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(54) **LUBRICANT COMPOSITION**

(57) Provided is a lubricating oil composition having excellent wear resistance, the lubricating oil composition containing a base oil (A), an overbased metal detergent (B), a sulfur-phosphorus extreme pressure agent (C)

having a carboxylic acid ester group, and a sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end.

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Description

Technical Field

5 **[0001]** The present invention relates to a lubricating oil composition.

Background Art

10 **[0002]** Hydraulic equipment installed in construction machinery such as hydraulic excavators, cranes, wheel loaders, and bulldozers, as well as gears and bearings installed in drive apparatus, are required to operate under high pressure, high temperature, high speed, and heavy load.

[0003] Therefore, a lubricating oil composition used as a power transmission medium in these apparatus is required to have wear resistance that does not impair the performance of the apparatus even when used for a long period of time under high pressure, high temperature, high speed, and heavy load.

15 **[0004]** For example, PTL 1 proposes a lubricating oil composition used in hydraulic equipment such as construction machinery with an operating pressure of 30 MPa or more, which contains a hindered phenol-based antioxidant, an imide compound, and an extreme pressure agent.

[0005] PTL 1 describes that the lubricating oil composition is capable of exhibiting good sludge suppression properties and wear resistance properties evaluated by scoring resistance and seizure resistance over a long period of time.

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Citation List

Patent Literature

25 **[0006]** PTL 1: JP 2021-161289 A

Summary of Invention

Technical Problem

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[0007] In recent years, there has been a trend towards higher performance in the above apparatus, such as higher pressure, smaller size, higher speed, and higher precision, and therefore, the performance requirements for the lubricating oil composition used are becoming more severe.

35 **[0008]** From this point of view, in recent years, phosphate treatment has been sometimes applied to sliding parts of apparatus to improve wear resistance and the like; however, a sliding member that has been subjected to such phosphate treatment may have different wear properties in the presence of a lubricating oil composition from that of a sliding member not subjected to such treatment.

[0009] Nevertheless, such consideration is not sufficiently conducted in PTL 1.

[0010] An object of the present invention is to provide a lubricating oil composition with excellent wear resistance.

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Solution to Problem

45 **[0011]** As a result of extensive studies, an inventor of the present invention has discovered that the above problems can be solved by a lubricating oil composition containing an overbased metal detergent, a sulfur-phosphorus extreme pressure agent having a carboxylic acid ester group, and a sulfur-phosphorus extreme pressure agent having a carboxy group at an end.

[0012] Specifically, the present invention provides the following [1] and [2].

50 [1] A lubricating oil composition containing a base oil (A), an overbased metal detergent (B), a sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group, and a sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end.

[2] A lubrication method for lubricating an apparatus equipped with a sliding member having a phosphate coating on at least a part of a sliding surface using the lubricating oil composition according to the above [1].

55 Advantageous Effects of Invention

[0013] According to the present invention, it is possible to provide a lubricating oil composition with excellent wear resistance.

Description of Embodiments

[0014] In the present description, lower limit values and upper limit values described in stages for preferred numerical ranges (for example, ranges of content) can be independently combined. For example, the expression of "preferably 10 to 90, more preferably 30 to 60" can mean "10 to 60" by combining "the preferable lower limit value (10)" and "the more preferable upper limit value (60)". Similarly, in the present description, numerical values with the expressions of "or more", "or less", "less than", and "more than" regarding the recitation of numerical ranges can be arbitrarily combined.

[Lubricating Oil Composition]

[0015] A lubricating oil composition of the present embodiment contains a base oil (A), an overbased metal detergent (B), a sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group, and a sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end.

[0016] In the following explanation, the "base oil (A)", the "overbased metal detergent (B)", the "sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group", and the "sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end" will also be referred to as "component (A)", "component (B)", "component (C)", and "component (D)", respectively.

[0017] The lubricating oil composition of the present embodiment may be composed of only the "component (A)", the "component (B)", the "component (C)", and the "component (D)"; however, within a range that does not impair the effects of the present invention, the lubricating oil composition may contain additional components other than the "component (A)", the "component (B)", the "component (C)", and the "component (D)".

[0018] In the lubricating oil composition of the present embodiment, from the viewpoint of more easily improving the effects of the present invention, a total content of the "component (A)", the "component (B)", the "component (C)", and the "component (D)" is preferably 70.0% by mass or more, more preferably 80.0% by mass or more, even more preferably 90.0% by mass or more, and still more preferably 95.0% by mass or more, based on a whole amount of the lubricating oil composition.

[0019] The upper limit value of the total content of the component (A), the component (B), the component (C), and the component (D) may be adjusted in balance with additional components other than the component (A), the component (B), the component (C), and the component (D), and is preferably 99.8% by mass or less, more preferably 99.5% by mass or less, and still more preferably 99.0% by mass or less, based on the whole amount of the lubricating oil composition.

[0020] Hereinafter, the base oil (A), the overbased metal detergent (B), the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group, the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end, and further additional components will be described in detail.

[Base Oil (A)]

[0021] As the base oil (A), one or more selected from mineral oils and synthetic oils conventionally used as base oils of lubricating oil can be used without any particular restrictions.

[0022] Examples of the mineral oil include atmospheric pressure residual oils obtained by atmospheric distillation of crude oils such as paraffinic crude oils, intermediate base crude oils, and naphthenic crude oils; distillate oils obtained by vacuum distillation of these atmospheric residual oils; and mineral oils obtained by subjecting the distillate oils to one or more refining treatments such as solvent de-asphalting, solvent extraction, hydrocracking, solvent dewaxing, catalytic dewaxing, and hydro-refining.

[0023] Examples of the synthetic oil include poly- α -olefins such as an α -olefin homopolymer and an α -olefin copolymer (for example, α -olefin copolymers having 8 to 14 carbon atoms such as an ethylene- α -olefin copolymer); isoparaffines; various esters such as a polyol ester and a dibasic acid ester; various ethers such as polyphenyl ether; polyalkylene glycols; alkylbenzenes; alkylnaphthalenes; and GTL base oils obtained by isomerization of wax (GasToLiquids (GTL) wax) produced from natural gas by the Fischer-Tropsch process and the like.

[0024] As the base oil (A), the mineral oil may be used alone or a plurality of kinds of the mineral oils may be used in combination, and the synthetic oil may be used alone or a plurality of kinds of the synthetic oils may be used in combination. In addition, one or more mineral oils may be used in combination with one or more synthetic oils.

[0025] From the viewpoint of further improving the oxidation stability of the lubricating oil composition, the base oil (A) is preferably one or more selected from base oils classified into Groups II, III, and IV in the American Petroleum Institute (API) base oil category, and more preferably one or more selected from base oils classified into Groups II and III.

[0026] The kinematic viscosity of the base oil (A) at 40°C (hereinafter also referred to as "40°C kinematic viscosity") is preferably 10 mm²/s to 150 mm²/s, more preferably 15 mm²/s to 100 mm²/s, even more preferably 20 mm²/s to 70 mm²/s, and particularly preferably 30 mm²/s to 60 mm²/s.

[0027] When the 40°C kinematic viscosity of the base oil (A) is 10 mm²/s or more, it is easy to obtain a lubricating oil

composition with a high flash point and excellent lubricating performance.

[0028] Furthermore, when the 40°C kinematic viscosity of the base oil (A) is 150 mm²/s or less, the viscous resistance at low temperatures does not become so large, making it easier to maintain good machine operation.

[0029] The viscosity index of the base oil (A) is preferably 80 or more, more preferably 90 or more, even more preferably 100 or more, and still more preferably 105 or more. When the viscosity index of the base oil (A) is within the above range, changes in viscosity due to temperature changes can be suppressed, making it easier to form an oil film at high temperatures and to improve wear resistance.

[0030] In addition, when the base oil (A) is a mixed base oil containing two or more kinds of base oils, the 40°C kinematic viscosity and the viscosity index of the mixed base oil are preferably within the above ranges.

[0031] In the present description, the 40°C kinematic viscosity and the viscosity index mean values measured or determined in accordance with JIS K 2283:2000.

[0032] The base oil (A) preferably contains mineral oil. When the base oil (A) contains mineral oil, the content of the mineral oil based on the whole amount of the base oil (A) is preferably 50% by mass or more, more preferably 70% by mass or more, and even more preferably 90% by mass or more.

[0033] In the lubricating oil composition of the present embodiment, the content of the base oil (A) is preferably 80.0% by mass to 99.5% by mass, more preferably 83.0% by mass to 99.0% by mass, and even more preferably 85.0% by mass to 98.8% by mass, based on the whole amount of the lubricating oil composition.

[Overbased Metal Detergent (B)]

[0034] The overbased metal detergent (B) means a metal detergent made by reacting a metal with an acidic organic compound and containing an excess amount of metal than the stoichiometric amount required to neutralize the metal and the acidic organic compound.

[0035] Specifically, as the overbased metal detergent (B), those having a base number of 100 mgKOH/g or more as measured by the perchloric acid method in accordance with JIS K 2501:2003 are preferably used, those having a base number of 150 to 600 mgKOH/g are more preferred, and those having a base number of 200 to 500 mgKOH/g are even more preferred.

[0036] From the viewpoint of improving the wear resistance of the lubricating oil composition, the overbased metal detergent (B) is preferably one or more selected from an alkaline earth metal sulfonate, an alkaline earth metal phenate, and an alkaline earth metal salicylate, and more preferably one or more selected from calcium sulfonate, calcium phenate, and calcium salicylate.

[0037] The overbased metal detergent (B) is particularly preferably one or more selected from an overbased calcium sulfonate with a base number of 100 mgKOH/g or more and an overbased calcium salicylates with a base number of 100 mgKOH/g or more, from the viewpoint of easily improving the wear resistance.

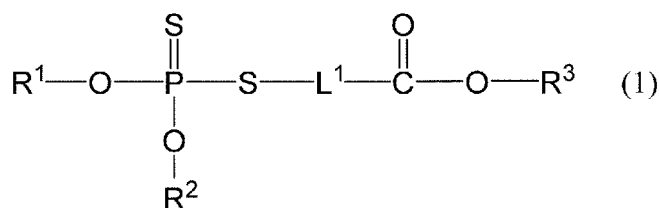
[0038] In addition, the overbased calcium sulfonate with a base number of 100 mgKOH/g or more and the overbased calcium salicylates with a base number of 100 mgKOH/g or more may be used in combination, but are preferably used alone.

[0039] From the viewpoint of more easily exhibiting the effects of the present invention, the content of metal atoms derived from the overbased metal detergent (B) in the lubricating oil composition of the present embodiment is, based on the whole amount of the lubricating oil composition, preferably 5 ppm by mass to 1,000 ppm by mass, more preferably 10 ppm by mass to 980 ppm by mass, and even more preferably 15 ppm by mass to 970 ppm by mass.

[0040] The content of the overbased metal detergent (B) in the lubricating oil composition of the present embodiment is preferably 0.01% by mass to 0.53% by mass, more preferably 0.01% by mass to 0.52% by mass, and even more preferably 0.01% by mass to 0.51% by mass, based on the whole amount of the lubricating oil composition.

[Sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group]

[0041] As the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group, a thiophosphoric acid ester having a carboxylic acid ester group is preferably used, and a thiophosphoric acid ester represented by the following general formula (1) is particularly preferably used.



[0042] In the above general formula (1), R¹ to R³ each independently represent a hydrocarbon group having 3 to 20 carbon atoms, and L¹ represents a linear or branched alkylene group having 1 to 8 carbon atoms.

[0043] From the viewpoint of improving solubility in base oil, L¹ is preferably a linear or branched alkylene group having 1 to 8 carbon atoms, and more preferably a linear or branched alkylene group having 2 to 4 carbon atoms. Specifically, preferred examples thereof include -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂CH₃)-, CH₂CH(CH₃)CH₂-, and -CH₂CH(CH₂CH₂CH₃)-, where -CH₂CH₂-, -CH₂CH(CH₃)-, and -CH₂CH(CH₃)CH₂- are more preferred, and -CH₂CH₂- is even more preferred.

[0044] In addition, from the viewpoint of achieving good extreme pressure performance and good solubility in base oil, R¹ to R³ each independently are preferably a linear or branched alkyl group having 1 to 8 carbon atoms, and specifically, those selected from the group consisting of a methyl group, an ethyl group, an n-propyl group, an isopropyl group, a butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, a hexyl group, 2-ethylbutyl group, 1-methylpentyl group, 1,3-dimethyl butyl group, and 2-ethylhexyl group are preferred. Among these, a linear or branched alkyl group having 2 to 5 carbon atoms is more preferred, and an ethyl group or an isobutyl group is even more preferred.

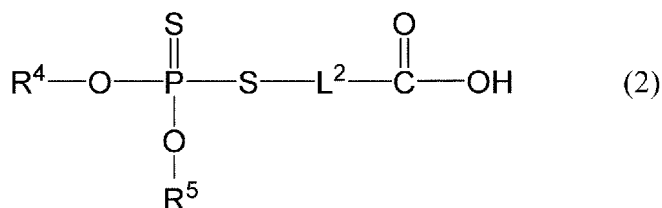
[0045] The sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group may be used alone or may be used in combination of two or more thereof.

[0046] The content of the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group in the lubricating oil composition of the present embodiment is preferably 0.01% by mass to 1.0% by mass, more preferably 0.05% by mass to 0.80% by mass, and even more preferably 0.10% by mass to 0.50% by mass, based on the whole amount of the lubricating oil composition.

[0047] When the content of the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group is equal to or more than the above lower limit value, the lubricating oil composition will have excellent wear resistance, and when the content is equal to or less than the above upper limit value, sludge generation will be easily suppressed.

[Sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end]

[0048] As the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end, a thiophosphoric acid ester having a carboxy group at an end is preferably used, and a thiophosphoric acid ester represented by the following general formula (2) is particularly preferably used.



[0049] In the above general formula (2), R⁴ and R⁵ each independently represent a hydrocarbon group having 3 to 20 carbon atoms, and L² represents a linear or branched alkylene group having 1 to 8 carbon atoms.

[0050] From the viewpoint of improving solubility in base oil, L² is preferably a linear or branched alkylene group having 1 to 8 carbon atoms, and more preferably a linear or branched alkylene group having 2 to 4 carbon atoms. Specifically, preferred examples thereof include -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂CH₃)-, CH₂CH(CH₃)CH₂-, and -CH₂CH(CH₂CH₂CH₃)-, where -CH₂CH(CH₃)-, and -CH₂CH(CH₃)CH₂- are more preferred, and -CH₂CH(CH₃)- is even more preferred.

[0051] In addition, from the viewpoint of achieving good extreme pressure performance and good solubility in base oil, R⁴ and R⁵ each independently are preferably a linear or branched alkyl group having 1 to 8 carbon atoms, and specifically, those selected from the group consisting of a methyl group, an ethyl group, an n-propyl group, an isopropyl group, a butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, a hexyl group, 2-ethylbutyl group, 1-methylpentyl group, 1,3-dimethyl butyl group, and 2-ethylhexyl group are preferred. Among these, a linear or branched alkyl group having 2 to 5 carbon atoms is more preferred, and an isobutyl group is even more preferred.

[0052] The sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end may be used alone or may be used in combination of two or more thereof.

[0053] The content of the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end in the lubricating oil composition of the present embodiment is, based on the whole amount of the lubricating oil composition, preferably 0.01% by mass or more, more preferably 0.03% by mass or more, even more preferably 0.04% by mass or more, and still more preferably 0.05% by mass or more, and is preferably 0.50% by mass or less, more preferably 0.20% by mass or less, even more preferably 0.12% by mass or less, and still more preferably 0.08% by mass or less. These upper limit values and lower limit values can be arbitrarily combined, and specifically, the content thereof is preferably 0.01% by mass to 0.50% by mass, more preferably 0.03% by mass to 0.20% by mass, even more preferably 0.04% by mass to 0.12% by mass, and still more preferably 0.05% by mass to 0.08% by mass.

[0054] When the content of the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end is equal to or more than the above lower limit value, the lubricating oil composition will have excellent wear resistance, and when the content is equal to or less than the above upper limit value, sludge generation will be easily suppressed.

[0055] The ratio between the content of the overbased metal detergent (B) and the content of the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group is, in terms of a mass ratio of the content of the component (B) to a total content of the component (B) and the component (C), preferably 5 to 50% by mass, more preferably 15 to 40% by mass, and even more preferably 20 to 40% by mass.

[0056] The ratio between the content of the overbased metal detergent (B) and the content of the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end is, in terms of a mass ratio of the content of the component (B) to a total content of the component (B) and the component (D), preferably 40 to 80% by mass, more preferably 45 to 75% by mass, and even more preferably 50 to 70% by mass.

[0057] The lubricating oil composition of the present embodiment is required to contain both the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group and the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end, and in the case where these are not contained, the solubility in the base oil will be poor and the necessary extreme pressure performance will not be obtained.

[0058] The content of the overbased metal detergent (B) is, in terms of a mass ratio of the content of the component (B) to a total content of the component (B), the component (C) and the component (D), preferably 10 to 60% by mass, more preferably 15 to 45% by mass, and even more preferably 20 to 35% by mass.

[0059] The ratio between the content of the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group and the content of the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end is, in terms of a mass ratio of the content of the component (C) to a total content of the component (C) and the component (D), preferably 50 to 95% by mass, more preferably 55 to 85% by mass, and even more preferably 60 to 80% by mass.

[0060] It is preferable that the above ratio is equal to or more than the above lower limit value from the viewpoint of solubility of the component (D), and it is more preferable that the ratio is equal to or less than the above upper limit value from the viewpoint of extreme pressure properties and wear resistance.

[Hindered Phenol-based Antioxidant]

[0061] It is preferable that the lubricating oil composition of the present embodiment further contains a hindered phenol-based antioxidant.

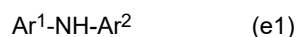
[0062] The hindered phenol-based antioxidant is preferably one or more selected from 2,6-di-tert-butylphenol and 2,6-di-tert-butyl-p-cresol, and particularly preferably 2,6-di-tert-butyl-p-cresol.

[0063] From the viewpoint of sludge suppressing properties, the content of the hindered phenol-based antioxidant in the lubricating oil composition of the present embodiment is preferably 0.05% by mass to 1.0% by mass, more preferably 0.10% by mass to 0.80% by mass, and even more preferably 0.20% by mass to 0.60% by mass, based on the whole amount of the lubricating oil composition.

[Amine-based Antioxidant]

[0064] It is preferable that the lubricating oil composition of the present embodiment further contains an amine-based antioxidant. When the lubricating oil composition contains an amine-based antioxidant, the sludge suppressing properties can be further easily improved.

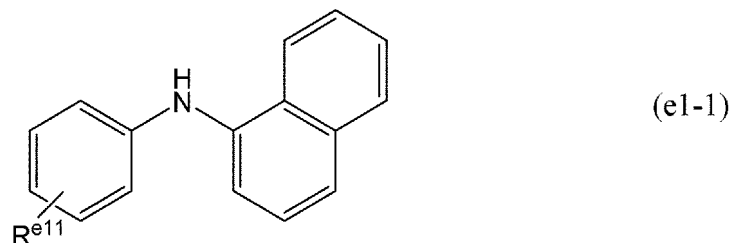
[0065] The amine-based antioxidant is preferably a compound represented by the following general formula (e1), for example.



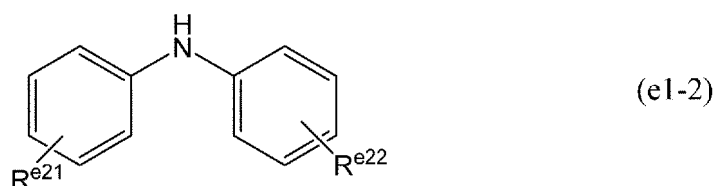
[0066] In the above general formula (e1), Ar¹ and Ar² each independently are an aryl group having 6 to 24 carbon atoms

selected from a phenyl group, an alkyl-substituted phenyl group substituted with an alkyl group, an aralkyl-substituted phenyl group substituted with an aralkyl group, naphthyl group and an alkyl-substituted naphthyl group substituted with an alkyl group.

[0067] Further, more specifically, the amine-based antioxidant is preferably one selected from the group consisting of phenyl- α -naphthylamines represented by the following general formula (e1-1) and diphenylamines represented by the general formula (e1-2).



[0068] In the above general formula (e1-1), R^{e11} is a hydrogen atom or an alkyl group having 1 to 18 carbon atoms.



[0069] In the above general formula (e1-2), R^{e21} and R^{e22} each independently are selected from a hydrogen atom, an alkyl group having 1 to 18 carbon atoms, and an aralkyl group having 7 to 18 carbon atoms.

[0070] In the phenyl- α -naphthylamines represented by the above general formula (e1-1), R^{e11} is preferably a hydrogen atom or an alkyl group having 1 to 12 carbon atoms, and R^{e11} is preferably arranged in a para position.

[0071] Furthermore, in the diphenylamines represented by the above general formula (e1-2), R^{e21} and R^{e22} each independently are selected from a hydrogen atom, an alkyl group having 4 to 12 carbon atoms, and an α,α -dimethylbenzyl group. In addition, it is more preferable that both of them are arranged in the para position.

[0072] Specific examples of the amine-based antioxidant include dioctyldiphenylamine, phenyl- α -naphthylamine, diphenylamine, dinonyldiphenylamine, monobutylphenylmonooctylphenylamine, p-t-octylphenyl-1-naphthylamine, and 4,4'-bis(α,α -dimethylbenzyl)diphenylamine.

[0073] In addition to the above, a diamine-based antioxidant can also be used as the amine-based antioxidant. Specific examples thereof include N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N,N'-di-2-naphthyl-p-phenylenediamine, and N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine.

[0074] The amine-based antioxidant may be used alone or may be used in combination of two or more thereof.

[0075] From the viewpoint of more easily exhibiting the effects of the present invention, the content of the amine-based antioxidant in the lubricating oil composition of the present embodiment is preferably 0.01% by mass to 0.20% by mass, more preferably 0.02% by mass to 0.10% by mass, and even more preferably 0.03% by mass to 0.08% by mass, based on the whole amount of the lubricating oil composition.

[Imide Compound]

[0076] The lubricating oil composition of the present embodiment preferably further contains one or more imide compounds selected from the group consisting of a monoimide compound and a bisimide compound. When the lubricating oil composition contains an imide compound, the oxidation stability and sludge suppressing properties of the lubricating oil composition can be further easily improved.

[0077] Specifically, the monoimide compound is preferably one or more selected from the group consisting of an alkenyl succinic acid monoimide compound and an alkyl succinic acid monoimide compound.

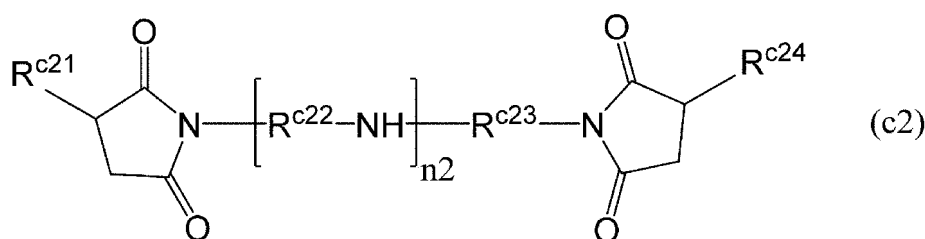
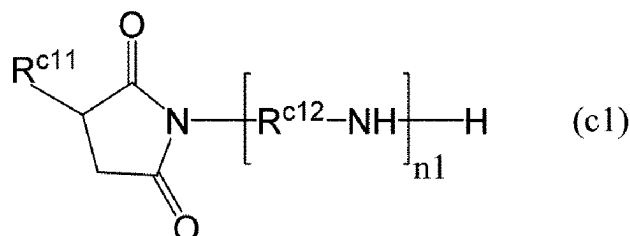
[0078] Moreover, the bisimide compound is preferably one or more selected from the group consisting of an alkenyl succinic acid bisimide compound and an alkyl succinic acid bisimide compound.

(Monoimide compound and bisimide compound)

[0079] As mentioned above, the monoimide compound is preferably one or more selected from the group consisting of

an alkenyl succinic acid monoimide compound and an alkyl succinic acid monoimide compound. The alkenyl succinic acid monoimide compound and the alkyl succinic acid monoimide compound are preferably compounds represented by the following general formula (c1), for example.

[0080] Moreover, the bisimide compound is preferably one or more selected from the group consisting of an alkenyl succinic acid bisimide compound and an alkyl succinic acid bisimide compound. The alkenyl succinic acid bisimide compound and the alkyl succinic acid bisimide compound are preferably compounds represented by the following general formula (c2), for example.



[0081] In the above general formula (c1), $\text{R}^{\text{c}11}$ is an alkenyl group or an alkyl group, $\text{R}^{\text{c}12}$ is an alkylene group having 1 to 6 carbon atoms, and $n1$ is an integer of 1 to 20. In addition, when $n1$ is 2 or more, a plurality of $\text{R}^{\text{c}12}$'s may be the same as or different from each other.

[0082] In the above general formula (c2), $\text{R}^{\text{c}21}$ and $\text{R}^{\text{c}24}$ each independently are an alkenyl group or an alkyl group, $\text{R}^{\text{c}22}$ and $\text{R}^{\text{c}23}$ each independently are an alkylene group having 1 to 6 carbon atoms, and $n2$ is an integer of 0 to 20. In addition, when $n2$ is 2 or more, a plurality of $\text{R}^{\text{c}22}$'s may be the same as or different from each other.

[0083] The alkenyl group or alkyl group that can be selected as $\text{R}^{\text{c}11}$ preferably has a mass average molecular weight (Mw) of 2,000 to 10,000, from the viewpoint of improving the solubility in the base oil (A) and more easily exhibiting the effects of the present invention, more preferably 3,000 to 9,000, and even more preferably 4,000 to 8,000.

[0084] On the other hand, the alkenyl group or alkyl group that can be selected as $\text{R}^{\text{c}21}$ and $\text{R}^{\text{c}24}$ preferably has a mass average molecular weight (Mw) of 500 to 8,000, from the viewpoint of improving the solubility in the base oil (A) and more easily exhibiting the effects of the present invention, more preferably 600 to 4,000, and even more preferably 700 to 2,000.

[0085] Examples of the alkenyl group that can be selected as $\text{R}^{\text{c}11}$, $\text{R}^{\text{c}21}$, and $\text{R}^{\text{c}24}$ include a polybutenyl group, a polyisobutenyl group, and an ethylene-propylene copolymer, and examples of the alkyl group include those obtained by hydrogenating these. As the polybutenyl group, a mixture of 1-butene and isobutene or one obtained by polymerizing high-purity isobutene is preferably used. Among these, the alkenyl group is preferably a polybutenyl group or an isobutenyl group, and examples of the alkyl group include those obtained by hydrogenating a polybutenyl group or an isobutenyl group.

[0086] In the lubricating oil composition of the present embodiment, from the viewpoint of more easily exhibiting the effects of the present invention, the groups that can be selected as $\text{R}^{\text{c}11}$, $\text{R}^{\text{c}21}$, and $\text{R}^{\text{c}24}$ are preferably alkenyl groups, and among the alkenyl groups, polybutenyl groups are more preferable.

[0087] From the viewpoint of improving the solubility in the base oil (A) and more easily exhibiting the effects of the present invention, the alkylene group having 1 to 6 carbon atoms that can be selected as $\text{R}^{\text{c}12}$, $\text{R}^{\text{c}22}$, and $\text{R}^{\text{c}23}$ is preferably a methylene group; various ethylene groups such as 1,1-ethylene groups and 1,2-ethylene groups; various propylene groups such as 1,3-propylene, 1,2-propylene, and 2,2-propylene; various butylene groups; various pentylene groups; and various hexylene groups.

[0088] Moreover, from the same viewpoint, the alkylene group that can be selected as $\text{R}^{\text{c}12}$, $\text{R}^{\text{c}22}$, and $\text{R}^{\text{c}23}$ preferably has 2 to 5 carbon atoms, more preferably 2 to 4 carbon atoms, and even more preferably 2 or 3 carbon atoms.

[0089] From the viewpoint of improving the solubility in the base oil (A) and more easily exhibiting the effects of the present invention, $n1$ in the above general formula (c1) is preferably 2 to 15, more preferably 3 to 10, even more preferably 3 to 5, and still more preferably 3 or 4.

[0090] From the viewpoint of improving solubility of the component (C2) represented by the above general formula (c2)

in base oil and more easily exhibiting the effects of the present invention, n_2 in the above general formula (c2) is preferably 1 to 15, more preferably 2 to 10, even more preferably 2 to 5, and still more preferably 3 or 4.

[0091] The alkenyl succinic acid monoimide, alkyl succinic acid monoimide, alkenyl succinic acid bisimide, or alkyl succinic acid bisimide can usually be produced by reacting an alkenyl succinic anhydride obtained from a reaction between a polyolefin and a maleic anhydride, or an alkyl succinic anhydride obtained by hydrogenating the same, with a polyamine. The monoimide and bisimide can be respectively produced by changing the reaction ratio of the alkenyl succinic anhydride or the alkyl succinic anhydride and the polyamine.

[0092] As an olefin monomer forming the polyolefin, one or more types selected from α -olefins having 2 to 8 carbon atoms can be mixed and used; however, a mixture of isobutene and 1-butene can be suitably used.

[0093] On the other hand, examples of the polyamine include diamines such as ethylene diamine, propylene diamine, butylene diamine, and pentylene diamine, and polyalkylene polyamines such as diethylenetriamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, di(methylethylene) triamine, dibutylene triamine, tributylene tetramine, and pentapentylene hexamine.

[0094] In the lubricating oil composition of the present embodiment, from the viewpoint of more easily exhibiting the effects of the present invention, a total content of the monoimide compound and the bisimide compound is preferably 0.10% by mass to 0.50% by mass, more preferably 0.13% by mass to 0.40% by mass, even more preferably 0.15% by mass to 0.35% by mass, and still more preferably 0.17% by mass to 0.30% by mass, based on the whole amount of the lubricating oil composition.

[0095] In the lubricating oil composition of the present embodiment, from the viewpoint of more easily exhibiting the effects of the present invention, the content ratio of the monoimide compound and the bisimide compound [monoimide compound content/bisimide compound content] is, in terms of mass ratio, preferably more than 0 to 2/1, more preferably 1/3 to 3/2, and even more preferably 2/3 to 3/2.

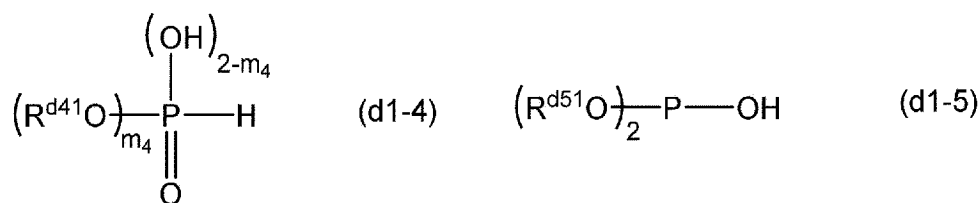
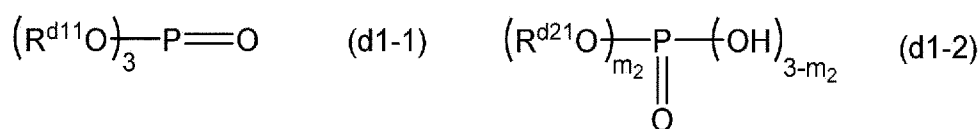
[Phosphorus-based extreme pressure agent that does not contain a sulfur atom]

[0096] It is preferable that the lubricating oil composition of the present embodiment further contains a phosphorus-based extreme pressure agent (hereinafter sometimes referred to as "phosphorus-based extreme pressure agent") that does not contain a sulfur atom.

[0097] When the lubricating oil composition contains the above extreme pressure agent, the lubricating oil composition can have even more excellent wear resistance.

[0098] Preferred examples of the phosphorus-based extreme pressure agent include phosphate ester compounds such as phosphate esters, acid phosphate esters, phosphite esters, and hydrogen phosphite esters, and amine salts of the phosphate ester compounds. More specifically, preferred examples of these phosphate esters, acid phosphate esters, phosphite esters, and hydrogen phosphite esters include phosphate esters represented by the following general formula (d1-1), acid phosphate esters represented by the general formula (d1-2), phosphite esters represented by the general formula (d1-3), and hydrogen phosphite esters represented by the general formulas (d1-4) and (d1-5), respectively.

[0099] The phosphorous-based extreme pressure agent may be used alone or may be used in combination of two or more thereof.



[0100] In the general formulas (d1-1) to (d1-5), R^{d11} , R^{d21} , R^{d31} , R^{d41} , and R^{d51} each independently represent a hydrocarbon group having 1 to 30 carbon atoms. Preferred examples of the hydrocarbon group include an alkyl group, an alkenyl group, an aryl group, and an arylalkyl group, from the viewpoint of obtaining more excellent wear resistance.

[0101] When R^{d11} , R^{d21} , R^{d31} , R^{d41} , and R^{d51} are alkyl groups, the carbon number is, from the viewpoint of obtaining more excellent wear resistance and also considering ease of acquisition and the like, preferably 2 to 20, and more preferably 2 to 10. The alkyl group may be linear, branched, or cyclic; however, in further consideration of ease of acquisition and the like, the alkyl group is preferably linear or branched.

[0102] When R^{d11} , R^{d21} , R^{d31} , R^{d41} , and R^{d51} are alkenyl groups, the carbon number is, from the viewpoint of obtaining more excellent wear resistance and also considering ease of acquisition and the like, preferably 2 to 20, and more preferably 2 to 10. The alkenyl group may be linear, branched, or cyclic, and is preferably linear or branched.

[0103] When R^{d11} , R^{d21} , R^{d31} , R^{d41} , and R^{d51} are aryl groups, the carbon number is, from the viewpoint of obtaining more excellent seizure resistance and wear resistance and also considering ease of acquisition and the like, preferably 6 to 20, and more preferably 6 to 15.

[0104] When R^{d11} , R^{d21} , R^{d31} , R^{d41} , and R^{d51} are arylalkyl groups, the carbon number is, from the viewpoint of obtaining more excellent seizure resistance and wear resistance and also considering ease of acquisition and the like, preferably 6 to 20, and more preferably 6 to 15.

[0105] A plurality of R^{d11} 's, R^{d31} 's, and R^{d51} 's may be the same as or different from each other, and when there are a plurality of R^{d21} 's and R^{d41} 's, they may be the same as or different from each other.

[0106] Furthermore, in the general formula (d1-2), m_2 represents 1 or 2, and in the general formula (d1-4), m_4 represents 1 or 2.

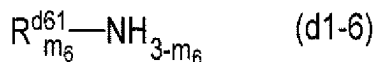
[0107] Examples of the phosphate esters represented by the general formula (d1-1) include triphenyl phosphate, tricresyl phosphate, benzyl diphenyl phosphate, ethyl diphenyl phosphate, tributyl phosphate, ethyl dibutyl phosphate, tert-butylphenyl diphenyl phosphate, di-tert-butylphenyl monophenyl phosphate, cresyl diphenyl phosphate, dicresyl monophenyl phosphate, ethylphenyl diphenyl phosphate, diethylphenyl monophenyl phosphate, triethylphenyl phosphate, trihexyl phosphate, tri(2-ethylhexyl) phosphate, tridecyl phosphate, trilauryl phosphate, trimyristyl phosphate, tripalmityl phosphate, tristearyl phosphate, and trioleyl phosphate.

[0108] Examples of the acid phosphate esters represented by the general formula (d1-2) include mono(di)ethyl acid phosphate, mono(di)n-propyl acid phosphate, mono(di)2-ethylhexyl acid phosphate, mono(di)butyl acid phosphate, mono(di)oleyl acid phosphate, mono(di)isodecyl acid phosphate, mono(di)lauryl acid phosphate, mono(di)stearyl acid phosphate, and mono(di)isostearyl acid phosphate.

[0109] Examples of the phosphite ester represented by the general formula (d1-3) include triethyl phosphite, tributyl phosphite, triphenyl phosphite, tricresyl phosphite, tri(nonylphenyl) phosphite, tri(2-ethylhexyl) phosphite, tridecyl phosphite, trilauryl phosphite, triisooctyl phosphite, diphenylisodecyl phosphite, tristearyl phosphite, and trioleylphosphite.

[0110] Examples of the hydrogen phosphite esters represented by the general formulas (d1-4) and (d1-5) include mono(di)ethyl hydrogen phosphite, mono(di)-n-propyl hydrogen phosphite, mono(di)-n-butyl hydrogen phosphite, mono(di)-2-ethylhexyl hydrogen phosphite, mono(di)lauryl hydrogen phosphite, mono(di)oleyl hydrogen phosphite, mono(di)stearyl hydrogen phosphite, and mono(di)phenyl hydrogen phosphite.

[0111] In addition, examples of amine salts of the phosphate ester compounds such as phosphate esters, acid phosphate esters, phosphite esters, and hydrogen phosphite esters include amine salts formed from these phosphate ester compounds and amines. Here, examples of amines used to form amine salts include primary amines, secondary amines, tertiary amines, and polyalkylene amines, and examples of the primary amines, secondary amines, and tertiary amines include amines represented by the following general formula (d1-6).



[0112] In the general formula (d1-6), R^{d61} represents a hydrocarbon group having 1 to 30 carbon atoms. When the hydrocarbon group is an alkyl group, it may be a hydroxyalkyl group in which at least one of the hydrogen atoms of the alkyl group is substituted with a hydroxy group.

[0113] R^{a61} is preferably an alkyl group having 6 to 18 carbon atoms, an alkenyl group having 6 to 18 carbon atoms, an aryl group having 6 to 18 ring carbon atoms, an arylalkyl group having 7 to 18 carbon atoms, or a hydroxyalkyl group having 6 to 18 carbon atoms, and among these, an alkyl group having 6 to 18 carbon atoms is more preferable.

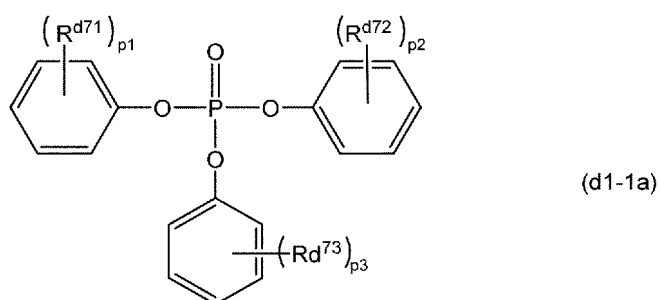
[0114] Further, m_6 is 1, 2 or 3; when m_6 is 1, it is a primary amine, when m_6 is 2, it is a secondary amine, and when m_6 is 3, it is a tertiary amine.

[0115] Examples of the polyalkylene amines include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexaethyleneheptamine, heptaethyleneoctamine, tetrapropylenepentamine, and hexabutyleneheptamine.

[0116] Among these, from the viewpoint of imparting more excellent wear resistance to the lubricating oil composition, it is preferable to use one or more selected from the group consisting of amine salts of phosphate esters and acid phosphate esters.

[0117] The phosphate ester is preferably a compound represented by the above general formula (d1-1), and more

preferably a compound represented by the following general formula (d1-1a).



[0118] In the general formula (d1-1a) above, R^{d71} to R^{d73} each independently are an alkyl group having 1 to 12 carbon atoms. p_1 to p_3 each independently are an integer of 0 to 5.

[0119] Among the compounds represented by the above general formula (d1-1a), from the viewpoint of more easily exhibiting the effects of the present invention, R^{d71} to R^{d73} each independently are preferably an alkyl group having 1 to 10 carbon atoms, more preferably an alkyl group having 1 to 6 carbon atoms, and even more preferably an alkyl group having 1 to 4 carbon atoms.

[0120] Further, it is preferable that p_1 to p_3 each independently are an integer of 0 to 1.

[0121] Here, when a phosphate ester is used alone, it is preferable that one or two of p_1 to p_3 are 0 and the rest is 1. Further, in this case, the alkyl group that can be selected as R^{d71} to R^{d73} is preferably a tert-butyl group.

[0122] In the lubricating oil composition of the present embodiment, the content of the phosphorus-based extreme pressure agent is preferably 0.01% by mass to 1.00% by mass, more preferably 0.05% by mass to 0.60% by mass, and even more preferably 0.10% by mass to 0.40% by mass, based on the whole amount of the lubricating oil composition.

[0123] When the content of the phosphorus-based extreme pressure agent is equal to or more than the above lower limit value, a lubricating oil composition with excellent wear resistance can be easily obtained. Moreover, when the content of the phosphorus-based extreme pressure agent is equal to or less than the above upper limit value, sludge generation can be easily suppressed.

[Additional Extreme Pressure Agent]

[0124] The lubricating oil composition of the present embodiment may further contain an additional extreme pressure agent other than the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group, the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end, and a phosphorus-based extreme pressure agent.

[0125] Examples of the additional extreme pressure agent include an organometallic extreme pressure agent and a sulfur-based extreme pressure agent.

[0126] Examples of the organometallic extreme pressure agent include one or more selected from an organomolybdenum compound such as molybdenum dialkyldithiocarbamate (MoDTC) and molybdenum dialkyldithiophosphate (MoDTP), and an organic zinc compound such as zinc dialkyldithiocarbamate (ZnDTC) and zinc dialkyldithiophosphate (ZnDTP).

[0127] Examples of the sulfur-based extreme pressure agent include one or more selected from sulfurized fats and oils, sulfurized fatty acids, sulfurized esters, sulfurized olefins, monosulfides, polysulfides, dihydrocarbyl polysulfides, thiazole compounds, alkylthiocarbamoyl compounds, thiocarbamate compounds, thioterpene compounds, and dialkylthiodipropionate compounds.

[0128] However, the lubricating oil composition of the present embodiment preferably has a small content of the organometallic extreme pressure agent and the sulfur-based extreme pressure agent. Specifically, the contents of the organometallic extreme pressure agent and the sulfur-based extreme pressure agent each are preferably less than 0.1% by mass, more preferably less than 0.01% by mass, even more preferably less than 0.001% by mass, and still more preferably containing no organometallic extreme pressure agent or sulfur-based extreme pressure agent, based on the whole amount of the lubricating oil composition.

[Other additives]

[0129] The lubricating oil composition of the present embodiment may contain an additional additive for lubricating oil other than the above components as long as the effects of the present invention are not impaired.

[0130] Examples of the additive for lubricating oil include a viscosity index improver, a pour point depressant, a rust

inhibitor, a metal deactivator, an anti-foaming agent, and an antioxidant other than the above-mentioned hindered phenol-based antioxidant and the amine-based antioxidant.

[0131] These additives for lubricating oil may be used alone or may be used in combination of two or more thereof.

[0132] In the present description, an additive such as a viscosity index improver and an anti-foaming agent may be in a form of a solution in which the additive is diluted with and dissolved in part of the base oil (A), taking into consideration handleability and the solubility in the base oil (A). In such a case, the above-described content of the additive such as an anti-foaming agent and a viscosity index improver means a content in terms of active ingredient (in terms of resin content) excluding the diluent oil, in the present description.

(Viscosity index improver)

[0133] Examples of the viscosity index improver include polymers such as a non-dispersant-type polymethacrylate, a dispersant-type polymethacrylate, an olefinic copolymer (e.g., an ethylene-propylene copolymer), a dispersant-type olefinic copolymer, and a styrene-based copolymer (e.g., a styrene-diene copolymer and a styrene-isoprene copolymer).

[0134] When the lubricating oil composition of the present embodiment contains a viscosity index improver, the content of the viscosity index improver in terms of resin content is preferably 0.01 to 10% by mass, more preferably 0.02 to 5.0% by mass, and even more preferably 0.03 to 2.0% by mass, based on the whole amount of the lubricating oil composition.

(Pour point depressant)

[0135] Examples of the pour point depressant include polymethacrylate having a mass average molecular weight of about 50,000 to 150,000. When the lubricating oil composition according to one embodiment of the present invention contains a pour point depressant, the content of the pour point depressant is preferably 0.01 to 5% by mass, and more preferably 0.02 to 2% by mass, based on the whole amount of the lubricating oil composition.

(Rust inhibitor)

[0136] Examples of the rust inhibitor include metal sulfonates, alkylbenzene sulfonates, dinonylnaphthalene sulfonates, organic phosphite esters, organic phosphate esters, organic sulfonic acid metal salts, organic phosphoric acid metal salts, alkenyl succinic acid esters, and alkenyl succinic acid polyhydric alcohol esters.

[0137] When the lubricating oil composition of the present embodiment contains a rust inhibitor, the content of the rust inhibitor is preferably 0.01 to 10.0% by mass, and more preferably 0.03 to 5.0% by mass, based on the whole amount of the lubricating oil composition.

(Metal deactivator)

[0138] Examples of the metal deactivator include a benzotriazole compound, a tolyltriazole compound, a thiadiazole compound, an imidazole compound, and a pyrimidine compound.

[0139] When the lubricating oil composition of the present embodiment contains a metal deactivator, the content of the metal deactivator is preferably 0.001 to 1.0% by mass, and more preferably 0.005 to 0.50% by mass, based on the whole amount of the lubricating oil composition.

(Anti-foaming agent)

[0140] Examples of the anti-foaming agent include a silicone anti-foaming agent, a fluorine-based anti-foaming agent such as fluorosilicone oil and a fluoroalkyl ether, and a polyacrylate-based anti-foaming agent.

[0141] When the lubricating oil composition of the present embodiment contains an anti-foaming agent, the content of the anti-foaming agent in terms of resin content is preferably 0.0001 to 0.1% by mass, and more preferably 0.0010 to 0.0300% by mass, based on the whole amount of the lubricating oil composition.

(Antioxidant other than hindered phenol-based antioxidant and amine-based antioxidant)

[0142] Examples of the antioxidant other than the hindered phenol-based antioxidant and the amine-based antioxidant include a metal-based antioxidant and a sulfur-based antioxidant.

[0143] In addition, from the viewpoint of more easily exhibiting the effects of the present invention, the content of the metal-based antioxidant and the sulfur-based antioxidant is preferably small.

[0144] Specifically, the contents of the metal-based antioxidant and the sulfur-based antioxidant each are preferably less than 0.1% by mass, more preferably less than 0.01% by mass, even more preferably less than 0.001% by mass, and

still more preferably containing no metal-based antioxidant or sulfur-based antioxidant, based on the whole amount of the lubricating oil composition.

[Various physical properties of lubricating oil composition]

(40°C kinematic viscosity)

[0145] The kinematic viscosity at 40°C of the lubricating oil composition of the present embodiment is preferably 19.8 mm²/s to 165 mm²/s, more preferably 28.8 mm²/s to 110 mm²/s, and even more preferably 41.4 mm²/s to 74.8 mm²/s.

[0146] When the 40°C kinematic viscosity of the lubricating oil composition is 19.8 mm²/s or more, it is easy to obtain a lubricating oil composition with a high flash point and excellent lubricating performance.

[0147] Furthermore, when the 40°C kinematic viscosity of the lubricating oil composition is 110 mm²/s or less, the viscous resistance at low temperatures does not become so large, making it easier to maintain good operation of hydraulic equipment.

(Viscosity index)

[0148] The viscosity index of the lubricating oil composition of the present embodiment is preferably 80 or more, more preferably 90 or more, even more preferably 100 or more, and still more preferably 105 or more.

[0149] In the lubricating oil composition of the present embodiment, it is preferable that the time required for the coefficient of friction to exceed 0.30 in the SRV friction test measured under the following conditions is 35.0 minutes or more, more preferably 40.0 minutes or more, and even more preferably 45.0 minutes or more.

(SRV friction test)

[0150] Abreak-in operation was performed for 1 minute at a load of 50 N using an SRV testing machine (manufactured by Optimol) and using the prepared lubricating oil composition. Thereafter, a friction test was performed while sliding under the following conditions, and the time required for the coefficient of friction to exceed 0.30 was measured.

- Ball: SUJ2 coated with manganese phosphate
- Disc: SUJ2
- Load: 200 N
- Amplitude: 0.1 mm
- Frequency: 100 Hz
- Temperature: 100°C
- Test time: maximum 2 hours

[Method for Producing Lubricating Oil Composition]

[0151] The method for producing the lubricating oil composition of the present invention is not particularly limited, and is a method for producing a lubricating oil composition including a step of mixing the base oil (A), the overbased metal detergent (B), the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group, and the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end.

[0152] The method for mixing the above components is not particularly limited, and examples thereof include a method including a step of blending the component (B), the component (C), and the component (D) into the base oil (A). The component (B), the component (C), and the component (D) may be blended into the base oil (A) simultaneously or separately. The same applies to components other than the component (B), the component (C), and the component (D). Each component may also be blended in a form of a solution (dispersion) with the addition of dilution oil or other substances. After blending each component, it is preferable to stir and uniformly disperse the components by a known method.

[Application of Lubricating Oil Composition]

[0153] The lubricating oil composition of the present embodiment can be used in an apparatus such as hydraulic equipment, gear oil, and bearings. Preferably, among these, the lubricating oil composition can be suitably used in apparatus such as hydraulic equipment, gear mechanisms, and bearings that are equipped with a sliding member having a phosphate coating on at least a part of a sliding surface.

[0154] Therefore, according to the present invention, the following methods for using are provided.

- A method of using the lubricating oil composition of the present embodiment in an apparatus such as hydraulic equipment, gear oil, and bearings.
- A method of using the lubricating oil composition of the present invention in an apparatus equipped with a sliding member having a phosphate coating on at least a part of a sliding surface.

Examples

[0155] The present invention will be more specifically described by the following Examples; however, the present invention is not limited to the following Examples.

[Measurement Method of Various Physical Property Values]

[0156] The measurement of each property of each raw material used in each of Examples and Comparative Examples and the lubricating oil composition of each of Examples and Comparative Examples was performed according to the following procedure.

(1) 40°C kinematic viscosity, 100°C kinematic viscosity, and viscosity index

[0157] Measurement and determination were performed in accordance with JIS K 2283:2000.

(2) Calcium content and phosphorus content

[0158] The calcium content and phosphorus content of the lubricating oil composition were measured using an ICP plasma emission spectrometer.

(3) Acid value of lubricating oil composition

[0159] The acid value of the lubricating oil composition was measured in accordance with JIS K 2501:2003 (indicator method).

(4) Base number of lubricating oil composition

[0160] The base number of the lubricating oil composition was measured in accordance with JIS K 2501:2003 (hydrochloric acid method).

[Examples 1 to 4, Comparative Examples 1 to 3]

[0161] Base oils and various additives shown below were thoroughly mixed in blending amounts (% by mass) shown in Table 1 to prepare lubricating oil compositions respectively.

[0162] Details of the base oils and various additives used in Examples 1 to 4 and Comparative Examples 1 to 3 are as follows.

<Base Oil (A)>

[0163]

· Base oil 1: mineral oil that is classified into Group II in API base oil category and has been subjected to a hydrogenation refining treatment (kinematic viscosity at 40°C = 30.60 mm²/s, kinematic viscosity at 100°C = 5.285 mm²/s, viscosity index = 104).

· Base oil 2: mineral oil that is classified into Group II in API base oil category and has been subjected to a hydrogenation refining treatment (kinematic viscosity at 40°C = 90.51 mm²/s, kinematic viscosity at 100°C = 10.89 mm²/s, viscosity index = 107).

<Overbased Metal Detergent (B)>

[0164]

· Ca sulfonate: overbased calcium sulfonate, base number: 294 mgKOH/g, content of calcium atom: 12.0% by mass.

- Ca salicylate: overbased calcium salicylate, base number: 219 mgKOH/g, content of calcium atom: 8.0% by mass.
- Ca phenate: overbased calcium phenate, base number: 366 mgKOH/g, content of calcium atom: 14.3% by mass.

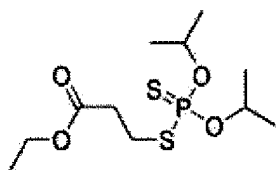
<Neutral Metal Detergent (B')>

[0165]

- Ca sulfonate: neutral calcium sulfonate, base number: 11.3 mgKOH/g, content of calcium atom: 2.15% by mass.

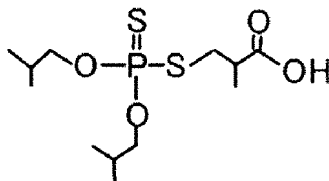
<Sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group>

[0166] A compound represented by the following formula was used as the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group.



<Sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end>

[0167] A compound represented by the following formula was used.



[0168] The compound represented by the above formula is a compound in which L² is -CH₂CH(CH₃)- and R⁴ and R⁵ are an isobutyl group in the general formula (2).

<Imide Compound>

[0169]

- Monoimide compound: a polybutenyl succinic acid monoimide compound having a mass average molecular weight (Mw) of polybutenyl groups of 6,300, a nitrogen atom content of 1.75% by mass, and a base number of 40.0 mgKOH/g.
- Bisimide compound: a polybutenyl succinic acid bisimide compound having a mass average molecular weight (Mw) of polybutenyl groups of 1,000, a nitrogen atom content of 1.15% by mass, and a base number of 19.5 mgKOH/g.

[0170] The mass average molecular weight of polybutenyl groups is a value obtained by measuring the mass average molecular weight (Mw) of polybutene, which is a raw material for the polybutenyl group, under the following conditions and evaluating the measured result as a mass average molecular weight (Mw) in terms of standard polystyrene.

- SEC device: HLC-8220GPC manufactured by Tosoh Corporation
- Column: TSKguardcolumn HXL-H + TSKgel GMH-XL 2 pieces + G2000H-XL 1 piece manufactured by Tosoh Corporation
- Solvent: tetrahydrofuran (special grade without stabilizers, manufactured by Wako Pure Chemical Corporation)
- Detector: differential refractive index (RI) detector, UV detector
- Concentration: 0.1 w/v%
- Injection volume: 100 μL
- Flow rate: 1.0 mL/min
- Column temperature: 40°C
- Standard sample for calibration curve: TSK standard polystyrene manufactured by Tosoh Corporation

· Analysis software: GPC-8020 model II

<Other Additives>

[0171]

- Phosphorus-based extreme pressure agent: tricresyl phosphate
- Pour point depressant: polymethacrylate with a mass average molecular weight (Mw) of 69,000
- Hindered phenol-based antioxidant: 2,6-di-tert-butyl-p-cresol
- Amine-based antioxidant: monobutylphenyl mono-octylphenylamine
- Metal deactivator: N-dialkylaminomethylbenzotriazole
- Anti-foaming agent: polyacrylate-based anti-foaming agent (active ingredient concentration: 5% by mass or less)

[Evaluation]

[0172] Regarding the lubricating oil compositions obtained in Examples 1 to 4 and Comparative Examples 1 to 3, the various physical property values described above were measured, and the following SRV friction test and shell wear test were also conducted. The results are shown in Table 1.

(SRV friction test)

[0173] Abreak-in operation was performed for 1 minute at a load of 50 N using an SRV testing machine (manufactured by Optimol) and using the prepared lubricating oil composition. Thereafter, a friction test was performed while sliding under the following conditions, and the time required for the coefficient of friction to exceed 0.30 was measured.

- Ball material: SUJ2 coated with manganese phosphate
- Disc material: SUJ2
- Load: 200 N
- Amplitude: 0.1 mm
- Frequency: 100 Hz
- Temperature: 100°C
- Test time: maximum 2 hours

(Shell wear test)

[0174] Using a shell wear tester, the wear resistance of the lubricating oil composition was evaluated under the following test conditions in accordance with ASTM D 4172. The results were expressed as a wear mark diameter (mm) of a test hard ball.

- Load: 294 N
- Rotation speed: 1,200 rpm
- Temperature: 50°C
- Test time: 30 minutes

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Table 1

			Example 1	Example 2	Example 3	Example 4
Composition of lubricating oil composition (% by mass)	Base oil (A)	Base oil 1	60.92	60.92	60.89	60.92
		Base oil 2	37.45	37.45	37.45	37.45
	Overbased metal detergent (B)	Ca sulfonate	0.10		0.10	
		Ca salicylate		0.10		
		Ca phenate				0.10
	Neutral metal detergent (B')	Ca sulfonate				
	Sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group		0.20	0.20	0.20	0.20
	Sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end		0.07	0.07	0.10	0.07
	Imide compound	Monoimide compound	0.10	0.10	0.10	0.10
		Bisimide compound	0.10	0.10	0.10	0.10
	Phosphorus-based extreme pressure agent		0.20	0.20	0.20	0.20
	Pour point depressant		0.30	0.30	0.30	0.30
	Hindered phenol-based antioxidant		0.40	0.40	0.40	0.40
	Amine-based antioxidant		0.05	0.05	0.05	0.05
	Metal deactivator		0.01	0.01	0.01	0.01
	Anti-foaming agent		0.10	0.10	0.10	0.10
	Total		100.00	100.00	100.00	100.00
	Physical properties	40°C kinematic viscosity	mm ² /s	46.36	46.56	46.47
100°C kinematic viscosity		mm ² /s	7.018	7.066	7.055	7.062
Viscosity index			109	110	110	110
Acid value		mgKOH/g	0.12	0.12	0.18	0.12
Base number		mgKOH/g	0.33	0.25	0.34	0.37
Calcium content		ppm by mass	128	85	129	135
Phosphorus content		ppm by mass	422	424	452	421
Evaluation	SRV friction test	minute	49.0	49.1	37.0	37.4
	Shell wear test	mm	0.43	0.39	0.37	0.40

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(continued)

				Comparative Example 1	Comparative Example 2	Comparative Example 3
5	Composition of lubricating oil composi- tion (% by mass)	Base oil (A)	Base oil 1	60.92	61.12	60.99
			Base oil 2	37.45	37.45	37.45
		Overbased metal deter- gent (B)	Ca sulfonate		0.10	0.10
10			Ca salicylate			
			Ca phenate			
		Neutral metal detergent (B')	Ca sulfonate	0.10		
15		Sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group		0.20		0.20
		Sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end		0.07	0.07	
20		Imide com- pound	Monoimide compound	0.10	0.10	0.10
			Bisimide compound	0.10	0.10	0.10
25		Phosphorus-based extreme pressure agent		0.20	0.20	0.20
		Pour point depressant		0.30	0.30	0.30
30		Hindered phenol-based antioxi- dant		0.40	0.40	0.40
		Amine-based antioxidant		0.05	0.05	0.05
		Metal deactivator		0.01	0.01	0.01
35		Anti-foaming agent		0.10	0.10	0.10
		Total		100.00	100.00	100.00
40	Physical properties	40°C kine- matic viscosity	mm ² /s	46.54	46.78	46.73
		100°C kine- matic viscosity	mm ² /s	7.063	7.084	7.058
		Viscosity index		110	109	109
45		Acid value	mgKOH/g	0.16	0.11	0.03
		Base number	mgKOH/g	0.08	0.34	0.35
		Calcium con- tent	ppm by mass	23	127	130
50		Phosphorus content	ppm by mass	423	232	361
	Evaluation	SRV friction test	minute	33.0	30.1	19.4
55		Shell wear test	mm	0.37	0.37	0.46

[0175] The following can be seen from Table 1.

[0176] It can be seen that in the lubricating oil compositions of Examples 1 to 4, the time required for the coefficient of

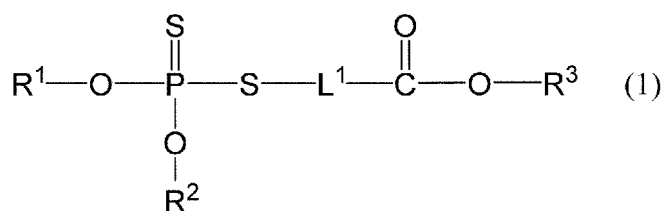
friction to exceed 0.30 in the SRV friction test was 37.0 minutes or more, and the lubricating oil compositions have excellent wear resistance when a sliding member having a phosphate coating was used. In particular, in Examples 1 and 2, the above-mentioned required time was 49.0 minutes or more, which shows that the wear resistance is more excellent when a sliding member having a phosphate coating was used.

[0177] In contrast, in the lubricating oil compositions of Comparative examples 1 to 3, in which any of the overbased metal detergent (B), the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group, and the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end is not blended, the time required for the coefficient of friction to exceed 0.30 in the SRV friction test was 33.0 minutes or less.

[0178] Further, in the shell wear test, the wear mark diameters in Examples 1 to 4 were 0.37 to 0.43 mm, whereas the wear mark diameters in Comparative Examples 1 to 3 were 0.37 to 0.46 mm.

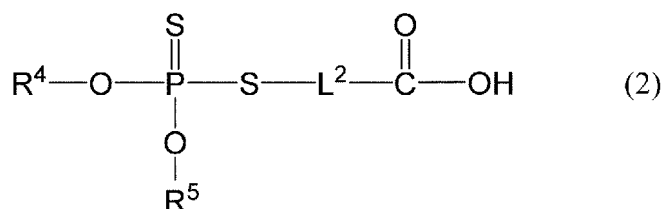
Claims

1. A lubricating oil composition comprising a base oil (A), an overbased metal detergent (B), a sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group, and a sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end.
2. The lubricating oil composition according to claim 1, wherein the overbased metal detergent (B) is one or more selected from an overbased calcium sulfonate with a base number of 100 mgKOH/g or more and an overbased calcium salicylates with a base number of 100 mgKOH/g or more.
3. The lubricating oil composition according to claim 1 or 2, wherein the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group is a thiophosphoric acid ester having a carboxylic acid ester group.
4. The lubricating oil composition according to any one of claims 1 to 3, wherein the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group is a thiophosphoric acid ester represented by the following general formula (1),



In the above general formula (1), R¹ to R³ each independently represent a hydrocarbon group having 3 to 20 carbon atoms, and L¹ represents a linear or branched alkylene group having 1 to 8 carbon atoms.

5. The lubricating oil composition according to any one of claims 1 to 4, wherein the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end is a thiophosphoric acid ester having a carboxy group at an end.
6. The lubricating oil composition according to any one of claims 1 to 5, wherein the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end is a thiophosphoric acid ester represented by the following general formula (2),



In the above general formula (2), R⁴ and R⁵ each independently represent a hydrocarbon group having 3 to 20 carbon atoms, and L² represents a linear or branched alkylene group having 1 to 8 carbon atoms.

7. The lubricating oil composition according to any one of claims 1 to 6, wherein a ratio between a content of the sulfur-phosphorus extreme pressure agent (C) having a carboxylic acid ester group and a content of the sulfur-phosphorus extreme pressure agent (D) having a carboxy group at an end is, in terms of a mass ratio of the content of the component (C) to a total content of the component (C) and component (D), 50 to 95% by mass.
8. The lubricating oil composition according to any one of claims 1 to 7, wherein an organometallic extreme pressure agent has a content of less than 0.1% by mass based on a whole amount of a hydraulic oil composition.
9. The lubricating oil composition according to any one of claims 1 to 8, further comprising a hindered phenol-based antioxidant.
10. The lubricating oil composition according to any one of claims 1 to 9, further comprising an amine-based antioxidant.
11. The lubricating oil composition according to any one of claims 1 to 10, further comprising an imide compound.
12. The lubricating oil composition according to any one of claims 1 to 11, used in an apparatus equipped with a sliding member having a phosphate coating on at least a part of a sliding surface.
13. A lubrication method for lubricating an apparatus equipped with a sliding member having a phosphate coating on at least a part of a sliding surface using the lubricating oil composition according to any one of claims 1 to 12.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/011901

A. CLASSIFICATION OF SUBJECT MATTER

C10M 169/04(2006.01)i; *C10M 129/10*(2006.01)i; *C10M 133/12*(2006.01)i; *C10M 133/16*(2006.01)i;
C10M 133/56(2006.01)i; *C10M 137/10*(2006.01)i; *C10M 159/22*(2006.01)i; *C10M 159/24*(2006.01)i;
C10N 30/06(2006.01)n; *C10N 40/02*(2006.01)n; *C10N 40/04*(2006.01)n; *C10N 40/08*(2006.01)n
 FI: C10M169/04; C10M129/10; C10M133/12; C10M133/16; C10M133/56; C10M137/10 Z; C10M159/22; C10M159/24;
 C10N30/06; C10N40/02; C10N40/04; C10N40/08

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; C10M129/10; C10M133/12; C10M133/16; C10M133/56; C10M137/10; C10M159/22; C10M159/24;
 C10N30/06; C10N40/02; C10N40/04; C10N40/08

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2023
 Registered utility model specifications of Japan 1996-2023
 Published registered utility model applications of Japan 1994-2023

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

CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 7-150175 A (TONEN CORP.) 13 June 1995 (1995-06-13) claims, paragraph [0011], examples	1-13
A	JP 2011-162617 A (JX NIPPON OIL & ENERGY CORP.) 25 August 2011 (2011-08-25) claims, example 6	1-13
A	JP 2020-164620 A (IDEMITSU KOSAN CO., LTD.) 08 October 2020 (2020-10-08) claims, paragraphs [0033]-[0035], example 5	1-13
A	JP 2016-180101 A (CHEVRON JAPAN LTD.) 13 October 2016 (2016-10-13) claims, examples	1-13
A	JP 2014-118534 A (IDEMITSU KOSAN CO., LTD.) 30 June 2014 (2014-06-30) claims, examples, comparative examples	1-13

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

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“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

15 May 2023

Date of mailing of the international search report

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Name and mailing address of the ISA/JP

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International application No.
PCT/JP2023/011901

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2009-161729 A (SHOWA SHELL SEKIYU KK) 23 July 2009 (2009-07-23) claims, paragraphs [0021], [0022], examples	1-13
A	JP 2018-95751 A (IDEMITSU KOSAN CO., LTD.) 21 June 2018 (2018-06-21) claims, examples	1-13

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2023/011901

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 7-150175 A	13 June 1995	(Family: none)	
JP 2011-162617 A	25 August 2011	(Family: none)	
JP 2020-164620 A	08 October 2020	(Family: none)	
JP 2016-180101 A	13 October 2016	US 2016/0281022 A1 claims, examples EP 3072949 A1 CN 105985830 A	
JP 2014-118534 A	30 June 2014	US 2015/0337231 A1 claims, examples, comparative examples WO 2014/098152 A1 EP 2937410 A1 CN 104837971 A KR 10-2015-0096397 A	
JP 2015-25115 A	05 February 2015	(Family: none)	
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Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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