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## (54) LUBRICATING OIL COMPOSITION

(57) Provided is a lubricating oil composition containing (A) 70 mass% or more and 95 mass% or less of a poly- $\alpha$ -olefin base oil, (B) 5 mass% or more and 20 mass% or less of an ester-based base oil, and (C) an ester-based defoaming agent, the poly- $\alpha$ -olefin base oil

(A) being a polymer of an  $\alpha$ -olefin having 8 to 12 carbon atoms. The lubricating oil composition is able to keep excellent defoaming performance over a long period of time and is suitable as a step-up gear oil composition for wind power generation.

#### Description

#### **TECHNICAL FIELD**

[0001] The present invention relates to a lubricating oil composition, and particularly to a lubricating oil composition which is suitable as a step-up gear oil composition for wind power generation.

#### **BACKGROUND ART**

10 [0002] Wind power generation, making use of renewable energy, is expected to increase in demand, from the viewpoints of reduction of the environment load and the conservation of fossil fuel which have been argued in recent years.

[0003] In wind power generation employing wind force, kinetic energy of wind is transformed into power by means of rotors including propellers which are rotated by wind. By means of the generated power, a power generator is operated to produce electric energy.

[0004] In the wind power generation, a step-up gear is employed to elevate the rotation rate of rotors, which is relatively slow, so as to improve power generation efficiency of the power generator. Actually, a variety of step-up gears are known in the art, and of those, a planetary gear-type power transmission apparatus is widely employed.

[0005] A step-up gear oil composition for wind power generation which is used for such a planetary gear-type power transmission apparatus or the like is required to be maintenance-free and operable over a long period of time.

[0006] As the lubricating oil composition which is used for a step-up gear for wind power generation, PTL 1 discloses those containing a poly- $\alpha$ -olefin and a polyol ester in the working examples.

CITATION LIST

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25 PATENT LITERATURE

[0007] PTL 1: WO 2008/038701 A1

SUMMARY OF INVENTION

#### **TECHNICAL PROBLEM**

[0008] However, as a result of extensive and intensive investigations made by the present inventor, it has been found that if a lubricating oil composition containing a poly-α-olefin and an ester-based base oil is used for an application of a step-up gear oil for wind power generation, there is a concern that seizure attributable to foaming is generated. Furthermore, it has been found that even in the case where a defoaming agent is added for the purpose of inhibiting the foaming, the defoaming performance is significantly deteriorated during a long-term operation depending upon the kind of a

[0009] Under such circumstances, an object of the present invention is to provide a lubricating oil composition which is able to keep excellent defoaming performance over a long period of time and which is suitable as a step-up gear oil composition for wind power generation.

#### SOLUTION TO PROBLEM

45 [0010] In order to develop a lubricating oil composition having the aforementioned excellent performances, the present inventor made extensive and intensive investigations. As a result, it has been found that the aforementioned problem can be solved by a combination of (A) a poly-α-olefin base oil, (B) an ester-based base oil, and (C) an ester-based defoaming agent. The present invention has been accomplished on the basis of such finding.

[0011] Specifically, the present invention provides the following.

- [1] A lubricating oil composition containing (A) 70 mass% or more and 95 mass% or less of a poly-α-olefin base oil,
- (B) 5 mass% or more and 20 mass% or less of an ester-based base oil, and (C) an ester-based defoaming agent, the poly- $\alpha$ -olefin base oil (A) being a polymer of an  $\alpha$ -olefin having 8 to 12 carbon atoms.
- [2] The lubricating oil composition as described in [1] above, wherein a sum total of the poly- $\alpha$ -olefin base oil (A) and the ester-based base oil (B) is 90 mass% or more on the basis of the total amount of the composition.
- [3] The lubricating oil composition as described in [1] or [2] above, wherein the ester-based defoaming agent (C) is composed of a (meth)acrylate polymer having a weight average molecular weight of 10,000 or more and 100,000 or less.

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- [4] The lubricating oil composition as described in any of [1] to [3] above, wherein the poly- $\alpha$ -olefin base oil (A) is a decene oligomer.
- [5] The lubricating oil composition as described in any of [1] to [4] above, wherein the ester-based base oil (B) is a polyol ester.
- [6] The lubricating oil composition as described in any of [1] to [5] above, which is a step-up gear oil composition for wind power generation.

#### ADVANTAGEOUS EFFECTS OF INVENTION

[0012] According to the present invention, it is possible to provide a lubricating oil composition which is able to keep excellent defoaming performance over a long period of time and which is suitable as a step-up gear oil composition for wind power generation.

#### **DESCRIPTION OF EMBODIMENTS**

**[0013]** The lubricating oil composition of the present invention contains (A) 70 mass% or more and 95 mass% or less of a poly- $\alpha$ -olefin base oil, (B) 5 mass% or more and 20 mass% or less of an ester-based base oil, and (C) an ester-based defoaming agent.

20 [(A) Poly-α-olefin base oil]

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[0014] The poly- $\alpha$ -olefin base oil (A) is a polymer obtained by using one or more  $\alpha$ -olefins having 8 to 12 carbon atoms. [0015] The poly- $\alpha$ -olefin base oil (A) is suitably one having a kinematic viscosity at 40°C in the range of 30 mm²/s or more and 800 mm²/s or less and a viscosity index of 80 or more. When the kinematic viscosity at 40°C is 30 mm²/s or more, an evaporation loss is small, whereas when it is 800 mm²/s or less, a power loss caused by viscous resistance does not excessively increase. The kinematic viscosity at 40°C is more preferably 32 mm²/s or more and 680 mm²/s or less, and especially preferably 100 mm²/s or more and 500 mm²/s or less. When the viscosity index is 80 or more, a variation in viscosity caused by a temperature variation is small. This viscosity index is more preferably 100 or more, and still more preferably 130 or more.

30 **[0016]** The poly-α-olefin base oil (A) preferably has a pour point of -25°C or lower. When the pour point is -25°C or lower, the lubricating oil composition of the present invention containing the same has sufficient fluidity even in a low-temperature environment. The pour point of the poly-α-olefin base oil (A) is more preferably -30°C or lower, and still more preferably -40°C or lower.

**[0017]** It is to be noted that the aforementioned kinematic viscosity and viscosity index are values as measured in accordance with JIS K2283, and the pour point is a value as measured in accordance with JIS K2265.

**[0018]** A content of the poly- $\alpha$ -olefin base oil (A) in the lubricating oil composition of the present invention is 70 mass% or more and 95 mass% or less, preferably 75 mass% or more and 95 mass% or less, and more preferably 80 mass% or more and 92 mass% or less on the basis of the total amount of the composition. When the content of the poly- $\alpha$ -olefin base oil (A) is less than 70 mass%, high anti-seizure performance and anti-fatigue performance which are required for the step-up gear oil for wind power generation are not obtained, and defoaming property becomes insufficient, whereas when it is more than 95 mass%, a content of the ester-based base oil (B) becomes insufficient.

[(B) Ester-based base oil]

[0019] As the ester-based base oil (B), a polyol ester is preferably used. Though the polyol ester may be either a partial ester of a polyol or a complete ester of a polyol, the use of a partial ester of a polyol is preferred from the viewpoint of sludge solubility.

**[0020]** Though the polyol serving as a raw material of the polyol ester is not particularly limited, it is preferably an aliphatic polyol. Examples of the polyol may include dihydric alcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, trimethylene glycol, tetramethylene glycol, neopentyl glycol, etc.; trihydric alcohols, such as glycerin, trimethylolethane, trimethylolpropane, etc.; and tetrahydric or polyhydric alcohols, such as diglycerin, triglycerin, pentaerythritol, dipentaerythritol, mannite, sorbit, etc.

**[0021]** The hydrocarbyl group constituting the polyol ester is preferably an alkyl group or an alkenyl group each having 6 to 30 carbon atoms, and more preferably an alkyl group or an alkenyl group each having 12 to 24 carbon atoms. Examples thereof may include various hexyl groups, octyl groups, decyl groups, dodecyl groups, tetradecyl groups, hexadecyl groups, hexadecyl groups, octadecyl groups, hexadecenyl groups, tetradecenyl groups, hexadecenyl groups, octadecenyl groups, and the like.

[0022] The alkyl group or alkenyl group may be linear or branched.

**[0023]** Specific examples of the complete ester of polyol may include, but are not limited to, neopentyl glycol dilaurate, neopentyl glycol dimyristate, neopentyl glycol dipalmitate, neopentyl glycol distearate, neopentyl glycol diisostearate, trimethylolpropane trilaurate, trimethylolpropane trimyristate, trimethylolpropane tripalmitate, trimethylolpropane trisearate, trimethylolpropane triisostearate, glycerin trilaurate, glycerin tristearate, glycerin triisostearate, and the like.

[0024] The partial ester of polyol is not particularly limited so long as at least one hydroxyl group remains.

**[0025]** Specific examples of the partial ester of polyol may include, but are not limited to, neopentyl glycol monolaurate, neopentyl glycol monomyristate, neopentyl glycol monopalmitate, neopentyl glycol monostearate, neopentyl glycol monostearate, trimethylolpropane mono- or dilaurate, trimethylolpropane mono- or dimyristate, trimethylolpropane mono- or disostearate, glycerin mono- or dilaurate, glycerin mono- or disostearate, and the like.

**[0026]** The polyol ester is preferably one represented by the following general formula (B-1) from the viewpoints of foaming prevention property and the like.

**[0027]** In the formula, R<sup>1</sup> is a hydrocarbon group having 6 to 30 carbon atoms; n is an integer of 2 to 4; and L is an n-valent hydrocarbon group.

**[0028]** R<sup>1</sup> is preferably an alkyl group or an alkenyl group each having 12 to 24 carbon atoms. n is preferably 3 or 4.

[0029] L is preferably an n-valent hydrocarbon group having 3 to 10 carbon atoms.

**[0030]** In the lubricating oil composition of the present invention, the polyol ester may be used singly or in combination of two or more thereof as the ester-based base oil (B). A blending amount thereof is 5 mass% or more and 20 mass% or less, and preferably 7 mass% or more and 15 mass% or less on the basis of the total amount of the composition. When the content of the ester-based base oil is less than 5 mass%, the sludge solubility becomes insufficient, and the solubility of an additive becomes insufficient.

**[0031]** In the lubricating oil composition of the present invention, a sum total of the poly- $\alpha$ -olefin base oil (A) and the ester-based base oil (B) is preferably 90 mass% or more, more preferably 92 mass% or more and 99 mass% or less, and still more preferably 93 mass% or more and 98 mass% or less on the basis of the total amount of the composition.

30 [Other base oil]

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**[0032]** The lubricating oil composition of the present invention may contain other base oil than the aforementioned poly- $\alpha$ -olefin base oil (A) and ester-based base oil (B), and its content is preferably less than 25 mass%, more preferably 15 mass% or less, and still more preferably 10 mass% or less on the basis of the total amount of the composition.

**[0033]** The other base oil is not particularly limited with respect to its kind, and either a mineral oil or a synthetic oil may be used. A variety of conventional mineral oils may be used, and examples thereof include paraffin base mineral oils, intermediate mineral oils, naphthene base mineral oils, and the like. Specific examples thereof include solvent-refined or hydrogenated light neutral oils, medium neutral oils, heavy neutral oils, and bright stocks, and the like.

**[0034]** A variety of conventional synthetic oils may be used. For example, polybutene, phosphate esters, polyphenyl ethers, alkylbenzenes, alkylnaphthalenes, polyoxyalkylene glycols, neopentyl glycol, silicone oil, trimethylolpropane, pentaerythritol, hindered esters, and the like may be used. These base oils may be used singly or in combination of two or more thereof, and a mineral oil and a synthetic oil may be used in combination.

[(C) Ester-based defoaming agent]

[0035] The ester-based defoaming agent (C) is preferably one composed of a (meth)acrylate polymer. It is to be noted that in the present specification, the term "(meth)acrylate" means that all of "acrylate" and "methacrylate" are included. [0036] The (meth)acrylate polymer is preferably one having a weight average molecular weight of 10,000 or more and 100,000 or less, and more preferably one having a weight average molecular weight of 20,000 or more and 80,000 or less.

[(D) Sulfur compound]

[0037] The lubricating oil composition of the present invention may further contain (D) a sulfur compound.

**[0038]** Specific examples of the sulfur compound include (d-1) a sulfur compound containing no poly-sulfur bond which is equal to or longer than -S-S-S- in a molecule thereof and having an S content within the molecule of 15 mass% or more and (d-2) a thiophosphoric acid trihydrocarbyl ester represented by the following general formula (l).

[0039] In the formula, R represents a hydrocarbyl group having 6 to 20 carbon atoms.

[0040] Examples of the sulfur compound serving as the component (d-1) may include the following compounds.

- (1) Olefin mono- or disulfide
- (2) Dihydrocarbyl mono- or disulfide
- (3) Thiadiazole compound
- (4) Dithiocarbamate compound
- (5) Ester compound having a disulfide structure
- (6) Other sulfur compound

[Olefin mono- or disulfide]

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[0041] Examples of the olefin mono- or disulfide may include compounds represented by the following general formula (III) and the like.

$$R^1-S_a-R,^2...$$
 (III)

**[0042]** In the formula, R<sup>1</sup> represents an alkenyl group having 2 to 15 carbon atoms; R<sup>2</sup> represents an alkyl group or an alkenyl group each having 2 to 15 carbon atoms; and a represents 1 or 2.

**[0043]** Such a compound is obtained through a reaction between an olefin having 2 to 15 carbon atoms or a dimer to tetramer thereof and a sulfidizing agent, such as sulfur, sulfur chloride, etc., and the olefin is preferably propylene, isobutene, diisobutene, or the like.

<sup>25</sup> [Dihydrocarbyl mono- or disulfide]

[0044] Examples of the dihydrocarbyl mono- or disulfide include compounds represented by the following general formula (IV).

$$R^3-S_b-R,^4...$$
 (IV)

**[0045]** In the formula, R<sup>3</sup> and R<sup>4</sup>, which may be identical to or different from each other, each represent an alkyl group or a cyclic alkyl group each having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, an alkylaryl group having 7 to 20 carbon atoms, or an arylalkyl group having 7 to 20 carbon atoms; and b is 1 or 2.

**[0046]** Here, when R<sup>3</sup> and R<sup>4</sup> are each an alkyl group, the compound represented by the foregoing general formula (IV) is called an alkyl sulfide.

**[0047]** Preferred examples of the dihydrocarbyl mono- or disulfide represented by the foregoing general formula (IV) may include dibenzyl mono- or disulfide, various dinonyl mono- or disulfides, various didodecyl mono- or disulfides, various dibutyl mono- or disulfides, various dioctyl mono- or disulfide, dicyclohexyl mono- or disulfide, and the like.

[Thiadiazole compound]

**[0048]** Preferred examples of the thiadiazole compound may include 2,5-bis(n-hexyldithio)-1,3,4-thiadiazole, 2,5-bis(n-nonyldithio)-1,3,4-thiadiazole, 2,5-bis(n-nonyldithio)-1,5-bis(n-nonyldithio)-1,5-bis(n-nonyldithio)-1,5-bis(n-nonyldithio)-1,5-bis(n-nonyldithio)-1,5-bis(n-nonyl

2,5-bis(1,1,3,3-tetramethylbutyldithio)-1,3,4-thiadiazole,

3,5-bis(n-hexyldithio)-1,2,4-thiadiazole, 3,6-bis(n-octyldithio)-1,2,4-thiadiazole, 3,5-bis(n-nonyldithio)-1,2,4-thiadiazole, 3,5-bis(1,1,3,3-tetramethylbutyldithio)-1,2,4-thiadiazole,

4,5-bis(n-octyldithio)-1,2,3-thiadiazole, 4,5-bis(n-nonyldithio)-1,2,3-thiadiazole, 4,5-bis(1,1,3,3-tetramethylbutyldithio)-1,2,3-thiadiazole, and the like.

[Dithiocarbamate compound]

[0049] Examples of the dithiocarbamate compound include alkylene bisdialkyldithiocarbamates. Of those, dithiocarbamate compounds having an alkylene group having 1 to 3 carbon atoms, a linear or branched, saturated or unsaturated alkyl group having 3 to 20 carbon atoms, or a cyclic alkyl group having 6 to 20 carbon atoms are preferably used. Specific examples of such dithiocarbamate compounds include methylene bisdibutyldithiocarbamate, methylene bisdioctyldithiocarbamate, methylene bistridecyldithiocarbamate, and the like.

[Ester compound having a disulfide structure]

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[0050] As the ester compound having a disulfide structure, a disulfide compound represented by the general formula (V) and a disulfide compound represented by the general formula (VI) are suitably used.

(VI)

**[0051]** In the foregoing general formula (V), each of  $R^5$  and  $R^6$  independently represents a hydrocarbyl group having 1 to 30 carbon atoms, preferably a hydrocarbyl group having 1 to 20 carbon atoms, more preferably a hydrocarbyl group having 2 to 18 carbon atoms, and especially preferably a hydrocarbyl group having 3 to 18 carbon atoms. The hydrocarbyl group may be linear, branched, or cyclic and may contain an oxygen atom, a sulfur atom, or a nitrogen atom. Though  $R^5$  and  $R^6$  may be identical to or different from each other,  $R^5$  and  $R^6$  are preferably identical to each other from the standpoint of production.

**[0052]** Each of  $A^1$  and  $A^2$  is independently a group represented by  $CR^7R^8$  or  $CR^7R^8$ - $CR^9R^{10}$ , wherein each of  $R^7$  to  $R^{10}$  is independently a hydrogen atom or a hydrocarbyl group having 1 to 20 carbon atoms. The hydrocarbyl group is preferably a hydrocarbyl group having 1 to 12 carbon atoms, and more preferably a hydrocarbyl group having 1 to 8 carbon atoms. Though  $A^1$  and  $A^2$  may be identical to or different from each other,  $A^1$  and  $A^2$  are preferably identical to each other from the standpoint of production.

**[0053]** Meanwhile, in the general formula (VI), each of R<sup>11</sup>, R<sup>12</sup>, R<sup>16</sup>, and R<sup>17</sup> is independently a hydrocarbyl group having 1 to 30 carbon atoms, preferably a hydrocarbyl group having 1 to 20 carbon atoms, more preferably a hydrocarbyl group having 2 to 18 carbon atoms, and especially preferably a hydrocarbyl group having 3 to 18 carbon atoms. The hydrocarbyl group may be linear, branched, or cyclic and may contain an oxygen atom, a sulfur atom, or a nitrogen atom. Though R<sup>11</sup>, R<sup>12</sup>, R<sup>16</sup>, and R<sup>17</sup> may be identical to or different from each other, R<sup>11</sup>, R<sup>12</sup>, R<sup>16</sup>, and R<sup>17</sup> are preferably identical to each other from the standpoint of production.

**[0054]** Each of  $R^{13}$  to  $R^{15}$  and  $R^{18}$  to  $R^{20}$  is independently a hydrogen atom or a hydrocarbyl group having 1 to 5 carbon atoms. Each of  $R^{13}$  to  $R^{15}$  and  $R^{18}$  to  $R^{20}$  is preferably a hydrogen atom from the standpoint of easiness of availability of raw materials.

[0055] Specific examples of the disulfide compound represented by the foregoing general formula (V) may include bis(methoxycarbonylmethyl) disulfide, bis(ethoxycarbonylmethyl) disulfide, bis(n-propoxycarbonylmethyl) disulfide, bis(isopropoxycarbonylmethyl) disulfide, 1,1-bis(1-methoxycarbonylethyl) disulfide, 1,1-bis(1-methoxycarbonylethyl) disulfide, 1,1-bis(1-methoxycarbonylen-butyl) disulfide, 1,1-bis(1-methoxycarbonylen-butyl) disulfide, 1,1-bis(1-methoxycarbonylen-butyl) disulfide, 2,2-bis(2-methoxycarbonylen-propyl) disulfide,  $\alpha$ ,  $\alpha$ -bis( $\alpha$ -methoxycarbonylbenzyl) disulfide, 1,1-bis(2-methoxycarbonylethyl) disulfide, 1,1-bis(2-ethoxycarbonylethyl) disulfide, 1,1-bis(2-ethoxycarbonylethyl) disulfide, 1,1-bis(2-methoxycarbonylethyl) disulfide, 1,1-bis(2-methoxycarbonylethyl) disulfide, 1,1-bis(2-methoxycarbonylethyl) disulfide, 1,1-bis(2-methoxycarbonylethyl) disulfide, 2,2-bis(3-methoxycarbonylethyl) disulfide, 2,2-bis(3-methoxycarbonylethyl)

[0056] Specific examples of the disulfide compound represented by the foregoing general formula (VI) may include tetramethyl dithiomalate, tetra-thyl dithiomalate, tetra-1-propyl dithiomalate, tetra-2-propyl dithiomalate, tetra-1-butyl dithiomalate, tetra-2-butyl dithiomalate, tetra-1-hexyl dithiomalate, tetra-1-octyl dithiomalate, tetra-1-cyl dithiomalate, tetra-1-decyl dithiomalate, tetra-1-decyl dithiomalate, tetra-1-decyl dithiomalate, tetra-1-decyl dithiomalate, tetra-1-cotadecyl dithiomalate, tetra-1-cyl dithiomalate, tetra-1-cyl dithiomalate, tetra-1-(2-methoxy)ethyl dithiomalate, tetra-1-(2-ethoxy)ethyl dithiomalate, tetra-1-(2-butoxy-butoxy)ethyl dithiomalate, tetra-1-(2-phenoxy)ethyl dithiomalate, and the like.

[Other sulfur compound]

**[0057]** Examples of the other sulfur compound may include sulfidized fats and oils, such as sulfidized lard, sulfidized rape seed oil, sulfidized castor oil, sulfidized soy bean oil, sulfidized rice bran oil, etc.; sulfidized fatty acids, such as thioglycolic acid, oleic acid sulfide, etc.; dialkyl thiodipropionate compounds, such as dilauryl thiodipropionate, distearyl thiodipropionate, dimyristyl thiodipropionate, etc.; a thioterpene compound formed through a reaction between phosphorus pentasulfide and pinene; and the like.

**[0058]** In the lubricating oil composition of the present invention, the aforementioned sulfur compounds may be used singly or in combination of two or more thereof as the sulfur compound serving as the component (d-1). As for a blending amount of this component (d-1), the sulfur compound is contained in an amount of preferably 0.2 mass% or more and

0.6 mass% or less, and more preferably 0.3 mass% or more and 0.5 mass% or less in terms of a sulfur atom on the basis of the total amount of the lubricating oil composition. When this sulfur atom content is 0.2 mass% or more, the anti-seizure performance is improved. On the other hand, when it is 0.6 mass% or less, not only the anti-fatigue performance is improved, but also the generation of sludge is inhibited.

[0059] If desired, the lubricating oil composition of the present invention may contain a thiophosphoric acid trihydro-carbyl ester represented by the general formula (I) as the component (d-2).

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[0060] In the general formula (I), R represents a hydrocarbyl group having 6 to 20 carbon atoms. Examples of this hydrocarbyl group include a linear, branched, or cyclic alkyl group or alkenyl group having 6 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, and an aralkyl group having 7 to 20 carbon atoms. In the aryl group and aralkyl group, one or more alkyl groups may be introduced onto the aromatic ring. Three R-O- groups may be identical to or different from each other.

**[0061]** Examples of the alkyl group and the alkenyl group each having 6 to 20 carbon atoms include various hexyl groups, various octyl groups, various decyl groups, various dodecyl groups, various tetradecyl groups, various hexadecyl groups, various octadecyl groups, a cyclohexyl group, various hexenyl groups, various octenyl groups, various dodecenyl groups, various tetradecenyl groups, various hexadecenyl groups, various octadecenyl groups, a cyclohexenyl group, and the like.

**[0062]** Examples of the aryl group having 6 to 20 carbon atoms include a phenyl group, a tolyl group, a xylyl group, a decylphenyl group, a 2,4-didecylphenyl group, a naphthyl group, and the like. Examples of the aralkyl group having 7 to 20 carbon atoms include a benzyl group, a phenethyl group, a naphthylmethyl group, a methylphenethyl group, a methylnaphthylmethyl group, and the like.

[0063] Specific examples of the thiophosphoric acid trihydrocarbyl ester represented by the foregoing general formula (I) include trihexyl thiophosphate, tri-2-ethylhexyl thiophosphate, tris(decyl) thiophosphate, trilauryl thiophosphate, trimyristyl thiophosphate, tripalmityl thiophosphate, tristearyl thiophosphate, trioleyl thiophosphate, tricresyl thiophosphate, trixylyl thiophosphate, tris(decylphenyl) thiophosphate, tris[2,4-isoalkyl( $C_9$ ,  $C_{10}$ )phenyl] thiophosphate, and the like. These thiophosphoric acid trihydrocarbyl phosphates may be used singly or in combination of two or more thereof.

[0064] In the lubricating oil composition of the present invention, the thiophosphoric acid trihydrocarbyl ester serving as the component (d-2) is optionally added for the purpose of further enhancing the addition effect of the sulfur compound serving as the component (d-1). Its addition amount is preferably in the range of 0.1 mass% or more and 1.0 mass% or less, and more preferably 0.2 mass% or more and 0.5 mass% or less on the basis of the total amount of the lubricating oil composition. A content of the whole of the sulfur atoms in the lubricating oil composition is preferably 150 ppm by mass or more and 500 ppm by mass or less.

[(E) Acidic phosphate ester amine salt]

[0065] It is preferred that the lubricating oil composition of the present invention further contains (E) an acidic phosphate ester amine salt.

[0066] As the acidic phosphate ester amine salt (E), a compound obtained by allowing (e-1) an acidic alkyl phosphate ester in which an alkyl group thereof has 6 to 20 carbon atoms and (e-2) a dialkylamine and/or a trialkylamine to react with each other in advance may be blended. By blending such a compound in the lubricating oil composition of the present invention, the acidic phosphate ester amine salt (E) may also be contained.

[(e-1) Acidic alkyl phosphate ester]

[0067] As the acidic alkyl phosphate ester (e-1), a compound represented by the following general formula (II) is preferred.

H-O  

$$X^1$$
-O  
 $X^2$ -O

P=O

...(II)

**[0068]** In the general formula (II),  $X^1$  represents a hydrogen atom or an alkyl group having 6 to 20 carbon atoms; and  $X^2$  represents an alkyl group having 6 to 20 carbon atoms.

[0069] The alkyl group having 6 to 20 carbon atoms may be linear, branched, or cyclic. Examples thereof include

various hexyl groups, octyl groups, decyl groups, dodecyl groups, tetradecyl groups, hexadecyl groups, octadecyl groups, eicosyl groups, and the like. Of those, alkyl groups having 10 to 18 carbon atoms are preferred.

**[0070]** Examples of the acidic alkyl phosphate ester represented by the foregoing general formula (II) may include acidic phosphate monoesters, such as monooctyl acid phosphate, monodecyl acid phosphate, monoisodecyl acid phosphate, monolauryl acid phosphate, monoyl acid phosphate, monopalmityl acid phosphate, monostearyl acid phosphate, etc.; and acidic phosphate diesters, such as dioctyl acid phosphate, didecyl acid phosphate, dilauryl acid phosphate, di(tridecyl) acid phosphate, dipalmityl acid phosphate, distearyl acid phosphate, etc.

**[0071]** In the present invention, the aforementioned acidic phosphate ester serving as the component (e-1) may be used singly or in combination of two or more thereof. A blending amount thereof is preferably 150 ppm by mass or more and 500 ppm by mass or less in terms of a content of the whole of the phosphorus atom in the lubricating oil composition. When the content of the phosphorus atoms is 150 ppm by mass or more, the anti-seizure performance is improved, whereas when it is 500 ppm by mass or less, the anti-fatigue performance is improved. The content of the phosphorus atom is more preferably 250 ppm by mass or more and 450 ppm by mass or less, and still more preferably 350 ppm by mass or more and 400 ppm by mass or less.

[(e-2) Dialkylamine and/or trialkylamine]

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[0072] The dialkylamine and/or the trialkylamine which is used as the component (e-2) is preferably one in which an alkyl group thereof has 6 to 20 carbon atoms.

**[0073]** Examples of the dialkylamine may include dihexylamine, dicyclohexylamine, dioctylamine, dilaurylamine, distearylamine, and the like. Examples of the trialkylamine may include trihexylamine, tricyclohexylamine, trioctylamine, trilaurylamine, tristearylamine, and the like.

**[0074]** In the lubricating oil composition of the present invention, the aforementioned dialkylamine and/or trialkylamine serving as the component (e-2) may be used singly or in combination of two or more thereof. Of those, trialkylamines are preferred from the standpoint of performances. In the case of using a monoalkylamine, the anti-seizure performance is impaired.

**[0075]** In the lubricating oil composition of the present invention, so long as the object of the present invention is not impaired, various additives, for example, at least one selected from an ashless detergent-dispersant, an antioxidant, a rust inhibitor, a metal deactivator, a pour point depressant, and the like, may be blended, if desired.

**[0076]** Examples of the ashless detergent-dispersant include succinimides, boron-containing succinimides, benzylamines, boron-containing benzylamines, succinate esters, amides of a mono- or divalent carboxylic acid represented by a fatty acid or succinic acid, and the like.

[0077] An amine-based antioxidant, a phenol-based antioxidant, or a sulfur-containing antioxidant, all of which are conventionally used in lubricating oils, may be used as the antioxidant. These antioxidants may be used singly or in combination of two or more thereof. Examples of the amine-based antioxidant include monoalkyldiphenylamine-based compounds, such as monooctyldiphenylamine, monononyldiphenylamine, etc.; dialkyldiphenylamine-based compounds, such as 4,4'-dibutyldiphenylamine, 4,4'-dipentyldiphenylamine, 4,4'-dihexyldiphenylamine, 4,4'-dihexyldiphenylamine-based compounds, such as tetrabutyldiphenylamine, tetrahexyldiphenylamine, tetraoctyldiphenylamine, tetranonyldiphenylamine, etc.; and naphthylamine-based compounds, such as  $\alpha$ -naphthylamine, phenyl- $\alpha$ -naphthylamine, butylphenyl- $\alpha$ -naphthylamine, pentylphenyl- $\alpha$ -naphthylamine, hexylphenyl- $\alpha$ -naphthylamine, octylphenyl- $\alpha$ -naphthylamine, nonylphenyl- $\alpha$ -naphthylamine, etc.

**[0078]** Examples of the phenol-based antioxidant include monophenol-based compounds, such as 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, etc.; and diphenol-based compounds, such as 4,4'-methylenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), etc.

**[0079]** Examples of the sulfur-based antioxidant include 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino)phenol; thioterpene-based compounds, such as a reaction product between phosphorus pentasulfide and pinene; dialkyl thiodipropionates, such as dilauryl thiodipropionate, distearyl thiodipropionate, etc.; and the like.

**[0080]** Examples of the rust inhibitor may include metal-based sulfonates, succinic acid esters, and the like, and examples of the metal deactivator may include benzotriazole, thiadiazole, and the like.

**[0081]** As the pour point depressant, polymethacrylates having a weight average molecular weight of about 50,000 or more and 150,000 or less and the like may be used.

**[0082]** The lubricating oil composition of the present invention is excellent in anti-seizure performance and anti-fatigue performance (e.g., FZG micropitting resistance, etc.) and is reduced in the formation of sludge in an oxidation test. Thus, the lubricating oil composition of the present invention can be used as various lubricating oils, for example, gear oil, bearing oil, or the like, and in particular, it is suitable as a lubricating oil for use in a planetary gear-type power transmission

apparatus in a wind power generator or the like.

#### **EXAMPLES**

5 [0083] The present invention is hereunder described in more detail by reference to the following Examples, but it should be construed that the present invention is not limited at all by these Examples.

**[0084]** Properties of the base oils employed in the respective Examples and various properties of the lubricating oil compositions obtained in the respective Examples were determined in accordance with the following methods.

- 10 <Properties of base oil>
  - (1) Kinematic viscosity and viscosity index

[0085] Determined in accordance with JIS K2283.

(2) Foaming test

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[0086] 300 mL of the lubricating oil composition was taken into a test tube for turbine oil oxidation stability test as prescribed in JIS K2839, and the volume of foams in a state where air was brown at a rate of 3 L/h via a diffuser as prescribed in JIS K2518 was measured.

[0087] A kind of each of the components used in the preparation of the lubricating oil composition is as follows.

- (A) Poly-α-olefin base oil 1 (PAO base oil 1): Decene oligomer, kinematic viscosity at 40°C = 390 mm<sup>2</sup>/s, viscosity index = 149, pour point = -50°C or lower Poly-α-olefin base oil 2 (PAO base oil 2): Decene oligomer, kinematic viscosity at 40°C = 46 mm<sup>2</sup>/s, viscosity index = 137, pour point = -50°C or lower
- Thickener 1: Ethylene-propylene oligomer, weight average molecular weight (Mw) = 14,400
- Thickener 2: Polybutene
- Thickener 3: Hydrogenated petroleum resin
- (B) Ester-based base oil: Ester of trimethylolpropane and isostearic acid (molar ratio: 1/2)
- (C) Ester-based defoaming agent: Defoaming agent component = 30 to 40 mass% (weight average molecular weight = 50,000), mineral oil = 60 to 70 mass%
  - Silicone-based defoaming agent: Refractive index at 20°C = 1.405, flash point (COC) = 370°C
     (D) Sulfur compound
  - (d-1) Sulfur compound: Methylene bis(dibutyldithiocarbamate)
  - (d-2) Sulfur compound: Tris(isoalkylphenol) thiophosphate ("IRGALUBE 211", available from BASF SE) (E) Acidic phosphate ester amine salt
  - (e-1) Acidic alkyl phosphate ester: Acidic (mono, di)isodecyl phosphate ester (mixing molar ratio of monoester to diester = 1/1)
  - (e-2) Amine: Tri-n-octylamine

Example 1 and Comparative Examples 1 to 4

[0088] Lubricating oil compositions having a blending composition shown in Table 1 were prepared, and foaming characteristics of the compositions were determined. The results are shown in Table 1.

Table 1

Example Comparative Example 1 2 3 4 Blending composition (mass%) (A) PAO base oil 1 86.29 86.29 67.29 PAO base oil 2 61.29 61.29 Thickener 1 15.00 15.00 Thickener 2 19.00 Thickener 3 10.00 10.00

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#### (continued)

	Example	Comparative Example			
	1	1	2	3	4
(B) Ester-based base oil	10.00	10.00	10.00	10.00	10.00
(C) Ester-based defoaming agent	0.01			0.01	
Silicone-based defoaming agent		0.01	0.01		0.01
(d-1) Sulfur compound	1.65	1.65	1.65	1.65	1.65
(d-2) Sulfur compound	0.40	0.40	0.40	0.40	0.40
(e-1) Acidic alkyl phosphate ester	0.22	0.22	0.22	0.22	0.22
(e-2) Amine	0.36	0.36	0.36	0.36	0.36
Foaming test					
Before filtration with Millipore filter					
After continuous foaming for 1 hour (mL)	20	20	20	20	20
After continuous foaming for 10 hours (mL)	20	70	250<	120	250<
After filtration with Millipore filter	_				
After continuous foaming for 1 hour (mL)	20	70	250<	20	250<
After continuous foaming for 10 hours (mL)	20	170	250<	120	250<

#### INDUSTRIAL APPLICABILITY

**[0089]** The lubricating oil composition of the present invention is able to keep excellent defoaming performance over a long period of time, and hence, it is especially suitable as a lubricating oil used for a step-up gear of a planetary geartype power transmission apparatus or the like to be used in a wind power generator.

# Claims

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- 1. A lubricating oil composition comprising (A) 70 mass% or more and 95 mass% or less of a poly-α-olefin base oil, (B) 5 mass% or more and 20 mass% or less of an ester-based base oil, and (C) an ester-based defoaming agent, the poly-α-olefin base oil (A) being a polymer of an α-olefin having 8 to 12 carbon atoms.
- **2.** The lubricating oil composition according to claim 1, wherein a sum total of the poly-α-olefin base oil (A) and the ester-based base oil (B) is 90 mass% or more on the basis of the total amount of the composition.
  - 3. The lubricating oil composition according to claim 1 or 2, wherein the ester-based defoaming agent (C) is composed of a (meth)acrylate polymer having a weight average molecular weight of 10,000 or more and 100,000 or less.
  - **4.** The lubricating oil composition according to any of claims 1 to 3, wherein the poly- $\alpha$ -olefin base oil (A) is a decene oligomer.
  - 5. The lubricating oil composition according to any of claims 1 to 4, wherein the ester-based base oil (B) is a polyol ester.
  - **6.** The lubricating oil composition according to any of claims 1 to 5, which is a step-up gear oil composition for wind power generation.

International application No.

INTERNATIONAL SEARCH REPORT

#### PCT/JP2014/078993 A. CLASSIFICATION OF SUBJECT MATTER 5 C10M169/04(2006.01)i, C10M105/32(2006.01)n, C10M105/38(2006.01)n, C10M107/10(2006.01)n, C10M145/14(2006.01)n, C10N20/04(2006.01)n, C10N30/18(2006.01)n, C10N40/04(2006.01)n According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) 10 C10M101/00-177/00, C10N10/00-80/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2015 15 Kokai Jitsuyo Shinan Koho 1971-2015 Toroku Jitsuyo Shinan Koho 1994-2015 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 20 DOCUMENTS CONSIDERED TO BE RELEVANT Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. WO 2011/142345 A1 (Mitsui Chemicals, Inc.), 1-2,4-6 Χ 17 November 2011 (17.11.2011), 3 Α claims; paragraphs [0139], [0171]; examples 25 & US 2012/0135903 A1 & EP 2570472 A1 & CN 102858929 A Α JP 08-183985 A (Tonen Corp.), 1-6 16 July 1996 (16.07.1996), (Family: none) 30 WO 2010/084966 A1 (Idemitsu Kosan Co., Ltd.), 29 July 2010 (29.07.2010), 1-6 Α & US 2011/0275867 A1 & EP 2383328 A1 & CN 102292421 A 35 × Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents: 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 "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 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 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other 45 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 special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the document member of the same patent family priority date claimed Date of the actual completion of the international search Date of mailing of the international search report 50 27 January 2015 (27.01.15) 20 January 2015 (20.01.15) Name and mailing address of the ISA/ Authorized officer Japan Patent Office 55 Telephone No. Facsimile No

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# INTERNATIONAL SEARCH REPORT International application No. PCT/JP2014/078993

5	C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT						
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10	P,X P,A	JP 2013-256561 A (Idemitsu Kosan Co., Ltd.), 26 December 2013 (26.12.2013), claims; paragraphs [0065], [0073]; examples 4 to 11, 13 (Family: none)	1-2,5-6 3-4				
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