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(19) **United States**(12) **Patent Application Publication**  
**Watanabe et al.**(10) **Pub. No.: US 2019/0390131 A1**(43) **Pub. Date: Dec. 26, 2019**(54) **LUBRICANT COMPOSITION****Publication Classification**(71) Applicants: **ExxonMobil Research and Engineering Company**, Annandale, NJ (US); **Toyota Jidosha Kabushiki Kaisha**, Toyota-shi Aichi-ken (JP)(72) Inventors: **Honami Watanabe**, Kawasaki-shi (JP); **Ko Onodera**, Kawasaki-shi (JP); **Takehisa Sato**, Kawasaki-shi (JP); **Kazuo Yamamori**, Nagoya-shi, Aichi-ken (JP); **Toyoharu Kaneko**, Anjo-shi, Aichi-ken (JP); **Kazuyoshi Manabe**, Toyota-shi Aichi-ken (JP)(51) **Int. Cl.****C10M 141/10** (2006.01)  
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(57)

**ABSTRACT**

A lubricant composition which, in a sliding member, is interposed between a DLC-coated surface and another metal member, in particular, a steel material, the lubricant composition having good wear resistance as well as having a better friction reducing effect than conventional molybdenum friction modifier-containing lubricant compositions. The lubricant composition is characterized by containing a lubricating base oil, (A) molybdenum dialkyl dithiophosphate, and (B) zinc dialkyl dithiophosphate, wherein the amount of phosphorus with respect to the total mass of the lubricant composition is 300-1500 mass ppm.

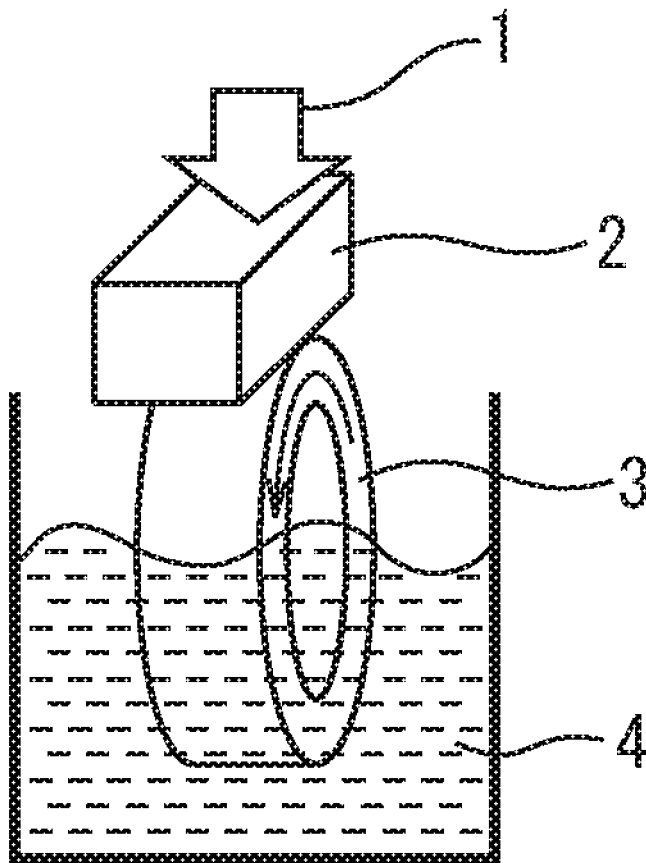
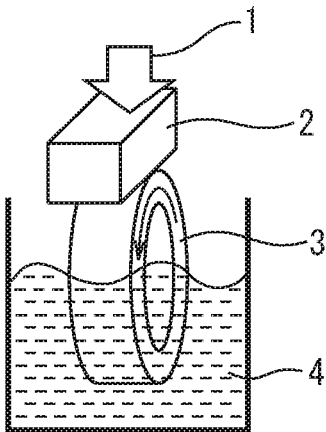


FIG. 1



## LUBRICANT COMPOSITION

### CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application is the National Phase entry of International Patent Application No. PCT/JP2018/003468 filed on Feb. 1, 2018, which claims priority to Japanese Patent Application No. 2017-016661 filed on Feb. 1, 2017, the entire contents of which are hereby incorporated by reference into this application.

### FIELD

[0002] The present disclosure relates to a lubricant composition. Specifically, the present disclosure provides a lubricant composition for sliding members, more specifically a lubricant composition for sliding members in internal combustion engines.

### BACKGROUND

[0003] Lubricant compositions are now widely used in automobile fields, such as for internal combustion engines, automatic transmissions, and gear oils. In recent years, lubricant compositions have been required to have lower viscosities in order to improve fuel consumption. However, lowering viscosity may result in thinned oil films and thus increased boundary friction, leading to inability to sufficiently reduce friction. Reduction of friction is important for improvement of fuel consumption, and thus surface modification technologies for sliding members are now receiving attention. For example, various hard films are investigated as measures for reduction of friction and wear of sliding parts. In particular, various attempts are being made to develop those using diamond-like carbon (hereinafter abbreviated as "DLC") films. For example, investigations are underway to obtain higher effect of reducing friction by optimizing the combination of DLC film and lubricant composition disposed between sliding members.

[0004] Published Japanese Translation of PCT International Publication for Patent Application (Kohyo) No. 2014-513173 (Patent Literature 1) discloses a lubricant composition containing an oil soluble organic molybdenum friction modifier and active sulfur of a surface active sulfur donor component, for use in reduction of friction and improvement of wear properties of DLC coating. As the oil soluble organic molybdenum friction modifier, molybdenum dithiocarbamates are used. Japanese Unexamined Patent Publication (Kokai) No. 2014-224239 (Patent Literature 2) discloses use of DLC-coated surface doped with specific elements and an oil soluble molybdenum compound having a chemical structure of trinuclear Mo for reduction of friction. Furthermore, Japanese Unexamined Patent Publication (Kokai) No. 2016-216653 (Patent Literature 3) discloses a lubricant composition containing a molybdenum dithiophosphate and an amine or amide friction modifier as essential components, which lubricant composition has low friction and wear resistance to DLC films, particularly DLC films comprising a hydrogenated amorphous carbon.

### CITATION LIST

#### Patent Literature

[0005] [Patent Literature 1] Published Japanese Translation of PCT International Publication for Patent Application (Kohyo) No. 2014-513173

[0006] [Patent Literature 2] Japanese Unexamined Patent Publication (Kokai) No. 2014-224239

[0007] [Patent Literature 3] Japanese Unexamined Patent Publication (Kokai) No. 2016-216653

### SUMMARY

#### Technical Problem

[0008] However, lubricant compositions containing a molybdenum dithiocarbamate or a trinuclear Mo compound as a friction modifier still does not have sufficient friction reducing effects. In addition, lubricant compositions containing a molybdenum dithiocarbamate are effective for sliding contact between steel materials, but may increase the wear amount by sliding contact between a DLC film and a steel material. Further, use of a lubricant composition containing an amine or amide friction modifier at a content described in Examples in Japanese Unexamined Patent Publication (Kokai) No. 2016-216653 (Patent Literature 3) onto a DLC film surface containing boron may lead to higher coefficient of friction and increased wear amount.

[0009] In view of the above, an object of the present disclosure is to provide a lubricant composition which is provided between a DLC-coated surface and another metal member (in particular a steel material) of sliding members, and which lubricant composition has both a better friction reducing effect than that of conventional lubricant compositions containing molybdenum friction modifiers and a good wear resistance.

#### Solution to Problem

[0010] In order to solve the above problems, the present inventors have intensively studied to find that a lubricant composition containing molybdenum dialkyldithiophosphate and zinc dialkyldithiophosphate can solve the above problems, thereby completing the present disclosure.

[0011] The present disclosure provides a lubricant composition comprising a lubricant base oil, (A) molybdenum dialkyldithiophosphate, and (B) zinc dialkyldithiophosphate, and having a phosphorus content of 300 to 1500 ppm by weight based on the total weight of the lubricant composition.

[0012] Further, the present disclosure provides lubricant compositions further having at least one characteristics of the following (a) to (h):

[0013] (a) the lubricant composition, which further comprises, or does not comprise at all, (A') at least one selected from the group consisting of an amine friction modifier and an amide friction modifier at a content of less than 0.1% by weight based on the total weight of the lubricant composition;

[0014] (b) the lubricant composition, comprising component (A) at a content of 400 to 1300 ppm by weight in terms of ppm by weight of molybdenum based on the total weight of the lubricant composition, and component (B) at a content of 200 to 1000 ppm by weight in terms of ppm by weight of phosphorus based on the total weight of the lubricant composition;

[0015] (c) the lubricant composition, for use in lubrication of diamond-like carbon (DLC) films;

[0016] (d) the lubricant composition, for use in lubrication of opposed sliding surfaces of sliding members, wherein the sliding members are a pair of sliding members having

opposed sliding surfaces which can move relative to each other, and wherein at least one of the sliding surfaces comprises a surface coated with a diamond-like carbon (DLC) film;

[0017] (e) the lubricant composition of (c) or (d), wherein the DLC comprises boron;

[0018] (f) the lubricant composition, which has a high temperature high shear viscosity (HTHS viscosity) at 150° C. of 1.4 to 2.9 mPa·s;

[0019] (g) the lubricant composition, which has a kinematic viscosity at 100° C. of 9.3 mm<sup>2</sup>/s or less;

[0020] (h) the lubricant composition, for use in internal combustion engines.

[0021] In the present disclosure, the sliding member means a pair of members having opposed sliding surfaces which can move relative to each other while being in sliding contact with each other, such as a shaft and a bearing, and a piston and a liner. The sliding members wherein at least one of the sliding surfaces comprises a surface coated with a diamond-like carbon (DLC) film in (d) above means that the surface of one of a pair of opposed members, in sliding contact with the other member is coated with a DLC film. The lubricant composition for use in lubrication of opposed sliding surfaces means a lubricant composition for use in lubrication between opposed sliding surfaces of a pair of members. The lubricant composition may be disposed between the opposed sliding surfaces.

#### Technical Effects

[0022] The lubricant composition of the present disclosure can reduce a coefficient of friction between sliding surfaces. In particular, the lubricant composition of the present disclosure can provide a lower coefficient of friction in sliding surfaces between a DLC-coated surface and another metal member (in particular, a steel material) than a lubricant composition only containing a molybdenum dithiocarbamate or a trinuclear Mo compound as a friction modifier, and also is excellent in wear resistance. The lubricant composition of the present disclosure can be suitably used as a lubricant composition particularly for use in internal combustion engines.

#### BRIEF DESCRIPTION OF DRAWING

[0023] FIG. 1 is a schematic view of a Block-on-Ring friction test.

#### DESCRIPTION OF EMBODIMENTS

[0024] The lubricant composition of the present disclosure will be described in detail.

[0025] Lubricant Base Oil

[0026] Any lubricant base oils may be used, including mineral oils, synthetic oils, and mixed oils thereof. Examples of the mineral base oils include lubricant base oils such as paraffin oils and naphthene oils, obtained by subjecting crude oil to atmospheric distillation and vacuum distillation and purifying the obtained lubricant oil fractions in appropriate combination of purification processes such as solvent deasphalting, solvent extraction, hydrogenolysis, solvent dewaxing, catalytic dewaxing, hydrogenation refining, sulfuric acid cleaning, clay treatment; and lubricant base oils obtained by isomerization and dewaxing of waxes obtained by solvent dewaxing. The kinematic viscosities of the mineral base oils at 100° C. are, but not limited to, 1 to

6 mm<sup>2</sup>/s, or from 2 to 6 mm<sup>2</sup>/s, in order to obtain a lubricant composition having a low viscosity.

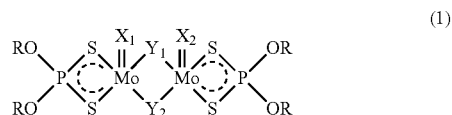
[0027] Examples of the synthetic base oils which can be used include isoparaffins, alkylbenzenes, alkylnaphthalenes, monoesters, diesters, polyol esters, polyoxyalkylene glycols, dialkyl diphenyl ethers, and polyphenyl ethers. GTL (Gas to Liquid) base oils, ATL (Asphalt to Liquid) base oils, BTL (Biomass to Liquid) base oils and CTL (Coal to Liquid) base oils can also be used, and the processes for using them as raw materials are described in U.S. Pat. Nos. 4,594,172 and 4,943,672. The kinematic viscosities of the synthetic base oils are not particularly limited. Poly- $\alpha$ -olefins or  $\alpha$ -olefin copolymers having a kinematic viscosity of less than 6 mm<sup>2</sup>/s or more than 80 mm<sup>2</sup>/s at 100° C. can also be used. The kinematic viscosities of the synthetic base oils are 1 to 6 mm<sup>2</sup>/s, or from 2 to 6 mm<sup>2</sup>/s, in order to obtain a lubricant composition having a low viscosity.

[0028] The above-described base oils which can be used in combination may be used alone or in combination of two or more. When two or more are used, two or more mineral base oils; two or more synthetic base oils; and one or more mineral base oils and one or more synthetic base oils can be used.

[0029] In order to obtain a lubricant composition having a low viscosity, the lubricant base oils as a whole have a kinematic viscosity at 100° C. from 1 to 6 mm<sup>2</sup>/s, from 2 to 6 mm<sup>2</sup>/s, or from 2.5 to 6 mm<sup>2</sup>/s.

[0030] (A) Molybdenum Dialkyldithiophosphate

[0031] The present disclosure is characterized in that the lubricant composition comprises molybdenum dialkyldithiophosphate (MoDTP) as a component. For example, MoDTP is a compound represented by following formula (1).



[0032] Friction modifiers include organic molybdenum compounds, complexes of a molybdenum compound and a sulfur-containing organic compound or other organic compound, and complexes of a sulfur-containing molybdenum compound such as sulfurized molybdate and an alkenylsuccinimide. Examples of the organic molybdenum compounds include a molybdenum dialkyldithiophosphate (MoDTP) and a molybdenum dithiocarbamate (MoDTC). Among them, a molybdenum dithiocarbamate (MoDTC) has been used. This is because MoDTP contains phosphorus as shown in formula (1). Because phosphorus poisons three-way catalysts for exhaust gas purification, the content of phosphorus in a lubricant composition is regulated. In addition, since conventional lubricant compositions have often been blended with an organophosphorus compound as anti-wear agents, a molybdenum dithiophosphate has been avoided from aggressive use in order to reduce the content of phosphorus contained in a lubricant composition. From these reasons, a molybdenum dithiocarbamate (MoDTC) has been used as friction modifiers in conventional lubricant compositions. However, as described above, a lubricant composition containing a molybdenum dithiocarbamate (MoDTC) may cause significant wear between sliding sur-

faces of a DLC-coated surface and a steel material. In addition, the friction reducing effect of the lubricant compositions is insufficient. On the other hand, a lubricant composition containing a molybdenum dithiophosphate, as compared with a lubricant composition containing a molybdenum dithiocarbamate, can give an excellent friction reducing effect to a sliding surface having a DLC film and improve the wear resistance.

**[0033]** As described above, the lubricant composition of the present disclosure comprises a molybdenum dialkyldithiophosphate and a zinc dialkyldithiophosphate. The total content of phosphorus contained in the lubricant composition is from 300 to 1500 ppm by weight, from 400 to 1400 ppm by weight, from 500 to 1300 ppm by weight, from 600 to 1200 ppm by weight, or from 600 to 1000 ppm by weight based on the total weight of the lubricant composition. When a molybdenum dialkyldithiophosphate and a zinc dialkyldithiophosphate are combined at such contents that the total content of phosphorus is within the above ranges, both an improved effect of reducing the friction between sliding surfaces and an excellent wear resistance can be obtained without catalyst poisoning.

**[0034]** In formula (1) above, Rs are each independently a monovalent  $C_{1-30}$  hydrocarbon group. The hydrocarbon group may be linear or branched. Examples of the monovalent hydrocarbon group include linear or branched  $C_{1-30}$  alkyl groups;  $C_{2-30}$  alkenyl groups;  $C_{4-30}$  cycloalkyl groups;  $C_{6-30}$  aryl groups, alkylaryl groups and arylalkyl groups. When the monovalent hydrocarbon group is an arylalkyl group, the alkyl group is bound to any position. More specifically, examples of the alkyl group include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl, and branched alkyl thereof. In particular, in some embodiments, Rs are each independently  $C_{3-8}$  alkyl groups.  $X_1$  and  $X_2$  are oxygen atoms or sulfur atoms. In some embodiments,  $X_1$  and  $X_2$  are oxygen atoms.  $Y_1$  and  $Y_2$  are oxygen atoms or sulfur atoms. In some embodiments,  $Y_1$  and  $Y_2$  are sulfur atoms.

**[0035]** The content of the above (A) MoDTP in the lubricant composition of the present disclosure, in terms of ppm by weight of molybdenum based on the total weight of the lubricant composition, is from 400 to 1300 ppm by weight, from 500 to 1200 ppm by weight, from 600 to 1100 ppm by weight, or from 650 to 1050 ppm by weight. When the content of MoDTP is below the lower limit, insufficient effect of reducing the friction between sliding surfaces may be obtained. When the content of MoDTP is above the upper limit, wearing between sliding surfaces is undesirably increased.

**[0036]** The lubricant composition of the present disclosure can comprise a molybdenum friction modifier other than (A), such as a molybdenum dithiocarbamate (MoDTC), and a trinuclear molybdenum compound as optional components in combination with the molybdenum dialkyldithiophosphate (MoDTP). The content of the molybdenum friction modifier other than (A) is within the range not impairing the friction reducing effect obtained by the present disclosure and the wear resistance, and may be adjusted as appropriate without exceeding the content of MoDTP.

**[0037]** As described above, conventional lubricant compositions containing a molybdenum dithiocarbamate (MoDTC) alone may provide an insufficient effect of reducing the friction and cause a significant wearing between

sliding surfaces of a DLC-coated surface and a steel material. When MoDTC is used in combination with MoDTP, the friction between sliding surfaces of a DLC-coated surface and a steel material can be further reduced, and the wearing therebetween can be reduced. The content of MoDTC, in terms of ppm by weight of molybdenum derived from MoDTC based on the total weight of the lubricant composition, is 100 ppm by weight or less, 70 ppm by weight or less, or 50 ppm by weight or less. The lower limit of the content is, but not limited to, 1 ppm by weight or more, 5 ppm by weight or more, or 10 ppm by weight or more. When the content of MoDTC is above the upper limit, wearing between sliding surfaces may be undesirably increased.

**[0038]** The lubricant composition can comprise a trinuclear molybdenum compound in combination with MoDTP, and thereby can further reduce the friction between sliding surfaces as compared with a lubricant composition comprising a trinuclear molybdenum compound alone. However, a lubricant composition comprising a trinuclear molybdenum compound may result in larger wearing even in combination with MoDTP. Thus, when the lubricant composition comprises a trinuclear molybdenum compound, the content of the compound is very small without impairing the effects of the present disclosure. More specifically, in terms of ppm by weight of molybdenum derived from the molybdenum dithiocarbamate based on the total weight of the lubricant composition, the content is less than 50 ppm by weight, 40 ppm by weight or less, or 20 ppm by weight or less. The lower limit is not particularly limited. For example, the content is 1 ppm by weight or more, 5 ppm by weight or more, or 10 ppm by weight or more.

**[0039]** (A') Amide Friction Modifier and Amine Friction Modifier

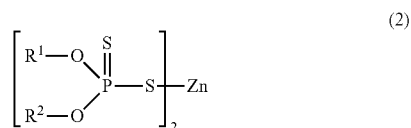
**[0040]** The lubricant composition of the present disclosure may further comprise, in addition to the above, at least one selected from the group consisting of an amide friction modifier and an amine friction modifier in less than a specific content, or may not comprise any of them at all. When the lubricant composition comprises an amide friction modifier or an amine friction modifier, the total content of them is 0.1% by weight or less, 0.05% by weight or less, or 0.01% by weight or less based on the total amount of the lubricant composition. Use of a lubricant compositions comprising an amide friction modifier or an amine friction modifier at a content not less than the above content, especially to DLC films doped with boron, may cause the coefficient of friction to become higher and the wearing to become larger. The contents of the amide friction modifier and the amine friction modifier is as small as possible, and some embodiments may not comprise any of them at all.

**[0041]** Any amine friction modifiers and amide friction modifiers may be used. Examples include alkylamines having a linear or branched alkyl group with a carbon number from 1 to 30, from 4 to 28, or from 6 to 25, such as methylamine, ethylamine, and propylamine; alkenyl amines having an alkenyl group with a carbon number from 2 to 30, from 4 to 28, or from 6 to 25, which may be branched, such as ethenylamine, propenylamine, and oleylamine; alicyclic amines such as cyclohexylamine; alkylenediamines having an alkylene group with a carbon number from 1 to 30, such as butylenediamine; polyamines such as pentaethylenehexamine; and mixtures thereof. Examples of the amide friction modifiers include saturated fatty acid amides having a linear or branched alkyl group with a carbon number from 1 to 30,

from 4 to 28, or from 6 to 25, such as ethanamide and propanamide; unsaturated fatty acid amides having an alkenyl group with a carbon number from 2 to 30, from 4 to 28, or from 6 to 25, which may be branched, such as oleamide and erucamide; and mixtures thereof.

**[0042]** (B) Zinc Dialkyldithiophosphate

**[0043]** The lubricant composition of the present disclosure comprises a zinc dialkyldithiophosphate (ZnDTP (also referred to as ZDDP)). This compound is known as an anti-wear agent for lubricant compositions and is represented by following formula (2).

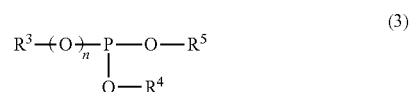


**[0044]** In formula (2), R<sup>1</sup> and R<sup>2</sup>, which may be the same or different, are each a hydrogen atom or a monovalent C<sub>1-26</sub> hydrocarbon group. For example, the monovalent hydrocarbon group is a hydrocarbon group containing a primary or secondary C<sub>1-26</sub> alkyl group; a C<sub>2-26</sub> alkenyl group; a C<sub>6-26</sub> cycloalkyl group; a C<sub>6-26</sub> aryl, alkylaryl or arylalkyl group; and an ester linkage, an ether linkage, an alcohol group or a carboxyl group. R<sup>1</sup> and R<sup>2</sup> each is a primary or secondary alkyl group with a carbon number from 2 to 12, a C<sub>8-18</sub> cycloalkyl group, or a C<sub>8-18</sub> alkylaryl group, and may be the same or different. In some embodiments, R<sup>1</sup> and R<sup>2</sup> may be zinc dialkyldithiophosphates, and the primary alkyl group has a carbon number from 3 to 12, or from 4 to 10. The secondary alkyl group has a carbon number from 3 to 12, or from 3 to 10. A zinc dithiocarbamate (ZnDTC) may also be used in combination.

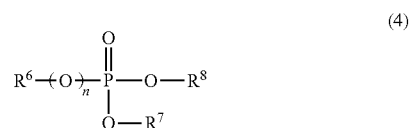
**[0045]** The content of the zinc dialkyldithiophosphate in the present lubricant composition is such a content that the total content of phosphorus satisfies the above-described ranges based on the total weight of the lubricant composition. In some embodiments, the content is such that the content of phosphorus derived from the ZnDTP is from 200 to 1000 ppm by weight, from 300 to 900 ppm by weight, from 350 to 850 ppm by weight, or from 400 to 800 ppm by weight, based on the total weight of the lubricant composition. When the lubricant composition comprises the zinc dialkyldithiophosphate at a content satisfying the above ranges, both an improved effect of reducing the friction between sliding surfaces and an excellent wear resistance can be obtained without catalyst poisoning. It is noted that the lubricant composition of the present disclosure may comprise one of zinc dialkyldithiophosphates having a primary alkyl group (Pri-ZnDTPs) and zinc dialkyldithiophosphates having a secondary alkyl group (Sec-ZnDTPs) alone, or two or more of them in combination. When the lubricant composition comprises them in combination, the combination ratio is not particularly limited. When combined with a molybdenum dialkyldithiophosphate, use of any of Pri-ZnDTP and Sec-ZnDTP can equally result in both an excellent friction reducing effect and wear resistance. In some embodiments, the lubricant compositions may include a Sec-ZnDTP, in which the content of phosphorus derived from the Sec-ZnDTP is, but not limited to, from 200 to 1000

ppm by weight, from 250 to 900 ppm by weight, or from 300 to 800 ppm by weight based on the total weight of the lubricant composition.

**[0046]** In combination with the zinc dialkyldithiophosphate, at least one compounds selected from phosphate- and phosphite-phosphorus compounds represented by following formulae (3), (4) and (5), and metal salts and amine salts thereof can also be used. However, the contents of these compounds are limited in such amounts that the total weight of phosphorus in the whole lubricant composition satisfies the ranges described above. For example, the total content is less than 0.1% by weight, less than 0.05% by weight, or less than 0.01% by weight, based on the total amount of the lubricant composition. In some embodiments, these compounds are not contained at all.



**[0047]** In formula (3) above, R<sup>3</sup> is a monovalent C<sub>1-30</sub> hydrocarbon group; R<sup>4</sup> and R<sup>5</sup> are each independently a hydrogen atom or a monovalent C<sub>1-30</sub> hydrocarbon group; and m is 0 or 1.



**[0048]** In formula (4) above, R<sup>6</sup> is a monovalent C<sub>1-30</sub> hydrocarbon group; R<sup>7</sup> and R<sup>8</sup> are each independently a hydrogen atom or a monovalent C<sub>1-30</sub> hydrocarbon group; and n is 0 or 1.



**[0049]** In formula (5) above, R<sup>6</sup> is as described above.

**[0050]** Examples of the monovalent C<sub>1-30</sub> hydrocarbon group represented as R<sup>3</sup> to R<sup>8</sup> in formulae (3), (4) and (5) include alkyl, cycloalkyl, alkenyl, alkyl-substituted cycloalkyl, aryl, alkyl-substituted aryl, and arylalkyl groups. In particular, the monovalent C<sub>1-30</sub> hydrocarbon group may be a C<sub>1-30</sub> alkyl group or a C<sub>6-24</sub> aryl group, a C<sub>3-18</sub> alkyl group, or a C<sub>4-15</sub> alkyl group.

**[0051]** Examples of the phosphorus compound represented by formula (3) above include phosphorous acid monoesters and (hydrocarbyl)phosphonous acids having one C<sub>1-30</sub> hydrocarbon group described above; phosphorous acid diesters, monothiophosphorous acid diesters, and (hydrocarbyl)phosphonous acid monoesters having two C<sub>1-30</sub> hydrocarbon group described above; phosphorous acid triesters and (hydrocarbyl)phosphonous acid diesters having three C<sub>1-30</sub> hydrocarbon group described above; and combinations thereof.

**[0052]** As described above, the lubricant composition of the present disclosure comprises a lubricant base oil, (A) a molybdenum dialkyldithiophosphate, and (B) a zinc dialkyldithiophosphate. The lubricant composition can further comprise an amide friction modifier and an amine friction modifier in less than the specific content described above, but, in some embodiments, the lubricant composition does not comprise them at all. In addition, the lubricant composition may comprise one or more selected from (C) a viscosity index improver, (D) an ashless dispersant, and (E) a metal detergent, as optional components.

**[0053]** (C) Viscosity Index Improver

**[0054]** Examples of the viscosity index improver include so-called non-dispersion viscosity index improvers such as polymers or copolymers of one or more monomers selected from various methacrylic acid esters, and hydrogenated products thereof; and so-called dispersion viscosity index improvers obtained by copolymerizing various methacrylic acid esters including nitrogen compounds; non-dispersion or dispersion ethylene- $\alpha$ -olefin copolymers (the  $\alpha$ -olefin includes propylene, 1-butene, and 1-pentene), and hydrogenated products thereof; polyisobutenes and hydrogenated products thereof; hydrogenated products of styrene-diene copolymers; styrene-maleic anhydride ester copolymers; star-shaped isoprenes; and polyalkylstyrenes. Furthermore, comb polymers comprising at least a polyolefin macromer-based repeating unit and a repeating unit based on alkyl (meth)acrylate having a  $C_{1-30}$  alkyl group in the main chain can be used.

**[0055]** The molecular weight of the viscosity index improver is selected in consideration of the shear stability of the lubricant composition. For example, viscosity index improvers are used, which have a weight average molecular weight of usually from 5,000 to 1,000,000, or from 100,000 to 900,000 for dispersion and non-dispersion polymethacrylates; usually from 800 to 5,000, or from 1,000 to 4,000 for polyisobutenes or hydrogenated products thereof; and usually from 800 to 500,000, or from 3,000 to 200,000 for ethylene- $\alpha$ -olefin copolymers or hydrogenated products thereof.

**[0056]** Among the viscosity index improvers, when an ethylene- $\alpha$ -olefin copolymer or a hydrogenated product thereof is used, a lubricant composition having particularly excellent shear stability can be obtained. Any one or more compound(s) selected from the viscosity index improvers described above can be contained in any content(s).

**[0057]** The content of the viscosity index improver in the lubricant composition is from 0.01 to 20% by weight, from 0.02 to 10% by weight, or from 0.05 to 5% by weight, based on the total weight of the composition.

**[0058]** (D) Ashless Dispersant

**[0059]** The lubricant composition of the present disclosure can further comprise an ashless dispersant. Any ashless dispersants may be used without limitation. Examples of the ashless dispersant include nitrogen-containing compounds having at least one linear or branched  $C_{40-400}$  alkyl or alkenyl group in the molecules, and derivatives thereof, and succinimides and modified products thereof. The ashless dispersants may be used alone or in combination of two or more. Boronated ashless dispersants can also be used. The boronated ashless dispersants are obtained by boronation of any ashless dispersants used in lubricants. Boronation is

generally carried out by reacting an imide compound with boric acid to neutralize a part or all of the remaining amino groups and/or imino groups.

**[0060]** The carbon number of the alkyl or alkenyl group described above is from 40 to 400, or from 60 to 350. When the carbon number of the alkyl or alkenyl group is below the lower limit, the solubility of the compound in a lubricant base oil tends to decrease. On the other hand, when the carbon number of the alkyl or alkenyl group is above the upper limit, the low-temperature fluidity of the lubricant composition tends to deteriorate. The alkyl and alkenyl groups may have linear or branched structures. In some embodiments, a branched alkyl or alkenyl group derived from an oligomer of an olefin such as propylene, 1-butene, or isobutene, or a co-oligomer of ethylene and propylene is used.

**[0061]** The succinimides include so-called mono-succinimides which are reaction products between one end of polyamines and succinic anhydride, and so-called bis-succinimides which are reaction products between both ends of polyamines and succinic anhydride. The lubricant composition of the present disclosure may comprise either one or both of the mono- and bis-succinimides.

**[0062]** The modified products of succinimides are, for example, those obtained by modifying a succinimide with a boron compound (hereinafter also referred to as boronated succinimide). Modification with a boron compound refers to boronation. Boronated succinimides may be used alone or in combination of two or more. When used in combination, two or more boronated succinimides may be combined. Both a boronated mono-succinimide and a bis-succinimide may be contained. Alternatively, boronated mono-succinimides may be combined, or boronated bis-succinimides may be combined. A boronated succinimide and a non-boronated succinimide may be combined.

**[0063]** For example, methods for producing boronated succinimides include those disclosed in, for example, Japanese Examined Patent Publication (Kokoku) Nos. S42-8013 and S42-8014, and Japanese Unexamined Patent Publication (Kokai) Nos. S51-52381 and S51-130408. Specifically, for example, a boronated succinimide can be obtained by mixing an organic solvent such as alcohol, hexane, or xylene, a light lubricant base oil or the like, with a polyamine, a succinic anhydride (derivative), and a boron compound such as boric acid, a borate ester, or a borate salt, and heat-treating the resultant mixture under appropriate conditions. Thus-obtained boronated succinimide can usually have a boron content from 0.1 to 4% by weight. In accordance with the present disclosure, boron-modified compounds of alkenyl-succinimide compounds (boronated succinimides) may enable excellent heat resistance, antioxidant properties and anti-wear properties to be achieved.

**[0064]** The content of boron contained in the boronated ashless dispersant is not particularly limited. Usually, the content is from 0.1 to 3% by weight based on the weight of the ashless dispersant. In one embodiment of the present disclosure, the boron content in the ashless dispersant is 0.2% by weight or more, or 0.4% by weight or more, and is 2.5% by weight or less, 2.3% by weight or less, or 2.0% by weight or less. The boronated ashless dispersant may be a boronated succinimide, such as a boronated bis-succinimide.

**[0065]** The boronated ashless dispersant has a weight ratio of boron to nitrogen (B/N ratio) of 0.1 or more, 0.2 or more, and less than 1.0, or 0.8 or less.

**[0066]** The content of the ashless dispersant may be adjusted as appropriate and, for example, is from 0.01 to 20% by weight, or from 0.1 to 10% by weight based on the total weight of the lubricant composition. When the content of the ashless dispersant is below the lower limit, the sludge dispersibility may be insufficient. On the other hand, when the content is above the upper limit, the lubricant composition may deteriorate certain rubber materials, or deteriorate the low-temperature fluidity.

**[0067]** (E) Metal Detergent

**[0068]** Examples of the metal detergent include detergents containing an alkali metal or an alkaline earth metal. Examples include, but are not limited to, sulfonates containing an alkali metal or an alkaline earth metal, salicylates containing an alkali metal or an alkaline earth metal, phenates containing an alkali metal or an alkaline earth metal. Examples of the alkali metal or alkaline earth metal include, but are not limited to, magnesium, barium, sodium, and calcium.

**[0069]** More specifically, calcium sulfonate, magnesium sulfonate, calcium salicylate, magnesium salicylate, calcium phenate, and magnesium phenate are used. The metal detergents may be used alone or in combination of two or more. The content of an alkali metal or alkaline earth metal contained in the metal detergent is, but not limited to, from 0.1 to 20% by weight, from 0.5 to 15% by weight, or from 1.0 to 15% by weight.

**[0070]** The metal detergent has a total base number, but not limited to, from 20 to 600 mgKOH/g, from 50 to 500 mgKOH/g, from 100 to 450 mgKOH/g, or from 150 to 400 mgKOH/g. Such metal detergents allow the lubricant composition to have an acid neutralizing property, a high-temperature detergency, and an anti-rust property.

**[0071]** The metal detergent may be contained in the lubricant composition at any percentage. For example, the percentage is from 0.01 to 5% by weight, from 0.1 to 4% by weight, or from 0.2 to 3% by weight.

**[0072]** In addition to the above, the lubricant composition of the present disclosure may further comprise other additives. Examples of the other additives include oily agents, rust preventives, antioxidants, extreme pressure agents, corrosion inhibitors, metal deactivators, pour point depressants, anti-foaming agents, coloring agents, and additive packages for automatic transmission fluid. Additive packages for various lubricants containing at least one of them can also be added. When additives containing phosphorus are used, the total content of phosphorus is adjusted to a range from 300 to 1500 ppm by weight, from 400 to 1400 ppm by weight, from 500 to 1300 ppm by weight, from 600 to 1200 ppm by weight, or from 600 to 1000 ppm by weight, based on the total weight of the lubricant composition.

**[0073]** The high temperature high shear viscosity (HTHS viscosity) at 150° C. of the lubricant composition of the present disclosure is, but not limited to, from 1.4 to 2.9 mPa·s, or from 1.7 to 2.6 mPa·s.

**[0074]** The kinematic viscosity at 100° C. of the lubricant composition of the present disclosure is, but not limited to, from 3 to 9.3 mm<sup>2</sup>/s, from 3 to 8.2 mm<sup>2</sup>/s, or from 4 to 8.2 mm<sup>2</sup>/s. When the kinematic viscosity at 100° C. of the lubricant composition is below the lower limit, there is a possibility that a sufficient coefficient of friction cannot be obtained. On the other hand, when the kinematic viscosity at 100° C. is above the upper limit, the viscosity resistance is increased, and the fuel consumption is worsened.

**[0075]** The viscosity index of the lubricant composition of the present disclosure is, but not limited to, 120 or more, or 160 or more. When the viscosity index of the lubricant composition is below the lower limit, there is a possibility that sufficient low-temperature characteristics cannot be obtained. The upper limit is, but not limited to, 250.

**[0076]** The lubricant composition of the present disclosure, though being made low-viscosity, exhibits an excellent friction reducing effect, and also has an excellent wear resistance. The lubricant composition of the present disclosure is suitably used as an oil disposed between sliding surfaces of sliding members. The lubricant composition of the present disclosure also suitably functions as a lubricant for diamond-like carbon (DLC) films. In particular, the lubricant composition of the present disclosure can be disposed between a DLC-coated sliding surface of a sliding member, which has at least one sliding surface coated with a diamond-like carbon (DLC) film, and a sliding surface of the other metal member (in particular, a steel material), so that the friction between the sliding surfaces can be further reduced and an excellent wear resistance can be obtained. Thus, in some embodiments of the present disclosure, a diamond-like carbon (DLC) film and the lubricant composition are combined.

**[0077]** The diamond-like carbon (DLC) film in the present disclosure may be a DLC film having an amorphous structure. The DLC film is formed on at least one sliding surface of sliding members. The DLC film can be doped with a predetermined element. Examples of the element include boron (B), titanium (Ti), vanadium (V), and molybdenum (Mo). In some embodiments, the element is boron. In other embodiments of the present disclosure, a DLC film doped with boron and the lubricant composition are combined, so that both better friction reducing effect and wear resistance are obtained.

**[0078]** The content of boron is from 1 to 30%, or from 4 to 25% when the entire DLC film is considered as 100 atom %. When the content of boron is below the lower limit, insufficient friction reducing effect and wear resistance may be obtained. On the other hand, when the content of boron is above the upper limit, a good DLC film may not be formed.

**[0079]** The DLC film in the present disclosure may be a DLC not containing hydrogen, so-called hydrogen-free DLC, but a DLC containing hydrogen may be used because the friction reducing effect can be easily obtained. The content of hydrogen is from 0 to 25%, from 5 to 25%, from 10 to 22%, or from 15 to 20%, when the entire film is considered as 100 atom %. As the content of hydrogen in the DLC film increases, there is a tendency that the low-friction characteristics can be improved. However, when the content of hydrogen is excessive, the DLC film may be excessively softened to have a reduced wear resistance.

**[0080]** The DLC film in the present disclosure may contain a modification element for improving the sliding characteristics and the like and/or inevitable impurities. Examples of the element include O, Al, Mn, Si, Cr, W, and Ni. The content of the element is not particularly limited, and may be adjusted within a range not impairing the effects of the present disclosure. In particular, the content is less than 8 atom %, or less than 4 atom %. The composition of the DLC film may be homogeneous, slightly changed, or even inclined, with respect to the thickness direction.

**[0081]** A substrate on which the DLC film is formed (i.e., a substrate of a sliding member) is not particularly limited. The DLC film is harder than the substrate, and has a smaller modulus of elasticity than the substrate. Such substrates can improve the wear resistance, the toughness, the impact resistance or the like of the DLC-coated surface. For example, the DLC film in the present disclosure has a hardness from 10 to 30 GPa, or from 14 to 25 GPa. When the hardness is too low, the wear resistance is reduced. When the hardness is too high, the DLC film is likely to occur cracks or the like. From the same viewpoint, for example, the modulus of elasticity of the DLC film is from 100 to 200 GPa, from 110 to 190 GPa, from 120 to 180 GPa, or from 130 to 170 GPa.

**[0082]** The DLC film may be formed according to a known method. For example, a method described in Japanese Unexamined Patent Publication (Kokai) No. 2014-224239 can be followed. Specifically, a dense DLC film can be efficiently formed by sputtering, or by unbalanced magnetron sputtering (UBMS). The inside of the chamber is evacuated to  $10^{-5}$  Pa or less before formation of the DLC film, or a hydrogen gas is introduced into the chamber to remove the remaining oxygen and water in the chamber before film formation. The amount of the hydrogen gas introduced may be adjusted according to the content of H in the DLC film.

**[0083]** As the sputtering gas, for example, one or more rare gases such as argon (Ar) gas, helium (He) gas, and nitrogen ( $N_2$ ) gas can be used. As a H-containing gas, one or more hydrocarbon gases such as methane ( $CH_4$ ), acetylene ( $C_2H_2$ ), and benzene ( $C_6H_6$ ) can be used. The gas flow rate, the DLC film formation temperature, and the like may be selected as appropriate according to known methods.

**[0084]** The lubricant composition of the present disclosure can be applied to sliding members in a wide variety of machines. In particular, a sliding machine comprising the lubricant composition of the present disclosure and a sliding member coated with a DLC film (in particular, a boron-containing DLC film) has a very small coefficient of friction between the sliding surfaces and an excellent wear resistance, and thus the lubricant composition is suitable for applications where mechanical loss due to sliding is to be reduced. For example, the lubricant composition can be applied to pistons, piston rings, piston pins, crank shafts, gears, rotors, rotor housings, cams, and valve lifters. In particular, the lubricant composition of the present disclosure can be suitably used for use in internal combustion engines.

## EXAMPLES

**[0085]** The present disclosure will now be described in detail by showing Examples and Comparative Examples, but is not limited thereto.

**[0086]** Evaluation materials for the Block-on-Ring friction test shown below were prepared as test samples used as sliding members in the following Examples and Comparative Examples.

**[0087]** As a substrate, a block-shaped (6.3 mm by 15.7 mm by 10.1 mm) steel material (SUS440C) subjected to a quenching treatment was prepared. A DLC film was deposited on a mirror-finished surface (surface roughness  $R_{zjs}$  0.1  $\mu m$ /sliding surface) of the steel material using an unbalanced magnetron sputtering apparatus (UBMS 504 manufactured by Kobe Steel, Ltd.). B4C was used as a doping

target to deposit a boron-doped DLC film. Deposition of the DLC film by sputtering was done according to a method described in Japanese Unexamined Patent Publication (Kokai) No. 2014-224239. Thus, the evaluation material on which the boron-doped DLC film (containing hydrogen) was deposited was obtained. The thickness of the DLC film was about 2  $\mu m$ . For the composition of the obtained film, the content of boron in the boron-doped DLC film was 6% as a boron content when the entire film was considered as 100 atom %.

**[0088]** As evaluation materials not coated with a DLC film, a standard test piece made of a steel material (SAE4620) manufactured by Falex Corporation (hardness: RC58-63) was prepared as a ring test piece, and a standard test piece made of a steel material (SAE O1) manufactured by Falex Corporation (hardness: RC58-63) was also prepared as a block test piece.

**[0089]** In the tables below, test pieces coated with a boron-doped DLC film are represented as "B-DLC," and test pieces not coated with a DLC film (steel materials) are represented as "Steel."

**[0090]** Lubricant compositions in Examples and Comparative Examples comprise the following components. Lubricant Base Oil a GTL-derived base oil having a kinematic viscosity at 100° C. of 4.1  $mm^2/s$ , and VI of 127

### (A) Molybdenum Dialkylidithiophosphate (MoDTP)

**[0091]** a compound containing molybdenum at a content of 9% by weight, and represented by formula (1) above, wherein  $X_1$  and  $X_2$  are each an oxygen atom,  $Y_1$  and  $Y_2$  are each a sulfur atom, each R is a monovalent  $C_8$  hydrocarbon group

Friction Modifiers Other than (A) Above

**[0092]** a molybdenum dithiocarbamate MoDTC having a molybdenum content of 10% by weight

**[0093]** a trinuclear Mo compound having a molybdenum content of 5.5% by weight

**[0094]** oleylamine

**[0095]** oleamide

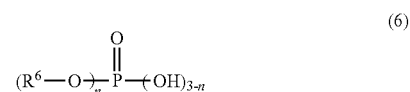
### (B) Zinc Dialkylidithiophosphate

**[0096]** a Pri-ZnDTP (a zinc dialkylidithiophosphate having a primary alkyl group)

**[0097]** a Sec-ZnDTP (a zinc dialkylidithiophosphate having a secondary alkyl group)

### (B') Acidic Phosphate Ester

**[0098]** a mixture of compounds represented by following formula (6), wherein  $R^6$  is a 2-ethylhexyl group, and n is 1 or 2



### (C) Metal Detergent

**[0099]** Ca salicylate having a total base number of 180 mgKOH/g, and a Ca content of 6.3% by weight

**[0100]** Mg sulfonate having a total base number of 400 mgKOH/g, and a Mg content of 9.4% by weight

(D) Ashless Dispersant

**[0101]** boronated succinimide having a B content of 0.7% by weight, and a N content of 2.0% by weight

**[0102]** non-boronated succinimide having a N content of 1.0% by weight

(E) Viscosity Index Improver

**[0103]** polymethacrylate having Mw of 300,000

(F) Other Additive Packages

**[0104]** Antioxidants: phenolic antioxidant and amine antioxidant

**[0105]** Anti-foaming agent: dimethyl silicone

Examples 1 to 14 and Comparative Examples 1 to 5

**[0106]** Lubricant compositions were prepared by mixing the components described above at the compositions and the contents described in the tables.

**[0107]** The contents shown in the tables are described below.

**[0108]** The content of a molybdenum friction modifier is in terms of ppm by weight of molybdenum based on the total amount of the lubricant composition. For a MoDTP, the content of phosphorus derived from the MoDTP in ppm by weight based on the total amount of the lubricant composition is also shown.

**[0109]** The content of a zinc dialkyldithiophosphate is in terms of ppm by weight of phosphorus derived from the zinc dialkyldithiophosphate based on the total amount of the lubricant composition.

**[0110]** The contents of oleylamine, oleamide, and an acidic phosphate ester are in % by weight based on the total amount of the lubricant composition.

**[0111]** The contents of metal detergents are in terms of % by weight of calcium and magnesium based on the total amount of the lubricant composition.

**[0112]** The content of an ashless dispersant is shown in terms of ppm by weight of boron based on the total amount

of the lubricant composition, and in terms of ppm by weight of nitrogen based on the total amount of the lubricant composition.

**[0113]** The tables also show the total content of phosphorus in ppm by weight based on the total amount of the lubricant composition.

**[0114]** These lubricant compositions were tested as described below. The results are shown in the tables.

(1) The kinematic viscosity at 100° C. (KV100) was measured according to ASTM D445.

(2) The high temperature high shear viscosity (HTHS viscosity) at 150° C. was measured according to ASTM D4683.

(3) Determination of Minimum Coefficient of Friction

**[0115]** A Block-on-Ring friction test was carried out using a block test piece having a sliding surface width of 6 mm (a test piece coated with a DLC film or a test piece not coated with a DLC film (a standard test piece made of a steel material (SAE O1) manufactured by Falex Corporation (hardness: RC58-63)); and as a counterpart, a ring test piece made of a steel material having an outer diameter of 35 mm and a width of 9 mm (a standard test piece made of a steel material (SAE4620) manufactured by Falex Corporation (hardness: RC58-63)). An embodiment of the Block-on-Ring friction test is schematically depicted in FIG. 1. A Block-on-Ring friction test was conducted for 30 minutes with a test load of 294 N, a sliding velocity of 0.3 m/s, and an oil temperature of 80° C. (constant), and the minimum coefficient of friction during 30 minutes was taken as the minimum coefficient of friction in this test.

(4) Evaluation of Wear Amount

**[0116]** Block test pieces before and after the Block-on-Ring friction test were measured for the surface roughness on a surface roughness tester (SURFTEST SV-3200 manufactured by Mitutoyo Corporation), and the wear amount was determined. For the wear amount, measurements were made at a total of three places, one at the central portion of the sliding mark and two portions at 1 mm from the both ends toward the central portion of the sliding mark, and the average value was taken as the wear amount in this test.

TABLE 1

|                                         |                                     |               | Example 1 | Example 2 | Example 3 | Example 4 | Example 5 | Example 6 | Example 7 | Example 8 |
|-----------------------------------------|-------------------------------------|---------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Mo friction modifier                    | lubricant base oil                  |               |           |           |           |           |           |           |           |           |
|                                         | MoDTP                               | (Mo)          | balance   | balance   | balance   | balance   | balance   | balance   | balance   | balance   |
|                                         |                                     | ppm by weight | 700       | 700       | 700       | 700       | 700       | 700       | 700       | 700       |
|                                         |                                     | (P)           | 250       | 250       | 250       | 250       | 250       | 250       | 250       | 250       |
|                                         |                                     | ppm by weight |           |           |           |           |           |           |           |           |
| ZnDTP (P content)                       | Primary ZnDTP                       | ppm by weight | 300       | 200       | 750       | —         | —         | 300       | 300       | 300       |
|                                         | Secondary ZnDTP                     | ppm by weight | 450       | 300       | —         | 750       | 450       | 450       | 450       | 450       |
|                                         |                                     |               |           |           |           |           |           |           |           |           |
|                                         | P content total                     | ppm by weight | 750       | 500       | 750       | 750       | 450       | 750       | 750       | 750       |
| metal detergent (metal element content) | Ca salicylate                       | % by weight   | 0.14      | 0.14      | 0.14      | 0.14      | 0.14      | 0.14      | —         | 0.20      |
|                                         | Mg sulfonate                        | % by weight   | 0.06      | 0.06      | 0.06      | 0.06      | 0.06      | —         | 0.06      | —         |
|                                         |                                     |               |           |           |           |           |           |           |           |           |
| dispersant (N content/B content)        | B dispersant                        | ppm by weight | 600/200   | 600/200   | 600/200   | 600/200   | 600/200   | 600/200   | 600/200   | 600/200   |
|                                         | non-B dispersant                    | ppm by weight | 200/0     | 200/0     | 200/0     | 200/0     | 200/0     | 200/0     | 200/0     | 200/0     |
|                                         |                                     |               |           |           |           |           |           |           |           |           |
|                                         | viscosity index improver            | % by weight   | 1         | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
|                                         | other additives                     | % by weight   | 1         | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
|                                         |                                     |               |           |           |           |           |           |           |           |           |
|                                         | Mo content in the whole composition | ppm by weight | 700       | 700       | 700       | 700       | 700       | 700       | 700       | 700       |
|                                         | P content in the whole composition  | ppm by weight | 1000      | 750       | 1000      | 1000      | 700       | 1000      | 1000      | 1000      |

TABLE 1-continued

|            |                   |                    | Example 1 | Example 2 | Example 3 | Example 4 | Example 5 | Example 6 | Example 7 | Example 8 |
|------------|-------------------|--------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| evaluation | KV100             | mm <sup>2</sup> /s | 6.5       | 6.5       | 6.5       | 6.7       | 6.5       | 6.5       | 6.2       | 6.6       |
| results    | HTHS150           | mPa · s            | 2.3       | 2.3       | 2.3       | 2.3       | 2.3       | 2.3       | 2.3       | 2.3       |
|            | B- minimum        | —                  | 0.042     | 0.042     | 0.041     | 0.041     | 0.041     | 0.044     | 0.045     | 0.046     |
|            | DLC/ coefficient  |                    |           |           |           |           |           |           |           |           |
|            | Steel of friction |                    |           |           |           |           |           |           |           |           |
|            | wear amount       | μm                 | 0.27      | 0.40      | 0.67      | 0.33      | 0.46      | 0.50      | 0.32      | 0.55      |
|            | Steel/ minimum    | —                  | 0.057     | 0.059     | 0.054     | 0.051     | 0.053     | 0.041     | 0.059     | 0.052     |
|            | Steel coefficient |                    |           |           |           |           |           |           |           |           |
|            | of friction       |                    |           |           |           |           |           |           |           |           |
|            | wear amount       | μm                 | 1.00      | 0.90      | 0.73      | 0.37      | 0.73      | 0.63      | 0.50      | 0.93      |

TABLE 2

|                 |                                     |                    | Example 9 | Example 10 | Example 11 | Example 12 | Example 13 |
|-----------------|-------------------------------------|--------------------|-----------|------------|------------|------------|------------|
| Mo friction     | lubricant base oil                  |                    | balance   | balance    | balance    | balance    | balance    |
| modifier        | MoDTP                               | (Mo)               | 700       | 1000       | 700        | 650        | 600        |
|                 |                                     | ppm by weight      |           |            |            |            |            |
|                 |                                     | (P)                | 250       | 360        | 250        | 230        | 210        |
|                 | Mo-trimer                           | ppm by weight      |           |            |            |            |            |
|                 |                                     | (Mo)               | —         | —          | —          | —          | —          |
|                 | MoDTC                               | ppm by weight      |           |            |            | 50         | 100        |
|                 |                                     | (Mo)               | —         | —          | —          |            |            |
| ZnDTP           | Primary ZnDTP                       | ppm by weight      | 300       | 200        | 300        | 200        | 200        |
| (P content)     | Secondary ZnDTP                     | ppm by weight      | 450       | 300        | 450        | 300        | 300        |
|                 |                                     | ppm by weight      |           |            |            |            |            |
| metal detergent | P content total                     | ppm by weight      | 750       | 500        | 750        | 500        | 500        |
| (metal element  | Ca salicylate                       | % by weight        | —         | 0.14       | 0.14       | 0.14       | 0.14       |
| content)        | Mg sulfonate                        | % by weight        | 0.20      | 0.06       | 0.06       | 0.06       | 0.06       |
| dispersant      | B dispersant                        | ppm by weight      | 600/200   | 600/200    | —          | 600/200    | 600/200    |
| (N content/B    | non-B dispersant                    | ppm by weight      | 200/0     | 200/0      | 500/0      | 200/0      | 200/0      |
| content)        |                                     |                    |           |            |            |            |            |
|                 | viscosity index improver            | % by weight        | 1         | 1          | 1          | 1          | 1          |
|                 | other additives                     | % by weight        | 1         | 1          | 1          | 1          | 1          |
|                 | Mo content in the whole composition | ppm by weight      | 700       | 1000       | 700        | 700        | 700        |
|                 | P content in the whole composition  | ppm by weight      | 1000      | 860        | 1000       | 730        | 710        |
| evaluation      | KV100                               | mm <sup>2</sup> /s | 6.4       | 6.5        | 6.7        | 6.6        | 6.5        |
| results         | HTHS150                             | mPa · s            | 2.3       | 2.3        | 2.3        | 2.3        | 2.3        |
|                 | B-DLC/Steel                         | minimum            | 0.047     | 0.045      | 0.046      | 0.046      | 0.048      |
|                 |                                     | coefficient        |           |            |            |            |            |
|                 |                                     | of friction        |           |            |            |            |            |
|                 | wear amount                         | μm                 | 0.37      | 0.47       | 0.47       | 0.43       | 0.70       |
|                 | Steel/Steel                         | minimum            | 0.061     | 0.049      | 0.061      | 0.053      | 0.051      |
|                 |                                     | coefficient        |           |            |            |            |            |
|                 |                                     | of friction        |           |            |            |            |            |
|                 | wear amount                         | μm                 | 0.73      | 0.67       | 0.57       | 0.57       | 0.67       |

TABLE 3

|             |                    |               | Comparative Example 1 | Comparative Example 2 | Comparative Example 3 | Comparative Example 4 |
|-------------|--------------------|---------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Mo friction | lubricant base oil |               | balance               | balance               | balance               | balance               |
| modifier    | MoDTP              | (Mo)          | —                     | —                     | —                     | 1400                  |
|             |                    | ppm by weight |                       |                       |                       |                       |
|             |                    | (P)           |                       |                       |                       | 500                   |
|             |                    | ppm by weight |                       |                       |                       |                       |
|             | Mo-trimer          | (Mo)          | 700                   | —                     | 100                   | —                     |
|             |                    | ppm by weight |                       |                       |                       |                       |
|             | MoDTC              | (Mo)          | —                     | 700                   | —                     | —                     |
|             |                    | ppm by weight |                       |                       |                       |                       |

TABLE 3-continued

|                                            |                                     |                                 |                       |                       |                       |                       |
|--------------------------------------------|-------------------------------------|---------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| ZnDTP<br>(P content)                       | Primary ZnDTP                       | ppm by weight                   | 300                   | 300                   | 300                   | 300                   |
|                                            | Secondary ZnDTP                     | ppm by weight                   | 450                   | 450                   | 450                   | 450                   |
|                                            |                                     |                                 |                       |                       |                       |                       |
|                                            | P content total                     | ppm by weight                   | 750                   | 750                   | 750                   | 750                   |
| metal detergent<br>(metal element content) | Ca salicylate                       | % by weight                     | 0.14                  | 0.14                  | 0.14                  | 0.14                  |
|                                            | Mg sulfonate                        | % by weight                     | 0.06                  | 0.06                  | 0.06                  | 0.06                  |
| dispersant<br>(N content/B content)        | B dispersant                        | ppm by weight                   | 600/200               | 600/200               | 600/200               | 600/200               |
|                                            | non-B dispersant                    | ppm by weight                   | 200/0                 | 200/0                 | 200/0                 | 200/0                 |
|                                            | viscosity index improver            | % by weight                     | 1                     | 1                     | 1                     | 1                     |
|                                            | oleylamine                          | % by weight                     | —                     | —                     | —                     | —                     |
|                                            | acidic phosphate ester              | % by weight                     | —                     | —                     | —                     | —                     |
|                                            | oleamide                            | % by weight                     | —                     | —                     | —                     | —                     |
|                                            | other additives                     | % by weight                     | 1                     | 1                     | 1                     | 1                     |
|                                            | Mo content in the whole composition | ppm by weight                   | 700                   | 700                   | 100                   | 1400                  |
|                                            | P content in the whole composition  | ppm by weight                   | 750                   | 750                   | 750                   | 1250                  |
| evaluation results                         | KV100                               | mm <sup>2</sup> /s              | 6.6                   | 6.6                   | 6.6                   | 6.5                   |
|                                            | HTHS150                             | mPa · s                         | 2.3                   | 2.3                   | 2.3                   | 2.3                   |
|                                            | B-DLC/Steel                         | minimum coefficient of friction | 0.055                 | 0.051                 | 0.052                 | 0.047                 |
|                                            |                                     | wear amount                     | μm                    | 0.93                  | 1.57                  | 0.57                  |
|                                            | Steel/Steel                         | minimum coefficient of friction | 0.065                 | 0.058                 | 0.088                 | —                     |
|                                            |                                     | wear amount                     | μm                    | 0.63                  | 0.93                  | 0.80                  |
|                                            |                                     |                                 |                       |                       |                       |                       |
|                                            |                                     |                                 |                       |                       |                       |                       |
|                                            |                                     |                                 | Comparative Example 5 | Comparative Example 6 | Comparative Example 7 | Comparative Example 8 |
| Mo friction modifier                       | lubricant base oil                  |                                 | balance               | balance               | balance               | balance               |
|                                            | MoDTP                               | (Mo) ppm by weight              | 350                   | 700                   | 700                   | 700                   |
|                                            |                                     | (P) ppm by weight               | 125                   | 250                   | 250                   | 250                   |
|                                            | Mo-trimer                           | (Mo) ppm by weight              | —                     | —                     | —                     | —                     |
|                                            | MoDTC                               | (Mo) ppm by weight              | —                     | —                     | —                     | —                     |
| ZnDTP<br>(P content)                       | Primary ZnDTP                       | ppm by weight                   | 300                   | 300                   | 300                   | 300                   |
|                                            | Secondary ZnDTP                     | ppm by weight                   | 450                   | 450                   | 450                   | 450                   |
|                                            |                                     |                                 |                       |                       |                       |                       |
|                                            | P content total                     | ppm by weight                   | 750                   | 750                   | 750                   | 750                   |
| metal detergent<br>(metal element content) | Ca salicylate                       | % by weight                     | 0.14                  | 0.14                  | 0.14                  | 0.14                  |
|                                            | Mg sulfonate                        | % by weight                     | 0.06                  | 0.06                  | 0.06                  | 0.06                  |
| dispersant<br>(N content/B content)        | B dispersant                        | ppm by weight                   | 600/200               | 600/200               | 600/200               | 600/200               |
|                                            | non-B dispersant                    | ppm by weight                   | 200/0                 | 200/0                 | 200/0                 | 200/0                 |
|                                            | viscosity index improver            | % by weight                     | 1                     | 1                     | 1                     | 1                     |
|                                            | oleylamine                          | % by weight                     | —                     | 0.19                  | 0.19                  | —                     |
|                                            | acidic phosphate ester              | % by weight                     | —                     | —                     | 0.16                  | —                     |
|                                            | oleamide                            | % by weight                     | —                     | —                     | —                     | 0.19                  |
|                                            | other additives                     | % by weight                     | 1                     | 1                     | 1                     | 1                     |
|                                            | Mo content in the whole composition | ppm by weight                   | 350                   | 700                   | 700                   | 700                   |
|                                            | P content in the whole composition  | ppm by weight                   | 875                   | 1000                  | 1200                  | 1000                  |

TABLE 3-continued

|            |             |                                 |       |       |       |       |
|------------|-------------|---------------------------------|-------|-------|-------|-------|
| evaluation | KV100       | mm <sup>2</sup> /s              | 6.5   | 6.6   | 6.6   | 6.6   |
| results    | HTHS150     | mPa · s                         | 2.3   | 2.3   | 2.3   | 2.3   |
|            | B-DLC/Steel | minimum coefficient of friction | 0.099 | 0.054 | 0.059 | 0.061 |
|            |             | wear amount                     | μm    | 0.13  | 0.83  | 1.50  |
|            | Steel/Steel | minimum coefficient of friction | —     | —     | —     | —     |
|            |             | wear amount                     | μm    | —     | —     | —     |

[0117] As shown in Comparative Example 2, the lubricant composition comprising a molybdenum dithiocarbamate (MoDTC) alone provided an insufficient effect of reducing the friction and caused a significant wear between the sliding surfaces of the DLC-coated surface and the steel material. As shown in Comparative Example 1, the lubricant composition comprising a trinuclear molybdenum compound alone resulted in increased friction between the sliding surfaces. Further, the wear between the sliding surfaces of the DLC-coated surface and the steel material was increased. As shown in Comparative Example 3, even where the content of a trinuclear molybdenum compound in the lubricant composition comprising a trinuclear molybdenum compound alone was decreased, the friction between the sliding surfaces was still large. In addition, as shown in Comparative Examples 6 to 8, the lubricant compositions comprising an amino friction modifier or an amide friction modifier at a content described in Example in Japanese Unexamined Patent Publication (Kokai) No. 2016-216653 (Patent Literature 3) resulted in high coefficients of friction between the sliding surfaces of the B-DLC-coated surface and the steel material, and the wear amount was large.

[0118] Compared to them, as shown in Tables 1 and 2, the lubricant composition of the present disclosure possibly gave excellent friction reducing effects not only between the sliding surfaces of the steel material and the steel material but also between the sliding surfaces of the B-DLC-coated surface and the steel material, and possibly improved the wear resistance.

#### INDUSTRIAL APPLICABILITY

[0119] In particular, the lubricant composition of the present disclosure can provide sliding surfaces between a DLC-coated surface and another metal member (in particular, a steel material) with a lower coefficient of friction than a lubricant composition only comprising a molybdenum dithiocarbamate or a trinuclear Mo compound as a friction modifier, and also is excellent in wear resistance. The lubricant composition of the present disclosure is suitably used as a lubricant composition particularly for use in internal combustion engines.

#### REFERENCE SIGNS LIST

- [0120] 1: Load
- [0121] 2: Block test piece
- [0122] 3: Ring test piece
- [0123] 4: Lubricant composition

1. A lubricant composition comprising a lubricant base oil, (A) a molybdenum dialkyldithiophosphate, and (B) a

zinc dialkyldithiophosphate, and having a phosphorus content of 300 to 1500 ppm by weight based on a total weight of the lubricant composition.

2. The lubricant composition according to claim 1, wherein the lubricant composition further comprises (A') at least one selected from the group consisting of an amine friction modifier and an amide friction modifier at a content of less than 0.1% by weight based on the total weight of the lubricant composition.

3. The lubricant composition according to claim 1, comprising component (A) at a content of 400 to 1300 ppm by weight in terms of ppm by weight of molybdenum based on the total weight of the lubricant composition, and component (B) at a content of 200 to 1000 ppm by weight in terms of ppm by weight of phosphorus based on the total weight of the lubricant composition.

4. The lubricant composition according to claim 1, for use in lubrication of diamond-like carbon (DLC) films.

5. The lubricant composition according to claim 1, for use in lubrication of opposed sliding surfaces of sliding members, wherein the sliding members are a pair of sliding members having opposed sliding surfaces which can move relative to each other, and wherein at least one of the sliding surfaces comprises a surface coated with a diamond-like carbon (DLC) film.

6. The lubricant composition according to claim 4, wherein the DLC film comprises boron.

7. The lubricant composition according to claim 1, wherein the lubricant composition has a high temperature high shear viscosity (HTHS viscosity) at 150° C. of 1.4 to 2.9 mPa·s.

8. The lubricant composition according to claim 1, wherein the lubricant composition has a kinematic viscosity at 100° C. of 9.3 mm<sup>2</sup>/s or less.

9. The lubricant composition according to claim 1, for use in internal combustion engines.

10. The lubricant composition according to claim 1, wherein the lubricant composition does not comprise (A') at least one selected from the group consisting of an amine friction modifier and an amide friction modifier.

11. The lubricant composition according to claim 2, comprising component (A) at a content of 400 to 1300 ppm by weight in terms of ppm by weight of molybdenum based on the total weight of the lubricant composition, and component (B) at a content of 200 to 1000 ppm by weight in terms of ppm by weight of phosphorus based on the total weight of the lubricant composition.

**12.** The lubricant composition according to claim 2, wherein the lubricant composition has a high temperature high shear viscosity (HTHS viscosity) at 150° C. of 1.4 to 2.9 mPa·s.

**13.** The lubricant composition according to claim 3, wherein the lubricant composition has a high temperature high shear viscosity (HTHS viscosity) at 150° C. of 1.4 to 2.9 mPa·s.

**14.** The lubricant composition according to claim 4, wherein the lubricant composition has a high temperature high shear viscosity (HTHS viscosity) at 150° C. of 1.4 to 2.9 mPa·s.

**15.** The lubricant composition according to claim 5, wherein the lubricant composition has a high temperature high shear viscosity (HTHS viscosity) at 150° C. of 1.4 to 2.9 mPa·s.

**16.** The lubricant composition according to claim 6, wherein the lubricant composition has a high temperature high shear viscosity (HTHS viscosity) at 150° C. of 1.4 to 2.9 mPa·s.

**17.** The lubricant composition according to claim 2, wherein the lubricant composition has a kinematic viscosity at 100° C. of 9.3 mm<sup>2</sup>/s or less.

**18.** The lubricant composition according to claim 3, wherein the lubricant composition has a kinematic viscosity at 100° C. of 9.3 mm<sup>2</sup>/s or less.

**19.** The lubricant composition according to claim 4, wherein the lubricant composition has a kinematic viscosity at 100° C. of 9.3 mm<sup>2</sup>/s or less.

**20.** The lubricant composition according to claim 5, wherein the lubricant composition has a kinematic viscosity at 100° C. of 9.3 mm<sup>2</sup>/s or less.

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