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(54) LUBRICATING OIL COMPOSITION

(57) The present invention provides a lubricating oil composition exhibit excellent friction reduction properties with a small amount of molybdenum. The lubricating oil composition comprises a lubricating base oil, (A) a phosphoric acid ester metal salt represented by formula (1) and (B) an organic molybdenum compound with a ratio of molybdenum to sulfur of 1 : 3.5 or greater. (In formula 1, R_1 to R_4 are each a hydrocarbon group having 1 to 30 carbon atoms, an alkyl or alkenyl group having 1 to 30 carbon atoms, or an alkylthioethyl comprising an alkyl group having 1 to 30 carbon atoms and may be the same or different from each other; X_1, X_2, X_3 and X_4 are each sulfur or oxygen, either X_1 or X_2 is oxygen or both are oxygen, and either X_3 or X_4 is oxygen or both are oxygen; and Y is a metal element.)

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Description

Technical Field

[0001] The present invention relates to a novel lubricating oil composition, more specifically such a lubricating oil composition produced by blending a base oil with a phosphoric acid ester metal salt and a molybdenum friction modifier with a specific structure and having excellent friction-reducing properties. In particular, the present invention relates to a lubricating oil composition suitably used as an internal combustion engine lubricating oil.

Background Art

[0002] Conventionally, lubricating oil has been used in an internal combustion engine, a transmission or grease to allow the smooth operation thereof. In particular, a lubricating oil (engine oil) for an internal combustion engine is required to exhibit performances of higher levels because internal combustion engines have been improved in performances, enhanced in output and used under severe working conditions. In order to meet such demands, conventional engine oils have contained various additives such as an antiwear agent, a metallic detergent, an ashless dispersant, and an anti-oxidant (for example, see Patent Literatures 1 to 3 below). For a fuel saving engine oil, a lubricating oil has been used, which contains various additives such as a friction modifier (FM) in combination for reducing the friction loss and fuel consumption since energy loss is large at friction parts where the oil is involved (see, for example, Patent Literature 4). A friction reducing technique where zinc dialkyldithiophosphate (ZDTP) is used in combination with a molybdenum compound is most common, but unless the molybdenum compound is blended in a relatively large amount, excellent friction-reducing properties cannot be obtained.

[0003] Furthermore, both the molybdenum compound and ZDTP are metal-based and if used in a lubricating oil for an internal combustion engine causes a trouble that they contaminate an exhaust-gas after-treatment system and consequently reduce the purification efficiency thereof. The use of a molybdenum compound in a large amount may possibly lead to an increase in deposit or adversely affect sealing materials due to its degradation, and thus a sufficient friction reducing effect is desirously exhibited with the molybdenum compound in an amount as small as possible.

Citation List

Patent Literature

[0004]

Patent Literature 1: Japanese Patent Application Laid-Open Publication 2001-279287
Patent Literature 2: Japanese Patent Application Laid-Open Publication 2002-129182
Patent Literature 3: Japanese Patent Application Laid-Open Publication No. 08-302378
Patent Literature 4: Japanese Patent Application Laid-Open Publication No. 06-306384

Summary of Invention

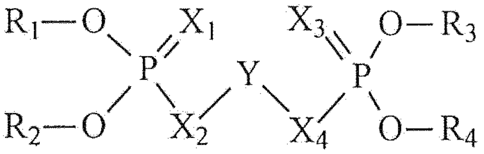
Technical Problem

[0005] The present invention has an object to provide a lubricating oil composition to be used for internal combustion engines, automatic transmissions or in greases that can exhibit excellent friction-reducing properties even with a small amount of molybdenum and is particularly suitably used as an internal combustion engine lubricating oil.

Solution to Problem

[0006] As the result of extensive research and study of the above-described problems, the inventors of the present invention has accomplished the present invention.

[0007] That is, the present invention relates to a lubricating oil composition comprising a lubricating base oil, (A) a phosphoric acid ester metal salt represented by formula (1) and (B) an organic molybdenum compound with a ratio of molybdenum to sulfur of 1: 3.5 or greater:



(1)

wherein R_1 to R_4 are each a hydrocarbon group having 1 to 30 carbon atoms, an alkyl or alkenyl group having 1 to 30 carbon atoms, or an alkylthioethyl comprising an alkyl group having 1 to 30 carbon atoms and may be the same or different from each other; X_1, X_2, X_3 and X_4 are each sulfur or oxygen, either X_1 or X_2 is oxygen or both are oxygen, and either X_3 or X_4 is oxygen or both are oxygen; and Y is a metal element.

Advantageous Effect of Invention

[0008] The present invention can provide a lubricating oil composition which can suppress the properties thereof from degrading and alleviate the adverse effect on an exhaust-gas after-treatment system with a small amount of molybdenum and further can decrease sufficiently friction under mixed lubricating conditions and is excellent in friction loss reduction and fuel consumption reduction properties.

Description of Embodiments

[0009] The present invention will be described in more detail below.

[0010] Examples of lubricating base oils used in the lubricating oil composition of the present invention (hereinafter referred to as "the lubricating base oil of the present invention") include mineral base oils and/or synthetic base oils.

[0011] Examples of the mineral base oil include paraffinic mineral base oils which can be produced by subjecting a lubricating oil fraction produced by atmospheric- and/or vacuum-distillation of a crude oil, to any one of or any suitable combination of refining processes selected from solvent deasphalting, solvent extraction, hydrocracking, hydroisomerizing, solvent dewaxing, catalytic dewaxing, hydrorefining, sulfuric acid treatment, and clay treatment; n-paraffins; and iso-paraffins.

[0012] Examples of preferred mineral base oils include base oils produced by refining the following base oils (1) to (7) and/or lubricating oil fractions recovered therefrom in a given process to recover lubricating oil fractions:

(1) a whole vacuum gas oil (WVGO) produced by vacuum distillation of the topped crude of a paraffin-base crude oil and/or a mixed-base crude oil;
(2) a wax produced by dewaxing of lubricating oil (slack wax) and/or a synthetic wax produced through a gas to liquid (GTL) process (Fischer-Tropsch wax, GTL wax);
(3) a mixed oil of one or more types selected from the above base oils (1) and (2) or an oil produced by mild-hydrocracking the mixed oil;
(4) a mixed oil of two or more base oils selected from (1) to (3) above;
(5) a deasphalted oil (DAO) produced by deasphalting a vacuum residue of a topped crude of a paraffin-base crude oil and/or a mixed-base crude oil;
(6) an oil produced by mild-hydrocracking (MHC) the base oil (5);
(7) a mixed oil of two or more base oils selected from (1) to (6) above.

[0013] The above-mentioned given refining process is preferably hydrorefining such as hydrocracking or hydrofinishing, solvent refining such as furfural extraction, dewaxing such as solvent dewaxing and catalytic dewaxing, clay refining with acidic clay or active clay, or chemical (acid or alkali) refining such as sulfuric acid treatment and sodium hydroxide treatment. In the present invention, any one or more of these refining processes may be used in any combination and any order.

[0014] The mineral base oil is particularly preferably the following base oil (8) :

(8) a hydrocracked mineral oil produced by hydrocracking a base oil selected from the base oils (1) to (7) or a lubricating oil fraction recovered therefrom, and subjecting the resulting product or a lubricating oil fraction recovered therefrom by distillation, to a dewaxing treatment such as solvent or catalytic dewaxing, optionally followed by distillation.

[0015] If necessary, a solvent refining process and/or hydrofinishing process may be additionally carried out at appropriate timing upon production of the above lubricating base oil (8).

[0016] No particular limitation is imposed on the sulfur content of the mineral base oil, which is. however, preferably

100 ppm by mass or less, more preferably 50 ppm by mass or less, more preferably 10 ppm by mass or less, and particularly preferably 5 ppm by mass or less with the objective of further improving the thermal/oxidation stability and reducing the sulfur content.

[0017] The $\%C_A$ of the mineral base oil is preferably 2 or less, more preferably 1 or less, more preferably 0.8 or less, particularly preferably 0.5 or less, most preferably 0. If the $\%C_A$ is greater than 2, the resulting composition would tend to be degraded in viscosity-temperature characteristics, thermal/oxidation stability and fuel efficiency.

[0018] The lubricating base oil used in the present invention may be a synthetic base oil. Examples of synthetic base oils include poly-α-olefins and hydrogenated compounds thereof; isobutene oligomers and hydrogenated compounds thereof; paraffins; alkylbenzenes; alkylnaphthalenes; diesters such as ditridecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate and di-2-ethylhexyl sebacate; polyol esters such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol 2-ethylhexanoate and pentaerythritol pelargonate; polyoxyalkylene glycols; dialkyldiphenyl ethers; and polyphenyl ethers. Preferred synthetic lubricating base oils are poly-α-olefins. Typical examples of poly-α-olefins include oligomers or cooligomers of α-olefins having 2 to 32, preferably 6 to 16 carbon atoms, such as 1-octene oligomer, decene oligomer, ethylene-propylene cooligomer, and hydrogenated compounds thereof.

[0019] The viscosity index of the lubricating base oil used in the present invention is preferably 110 or greater, more preferably 120 or greater, more preferably 125 or greater and preferably 160 or less. A viscosity index of less than 110 would not only cause the viscosity-temperature characteristics, thermal/oxidation stability, anti-evaporation properties to degrade but also cause the friction coefficient to increase and cause the anti-wear properties to degrade. A viscosity index of greater than 160 would tend to degrade the low temperature viscosity characteristics.

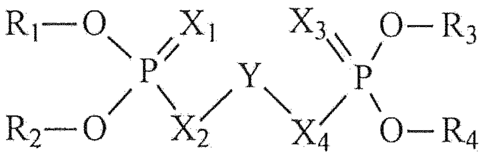
[0020] The viscosity index referred herein denotes the viscosity index measured in accordance with JIS K 2283-1993.

[0021] The 100°C kinematic viscosity of the lubricating base oil used in the present invention is preferably 10 mm^2/s or less, more preferably 6 mm^2/s or less, more preferably 5.0 mm^2/s or less, particularly preferably 4.5 mm^2/s or less, most preferably 4.2 mm^2/s or less. Whilst, the kinematic viscosity is preferably 1 mm^2/s or greater, more preferably 1.5 mm^2/s or greater, more preferably 2 mm^2/s or greater, particularly preferably 2. 5 mm^2/s or greater, most preferably 3 mm^2/s or greater. The 100°C kinematic viscosity referred herein denotes the kinematic viscosity at 100°C defined by ASTM D-445. If the lubricating base oil component has a 100°C kinematic viscosity of greater than 6 mm^2/s, the resulting composition would be degraded in low temperature viscosity characteristics and may not obtain sufficiently improved fuel economy. It the 100°C kinematic viscosity is less than 1 mm^2/s, the resulting lubricating oil composition would be poor in lubricity due to its insufficient oil film formation at lubricating sites and would be large in evaporation loss of the composition.

[0022] The above lubricating base oils may be used alone or in combination with one or more types of other base oils. When the base oil of the present invention is used in combination with the other base oils, the proportion of the base oil of the present invention in the mixed base oil is preferably 30 percent by mass or more, more preferably 50 percent by mass or more, more preferably 70 percent by mass or more.

[0023] No particular limitation is imposed on the other base oils used in combination with the base oil of the present invention. However, examples of the other mineral base oils include solvent-refined mineral oils, hydrocracked mineral oils, hydrorefined mineral oils, and solvent-dewaxed mineral oils, all of which have a 100°C kinematic viscosity of greater than 10 mm^2/s and 200 mm^2/s or less. Examples of the other synthetic base oils include those having a 100°C kinematic viscosity outside the range of 1 to 10 mm^2/s.

[0024] Component (A) of the lubricating oil composition of the present invention is a phosphoric acid ester metal salt represented by formula (1).



(1)

[0025] In formula(1), R_1 through R_4 are each a hydrocarbon group having 1 to 30 carbon atoms, an alkyl or alkenyl group having 1 to 30 carbon atoms, or an alkylthioethyl comprising an alkyl group having 1 to 30 carbon atoms and may be the same or different from each other; X_1, X_2, X_3 and X_4 are each sulfur or oxygen, either X_1 or X_2 is oxygen or both are oxygen, and either X_3 or X_4 is oxygen or both are oxygen; and Y is a metal element.

[0026] Specific examples of the hydrocarbon group having 1 to 30 carbon atoms represented by R_1 through R_4 include alkyl, cycloalkyl or alkenyl, alkyl-substituted cycloalkyl, aryl, alkyl-substituted aryl, and arylalkyl groups.

[0027] Examples of the alkyl group include those such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl groups (these alkyl groups may be straight-chain or branched).

[0028] Examples of the cycloalkyl group include those having 5 to 7 carbon atoms, such as cyclopentyl, cyclohexyl and cycloheptyl groups.

[0029] Examples of the alkylcycloalkyl group include those, of which the alkyl groups may bond to any position of the cycloalkyl group, having 6 to 11 carbon atoms, such as methylcyclopentyl, dimethylcyclopentyl, methylethylcyclopentyl, diethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, methylethylcyclohexyl, diethylcyclohexyl, methylcycloheptyl, dimethylcycloheptyl, methylethylcycloheptyl and diethylcycloheptyl groups.

[0030] Examples of the alkenyl group include those, which may be straight-chain or branched and the position of which the double bond may vary, such as butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, and octadecenyl groups.

[0031] Examples of the aryl group include those such as phenyl and naphthyl groups.

[0032] Examples of the alkylaryl group include those, of which the alkyl groups may be straight-chain or branched and bond to any position of the aryl group, having 7 to 18 carbon groups, such as tolyl, xylyl, ethylphenyl, propylphenyl, butylphenyl, pentylphenyl, hexylphenyl, heptylphenyl, octyphenyl, nonylphenyl, decylphenyl, undecylphenyl, and dodecylphenyl groups.

[0033] Examples of the arylalkyl group include those, of which the alkyl groups may be straight-chain or branched, having 7 to 12 carbon atoms, such as benzyl, phenylethyl, phenylpropyl, phneylbutyl, phenylpentyl and phenylhexyl groups.

[0034] The hydrocarbon group having 1 to 30 carbon atoms represented by R_1 through R_4 is preferably an alkyl group having 1 to 30 carbon atoms or an aryl group having 6 to 24 carbon atoms, more preferably an alkyl group having 3 to 18 carbon atoms, most preferably a straight-chain alkyl group having 4 to 8 carbon atoms.

[0035] Specific examples of the metal represented by Y include alkali metals such as lithium, sodium, potassium and cesium, alkaline earth metals such as calcium, magnesium and barium, and heavy metals such as zinc, copper, iron, lead, nickel, silver, manganese and molybdenum. Among these metals, preferred are zinc, molybdenum, and alkaline earth metals such as calcium. Particularly preferred is zinc.

[0036] With regard to the above-mentioned phosphorus compound metal salt, the coordination number of a phosphorus compound varies depending on the valence of the metal and for example, zinc and calcium, which are divalent presumably form complexes wherein two phosphorus compounds coordinate to one metal atom.

[0037] The content of Component (A) of the lubricating oil composition of the present invention is preferably 0.005 percent by mass or more, more preferably 0.02 percent by mass or more, particularly preferably 0.05 percent by mass or more and also preferably 0.5 percent by mass or less, more preferably 0.2 percent by mass or less, and particularly preferably 0.1 percent by mass or less, on the basis of phosphorus based on the total mass of the composition. If the content of Component (A) is less than 0.005 percent by mass on the basis of phosphorus based on the total mass of the composition, the resulting composition is less effective in anti-wear properties. If the content is more than 0.5 percent by mass, there may be a fear that phosphorus adversely affects an exhaust-gas after-treatment system.

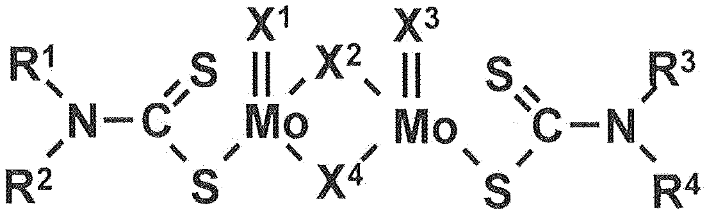
[0038] Among the aforesaid Components (A) used in the present invention, a sulfur-containing compound may also be contained within the above-described range of phosphorus amount, and the content of the compound is preferably 0.1 percent by mass or less, more preferably 0.08 percent by mass or less on the basis of sulfur.

[0039] In order to enhance significantly the base number retainability under a NOx atmosphere and exhibit the friction reducing effect intended by the present invention, most preferably such a sulfur-containing compound is not used.

[0040] Component (B) of the lubricating oil composition of the present invention is an organic molybdenum compound wherein the ratio of molybdenum to sulfur is 1: 3.5 or greater.

[0041] Examples of the organic molybdenum compound used as Component (B) include (B1) sulfurized molybdenum dithiocarbamates, (B2) sulfurized molybdenum dithiophosphates and (B3) oil-soluble trinuclear molybdenum-sulfur compounds.

[0042] Component (B1), i.e., the sulfurized molybdenum dithiocarbamate used in the present invention is an organic molybdenum compound represented by formula(2) below where the ratio of sulfur to molybdenum is 3.5 or greater.



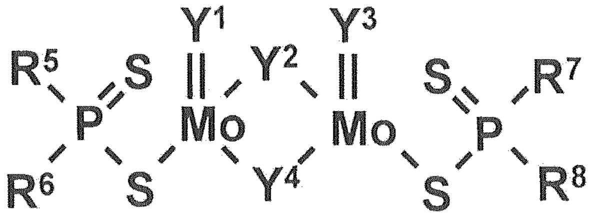
(2)

[0043] In formula (2) above, R^1, R^2, R^3 and R^4 may be the same or different from each other and are each a hydrocarbon group such as an alkyl group having 2 to 24, preferably 4 to 13 carbon atoms or an aryl group (including alkylaryl group) having 6 to 24, preferably 8 to 15carbon atoms. X^1, X^2, X^3 and X^4 may be the same or different from each other and are each sulfur or oxygen.

[0044] Preferred examples of the alkyl group include ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl groups. These alkyl groups may be primary, secondary or tertiary alkyl groups and straight-chain or branched. Preferred examples of the (alkyl)aryl groups include phenyl, tolyl, ethylphenyl, propylphenyl, butylphenyl, pentylphenyl, hexylphenyl, octylphenyl, nonylphenyl, decylphenyl, undecylphenyl, and dodecylphenyl groups, all of which alkyl groups may be primary, secondary or tertiary alkyl groups and straight-chain or branched. Furthermore, the (alkyl)aryl groups include all positional isomers wherein the aryl group may possess an alkyl substituent at any position.

[0045] Specific examples of Component (B1), i.e., sulfurized molybdenum dithiocarbamates include sulfurized molybdenum diethyldithiocarbamate, sulfurized molybdenum dipropyldithiocarbamate, sulfurized molybdenum dibutyldithiocarbamate, sulfurized molybdenum dipentyldithiocarbamate, sulfurized molybdenum dihexyldithiocarbamate, sulfurized molybdenum dioctyldithiocarbamate, sulfurized molybdenum didecyldithiocarbamate, sulfurized molybdenum didodecyldithiocarbamate, sulfurized molybdenum di(butylphenyl)dithiocarbamate, sulfurized molybdenum di(nonylphenyl)dithiocarbamate, sulfurized oxymolybdenum diethyldithiocarbamate, sulfurized oxymolybdenum dipropyldithiocarbamate, sulfurized oxymolybdenum dibutyldithiocarbamate, sulfurized oxymolybdenum dipentyldithiocarbamate, sulfurized oxymolybdenum dihexyldithiocarbamate, sulfurized oxymolybdenum dioctyldithiocarbamate, sulfurized oxymolybdenum didecyldithiocarbamate, sulfurized oxymolybdenum didodecyldithiocarbamate, sulfurized oxymolybdenum di(butylphenyl)dithiocarbamate, and sulfurized oxymolybdenum di(nonylphenyl)dithiocarbamate, all of which the alkyl groups may be straight-chain or branched and the alkyl groups may bond to any position of the phenyl groups, and mixtures thereof. Furthermore, those having in one molecule hydrocarbon groups each having a different carbon number and/or structure from each other are also preferably used.

[0046] Component (B2), i.e., the sulfurized molybdenum dithiophosphates used in the present invention is an organic molybdenum compound represented by formula(3) below wherein the ratio of sulfur to molybdenum is 3.5 or greater.



(3)

[0047] In formula (3) above, R^5, R^6, R^7 and R^8 may be the same or different from each other and are each a hydrocarbon group such as an alkyl group having 2 to 30, preferably 5 to 18, more preferably 5 to 12 carbon atoms or an aryl group (including alkylaryl group) having 6 to 18 carbon atoms. Y^1, Y^2, Y^3 and Y^4 may be the same or different from each other and are each sulfur or oxygen.

[0048] Preferred examples of the alkyl group include ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl groups. These alkyl groups may be primary, secondary or tertiary alkyl groups and straight-chain or branched. Preferred examples of the (alkyl)aryl groups include phenyl, tolyl, ethylphenyl, propylphenyl, butylphenyl, pentylphenyl, hexylphenyl, octylphenyl, nonylphenyl, decylphenyl, undecylphenyl, and dodecylphenyl groups, all of which alkyl groups may be primary, secondary or tertiary alkyl groups and straight--chain or branched. Furthermore, the (alkyl)aryl groups include all positional isomers wherein the aryl group may possess an alkyl substituent at any position.

[0049] Specific examples of Component (B2), i.e., the sulfurized molybdenum dithiophosphates include sulfurized molybdenum diethyldithiophosphate, sulfurized molybdenum dipropyldithiophosphate, sulfurized molybdenum dibutyldithiophosphate, sulfurized molybdenum dipentyldithiophosphate, sulfurized molybdenum dihexyldithiophosphate, sulfurized molybdenum dioctyldithiophosphate, sulfurized molybdenum didecyldithiophosphate, sulfurized molybdenum didodecyldithiophosphate, sulfurized molybdenum di(butylphenyl)dithlophosphate, sulfurized molybdenum di(nonylphenyl)dithiophosphate, sulfurized oxymolybdenum diethyldithiophosphate, sulfurized oxymolybdenum dipropyldithiophosphate, sulfurized oxymolybdenum dibutyldithiophosphate, sulfurized oxymolybdenum dipentyldithiophosphate, sulfurized oxymolybdenum dihexyldithiophosphate, sulfurized oxymolybdenum dioctyldithiophosphate, sulfurized oxymolybdenum didecyldithiophosphate, sulfurized oxymolybdenum didodecyldithiophosphate, sulfurized oxymolybdenum di(butylphenyl)dithiophosphate, sulfurized oxymolybdenum di(nonylphenyl)dithiophosphate, all of which the alkyl groups may be straight-chain or branched and the alkyl groups may bond to any position of the phenyl groups, and mixtures thereof. Furthermore, those having in per molecule hydrocarbon groups each having a different carbon number and/or structure from each other are preferably used.

[0050] Component (B3), i.e., oil-soluble trinuclear molybdenum-sulfur compounds used in the present invention is an organic molybdenum compound represented by formula (4) wherein the ratio of sulfur to molybdenum is 3.5 or greater.

$Mo_3S_kL_nQ_z$ (4)

[0051] In formula (4), L is a ligand having an organic group with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil and n is an integer of 1 to 4. When n is any of 2 to 4, Ls may be the same or different from each other. While k is an integer of 4 to 7, Q is selected from neutral electron-donating compounds such as water, amine, alcohol, phosphine and ether and z is an integer of 0 to 5 and includes non-stoichiometric values. When z is any of 2 to 5, Qs may be the same or different from each other.

[0052] L could be independently selected from the group consisting of -X-R, -(X1)(X2)CR, -(X1)(X2)CYR, -(X1)(X2)CN(R1)(R2), -(X1)(X2)P(OR1)(OR2), mixtures thereof and perthio derivatives thereof. X, X1, X2 and Y are each independently selected from oxygen and sulfur, and R, R1 and R2 are each independently selected from hydrogen and organic groups (may be the same or different type). Preferably, the organic group is a hydrocarbon group such as an alkyl (for example, in which the carbon atom attached to the remainder of the ligand is primary, secondary or tertiary), aryl, substituted aryl and ether groups. More preferably, all the ligands are the same.

[0053] Importantly, the organic groups of the ligands have a sufficient number of carbon atoms to render the compounds soluble or dispersible in the oil. For example, the carbon atom number in each group is generally from 1 to 100, preferably from 1 to 30, more preferably from 4 to 20. Preferred ligands include dialkyldithiophosphate, alkylxanthates and dialkyldithiocarbamates, among which particualry preferred are dialkyldithiocarbamates. An organic ligand containing two or more types of the aforesaid functionalities are also capable of binding to one or more core and serving as ligands. For the formation of the compound used in the present invention, appropriate ligands having suitable charge to balance the corresponding core's charge are preferably selected.

[0054] Although the sulfurized molybdenum dithiocarbamate, sulfurized molybdenum dithiophosphate or oil-soluble trinuclear molybdenum-sulfur compound may each be used alone as Component (B), the sulfurized molybdenum dithiocarbamate is preferred because of its effect or no phosphorus content. An oil-soluble trinuclear molybdenum-sulfur compound whose ligand contains no phosphorus compound is also preferred. Furthermore, this ligand is more preferably a dialkyldithiocarbamate.

[0055] However, the use of (B1) the sulfurized molybdenum dithiocarbamate in combination with (B2) the sulfurized molybdenum dithiophosphate is also effective from the viewpoint of properties. In this case, the ratio of the content of Component (B1) to the total amount of Components (B1) and (B2) is preferably from 50 to 95 percent by mass, more preferably from 60 to 95 percent by mass, more preferably from 70 to 95 percent by mass on the basis of molybdenum.

[0056] In the lubricating oil composition of the present invention, the ratio of the sulfur to the molybdenum in Component (B) is necessarily 3.5 or greater, preferably 4 or greater, more preferably 5 or greater. If the ratio of the sulfur to the molybdenum is less than 3.5, the low friction properties would be degraded.

[0057] The content of Component (B) in the lubricating oil composition of the present invention is preferably 10 ppm by mass or more, more preferably 50 ppm by mass or more, more preferably 100 ppm by mass or more, particularly preferably 200 ppm by mass or more on the basis of molybdenum based on the total mass of the lubricating oil composition from the viewpoint of friction reducing effect. Whilst, the content is preferably 600 ppm by mass or less, more preferably 500 ppm by mass or less, particularly preferably 300 ppm by mass or less from the viewpoint of solubility in the lubricating base oil, storage stability, oxidation stability, and further economic efficiency. If the content of Component (B) exceeds 600 ppm by mass and in particular if a polyα-olefin or a hydrogenated compound thereof is used as the lubricating base oil, Component (B) may not be sufficiently dissolved in the base oil and possibly precipitate during a long period of storage. Furthermore, the content is not preferred from the viewpoint of economic efficiency.

[0058] If necessary, the lubricating oil composition of the present invention may be blended with any additives that have been generally used in a lubricating oil depending on the purposes in order to further enhance the properties. Examples of such additives include metallic detergents, ashless dispersants, viscosity index improvers, antiwear agents (or extreme pressure additive), anti-oxidants, corrosion inhibitors, rust inhibitors, demulsifiers, metal deactivators, and anti-foaming agents.

[0059] Examples of the metallic detergents include normal or basic alkali metal or alkaline earth metal salicylates, normal or basic alkali metal or alkaline earth metal sulfonates, and normal or basic alkali metal or alkaline earth metal phenates. Examples of the alkali metal include sodium and potassium. Examples of the alkaline earth metal include magnesium, calcium and barium. Preferred are magnesium and calcium. Particularly preferred is calcium.

[0060] Among these metallic detergents, alkali metal or alkaline earth metal salicylate detergents (hereinafter referred to "metallic salicylate detergent") are preferred from the viewpoint of their friction reducing effect.

[0061] Examples of the metallic salicylate detergent include: a neutral metal salicylate produced by preparing a salicylic acid to which an equimolar amount of a hydrocarbon group (for example, olefin of 8 to 30 carbon atoms) has been added or alternatively a salicylic acid having one hydrocarbon group of 8 to 30 carbon atoms produced by adding to phenol an equimolar amount of a hydrocarbon group (for example, olefin having 8 to 30 carbon atoms), followed by carboxylation with carbon dioxide and then allowing such a salicylic acid to act with a stoichiometric amount of a metal salt or metal base; a basic metal salicylate produced by heating such a neutral metal salicylate with an excess amount of a metal salt or metal base (metal hydroxide or oxide) in the presence of water; and an overbased (ultrabasic) metal salicylate produced by reacting carbon dioxide, boric acid or borate with a base such as a metal hydroxide in the presence of the above neutral metal salicylate. These reactions are generally carried out in a solvent (aliphatic hydrocarbon solvents such as hexane, aromatic hydrocarbon solvents such as xylene, and light lubricating base oil).

[0062] The olefin having 8 to 30 carbon atoms used for the synthesis of salicylate is usually classified broadly to a group of olefins 8 to 19 carbon atoms and a group of olefins of 20 to 30 carbon atoms and thus a salicylic acid to which the hydrocarbon group of each olefin is added is synthesized.

[0063] The hydrocarbon group is preferably an alkyl group derived from a polymer or copolymer of ethylene, propylene or butylene, particularly preferably an alkyl group derived from a straight-chain α-olefin such as an ethylene polymer.

[0064] In the present invention, the metallic salicylate detergent may be a metal salicylate having a hydrocarbon group of 8 to 19 carbon atoms (for example, an alkyl group of 8 to 19 carbon atoms) (hereinafter often referred to as "metal salicylate C-a") or a metal salicylate having a hydrocarbon group of 20 to 30 carbon atoms (for example, an alkyl group of 20 to 30 carbon atoms) (hereinafter often referred to as "metal salicylate C-b"), either or both of which may be used alone or in combination. From the viewpoint of friction reducing effect, metal salicylate C-b is preferred. Whereas, with the objective of improving synergistically the storage stability and low temperature fluidity, metal salicylates C-a and C-b may be used in combination.

[0065] The metallic salicylate detergent is usually produced by being reacted in a diluent such as solvent or lubricating base oil. The lower limit of metal content of the metallic salicylate detergent produced in such a manner is preferably 1.0 percent by mass or more, more preferably 2.0 percent by mass or more, more preferably 5.0 percent by mass or more, particularly preferably 7.0 percent by mass or more based on the total mass of the metallic salicylate detergent. The upper limit metal content is preferably 20 percent by mass or less, more preferably 15 percent by mass or less, more preferably 12 percent by mass or less, particularly preferably 10 percent by mass or less.

[0066] With regard to the base number of the metallic salicylate detergent, it is preferred to use an overbased salicylate detergent adjusted in the lower limit base number to preferably 50 mgKOH/g or greater, more preferably 100 mgKOH/g or greater, more preferably 150 mgKOH/g or greater, particularly preferably 200 mgKOH/g or greater, as the main component. It is also preferred to use an overbased salicylate detergent adjusted in the upper limit base number to preferably 400 mgKOH/g or lower, more preferably 300 mgKOH/g or lower, more preferably 250 mgKOH/g or lower, as the main component. The term "base number" used herein denotes the value measured by the perchloric acid potentiometric titration method in accordance with section 7 of JIS K2501 "Petroleum products and lubricants-Determination of neutralization number".

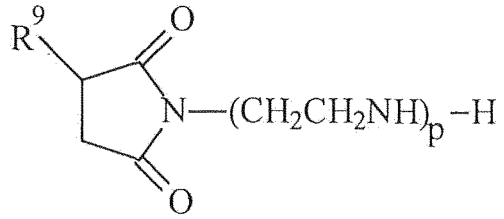
[0067] No particular limitation is imposed on the metal ratio of the metallic salicylate detergent. Generally, one or more types of detergents with a metal ratio of 20 or less may be used. The metal ratio is preferably less than 4.5, more preferably 3 or less. The term "metal ratio" used herein is represented by (valence of metal element in a salicylate detergent) x (metal element content (mole%)) / (soap group content (mole%)). The metal element denotes calcium and magnesium. The soap group denotes a salicylic acid group.

[0068] When a metallic salicylate detergent is blended with the lubricating oil composition of the present invention, the content of the detergent is preferably 0.1 percent by mass or more, more preferably 0.5 percent by mass or more, more preferably 1 percent by mass or more based on the total mass of the composition. The content is also preferably 15 percent by mass or less, more preferably 10 percent by mass or less, more preferably 5 percent by mass or less, particularly preferably 3 percent by mass or less. If the content is less than 0.1 percent by mass, the friction reducing effect would last only for a short period of time. If the content exceeds 15 percent by mass, an advantageous effect as balanced with the content would not be obtained. The lower limit metal content is preferably 0.01 percent by mass or more, more preferably 0.05 percent by mass or more, more preferably 0.1 percent by mass or more, particularly preferably 0.15 percent by mass or more. The upper limit is preferably 1.5 percent by mass or less, more preferably 1.0 percent by mass or less, more preferably 0.5 percent by mass or less, particularly preferably 0.3 percent by mass or less. If the metal content is less than 0.01 percent by mass, the friction reducing effect would last only for a short period of time. If the metal content exceeds 1.5 percent by mass, an advantageous effect as balanced with the content would not be obtained.

[0069] Examples of the ashless dispersant include nitrogen-containing compounds having in their molecules at least one straight-chain or branched alkyl or alkenyl group having 40 to 400 and derivatives thereof and modified products of alkenylsuccinicimides. Any one or more types selected from these ashless dispersants may be blended in the lubricating oil composition of the present invention.

[0070] The carbon number of the alkyl or alkenyl group of the ashless dispersant is preferably 40 to 400, more preferably 60 to 350. If the carbon number of the alkyl or alkenyl group is fewer than 40, the ashless dispersant would tend to be degraded in solubility in the lubricating base oil. Whereas, if the carbon number of the alkyl or alkenyl group is more than 400, the resulting lubricating oil composition would be degraded in low-temperature fluidity. The alkyl or alkenyl group may be straight-chain or branched but is preferably a branched alkyl or alkenyl group derived from oligomers of olefins such as propylene, 1-butene or isobutylene or a cooligomer of ethylene and propylene.

[0071] The succinimide includes a mono-type succinimide wherein a succinic anhydride is added to one end of a polyamine, as represented by formula (5) and a bis-type succinimide wherein a succinic anhydride is added to both ends of a polyamine, as represented by formula (6).



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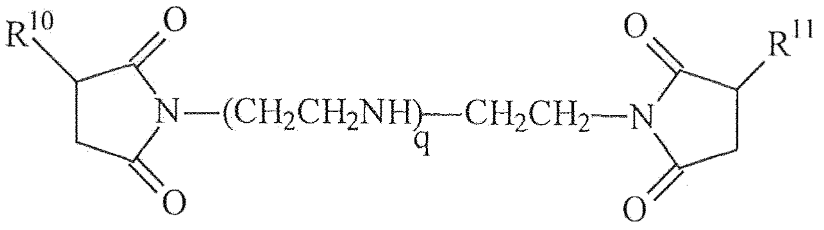


(6)

[0072] In formula (5), R^9 is an alkyl or alkenyl group having 40 to 400, preferably 60 to 350 carbon atoms, and p is an integer of 1 to 5, preferably 2 to 4.

[0073] In formula (6), R^{10} and R^{11} may be the same or different from one another and are each independently an alkyl or alkenyl group having 40 to 400, preferably 60 to 350 carbon atoms, and particularly preferably a polybutenyl group, and q is an integer of 0 to 4, preferably 1 to 3.

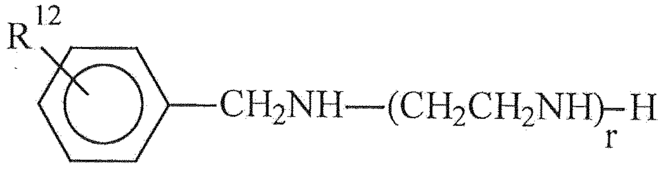
[0074] The lubricating oil composition of the present invention may contain either one or both of the mono-type and bis-type succinimides.

[0075] No particular limitation is imposed on the method of producing these succinimides. For example, a method may be used, wherein an alkyl or alkenyl succinimide produced by reacting a compound having an alkyl or alkenyl group having 40 to 400 carbon atoms with maleic anhydride at a temperature of 100 to 200°C is reacted with a polyamine. Examples of the polyamine include diethylene triamine, triethylene tetramine, tetraethylene pentamine, and pentaethylene hexamine.

[0076] In the present invention, any ashless dispersant selected from the above-described succinimide and/or derivatives thereof may be used, and their weight-average molecular weight is preferably 6,500 or greater, more preferably 7,000 or greater, more preferably 8,000 or greater, particularly preferably 9,000 or greater. If the weight-average molecular weight is smaller than 6,500, the molecular weight of the non-polar group polybutenyl groups would be smaller, and thus the sludge dispersibility would be poor and also the oxidation stability would be poor due to a relative increase in the amine portion of the polar groups, which could be active sites of oxidation degradation and thus would fail to obtain an working life extending effect. On the other hand, no particular limitation is imposed on the upper limit. However, it is preferably 20,000 or smaller, more preferably 15,000 or smaller with the objective of preventing the low temperature viscosity characteristics from degrading.

[0077] The weight-average molecular weight referred herein is the weight-average molecular weight based on polystyrene, as measured using a 150-CALC/GPC by Japan Waters Co., equipped with two GMHHR-M (7.8 mm IDx30 cm) columns by Tosoh Corp. in series, with tetrahydrofuran as the solvent, a temperature of 23°C, a flow rate of 1 mL/min, a sample concentration of 1% by mass, a sample injection rate of 75 μL and a differential refractometer (RI) as the detector.

[0078] The ashless dispersant may be a benzylamine. Preferred examples of the benzylamine include compounds represented by formula (7):



(7)

[0079] In formula (7), R^{12} is an alkyl or alkenyl group having 40 to 400, preferably 60 to 350 and r is an integer of 1 to 5, preferably 2 to 4.

[0080] No particular limitation is imposed on the method for producing the benzylamines. They may be produced by reacting a polyolefin such as a propylene oligomer, polybutene, or ethylene-α-olefin copolymer with a phenol so as to produce an alkylphenol and then subjecting the alkylphenol to Mannich reaction with formaldehyde and a polyamine such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, or pentaethylenehexamine.

[0081] Specific examples of the aforementioned polyamine include compounds represented by formula (8).

$$R^{13}\text{-NH-(CH}_2\text{CH}_2\text{NH)}_s\text{-H} \qquad (8)$$

[0082] In formula (8), R^{13} is an alkyl or alkenyl group having 40 to 400, preferably 60 to 350 and s is an integer of 1 to 5, preferably 2 to 4.

[0083] No particular limitation is imposed on the method for producing the polyamines. For example, the polyamines may be produced by chlorinating a polyolefin such as a propylene oligomer, polybutene, or ethylene-α-olefin copolymer and reacting the chlorinated polyolefin with ammonia or a polyamine such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and pentaethylenehexamine.

[0084] Specific examples of the other derivative include an organic acid-modified compound produced by allowing any of the above-described nitrogen-containing compounds to react with a monocarboxylic acid (fatty acids or the like) having 1 to 30 carbon atoms, a polycarboxylic acid having 2 to 30 carbon atoms, such as oxalic acid, phthalic acid, trimellitic acid, and pyromellitic acid or an oxygen-containing compound such as alcohol, aldehyde, ketone, alkylphenol, cyclic carbonate (for example, ethylene carbonate), hydroxy(poly)alkylene carbonate, so as to neutralize or amidize the whole or part of the remaining amino and/or imino groups; and a sulfur modified-compound produced by allowing any of the above-described nitrogen-containing compounds to react with a sulfur compound. Furthermore, a boron-modified compound may also be used.

[0085] However, for the lubricating oil composition of the present invention, the ashless dispersant is preferably any of the aforesaid nitrogen compounds that are not modified with boron.

[0086] When the lubricating oil composition of the present invention contains the ashless dispersant, the content thereof is preferably from 0.01 to 20 percent by mass, more preferably from 0.1 to 10 percent by mass based on the total mass of the lubricating oil composition. If the ashless dispersant content is less than 0.01 percent by mass, the resulting composition would be insufficient in friction-reducing effect. Whilst, if the content exceeds 20 percent by mass, the resulting lubricating oil composition would be extremely degraded in low temperature fluidity.

[0087] The viscosity index improver is specifically a non-dispersant type or dispersant type ester group-containing viscosity index improver. Examples of such a viscosity index improver include non-dispersant type or dispersant type poly(meth)acrylate viscosity index improvers, non-dispersant type or dispersant type olefin-(meth)acrylate copolymer viscosity index improvers, styrene-maleic anhydride ester copolymer viscosity index improvers, and mixtures thereof. Preferred are non-dispersant type or dispersant type poly(meth)acrylate viscosity index improvers. Particularly preferred are non-dispersant type or dispersant type poly(meth)acrylate viscosity index improvers.

[0088] Other examples of the viscosity index improver include non-dispersant type or dispersant type ethylene-α-olefin copolymers or hydrogenated compounds thereof, polyisobutylene and hydrogenated compounds thereof, styrene-diene hydrogenated copolymers and polyalkylstyrenes.

[0089] The antiwear agent (or extreme pressure additive) may be any anti-oxidant or extreme pressure additive that has been used for lubricating oil. For example, sulfuric-, phosphoric- and sulfuric-phosphoric extreme pressure additives may be used. Specific examples include zinc dialkyldithiophosphate (ZnDTP), phosphorus acid esters, thiophosphorus acid esters, dithiophosphorus acid esters, trithiophosphorus acid esters, phosphoric acid esters, thiophosphoric acid esters, dithiophosphoric acid esters, trithiophosphoric acid esters, amine salts, metal salts or derivatives thereof, dithiocarbamates, zinc dithiocaramates, MoDTC, disulfides, polysulfides, and sulfurized fats and oils. Among these antiwear agents, preferred are sulfuric extreme pressure additives, and particularly preferred are sulfurized fats and oils.

[0090] The anti-oxidant may be an ashless anti-oxidant such as a phenol- or amine-based anti-oxidant, or a metallic anti-oxidant such as a copper- or molybdenum-based anti-oxidant. Specific examples of the phenol-based anti-oxidant include 4,4'-methylene bis(2,6-di-tert-butylphenol) and 4,4'-bis(2,6-di-tert-butylphenol). Specific examples of the amine-based anti-oxidant include phenyl-α-naphthylamines, alkylphenyl-α-naphthylamines and dialkyldiphenylamines.

[0091] Examples of the corrosion inhibitor include benzotriazole-, tolyltriazole-, thiadiazole-, and imidazole-types compounds.

[0092] Examples of the rust inhibitor include petroleum sulfonates, alkylbenzene sulfonates, dinonylnaphthalene sulfonates, alkenyl succinic acid esters, and polyhydric alcohol esters.

[0093] Examples of the demulsifier include polyalkylene glycol-based non-ionic surfactants such as polyoxyethylenealkyl ethers, polyoxyethylenealkylphenyl ethers, and polyoxyethylenealkylnaphthyl ethers.

[0094] Examples of the metal deactivator include imidazolines, pyrimidine derivatives, alkylthiadiazoles, mercaptobenzothiazoles, benzotriazoles and derivatives thereof, 1,3,4-thiadiazolepolysulfide, 1,3,4-thiadiazolyl-2,5-bisdialkyldithiocarbamate, 2-(alkyldithio)benzoimidazole, and β-(o-carboxybenzylthio)propionitrile.

[0095] Examples of the anti-foaming agent include silicone oil with a 25°C kinematic viscosity of 1000 to 100,000 mm^2/s, alkenylsuccinic acid derivatives, esters of polyhydroxy aliphatic alcohols and long-chain fatty acids, aromatic amine salts of methylsalicylate and o-hydroxybenzyl alcohol.

[0096] When these additives are contained in the lubricating oil composition of the present invention, the anti-foaming agent is contained in an amount of 0.0005 to 1 percent by mass and the other additives are contained in an amount selected from the range of 0.01 to 10 percent by mass on the total composition mass basis.

Examples

[0097] The present invention will be described with reference to the following Examples and Comparative Examples but are not limited thereto.

(Examples 1 to 8, Comparative Examples 1 to 5)

[0098] Lubricating oil compositions according to the present invention (Examples 1 to 8) and lubricating oil composition (Comparative Examples 1 to 5) for comparison were prepared. These compositions were subjected to a friction test using a high-frequency, linear-oscillation friction tester (SRV, oil temperature: 110°C, load: 400 N, test time: 30 min), and the results are set forth in Table 1.

[0099] As apparent from the results set forth in Table 1, the lubricating oil composition of Examples 1 to 8 are excellent in friction coefficient improvement rate in comparison with the reference oil and is drastically superior in friction-reducing properties to the compositions of Comparative Examples 1 to 5 containing no Component (A) or Component (B).

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Lubricating base oil *1)	mass%	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
(A) Phosphorus compound I *2)	mass%	0.55	-	-	-	0.55	-	-	-	-	-	-	-	-
Amount on the basis of phosphorus	mass%	(0.07)	-	-	-	(0.07)	-	-	-	-	-	-	-	-
(A) Phosphorus compound II *3)	mass%	-	0.55	-	-	-	0.55	-	-	-	-	-	-	-
Amount on the basis of phosphorus	mass%	-	(0.07)	-	-	-	(0.07)	-	-	-	-	-	-	-
(A) Phosphorus compound III *4)	mass%	-	-	0.55	-	-	-	0.55	-	-	-	-	-	0.55
Amount on the basis of phosphorus	mass%	-	-	(0.07)	-	-	-	(0.07)	-	-	-	-	-	(0.07)
(A) Phosphorus compound IV *5)	mass%	-	-	-	0.55	-	-	-	0.55	-	-	-	-	-
Amount on the basis of phosphorus	mass%	-	-	-	(0.07)	-	-	-	(0.07)	-	-	-	-	-
Zinc dithiophospate *6)	mass%	-	-	-	-	-	-	-	-	0.97	0.97	0.97	0.97	-
Amount on the basis of phosphorus	mass%	-	-	-	-	-	-	-	-	(0.07)	(0.07)	(0.07)	(0.07)	-
(B) Sulfur-containing Mo complex-1 *7)	mass%	0.22	0.22	0.22	0.22	0.55	0.55	0.55	0.55	0.22	0.55	-	-	-
Amount on the basis of molybdenum	mass%	(0.02)	(0.02)	(0.02)	(0.02)	(0.05)	(0.05)	(0.05)	(0.05)	(0.02)	(0.05)	-	-	-
Sulfur-containing Mo complex-2 *8)	mass%	-	-	-	-	-	-	-	-	-	-	0.22	0.55	0.22
Amount on the basis of molybdenum	mass%	-	-	-	-	-	-	-	-	-	-	(0.02)	(0.05)	(0.02)
Metallic detergent *9)	mass%	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Ashless dispersant *10)	mass%	5	5	5	5	5	5	5	5	5	5	5	5	5
Anti-oxidant *11)	mass%	2	2	2	2	2	2	2	2	2	2	2	2	2
Viscosity index improver *12)	mass%	5	5	5	5	5	5	5	5	5	5	5	5	5
Demulsifier *13)	mass%	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Properties of composition														
Total sulfur content	mass%	0.03	0.03	0.1	0.1	0.07	0.07	0.14	0.14	0.17	0.22	0.17	0.21	0.1
Phosphorus content	mass%	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Boron content	mass%													
Friction coefficient (SRV), 110°C, 30 min		0.05	0.051	0.059	0.061	0.053	0.055	0.052	0.053	0.103	0.097	0.091	0.069	0.063

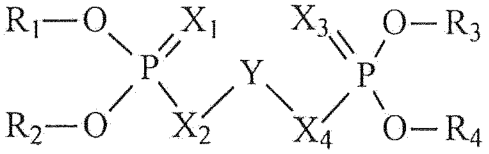
1) Hydrogenated refined mineral oil, total aromatic content: 1.2 mass%, sulfur content: 10 mass ppm, 100°C viscosity: 4.2 mm^2/s, viscosity index: 125
2) Zinc di-n-butylphosphate, phosphorus content: 12.8 mass%, sulfur content: 0 mass ppm, zinc content: 12.8 mass%
3) Zinc di-n-octylphosphate, phosphorus content: 8.8 mass%, sulfur content: 0 mass ppm, zinc content: 8.8 mass%
4) Zinc-di-n-hexylmonothiophosphate, phosphorus content: 10 mass%, sulfur content: 9.9 mass ppm, zinc content: 10 mass%
5) Zinc-di-octylmonothiophosphate, phosphorus content: 8.4 mass%, sulfur content: 8.2 mass ppm, zinc content: 8.4 mass%
6) Alkyl: sec-butyl/hexyl, phosphorus content: 7.2 mass%, sulfur content: 15.2 mass%, zinc content: 8.4 mass%
7) Molybdenum dithiocarbamate, Mo content: 9.0 mass%, sulfur content: 12.0 mass%, Mo:S=1:3.81
8) Molybdenum dithiocarbamate, Mo content: 9.0 mass%, sulfur content: 10 mass%, Mo:S=1:3.3
9) Calcium salicylate, total base number: 23.0 mgKOH/g, calcium content: 8.1%
10) Polybutenyl succinimide, number-average molecular weight of polybutenyl group: 1300
11) Phenol and amine-based anti-oxidants (1:1)
12) PMA, weight-average molecular weight: 400,000
13) Polyalkylene glycol-based

Industrial Applicability

[0100] The lubricating oil composition of the present invention can be generally used in lubricating oils that are required to exhibit a friction reducing effect. Furthermore, the composition can be suitably used not only as gear oils for transmissions or final reduction gears of automobiles and but also for internal combustion engines such as gasoline engines, diesel engines and gas engines for two- and four-wheeled vehicles, power generators and cogenerations. Furthermore, the composition is also useful for various engines such as those for ships and outboard motors.

Claims

1. A lubricating oil composition comprising a lubricating base oil, (A) a phosphoric acid ester metal salt represented by formula (1) and (B) an organic molybdenum compound with a ratio of molybdenum to sulfur of 1: 3.5 or greater:



(1)

wherein R_1 to R_4 are each a hydrocarbon group having 1 to 30 carbon atoms, an alkyl or alkenyl group having 1 to 30 carbon atoms, or an alkylthioethyl comprising an alkyl group having 1 to 30 carbon atoms and may be the same or different from each other; X_1, X_2, X_3 and X_4 are each sulfur or oxygen, either X_1 or X_2 is oxygen or both are oxygen, and either X_3 or X_4 is oxygen or both are oxygen; and Y is a metal element.

2. The lubricating oil composition according to claim 1 wherein R_1 through R_4 are each a straight-chain alkyl group having 4 to 8 carbon atoms.

3. The lubricating oil composition according to claim 1 or 2 further comprising an ashless dispersant containing no boron.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/051219

A. CLASSIFICATION OF SUBJECT MATTER

C10M141/12(2006.01)i, *C10M133/16*(2006.01)n, *C10M135/18*(2006.01)n, *C10M137/06*(2006.01)n, *C10M137/10*(2006.01)n, *C10M139/00*(2006.01)n, *C10N10/12*(2006.01)n, *C10N30/06*(2006.01)n, *C10N40/25*(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M101/00-177/00

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2004-83891 A (Nippon Oil Corp.), 18 March 2004 (18.03.2004), claims; paragraphs [0040] to [0053]; examples & US 2005/0107269 A1	1-3 1-3
Y	JP 2007-217604 A (Showa Shell Sekiyu Kabushiki Kaisha), 30 August 2007 (30.08.2007), claims; paragraphs [0011] to [0017]; examples & US 2007/0203034 A1 & WO 2007/093632 A2	1-3
Y	JP 2002-508384 A (Infineum USA LP), 19 March 2002 (19.03.2002), claims; examples & US 5906968 A & US 6110878 A & WO 1999/031113 A1	1-3

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 06 April, 2012 (06.04.12)	Date of mailing of the international search report 17 April, 2012 (17.04.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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- JP 2001279287 A **[0004]**
- JP 2002129182 A **[0004]**
- JP 8302378 A **[0004]**
- JP 6306384 A **[0004]**