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(54) LUBRICATING OIL COMPOSITION

(57) The present invention provides a lubricating oil composition having excellent oxidation stability, suitable as a lubricating oil for internal combustion engines and automatic transmissions, particularly internal combustion engines. The lubricating oil composition comprises a lubricating base oil and one or more type of phosphorus compound represented by formula (1) below as Component (A), the element ratio of sulfur derived from the compound of formula (1) to phosphorus in the oil (S/P molar ratio) being from 0.05 to 0.8 and the amount of phosphorus derived from Component (A) in the oil being from 0.01 to 0.5 percent by mass (in formula 1, R_1 through R_4 are each a hydrocarbon group with 1 to 30 carbon atoms or an alkylthioethyl group having an alkyl or alkenyl group with 1 to 30 carbon atoms and may be the same or different from one another, X_1 to X_4 are each independently sulfur or oxygen, and Y represents 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 thiophosphoric acid ester metal salt with a specific structure and having an excellent oxidation stability. In particular, the present invention relates to a lubricating oil composition suitably used as an internal combustion engine lubricating oil.

Background Art

[0002] Conventionally, a lubricating oil or grease has been used in an internal combustion engine or a transmission 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). In particular, since an engine oil contacts peroxides that are active species of oxidation degradation at piston-cylinder regions, it has been required to have oxidation resistivity. Zinc dialkyldithiophosphate (ZDTP) acting as a peroxide decomposer has, therefore, been used in engine oils. Molybdenum compounds are also known as a peroxide decomposer. ZDTP is an excellent antiwear agent, and molybdenum compound are known as excellent friction modifier reducing friction. Both are used in many engine oils.

Citation List

Patent Literature

[0003]

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

Summary of Invention

Technical Problem

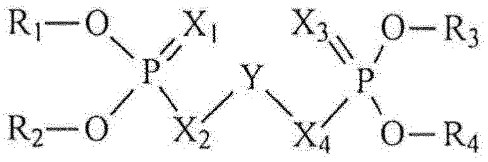
[0004] As described above, the ZDTP acts as an anti-oxidant or antiwear agent but rather decreases the base number of lubricating oil after being decomposed and also becomes a causes of deposit. The ZDTP is thus an additive that is extremely difficult to handle in lubricating oils, which are required to have a long working life.

[0005] Therefore, various ZDTPs with different alkyl groups have been produced and various lubricating oil compositions containing such ZDTPs have been created in combination with metallic detergents or other anti-oxidants, but have not come to solve the above-described problems yet.

Solution to Problem

[0006] As the results of extensive studies carried out to solve the above problems, the present invention has been accomplished.

[0007] That is, the present invention is a lubricating oil composition comprising a lubricating base oil and one or more type of phosphorus compound represented by formula (1) below as Component (A), the element ratio of sulfur derived from the compound of formula (1) to phosphorus in the oil (S/P molar ratio) being from 0.05 to 0.8 and the amount of phosphorus derived from Component (A) in the oil being from 0.01 to 0.5 percent by mass:



(1)

wherein R_1 through R_4 are each a hydrocarbon group with 1 to 30 carbon atoms or an alkylthioethyl group having an alkyl or alkenyl group with 1 to 30 carbon atoms and may be the same or different from one another, X_1 rough X_4 are each independently sulfur or oxygen, and Y represents a metal element.

Advantageous Effect of Invention

[0008] The present invention can provide a lubricating oil composition which can obtain an excellent oxidation stability that conventional lubricating oils containing zinc dialkyldithiophosphate (ZDTP) were not able to achieve, suitably used as a lubricating oil for internal combustion engines or automatic transmissions, particularly as a lubricating oil for internal combustion engines.

Description of Embodiments

[0009] The present invention will be described below.

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

[0011] Examples of the mineral lubricating base oil which may be used in the present invention include paraffinic mineral base oils which can be produced by subjecting a lubricating oil fraction produced by atmospheric- 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-paraffinic base oils; and iso-paraffinic base oils.

[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) one type or a mixed oil of two 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 base oils (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); and
(7) a mixed oil of two or more base oils selected from base oils (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) above 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.

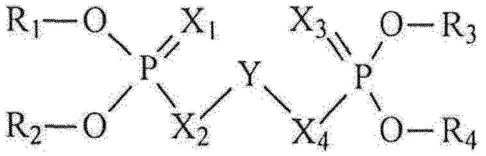
[0020] The viscosity index referred herein denotes the viscosity index measured in accordance with JIS K 2283-1993.

[0021] The 100°C kinematic viscosity of the lubricating base oil used in the present invention is preferably 20 mm^2/s or lower, more preferably 10 mm^2/s or lower, more preferably 6 mm^2/s or lower, particular preferably 5 mm^2/s or lower. Whilst, the kinematic viscosity is preferably 1 mm^2/s or higher, more preferably 1.5 mm^2/s or higher, more preferably 2 mm^2/s or higher, particularly preferably 2.5 mm^2/s or higher, most preferably 3 mm^2/s or higher. 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 higher than 20 mm^2/s, the resulting composition would be degraded in low temperature viscosity characteristics and may not obtain sufficiently improved fuel economy. It the 104°C kinematic viscosity is lower 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 type of other base oil. 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 higher than 20 mm^2/s and 200 mm^2/s or lower. Examples of the other synthetic base oils include those having a 100°C kinematic viscosity outside the range of 1 to 20 mm^2/s.

[0024] Component (A) of the lubricating oil composition of the present invention is a phosphoric



(1)

[0025] In formula (1), R_1 through R_4 are each a hydrocarbon group having 1 to 30 carbon atoms or an alkylthioethyl group having an alkyl or alkenyl group having 1 to 30 carbon atoms and may be the same or different from one another, X_1 through X_4 are each sulfur or oxygen and may be the same or different from one another, and Y represents a metal element.

[0026] Specific examples of the hydrocarbon group having 1 to 30 carbon atoms represented by R1 through R4 include alkyl, cycloalkyl, alkenyl, alkyl-substituted cycloalkyl, aryl, alkyl-substituted aryl, and arylalkyl groups.

[0027] Examples of the alkyl group (including the alkyl group of alkylthioethyl group having an alkyl or alkenyl group having 1 to 30 carbon atoms) 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 (including the alkyl group of an alkylthioethyl group having an alkyl or alkenyl group having 1 to 30 carbon atoms) 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 are zinc, molybdenum and a combination of zinc and molybdenum.

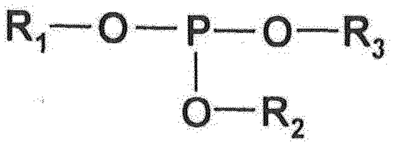
[0036] With regard to the above-mentioned phosphorus compound metal salt, the coordination number of a phosphorus compound varies depending on the valence of the metal and for example, zinc and calcium, which are divalent presumably form complexes wherein two phosphorus compounds coordinate to one metal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

[0037] In the lubricating oil composition of the present invention, the element ratio of sulfur derived from the compound of formula (1) to phosphorus in the oil (S/P molar ratio) is necessarily 0.05 or higher, preferably 0.07 or higher, more preferably 0.1 or higher and 0.8 or smaller, preferably 0.7 or smaller, more preferably 0.5 or smaller, particularly preferably 0.3 or smaller.

[0038] If the S/P molar ratio is smaller than 0.05, the resulting composition would fail to obtain a sufficient anti-oxidation effect due to the too less sulfur content while if the S/P molar ratio is higher than 0.8, the resulting composition would be degraded in oxidation stability due to the too much sulfur content.

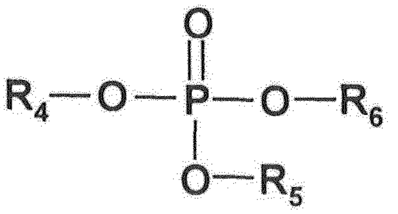
[0039] In the case where a sulfur-containing compound is used as Component (A), a compound of formula (1) where all X_1 through X_4 are oxygen or a sulfur-free phosphorus compound other than Component (A) is necessarily used in combination.

[0040] Examples of the sulfur-free phosphorus compound other than Component (A) used in the present invention include at least one type of compound selected from the group consisting of phosphorus compounds represented by formula (2), phosphorus compounds represented by formula (3), amine salts thereof and derivatives thereof.



$$\mathrm{R_1{-}O{-}\underset{\underset{\displaystyle O{-}R_2}{|}}{P}{-}O{-}R_3} \qquad (2)$$

[0041] In formula (2), R_1, R_2 and R_3 are each independently hydrogen or a hydrocarbon group having 1 to 30 carbon atoms.



$$\mathrm{R_4{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O{-}R_5}{|}}{P}}{-}O{-}R_6} \qquad (3)$$

[0042] In formula (3), R_4, R_5 and R_6 are each independently hydrogen or a hydrocarbon group having 1 to 30 carbon atoms.

[0043] Specific examples of the hydrocarbon group having 1 to 30 carbon atoms represented by R_1 through R_6 in formulas (2) and (3) include alkyl, cycloalkyl, alkenyl, alkyl-substituted cycloalkyl, aryl, alkyl-substituted aryl, and arylalkyl groups.

[0044] The hydrocarbon group having 1 to 30 carbon atoms is preferably an alkyl group having 1 to 30 carbon atoms or aryl group having 6 to 24 carbon atoms, more preferably an alkyl group having 3 to 18 carbon atoms, more preferably an alkyl group having 4 to 12 carbon atoms.

[0045] Examples of the phosphorus compound represented by formula (2) include phosphorus acid; phosphorus acid monoesters having one hydrocarbon group of 1 to 30 carbon atoms mentioned above; phosphorus acid diesters having two hydrocarbon groups of 1 to 30 carbon atoms mentioned above; phosphorus acid triesters having three hydrocarbon groups of 1 to 30 carbon atoms mentioned above; and mixtures thereof.

[0046] Phosphonic acid esters that are tautomers of phosphorus acid monoester and phosphorus acid diester are also included in the examples of the compound.

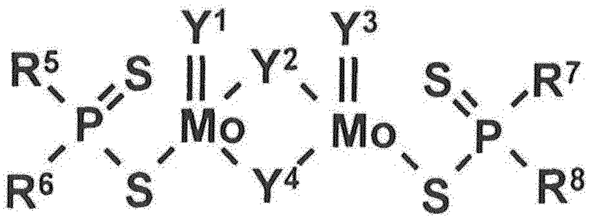
[0047] Examples of the phosphorus compound represented by formula (3) include phosphoric acid; phosphoric acid monoesters having one hydrocarbon group of 1 to 30 carbon atoms mentioned above; phosphoric acid diesters having two hydrocarbon groups of 1 to 30 carbon atoms mentioned above; phosphoric acid triesters having three hydrocarbon groups of 1 to 30 carbon atoms mentioned above; and mixtures thereof.

[0048] The content of Component (A) of the lubricating oil composition of the present invention is 0.005 percent by mass or more, preferably 0.02 percent by mass or more, particularly preferably 0.05 percent by mass or more on the basis of phosphorus on the total composition mass basis. Whilst, the content is 0.5 percent by mass or less, preferably 0.2 percent by mass or less, particularly preferably 0.1 percent by mass or less. If the content of Component (A) is less than 0.005 percent by mass on the basis of phosphorus, the resulting composition is less effective in anti-wear properties. If the content of Component (A) is more than 0.5 percent by mass, phosphorus may adversely affects an exhaust-gas after-treatment system.

[0049] In the case of using a sulfur-free phosphorus compound other than Component (A) in combination, the phosphorus content is 0.005 percent by mass or more, preferably 0.02 percent by mass or more, particularly preferably 0.05 percent by mass or more, on the basis of phosphorus on the total composition mass basis. Whilst, the content is 0.5 percent by mass or less, preferably 0.2 percent by mass or less, particularly preferably 0.1 percent by mass or less. If the content is less than 0.005 percent by mass on the basis of phosphorus, the resulting composition is less effective in anti-wear properties. If the content is more than 0. 5 percent by mass, phosphorus may adversely affects an exhaust-gas after-treatment system.

[0050] In the case where one type of metal of Component (A) used in the present invention is molybdenum, the content thereof is 0.03 percent by mass or less, preferably 0.02 percent by mass or less, more preferably 0.01 percent by mass or less on the basis of Mo. If the content exceeds 0.03 percent by mass, the resulting composition would rather be degraded in anti-oxidation effect.

[0051] In the case where the metal of Component (A) is molybdenum, molybdenum dithiophosphates represented by formula (4) may be used:



(4)

[0052] In formula (4), R^5, R^6, R^7 and R^8 may be the same or different from one another 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 one another and are each sulfur or oxygen.

[0053] 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.

[0054] Specific examples of 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)dithiophosphate, 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.

[0055] The lubricating oil composition of the present invention preferably contains an ashless anti-oxidant as Component (B). The anti-oxidant may be any of ashless anti-oxidants such as phenol- or amine-based anti-oxidants generally used in lubricating oils. Addition of an ashless anti-oxidant can further enhance the anti-oxidation properties of the lubricating oil composition of the present invention and also can enhance the suppression properties in respect of deposit generation, anti-corrosion or anti-wear properties for lead-containing metals, and base number retainability of the lubricating oil composition of the present invention.

[0056] Examples of phenol-based anti-oxidants include 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-nonylphenol), 2,2'-isobutylidenebis(4,6-dimethylphenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert-α-dimethylamino-p-cresol, 2,6-di-tert-butyl-4(N,N'-dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 4,4'-thiobis(3-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)sulfide, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, 2,2'-thio-diethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], tridecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, pentaerythrityl-tetraquis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], octyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, and 3-methyl-5-tert-butyl-4-hydroxyphenyl-substituted fatty acid esters. Two or more of these may be used.

[0057] Examples of the amine-based anti-oxidant include aromatic amine-based anti-oxidants such as phenyl-α-naphthylamines, alkylphenyl-α-naphthylamines and dialkyldiphenylamines. A mixture of two or more these compounds may also be used.

[0058] The above-described phenol-based anti-oxidant and amine-based anti-oxidant may be used in combination, but the sole use of an aromatic amine-based anti-oxidant is particularly preferred.

[0059] 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 viscosity index improvers, metallic detergents, ashless dispersants, antiwear agents (or extreme pressure additive), corrosion inhibitors, rust inhibitors, demulsifiers, metal deactivators, and anti-foaming agents.

[0060] 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.

[0061] Among these metallic detergents, alkali metal or alkaline earth metal salicylate detergents are preferred from the viewpoint of their friction reducing effect.

[0062] Examples of the metallic salicylate detergent include: a neutral salicylic acid metal salt produced by allowing a salicylic acid having one hydrocarbon group of 8 to 30 carbon atoms to act with an equimolar amount of a metal salt or metal base; a basic salicylic acid metal salt 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) salicylic acid metal salt produced by reacting carbon dioxide, boric acid or borate with a base such as a metal hydroxide in the presence of the above neutral salicylic acid metal salt.

[0063] Examples of the metal of the metal salt or metal base of the above-described salicylate (i.e., metal contained in the metallic salicylate detergent) include alkali metals such as sodium and potassium and alkaline earth metals such as calcium, magnesium and barium. Preferred are alkaline earth metals, and particularly preferred is calcium.

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

[0065] 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".

[0066] No particular limitation is imposed on the metal ratio of the metallic salicylate detergent. Generally, one or more type 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.

[0067] 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 6 percent by mass or less, particularly preferably 4 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.

[0068] 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] The lubricating oil composition of the present invention preferably contains an ashless dispersant.

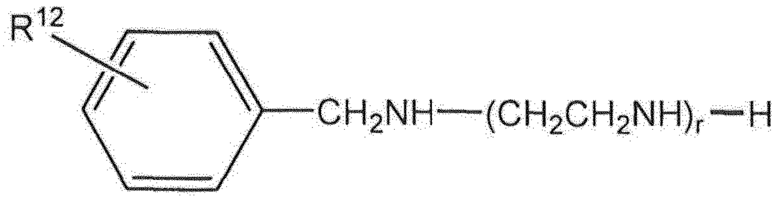
[0070] Examples of the ashless dispersant include nitrogen-containing compounds having in per molecule at least one straight-chain or branched alkyl or alkenyl group having 40 to 400 and derivatives thereof and modified products of alkenylsuccinicimides. Any one or more type selected from these ashless dispersants may be blended in the lubricating oil composition of the present invention.

[0071] 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.

[0072] The succinimide includes a mono-type succinimide wherein a succinic anhydride is added to one end of a polyamine and a bis-type succinimide wherein a succinic anhydride is added to both ends of a polyamine.

[0073] The lubricating oil composition of the present invention may contain either one or both of the mono-type and bis-type succinimides.

[0074] The ashless dispersant may be a benzylamine. Preferred examples of the benzylamine include compounds represented by formula (5):



(5)

[0075] In formula (5), 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.

[0076] Specific examples of the aforementioned polyamine include compounds represented by formula (6).

$$R^{13}\text{-NH-}(CH_2CH_2NH)_s\text{-H} \qquad (6)$$

[0077] In formula (6), R^{13} is an alkyl or alkenyl group having 40 to 400, preferably 60 to 350 carbon atoms and s is an integer of 1 to 5, preferably 2 to 4.

[0078] 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 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 included.

[0079] The boron-modified ashless dispersant is one produced by boronating any ashless dispersant used for lubricating oil.

[0080] Boronation is generally carried out by allowing the above-described nitrogen-containing compound to react with boric acid to neutralize the whole or part of the remaining amino and/or imino groups.

[0081] Examples of a method of producing a boric acid modified-succinimide are those disclosed in Japanese Patent Publication Nos. 42-8013 and 42-8014 and Japanese Laid-Open Patent Publication Nos. 51-52381 and 51-130408. More specifically, a boric acid modified-succinimide may be produced by mixing polyamine and polybutenylsuccinic acid (anhydride) with a boron compound such as boric acid, boric acid ester, or borate in a solvent including alcohols, organic solvent such as hexane or xylene, or a light fraction lubricating base oil and by heating the mixture under appropriate conditions. The boron content of the boron-modified succinimide obtained in this manner is generally from 0.1 to 4.0 percent by mass.

[0082] Boric acid-modified compounds of alkenylsuccinimides (boron-containing succinimide) is excellent in heat resistance, anti-oxidation properties and anti-wear properties.

[0083] 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.

[0084] In the case of using a boron-containing ashless dispersant such as the above-described boron-containing succinimide, no particular limitation is imposed on the boron content, which is usually from 0.1 to 3 percent by mass. However, in one embodiment of the present invention, it is desired to use a boron-containing ashless dispersant, preferably boron-containing succinimide, particularly preferably a boron-containing bis succinimide with a boron content of preferably 0.2 percent by mass or more, more preferably 0.4 percent by mass or more, and preferably 2 percent by mass or less, more preferably 1.5 percent by mass or less, more preferably 1.0 percent by mass or less, particularly preferably 0.6 percent by mass or less. In the case of using the above-mentioned boron-containing ashless dispersant, the boron content thereof is 0.01 percent by mass or more, preferably 0.02 percent by mass or more, more preferably 0.025 percent by mass or more and 0.15 percent by mass or less, preferably 0.1 percent by mass or less, particularly preferably 0.05 percent by mass or less on the basis of the total mass of the composition.

[0085] In the case of using a boron-containing ashless dispersant such as the above-described boron-containing succinimide, no particular limitation is imposed on the boron/nitrogen mass ratio (B/N ratio). The B/N ratio is usually from 0.05 to 5. However, in one embodiment of the present invention, it is desired to use a boron-containing ashless dispersant, preferably a boron-containing succinimide, particularly preferably a boron-containing bis succinimide with a B/N ratio of preferably 0.1 or higher, more preferably 0.2 or higher and preferably 1 or lower, more preferably 0.7 or lower, more preferably 0.5 or lower. In the case of using a boron-containing ashless dispersant as described above, the boron content thereof is 0.01 percent by mass or more, preferably 0.02 percent by mass or more, more preferably 0.025 percent by mass or more and 0.15 percent by mass or less, preferably 0.1 percent by mass or less, particularly preferably 0.05 percent by mass or less on the basis of the total mass of the composition.

[0086] With regard to the boron/nitrogen mass ratio (B/N ratio) of the boron-containing ashless dispersant such as boron-containing succinimides, in another embodiment, it is desired to use a boron-containing ashless dispersant, preferably a boron-containing succinimide, particularly preferably a boron-containing bis succinimide with a B/N ratio of 0.1 or higher, preferably 0.2 or higher and preferably lower than 0.5, more preferably 0.4 or lower.

[0087] If the B/N ratio exceeds 1, not only concerns about stability are arisen, but also concerns about influences on an exhaust-gas after-treatment system would be arisen accompanied with an increase in sulfated ash content due to the too much boron in the composition. If the B/N ratio is smaller than 0.1, the resulting composition would be less effective in improving the friction-reducing properties and thus desirously used in combination with another boric compound.

[0088] 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.

[0089] 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.

[0090] 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. However, the use thereof is acceptable within the range satisfying the phosphorus content of 0.01 to 0.5 percent by mass in the oil and the molar ratio of phosphorus to sulfur derived from Component (A) of 0.05 to 0.8.

[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 1,000 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 0.0001 to 0.01 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 4 and Comparative Examples 1 to 5]

[0098] Lubricating oil compositions of the present invention (Examples 1 to 4) and those for comparison (Comparative Examples 1 to 5) were prepared and evaluated with an engine test (high temperature. oxidation stability test) in accordance with JASO M333-93. The results are set forth in Table 1.

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Lubricating base oil *1)	Ratio	70	70	70	70	7C	70	70	70	100
Lubricating base oil *2)		30	30	30	30	30	30	30	30	
(A) Zinc alkylphosphate *3) on the basis of phosphorus	mass% mass%	0.34 (0.035)	0.5 (0.0525)	0.57 (0.06)	0.6 (0.063)	- -	033 (0.035)	- -	- -	0 67 (0.07)
(A) Zinc alkylmonothiophosphate *4) on the basis of phosphorus	mass% mass%	0.35 (0.035)	- -	- -	- -	0.7 (0.07)	- -	- -	- -	- -
(A) Zinc alkyldithiophosphate *5) on the basis of phosphorus	mass% mass%	- -	0.24 (0.0175)	- -	- -	- -	0.49 (0.035)	0.97 (0.07)	- -	- -
(A) Zinc alkyldithiophosphate *6) on the basis of phosphorus	mass% mass%	- -	- -	0.125 (0.010)	- -	- -	- -	- -	0.87 (0.07)	- -
(A) Mo alkyldithiophosphate *7) on the basis of phosphorus	mass% mass%	- -	- -	- -	0.115 (0.007)	- -	- -	- -	- -	- -
S/P ratio of phosphorus compoud		0.5	0.5	0.3	0.12	1	1	2	2	0
Metallic detergent *8)	mass%	3.3	3.3	3.3	3.33	3.3	3.3	3.3	3.3	3.33
Ashless dispersant *9)	mass%	5	5	5	5	5	0.5	5	5	5
(B) Anti-oxidant *10)	mass%	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Viscosity index improver *11)	mass%		3.5	3.5	5	3.5	3.5	3.5	3.5	3.8
Properties of composition										
Phosphorus content	mass%	07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Ca Content	mass%	0.2	0.2	0.2	0.2	0.	0.2	0.2	0	
JASO M333-93 tested oil properties		96 hours later								48 hours later

(continued)

		Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Viscosity increase (40°C)	%	55	20	26	1	231	1 0	152	145	440
Acid number increase	mgkOH/g	5.02	1.63	1.7	1	11.77	6.27	6.07	8.2	27
Base number (HCL)	mgKOH/g	0.12	1.44	1.32	1.28	0	0	0	0	0
Pentane insoluble (B method)	%	0.29	0.01	0.01	0.01	4.18	3.15	4.81	4.13	3.95

1) Hydrorefined mineral oil: total aromatic content 0.0 mass%, sulfur content 10 mass ppm 100°C kinematic viscosity: 4 8 mm^2/s, viscosity index: 128
2) Solvent refined mineral oil: total aromatic content 9.3 mass% sulfur content 0 6 mass ppm 100°C kinematic viscosity: 7 4 mm^2/s viscosity index: 95
3) Zinc di-n-hexylphosphate: phosphorus content: 10.4 mass%, zinc content 10.8 mass%
4) Zinc di-n-hexylmonothiophosphate: phosphorus content 9.9 mass% zinc content 10.2 mass%, sulfur content 10.2 mass%
5) Alkyl group sec-butyl/hexyl group phosphorus content: 7.2 mass% sulfur content 15.2 mass% zinc content 7 8 mass%
6) Zinc di-n-octyldithiophosphate: phosphorus content 8 0 mass%, sulfur content 16.0 mass% zinc content 8 3 mass%
7) Molybdenum di-2-ethylhexyldithiophosphate: phosphorus content: 5.5 mass%, sulfur content: 13.0 mass%, molybdenum zinc content 8 7 mass%
8) Calcium salicylate: total base number: 170 calcium content: 6.1 mass%
9) Boric acid-modified polybutenyl succinimide: number average molecular weight of polybutenyl group: 1300 B: 0 5 mass%
10) Amine-based anti-oxidant: akyldiphenyl amine 11) Mix polymer

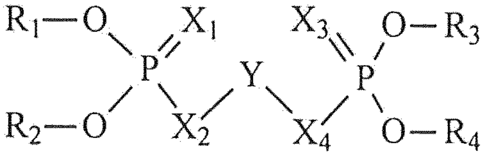
[0099] It is apparent from the results set forth in Table 1 that the lubricating oil compositions of Examples 1 to 4 of the present invention are less in viscosity increase and oxidation increase and excellent in retainability of the base number comparing with those of Comparative Examples 1 to 5.

Industrial Applicability

[0100] The lubricating oil composition of the present invention is used suitably as a lubricating oil for internal combustion engines and automatic transmissions.

Claims

1. A lubricating oil composition comprising a lubricating base oil and one or more type of phosphorus compound represented by formula (1) below as Component (A), the element ratio of sulfur derived from the compound of formula (1) to phosphorus in the oil (S/P molar ratio) being from 0.05 to 0.8 and the amount of phosphorus derived from Component (A) in the oil being from 0.01 to 0.5 percent by mass:



(1)

wherein R_1 through R_4 are each a hydrocarbon group with 1 to 30 carbon atoms or an alkylthioethyl group having an alkyl or alkenyl group with 1 to 30 carbon atoms and is the same or different from one another, X_1 to X_4 are each independently sulfur or oxygen, and Y represents a metal element.

2. The lubricating oil composition according to claim 1 wherein the metal element Y of the phosphorus compound represented by formula (1) is zinc, molybdenum or a combination of zinc and molybdenum.

3. The lubricating oil composition according to claim 1 or 2 wherein the phosphorus compounds represented by formula (1) are a compound where all of X_1 through X_4 are oxygen and a compound where at least one of X_1 through X_4 is sulfur.

4. The lubricating oil composition according to any one of claims 1 to 3 wherein at least one type of phosphorus compound represented by formula (1) is a compound where the metal element is molybdenum and contained in an amount of 0.03 percent by mass or less on the basis of Mo.

5. The lubricating oil composition according to any one of claims 1 to 4 further comprising (B) an ashless anti-oxidant.

6. The lubricating oil composition according to claim 5 wherein (B) the ashless anti-oxidant is an aromatic amine-based anti-oxidant.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/051220

A. CLASSIFICATION OF SUBJECT MATTER
C10M137/10(2006.01)i, *C10M137/04*(2006.01)i, *C10M141/10*(2006.01)i, *C10M133/12*(2006.01)n, *C10M137/06*(2006.01)n, *C10N10/04*(2006.01)n, *C10N10/12*(2006.01)n, *C10N30/10*(2006.01)n, *C10N40/04*(2006.01)n,
According to International Patent Classification (IPC) or to both national classification and IPC

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	JP 2005-220196 A (Nippon Oil Corp.), 18 August 2005 (18.08.2005), claims; paragraphs [0051], [0059]; examples & US 2006/0270567 A1 & EP 1712606 A1 & WO 2005/075611 A1 & CN 1926225 A	1-6
P,X	WO 2011/114848 A1 (JX Nippon Oil & Energy Corp.), 22 September 2011 (22.09.2011), claims; paragraphs [0035] to [0050]; examples (Family: none)	1-6

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

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"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		

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.

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INTERNATIONAL SEARCH REPORT

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

C10N40/25(2006.01)n

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

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- JP 8302378 A **[0003]**
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- JP 428014 A **[0081]**
- JP 51052381 A **[0081]**
- JP 51130408 A **[0081]**