA GAS CO., LTD.) 08 April 2004, claims, examples, reference examples, paragraph [0021]	1-4, 7-12																
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P, A		1-12																
35	<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.																	
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45	Date of the actual completion of the international search 25.05.2020																	
50	Date of mailing of the international search report 09.06.2020																	
55	Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan																	

INTERNATIONAL SEARCH REPORT Information on patent family members			International application No. PCT/JP2020/013227
Patent Documents referred to in the Report	Publication Date	Patent Family	Publication Date
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REFERENCES CITED IN THE DESCRIPTION

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