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(54) **LUBRICANT COMPOSITION**

(57) Provided is a lubricating oil composition capable of decreasing friction while ensuring anti-wear properties even if it is reduced in viscosity. The lubricating oil composition comprises a lubricant base oil, (A) a magnesium-based detergent, and (B) a molybdenum-based friction modifier, wherein the amount of component (A) is in the range of 200 to 1200 mass ppm in terms of a concentration in mass ppm of magnesium [Mg] in the lubricating oil composition, and the amount of component (B) is in the range of 500 to 1500 mass ppm in terms of a concentration in mass ppm of molybdenum [Mo] in the lubricating oil composition.

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**Description**

## FIELD

5 **[0001]** The present invention relates to a lubricating oil composition, more particularly to a lubricating oil composition for an internal combustion engine, and even more particularly to a lubricating oil composition for a gasoline engine.

## BACKGROUND

10 **[0002]** Lubricating oil compositions are widely used in the automotive field, such as for internal combustion engines, automatic transmissions, and gear oils. In recent years, viscosity reduction has been desired for an improvement in fuel economy. However, viscosity reduction causes a decrease in thickness of an oil film, and accordingly friction cannot be reduced sufficiently. Therefore, molybdenum dithiocarbamate (MoDTC) which can reduce friction by producing molybdenum disulfide under boundary lubrication conditions has been conventionally used. At that time, a calcium-based  
 15 detergent is normally used in combination therewith (e.g., Patent Document 1). However, in this combination, there is a limit in the reduction of friction, and accordingly fuel economy cannot be improved sufficiently.

**[0003]** It is also known to use a magnesium-based detergent as a detergent (e.g., Patent Documents 2 and 3). Although the use of a magnesium-based detergent can reduce friction more than calcium-based detergents, there is a problem that wear is likely to occur.

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[Prior Art Documents]

[Patent Documents]

25 **[0004]**

[Patent Document 1] Japanese Unexamined Patent Publication No. 2013-199594

[Patent Document 2] Japanese Unexamined Patent Publication No. 2011-184566

[Patent Document 3] Japanese Unexamined Patent Publication No. 2006-328265

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## DISCLOSURE OF THE INVENTION

[Problems to be Solved by the Invention]

35 **[0005]** An object of the present invention is to provide a lubricating oil composition capable of reducing friction while securing anti-wear properties, even if it is reduced in viscosity.

[Means for Solving the Problems]

40 **[0006]** As a result of intensive studies, the inventors have found that the above object can be achieved by adding a specific amount of a magnesium-based detergent and a specific amount of a molybdenum-based friction modifier to a lubricating oil base oil.

**[0007]** That is, the present invention provides a lubricating oil composition comprising a lubricant base oil, (A) a magnesium-based detergent, and (B) a molybdenum-based friction modifier, wherein the amount of component (A) is  
 45 in the range of 200 to 1200 mass ppm in terms of a concentration in mass ppm of magnesium [Mg] in the lubricating oil composition, and the amount of component (B) is in the range of 500 to 1500 mass ppm in terms of a concentration in mass ppm of molybdenum [Mo] in the lubricating oil composition.

**[0008]** In the preferred embodiments of the present invention, the lubricating oil composition further has at least one of the following features (1) to (7):

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(1) wherein the amount of component (A) is in the range of from 300 to 800 mass ppm in terms of the amount of magnesium in the lubrication oil composition.

(2) wherein the amount of component (B) is in the range of from 600 to 1200 mass ppm in terms of the amount of magnesium in the lubrication oil composition.

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(3) wherein it satisfies  $[Mg]/[Mo] \leq 2.4$ .

(4) wherein it further comprises a calcium-based detergent (A') and satisfies  $([Mg] + [Ca])/[Mo] < 3.0$ , wherein the [Ca] represents the concentration in mass ppm of the calcium in the lubricating oil composition.

(5) wherein it has a CCS viscosity at -35°C of less than or equal to 6.2 Pa●S.

(6) wherein it has a High-Temperature High-Shear Viscosity at 150°C (HTHS viscosity) of 1.7 to 2.9 mPa●s.

(7) wherein it has a kinematic viscosity at 100°C of less than 9.3 mm<sup>2</sup>/s.

(8) wherein it is for use in an internal combustion engine.

**[0009]** The present invention further relates to a method for reducing friction while maintaining low wearing properties by using the lubricating oil composition or a lubricating oil composition according to embodiments (1) to (8) described above.

[Effect of the Invention]

**[0010]** The lubricating oil composition of the present invention can reduce friction while securing anti-wear properties, even if it is reduced in viscosity, and can be suitably used for a lubricating oil composition particularly for an internal combustion engine.

## MODE FOR CARRYING OUT THE INVENTION

### Lubricating Oil Base Oil

**[0011]** The lubricating oil base oil in the present invention is not particularly limited. It may be any of mineral oils and synthetic oils and these oils may be used alone or may be used in combination.

**[0012]** The mineral oil includes, for example, those obtained by vacuum distilling an atmospheric residue oil obtained by topping crude oil to obtain a lubricating oil fraction, and refining the resulting lubricating oil fraction by subjecting it to one or more of treatments such as solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, hydrotreating, etc., as well as wax-isomerized mineral oil, GTL (Gas to Liquid) base oils, ATL (Asphalt to Liquid) base oils, vegetable oil-based base oils, or mixed base oils thereof.

**[0013]** The synthetic oil includes, for example, polybutene or hydrides thereof; poly- $\alpha$ -olefins or hydrides thereof, such as 1-octene oligomers, 1-decene oligomers, and the like; monoesters such as 2-ethylhexyl laurate, 2-ethylhexyl palmitate, 2-ethylhexyl stearate, and the like; diesters such as ditridecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate, di-2-ethylhexyl sebacate, and the like; polyol esters such as neopentyl glycol di-2-ethylhexanoate, neopentyl glycol di-n-octanoate, neopentyl glycol di-n-decanoate, trimethylolpropane tri-n-octanoate, trimethylolpropane tri-n-decanoate, pentaerythritol tetra-n-pentanoate, pentaerythritol tetra-n-hexanoate, pentaerythritol tetra-2-ethylhexanoate, and the like; aromatic synthetic oils such as alkylnaphthalenes, alkylbenzenes, aromatic esters, and the like; and mixtures thereof.

**[0014]** The kinematic viscosity (mm<sup>2</sup>/s) at 100°C of the lubricating base oil is not particularly limited, but is preferably 2 to 15 mm<sup>2</sup>/s, more preferably 3 to 10 mm<sup>2</sup>/s, even more preferably 3 to 8 mm<sup>2</sup>/s, and most preferably 3 to 6 mm<sup>2</sup>/s. This enables to obtain a lubricating oil composition which exhibits sufficient oil film formation, excellent lubricity, and even less evaporation loss.

**[0015]** The viscosity index (VI) of the lubricating oil base oil is not particularly limited, but is preferably 100 or more, more preferably 120 or more, and most preferably 130 or more. This enables to reduce the viscosity at low temperatures while securing an oil film at high temperatures.

### (A) Magnesium-Based Detergent

**[0016]** The magnesium-based detergent is not particularly limited, and any conventional one can be used. The magnesium-based detergent includes, for example, magnesium sulfonate, magnesium phenate, and magnesium salicylate. Among them, magnesium salicylate or magnesium sulphonate is preferred. A single magnesium-based detergent may be used alone or two or more magnesium-based detergents may be used in admixture.

**[0017]** By the inclusion of component (A), a high-temperature detergency and anti-rusting properties required for a lubricating oil can be ensured. Further, friction can be reduced, and consequently, torque can be reduced. This is particularly advantageous in terms of fuel economy characteristics.

**[0018]** Component (A) is added in such an amount that the concentration in mass ppm of magnesium [Mg] in the lubricating oil composition is in the range of 200 to 1200 mass ppm, preferably 250 to 1,000 mass ppm, and more preferably 300 to 800 mass ppm. An amount of component (A) above the upper limit indicated above may lead to an excessive wear, and an amount of component (A) lower than the lower limit indicated above may lead to a low friction reduction effect.

**[0019]** The amount of component (A) preferably satisfies the following formula (1):

$$[\text{Mg}]/[\text{Mo}] \leq 2.4 \quad (1)$$

wherein the [Mo] is the concentration in mass ppm of molybdenum in the lubricating oil composition. The value of the [Mg]/[Mo] is more preferably 2.0 or less, even more preferably 1.8 or less, and still more preferably 1.5 or less. The above value of more than 2.4 may lead to an excessive wear. The lower limit of the [Mg]/[Mo] is preferably 0.1, more preferably 0.2, and even more preferably 0.3.

**[0020]** The lubricating oil composition of the present invention may contain calcium-based detergent (A') as will be described later, as a metal detergent other than magnesium-based metal detergent (A). By the inclusion of the calcium-based detergent, a high-temperature detergency and anti-rusting properties required for a lubricating oil can be further ensured.

**[0021]** Component (A') is preferably added in an amount which satisfies the following formula (2):

$$([Mg] + [Ca])/[Mo] < 3.0 \quad (2)$$

wherein the [Ca] represents the concentration in mass ppm of calcium in the lubricating oil composition. The value of the  $([Mg] + [Ca])/[Mo]$  is more preferably less than 2.8, even more preferably less than 2.6, and particularly preferably less than 2.5. The above value of more than the upper limit indicated above may lead to a low torque reduction effect. The lower limit of the  $([Mg] + [Ca])/[Mo]$  is preferably 0.2 or more, more preferably 0.5, and even more preferably 1.0.

**[0022]** In particular, magnesium-based detergent (A) is preferably an overbased magnesium detergent. This enables to ensure acid neutralizing properties required for a lubricating oil. When an overbased magnesium-based detergent is used, a neutral, magnesium or calcium based detergent may be mixed therewith.

**[0023]** The total base number of magnesium-based detergent (A) is preferably 20 to 600 mg KOH/g, more preferably 50 to 500 mg KOH/g, and most preferably 100 to 450 mg KOH/g, but is not limited thereto. This enables to ensure acid neutralizing properties, high-temperature detergency, and anti-rusting properties required for a lubricating oil. When a mixture of two or more metal detergents are used, the base number obtained after mixing is preferably in the above ranges.

**[0024]** Magnesium-based detergent (A) has a magnesium content of preferably 0.5 to 20 mass %, more preferably 1 to 16 mass %, and most preferably 2 to 14 mass %, and it may be added to the lubricating oil composition so that magnesium in an amount within the above ranges is included in the lubricating oil composition.

**[0025]** Calcium-based detergent (A') is not particularly limited, and any conventional one may be used. The calcium-based detergent includes, for example, calcium sulfonate, calcium phenate, and calcium salicylate. One of the calcium-based detergents may be used or two or more of the calcium-based detergents may be used in admixture.

**[0026]** Calcium-based detergent (A') is preferably an overbased calcium detergent. This enables to ensure acid neutralizing properties required for a lubricating oil. When an overbased calcium-based detergent is used, a neutral calcium-based detergent may also be used in combination therewith.

**[0027]** The total base number of calcium-based detergent (A') is preferably 20 to 500 mg KOH/g, more preferably 50 to 400 mg KOH/g, and most preferably 100 to 350 mg KOH/g, but is not limited thereto. This enables to ensure acid neutralizing properties, a high-temperature detergency, and anti-rusting properties required for a lubricating oil. When a mixture of two or more metal detergents are used, the base number obtained after mixing is preferably in the above ranges.

**[0028]** Calcium-based detergent (A') has a calcium content of preferably 0.5 to 20 mass %, more preferably 1 to 16 mass %, and most preferably 2 to 14 mass %.

**[0029]** It is preferred that the amounts of magnesium and calcium in the lubricating oil composition of the present invention satisfy the following formula (3):

$$\{[Mg]/([Mg] + [Ca])\} * 100 \geq 5 \quad (3)$$

wherein the value of the  $\{[Mg]/([Mg] + [Ca])\} * 100$  is more preferably 10 or more, and even more preferably 15 or more. The above value of less than the lower limit indicated above may lead to a low friction reduction effect. The upper limit of the  $\{[Mg]/([Mg] + [Ca])\} * 100$  is preferably 100, more preferably 80, even more preferably 60, and still more preferably 50.

**[0030]** The lubricating oil composition of the present invention may contain a sodium-based detergent as a metal detergent other than those described above, provided that it does not impair the effects of the present invention. Sodium sulfonate, sodium phenate, and sodium salicylate are preferred as a sodium-based detergent. One of the sodium-based detergent may be used alone or two or more of the sodium-based detergents may be used in admixture. By the inclusion of a sodium-based detergent, a high-temperature detergency and anti-rusting properties required for a lubricating oil can be ensured. A sodium-based detergent(s) may be used in admixture with the magnesium-based detergents and optional calcium-based detergents as described above.

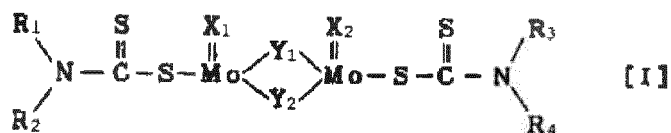
**[0031]** The total amount of the metal detergents in the lubricating oil composition of the present invention is such an amount that the amount of magnesium contained in the composition satisfies the specific range described above, and the amount of calcium-based detergent(s) is limited depending on the amount of the magnesium-based detergent(s).

## (B) Molybdenum-Based Friction Modifier

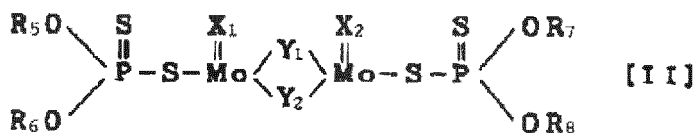
**[0032]** The molybdenum-based friction modifier is not particularly limited, and well-known molybdenum-based friction modifiers may be used. The molybdenum-based friction modifier includes, for example, sulfur-containing organic molybdenum compounds such as molybdenum dithiophosphate (MoDTP), molybdenum dithiocarbamate (MoDTC), and the like, complexes of a molybdenum compound with a sulfur-containing organic compound or other organic compounds, complexes of a sulfur-containing molybdenum compound such as molybdenum sulfide, molybdic acid sulfide, and the like, with an alkenyl succinimide, and the like. The molybdenum compound described above includes, for example, molybdenum oxides such as molybdenum dioxide, molybdenum trioxide, and the like, molybdic acids such as orthomolybdic acid, paramolybdic acid, (poly)molybdic acid sulfide, and the like, molybdate salts such as metal salts, ammonium salts, and the like, of these molybdic acids, molybdenum sulfides such as molybdenum disulfide, molybdenum trisulfide, molybdenum pentasulfide, molybdenum polysulfide, and the like, molybdic acid sulfides, metal salts and amine salts of molybdic acid sulfides, and molybdenum halides such as molybdenum chloride, and the like. The sulfur-containing organic compound described above includes, for example, alkyl(thio)xanthate, thiadiazole, mercaptothiadiazole, thio-carbonate, tetrahydrocarbylthiuram disulfide, bis(di(thio)hydrocarbyldithiophosphonate) disulfide, organic (poly)sulfides, and sulfide esters, and the like. In particular, organic molybdenum compounds such as molybdenum dithiophosphate (MoDTP) and molybdenum dithiocarbamate (MoDTC) are preferred.

**[0033]** Molybdenum dithiocarbamate (MoDTC) is a compound represented by formula [I] below, and molybdenum dithiophosphate (MoDTP) is a compound represented by formula [II] below.

[Formula 1]



[Formula 2]



**[0034]** In the above general formulae [I] and [II],  $\text{R}_1$  to  $\text{R}_8$  may be the same or different from each other, and represent monovalent hydrocarbon groups having 1 to 30 carbon atoms. The hydrocarbon groups may be linear or branched. The monovalent hydrocarbon groups include linear or branched alkyl groups having 1 to 30 carbon atoms; alkenyl groups having 2 to 30 carbon atoms; cycloalkyl groups having 4 to 30 carbon atoms; aryl, alkylaryl, or arylalkyl groups having 6 to 30 carbon atoms, and the like. The bonding site of the alkyl group in the arylalkyl groups are arbitrary. More specifically, the alkyl groups include, for example, methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group, octadecyl group, and the like, and branched alkyl groups thereof, and alkyl groups having 3 to 8 carbon atoms are particularly preferred. Further,  $\text{X}_1$  and  $\text{X}_2$  represent oxygen or sulfur atom, and  $\text{Y}_1$  and  $\text{Y}_2$  represent oxygen or sulfur atom.

**[0035]** Sulfur-free organic molybdenum compounds may also be used as component (B). Such compounds include, for example, molybdenum-amine complexes, molybdenum-succinimide complexes, molybdenum salts of organic acids, molybdenum salts of alcohols, and the like.

**[0036]** Further, trinuclear molybdenum compounds described in U.S. Patent No. 5,906,968 may be used as friction modifier (B) in the present invention.

**[0037]** Component (B) is added in an amount such that the concentration in mass ppm of molybdenum [Mo] in the lubricating oil composition is in the range of from 500 to 1500 mass ppm, and preferably from 600 to 1200 mass ppm. An amount of component (B) above the upper limit indicated above may lead to a deterioration in detergency, whereas an amount of component (B) lower than the lower limit indicated above may lead to an insufficient reduction in friction or a deterioration in detergency.

**[0038]** As described above for component (A), the amount of component (B) preferably satisfies the following formula (1):

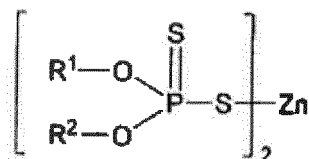
$$[\text{Mg}]/[\text{Mo}] \leq 2.4 \quad (1).$$

The value of the  $[\text{Mg}]/[\text{Mo}]$  is more preferably 2.0 or less, even more preferably 1.8 or less, and still more preferably 1.5 or less. The lower limit value of the  $[\text{Mg}]/[\text{Mo}]$  is preferably 0.1, more preferably 0.2, and even more preferably 0.3.

**[0039]** The lubricating oil composition of the present invention comprises the above lubricating oil base oil, component (A), and component (B), as essential components, and it may also contain conventional anti-wear agents, ashless dispersants, and viscosity index improvers as optional components.

**[0040]** Any well-known anti-wear agents may be used as the anti-wear agent. Among them, anti-wear agents having phosphorus are preferred, and zinc dithiophosphate (ZnDTP (also referred to as ZDDP)) represented by the following formula are particularly preferred.

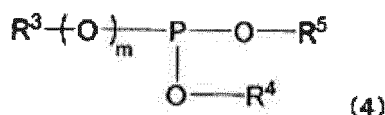
[Formula 3]



**[0041]** In the above formula,  $\text{R}^1$  and  $\text{R}^2$  may be the same or different from each other and represent hydrogen atom or monovalent hydrocarbon groups having 1 to 26 carbon atoms. The monovalent hydrocarbon groups include primary or secondary alkyl groups having 1 to 26 carbon atoms; alkenyl groups having 2 to 26 carbon atoms; cycloalkyl groups having 6 to 26 carbon atoms; aryl, alkylaryl, or arylalkyl groups having 6 to 26 carbon atoms; or hydrocarbon groups containing an ester bond, ether bond, alcohol group or carboxyl group.  $\text{R}^1$  and  $\text{R}^2$  preferably represent a primary or secondary alkyl group having 2 to 12 carbon atoms, a cycloalkyl group having 8 to 18 carbon atoms, or an alkylaryl group having 8 to 18 carbon atoms, and may be the same or different from each other. Zinc dialkyldithiophosphate is particularly preferred, and the primary alkyl group preferably has 3 to 12 carbon atoms and more preferably has 4 to 10 carbon atoms. The secondary alkyl group preferably has 3 to 12 carbon atoms and more preferably has 3 to 10 carbon atoms. One type of the zinc dithiophosphate described above may be used alone or two or more types may be used in admixture. Further, zinc dithiocarbamate (ZnDTC) may also be used in combination therewith.

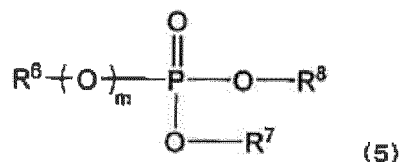
**[0042]** Further, at least one compound selected from phosphate- and phosphite-type phosphorous compounds represented by the following formulas (6) and (7), and metal salts and amine salts thereof, may also be used.

[Formula 4]



**[0043]** In the above general formula (4),  $\text{R}^3$  is a monovalent hydrocarbon group having 1 to 30 carbon atoms,  $\text{R}^4$  and  $\text{R}^5$  are independently hydrogen atom or a monovalent hydrocarbon group having 1 to 30 carbon atoms, and  $m$  is 0 or 1.

[Formula 5]



**[0044]** In formula (5),  $\text{R}^6$  is a monovalent hydrocarbon group having 1 to 30 carbon atoms,  $\text{R}^7$  and  $\text{R}^8$  are independently hydrogen atom or a monovalent hydrocarbon group having 1 to 30 carbon atoms, and  $n$  is 0 or 1.

**[0045]** In the above general formulae (4) and (5), the monovalent hydrocarbon groups having 1 to 30 carbon atoms represented by  $\text{R}^3$  to  $\text{R}^8$  include, for example, alkyl groups, cycloalkyl groups, alkenyl groups, alkyl-substituted cycloalkyl

groups, aryl groups, alkyl-substituted aryl groups, and arylalkyl groups. In particular, they are preferably an alkyl group having 1 to 30 carbon atoms, more preferably an aryl group having 6 to 24 carbon atoms, still more preferably an alkyl group having 3 to 18 carbon atoms, and most preferably an alkyl group having 4 to 15 carbon atoms.

**[0046]** The phosphorous compounds represented by the above general formula (4) include, for example, phosphite monoesters and (hydrocarbyl)phosphonous acids having one hydrocarbon group having 1 to 30 carbon atoms as described above; phosphite diesters, monothiophosphite diesters and (hydrocarbyl)phosphonous monoesters having two hydrocarbon groups having 1 to 30 carbon atoms as described above; phosphite triesters and (hydrocarbyl)phosphonous diesters having three hydrocarbon groups having 1 to 30 carbon atoms as described above, and mixtures thereof.

**[0047]** The metal salts or amine salts of the phosphorous compounds represented by the above general formula (4) or (5) can be obtained by allowing a metal base such as a metal oxide, metal hydroxide, metal carbonate, metal chloride, and the like; ammonia; a nitrogen compound such as an amine compound having in its molecule only a hydrocarbon or hydroxyl group-containing hydrocarbon group having 1 to 30 carbon atoms; or the like, to act on a phosphorous compound represented by general formula (4) or (5), to neutralize a part or all of the remaining acidic hydrogen. The metal in the above metal base includes, for example, alkali metals such as lithium, sodium, potassium, cesium, and the like; alkaline earth metals such as calcium, magnesium, barium, and the like; and heavy metals such as zinc, copper, iron, lead, nickel, silver, manganese, and the like (excluding molybdenum). Among these, alkaline metals such as calcium, magnesium, and the like, as well as zinc are preferred, and zinc is particularly preferred.

**[0048]** An anti-wear agent is formulated into the lubricating oil composition, typically at 0.1 to 5.0 mass %, and preferably at 0.2 to 3.0 mass %.

**[0049]** The ashless dispersant includes nitrogen-containing compounds having in its molecule at least one linear or branched alkyl or alkenyl group having 40 to 500 carbon atoms, preferably 60 to 350 carbon atoms, or a derivative thereof, Mannich dispersants, or mono- or bis-succinimides (e.g., alkenyl succinimides), benzylamines having in its molecule at least one alkyl or alkenyl group having 40 to 500 carbon atoms, or polyamines having in its molecule at least one alkyl or alkenyl group having 40 to 400 carbon atoms, or products modified with a boron compound, carboxylic acid, phosphoric acid, or the like. One or two or more optionally selected from them may be added. In particular, it preferably contains an alkenyl succinimide.

**[0050]** The method for preparing the succinimide is not particularly limited. For example, it is obtained by reacting a compound having an alkyl or alkenyl group having 40 to 500 carbon atoms with maleic anhydride at 100 to 200°C to produce an alkyl succinic acid or alkenyl succinic acid, and reacting the resulting alkyl succinic acid or alkenyl succinic acid with a polyamine. The polyamine includes diethylene triamine, triethylene tetramine, tetraethylene pentamine, and pentaethylene hexamine. The derivatives of the nitrogen-containing compounds exemplified above for the ashless dispersant include, for example, so-called oxygen-containing organic compound-modified compounds obtained by allowing a monocarboxylic acid having 1 to 30 carbon atoms, such as fatty acids, polycarboxylic acids having 2 to 30 carbon atoms, such as oxalic acid, phthalic acid, trimellitic acid, pyromellitic acid, and the like, or anhydrides or esters thereof, an alkyleneoxide having 2 to 6 carbon atoms, or hydroxy(poly)oxyalkylene carbonate to act on the nitrogen-containing compounds described above to neutralize or amidate a part or all of the remaining amino groups and/or imino groups therein; so-called boron-modified compounds obtained by allowing boric acid to act on the nitrogen-containing compounds described above to neutralize or amidate a part or all of the remaining amino groups and/or imino groups therein; so-called phosphoric acid-modified compounds obtained by allowing phosphoric acid to act on the nitrogen-containing compounds described above to neutralize or amidate a part or all of the remaining amino groups and/or imino groups therein; sulfur-modified compounds obtained by allowing a sulfur compound to act on the nitrogen-containing compounds described above; and modified compounds obtained by subjecting the nitrogen-containing compound described above to two or more modifications selected from a modification with an oxygen-containing organic compound, a modification with boron, a modification with phosphoric acid, a modification with sulfur. Among these derivatives, boron-modified compounds of alkenyl succinimides, in particular, bis-type boron-modified compounds of alkenyl succinimides can further improve heat resistance properties in combination with the base oil described above.

**[0051]** The amount of the ashless dispersant is 20 mass % or less, preferably 15 mass % or less, and more preferably 5 mass % or less, based on the total amount of the composition. Further, a boron-containing ashless dispersant may also be used as an ashless dispersant in admixture with a boron-free ashless dispersant. Moreover, when a boron-containing ashless dispersant is used, the content ratio thereof is not particularly limited. However, the amount of boron contained in the composition is preferably 0.001 to 0.2 mass %, more preferably 0.003 to 0.1 mass %, and most preferably 0.005 to 0.05 mass %, based on the total amount of the composition.

**[0052]** The number average molecular weight ( $M_n$ ) of the ashless dispersant is preferably 2000 or more, more preferably 2500 or more, even more preferably 3000 or more, and most preferably 5000 or more, and preferably 15000 or less. The number average molecular weight of the ashless dispersant of less than the lower limit indicated above may lead to an insufficient dispersibility. On the other hand, a number average molecular weight of the ashless dispersant of more than the upper limit indicated above may lead to an excessive viscosity, thereby resulting in insufficient fluidity, causing an increase in deposits.

**[0053]** The viscosity index improver includes, for example, those containing polymethacrylates, dispersed type polymethacrylates, olefin copolymers (polyisobutylene, ethylene-propylene copolymer), dispersed type olefin copolymers, polyalkyl styrene, styrene-butadiene hydrogenated copolymers, styrene-maleic anhydride ester copolymers, star-shaped isoprene, or the like. Further, it is also possible to use a comb-shaped polymer comprising in its main chain at least a repeating unit based on a polyolefin macromer and a repeating unit based on an alkyl (meth)acrylate having a C1-30 alkyl group.

**[0054]** The viscosity index improver is typically comprised of the above polymer and a diluent oil. The content of the viscosity index improver is preferably 0.01 to 20 mass %, more preferably from 0.02 to 10 mass %, and most preferably 0.05 to 5 mass %, as the amount of the polymer, based on the total amount of the composition. A content of the viscosity index improver of less than the lower limit indicated above may lead to a deterioration in viscosity-temperature characteristics and low-temperature viscosity characteristics. On the other hand, a content of the viscosity index improver of more than the upper limit indicated above may lead to a deterioration in viscosity-temperature characteristics and low-temperature viscosity characteristics, and may further lead to a significant increase in product cost.

**[0055]** The lubricating oil composition of the present invention may further contain other additives depending on the purpose in order to improve its performance. Additives that are commonly used in lubricating oil compositions can be used for the above other additives, and the above other additives include, for example, additives such as antioxidants, friction modifiers other than component (B), corrosion inhibitors, anti-rusting agents, pour point depressants, demulsifiers, metal deactivators, antifoaming agents, etc.

**[0056]** The antioxidants include ashless antioxidants of phenol-based type, amine-based type, etc., and metal-based antioxidants such as copper-based type, molybdenum-based type, and the like. For example, the phenol-based ashless antioxidants include 4,4'-methylene bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), isooctyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, and the like, and the amine-based ashless antioxidants include phenyl- $\alpha$ -naphthylamine, alkylphenyl- $\alpha$ -naphthylamine, dialkyldiphenylamines, and the like. The antioxidant(s) is typically incorporated in the lubricating oil composition at 0.1 to 5 mass %.

**[0057]** The friction modifiers other than component (B) include, for example, esters, amines, amides, sulfide esters, etc. The friction modifier(s) is typically incorporated in the lubricating oil composition at 0.01 to 3 mass %.

**[0058]** The corrosion inhibitors include, for example, benzotriazole, tolyltriazole-based, thiadiazole-based, imidazole-based compounds, and the like. The anti-rusting agents include, for example, petroleum sulfonates, alkylbenzene sulfonates, dinonyl naphthalene sulfonates, alkenyl succinic acid esters, polyhydric alcohol esters, and the like. The corrosion inhibitor(s) is typically incorporated in the lubricating oil composition at 0.01 to 5 mass %.

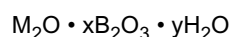
**[0059]** As the pour point depressants, for example, polymethacrylate-based polymers compatible with the lubricating oil base oil used can be used. The pour point depressant(s) is typically incorporated in the lubrication oil composition at 0.01 to 3 mass %.

**[0060]** The demulsifiers include, for example, polyalkylene glycol-based non-ionic surfactants such as polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, polyoxyethylene alkyl naphthyl ether, and the like. The demulsifier(s) is typically incorporated in the lubricating oil composition at 0.01 to 5 mass %.

**[0061]** The metal deactivators include, for example, imidazolines, pyrimidine derivatives, alkyl thiadiazoles, mercapto benzothiazole, benzotriazole or derivatives thereof, 1,3,4-thiadiazole polysulfides, 1,3,4-thiadiazolyl-2,5-bisdialkyl dithiocarbamate, 2-(alkyldithio)benzimidazole, beta-(o-carboxybenzylthio)propionitrile, and the like. The metal deactivator(s) is typically incorporated in the lubricating oil composition at 0.01 to 3 mass %.

**[0062]** The defoaming agents include, for example, silicone oils having a kinematic viscosity at 25°C of 1,000 to 100,000 mm<sup>2</sup>/s, alkenyl succinic acid derivatives, esters of a polyhydroxy aliphatic alcohol and a long-chain fatty acid, methyl salicylate, o-hydroxybenzyl alcohol, and the like. The defoamer(s) is typically incorporated in the lubricating oil composition at 0.001 to 1 mass %.

**[0063]** Alkali borate additives may be added as the above other additives. Alkali borate additives are those containing an alkali metal borate hydrate and can be represented by the following formula:



wherein M is an alkali metal, x is 2.5 to 4.5, and y is 1.0 to 4.8.

**[0064]** Specifically, it includes lithium borate hydrate, sodium borate hydrate, potassium borate hydrate, rubidium borate hydrate, cesium borate hydrate, and the like, and potassium borate hydrate and sodium borate hydrate are preferred, in particular, potassium borate hydrate is preferred. The alkali metal borate hydrate particles has an average particle diameter of generally 1 micron ( $\mu$ ) or less. In the alkali metal borate hydrate used in the present invention, the ratio of boron to alkali metal is preferably in the range of about from 2.5:1 to 4.5:1. The addition amount of the alkali borate additive is 0.002 to 0.05 mass % in terms of the amount of boron, based on the total amount of the lubricating oil composition.

**[0065]** The CCS viscosity at -35°C of the lubricating oil composition of the present invention is not limited, but is

preferably 6.2 Pa.s or less, more preferably 5.0 Pa.s or less, even more preferably 4.0 Pa.s or less, and most preferably 3.5 Pa.s or less.

**[0066]** In the lubricating oil composition of the present invention, the amount of the molybdenum contained in the lubricating oil composition and the CCS viscosity at -35°C preferably satisfy the following formula (6):

$$[\text{CCS Viscosity}]/[\text{Mo}] \leq 0.01 \quad (6)$$

wherein the [CCS Viscosity] represents the CCS viscosity value (Pa.s) at -35°C of the lubricating oil composition, and the [Mo] represents the concentration in mass ppm of the molybdenum in the lubricating oil composition.

**[0067]** The value of the [CCS viscosity]/[Mo] is more preferably 0.008 or less, and more preferably 0.005 or less. The above value of more than 0.01 may lead to a decrease in torque reduction rate or a deterioration in detergency. The lower limit of the [CCS Viscosity]/[Mo] is not limited, but is preferably 0.002, and more preferably 0.003.

**[0068]** The high-temperature high-shear viscosity (HTHS viscosity) at 150°C of the lubricating oil composition of the present invention is not limited, but is preferably 1.7 to 2.9 mPa.s, and more preferably 2.0 to 2.6 mPa.s.

**[0069]** The kinematic viscosity at 100°C of the lubricating oil composition of the present invention is not limited, but is preferably less than 9.3 mm<sup>2</sup>/s, and more preferably less than 8.2 mm<sup>2</sup>/s.

**[0070]** The lubricating oil composition of the present invention has sufficient frictional properties and wear properties even if it has a low viscosity, and exhibits an effect of yielding a high torque reduction rate, and therefore can be suitably used for an internal combustion engine.

## EXAMPLES

**[0071]** The present invention is illustrated in more detail below by way of Examples and Comparative Examples, but the present invention is not limited to the following examples.

**[0072]** Materials used in Examples and Comparative Examples are as follows.

Lubricating oil base oil

**[0073]** Lubricating oil base oil: Fischer-Tropsch derived base oil, kinematic viscosity at 100°C = 4.1 mm<sup>2</sup>/s, and VI = 127

Magnesium-based detergents (A)

**[0074]**

Magnesium-based detergent 1: magnesium salicylate (total base number 340 mg KOH/g, magnesium content 7.5 mass %)

Magnesium-based detergent 2: magnesium sulfonate (total base number 400 mg KOH/g, magnesium content 9.0 mass %)

Calcium-based detergents (A')

**[0075]**

Calcium-based detergent 1: calcium salicylate (total base number 350 mg KOH/g, calcium content 12.0 mass %)

Calcium-based detergent 2: calcium salicylate (total base number 220 mg KOH/g, magnesium content 8.0 mass %)

Molybdenum-based friction modifier (B)

**[0076]** Molybdenum-based friction modifier: MoDTC (molybdenum content 10 mass %)

Anti-wear agents

**[0077]**

Anti-wear agent 1: pri-ZnDTP (primary alkyl type)

Anti-wear agent 2: sec-ZnDTP (secondary alkyl type)

Other additives

**[0078]**

Antioxidant: phenolic antioxidant  
Ashless dispersant: succinimide  
Viscosity index improver: polymethacrylate  
Defoaming agent: dimethyl silicone

Examples 1 to 8 and Comparative Examples 1 to 6

**[0079]** Lubricating oil compositions were prepared by mixing the components in the amounts shown in Table 1. The amounts of the magnesium-based detergents, calcium-based detergents, and molybdenum-based friction modifier are respectively represented in terms of the content of magnesium, calcium, and molybdenum in mass ppm relative to the total lubricating oil composition amount, and the amounts of the anti-wear agents and the other additives are represented in parts by mass relative to the total lubricating oil composition amount (100 parts by mass). The amounts of magnesium-based detergents and calcium-based detergents were set so that the total molar amount of the magnesium and calcium contained in these detergents are identical in all the examples and comparative examples. The resulting compositions were subjected to the following tests. The results are shown in Table 1.

(1) High-Temperature High-Shear Viscosity at 150°C (HTHS150)

**[0080]** Measured in accordance with ASTM D4683.

(2) CCS Viscosity at -35°C (CCS viscosity)

**[0081]** Measured in accordance with ASTM D5293.

(3) Kinematic Viscosity at 100°C (KV100)

**[0082]** Measured at 100°C in accordance with ASTM D445.

(4) Torque Reduction Rate

**[0083]** The lubricating oil compositions obtained in the Examples and Comparative Examples were used as test compositions, and torque was measured by a motoring test using a gasoline engine. The engine was a Toyota 2ZR-FE 1.8L inline 4-cylinder engine, and a torque meter was installed between the motor and the engine, and then the torque was measured at an oil temperature of 80°C and an engine speed of 700 RPM. A commercially available GF-5 0W-20 oil was used as a standard oil, and the torque was measured in the same way. The torque (T) of the test composition was compared with the torque ( $T_0$ ) of the standard oil and the reduction rate ( $\{(T_0 - T)/T_0\} \times 100$ ) (%) relative to the torque of the standard oil was calculated. The higher the reduction rate, the better the fuel economy. Those exhibited a reduction rate of 5.5% or more were determined as passed.

(5) Shell Wear Scar Diameter

**[0084]** Measurements were conducted in accordance with the shell four-ball test (ASTM D4172), except that the rotational speed was set at 1800 rpm, the load was set at 40 kgf, the test temperature was set at 90°C, and the test time was set at 30 minutes. Those exhibited a wear scar diameter of 0.7 mm or less were determined as passed.

(6) Hot Tube Test (High-Temperature Detergency Evaluation)

**[0085]** A lubricating oil composition was continuously allowed to flow into a glass tube having an inner diameter of 2 mm at 0.3 ml/hr for 16 hours with flowing air at 10 ml/sec, while maintaining the temperature of the glass tube at 270°C. The lacquer deposited inside the glass tube was compared with a color sample and was rated as 10 for a transparent lacquer and rated as 0 for a black color lacquer. The higher the rating, the better the high temperature detergency. Those exhibited a rating of 5.0 or higher were determined as passed.

[Table 1]

|      | Ex. 1                              | Ex. 2   | Ex. 3   | Ex. 4   | Ex. 5   | Ex. 6   | Ex. 7   | Ex. 8   | Comp.<br>Ex. 1 | Comp.<br>Ex. 2 | Comp.<br>Ex. 3 | Comp.<br>Ex. 4 | Comp.<br>Ex. 5 | Comp.<br>Ex. 6 |
|------|------------------------------------|---------|---------|---------|---------|---------|---------|---------|----------------|----------------|----------------|----------------|----------------|----------------|
|      | Balance                            | Balance | Balance | Balance | Balance | Balance | Balance | Balance | Balance        | Balance        | Balance        | Balance        | Balance        | Balance        |
| (A)  | Magnesium-based detergent 1        | 300     | 600     | 300     | 300     | 1100    | 300     | 0       | 0              | 0              | 0              | 300            | 600            | 1500           |
|      | Magnesium-based detergent 2        | 0       | 0       | 0       | 0       | 0       | 0       | 300     | 0              | 0              | 0              | 0              | 0              | 0              |
| (A') | Calcium-based detergent 1          | 1400    | 900     | 1400    | 0       | 0       | 1400    | 1400    | 1900           | 1900           | 1900           | 1400           | 900            | 0              |
|      | Calcium-based detergent 2          | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0              | 0              | 0              | 0              | 0              | 0              |
| (B)  | Molybdenum-based friction modifier | 700     | 700     | 700     | 700     | 1000    | 1000    | 1000    | 700            | 1000           | 1000           | 300            | 300            | 700            |
|      | Anti-wear agent 1                  | 1       | 1       | -       | -       | 1       | -       | -       | 1              | 1              | -              | 1              | 1              | 1              |
|      | Anti-wear agent 2                  | -       | -       | 1       | 1       | -       | 1       | 1       | -              | -              | 1              | -              | -              | -              |
|      | Antioxidant                        | 0.6     | 0.6     | 0.6     | 0.6     | 0.6     | 0.6     | 0.6     | 0.6            | 0.6            | 0.6            | 0.6            | 0.6            | 0.6            |
|      | Ashless dispersant                 | 3.6     | 3.6     | 3.6     | 3.6     | 3.6     | 3.6     | 3.6     | 3.6            | 3.6            | 3.6            | 3.6            | 3.6            | 3.6            |
|      | Viscosity index improver           | 8.7     | 8.7     | 8.7     | 8.7     | 8.7     | 8.7     | 8.7     | 8.7            | 8.7            | 8.7            | 8.7            | 8.7            | 8.7            |
|      | Antifoaming agent                  | 0.1     | 0.1     | 0.1     | 0.1     | 0.1     | 0.1     | 0.1     | 0.1            | 0.1            | 0.1            | 0.1            | 0.1            | 0.1            |
|      | [Mg]/[Mo]                          | 0.43    | 0.86    | 0.43    | 0.43    | 1.10    | 0.30    | 0.30    | 0              | 0              | 0              | 1.00           | 2.00           | 2.14           |
|      | ([Mg] + [Ca])/[Mo]                 | 2.4     | 2.1     | 2.4     | 2.4     | 1.1     | 1.7     | 1.7     | 2.7            | 1.9            | 1.9            | 5.7            | 5.0            | 2.1            |
|      | [Mg]/([Mg] + [Ca])×100             | 17.6    | 40.0    | 17.6    | 17.6    | 100.0   | 17.6    | 17.6    | 0.0            | 0.0            | 0.0            | 17.6           | 40.0           | 100.0          |

(continued)

| Evaluation Results | Ex. 1                    | Ex. 2              | Ex. 3  | Ex. 4  | Ex. 5  | Ex. 6  | Ex. 7  | Ex. 8  | Comp. Ex. 1 | Comp. Ex. 2 | Comp. Ex. 3 | Comp. Ex. 4 | Comp. Ex. 5 | Comp. Ex. 6 |
|--------------------|--------------------------|--------------------|--------|--------|--------|--------|--------|--------|-------------|-------------|-------------|-------------|-------------|-------------|
|                    | KV100                    | mm <sup>2</sup> /s | 6.8    | 6.8    | 6.7    | 6.6    | 6.9    | 6.9    | 6.8         | 6.9         | 6.9         | 6.7         | 6.8         | 6.7         |
|                    | HTHS150                  | mPa.s              | 2.3    | 2.3    | 2.3    | 2.3    | 2.3    | 2.3    | 2.3         | 2.3         | 2.3         | 2.3         | 2.3         | 2.3         |
|                    | CCS Viscosity            | Pa.s               | 3.2    | 3.3    | 3.3    | 3.4    | 3.4    | 3.4    | 3.2         | 3.4         | 3.4         | 3.3         | 3.3         | 3.3         |
|                    | Torque reduction rate    | %                  | 5.99   | 6.40   | 7.40   | 7.43   | 7.45   | 8.66   | 0.86        | 2.91        | 5.3         | 1.7         | 3.4         | 6.5         |
|                    | Shell wear scar diameter | mm                 | 0.64   | 0.55   | 0.62   | 0.61   | 0.66   | 0.66   | 0.53        | 0.63        | 0.61        | 0.54        | 0.62        | 0.74        |
|                    | Hot tube                 | 270°C              | 7.5    | 5.5    | 5.5    | 8.5    | 5.5    | 5.5    | 6.5         | 6.5         | 4.0         | 3.0         | 4.0         | 8.5         |
|                    | [CCS Viscosity]/[Mo]     |                    | 0.0046 | 0.0047 | 0.0047 | 0.0034 | 0.0034 | 0.0034 | 0.0046      | 0.0034      | 0.0034      | 0.011       | 0.011       | 0.0047      |

**[0086]** As is evident from Table 1, the lubricating oil compositions of the present invention exhibited low wear as well as high torque reduction rate and high-temperature detergency, even though they had a low kinetic viscosity at 100°C

**[0087]** On the other hand, the compositions of Comparative Examples 1 to 3 that were free of magnesium-based detergent (A) exhibited a low torque reduction rate, and the composition of Comparative Example 6 containing magnesium-based detergent (A) in an amount higher than the upper limit of the present invention exhibited a large wear. Further, the compositions of Comparative Examples 4 and 5 containing molybdenum-based friction modifier (B) in an amount less than the lower limit of the present invention exhibited a low torque reduction rate and poor high-temperature detergency.

## Claims

1. A lubricating oil composition comprising a lubricant base oil, (A) a magnesium-based detergent, and (B) a molybdenum-based friction modifier, wherein the amount of component (A) is in the range of 200 to 1200 mass ppm in terms of a concentration in mass ppm of magnesium [Mg] in the lubricating oil composition, and the amount of component (B) is in the range of 500 to 1500 mass ppm in terms of a concentration in mass ppm of molybdenum [Mo] in the lubricating oil composition.

2. The lubricating oil composition of claim 1, wherein the lubricating oil composition satisfies the following formula (1):

$$[\text{Mg}]/[\text{Mo}] \leq 2.4 \quad (1).$$

3. The lubricating oil composition of claim 1 or 2, further comprising a calcium-based detergent (A'), and satisfying the following formula (2):

$$([\text{Mg}] + [\text{Ca}])/[\text{Mo}] < 3.0 \quad (2)$$

wherein the [Ca] represents a concentration in mass ppm of calcium in the lubricating oil composition.

4. The lubricating oil composition of any one of claims 1 to 3, having a CCS viscosity at -35°C of less than or equal to 6.2 Pa●s.

5. The lubricating oil composition of any one of claims 1 to 4, having a High-Temperature High-Shear Viscosity at 150°C (HTHS viscosity) of 1.7 to 2.9 mPa●s.

6. The lubricating oil composition of any one of claims 1 to 5, having a kinematic viscosity at 100°C of less than 9.3 mm<sup>2</sup>/s.

7. The lubricating oil composition of any one of claims 1 to 6, wherein the lubricating oil composition is for use in an internal combustion engine.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/086429

## A. CLASSIFICATION OF SUBJECT MATTER

C10M169/04(2006.01)i, C10M135/18(2006.01)i, C10M141/12(2006.01)i,  
C10M159/22(2006.01)i, C10N10/04(2006.01)n, C10N10/12(2006.01)n, C10N20/02  
(2006.01)n, C10N30/02(2006.01)n, C10N30/06(2006.01)n, C10N40/25(2006.01)n  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10M169/04, C10M135/18, C10M141/12, C10M159/22, C10N10/04, C10N10/12,  
C10N20/02, C10N30/02, C10N30/06, C10N40/25

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2017  
Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017

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

JSTPlus/JMEDPlus/JST7580(JDreamIII) Keyword: JUNKATSUYU SEIJOZAI,  
SARISHIRETO, SURUHONETO, JICHIOKARUBAMINSAN (in Japanese) and related terms

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                  | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | JP 2000-1690 A (Exxon Research & Engineering Co.),<br>07 January 2000 (07.01.2000),<br>claims; paragraphs [0027] to [0028], [0041] to [0046]; table 1; examples B to D<br>& US 5906969 A<br>claims; column 3, line 53 to column 4, line 21;<br>column 6, line 21 to column 7, line 16; table 1; examples B to D<br>& EP 955353 A1 & DE 69909363 T2<br>& SG 93829 A1 & CA 2263551 A1 | 1-7                   |

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

\* Special categories of cited documents:

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

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

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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

"&" document member of the same patent family

Date of the actual completion of the international search  
14 February 2017 (14.02.17)

Date of mailing of the international search report  
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Name and mailing address of the ISA/  
Japan Patent Office  
3-4-3, Kasumigaseki, Chiyoda-ku,  
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Authorized officer

Telephone No.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/086429

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                          | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | JP 2003-513150 A (Infimum International Ltd.),<br>08 April 2003 (08.04.2003),<br>claims; paragraphs [0001] to [0010], [0037] to<br>[0038]; table 1; examples 7 to 8<br>& US 6074993 A<br>claims; column 1, line 5 to column 3, line 59;<br>column 12, lines 27 to 63; table 1; examples 7<br>to 8<br>& WO 2001/030948 A1 & EP 1238047 A1<br>& CA 2388953 A1 | 1-7                   |
| X         | WO 2006/126651 A1 (Idemitsu Kosan Co., Ltd.),<br>30 November 2006 (30.11.2006),<br>claims; paragraphs [0008], [0033] to [0035];<br>table 1; example 3<br>& US 2009/0082233 A1<br>claims; paragraphs [0016], [0065]; table 1;<br>example 3<br>& JP 2006-328265 A & CN 101184830 A                                                                            | 1-2, 4-7              |
| X         | JP 2004-211006 A (Asahi Denka Co., Ltd.),<br>29 July 2004 (29.07.2004),<br>claims; paragraphs [0063] to [0064]; table 1;<br>example 12<br>(Family: none)                                                                                                                                                                                                    | 1-2, 6                |
| P, X      | WO 2016/152993 A1 (Idemitsu Kosan Co., Ltd.),<br>29 September 2016 (29.09.2016),<br>claims; paragraphs [0008], [0017] to [0018],<br>[0097] to [0099]; table 4; examples 2 to 8<br>& JP 2016-180070 A                                                                                                                                                        | 1-7                   |
| P, X      | WO 2016/159258 A1 (Idemitsu Kosan Co., Ltd.),<br>06 October 2016 (06.10.2016),<br>claims; paragraphs [0012] to [0014], [0097] to<br>[0099]; table 1; example 6<br>(Family: none)                                                                                                                                                                            | 1-7                   |
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