



(11)

EP 3 578 624 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:

11.12.2019 Bulletin 2019/50

(21) Application number: **18748169.2**

(22) Date of filing: **01.02.2018**

(51) Int Cl.:

C10M 137/10 (2006.01)	C10M 141/10 (2006.01)
C10M 133/04 (2006.01)	C10M 133/16 (2006.01)
C10N 10/04 (2006.01)	C10N 10/12 (2006.01)
C10N 20/02 (2006.01)	C10N 30/06 (2006.01)
C10N 40/25 (2006.01)	C10N 80/00 (2006.01)

(86) International application number:

PCT/JP2018/003468

(87) International publication number:

WO 2018/143365 (09.08.2018 Gazette 2018/32)

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

Designated Validation States:

MA MD TN

(30) Priority: **01.02.2017 JP 2017016661**

(71) Applicants:

- **ExxonMobil Research and Engineering Company**
Annandale, New Jersey 08801 (US)
- **TOYOTA JIDOSHA KABUSHIKI KAISHA**
Toyota-Shi,
Aichi-Ken 471-8571 (JP)

(72) Inventors:

- **WATANABE, Honami**
Kawasaki-shi
Kanagawa 210-9526 (JP)

• **ONODERA, Ko**

Kawasaki-shi
Kanagawa 210-9526 (JP)

• **SATO, Takehisa**

Kawasaki-shi
Kanagawa 210-9526 (JP)

• **YAMAMORI, Kazuo**

Toyota-shi
Aichi-ken 471-8571 (JP)

• **KANEKO, Toyoharu**

Toyota-shi
Aichi-ken 471-8571 (JP)

• **MANABE, Kazuyoshi**

Toyota-shi
Aichi-ken 471-8571 (JP)

(74) Representative: **Kuhnen & Wacker**

Patent- und Rechtsanwaltsbüro PartG mbB
Prinz-Ludwig-Straße 40A
85354 Freising (DE)

(54) **LUBRICANT COMPOSITION**

(57) The purpose of the present invention is to provide 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 present invention provides a lubricant composition 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.

EP 3 578 624 A1

Description

FIELD

5 **[0001]** The present invention relates to a lubricant composition. Specifically, the present invention provides a lubricant composition for sliding members, more specifically a lubricant composition for sliding members in internal combustion engines.

BACKGROUND

10 **[0002]** 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.

20 **[0003]** 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]

35 **[0004]**

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

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

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

SUMMARY

[TECHNICAL PROBLEM]

45 **[0005]** 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.

50 **[0006]** In view of the above, an object of the present invention 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]

[0007] 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 invention.

[0008] The present invention 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.

[0009] Further, the present invention provides lubricant compositions further having at least one characteristics of the following (a) to (h):

(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;

(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;

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

(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;

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

(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;

(g) the lubricant composition, which has a kinematic viscosity at 100°C of 9.3 mm²/s or less;

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

[0010] In the present invention, 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.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0011] The lubricant composition of the present invention can reduce a coefficient of friction between sliding surfaces. In particular, the lubricant composition of the present invention 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 invention can be suitably used as a lubricant composition particularly for use in internal combustion engines.

BRIEF DESCRIPTION OF DRAWING

[0012] [FIG. 1] FIG. 1 is a schematic view of a Block-on-Ring friction test.

DESCRIPTION OF EMBODIMENTS

[0013] The lubricant composition of the present invention will be described in detail.

Lubricant Base Oil

[0014] Any conventionally known 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 preferably, but not limited to, 1 to 6 mm²/s, more preferably 2 to 6 mm²/s, in order to obtain a lubricant composition having a low viscosity.

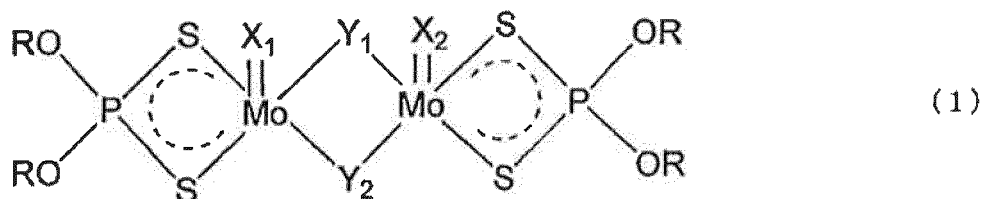
[0015] Examples of the synthetic base oils which can be used include isoparaffins, alkylbenzenes, alkylnaphthalenes, monoesters, diesters, polyol esters, polyoxyalkylene glycols, dialkyl diphenyl ethers, and polyphenyl ethers. GTL (Gas to Liquid) base oils, ATL (Asphalt to Liquid) base oils, BTL (Biomass 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 US Patent Nos. 4,594,172 and 4,943,672. The kinematic viscosities of the synthetic base oils are not particularly limited. Poly- α -olefins or α -olefin copolymers having a kinematic viscosity of less than 6 mm²/s or more than 80 mm²/s at 100°C can also be used. The kinematic viscosities of the synthetic base oils are preferably 1 to 6 mm²/s, more preferably 2 to 6 mm²/s, in order to obtain a lubricant composition having a low viscosity.

[0016] 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.

[0017] 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 mm²/s, preferably from 2 to 6 mm²/s, particularly preferably from 2.5 to 6 mm²/s.

(A) Molybdenum Dialkyldithiophosphate

[0018] The present invention is characterized in that the lubricant composition comprises molybdenum dialkyldithiophosphate (MoDTP) as an essential component. For example, MoDTP is a compound represented by following formula (1).



[0019] Conventionally known 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 conventionally and suitably 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 lubricant compositions conventionally 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 conventionally and commonly used as friction modifiers. However, as described above, a lubricant composition containing a molybdenum dithiocarbamate (MoDTC) may cause significant wear between sliding surfaces 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.

[0020] As described above, the lubricant composition of the present invention 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, preferably from 400 to 1400 ppm by weight, more preferably from 500 to 1300 ppm by weight, particularly preferably from 600 to 1200 ppm by weight, most preferably 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.

[0021] In formula (1) above, Rs are each independently a monovalent C₁₋₃₀ hydrocarbon group. The hydrocarbon group may be linear or branched. Examples of the monovalent hydrocarbon group include linear or branched C₁₋₃₀ alkyl groups; C₂₋₃₀ alkenyl groups; C₄₋₃₀ cycloalkyl groups; C₆₋₃₀ 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, C₃₋₈ alkyl groups are preferable. X₁ and X₂ are oxygen atoms or sulfur atoms, preferably oxygen atoms. Y₁ and Y₂ are oxygen atoms or sulfur atoms, preferably sulfur atoms.

[0022] The content of the above (A) MoDTP in the lubricant composition of the present invention, 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, preferably from 500 to 1200 ppm by weight, more preferably from 600 to 1100 ppm by weight, particularly preferably 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.

[0023] The lubricant composition of the present invention can comprise a conventionally known 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 required to be within the range not impairing the friction reducing effect obtained by the present invention and the wear resistance, and may be adjusted as appropriate without exceeding the content of MoDTP.

[0024] 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 preferably 100 ppm by weight or less, more preferably 70 ppm by weight or less, still more preferably 50 ppm by weight or less. The lower limit of the content is preferably, but not limited to, 1 ppm by weight or more, more preferably 5 ppm by weight or more, particularly preferably 10 ppm by weight or more. When the content of MoDTC is above the upper limit, wearing between sliding surfaces may be undesirably increased.

[0025] 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 preferably very small without impairing the effects of the present invention. 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 preferably less than 50 ppm by weight, more preferably 40 ppm by weight or less, still more preferably 20 ppm by weight or less. The lower limit is not particularly limited. For example, the content is preferably 1 ppm by weight or more, more preferably 5 ppm by weight or more, still more preferably 10 ppm by weight or more.

(A') Amide Friction Modifier and Amine Friction Modifier

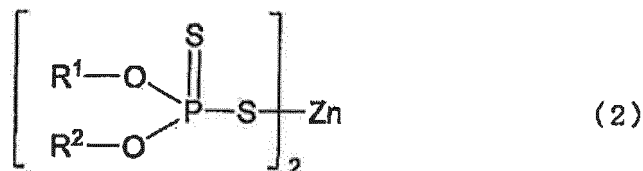
[0026] The lubricant composition of the present invention may further comprise, in addition to the above, at least one selected from the group consisting of an amide friction modifier and an amine friction modifier in less than a specific content, or may not comprise any of them at all. When the lubricant composition comprises an amide friction modifier or an amine friction modifier, the total content of them is preferably 0.1% by weight or less, more preferably 0.05% by weight or less, still more preferably 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 is not preferable, especially to DLC films doped with boron, because the coefficient of friction becomes higher and the wearing becomes larger. The contents of the amide friction modifier and the amine friction modifier is preferably as small as possible, and embodiments not comprising any of them at all are most preferable.

[0027] Any conventionally known 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, preferably 4 to 28, more preferably 6 to 25, such as methylamine, ethylamine, and propylamine; alkenyl amines having an alkenyl group with a carbon number from 2 to 30, preferably 4 to 28, more preferably 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, preferably from 4 to 28, more preferably 6 to 25, such as ethanamide and propanamide; unsaturated fatty acid amides having an alkenyl group with a carbon number from 2 to 30, preferably from 4 to 28, more preferably 6 to 25, which may be branched, such as oleamide and erucamide; and mixtures thereof.

(B) Zinc Dialkyldithiophosphate

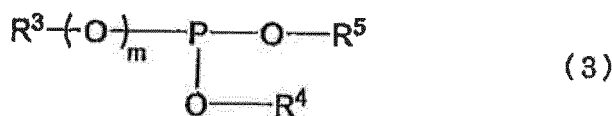
[0028] The lubricant composition of the present invention comprises a zinc dialkyldithiophosphate (ZnDTP (also referred to as ZDDP)). This compound is known as an anti-wear agent for lubricant compositions and is represented by following formula (2).



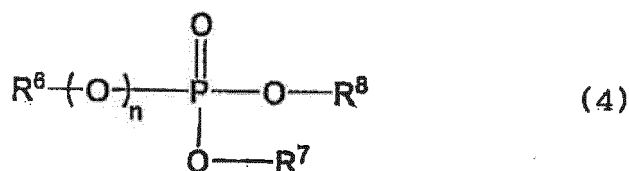
[0029] In formula (2), R¹ and R², which may be the same or different, are each a hydrogen atom or a monovalent C₁₋₂₆ hydrocarbon group. For example, the monovalent hydrocarbon group is a hydrocarbon group containing a primary or secondary C₁₋₂₆ alkyl group; a C₂₋₂₆ alkenyl group; a C₆₋₂₆ cycloalkyl group; a C₆₋₂₆ aryl, alkylaryl or arylalkyl group; and an ester linkage, an ether linkage, an alcohol group or a carboxyl group. R¹ and R² each is a primary or secondary alkyl group preferably with a carbon number from 2 to 12, a C₈₋₁₈ cycloalkyl group, or a C₈₋₁₈ alkylaryl group, and may be the same or different. In particular, zinc dialkyldithiophosphates are preferable, and the primary alkyl group preferably has a carbon number from 3 to 12, more preferably from 4 to 10. The secondary alkyl group preferably has a carbon number from 3 to 12, more preferably from 3 to 10. A zinc dithiocarbamate (ZnDTC) may also be used in combination.

[0030] 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. Preferably, the content is such that the content of phosphorus derived from the ZnDTP is from 200 to 1000 ppm by weight, preferably from 300 to 900 ppm by weight, more preferably from 350 to 850 ppm by weight, particularly preferably 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 invention 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. Embodiments essentially comprising a Sec-ZnDTP are particularly preferable, in which the content of phosphorus derived from the Sec-ZnDTP is preferably, but not limited to, from 200 to 1000 ppm by weight, more preferably from 250 to 900 ppm by weight, particularly preferably from 300 to 800 ppm by weight based on the total weight of the lubricant composition.

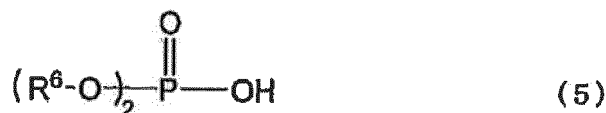
[0031] In combination with the zinc dialkyldithiophosphate, at least one compounds selected from phosphate- and phosphite-phosphorus compounds represented by following formulae (3), (4) and (5), and metal salts and amine salts thereof can also be used. However, the contents of these compounds are limited 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 preferably less than 0.1% by weight, more preferably less than 0.05% by weight, still more preferably less than 0.01% by weight, based on the total amount of the lubricant composition. Most preferably, these compounds are not contained at all.



[0032] In formula (3) above, R³ is a monovalent C₁₋₃₀ hydrocarbon group; R⁴ and R⁵ are each independently a hydrogen atom or a monovalent C₁₋₃₀ hydrocarbon group; and m is 0 or 1.



[0033] In formula (4) above, R^6 is a monovalent C_{1-30} hydrocarbon group; R^7 and R^8 are each independently a hydrogen atom or a monovalent C_{1-30} hydrocarbon group; and n is 0 or 1.



[0034] In formula (5) above, R^6 is as described above.

[0035] Examples of the monovalent C_{1-30} hydrocarbon group represented as R^3 to R^8 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_{1-30} hydrocarbon group is preferably a C_{1-30} alkyl group or a C_{6-24} aryl group, more preferably a C_{3-18} alkyl group, most preferably a C_{4-15} alkyl group.

[0036] Examples of the phosphorus compound represented by formula (3) above include phosphorous acid monoesters and (hydrocarbyl)phosphonous acids having one C_{1-30} hydrocarbon group described above; phosphorous acid diesters, monothiophosphorous acid diesters, and (hydrocarbyl)phosphonous acid monoesters having two C_{1-30} hydrocarbon group described above; phosphorous acid triesters and (hydrocarbyl)phosphonous acid diesters having three C_{1-30} hydrocarbon group described above; and combinations thereof.

[0037] As described above, the lubricant composition of the present invention essentially 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 most preferably 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.

(C) Viscosity Index Improver

[0038] 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- α -olefin copolymers (the α -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.

[0039] The molecular weight of the viscosity index improver is required to be 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, preferably from 100,000 to 900,000 for dispersion and non-dispersion polymethacrylates; usually from 800 to 5,000, preferably from 1,000 to 4,000 for polyisobutenes or hydrogenated products thereof; and usually from 800 to 500,000, preferably from 3,000 to 200,000 for ethylene- α -olefin copolymers or hydrogenated products thereof.

[0040] Among the viscosity index improvers, when an ethylene- α -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).

[0041] The content of the viscosity index improver in the lubricant composition is from 0.01 to 20% by weight, preferably from 0.02 to 10% by weight, more preferably from 0.05 to 5% by weight, based on the total weight of the composition.

(D) Ashless Dispersant

[0042] The lubricant composition of the present invention can further comprise an ashless dispersant. Any conventionally known ashless dispersants may be used without limitation. Examples of the ashless dispersant include nitrogen-

containing compounds having at least one linear or branched C₄₀₋₄₀₀ 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

[0043] The carbon number of the alkyl or alkenyl group described above is preferably 40 to 400, more preferably 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 preferable 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.

[0044] 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 invention may comprise either one or both of the mono- and bis-succinimides.

[0045] 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 combined. 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.

[0046] 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 invention, boron-modified compounds of alkenylsuccinimide compounds (boronated succinimides) are particularly preferable from the viewpoint that excellent heat resistance, anti-oxidant properties and anti-wear properties can be achieved.

[0047] 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 invention, the boron content in the ashless dispersant is preferably 0.2% by weight or more, more preferably 0.4% by weight or more, and is preferably 2.5% by weight or less, more preferably 2.3% by weight or less, still more preferably 2.0% by weight or less. The boronated ashless dispersant is preferably a boronated succinimide, particularly preferably a boronated bis-succinimide.

[0048] The boronated ashless dispersant has a weight ratio of boron to nitrogen (B/N ratio) of 0.1 or more, preferably 0.2 or more, and preferably less than 1.0, more preferably 0.8 or less.

[0049] The content of the ashless dispersant may be adjusted as appropriate and, for example, is preferably from 0.01 to 20% by weight, more preferably 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.

(E) Metal Detergent

[0050] 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.

[0051] More specifically, calcium sulfonate, magnesium sulfonate, calcium salicylate, magnesium salicylate, calcium phenate, and magnesium phenate are preferably 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 preferably, but not limited to, from 0.1 to 20% by weight, more preferably from 0.5 to 15% by weight, still more preferably from 1.0 to 15% by weight.

[0052] The metal detergent has a total base number preferably, but not limited to, from 20 to 600 mgKOH/g, more preferably from 50 to 500 mgKOH/g, still more preferably from 100 to 450 mgKOH/g, particularly preferably 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 which are required for a lubricant.

[0053] 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, more preferably from 0.1 to 4% by weight, still more preferably from 0.2 to 3% by weight.

[0054] In addition to the above, the lubricant composition of the present invention 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, preferably from 400 to 1400 ppm by weight, more preferably from 500 to 1300 ppm by weight, particularly preferably from 600 to 1200 ppm by weight, most preferably from 600 to 1000 ppm by weight, based on the total weight of the lubricant composition.

[0055] The high temperature high shear viscosity (HTHS viscosity) at 150°C of the lubricant composition of the present invention is preferably, but not limited to, from 1.4 to 2.9 mPa·s, more preferably from 1.7 to 2.6 mPa·s.

[0056] The kinematic viscosity at 100°C of the lubricant composition of the present invention is preferably, but not limited to, from 3 to 9.3 mm²/s, more preferably from 3 to 8.2 mm²/s, still more preferably from 4 to 8.2 mm²/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.

[0057] The viscosity index of the lubricant composition of the present invention is preferably, but not limited to, 120 or more, more preferably 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 preferably, but not limited to, 250.

[0058] The lubricant composition of the present invention, though being made low-viscosity, exhibits an excellent friction reducing effect, and also has an excellent wear resistance. The lubricant composition of the present invention is suitably used as an oil disposed between sliding surfaces of sliding members. The lubricant composition of the present invention also suitably functions as a lubricant for diamond-like carbon (DLC) films. In particular, the lubricant composition of the present invention 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 particularly preferable embodiments of the present invention, a diamond-like carbon (DLC) film and the lubricant composition are combined.

[0059] The diamond-like carbon (DLC) film in the present invention may be a conventionally known DLC film having an amorphous structure. The DLC film is formed on at least one sliding surface of sliding members. The DLC film is preferably doped with a predetermined element. Examples of the element include boron (B), titanium (Ti), vanadium (V), and molybdenum (Mo). Particularly preferably, the element is boron. In further preferable embodiments of the present invention, a DLC film doped with boron and the lubricant composition are combined, so that both better friction reducing effect and wear resistance are obtained.

[0060] The content of boron is preferably from 1 to 30%, more preferably 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.

[0061] The DLC film in the present invention may be a DLC not containing hydrogen, so-called hydrogen-free DLC, but a DLC containing hydrogen is preferably used because the friction reducing effect can be easily obtained. The content of hydrogen is preferably from 0 to 25%, more preferably from 5 to 25%, still more preferably from 10 to 22%, still more preferably 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.

[0062] The DLC film in the present invention 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 invention. In particular, the content is preferably less than 8 atom%, more preferably less than 4 atom%. The composition of the DLC film may be homogeneous, slightly changed, or even inclined, with respect to the thickness direction.

[0063] A substrate on which the DLC film is formed (i.e., a substrate of a sliding member) is not particularly limited. Preferably, 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 invention has a hardness preferably from 10 to 30 GPa, more preferably 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 preferably from 100 to 200 GPa, more preferably from 110 to 190 GPa, still more preferably from 120 to 180 GPa, still more preferably from 130 to 170 GPa.

[0064] The DLC film may be formed according to a conventionally 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, particularly preferably by unbalanced magnetron sputtering (UBMS). Preferably, 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.

[0065] 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 conventionally known methods.

[0066] The lubricant composition of the present invention can be applied to sliding members in a wide variety of machines. In particular, a sliding machine comprising the lubricant composition of the present invention 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 required 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 invention can be suitably used for use in internal combustion engines.

EXAMPLES

[0067] The present invention will now be described in detail by showing Examples and Comparative Examples, but is not limited thereto.

[0068] 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.

[0069] 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 μm /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 μm . 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%.

[0070] 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.

[0071] 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."

[0072] Lubricant compositions in Examples and Comparative Examples comprise the following components.

Lubricant Base Oil

[0073] a GTL-derived base oil having a kinematic viscosity at 100°C of 4.1 mm^2/s , and VI of 127

(A) Molybdenum Dialkyldithiophosphate (MoDTP)

[0074] 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 Cs hydrocarbon group

Friction Modifiers Other Than (A) Above

[0075] a molybdenum dithiocarbamate MoDTC having a molybdenum content of 10% by weight
a trinuclear Mo compound having a molybdenum content of 5.5% by weight oleylamine

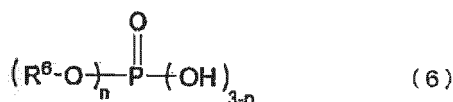
oleamide

(B) Zinc Dialkyldithiophosphate

- 5 **[0076]** a Pri-ZnDTP (a zinc dialkyldithiophosphate having a primary alkyl group)
a Sec-ZnDTP (a zinc dialkyldithiophosphate having a secondary alkyl group)

(B') Acidic Phosphate Ester

- 10 **[0077]** a mixture of compounds represented by following formula (6), wherein R⁶ is a 2-ethylhexyl group, and n is 1 or 2



(C) Metal Detergent

- 20 **[0078]** Ca salicylate having a total base number of 180 mgKOH/g, and a Ca content of 6.3% by weight
[0079] Mg sulfonate having a total base number of 400 mgKOH/g, and a Mg content of 9.4% by weight

(D) Ashless Dispersant

- 25 **[0080]** boronated succinimide having a B content of 0.7% by weight, and a N content of 2.0% by weight
non-boronated succinimide having a N content of 1.0% by weight

(E) Viscosity Index Improver

- 30 **[0081]** polymethacrylate having Mw of 300,000

(F) Other Additive Packages

[0082] Antioxidants: phenolic antioxidant and amine antioxidant
Anti-foaming agent: dimethyl silicone

35 [Examples 1 to 14 and Comparative Examples 1 to 5]

[0083] Lubricant compositions were prepared by mixing the components described above at the compositions and the contents described in the tables.

40 **[0084]** The contents shown in the tables are described below.

[0085] 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.

45 **[0086]** 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.

[0087] The contents of oleylamine, oleamide, and an acidic phosphate ester are in % by weight based on the total amount of the lubricant composition.

[0088] The contents of metal detergents are in terms of % by weight of calcium and magnesium based on the total amount of the lubricant composition.

50 **[0089]** 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.

[0090] The tables also show the total content of phosphorus in ppm by weight based on the total amount of the lubricant composition.

55 **[0091]** 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

[0092] 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

[0093] 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
balance		balance	balance	balance	balance	balance	balance	balance
Mo friction modifier	(Mo) ppm by weight	700	700	700	700	700	700	700
	(P) ppm by weight	250	250	250	250	250	250	250
ZnDTP (P content)	Primary ZnDTP	300	750	-	-	300	300	300
	Secondary ZnDTP	450	-	750	450	450	450	450
	P content total	750	750	750	450	750	750	750
metal detergent (metal element content)	% by weight	0.14	0.14	0.14	0.14	0.14	-	0.20
	% by weight	0.06	0.06	0.06	0.06	-	0.06	-
dispersant (N content/B content)	B dispersant	600/200	600/200	600/200	600/200	600/200	600/200	600/200
	non-B dispersant	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
other additives	% by weight	1	1	1	1	1	1	1
Mo content in the whole composition	ppm by weight	700	700	700	700	700	700	700
P content in the whole composition	ppm by weight	1000	750	1000	700	1000	1000	1000

(continued)

lubricant base oil		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
evaluation results	KV100	balance	balance	balance	balance	balance	balance	balance	balance
		6.5	6.5	6.5	6.7	6.5	6.5	6.2	6.6
	HTHS150	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
	minimum coefficient of friction	0.042	0.042	0.041	0.041	0.041	0.044	0.045	0.046
	wear amount	0.27	0.40	0.67	0.33	0.46	0.50	0.32	0.55
	minimum coefficient of friction	0.057	0.059	0.054	0.051	0.053	0.041	0.059	0.052
	wear amount	1.00	0.90	0.73	0.37	0.73	0.63	0.50	0.93

EP 3 578 624 A1

Table 2

			Example 9	Example 10	Example 11	Example 12	Example 13
lubricant base oil			balance	balance	balance	balance	balance
Mo friction modifier	MoDTP	(Mo) ppm by weight	700	1000	700	650	600
		(P) ppm by weight	250	360	250	230	210
	Mo-trimer	(Mo) ppm by weight	-	-	-	-	-
	MoDTC	(Mo) ppm by weight	-	-	-	50	100
ZnDTP (P content)	Primary ZnDTP	ppm by weight	300	200	300	200	200
	Secondary ZnDTP	ppm by weight	450	300	450	300	300
	P content total	ppm by weight	750	500	750	500	500
metal detergent	Ca salicylate	% by weight	-	0.14	0.14	0.14	0.14
(metal element 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 content)	non-B dispersant	ppm by weight	200/0	200/0	500/0	200/0	200/0
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

EP 3 578 624 A1

(continued)

				Example 9	Example 10	Example 11	Example 12	Example 13
lubricant base oil				balance	balance	balance	balance	balance
evaluation results	KV100		mm ² /s	6.4	6.5	6.7	6.6	6.5
	HTHS150		mPa·s	2.3	2.3	2.3	2.3	2.3
	B-DLC/ Steel	minimum coefficient of friction	-	0.047	0.045	0.046	0.046	0.048
		wear amount	μm	0.37	0.47	0.47	0.43	0.70
	Steel/ Steel	minimum coefficient of friction	-	0.061	0.049	0.061	0.053	0.051
		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	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
	balance	balance	balance	balance	balance	balance	balance	balance	balance
lubricant base oil									
	(Mo) ppm by weight		-	-	1400	350	700	700	700
	(P) ppm by weight				500	125	250	250	250
Mo friction									
modifier	(Mo) ppm by weight		-	100	-	-	-	-	-
	(Mo) ppm by weight		700	-	-	-	-	-	-
	ppm by weight	Primary ZnDTP	300	300	300	300	300	300	300
ZnDTP	ppm by weight	Secondary ZnDTP	450	450	450	450	450	450	450
(P content)	ppm by weight	P content total	750	750	750	750	750	750	750
metal detergent	% by weight	Ca salicylate	0.14	0.14	0.14	0.14	0.14	0.14	0.14
(metal element content)	% by weight	Mg sulfonate	0.06	0.06	0.06	0.06	0.06	0.06	0.06
dispersant	ppm by weight	B dispersant	600/200	600/200	600/200	600/200	600/200	600/200	600/200
(N content/B content)	ppm by weight	non-B dispersant	200/0	200/0	200/0	200/0	200/0	200/0	200/0

(continued)

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
	balance	balance	balance	balance	balance	balance	balance	balance
lubricant base oil								
viscosity index improver	1	1	1	1	1	1	1	1
oleylamine	-	-	-	-	-	0.19	0.19	-
acidic phosphate ester	-	-	-	-	-	-	0.16	-
oleamide	-	-	-	-	-	-	-	0.19
other additives	1	1	1	1	1	1	1	1
Mo content in the whole composition	700	700	100	1400	350	700	700	700
P content in the whole composition	750	750	750	1250	875	1000	1200	1000
evaluation results	KV100	mm ² /s	6.6	6.5	6.5	6.6	6.6	6.6
	HTHS150	mPa·s	2.3	2.3	2.3	2.3	2.3	2.3
	B-DLC/Steel	minimum coefficient of friction	0.055	0.051	0.052	0.047	0.099	0.054
		wear amount	0.93	1.57	0.57	0.77	0.13	0.83
	Steel/Steel	minimum coefficient of friction	0.065	0.058	0.088	-	-	-
		wear amount	0.63	0.93	0.80	-	-	-

[0094] 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.

[0095] Compared to them, as shown in Tables 1 and 2, the lubricant composition of the present invention 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

[0096] In particular, the lubricant composition of the present invention 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 invention is suitably used as a lubricant composition particularly for use in internal combustion engines.

REFERENCE SIGNS LIST

[0097]

- 1: Load
- 2: Block test piece
- 3: Ring test piece
- 4: Lubricant composition

Claims

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 the total weight of the lubricant composition.
2. The lubricant composition according to claim 1, wherein the composition 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.
3. The lubricant composition according to claim 1 or 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.
4. The lubricant composition according to any one of claims 1 to 3, for use in lubrication of diamond-like carbon (DLC) films.
5. The lubricant composition according to any one of claims 1 to 3, 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 or 5, wherein the DLC film comprises boron.

EP 3 578 624 A1

7. The lubricant composition according to any one of claims 1 to 6, wherein the 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 any one of claims 1 to 7, wherein the composition has a kinematic viscosity at 100°C of 9.3 mm²/s or less.
9. The lubricant composition according to any one of claims 1 to 8, for use in internal combustion engines.

5

10

15

20

25

30

35

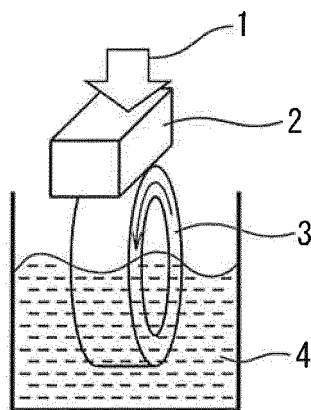
40

45

50

55

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/003468

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C10M137/10 (2006.01) i, C10M141/10 (2006.01) i, C10M133/04 (2006.01) n,
C10M133/16 (2006.01) n, C10N10/04 (2006.01) n, C10N10/12 (2006.01) n,
C10N20/02 (2006.01) n, C10N30/06 (2006.01) n, C10N40/25 (2006.01) n,
C10N80/00 (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)

Int.Cl. C10M137/10, C10M141/10, C10M133/04, C10M133/16, C10N10/04, C10N10/12,
C10N20/02, C10N30/06, C10N40/25, C10N80/00

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2018

Registered utility model specifications of Japan 1996-2018

Published registered utility model applications of Japan 1994-2018

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2002-129182 A (NIPPON MITSUBISHI OIL CORP.) 09 May 2002, claims 1-3, example 7 (Family: none)	1-3, 9 4-8
X A	JP 2000-282075 A (TONEN CORPORATION) 10 October 2000, claims 1-2, example 5 & US 6329328 B1, claims 1-2, example 5 & EP 1203805 A1	1-3, 9 4-8



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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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
25.04.2018Date of mailing of the international search report
15.05.2018

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/003468

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2000-53991 A (IDEMITSU KOSAN CO.) 22 February 2000, claims 1-2, example 8 (Family: none)	1-3, 9 4-8
X A	JP 2014-43526 A (NTN CORPORATION) 13 March 2014, claims 1-6, examples 1, 3 & US 2015/0218483 A1, claims 1-10, examples 1, 3 & WO 2014/034647 A1 & EP 2891705 A1 & KR 10-2015-0046079 A & CN 104583381 A	1-3 4-9
X A	JP 9-59662 A (ASAHI DENKA KOGYO KK) 04 March 1997, claims 1-5, examples 3, 7, 9, 11, 12, 14 & US 5858931 A, claims 1-16, table 4 & EP 761804 A1 & CA 2182916 A1	1-2, 9 3-8
X A	JP 1-48895 A (KIYOUSEKI SEIHIN GIJUTSU KENKYUSHO KK) 23 February 1989, claim 1, examples 1-3 & US 4925596 A, claims 1-4, examples 1-3 & EP 304011 A1 & CA 1295989 A1	1-2, 9 3-8
X A	JP 2013-35973 A (NTN CORPORATION) 21 February 2013, claims 1-14, examples 2, 3 (Family: none)	1-2 3-9
A	WO 2012/073717 A1 (HONDA MOTOR CO., LTD.) 07 June 2012, claim 1 & US 2013/0252860 A1, claim 1 & EP 2647738 A1 & CN 103228817 A	1-9
P, X	WO 2017/146232 A1 (IDEMITSU KOSAN CO.) 31 August 2017, claims 1-15, examples 5, 7, 10-13 & JP 2017-149830 A	1-3, 8-9

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

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2014513173 PCT [0003] [0004]
- JP 2014224239 A [0003] [0004] [0064] [0069]
- JP 2016216653 A [0003] [0004] [0005] [0094]
- US 4594172 A [0015]
- US 4943672 A [0015]
- JP S428013 B [0046]
- JP S428014 B [0046]
- JP S5152381 B [0046]
- JP S51130408 B [0046]