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(54) LUBRICATING OIL COMPOSITION

(57) The lubricating oil composition contains a base oil; (A) an acidic alkyl phosphate ester having a C6 to C20 alkyl group; (B) a dialkylamine and/or a trialkylamine; and (C) (c-1) a sulfur compound in an amount of 0.2 to 0.6 mass% as reduced to S, the 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 of the molecule of 15 mass% or more and (c-2) an optional thiophosphoric acid trihydrocarbyl ester in an amount of 0.1 to 1.0 mass%, the ester being represented by formula (I):

$$(R\text{-}O\text{-})_3P{=}S \qquad \text{(I)}$$

(wherein R represents a C6 to C20 hydrocarbyl group) and having a P content of the composition of 150 to 500 ppm by mass

The lubricating oil composition has excellent anti-seizure performance, excellent anti-fatigue performance (e.g., anti-FZG-micropitting performance), and reduced sludge formation in an oxidation test.

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Description

[Technical Field]

[0001] The present invention relates to a lubricating oil composition and, more particularly, to a lubricating oil composition which exhibits excellent anti-seizure performance, excellent anti-fatigue performance, and reduced sludge formation in an oxidation test, and which is particularly suitable for use with a step-up gear for wind power generation.

[Background Art]

[0002] Wind power generation, making use of renewable energy, is expected to increase in demand, as it will reduce the environment load and contribute to the conservation of fossil fuel, which have become important issues in recent years. 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.
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 among them, a planetary gear-type power transmission apparatus is widely employed.
In such apparatus (e.g., planetary gear-type power transmission apparatus) as employed in wind power generation, a step-up gear oil composition is used and is required to exhibit excellent anti-seizure performance and anti-fatigue performance, such as anti-FZG-micropitting performance, and to ensure minimization in amount of formed sludge in an oxidation test.
There has been proposed a lubricating oil composition for use in a step-up gear used in a wind power generator, which composition contains (a) an extreme pressure compound including a sulfur compound, (b) a mixture of a hydrocarbylamine compound and an alkyl phosphorothioate compound, (c) a friction-controlling compound, and (d) a base oil (see, for example, Patent Document 1).
However, the proposed lubricating oil composition is not thought to exhibit completely satisfactory performance required for step-up gear oil compositions for wind power generation.
[0003]

[Patent Document 1]
Japanese Patent Application Laid-Open (*kokai*) No. 2005-126709

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0004] Under such circumstances, an object of the present invention is to provide a lubricating oil composition which has excellent anti-seizure performance, anti-fatigue performance, and reduced sludge formation in an oxidation test, and which is suitably used with a step-up gear for wind power generation.

[Means for Solving the Problems]

[0005] The present inventor has carried out extensive studies for the development of a lubricating oil composition which is excellent in the aforementioned characteristics, and has found that the object can be attained by a lubricating oil composition containing a base oil and a specific acidic alkyl phosphate ester, a specific alkylamine, and a specific sulfur compound, in combination, and having a specific P/S ratio. The present invention has been accomplished on the basis of this finding.
Accordingly, the present invention provides the following.

[1] A lubricating oil composition characterized by comprising: a base oil; (A) an acidic alkyl phosphate ester having a C6 to C20 alkyl group; (B) a dialkylamine and/or a trialkylamine; and (C) (c-1) a sulfur compound in an amount of 0.2 to 0.6 mass% as reduced to S, the 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 of the molecule of 15 mass% or more and (c-2) an optional thiophosphoric acid trihydrocarbyl ester in an amount of 0.1 to 1.0 mass%, the ester being represented by formula (I):

$$(R\text{-}O\text{-})_3P{=}S \qquad (I)$$

(wherein R represents a C6 to C20 hydrocarbyl group) and having a P content of the composition of 150 to 500 ppm by mass.

[2] A lubricating oil composition as described in [1] above, which contains component (B) in such an amount that the ratio by mass of P contained in component (A) to N contained in component (B) is adjusted to 1.7 to 2.1.

[3] A lubricating oil composition as described in [1] or [2] above, wherein component (B) is a trialkylamine having a C6 to C20 alkyl group.

[4] A lubricating oil composition as described in any of [1] to [3] above, which further contains (D) a polyol partial ester in an amount of 5 to 20 mass%.

[5] A lubricating oil composition as described in any of [1] to [4] above, which is used as a step-up gear oil composition for wind power generation.

[Effects of the Invention]

[0006] The present invention can provide a lubricating oil composition which has excellent anti-seizure performance, excellent anti-fatigue performance (e.g., anti-FZG-micropitting performance), and reduced sludge formation in an oxidation test, and which is suitably used with a step-up gear for wind power generation.

[Best Modes for Carrying Out the Invention]

[0007] The lubricating oil composition of the present invention is characterized by comprising: a base oil; (A) an acidic alkyl phosphate ester having a C6 to C20 alkyl group; (B) a dialkylamine and/or a trialkylamine; and (C) (c-1) a sulfur compound in an amount of 0.2 to 0.6 mass% as reduced to S, the sulfur compound containing no poly-sulfur bond which is equal to or longer than -S-S-S- in a molecule thereof and having a S content of the molecule of 15 mass% or more and (c-2) an optional thiophosphoric acid trihydrocarbyl ester in an amount of 0.1 to 1.0 mass%, the ester being represented by formula (z):

$$(R\text{-}O\text{-})_3P{=}S \qquad (I)$$

(wherein R represents a C6 to C20 hydrocarbyl group) and having a P content of the composition of 150 to 500 ppm by mass.

The base oil employed in the lubricating oil composition of the present invention preferably has a kinematic viscosity as determined at 40°C of 30 to 800 mm^2/s and a viscosity index of 80 or higher. When the kinematic viscosity (40°C) is 30 mm^2/s or higher, evaporation loss is small, whereas when it is 800 mm^2/s or lower, power loss due to viscous resistance does not excessively increase. The kinematic viscosity (40°C) is more preferably 32 to 680 mm^2/s, particularly preferably 100 to 500 mm^2/s. When the viscosity index is 80 or higher, variation in viscosity to temperature variation is small. The viscosity index is more preferably 100 or higher, still more preferably 130 or higher.

The pour point is preferably -25°C or lower. When the pour point is -25°C or lower, the produced lubricating oil composition can possess sufficient fluidity event at low temperature. The pour point is more preferably -30°C or lower, still more preferably -40°C or lower.

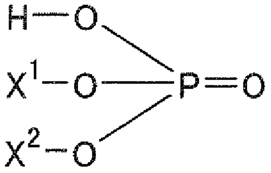
The aforementioned kinematic viscosity and viscosity index are determined in accordance with JIS K 2283, and the pour point is determined in accordance with JIS K 2265.

[0008] No particular limitation is imposed on the type of the base oil, and either mineral oil or synthetic oil may be used. A variety of conventional mineral oils may be employed. Examples of the mineral oil include paraffin-base mineral oil, intermediate mineral oil, and naphthene-base mineral oil. Specific examples include solvent-refined or hydrogenated light neutral oil, medium neutral oil, heavy neutral oil, and bright stock.

Also, a variety of conventional synthetic oils may be employed. Examples of the synthetic oil include poly-α-olefin, polybutene, polyol ester, dibasic acid esters, phosphate esters, polyphenyl ethers, alkylbenzenes, alkylnaphthalenes, polyoxyalkylene glycols, neopentyl glycol, silicone oil, trimethylolpropane, pentaerytheritol, and hindered esters. These base oils may be used singly or in combination of two or more species, and mineral oil and synthetic oil may be used in combination.

[0009] In the lubricating oil composition of the present invention, the C6 to C20 acidic alkyl phosphate ester serving as component (A) may be a compound represented by formula (I):

[0010]



···(II)

[0011] (wherein X^1 represents a hydrogen atom or a C6 to C20 alkyl group, and X^2 represents a C6 to C20 alkyl group). The C6 to C20 alkyl group may be linear, branched, or cyclic. Examples of the alkyl group include hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, and icosyl. Of these, C10 to C18 alkyl groups are preferred.

Examples of the acidic alkyl phosphate ester represented by formula (II) include acidic phosphate monoesters such as monooctyl acid phosphate, monodecyl acid phosphate, monoisodecyl acid phosphate, monolauryl acid phosphate, mono (tridecyl) acid phosphate, monomyristyl acid phosphate, monopalmityl acid phosphate, monostearyl acid phosphate; and acidic phosphate diesters such as dioctyl acid phosphate, didecyl acid phosphate, diisodecyl acid phosphate, dilauryl acid phosphate, di(tridecyl) acid phosphate, dipalmityl acid phosphate, and distearyl acid phosphate.

[0012] In the present invention, the aforementioned acidic alkyl phosphate esters serving as component (A) may be used singly or in combination of two or more species. The amount(s) of the phosphate ester(s) as reduced to P is (are) 150 to 500 ppm by mass with respect to the amount of lubricating oil composition. When the P content of the composition is less than 150 ppm by mass, anti-seizure performance is insufficient, whereas when the P content is in excess of 500 ppm by mass, anti-fatigue performance (anti-FZG-micropitting performance) decreases. The P content is preferably 250 to 450 ppm by mass, more preferably 350 to 400 ppm by mass.

The anti-seizure performance and anti-fatigue performance are assessed through the following test methods.

<Anti-seizure performance>

(1) FZG seizure test

[0013] The test is performed in accordance with ASTM D 5182-91, at 90°C and 1,450 rpm for 15 minutes. The score is represented by a load stage at which scuffing occurs.

(2) Timken test

[0014] The test is performed in accordance with ASTM D 2782, at 800 rpm for 10 minutes. The score is represented by the maximum load (lbs) at which no seizure occurs.

<Anti-fatigue performance>

(3) FZG micropitting test

[0015] The test is performed through the same procedure as employed in the aforementioned FZG seizure test, except that the score is represented by a load stage at which micropitting occurs.

[0016] In the lubricating oil composition of the present invention, the dialkylamine and/or trialkylamine serving as component (B) preferably has a C6 to C20 alkyl group.

Examples of the dialkylamine include dihexylamine, dicyclohexylamine, dioctylamine, dilaurylamine, and distearylamine. Examples of the trialkylamine include trihexylamine, tricyclohexylamine, trioctylamine, trilaurylamine, and tristearylamine. In the lubricating oil composition the present invention, the aforementioned dialkylamines and/or trialkylamines serving as component (B) may be used singly or in combination of two or more species. Of these, trialkylamines are preferred from the viewpoint of performance. When a monoalkylamine is employed, anti-seizure performance is impaired.

Component (B) is preferably incorporated into the composition in such an amount that the ratio by mass of P contained in component (A) to N contained in component (B) is adjusted to 1.7 to 2.1. When the mass ratio is 1.7 or higher, good anti-seizure performance is attained, whereas when the mass ratio is 2.1 or less, sludge formation in an oxidation test is prevented.

[0017] In the lubricating oil composition of the present invention, as sulfur compounds serving as component (C), (c-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 of the molecule of 15 mass% or more and (c-2) an optional thiophosphoric acid trihydrocarbyl ester represented by formula (I):

$(R\text{-}O\text{-})_3P{=}S \qquad \text{(I)}$

(wherein R represents a C6 to C20 hydrocarbyl group) is employed.
When the sulfur compound serving as component (c-1) has a poly-sulfur bond which is equal to or longer than -S-S-S-, a large amount of sludge forms in the Indiana oxidation test, and anti-FZG-micropitting performance decreases. When the S content of the molecule is less than 15 mass%, the effect of the sulfur compound commensurate with the amount of addition cannot be attained, and in some cases, anti-seizure performance is poor.
Examples of the sulfur compound serving as component (c-1) and having the aforementioned properties include the following compounds:

(1) olefin mono- or disulfides,
(2) dihydrocarbyl mono- or disulfides,
(3) thiadiazole compounds,
(4) dithiocarbamate compounds,
(5) ester compounds having a disulfide structure, and
(6) other sulfur compounds.

[Olefin mono- or disulfide]

[0018] Examples of the olefin sulfide include compounds represented by formula (III):

$R^1\text{-}S_a\text{-}R^2 \qquad \text{(I)}$

(wherein R^1 represents a C2 to C15 alkenyl group, R^2 represents a C2 to C15 alkyl group or alkenyl group, and a is 1 or 2). These compounds are produced through reaction between a C2 to C15 olefin or a dimer to tetramer thereof and a sulfidizing agent such as sulfur or sulfur chloride. Examples of preferred olefins include propylene, isobutene, and diisobutene.

[Dihydrocarbyl mono- or disulfide]

[0019] Examples of the dihydrocarbyl mono- or disulfide include compounds represented by formula (IV):

$R^3\text{-}S_b\text{-}R^4 \qquad \text{(IV)}$

(wherein R^3 and R^4, which may be identical to or different from each other, each represent a C1 to C20 alkyl group, a cycloalkyl group, a C6 to C20 aryl group, a C7 to C20 alkylaryl group, or a C7 to C20 arylalkyl group, and b is 1 or 2). When R^3 and R^4 are alkyl groups, these compounds are called alkyl sulfide.
Examples of preferred dihydrocarbyl mono- or disulfides represented by formula (IV) include dibenzyl mono- or disulfide, various dinonyl mono- or disulfides, various didodecyl mono- or disulfides, various dibutyl mono- or disulfides, various dioctyl mono- or disulfides, various diphenyl mono- or disulfide, and various dicyclohexyl mono-or disulfide.

[Thiadiazole compound]

[0020] Examples of preferred thiadiazole compounds include 2,5-bis(n-hexyldithio)-1,3,4-thiadiazole, 2,5-bis(n-octyldithio)-1,3,4-thiadiazole, 2,5-bis(n-nonyldithio)-1,3,4-thiadiazole, 2,5-bis(1,1,3,3-tetramethylbutyldithio)-1,3,4-thiadiazole, 3,5-bis(n-hexyldithioy)-1,2,4-thiadiazole, 3,6-bis(n-octyldithio)-1,2,4-thiadiazole, 3,5-bis(n-noyldithio)-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, and 4,5-bis(1,1,3,3-tetramethylbutyldithio)-1,2,3-thiadiazole.

[Dithiocarbamate compound]

[0021] Examples of the dithiocarbamate compound include alkylene bisdialkyldithiocarbamates. Among them, those having a C1 to C3 alkylene group, a C3 to C20 linear or branched, saturated or unsaturated alkyl group, or a C6 to C20 cycloalkyl group are preferably employed. Specific examples of such dithiocarbamate compounds include methylene bisdibutyldithiocarbamate, methylene bis dioctyldithiocarbamate, and methylene bistridecyldithiocarbamate.

[Ester compound having a disulfide structure]

[0022] Examples of the ester compound having a disulfide structure employed include disulfide compounds represented by formula (V):

$$R^5OOC\text{-}A^1\text{-}S\text{-}S\text{-}A^2\text{-}COOR^6 \qquad (V)$$

and disulfide compounds represented by formula (vet):

$$R^{11}OOC\text{-}CR^{13}R^{14}\text{-}CR^{15}(COOR^{12})\text{-}S\text{-}S\text{-}R^{20}(COOR^{17})\text{-}CR^{18}R^{19}\text{-}COOR^{16} \qquad (VI).$$

In formula (V), each of R^5 and R^6 represents a C1 to C30 hydrocarbyl group (preferably a C1 to C20, more preferably a C2 to C18, particularly preferably a C3 to C18 hydrocarbyl group). The hydrocarbyl group may be linear, branched, or cyclic, and may contain an oxygen atom, a sulfur atom, or a nitrogen atom. R^5 and R^6 may be identical to or different from each other. From the viewpoint of production of the above compounds, the two groups are preferably identical to each other.

Each of A^1 and A^2 represents CR^7R^8 or $CR^7R^8\text{-}CR^9R^{10}$, wherein each of R^7 to R^{10} represents a hydrogen atom or a C1 to C20 hydrocarbyl group. The hydrocarbyl group is preferably a C1 to C12 hydrocarbyl group, more preferably a C1 to C8 hydrocarbyl group. A^1 and A^2 may be identical to or different from each other. From the viewpoint of production of the above compounds, the two groups are preferably identical to each other.

[0023] In formula (VI), each of R^{11}, R^{12}, R^{16}, and R^{17} represents a C1 to C30 hydrocarbyl group (preferably a C1 to C20, more preferably a C2 to C18, particularly preferably a C3 to C18 hydrocarbyl group). The hydrocarbyl group may be linear, branched, or cyclic, and may contain an oxygen atom, a sulfur atom, or a nitrogen atom. R^{11}, R^{12}, R^{16}, and R^{17} may be identical to or different from one another. From the viewpoint of production of the above compounds, these groups are preferably identical to one another.

Each of R^{13} to R^{15} and R^{18} to R^{20} represents a hydrogen atom or a C1 to C5 hydrocarbyl group. For the reason of availability, these groups are preferably hydrogen atoms.

[0024] Specific examples of the disulfide compound represented by formula (V) include bas (methoxycarbonylmethyl) disulfide, bis(ethoxycarbonylmethyl) disulfide, bis(n-propoxycarbonylmethyl) disulfide, bis(isopropoxycarbonylmethyl) disulfide, bis(cyclopropoxycarbonylmethyl) disulfide, 1,1-bis(1-methoxycarbonylethyl) disulfide, 1,1-bis(1-methoxycarbonyl-n-propyl) disulfide, 1,1-bis(1-methoxycarbonyl-n-butyl) disulfide, 1,1-bis(1-methoxycarbonyl-n-hexyl) disulfide, 1,1-bis(1-methoxycarbonyl-n-octyl) disulfide, 2,2-bis(2-methoxycarbonyl-n-propyl) disulfide, α,α-bis(α-methoxycarbonylbenzyl) disulfide, 1,1-bis(2-methoxycarbonylethyl) disulfide, 1,1-bis(2-ethoxycarbonylethyl) disulfide, 1,1-bis(2-n-propoxycarbonylethyl) disulfide, 1,1-bis(2-isopropoxycarbonylethyl) disulfide, 1,1-bis(2-cyclopropoxycarbonylethyl) disulfide, 1,1-bis(2-methoxycarbonyl-n-propyl) disulfide, 1,1-bins(2-methoxycarbonyl-n-butyl) disulfide, 1,1-bis(2-methoxycarbonyl-n-hexyl) disulfide, 1,1-bis(2-methoxycarbonyl-n-propyl) disulfide, 2,2-bis(3-methoxycarbonyl-n-pentyl) disulfide, and 1,1-bis(2-methoxycarbonyl-1-phenylethyl) disulfide.

[0025] Specific examples of the disulfide compound represented by formula (VI) include tetramethyl dithiomalate, tetraethyl dithiomalate, tetra-1-propyl dithiomalate, tetra-2-propyl dithiomalate, tetra-1-butyl dithiomalate, tetra-2-butyl dithiomalate, tetraisobutyl dithiomalate, tetra-1-hexyl dithiomalate, tetra-1-octyl dithiomalate, tetra-1-(2-ethyl)hexyl dithiomalate, tetra-1-(3,5,5-trimethyl)hexyl dithiomalate, tetra-1-decyl dithiomalate, tetra-1-dodecyl dithiomalate, tetra-1-hexadecyl dithiomalate, terra-1-octadecyl dithiomalate, tetrabenzyl dithiomalate, tetra-α-(methyl)benzyl dithiomalate, tetra α,α-dimethylbenzyl dithiomalate, tetra-1-(2-methoxy)ethyl dithiomalate, tetra-1-(2-ethoxy)ethyl dithiomalate, tetra-1-(2-butoxy)ethyl dithiomalate, tetra-1-(2-ethoxy)ethyl dithiomalate, tetra-1-(2-butoxy-butoxy)ethyl dithiomalate, and tetra-1-(2-phenoxy)ethyl dithiomalate.

[Other sulfur compounds]

[0026] Other sulfur compounds include sulfidized fats and oils such as sulfidized lard, sulfidized rape seed oil, sulfidized castor oil, sulfidized soy bean oil, and sulfidized rice bran oil; sulfidized fatty acids such as thioglycolic acid and thiooleic acid; dialkyl thiodipropionate compounds such as dilauryl thiodipropionate, distearyl thiodipropionate, and dimyristyl thiodipropionate; and a thioterpene compound formed through reaction between phosphorus pentasulfide and pinene.

In the lubricating oil composition of the present invention, the aforementioned sulfur compounds serving as component (c-1) may be used singly or in combination of two or more species. The component (c-1) is required to be incorporated into the lubricating oil composition in an amount of composition 0.2 to 0.6 mass% as reduced to S. When the S content is less than 0.2 mass%, anti-seizure performance is unsatisfactory, whereas when the S content is in excess of 0.6 mass%, anti-fatigue performance such as FZG micropitting resistance is impaired, and a large amount of sludge is generated in the Indiana oxidation test. Thus, the S content is preferably 0.3 to 0.5 mass%.

The Indiana oxidation test is carried out through the following procedure.

<Indiana oxidation test>

[0027] The test is carried out in accordance with the Indiana oxidation test method (Standard Oil Co.). Specifically, air is introduced into a sample (300 mL) at 10 L/hour and 121°C for 312 hours for causing forced deterioration. After the experiment, generated sludge is recovered by means of a Millipore filter and weighed.

[0028] In the lubricating oil composition of the present invention, a thiophosphoric acid trihydrocarbyl ester represented by formula (I):

$$(R\text{-}O\text{-})_3P{=}S \qquad (I)$$

is employed as an optional component (c-2).

In formula (I), R represents a C6 to C20 hydrocarbyl group. The hydrocarbyl group represents a linear, branched, or cyclic C6 to C20 alkyl group or alkenyl group, a C6 to C20 aryl group, or a C7 to C20 aralkyl group. In the aryl group and aralkyl group, one or more alkyl groups may be attached to the corresponding aromatic ring. Three R-O- groups may be identical to or different from one another.

Examples of the C6 to C20 alkyl group and alkenyl group include hexyls, octyls, decyls, dodecyls, tetradecyls, hexadecyls, octadecyls, cyclohexyl, hexenyls, octenyls, decenyls, dodecenyls, tetradecenyls, hexadecenyls, octadecenyls, and cyclohexenyl.

Examples of the C6 to C20 aryl group include phenyl, tolyl, xylyl, decylphenyl, 2,4-didecylphenyl, and naphthyl. Examples of the C7 to C20 aralkyl group include benzyl, phenethyl, naphthylmethyl, methylbenzyl, methylphenethyl, and methylnaphthylmethyl.

Specific examples of the thiophosphoric acid trihydrocarbyl ester represented by 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, and tris[2,4-isoalkyl(C_9, C_{10})phenyl] thiophosphate. These thiophosphoric acid trihydrocarbyl phosphates may be used singly or in combination of two or more species.

In the lubricating oil composition of the present invention, the thiophosphoric acid trihydrocarbyl ester serving as component (c-2) is optionally added to the composition for further enhancing the effect of the sulfur compound serving as component (c-1). The amount of component (c-2) compound is preferably 0.1 to 1.0 mass% based on the total amount of the lubricating oil composition, more preferably 0.2 to 0.5 mass%. However, the total amount of P in the lubricating oil composition is adjusted to 150 to 500 ppm by mass.

[0029] If required, the lubricating oil composition of the present invention may further contain a polyol partial ester serving as component (D). The component (D) further prevents sludge formation in the Indiana oxidation test.

No particular limitation is imposed on the polyol serving as a raw material of the polyol partial ester, and an aliphatic polyol is preferred. Examples of the polyol include dihydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, trimethylene glycol, tetramethylene glycol, and neopentyl glycol; trihydric alcohols such as glycerin, trimethylolethane, and trimethylolpropane; and polyhydric (≥4-valent) alcohols such as diglycerin, triglycerin, pentaerythritol, dipentaerythritol, mannit, and sorbit.

No particular limitation is imposed on the number of ester bonds in the partial ester, so long as at least one hydroxyl group remains. The hydrocarbyl group forming the ester bond(s) is preferably a C6 to C20 alkyl group or alkenyl group. Examples include hexyls, octyls, decyls, dodecyls, tetradecyls, hexadecyls, octadecyls, hexenyls, octenyls, decenyls, dodecenyls, tetradecenyls, hexadecenyls, and octadecenyls.

Specific examples of the polyol partial ester include, but are not limited to, neopentyl glycol monolaurate, neopentyl glycol monomyristate, neopentyl glycol monopalmitate, neopentyl glycol monostearate, neopentyl glycol monoisostearate, trimethylolpropane mono- or dilaurate, trimethylolpropane mono- or dimyristate, trimethylolpropane mono- or dipalmitate, trimethylolpropane mono- or distearate, trimethylolpropane mono- or diisostearate, glycerin mono- or dilaurate, glycerin mono- or distearate, and glycerin mono-or diisostearate.

In the lubricating oil composition of the present invention, these polyol partial esters may be used singly or in combination of two or more species as component (D). The amount of polyol partial ester(s) incorporated into the composition is generally about 5 to about 20 mass%, based on the total amount of the composition, more preferably 7 to 15 mass%, from the viewpoint of prevention of sludge formation in the Indiana oxidation test.

[0030] Into the lubricating oil composition of the present invention, so long as the objects of the present invention are not impaired, at least one additive may be incorporated in accordance with needs, the additive being selected from among an ashless detergent-dispersant, an antioxidant, an anticorrosive, a metal deactivator, a viscosity index improver, a pour point depressant, a defoaming agent, etc.

Examples of the ashless detergent-dispersant include succinimides, boron-containing succinimides, benzylamines, boron-containing benzylamines, succinate esters, and mono- or divalent carboxamides including fatty acid amides and succinamides.

[0031] The antioxidant employed may be an amine-based antioxidant, a phenol-based antioxidant, or a sulfur-containing antioxidant, which are conventionally employed in lubricating oil. These antioxidants may be used singly or in combination of two or more species. Examples of the amine-based antioxidant include monoalkyldiphenylamine compounds such as monooctyldiphenylamine and monononyldiphenylamine; dialkyldiphenylamine compounds such as 4,4'-dibutyldiphenylamine, 4,4'-dipentyldiphenylatnine, 4,4'-dihexyldiphenylamine, 4,4'-diheptyldiphenylamine, 4,4'-dioctyldiphenylamine, and 4,4'-dinonyldiphenylamine; polyalkyldiphenylamine compounds such as tetrabutyldiphenylamine, tetrahexyldiphenylamine, tetraoctyldiphenylamine, and tetranonyldiphenylamine; and naphthylamine compounds such as α-naphthylamine, phenyl-α-naphthylamine, butylphenyl-α-naphthylamine, pentylphenyl-α-naphthylamine, hexylphenyl-α-naphthylamine, heptylphenyl-α-naphthylamine, octylphenyl-α-naphthylamine, and nonylphenyl-α-naphthylamine.

[0032] Examples of the phenol-based antioxidant include monophenol compounds such as 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, and octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate; and diphenol compounds such as 4,4'-methylenebis(2,6-di-tert-butylphenol) and 2,2'-methylenebis(4-ethyl-6-tert-butylphenol).

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

[0033] Examples of the anticorrosive include metal sulfonates and succinic acid esters, and examples of the metal deactivator include benzotriazole and thiadiazole.

Examples of the viscosity index improver include polymethacrylates, dispersion-type polymethacrylates, olefin copolymers (e.g., etylene-propylene copolymer), dispersion-type olefin copolymers, and styrene copolymers (e.g., styrene-diene hydrogenated copolymer).

Examples of the pour point depressant employed in the invention include polymethacrylates having a weight average molecular weight of 50,000 to 150,000.

The defoaming agent is preferably a high-molecular-weight silicone defoaming agent or a polyacrylate defoaming agent. Incorporation of a defoaming agent such as a high-molecular-weight silicone defoaming agent into the composition of the invention effectively attains defoaming property.

Examples of the high-molecular-weight silicone defoaming agent include organopolysiloxanes. Of these, fluorine-containing organopolysiloxanes such as trifluoropropylmethyl silicone oil are particularly preferred.

The lubricating oil composition of the present invention is excellent in anti-seizure performance, excellent anti-fatigue performance (e.g., FZG micropitting resistance), and reduced sludge formation in an oxidation test. Thus, the composition can be employed as lubricating oils such as gear oil and bearing oil, and particularly suitable for a lubricating oil for use in a planetary gear-type power transmission apparatus in a wind power generator.

[0034] As described hereinabove, the present invention is directed to a lubricating oil composition comprising a base oil, components (A) to (C), and an optional component (D). Generally, the lubricating oil composition comprises a base oil, components (A) to (C), and a component (D).

Examples

[0035] The present invention will next be described in more detail by way of examples, which should not be construed as limiting the invention thereto.

Properties of the base oils employed in the Examples and those of the lubricating oil compositions obtained in the Examples were determined through the following methods.

<Properties of base oils>

(1) Kinematic viscosity and viscosity index

[0036] Determined in accordance with JIS K 2283.

(2) Pour point

[0037] Determined in accordance with JIS K 2265.

<Performance of lubricating oil compositions>

(3) FZG seisure test

[0038] The test was carried out in accordance with a method described in the present specification. Stage 13 is a pass level.

(4) Timken test

[0039] The test was carried out in accordance with a method described in the present specification. The pass level is 45 lbs or higher.

(5) FZG micropitting test

[0040] The test was carried out in accordance with a method described in the present specification. Stage 9 is a pass level.

(6) Indiana oxidation test

[0041] The test was carried out in accordance with a method described in the present specification. Sludge level (determined by means of a Millipore filter) of 10 or less is a pass level.

[0042] The following components were employed for preparing the lubricating oil compositions.

(1) Base oil: PAO, α-olefin oligomer, kinematic viscosity (40°C) of 390 mm^2/s, viscosity index of 149, and pour point of -50°C or lower

(2) Acidic phosphate esters

·Isodecyl : acidic (mono, di)isodecyl phosphate ester(mono : di (mole) = 1 : 1)
·Tridecyl: acidic (mono, di)tridecyl phosphate ester(mono : di (mole) = 1 : 1)
·Isoamyl: acidic (mono, di)isoamyl phosphate ester(mono : di (mole) = 1 : 1)
·2-Ethylhexyl: acidic (mono, di)-2-ethylhexyl phosphate ester(mono : di (mole) = 1 : 1)
·Oleyl: acidic (mono, di)oleyl phosphate ester(mono : di (mole) = 1 : 1)

(3) Amines

·Trioctylamine
·Dadecylamine

(4) Sulfur compounds

·Dithiocarbamate: methylenebisdibutyl dithiocarbamate: S content of 30 mass%
·Thiophosphate: tris(2,4-diisoalkyl(C_9, C_{10})phenyl) thiophosphate, S content of 44 mass%
·Dibutyl dithioglycolate: S content of 20 mass%
·thiadiazole: 2,5-bis(1,1,3,3-tetramethylbutanedithio)-1,3,4-thiadiazole, S content of 39 mass%
·Butene sulfide: trisulfide bond-containing (mono, di, tri, and tetrasulfides, S_X: average of x of 2.3), S content 40 mass%

(5) Polyol ester

Partial ester: Ester from trimethylolpropane and isostearic acid (1:2 (mole))
Complete ester: Ester from trimethylolpropane and isostearic acid (1:3 (mole))

(6) Antioxidant

A: Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate
B: 4,4'-Dioctyldiphenylamine

(7) Anticorrosive: dialkylaminomethylbenzotriazole

Examples 1 to 8 and Comparative Examples 1 to 7

[0043] Lubricating oil compositions having a formulation shown in Table 1 were prepared, and characteristics of the compositions were assessed. Table 1 shows the results.

[Table 1]

[0044]

Table 1-1

			Examples				
			1	2	3	4	5
Formulation (mass%)	Base oil (PAO)		86.32	86.28	86.68	86.33	86.93
	Acidic phosphate ester (A)	isodecyl	0.22	--	--	--	--
		tridecyl	--	0.26	0.26	0.26	0.26
		isoamyl	--	--	--	--	--
		2-ethylhexyl	--	--	--	--	--
		oleyl	--	--	--	--	--
	Amine (B)	octylamine	0.36	0.36	0.36	0.36	0.36
		dodecylamine	--	--	--	--	--
	Sulfur compound (C)	dithiocarbamate	1.65	1.65	1.65	--	--
		thiophosphate	0.40	0.40	--	--	--
		dibutyl dithioglycolate	--	--	--	2.00	--
		thiadiazole	--	--	--	--	1.50
		butene sulfide	--	--	--	--	--
	Polyol ester (D)	partial ester	10	10	10	10	10
		complete ester	--	--	--	--	--
	Antioxidant	A	0.5	0.5	0.5	0.5	0.5
		B	0.5	0.5	0.5	0.5	0.5
	Anticorrosive		0.05	0.05	0.05	0.05	0.05
P content of composition (mass ppm)			380	380	220	220	220
S content of compositions (mass ppm)			0.51	0.51	0.49	0.40	0.45
[P in (A)]/[N in (B)] (by mass)			1.9	1.9	1.9	1.9	1.9
Performance	Timken test (lbs)		65	60	45	50	45
	FZG seizure test	stage 12	pass	pass	pass	pass	pass
		stage 13	pass	pass	pass	pass	pass
		stage 14	pass	pass	fail	pass	pass
	FZG micropitting test	stage 8	pass	pass	pass	pass	pass
		stage 9	pass	pass	pass	pass	pass
		stage 10	pass	pass	pass	fail	fail
	Indiana oxidation test	Millipore filter	2	1	4	7	5

[Table 2]

[0045]

Table 1-2

			Examples			Comp. Exs.	
			6	7	8	1	2
Formulation (mass%)	Base oil (PAO)		96.28	86.28	86.37	86.42	85.66
	Acidic phosphate ester (A)	isodecyl	--	--	--	--	--
		tridecyl	0.26	0.26	--	--	0.52
		isoamyl	--	--	--	0.12	--
		2-ethylhexyl	--	--	0.17	--	--
		oleyl	--	--	--	--	--
	Amino (B)	trioctylamine	0.36	0.36	0.36	0.36	0.72
		dodecylamine	--	--	--	--	--
	Sulfur compound (C)	dithiocarbamate	1.65	1.65	1.65	1.65	1.65
		thiophosphate	0.40	0.40	0.40	0.40	0.40
		dibutyl dithioglycolate	--	--	--	--	--
		thiadiazole,	--	--	--	--	--
		butene sulfide	--	--	--	--	--
	Polyol ester (D)	partial ester	--	--	10	10	10
		complete ester	--	10	--	--	--
	Antioxidant	A	0.5	0.5	0.5	0.5	0.5
		B	0.5	0.5	0.5	0.5	0.5
	Anticorrosive		0.05	0.05	0.05	0.05	0.05
P content of composition (mass ppm)			380	380	380	380	600
S content of composition (mass ppm)			0.51	0.51	0.51	0.51	0.51
[P in (A)]/[N in (B)] (by mass)			1.9	1.9	1.9	1.9	1.9
Performance	Timken test (lbs)		55	60	50	70	65
	FZG seizure test	stage 12	pass	pass	pass	pass	pass
		stage 13	pass	pass	pass	pass	pass
		stage 14	fail	pass	pass	pass	pass
	FZG micropitting test	stage 8	pass	pass	pass	pass	pass
		stage 9	pass	pass	pass	fail	fail
		stage 10	pass	pass	pass	fail	fail
	Indiana oxidation test	Millipore filter	40	35	15	100	18

[Table 3]

[0046]

Table 1-3

			Comp. Exs.				
			3	4	5	6	7
ormulation (mass%)	Base oil (PAO)		87.08	86.21	86.47	87.51	Commercial oil
	Acidic phosphate ester (A)	isodecyl	—	—	—	—	
		tridecyl	0.26	—	0.26	0.26	
		isoamyl	—	—	—	—	
		2-ethylhexyl	—	—	—	—	
		oleyl	—	0.33	—	—	
	Amine (B)	trioctylamine	0.36	0.36	—	0.36	
		dodecylamine	—	—	0.17	—	
	Sulfur compound (C)	dithiocarbamate	—	1.65	1.65	0.82	
		thiophosphate	—	0.40	0.40	—	
		dibutyl dithioglycolate	—	—	—	—	
		thiadiazole	—	—	—	—	
		butene sulfide	1.25	—	—	—	
	Polyol ester (D)	partial ester	10	10	10	10	
		complete ester	—	—	—	—	
	Antioxidant	A	0.5	0.5	0.5	0.5	
		B	0.5	0.5	0.5	0.5	
	Anticorrosive		0.05	0.05	0.05	0.05	
P content of composition (mass ppm)			220	380	380	220	570
S content of composition (mass ppm)			0.51	0.51	0.51	0.17	0.44
[P in (A)]/[N in (B)] (by mass)			1.9	1.9	1.9	1.9	—
Performance	Timken test (lbs)		60	40	50	35	45
	FZG seizure test	stage 12	pass	pass	pass	pass	pass
		stage 13	pass	pass	fail	fail	pass
		stage 14	pass	fail	fail	fail	fail
	FZG micropitting test	stage 8	pass	pass	pass	pass	pass
		stage 9	fail	pass	pass	pass	pass
		stage 10	fail	pass	pass	pass	pass
	Indiana oxidation test	Millipore filter	90	50	4	6	120

[0047] As is clear from Table 1, the lubricating oil compositions of Examples 1 to 5 all passed the Timken test, FZG seizure test, FZG micropitting test, and Indiana oxidation test. The lubricating oil composition of Example 6 contains no polyol partial ester, and that of Example 7 contains a polyol complete ester. These two compositions give a relatively large amount of sludge in the Indiana oxidation test. The lubricating oil composition of Example 8, which contains 2-ethylhexyl (C8 alkyl) acid phosphate as an acidic phosphate ester, gives a slightly large amount of sludge in the Indiana oxidation test.

The lubricating oil compositions of Comparative Examples 1 to 6 have at least one property falling outside the scope of the present invention. Thus, performance thereof is inferior to that of the compositions of the Examples.

A commercial product (Comparative Example 7) gives a considerable amount of sludge in the Indiana oxidation test.

[Industrial Applicability]

[0048] The lubricating oil composition of the present invention has excellent anti-seizure performance, excellent anti-fatigue performance (e.g., anti-FZG-micropitting performance), and reduced sludge formation in an oxidation test, and is suitably used as a lubricating oil such as gear oil or bearing oil. The composition is particularly suitable as a lubricating oil for use with a step-up gear (e.g., planetary gear-type power transmission apparatus) in a wind power generator.

Claims

1. A lubricating oil composition **characterized by** comprising: a base oil; (A) an acidic alkyl phosphate ester having a C6 to C20 alkyl group; (B) a dialkylamine and/or a trialkylamine; and (C) (c-1) a sulfur compound in an amount of 0.2 to 0.6 mass% as reduced to S, the 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 of the molecule of 15 mass% or more and (c-2) an optional thiophosphoric acid trihydrocarbyl ester in an amount of 0.1 to 1.0 mass%, the ester being represented by formula (I):

   $$(R\text{-}O\text{-})_3P{=}S \qquad (I)$$

   (wherein R represents a C6 to C20 hydrocarbyl group) and having a P content of the composition of 150 to 500 ppm by mass.

2. A lubricating oil composition as described in claim 1, which contains component (B) in such an amount that the ratio by mass of P contained in component (A) to N contained in component (B) is adjusted to 1.7 to 2.1.

3. A lubricating oil composition as described in claim 1, wherein component (B) is a trialkylamine having a C6 to C20 alkyl group.

4. A lubricating oil composition as described in claim 1, which further contains (D) a polyol partial ester in an amount of 5 to 20 mass%.

5. A lubricating oil composition as described in any of claims 1 to 4, which is used as a step-up gear oil composition for wind power generation.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/068779

A. CLASSIFICATION OF SUBJECT MATTER
See extra sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M169/04, C10M129/76, C10M133/06, C10M133/10, C10M135/04, C10M135/06, C10M135/18, C10M135/22, C10M135/28, C10M135/36, C10M137/04, C10M137/10, C10N30/00, C10N30/06, C10N30/10, C10N40/04

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

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Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2005-126709 A (Afton Chemical Corp.), 19 May, 2005 (19.05.05), & EP 1528098 A1 & CA 2483063 A1 & US 2005/090410 A1 & SG 111264 A1 & BR 200404643 A & CN 1637125 A	1-5
A	JP 2002-338983 A (Showa Shell Sekiyu Kabushiki Kaisha), 27 November, 2002 (27.11.02), & WO 02/092735 A1 & EP 1385926 A1 & KR 2003096370 A & AU 2002316899 A1 & US 2004/214733 A1 & CN 1522295 A & DE 60209497 E & ES 2259375 T3	1-5

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

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Date of the actual completion of the international search 19 October, 2007 (19.10.07)	Date of mailing of the international search report 30 October, 2007 (30.10.07)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/068779

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 6-100880 A (Asahi Denka Kogyo Kabushiki Kaisha), 12 April, 1994 (12.04.94), (Family: none)	1-5

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/068779

Continuation of A. CLASSIFICATION OF SUBJECT MATTER
(International Patent Classification (IPC))

C10M169/04(2006.01)i, *C10M129/76*(2006.01)i, *C10M133/06*(2006.01)i, *C10M133/10*(2006.01)i, *C10M135/04*(2006.01)i, *C10M135/06*(2006.01)i, *C10M135/18*(2006.01)i, *C10M135/22*(2006.01)i, *C10M135/28*(2006.01)i, *C10M135/36*(2006.01)i, *C10M137/04*(2006.01)i, *C10M137/10*(2006.01)i, *C10N30/00*(2006.01)n, *C10N30/06*(2006.01)n, *C10N30/10*(2006.01)n, *C10N40/04*(2006.01)n

(According to International Patent Classification (IPC) or to both national classification and IPC)

REFERENCES CITED IN THE DESCRIPTION

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