

DESCRIPTION

TITLE

LUBRICATING OIL COMPOSITION

5

FIELD

[0001]

10 The present invention relates to a lubricating oil composition. In particular, the present invention relates to an automobile lubricating oil composition having a reduced viscosity, which can be applied to differential gears.

BACKGROUND

[0002]

15 Lubricating oil compositions are used in a wide variety of applications including automobiles and machines. In recent years, from the standpoint of improving fuel efficiency, a reduction in viscosity is demanded in automobile lubricating oil compositions. However, a reduction in the viscosity of a lubricating oil composition affects the oil film-forming capability. Particularly in the field of automobile gear oils, more particularly in those lubricating oils used for differential gears, a reduction in the viscosity of a lubricating oil causes problems, such as
20 occurrence of wear of bearings and the like and occurrence of scoring on gear tooth surfaces, and it is thus difficult to implement a reduction in viscosity. Therefore, it is desired to develop an automobile gear oil composition, particularly a differential gear oil composition, which is capable of, even at a low viscosity, suppressing wear of bearings and the like under high-temperature conditions where formation of an oil film is difficult.

25 [0003]

The present inventors previously discovered that, by using a low-viscosity base oil and a high-viscosity base oil in combination, the viscosity of a lubricating oil can be reduced and, particularly, an improvement in the bearing fatigue life characteristics affected by the oil film-forming capability and an improvement in fuel efficiency can be achieved at the same time,
30 thereby completing the invention disclosed in Japanese Unexamined Patent Publication (Kokai) No. 2007-039480 (PLT 1). However, in the lubricating oil composition disclosed in PLT 1, there was still room for improvement in terms of inhibition of wear of bearings and the like, as well as inhibition of scoring on gear tooth surfaces and the like.

[0004]

35 Japanese Unexamined Patent Publication (Kokai) No. 2014-012855 (PLT 2) discloses a lubricating oil composition that includes: a specific acid alkyl phosphate; a dialkylamine and/or a

trialkylamine; a specific sulfur compound containing no poly-sulfur bond that is equal to or longer than -S-S-S-; and, depending on the case, a specific trihydrocarbyl thiophosphate. The lubricating oil composition disclosed in PLT 2, however, relates to a step-up gear oil composition for wind power generation, for which seizure resistance and fatigue resistance are required, and PLT2 offers no description at all with regard to scoring.

[CITATION LIST]

[PATENT LITERATURES]

[0005]

[PLT 1] Japanese Unexamined Patent Publication (Kokai) No. 2007-039480

[PLT 2] Japanese Unexamined Patent Publication (Kokai) No. 2014-012855

SUMMARY

[TECHNICAL PROBLEM]

[0006]

In view of the above, the present inventors aim at providing a lubricating oil composition that is capable of suppressing wear of bearings and the like, as well as scoring on gear tooth surfaces and the like even at a reduced viscosity.

[SOLUTION TO PROBLEM]

[0007]

The present inventors discovered that the above-described object can be achieved by incorporating a combination of a specific amount of an extreme pressure agent having a specific active sulfur content and a specific amount of a phosphorus-based extreme pressure agent into a lubricating oil composition, thereby completing the present invention.

[0008]

In other words, the present invention provides a lubricating oil composition comprising: (A) a lubricating base oil; (B) a sulfur-based extreme pressure agent; and (C) a phosphorus-based extreme pressure agent, wherein the sulfur-based extreme pressure agent (B) has an active sulfur content of 5 to 30% by weight; the sulfur-based extreme pressure agent (B) is contained in the composition in an amount of 5 to 15% by weight based on a total weight of the lubricating oil composition; and the phosphorus-based extreme pressure agent (C) is contained in the composition in an amount of 1.5 to 8% by weight based on the total weight of the lubricating oil composition.

[0009]

Preferred embodiments of the present invention include at least one of following

characteristic features (1) to (9):

(1) the sulfur-based extreme pressure agent (B) is a sulfurized olefin;

(2) the phosphorus-based extreme pressure agent (C) is at least one selected from phosphate esters, acid phosphate esters, phosphite esters, acid phosphite esters, thiophosphate esters, acid thiophosphate esters, thiophosphite esters, acid thiophosphite esters, amine salts of acid phosphate esters, amine salts of acid phosphite esters, amine salts of acid thiophosphate esters, and amine salts of acid thiophosphite esters;

(3) the phosphorus-based extreme pressure agent (C) is at least one selected from amine salts of acid phosphate esters, amine salts of acid phosphite esters, amine salts of acid thiophosphate esters, and amine salts of acid thiophosphite esters;

(4) the lubricating oil composition has a kinematic viscosity at 100°C of 3 to 40 mm²/s;

(5) the lubricating base oil (A) is at least partially a GTL (Gas to Liquid)-derived base oil;

(6) the lubricating base oil (A) is at least partially a poly- α -olefin (PAO) base oil;

(7) the lubricating base oil (A) has a kinematic viscosity at 100°C of 3 to 40 mm²/s;

(8) the lubricating oil composition is used for a transmission; and

(9) the lubricating oil composition is used for a differential gear.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0010]

The lubricating oil composition of the present invention can suppress wear of bearings and the like as well as scoring on gear tooth surfaces and the like even at a reduced viscosity. The lubricating oil composition of the present invention can be preferably used as a lubricating oil for automobiles, and is also suitable as a transmission gear oil and as a differential gear oil.

DESCRIPTION OF EMBODIMENTS

[0011]

The present invention will now be described in more detail.

[0012]

(A) Lubricating Base Oil

In the present invention, the lubricating base oil is not particularly restricted, and any conventionally known lubricating base oil can be used. The lubricating base oil may be, for example, a mineral base oil, a synthetic base oil or a mixed base oil thereof.

[0013]

A method of producing the mineral base oil is not restricted. The mineral base oil is

preferably a highly refined paraffinic mineral oil (high-viscosity-index mineral oil-based lubricating base oil) obtained by performing a treatment, such as solvent dewaxing or hydrodewaxing, on a hydrotreated oil, a catalytically isomerized oil or the like. Examples of mineral base oils other than the above-described one include raffinates obtained by solvent refining of a lubricating oil raw material with an aromatic extraction solvent, such as phenol or furfural; and hydrotreated oils obtained by hydrotreatment using a hydrotreatment catalyst, such as cobalt or molybdenum supported on a silica-alumina carrier. Examples thereof include 100 neutral oil, 150 neutral oil, and 500 neutral oil.

[0014]

Examples of the synthetic base oil include base oils (so-called GTL-derived base oils) that are obtained by hydrocracking and hydroisomerization of a raw material (e.g., a wax) obtained from a natural gas (e.g., methane) by Fischer-Tropsch synthesis; PAO base oils, polybutenes, alkylbenzenes, polyol esters, polyglycol esters, dibasic acid esters, fatty acid esters, phosphoric acid esters, and silicon oils. Thereamong, GTL-derived base oils and PAO base oils are preferred.

[0015]

The lubricating base oil may be any one of, or any combination of two or more of the above-described base oils, as long as it is selected from the above-described mineral base oils, the above-described synthetic base oils, and combinations thereof. When two or more lubricating base oils are used in combination, they may be a combination of mineral base oils, a combination of synthetic base oils, or a combination of a mineral base oil and a synthetic base oil, and the mode thereof is not restricted. In particular, a combination of a mineral base oil and a synthetic base oil is preferred.

[0016]

When a mineral base oil and a synthetic base oil are used in combination, it is appropriate to use at least one selected from GTL-derived base oils and PAO base oils as the synthetic base oil. Preferred modes of such a combination use are:

- (1) a combination of a mineral base oil and a GTL-derived base oil,
- (2) a combination of a mineral base oil and a PAO base oil,
- (3) a combination of a mineral base oil, a GTL-derived base oil and a PAO base oil, and
- (4) a combination of a GTL-derived base oil and a PAO base oil.

Thereamong, (3) a combination of a mineral base oil, a GTL-derived base oil and a PAO base oil is particularly preferred.

[0017]

The mineral base oil is not restricted to be one produced by the above-described production method; however, it is appropriate that the mineral base oil have a kinematic

viscosity at 100°C of preferably 2 to 35 mm²/s, more preferably 2 to 20 mm²/s, still more preferably 3 to 10 mm²/s.

[0018]

The GTL-derived base oil is not particularly restricted; however, it is appropriate that the GTL-derived base oil have a kinematic viscosity at 100°C of preferably 2 to 40 mm²/s, more preferably 2 to 20 mm²/s, still more preferably 2 to 10 mm²/s.

[0019]

The PAO base oil is also not particularly restricted and, for example, a 1-octene oligomer, a 1-decene oligomer, an ethylene- α -olefin oligomer, an ethylene-propylene oligomer, an isobutene oligomer, or a hydrogenated product thereof can be used. It is appropriate that the PAO base oil have a kinematic viscosity at 100°C of preferably 2 to 200 mm²/s, more preferably 2 to 150 mm²/s, still more preferably 4 to 50 mm²/s.

[0020]

The kinematic viscosity of the lubricating base oil is not restricted as long as the gist of the present invention is not impaired. In particular, in order to obtain a low-viscosity lubricating oil composition, it is appropriate that the whole lubricating base oil have a kinematic viscosity at 100°C of preferably 3 to 40 mm²/s, more preferably 4 to 20 mm²/s, still more preferably 5 to 15 mm²/s, particularly preferably 6 to 12 mm²/s. When the kinematic viscosity at 100°C of the lubricating base oil is higher than the above-described upper limit value, it is difficult to reduce the viscosity of the lubricating oil composition, and this can make it difficult to achieve an improvement in fuel efficiency. Meanwhile, when the kinematic viscosity at 100°C is less than the above-described lower limit value, an improvement in fuel efficiency can be achieved; however, it may be difficult to ensure anti-wear performance and anti-scoring performance.

[0021]

(B) Sulfur-Based Extreme Pressure Agent

The lubricating oil composition of the present invention comprises a sulfur-based extreme pressure agent as an indispensable component. The sulfur-based extreme pressure agent used in the present invention is required to have an active sulfur content of 5 to 30% by weight, and the active sulfur content is preferably 5 to 20% by weight, more preferably 5 to 15% by weight, particularly preferably 8 to 12% by weight. When the active sulfur content is higher than the above-described upper limit value, not only the sulfur-based extreme pressure agent causes metal corrosion but also it is difficult to ensure anti-wear performance. Meanwhile, when the active sulfur content is less than the above-described lower limit value, it is difficult to ensure anti-scoring performance.

[0022]

The active sulfur content is determined by the method prescribed in ASTM D1662. More

specifically, the active sulfur content based on ASTM D1662 can be determined by the following procedures.

(1) To a 200-ml beaker, 50 g of a sample and 5 g of copper powder (purity: 99% or higher, particle size: 75 μ m or smaller) are added, and these materials are heated to 150°C with stirring using a stirrer (500 rpm);

(2) Once the temperature reached 150°C, 5 g of copper powder is further added, followed by 30-minute stirring;

(3) The stirring is terminated, and a copper plate according to ASTM D130 is placed and immersed in the beaker for 10 minutes. In this process, if discoloration of the copper plate is observed, 5 g of copper powder is further added, followed by 30-minute stirring (this operation is continued until discoloration of the copper plate is no longer observed); and

(4) Once discoloration of the copper plate is no longer observed, the copper powder in the sample is removed by filtration, and the amount of sulfur contained in the resulting filtrate is measured.

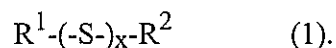
The active sulfur content (% by weight) is calculated based on “Amount (% by weight) of sulfur contained in the original sample (Procedure (1)) - Amount (% by weight) of sulfur contained in the filtrate (Procedure (4)) after the reaction with copper powder.”

[0023]

In the present invention, the sulfur-based extreme pressure agent may be any sulfur-based extreme pressure agent as long as it has the above-described specific active sulfur content, and the sulfur-based extreme pressure agent can be selected from known sulfur-based extreme pressure agents. The sulfur-based extreme pressure agent is preferably at least one selected from sulfide compounds that are represented by sulfurized olefins and sulfurized esters that are represented by sulfurized oils and fats, and the sulfur-based extreme pressure agent is particularly preferably a sulfurized olefin. It is noted here that, in the present invention, extreme pressure agents containing sulfur and phosphorus, such as thiophosphate esters, are included in the below-described phosphorus-based extreme pressure agent (C), and are thus not included in the sulfur-based extreme pressure agent (B). Further, the sulfur-based extreme pressure agent of the present invention does not encompass zinc dithiophosphate.

[0024]

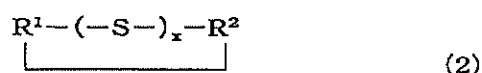
The sulfur-based extreme pressure agent used in the present invention is represented by, for example, following Formula (1):



In Formula (1), R^1 and R^2 each independently represent a monovalent substituent that contains at least one element of carbon, hydrogen, oxygen and sulfur. Specific examples thereof include saturated or unsaturated hydrocarbon groups that have 1 to 40 carbon atoms and a linear

or branched structure, and the monovalent substituent may be an aliphatic hydrocarbon group, an aromatic hydrocarbon group, or an aromatic group-containing aliphatic hydrocarbon group. An oxygen atom and/or a sulfur atom may also be contained therein. R¹ and R² are optionally bound to each other and, when R¹ and R² form a single bond, the sulfur-based extreme pressure agent is represented by, for example, following Formula (2):

[0025]



[0026]

In Formulae (1) and (2), x represents an integer of 1 or larger, preferably an integer of 1 to 12. When x is small, the extreme pressure performance is deteriorated, whereas when x is excessively large, the thermal oxidation stability tends to be reduced. In order to attain both satisfactory extreme pressure performance and satisfactory thermal oxidation stability, x is preferably an integer of 1 to 6, more preferably an integer of 2 to 5. The sulfur-based extreme pressure agent represented by Formula (1) or (2) is usually not a compound having a single x but a mixture of compounds having various numbers of sulfur atoms, and it is believed that, among such compounds, one having a specific number of sulfur atoms functions as active sulfur.

[0027]

Examples of the sulfur-based extreme pressure agent are further described below.

[0028]

Sulfurized olefins are obtained by sulfurization of olefins and generally referred to as "sulfide compounds", including those compounds that are obtained by sulfurization of hydrocarbon-based raw materials other than olefins. Examples of the sulfurized olefins include those obtained by sulfurizing olefins, such as polyisobutenes and terpenes, with sulfur or other sulfurizing agent.

[0029]

Examples of sulfide compounds other than the sulfurized olefins include diisobutyl polysulfides, dioctyl polysulfides, di-*tert*-butyl polysulfides, diisobutyl polysulfides, dihexyl polysulfides, di-*tert*-nonyl polysulfides, didecyl polysulfides, didodecyl polysulfides, diisobutene polysulfides, dioctenyl polysulfides, and dibenzyl polysulfides.

[0030]

Sulfurized oils and fats are a reaction product of an oil or a fat and sulfur, and examples of the oil or the fat include animal and vegetable oils and fats, such as lard, beef tallow, whale oil, palm oil, coconut oil, and rapeseed oil. The reaction product is not composed of a single

substance species, but is a mixture of various substances, and its chemical structure itself is not necessarily clear.

[0031]

Examples of sulfurized esters other than the above-described sulfurized oils and fats include those obtained by sulfurizing, with sulfur or other sulfurizing agent, ester compounds each generated by a reaction between an organic acid (e.g., a saturated fatty acid, an unsaturated fatty acid, a dicarboxylic acid, or an aromatic carboxylic acid) and an alcohol. The chemical structures of such sulfurized esters themselves are not necessarily clear as in the case of sulfurized oils and fats.

[0032]

In the lubricating oil composition of the present invention, the content of the sulfur-based extreme pressure agent is 5% by weight to 15% by weight, preferably 6% by weight to 12% by weight, based on the weight of the whole lubricating oil composition, and the present invention is also characterized in that the content of the sulfur-based extreme pressure agent is higher as compared to conventional lubricating oil compositions. The above-described sulfur-based extreme pressure agents may be used singly, or in combination of two or more thereof as a mixture. When the content is higher than the above-described upper limit value, not only the thermal oxidation stability is reduced and a sludge is thus more likely to be generated, but also the composition is more likely to cause metal corrosion; therefore, such a high content is not preferred. Meanwhile, a content of less than the above-described lower limit value is also not preferred since it leads to deterioration of the anti-scoring performance.

[0033]

(C) Phosphorus-Based Extreme Pressure Agent

The lubricating oil composition of the present invention contains a phosphorus-based extreme pressure agent as an indispensable component. By incorporating the below-described amount of the phosphorus-based extreme pressure agent along with the above-described sulfur-based extreme pressure agent, satisfactory anti-wear performance and anti-scoring performance can be attained in a well-balanced manner. It is noted here that, in the present invention, extreme pressure agents containing sulfur and phosphorus, such as thiophosphate esters, are included in the phosphorus-based extreme pressure agent (C), not in the sulfur-based extreme pressure agent (B). Further, the phosphorus-based extreme pressure agent of the present invention does not encompass zinc dithiophosphate.

[0034]

The phosphorus-based extreme pressure agent is not particularly restricted and may be any conventionally known phosphorus-based extreme pressure agent. It is appropriate that the phosphorus-based extreme pressure agent be, for example, at least one selected from phosphate

esters, acid phosphate esters, phosphite esters, acid phosphite esters, thiophosphate esters, acid thiophosphate esters, thiophosphite esters, acid thiophosphite esters, amine salts of acid phosphate esters, amine salts of acid phosphite esters, amine salts of acid thiophosphate esters, and amine salts of acid thiophosphite esters. The phosphorus-based extreme pressure agent is preferably at least one selected from amine salts of acid phosphate esters, amine salts of acid phosphite esters, amine salts of acid thiophosphate esters, and amine salts of acid thiophosphite esters.

[0035]

The phosphate esters and the acid phosphate esters are represented by

$(R^1O)_aP(=O)(OH)_{3-a}$, wherein a is 0, 1, 2 or 3, and R^1 each independently represents a monovalent hydrocarbon group having 1 to 30 carbon atoms. This formula represents a phosphate ester when $a = 3$, an acid phosphate ester when $a = 1$ or 2, or phosphoric acid when $a = 0$.

[0036]

The phosphite esters and the acid phosphite esters are represented by

$(R^2O)_bP(=O)(OH)_{2-b}H$, wherein b is 0, 1 or 2, and R^2 each independently represents a monovalent hydrocarbon group having 1 to 30 carbon atoms. This formula represents a phosphite ester when $b = 2$, an acid phosphite ester when $b = 1$, or phosphorous acid when $b = 0$.

[0037]

The thiophosphate esters and the acid thiophosphate esters are represented by

$(R^3X^1)(R^4X^2)(R^5X^3)P(=X^4)$, wherein R^3 , R^4 and R^5 each independently represent a hydrogen atom or a monovalent hydrocarbon group having 1 to 30 carbon atoms. This formula represents an acid thiophosphate ester when one or two of R^3 , R^4 and R^5 is/are a hydrogen atom(s), or thiophosphoric acid when all three of R^3 , R^4 and R^5 are hydrogen atoms. Further, X^1 , X^2 , X^3 and X^4 each independently represent an oxygen atom or a sulfur atom, with a proviso that at least one of X^1 , X^2 , X^3 and X^4 is a sulfur atom.

[0038]

The thiophosphite esters and the acid thiophosphite esters are represented by

$(R^6X^5)(R^7X^6)P(=X^7)H$, wherein R^6 and R^7 each independently represent a hydrogen atom or a monovalent hydrocarbon group having 1 to 30 carbon atoms. This formula represents an acid thiophosphite ester when one of R^6 and R^7 is a hydrogen atom, or thiophosphorous acid when both of R^6 and R^7 are hydrogen atoms. Further, X^5 , X^6 and X^7 each independently represent an oxygen atom or a sulfur atom, with a proviso that at least one of X^5 , X^6 and X^7 is a sulfur atom.

[0039]

The term “monovalent hydrocarbon group having 1 to 30 carbon atoms” used above specifically refers to, for example, a methyl group, an ethyl group, a propyl group, a butyl group,

a pentyl group, a hexyl group, a heptyl group, an octyl group, a decyl group, a dodecyl group, a tridecyl group, an octadecyl group, an eicosyl group, an isobutyl group, an isohexyl group, an isodecyl group, an isoctadecyl group, a neopentyl group, a 2-ethylhexyl group, or an oleyl group, preferably a monovalent hydrocarbon group having 4 to 20 carbon atoms.

5 [0040]

The phosphate esters and the acid phosphate esters are preferably, but not limited to, monoalkyl phosphates, dialkyl phosphates, and trialkyl phosphates.

[0041]

10 The phosphite esters and the acid phosphite esters are preferably, but not limited to, monoalkyl phosphites and dialkyl phosphites.

[0042]

The thiophosphate esters and the acid thiophosphate esters are preferably, but not limited to, monoalkyl thiophosphates, dialkyl thiophosphates, and trialkyl thiophosphates.

[0043]

15 The thiophosphite esters and the acid thiophosphite esters are preferably, but not limited to, monoalkyl thiophosphites and dialkyl thiophosphites.

[0044]

20 More specific examples of the phosphate esters, phosphite esters, thiophosphate esters and thiophosphite esters include, but not limited to, monooctyl phosphate, dioctyl phosphate, trioctyl phosphate, monooctyl phosphite, dioctyl phosphite, monooctyl thiophosphate, dioctyl thiophosphate, trioctyl thiophosphate, monooctyl thiophosphite, dioctyl thiophosphite, monododecyl phosphate, didodecyl phosphate, tridodecyl phosphate, monododecyl phosphite, didodecyl phosphite, monododecyl thiophosphate, didodecyl thiophosphate, tridodecyl thiophosphate, monododecyl thiophosphite, didodecyl thiophosphite, monooctadecenyl phosphate, dioctadecenyl phosphate, trioctadecenyl phosphate, monooctadecenyl phosphite, dioctadecenyl phosphite, monooctadecenyl thiophosphate, dioctadecenyl thiophosphate, trioctadecenyl thiophosphate, monooctadecenyl thiophosphite, and dioctadecenyl thiophosphite.

[0045]

30 Moreover, alkylamine salts and alkenylamine salts of the above-described compounds that are partially esterified can also be preferably used. In other words, amine salts of the above-described acid phosphate esters, amine salts of the above-described acid phosphite esters, amine salts of the above-described acid thiophosphate esters, and amine salts of the above-described acid thiophosphite esters can be used; however, the phosphorus-based extreme pressure agent is not restricted thereto.

35 [0046]

More specific examples thereof include amine salts of monooctyl phosphate, amine salts

of dioctyl phosphate, amine salts of mono-octyl phosphite, amine salts of mono-octyl thiophosphate, amine salts of dioctyl thiophosphate, amine salts of mono-octyl thiophosphite, amine salts of monododecyl phosphate, amine salts of didodecyl phosphate, amine salts of monododecyl phosphite, amine salts of monododecyl thiophosphate, amine salts of didodecyl thiophosphate, amine salts of mono-octadecenyl phosphate, amine salts of dioctadecenyl phosphate, amine salts of mono-octadecenyl phosphite, amine salts of mono-octadecenyl thiophosphate, amine salts of dioctadecenyl thiophosphate, and amine salts of mono-octadecenyl thiophosphite.

Amines of the above-described amine salts are represented by $R^8R^9R^{10}N$, wherein R^8 , R^9 and R^{10} each independently represent a hydrogen atom, or a saturated or unsaturated aliphatic, aromatic or aromatic-aliphatic hydrocarbon group that has 1 to 20 carbon atoms and a linear structure or a branched chain. More particularly, examples of R^8 , R^9 and R^{10} include a methyl group, an ethyl group, a propyl group, a butyl group, an octyl group, a nonyl group, a dodecyl group, a stearyl group, and an oleyl group.

[0047]

The above-described phosphorus-based extreme pressure agents may be used singly, or in combination of two or more thereof. When a combination of the above-described phosphorus-based extreme pressure agents is used, examples of a mode thereof include, but not limited to, the following:

(1) combinations of a thiophosphate ester amine salt and a phosphate ester amine salt, particularly an alkyl group-containing thiophosphate ester amine salt and an alkyl group-containing phosphate ester amine salt;

(2) combinations of a thiophosphate ester amine salt and a phosphate ester, particularly an alkyl group-containing thiophosphate ester amine salt and an alkyl group-containing phosphate ester;

(3) combinations of a phosphate ester amine salt and a thiophosphate ester, particularly an alkyl group-containing phosphate ester amine salt and an alkyl group-containing thiophosphate ester; and

(4) combinations of a thiophosphate ester and a phosphate ester, particularly an alkyl group-containing thiophosphate ester and an alkyl group-containing phosphate ester.

[0048]

The amount of the phosphorus-based extreme pressure agent(s) to be added is 1.5 to 8% by weight, preferably 1.8 to 7% by weight, more preferably 2 to 6% by weight, based on the total weight of the lubricating oil composition. When the amount of the phosphorus-based extreme pressure agent(s) is greater than the above-described upper limit value, the anti-scoring performance on gear tooth surfaces and the like may be deteriorated; therefore, such a large

amount is not preferred. Meanwhile, by controlling the amount to be not less than the above-described lower limit value based on the total weight of the lubricating oil composition, the phosphorus-based extreme pressure agent(s) further contribute to an improvement of the anti-wear performance. When the amount of the phosphorus-based extreme pressure agent(s) is less
5 than the lower limit value, a reaction film is not sufficiently formed, and the anti-wear performance thus deteriorates.

[0049]

The lubricating oil composition of the present invention is characterized by containing a combination of the sulfur-based extreme pressure agent (B) and the phosphorus-based extreme
10 pressure agent (C) in the above-described respective specific amounts. When the amount of at least one of components (B) and (C) is excessively small or excessively large, the anti-wear performance or the anti-scoring performance is insufficient. A total content of the sulfur-based extreme pressure agent (B) and the phosphorus-based extreme pressure agent (C) is preferably 7 to 20% by weight, more preferably 8 to 18% by weight, still more preferably 9 to 16% by
15 weight, based on the total weight of the lubricating oil composition. Further, the use ratio (weight ratio) of the sulfur-based extreme pressure agent (B) and the phosphorus-based extreme pressure agent (C), (B)/(C), is preferably 1 to 10, more preferably 1.1 to 8, still more preferably 1.2 to 7, particularly preferably 1.4 to 5.

[0050]

The lubricating oil composition of the present invention may further contain an extreme
20 pressure agent other than the sulfur-based extreme pressure agent (B) and the phosphorus-based extreme pressure agent (C), in combination with components (B) and (C). For example, zinc dithiophosphate (ZnDTP) can be used. The content of ZnDTP is preferably 0.1 to 5% by weight, more preferably 0.2 to 3% by weight, still more preferably 0.3 to 1% by weight, based on the
25 total weight of the lubricating oil composition.

[0051]

(D) Ashless Dispersant

The lubricating oil composition of the present invention may further contain an ashless
dispersant. As the ashless dispersant, any conventionally known ashless dispersant can be used,
30 and the ashless dispersant is not particularly restricted. Examples thereof include nitrogen-containing compounds having at least one linear or branched alkyl or alkenyl group having 40 to 400 carbon atoms, and derivatives thereof; and succinimides and modified products thereof. These ashless dispersants may be used singly, or in combination of two or more thereof. In addition, a boronated ashless dispersant can also be used. The boronated ashless dispersant is
35 obtained by boronation of an arbitrary ashless dispersant used in a lubricating oil. The boronation is generally performed by allowing boric acid to react with an imide compound and neutralizing

some or all of residual amino groups and/or imino groups.

[0052]

The number of carbon atoms in the above-described alkyl or alkenyl group is preferably 40 to 400, more preferably 60 to 350. When the number of carbon atoms in the alkyl or alkenyl group is less than the above-described lower limit value, the solubility of the compound in the lubricating base oil tends to be reduced. Meanwhile, when the number of carbon atoms in the alkyl or alkenyl group is greater than the above-described upper limit value, the low-temperature fluidity of the lubricating oil composition tends to be deteriorated. The alkyl or alkenyl group may have a linear structure or a branched structure. Examples of a preferred mode thereof include branched alkyl groups and branched alkenyl groups, which are derived from olefin oligomers, such as propylene, 1-butene and isobutene, and co-oligomers of ethylene and propylene.

[0053]

The above-described succinimides encompass so-called mono-type succinimides that are reaction products between one end of a polyamine and succinic anhydride, and so-called bis-type succinimides are reaction products between both ends of a polyamine and succinic anhydride. The lubricating oil composition of the present invention may contain either one of, or both of a mono-type succinimide and a bis-type succinimide.

[0054]

Examples of the above-described modification products of succinimides include succinimides modified with a boron compound (hereinafter, may be referred to as “boronated succinimides”). The phrase “modified with a boron compound” used herein means to perform boronation. The boronated succinimides may be used singly, or in combination of two or more thereof. When a combination of boronated succinimides is used, it may be a combination of two or more boronated succinimides. The combination may contain both a mono-type succinimide and a bis-type succinimide, or may be a combination of mono-type succinimides or a combination of bis-type succinimides. A combination of a boronated succinimide and a non-boronated succinimide may be used as well.

[0055]

Examples of a method of producing a boronated succinimide include the methods disclosed in Japanese Examined Patent Publication (Kokoku) No. S42-8013, Japanese Examined Patent Publication (Kokoku) No. S42-8014, Japanese Unexamined Patent Publication (Kokai) No. S51-52381, Japanese Unexamined Patent Publication (Kokai) No. S51-130408, and the like. Specifically, a boronated succinimide can be obtained by, for example, mixing an organic solvent (e.g., an alcohol, hexane, or xylene), a light lubricating base oil and the like with a polyamine, succinic anhydride (derivative) and a boron compound (e.g., boric acid, a borate

ester, or a borate salt), and heat-treating the resulting mixture under appropriate conditions. The boron content in the boronated succinimide obtained in this manner can usually be 0.1 to 4% by weight. In the present invention, a boron-modified compound of an alkenylsuccinimide (boronated succinimide) is particularly preferred because of its excellent heat resistance, anti-oxidation performance and anti-wear performance.

[0056]

The boron content in the boronated ashless dispersant is not particularly restricted, and it is usually 0.1 to 3% by weight based on the weight of the ashless dispersant. In one mode of the present invention, the boron content in the ashless dispersant is preferably not less than 0.2% by weight, more preferably not less than 0.4% by weight, but 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.

[0057]

The boronated ashless dispersant has a boron/nitrogen weight ratio (B/N ratio) of 0.1 or higher, preferably 0.2 or higher, but preferably lower than 1.0, more preferably 0.8 or lower.

[0058]

The content of the ashless dispersant in the composition may be adjusted as appropriate, and it is, for example, preferably 0.01 to 20% by weight, more preferably 0.1 to 10% by weight, based on the total weight of the lubricating oil composition. When the content of the ashless dispersant is less than the above-described lower limit value, the sludge dispersibility may be insufficient. Meanwhile, a content of higher than the above-described upper limit value may cause degradation of a specific rubber material and deteriorate the low-temperature fluidity.

[0059]

(E) Other Additives

The lubricating oil composition of the present invention may comprise, as additives other than the above-described components (A) to (D), a viscosity index improver, an antioxidant, a metallic detergent, a friction modifier, a corrosion inhibitor, a rust inhibitor, a demulsifier, a metal deactivator, an antifoaming agent, and a pour-point depressant. It is noted here, however, that the lubricating oil composition of the present invention is not a grease and thus contains no thickening agent. The thickening agent is, for example, a metallic soap or a metal salt.

[0060]

Examples of the viscosity index improver include so-called non-dispersion-type viscosity index improvers, such as polymers and copolymers of one or more monomers selected from various methacrylic acid esters, and hydrogenated products thereof; so-called dispersion-type viscosity index improvers obtained by copolymerizing various methacrylic acid esters containing

nitrogen compounds; non-dispersion-type or dispersion-type ethylene- α -olefin copolymers (examples of α -olefin include 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; and polyalkylstyrenes.

5 [0061]

The molecular weight of the viscosity index improver is required to be selected taking into consideration the shear stability of the lubricating oil composition. For example, the weight-average molecular weight of the viscosity index improve is usually 5,000 to 1,000,000, preferably 100,000 to 900,000, when a dispersion-type or non-dispersion-type polymethacrylate is used; usually 800 to 5,000, preferably 1,000 to 4,000, when a polyisobutene or a hydrogenated product thereof is used; or usually 800 to 500,000, preferably 3,000 to 200,000, when an ethylene- α -olefin copolymer or a hydrogenated product thereof is used.

[0062]

15 Among the above-described viscosity index improvers, when an ethylene- α -olefin copolymer or a hydrogenated product thereof is used, a lubricating oil composition having particularly excellent shear stability can be obtained. Any one or more compounds selected from the above-described viscosity index improvers can be incorporated in any amount.

The content of the viscosity index improver(s) in the lubricating oil composition is 0.01 to 20% by weight, preferably 0.02 to 10% by weight, more preferably 0.05 to 5% by weight, based on the total amount of the composition.

20 [0063]

The antioxidant may be any antioxidant that is generally used in lubricating oils, and examples thereof include ashless antioxidants, such as phenolic antioxidants and amine-based antioxidants, and organometallic antioxidants. By adding an antioxidant, the oxidation stability of the lubricating oil composition can be further improved.

[0064]

30 Examples the metallic detergent include those containing a compound selected from sulfonates, phenates, salicylates and carboxylates of calcium, magnesium, barium and the like, and compounds having different base numbers, such as overbased salts, basic salts and neutral salts, can be selected arbitrarily. The metallic detergent is incorporated into the lubricating oil composition usually in an amount of 0.01 to 1% by weight in terms of metal amount.

[0065]

35 Examples of the friction modifier include organic molybdenum compounds, fatty acids, fatty acid esters, alcohols, amines, and amides. The friction modifier is incorporated into the lubricating oil composition usually in an amount of 0.01 to 5% by weight.

[0066]

Examples of the corrosion inhibitor include benzotriazole-based, tolyltriazole-based, thiadiazole-based, and imidazole-based compounds. The corrosion inhibitor is incorporated into the lubricating oil composition usually in an amount of 0.1 to 5% by weight.

[0067]

5 Examples of the rust inhibitor include petroleum sulfonates, salts of an alkylsulfonic acid, fatty acids, fatty acid soaps, fatty acid amines, alkyl polyoxyalkylenes, alkenylsuccinates, and polyhydric alcohol fatty acid esters. The rust inhibitor is incorporated into the lubricating oil composition usually in an amount of 0.01 to 5% by weight.

[0068]

10 Examples of the demulsifier include polyalkylene glycol-based nonionic surfactants, such as polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, and polyoxyethylene alkylnaphthyl ethers. The demulsifier is incorporated into the lubricating oil composition usually in an amount of 0.01 to 5% by weight.

[0069]

15 Examples of the metal deactivator include pyrroles, imidazoles, pyrazoles, pyrazines, pyrimidines, pyridazines, triazines, triazoles, thiazoles, and thiadiazoles. The metal deactivator is incorporated into the lubricating oil composition usually in an amount of 0.01 to 3% by weight.

[0070]

20 Examples of the antifoaming agent include polydimethylsiloxanes and fluorinated derivatives thereof; polyacrylates and fluorinated derivatives thereof; and perfluoropolyethers. The antifoaming agent is incorporated into the lubricating oil composition usually in an amount of 0.001 to 1% by weight.

[0071]

25 As the pour-point depressant, for example, a polymethacrylate-based polymer that is compatible with the lubricating base oil to be used can be selected. The pour-point depressant is incorporated into the lubricating oil composition usually in an amount of 0.01 to 3% by weight.

[0072]

30 The kinematic viscosity at 40°C of the lubricating oil composition of the present invention is preferably 20 to 120 mm²/s, more preferably 30 to 100 mm²/s, still more preferably 40 to 80 mm²/s.

[0073]

35 The kinematic viscosity at 100°C of the lubricating oil composition of the present invention is preferably 3 to 40 mm²/s, more preferably 4 to 20 mm²/s, still more preferably 5 to 15 mm²/s, particularly preferably 6 to 12 mm²/s.

EXAMPLES

[0074]

The present invention will now be described in more detail by way of Examples and Comparative Examples thereof; however, the present invention is not restricted to the below-described Examples.

5 [0075]

The components used in Examples and Comparative Examples are as follows. Lubricating oil compositions were prepared by mixing the following components according to the respective formulations shown in Table 1 below. In the followings, “KV40”, “KV100” and “VI” mean a kinematic viscosity at 40°C, a kinematic viscosity at 100°C and a viscosity index, respectively.

10 (A) Lubricating Base Oils

- Mineral base oil 1: KV40 = 19 mm²/s, KV100 = 4 mm²/s
- Synthetic base oil 1: a GTL-derived base oil, KV100 = 8 mm²/s
- Synthetic base oil 2: an ethylene- α -olefin base oil, KV100 = 40 mm²/s

15 [0076]

(B) Sulfur-Based Extreme Pressure Agents

The below-described values of active sulfur content were each determined by a method according to ASTM D1662 and represent an amount of active sulfur in each sulfur-based extreme pressure agent.

- 20
- Sulfur-based extreme pressure agent 1: a sulfurized olefin (active sulfur content = 11% by weight)
 - Sulfur-based extreme pressure agent 2: a sulfurized olefin (active sulfur content = 32% by weight)

[0077]

25 (C) Phosphorus-Based Extreme Pressure Agents

- Phosphorus-based extreme pressure agent 1: a salt of an acid phosphate ester (having a C4 to C8 alkyl group) and an amine (having a C8 to C18 alkyl group)
- Phosphorus-based extreme pressure agent 2: a salt of an acid thiophosphate ester (having a C4 to C8 alkyl group) and an amine (having a C8 to C18 alkyl group)

30 [0078]

(D) Ashless Dispersant

- Boronated polyisobutenylsuccinimide (bisimide-type): polybutenyl group molecular weight = 1,400, boron = 1.8% by weight, nitrogen = 2.4% by weight

[0079]

35 (E) Other Additives

antifoaming agent, pour-point depressant, rust inhibitor

[0080]

[Table 1]

	(% by weight)	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
(A)	Mineral base oil 1	10.0	10.2	9.5	9.7	9.8	10.3	10.5	9.1	10.0	10.0	10.0
	Synthetic base oil 1	52.8	54.1	50.5	51.0	51.8	52.5	55.2	48.0	52.8	53.6	50.7
	Synthetic base oil 2	24.8	25.3	23.6	24.0	23.1	23.8	25.9	22.5	24.8	25.5	21.2
	Kinematic viscosity of base oil, KV100*	12	12	12	12	12	12	12	12	12	12	12
(B)	Sulfur-based extreme pressure agent 1	8.3	6.3	12.3	8.3	8.3	8.3	4.3	16.3		8.3	8.3
	Sulfur-based extreme pressure agent 2									8.3		
(C)	Phosphorus-based extreme pressure agent 1	1.8	1.8	1.8	3.6	5.8	0	1.8	1.8	1.8	0.9	5.4
	Phosphorus-based extreme pressure agent 2	1.1	1.1	1.1	2.2	0	3.9	1.1	1.1	1.1	0.5	3.2
(D)	Ashless dispersant	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Other additives	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
	Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	(B) + (C)	11.2	9.2	15.2	14.1	14.1	12.2	7.2	19.2	11.2	9.7	16.9
	(B)/(C)	2.86	2.17	4.24	1.43	1.43	2.13	1.48	5.62	2.86	5.93	0.97

*unit = mm²/s

[0081]

For each lubricating oil composition, various properties were measured in accordance with the below-described methods. The results thereof are shown in Table 2.

(1) Kinematic Viscosity at 40°C (KV40)

5 The kinematic viscosity at 40°C was measured in accordance with ASTM D445.

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

 The kinematic viscosity at 100°C was measured in accordance with ASTM D445.

(3) Viscosity Index

 The viscosity index was measured in accordance with ASTM D2270.

10 (4) Evaluation of Anti-wear Performance

 A test was conducted in accordance with ASTM D2714 under the following conditions, and the width of wear made on each tested block test piece was evaluated: oil temperature = 120°C, load = 20 lbf, rotation speed = 1,000 rpm, time = 1 hour. A wear width (mm) of 0.5 or less was regarded as satisfactory.

15 (5) Evaluation of Anti-scoring Performance

 A test was conducted using a four-ball wear tester prescribed in ASTM D4172 under the following conditions, and the rotation speed at which seizure occurred was recorded: oil temperature = room temperature, load = 100 kgf, rotation speed = increased by 100 rpm every 30 seconds. A rotation speed (rpm) of higher than 1,000 was regarded as satisfactory.

20 (6) Oxidation Stability

 A test was conducted in accordance with JIS K2514-1 under the following conditions, and the pentane-insoluble content was measured for each tested sample oil in accordance with ASTM D893 (B method): oil temperature = 135°C, time = 96 hours. A pentane-insoluble content (% by weight) of 2.4 or less was regarded as satisfactory.

[0082]

[Table 2]

Evaluation results	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Kinematic viscosity (KV40)*	74	75	71	75	70	72	74	69	71	74	75
Kinematic viscosity (KV100)*	11	12	11	11	11	11	11	11	11	11	11
Viscosity index (VI)	146	146	145	144	147	148	146	145	146	146	142
Anti-wear performance Wear width (mm)	0.37	0.38	0.39	0.40	0.37	0.33	-	-	0.63	0.79	-
Anti-scoring performance Seizure-causing rotation speed (rpm)	1,250	1,113	1,500	1,138	1,400	1,150	1,000	-	-	-	1,000
Oxidation stability Pentane-insoluble content (% by weight)	0.4	0.2	1.2	0.9	0.5	2.2	-	2.5	-	-	-

*unit = mm²/s

[0083]

As shown in Table 2, the composition of Comparative Example 1 having a low content of sulfur-based extreme pressure agent did not have sufficient anti-scoring performance. The composition of Comparative Example 2 having an excessively high content of sulfur-based extreme pressure agent exhibited poor oxidation stability. The composition of Comparative Example 3, in which a sulfur-based extreme pressure agent containing a large amount of active sulfur was used, did not have sufficient anti-wear performance. Moreover, the composition of Comparative Example 4 having a low content of phosphorus-based extreme pressure agent had a large width of wear and exhibited poor anti-wear performance. The composition of Comparative Example 5 having a high content of phosphorus-based extreme pressure agent did not have sufficient anti-scoring performance. In contrast to these, the lubricating oil compositions according to the present invention were excellent in all of anti-wear performance, anti-scoring performance, and oxidation stability.

INDUSTRIAL APPLICABILITY

[0084]

The lubricating oil composition of the present invention is capable of suppressing wear of bearings and the like as well as scoring on gear tooth surfaces and the like even at a reduced viscosity. The lubricating oil composition of the present invention can, therefore, be preferably used as a lubricating oil for automobiles, and is also suitable as a transmission gear oil and as a differential gear oil.

CLAIMS

[Claim 1]

A lubricating oil composition comprising:

(A) a lubricating base oil;

(B) a sulfur-based extreme pressure agent; and

(C) a phosphorus-based extreme pressure agent,

wherein the sulfur-based extreme pressure agent (B) has an active sulfur content of 5 to 30% by weight,

the sulfur-based extreme pressure agent (B) is contained in the composition in an amount of 5 to 15% by weight, based on a total weight of the lubricating oil composition, and

the phosphorus-based extreme pressure agent (C) is contained in the composition in an amount of 1.5 to 8% by weight, based on the total weight of the lubricating oil composition.

[Claim 2]

The lubricating oil composition according to claim 1, wherein the sulfur-based extreme pressure agent is a sulfurized olefin.

[Claim 3]

The lubricating oil composition according to claim 1 or 2, wherein the phosphorus-based extreme pressure agent (C) is at least one selected from phosphate esters, acid phosphate esters, phosphite esters, acid phosphite esters, thiophosphate esters, acid thiophosphate esters, thiophosphite esters, acid thiophosphite esters, amine salts of acid phosphate esters, amine salts of acid phosphite esters, amine salts of acid thiophosphate esters, and amine salts of acid thiophosphite esters.

[Claim 4]

The lubricating oil composition according to claim 3, wherein the phosphorus-based extreme pressure agent (C) is at least one selected from amine salts of acid phosphate esters, amine salts of acid phosphite esters, amine salts of acid thiophosphate esters, and amine salts of acid thiophosphite esters.

[Claim 5]

The lubricating oil composition according to any one of claims 1 to 4, which has a kinematic viscosity at 100°C of 3 to 40 mm²/s.

[Claim 6]

The lubricating oil composition according to any one of claims 1 to 5, wherein the lubricating base oil (A) is at least partially a GTL (Gas to Liquid)-derived based oil.

[Claim 7]

5 The lubricating oil composition according to any one of claims 1 to 6, wherein the lubricating base oil (A) is at least partially a poly- α -olefin (PAO) base oil.

[Claim 8]

10 The lubricating oil composition according to any one of claims 1 to 7, wherein the lubricating base oil (A) has a kinematic viscosity at 100°C of 3 to 40 mm²/s.

[Claim 9]

15 The lubricating oil composition according to any one of claims 1 to 8, which is used for a transmission.

[Claim 10]

 The lubricating oil composition according to any one of claims 1 to 8, which is used for a differential gear.