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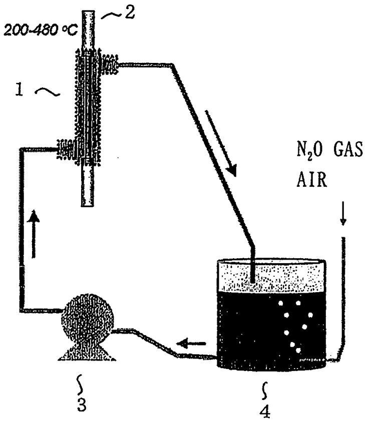
(54) LUBRICANT COMPOSITION FOR INTERNAL COMBUSTION ENGINES

(57) Provided is a lubricating oil composition for an internal combustion engine, including: an organic molybdenum compound as a component (A); a base oil having a kinematic viscosity at 100°C of 25 mm^2/s or more as a component (B) ; and a base oil having a kinematic viscosity at 100°C of less than 12.5 mm^2/s as a component (C), in which the composition has a kinematic viscosity at 100°C of 5 mm^2/s to 12.5 mm^2/s and a phosphorus content of 800 ppm or less.

Fig. 1



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Description

Technical Field

[0001] The present invention relates to a lubricating oil composition for an internal combustion engine, and more specifically, to a lubricating oil composition for an internal combustion engine having excellent fuel-saving property and high-temperature deposit-preventing performance.

Background Art

[0002] A lubricating oil for internal combustion engines of automobiles or the like plays roles such as the lubrication and cooling of the inside of the engine, and the cleaning and dispersion of combustion products. In recent years, to prevent global warming, there has been a growing demand for the suppression of carbon dioxide emissions through improvements in the fuel efficiency of automobiles or the like. Accordingly, a fuel-saving-type lubricating oil for an internal combustion engine obtained by providing a lubricating oil for an internal combustion engine with a function of improving fuel efficiency has been studied and used.

[0003] Fuel-saving-type lubricating oils for internal combustion engines reduce friction occurring in an internal combustion engine to improve the fuel efficiency of the engine. Specifically, an organic molybdenum-based friction modifier such as a molybdenum dithiocarbamate is generally blended as an additive (friction modifier) for reducing the friction. However, lubricants for internal combustion engines blended with organic molybdenum-based friction modifiers are apt to generate high-temperature deposits because of poor oxidation stability under high temperatures. In particular, recent lean-burn engines, direct-injection engines, or the like have higher efficiency than conventional engines, and their combustion temperatures tend to increase. Accordingly, problems due to generation of high-temperature deposits have become serious.

[0004] In view of the foregoing, various methods have been proposed for reducing the high-temperature deposits. For example, Patent Document 1 discloses a multigrade engine oil composition for an engine with a turbocharger, the composition being characterized by using a mineral oil and/or a synthetic oil having a kinematic viscosity of 1.5 to 13 cSt (100°C) as a base oil, and containing, as essential components, 3 to 40 mass% of (A) a mineral oil and/or a synthetic oil having a kinematic viscosity of 16 to 45 cSt (100°C) and 0.5 to 15 mass% of (B) a viscosity index improver. In addition, Patent Document 2 discloses a lubricating oil composition for an internal combustion engine characterized by using, as a base oil, a lubricating oil component that has a kinematic viscosity at 100°C of 2 cSt to 13 cSt and contains 1 mass% or more of a heavy component having a boiling point of 480°C or more in a boiling point range measured by gas chromatograph distillation with reference to the total mass of the lubricating oil base oil. In addition, the paragraphs [0021] to [0026] of Patent Document 2 disclose that an organic molybdenum-based compound can be used as a friction modifier.

Prior Art Documents

Patent Documents

[0005]

Patent Document 1: JP 59-122595 A
Patent Document 2: JP 09-328694 A

Summary of the Invention

Problem to be Solved by the Invention

[0006] However, even when an organic molybdenum-based friction modifier is blended with the compositions described in Patent Documents 1 and 2, the high-temperature deposits cannot sufficiently be reduced, and hence fuel-saving-type lubricating oil compositions for internal combustion engines capable of additionally reducing high-temperature deposits are still desired.

[0007] Therefore, a problem to be solved by the present invention is to provide a lubricating oil composition for an internal combustion engine having high-temperature deposit-preventing performance while maintaining excellent fuel-saving property.

Means for Solving the Problem

[0008] In view of the foregoing, the present inventors have made extensive studies to find that excellent fuel-saving performance and high-temperature deposit-preventing performance can be imparted by blending a lubricating oil composition for an internal combustion engine with an organic molybdenum compound and a plurality of base oils each having a specific viscosity. Thus, the inventors have reached the present invention.
That is, the present invention provides a lubricating oil composition for an internal combustion engine, including: an organic molybdenum compound as a component (A); a base oil having a kinematic viscosity at 100°C of 25 mm^2/s or more as a component (B); and a base oil having a kinematic viscosity at 100°C of less than 12.5 mm^2/s as a component (C), in which the composition has a kinematic viscosity at 100°C of 5 mm^2/s to 12.5 mm^2/s and a phosphorus content of 800 ppm or less.

Effects of the Invention

[0009] An effect of the present invention resides in the provision of the lubricating oil composition for an internal combustion engine having high-temperature deposit-preventing performance while maintaining excellent fuel-saving property.

Brief Description of Drawings

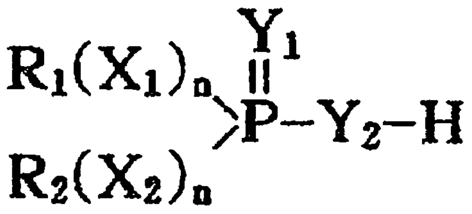
[0010]

FIG. 1 is a schematic view of a TEOST33C tester.
FIG. 2 is a graph showing a temperature change during 1 cycle in a case in a TEOST33C test.

Best Mode for Carrying Out the Invention

[0011] A lubricating oil composition for an internal combustion engine of the present invention contains an organic molybdenum compound as a component (A). Any one of the known organic molybdenum compounds can be used as the organic molybdenum compound, and examples thereof include: a molybdenum dithiocarbamate; a molybdenum dithiophosphate; a molybdenum amine compound listed in JP 05-62639 B or the like [an oil-soluble molybdenum compound obtained by reacting one or more kinds of hexavalent molybdenum compounds selected from molybdenum trioxide, and molybdic acid and an alkali salt thereof, and an amino compound represented by $R^1R^2R^3N$ (R^1, R^2, and R^3 each represent a hydrogen atom or a hydrocarbon group having 1 to 30 carbon atoms and may be identical to or different from one another, and the total number of carbon atoms of R^1, R^2, and R^3 is 4 or more) with each other] ; and a molybdenum compound containing phosphorus and sulfur listed in JP 04-30959 B or the like [a compound obtained by reacting (a) at least one hexavalent molybdenum compound; (b) at least one compound selected from hydrogen sulfide, an alkali hydrosulfide, and an alkali sulfide represented by M_2S (M represents an alkali metal or an ammonium group); (c) a compound represented by the following formula or a salt thereof,

[Chem. 1]

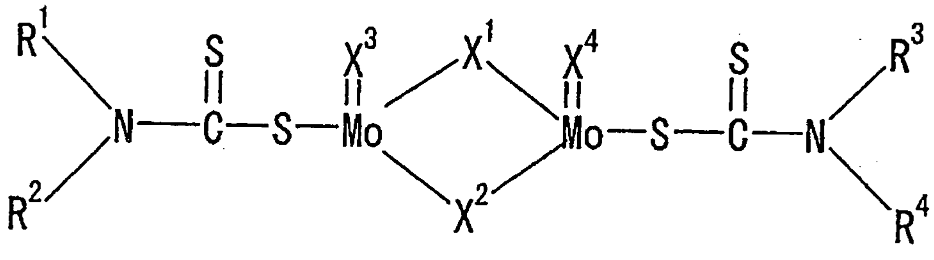


$$\begin{array}{l} R_1(X_1)_n \\ \qquad\qquad \overset{\overset{\displaystyle Y_1}{\|}}{>P}-Y_2-H \\ R_2(X_2)_n \end{array}$$

where X_1, X_2, Y_1 and Y_2 each represent an oxygen or sulfur atom and may be identical to or different from one another, n represents 0 or 1, and R_1 and R_2 each represent an organic residue and may be identical to or different from each other; and (d) a reducing agent capable of reducing the hexavalent molybdenum compound to pentavalent or tetravalent (provided that the components b and c are excluded) with one another].

[0012] Among such organic molybdenum compounds, a molybdenum dithiocarbamate represented by the following general formula (1) is preferred because of its large friction-reducing effect.

[Chem. 2]


(1)

where R^1 to R^4 each represent a linear or branched alkyl group or alkenyl group having 4 to 18 carbon atoms, and X^1 to X^4 each represent an oxygen atom or a sulfur atom.

[0013] R^1 to R^4 of the general formula (1) represent a linear or branched alkyl group or alkenyl group having 4 to 18 carbon atoms. Examples of such group include: alkyl groups such as a butyl group, an isobutyl group, a tertiarybutyl group, a pentyl group, an isopentyl group, a neopentyl group, a tertiary pentyl group, a hexyl group, an isohexyl group, a heptyl group, an isoheptyl group, an octyl group, a 2-ethylhexyl group, an isooctyl group, a nonyl group, an isononyl group, a decyl group, an isodecyl group, an undecyl group, an isoundecyl group, a dodecyl group, an isododecyl group, a tridecyl group, an isotridecyl group, a tetradecyl group, an isotetradecyl group, a hexadecyl group, an isohexadecyl group, a stearyl group, a 2-butyloctyl group, a 2-butyldecyl group, a 2-hexyloctyl group, a 2-hexyldecyl group, a 2-octyldecyl group, a 2-hexyldodecyl group, and a monomethyl branched-isostearyl group; and alkenyl groups such as a butenyl group, an isobutenyl group, a pentenyl group, an isopentenyl group, a hexenyl group, a heptenyl group, an octenyl group, a nonenyl group, a decenyl group, an undecenyl group, a dodecenyl group, a tetradecenyl group, and an oleyl group. Among them, an alkyl group is preferred because of its high friction-reducing effect, an alkyl group having 6 to 16 carbon atoms is more preferred, and an alkyl group having 8 to 13 carbon atoms is still more preferred. It should be noted that R^1 to R^4 may be identical to or different from one another.

[0014] X^1 to X^4 each represent an oxygen atom or a sulfur atom, all of X^1 to X^4 may be oxygen atoms or sulfur atoms, and X^1 to X^4 may be a mixture of oxygen atoms and sulfur atoms. However, the ratio of oxygen atom/sulfur atom (molar ratio) preferably falls within the range of 1/3 to 3/1 because a high friction-reducing effect and low corrosiveness are obtained.

[0015] The organic molybdenum compound may be one kind or a mixture of two or more kinds. The amount of the compound to be added to the lubricating oil composition for an internal combustion engine of the present invention is not specified. However, when the addition amount is small, there are cases where a friction-reducing effect is not obtained. In addition, when the addition amount is excessively large, high-temperature deposits outstripping the effect of the high-temperature deposit-preventing performance of the lubricating oil composition for an internal combustion engine of the present invention may be generated. Accordingly, the compound is added at a molybdenum content of preferably 200 to 2, 000 ppm, more preferably 200 to 1, 500 ppm, still more preferably 300 to 1, 000 ppm with respect to the total amount of the lubricating oil composition for an internal combustion engine of the present invention.

[0016] The component (B) used in the present invention is a base oil having a kinematic viscosity at 100°C of 25 mm^2/s or more, and a mineral oil-based base oil, a synthetic base oils, or a mixed oil thereof can be used as such base oil. A paraffin-based mineral oil and a naphthene-based mineral oil can be given as examples of the mineral oil-based base oil, and a solvent-refined oil, oil obtained by a hydrogenation treatment, wax-isomerized oil, or the like of any such oil may be used. For example, a poly-α-olefin, a polyisobutylene (polybutene), a diester, a polyol ester, or a polyphenyl ether can be used as the synthetic base oil. Among them, a paraffin-based mineral oil such as a bright stock and a high-viscosity poly-α-olefin are preferred.

[0017] One kind of these base oils can be used alone, or a mixture of two or more kinds thereof can be used, as the component (B). However, the kinematic viscosity at 100°C of the component must be 25 mm^2/s or more, and is preferably 25 to 100 mm^2/s, more preferably 25 to 80 mm^2/s, still more preferably 30 to 60 mm^2/s. When the kinematic viscosity at 100°C is less than 25 mm^2/s, the high-temperature deposit-preventing performance is not sufficiently exerted. In addition, when the viscosity is excessively high, there are problems such as cases where it may be difficult to handle the component or it takes a long time to uniformly blend the component. Accordingly, the kinematic viscosity is preferably 100 mm^2/s or less.

[0018] The blending amount of the component (B) is not particularly specified. However, when the blending amount is excessively small, there are cases where the effect of the high-temperature deposit-preventing performance may not be exerted. In addition, when the blending amount is excessively large, it may be difficult to set the kinematic viscosity at 100 °C of the lubricating oil composition for an internal combustion engine of the present invention to 12.5 mm^2/s or less, or its low-temperature viscosity may increase to reduce its fuel-saving effect. In view of the foregoing, the blending amount of the component (B) is preferably 1 to 30 mass%, more preferably 3 to 25 mass%, still more preferably 5 to 20 mass% with respect to the total amount of the lubricating oil composition for an internal combustion engine of the present invention.

[0019] The component (C) used in the present invention is a base oil having a kinematic viscosity at 100°C of less than 12.5 mm^2/s. A mineral oil-based base oil, a synthetic base oil, or a mixed oil thereof can be used as such base oil, and examples of such base oil include: mineral oil-based base oils such as a paraffin-based mineral oil and a naphthene-based mineral oil, oils obtained by subjecting these mineral oils to a solvent refining treatment, a hydrogenation treatment, and a wax isomerization treatment, and a mineral oil obtained by combining two or more of these treatments; and synthetic oils such as poly-α-olefins and polyisobutylenes.

[0020] When the kinematic viscosity of the component (C) is 12.5 mm^2/s or more, a lubricating oil composition having a kinematic viscosity in the range specified in the present invention cannot be produced. In addition, even when the kinematic viscosity of the component (C) is less than 12.5 mm^2/s, in the case where the component is a base oil having an excessively high viscosity, the amount of the high-viscosity base oil that can be added is reduced, and hence it may be unable to efficiently alleviate the generation of high-temperature deposits or the low-temperature viscosity of the lubricating oil composition for an internal combustion engine of the present invention may increase to reduce its fuel-saving effect. Accordingly, the kinematic viscosity at 100°C of the component (C) is preferably 1 to 11 mm^2/s, more preferably 2 to 8 mm^2/s, still more preferably 2 to 5 mm^2/s.

[0021] Further, the viscosity index of the component (C) is preferably 100 or more, more preferably 110 or more, still more preferably 120 or more from the viewpoint of improving fuel-saving properties. When the viscosity index of the low-viscosity base oil is less than 100, the low-temperature viscosity of the lubricating oil composition for an internal combustion engine as the end product increases, with the result that the fuel-saving effect is not obtained in some cases.

[0022] The component (C) has only to be blended in such an amount that the lubricating oil composition for an internal combustion engine of the present invention blended with any other additive or the like has a kinematic viscosity at 100°C of 5 mm^2/s to 12.5 mm^2/s. Specifically, the component has only to be blended in an amount of 50 to 95 mass%, preferably 60 to 85 mass% with respect to the total amount of the lubricating oil composition of the present invention.

[0023] In addition, the lubricating oil composition for an internal combustion engine of the present invention containing the components (A) to (C) must have a phosphorus content of 800 ppm or less. Although trace amounts of phosphorus may be present in a base oil, most of phosphorus is derived from a phosphorus-based additive to be added to the lubricating oil composition for an internal combustion engine. Examples of the phosphorus-based additive include metal-containing additives such as molybdenum dithiophosphate and zinc dithiophosphate; extreme-pressure agents such asmonooctylphosphate,dioctylphosphate,monooleyl phosphate, dioleyl phosphate, tributyl phosphate, triphenyl phosphate, tricresyl phosphate, triphenyl phosphite, tributyl phosphite, tricresyl phosphite, and a thiophosphoric acid ester; and detergents such as calcium phosphate, magnesium phosphate, and barium phosphate.

[0024] Although one or more kinds of those phosphorus-based additives may be added, the addition amount thereof must be 800 ppm or less in terms of a phosphorus content. As long as the addition amount is 800 ppm or less, the amount of high-temperature deposits generated is nearly immune to the phosphorus concentration. However, when the phosphorus concentration exceeds 800 ppm, the amount of high-temperature deposits generated abruptly increases. However, when the phosphorus concentration is excessively low, the lubricating oil for an internal combustion engine may be poor in wear resistance or oxidation-preventing property. Accordingly, phosphorus is preferably present in a certain amount or more. Specifically, the phosphorus content is preferably 300 to 800 ppm, more preferably 500 to 800 ppm. Further, the phosphorus compound most suitable for the addition is a zinc dithiophosphate excellent in wear resistance and oxidation-preventing property.

[0025] The lubricating oil composition for an internal combustion engine of the present invention has a kinematic viscosity at 100°C of 5 mm^2/s to 12.5 mm^2/s. When the kinematic viscosity is less than 5 mm^2/s, there is a possibility that oil film does not sufficiently form and hence wear occurs at sliding surfaces. When the kinematic viscosity is more than 12.5 mm^2/s, the following problem arises. The oil film becomes so thick that friction loss increases to impair fuel-saving performance.

[0026] The term "high-temperature deposit" as used in the present invention refers to insoluble matter resulting from the lubricating oil composition for an internal combustion engine, the insoluble matter being produced at high temperatures of 300°C or 400°C or more. The adhesion and deposition of such high-temperature deposits to, for example, the inside of an engine or the bearings of a supercharger may induce a reduction in performance of the engine or the supercharger, or trouble in the engine or the supercharger.

[0027] The major feature of the lubricating oil composition for an internal combustion engine of the present invention is that the amount of high-temperature deposits generated is small. Although the composition may be evaluated by any one of the known tests for observing high-temperature deposits, the composition is preferably evaluated by a TEOST33C test (ASTM D6335) adopted by the International Lubricant Standardization and Approval Committee (ILSAC) because an additionally strict evaluation can be performed. The smaller the amount of high-temperature deposits, the better.

Specifically, the amount is preferably 40 mg or less, more preferably 30 mg or less in the TEOST33C test because nearly no reduction in performance of an engine or in performance of a supercharger is observed at the time of practical use.

[0028] One or more kinds of additives such as viscosity index improvers, pour point depressants, extreme-pressure agents, oiliness improvers, antioxidants, metal-based detergents, ashless dispersants, metal deactivators, rust inhibitors, and anti-foaming agents are preferably added to the lubricating oil composition for an internal combustion engine of the present invention as long as the effects of the present invention are not impaired. Further, when any such additive is blended, particular attention needs to be paid so that the phosphorus content with respect to the total amount of the lubricating oil composition for an internal combustion engine will be 800 ppm or less, preferably 300 to 800 ppm.

[0029] Examples of viscosity index improvers include poly(C1 to C18)alkyl methacrylates, (C1 to C18)alkyl crylate/(C1 to C18)alkyl methacrylate copolymers, diethylaminoethyl methacrylate/(C1 to C18)alkyl methacrylate copolymers, ethylene/(C1 to C18)alkyl methacrylate copolymers, polyisobutylenes, polyalkylstyrenes, ethylene/propylene copolymers, styrene/maleic acid ester copolymers, and styrene/isoprene hydrogenated copolymers. Alternatively, a dispersion-type or multi-functional viscosity index improver to which dispersing performance has been imparted may be used. Its weight-average molecular weight is about 10,000 to 1,500,000, preferably about 30,000 to 1,000, 000. Such viscosity index improver is blended in an amount of preferably 0.1 to 20 mass%, more preferably 0.3 to 15 mass% with respect to the lubricating oil composition for an internal combustion engine.

[0030] Examples of pour point depressants include polyalkyl methacrylates, polyalkyl acrylates, polyalkylstyrenes, and polyvinyl acetates. Its weight-average molecular weight is about 1,000 to 100, 000, preferably about 3, 000 to 80, 000. Such pour point depressant is blended in an amount of preferably 0.005 to 3 mass%, more preferably 0.01 to 2 mass%, with respect to the lubricating oil composition for an internal combustion engine.

[0031] Examples of extreme-pressure agents include: sulfur-based additives such as sulfurized oils and fats, olefin polysulfides, and dibenzyl sulfides; phosphorus-based compounds such as monooctyl phosphate, tributyl phosphate, triphenylphosphite, tributyl phosphite, and thiophosphoric acid esters; and organic metal compounds such as metal salts of thiophosphoric acid, metal salts of thiocarbamic acid, and metal salts of an acidic phosphoric acid ester. Such extreme-pressure agent is blended in an amount of preferably 0.01 to 2 mass%, more preferably 0.05 to 1 mass% with respect to the lubricating oil composition for an internal combustion engine.

[0032] Examples of oiliness improvers include: higher alcohols such as oleyl alcohol and stearyl alcohol; fatty acids such as oleic acid and stearic acid; esters such as oleyl glycerine ester, stearyl glycerine ester, and lauryl glycerine ester; amides such as lauryl amide, oleyl amide, and stearyl amide; amines such as laurylamine, oleylamine, and stearylamine; and ethers such as lauryl glycerine ether and oleyl glycerine ether. Such oiliness improver is blended in an amount of preferably 0.1 to 5 mass%, more preferably 0.2 to 3 mass% with respect to the lubricating oil composition for an internal combustion engine.

[0033] Examples of antioxidants include: phenol-based antioxidants such as 2,6-ditertiary butylphenol (hereinafter, tertiary butyl is abbreviated as t-butyl), 2, 6-di-t-butyl-p-cresol, 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butyl-4-ethylphenol, 2,4-dimethyl-6-t-butylphenol, 4,4'-methylene bis(2,6-di-t-butylphenol), 4,4'-bis(2,6-di-t-butylphenol), 4,4'-bis(2-methyl-6-t-butylphenol), 2,2'-methylene bis(4-methyl-6-t-butylphenol), 2,2'-methylene bis(4-ethyl-6-t-butylphenol), 4,4'-butylidene bis(3-methyl-6-t-butylphenol), 4,4'-isopropylidene bis(2,6-di-t-butylphenol), 2,2'-methylene bis(4-methyl-6-cyclohexylphenol), 2,2'-methylene bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene bis(4,6-dimethylphenol), 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)-4-methylphenol, 3-t-butyl-4-hydroxyanisole, 2-t-butyl-4-hydroxyanisole, octyl 3-(4-hydroxy-3,5-di-t-butylphenyl)propionate, stearyl 3-(4-hydroxy-3,5-di-t-butylphenyl)propionate, oleyl 3-(4-hydroxy-3,5-di-t-butylphenyl)propionate, dodecyl 3-(4-hydroxy-3,5-di-t-butylphenyl)propionate, decyl 3-(4-hydroxy-3,5-di-t-butylphenyl)propionate, octyl 3-(4-hydroxy-3,5-di-t-butylphenyl)propionate, tetrakis{3-(4-hydroxy-3,5-di-t-butylphenyl)propionyl oxymethyl} methane, 3-(4-hydroxy-3,5-di-t-butylphenyl)propionic acid glycerine monoester, an ester of 3-(4-hydroxy-3,5-di-t-butylphenyl)propionic acid and glycerine monooleylether,3-(4-hydroxy-3,5-di-t-butylphenyl)propionic acid butylene glycol diester, 3-(4-hydroxy-3,5-di-t-butylphenyl)propionic acid thiodiglycol diester, 4,4'-thiobis(3-methyl-6-t-butylphenol), 4,4'-thiobis(2-methyl-6-t-butylphenol), 2,2'-thiobis(4-methyl-6-t-butylphenol), 2,6-di-t-butyl-α-dimethylamino-p-cresol, 2,6-di-t-butyl-4-(N,N'-dimethylaminomethylphenol), bis(3,5-di-t-butyl-4-hydroxybenzyl)sulfide, tris{(3,5-di-t-butyl-4-hydroxyphenyl)propionyl-oxyethyl} isocyanurate, tris(3,5-di-t-butyl-4-hydroxyphenyl) isocyanurate, 1,3,5-tris(3,5-di-t-butyl-4-hydroxybenzyl) isocyanurate, a bis{2-methyl-4-(3-n-alkylthiopropionyloxy)-5-t-butylphenyl}sul fide, 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, tetraphthaloyl-di(2,6-dimethyl-4-t-butyl-3-hydroxybenzyl sulfide), 6-(4-hydroxy-3,5-di-t-butyl anilino)-2,4-bis(octylthio)-1,3,5-triazine, 2,2-thio-{diethyl-bis-3-(3,5-di-t-butyl-4-hydroxyphenyl)} propionate, N,N'-hexamethylene bis(3,5-di-t-butyl-4-hydroxy-hydrocinnamide), 3,5-di-t-butyl-4-hydroxy-benzyl-phosphate diester, bis(3-methyl-4-hydroxy-5-t-butylbenzyl)sulfide, 3,9-bis[1,1-dimethyl-2-{β-(3-t-butyl-4-hydroxy-5-methylphenyl) propionyloxy}ethyl]-2,4,8,10-tetraoxaspiro[5,5]undecane, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benz ene, and bis{3,3'-bis-(4'-hydroxy-3'-t-butylphenyl)butyric acid} glycol ester; naphthylamine-based antioxidants such as 1-naphthylamine, phenyl-1-naphthylamine, p-octylphenyl-1-naphthylamine, p-nonylphenyl-1-naphthylamine, p-dodecylphenyl-1-napythylamine, and phenyl-2-naphthylamine; phenylenediamine-based antioxidants such as N,N'-diisopropyl-p-phenylenediamine, N,N'-diisobutyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di-β-naphthyl-p-phenylenediamine, N-phenyl-N'-isopropyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine, dioctyl-p-phenylenediamine, phenylhexyl-p-phenylenediamine, and phenyloctyl-p-phenylenediamine; diphenylamine-based antioxidants such as dipyridylamine, diphenylamine, p,p'-di-n-butyldiphenylamine, p,p'-di-t-butyldiphenylamine, p,p'-di-t-pentyldiphenylamine, p,p'-dioctyldiphenylamine, p,p'-dinonyldiphenylamine, p,p'-didecyldiphenylamine, p,p'-didodecyldiphenylamine, p,p'-distyryldiphenylamine, p,p'-dimethoxydiphenylamine, 4,4'-bis(4-α,α-dimethylbenzoyl)diphenylamine, p-isopropoxydiphenylamine, and dipyridylamine; phenothiazine-based antioxidants such as phenothiazine, N-methylphenothiazine, N-ethylphenothiazine, 3,7-dioctylphenothiazine, phenothiazine carboxylic acid ester, and phenoselenazine; and zinc dithiophosphate. Such antioxidant is blended in an amount of preferably 0.01 to 5 mass%, more preferably 0.05 to 4 mass% with respect to the lubricating oil composition for an internal combustion engine.

[0034] Examples of metal-based detergents include sulfonates, phenates, salicylates, and phosphates of calcium, magnesium, and barium, and perbasic salts thereof. Of those, perbasic salts are preferred. Of the perbasic salts, a perbasic salt having a total basic number (TBN) of 30 to 500 mgKOH/g is more preferred. A salicylate-based detergent free of phosphorus and sulfur atoms is still more preferred. Such metal-based detergent is blended in an amount of preferably 0.5 to 10 mass%, more preferably 1 to 8 mass% with respect to the lubricating oil composition for an internal combustion engine.

[0035] Examples of ashless dispersants include succinimide, a succinic acid ester, and benzylamine to each of which an alkyl group or an alkenyl group has been added and each of which has a weight-average molecular weight of about 500 to 3,000, and boron-denatured products thereof. Such ashless dispersant is blended in an amount of preferably 0.5 to 10 mass%, more preferably 1 to 8 mass% with respect to the lubricating oil composition for an internal combustion engine.

[0036] Examples of metal deactivators include benzotriazole, benzimidazole, benzothiazole, and a tetraalkylthiuram disulfide. Such metal deactivator is blended in an amount of preferably 0.01 to 3 mass%, more preferably 0.02 to 2 mass% with respect to the lubricating oil composition for an internal combustion engine.

[0037] Examples of rust inhibitors include sodium nitrite, oxidized paraffin wax calcium salts, oxidized paraffin wax magnesium salts, beef tallow fatty acid alkali metal salts, alkaline earth metal salts, or amine salts, alkenyl succinic acids or alkenyl succinic acid half esters (the molecular weight of the alkenyl group is about 100 to 300), sorbitan monoester, nonylphenol ethoxylate, and calcium salt of a lanolin fatty acid. Such rust inhibitor is blended in an amount of preferably 0.01 to 3 mass%, more preferably 0.02 to 2 mass% with respect to the lubricating oil composition for an internal combustion engine.

[0038] Examples of anti-foaming agents include polydimethylsilicone, trifluoropropylmethylsilicone, colloidal silica, polyalkyl acrylate, polyalkyl methacrylate, alcohol ethoxy/propoxylate, fatty acid ethoxy/propoxylate, and sorbitan partial fatty acid ester. Such anti-foaming agent is blended in an amount of preferably 0.001 to 0.1 mass%, more preferably 0.001 to 0.01 mass% with respect to the lubricating oil composition for an internal combustion engine.

[0039] The lubricating oil composition for an internal combustion engine of the present invention can be used as a lubricating oil for any internal combustion engine as long as the internal combustion engine is, for example, a gasoline engine, a diesel engine, and a natural gas engine (liquefied petroleum gas engine) and among these the composition can be favorably used as an engine oil for gasoline engines.

Examples

[0040] Hereinafter, the present invention is specifically described by way of examples. It should be noted that the term "%" in the following examples and the like refers to "mass%" unless otherwise stated.

Lubricating oil compositions for internal combustion engines (test oils) used in tests were produced in accordance with the recipes shown in Table 1 and Table 2 below, and were then subjected to the TEOST33C test and a fuel-saving property test by the following methods . Table 1 and Table 2 show the results. It should be noted that Table 3 shows a base oil used in blending and its properties.

<TEOST33C test: high-temperature deposit test>

[0041] A test was performed in conformity with the test method of ASTM D6335 with a TEOST33C tester (manufactured by Tannas Co.). FIG. 1 is a schematic view of the TEOST33C tester. The specific test method is as described below. While a rod (metal rod) (2) in a case (1) of the apparatus illustrated in FIG. 1 was heated and cooled so that its temperature was as shown in FIG. 2, a certain amount of a test oil was made to flow from a reaction chamber (4) storing the test oil into the rod (2) in the case (1) by a pump (3). The step is defined as 1 cycle and the cycle was repeated 12 times. After that, the rod was taken out, and then the mass of deposits adhering thereto and the mass of deposits in the test oil obtained by filtering the total amount of the test oil through a filter were measured. The total of the masses was defined as a high-temperature deposit amount. Further, certain amounts of air containing moisture and a nitrogen monoxide gas

were blown into the test oil in the reaction chamber (4). Further, air bubbled in 30 ml of water in a 50-ml flask was used as the air containing moisture .
Detailed test conditions are described below.

(Test condition)

[0042]

Temperature: 200 to 480°C
Test cycle: 12 cycles
Testing time: 9. 5 minutes per cycle (total testing time: 114 minutes)
Amount of test oil: 106 ml
Catalyst: iron naphthenate (added to the test oil in an amount of 100 ppm in terms of iron content)
Pump rate: 0.49 ml/min
Flow rate of N_2O gas: 3.5 ml/min
Flow rate of air: 3.5 ml/min

<Fuel-saving property test>

[0043] The coefficient of friction of each test oil was measured with an SRV tester under the following conditions. A lower coefficient of friction means higher fuel-saving property.
Upper test piece: a columnar test piece (φ15×22 mm, material: SUJ-2) Lower test piece: a disc-like test piece (φ24×6.85 mm, material: SUJ-2)

Load: 200 N
Amplitude: 1.0 mm
Cycle: 50 Hz
Measurement temperature: 80°C
Measurement time: 15 minutes

[0044] [Table 1]

Table 1

		Inventive Product					
		1	2	3	4	5	6
Viscosity index improver		3.4	3.4	3.4	3.4	3.4	3.4
Detergent		2.0	2.0	2.0	2.0	2.0	2.0
Dispersant		4.0	4.0	4.0	4.0	4.0	4.0
Antioxidant		2.0	2.0	2.0	2.0	2.0	2.0
Zinc dithiophosphate		0.9	0.9	0.7	0.9	0.9	0.9
Molybdenum dithiocarbamate		0.4	0.4	0.4	0.4	0.4	0.4
Base oil	Mineral oil 1	9		9	28	1	9
	Synthetic oil 1		9				
	Mineral oil 2	Balance	Balance	Balance	Balance		
	Mineral oil 3						Balance
	Synthetic oil 2					Balance	
Phosphorus content (ppm)		780	780	600	780	780	780
Mo content (ppm)		700	700	700	700	700	700
Test result	Product viscosity at 100°C (mm^2/s)	9.7	8.1	9.7	12.1	9.7	9.8
	High-temperature deposit amount (mg)	22	26	23	23	34	22
	Fuel-saving property test	0.52	0.53	0.52	0.58	0.52	0.56

* The amount of the entirety was adjusted to 100 with the base oil described as "balance."

[0045] [Table 2]

Table 2

		Comparative Product					
		1	2	3	4	5	6
Viscosity index improver		3.4	3.4	3.4	3.4	3.4	3.4
Detergent		2.0	2.0	2.0	2.0	2.0	2.0
Dispersant		4.0	4.0	4.0	4.0	4.0	4.0
Antioxidant		2.0	2.0	2.0	2.0	2.0	2.0
Zinc dithiophosphate		0.9	0.9	0.9	1.1	0.9	0.9
Tricresyl phosphate						0.5	
Molybdenum dithiocarbamate		0.4	0.4	0.4	0.4	0.4	
Base oil	Mineral oil 1				9	9	
	Synthetic oil 1						
	Mineral oil 2	Balance			Balance	Balance	Balance
	Mineral oil 3		Balance				
	Synthetic oil 2			Balance			
Phosphorus content (ppm)		780	780	780	950	1,200	780
Mo content (ppm)		700	700	700	700	700	700
Test result	Product viscosity at 100°C (mm^2/s)	8.6	7.0	5.2	9.7	9.7	8.6
	High-temperature deposit amount (mg)	60	63	92	44	58	21
	Fuel-saving property test	0.52	0.52	0.53	0.52	0.52	1.08

* The amount of the entirety was adjusted to 100 with the base oil described as "balance."

[0046] Further, the details of each component included in the products of the present invention and the comparative products are as follows.
Viscosity index improver: polymethacrylate-based viscosity index improver
Detergent: calcium salicylate (TBN280)
Dispersant: polyalkenyl succinimide
Antioxidant: mixture of benzenepropanoic acid 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxyoctyl ester and dioctyldiphenylamine (mass ratio: 1/1)
Zinc dithiophosphate: zinc dialkyldithiophosphate whose alkyl group is linear and a mixture of alkyl groups having 4 to 6 carbon atoms (phosphorus content: 8.67%)
Molybdenum dithiocarbamate: molybdenum dithiocarbamate of the general formula (1) in which R^1 to R^4 each represent a mixture of groups having 8 or 13 carbon atoms, X^1 and X^2 each represent an oxygen atom, and X^3 and X^4 each represent a sulfur atom (molybdenum content: 17.5%)
The kind and properties of each base oil used in the experiments are as described in Table 3 below.

[0047] [Table 3]

Table 3

		Kinematic viscosity at 100°C (mm²/s)	Viscosity Index
Component B	Mineral oil 1 (bright stock)	32.8	95
	Synthetic oil 1 (PAO)	39.5	149
Component C	Mineral oil 2 (hydrocracked oil)	4.24	122
	Mineral oil 3 (solvent-refined oil)	4.39	102
	Synthetic oil 2 (PAO)	4.04	119
PAO: Poly-α-olefin			

Claims

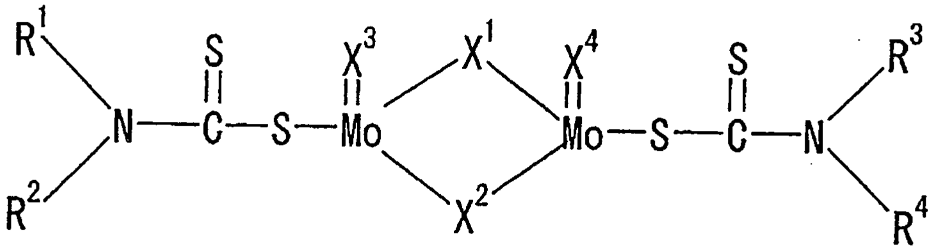
1. A lubricating oil composition for an internal combustion engine, comprising:

   an organic molybdenum compound as a component (A);
   a base oil having a kinematic viscosity at 100°C of 25 mm²/s or more as a component (B); and
   a base oil having a kinematic viscosity at 100°C of less than 12.5 mm²/s as a component (C),
   wherein the composition has a kinematic viscosity at 100°C of 5 mm²/s to 12.5 mm²/s and a phosphorus content of 800 ppm or less.

2. The lubricating oil composition for an internal combustion engine according to claim 1, wherein the lubricating oil composition for an internal combustion engine contains 200 to 2, 000 ppm in terms of a molybdenum content of the component (A), 1 to 30 mass% of the component (B), and 50 to 95 mass% of the component (C) with respect to a total amount thereof.

3. The lubricating oil composition for an internal combustion engine according to claim 1 or 2, wherein the component (A) comprises a compound represented by the following general formula (1):

[Chem. 1]



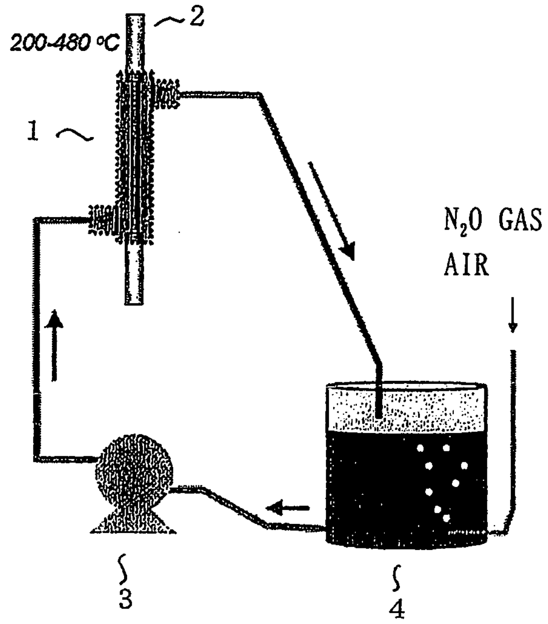
(1)

where R^1 to R^4 each represent a linear or branched alkyl group or alkenyl group having 4 to 18 carbon atoms, and X^1 to X^4 each represent an oxygen atom or a sulfur atom.

4. The lubricating oil composition for an internal combustion engine according to any one of claims 1 to 3, wherein the lubricating oil composition for an internal combustion engine further comprises one or more kinds of additives selected from the group consisting of a viscosity index improver, a pour point depressant, an extreme-pressure agent, an oiliness improver, an antioxidant, a metal-based detergent, an ashless dispersant, a metal deactivator, a rust inhibitor, and an anti-foaming agent.

5. The lubricating oil composition for an internal combustion engine according to claim 4, wherein the lubricating oil composition for an internal combustion engine contains 300 to 800 ppm in terms of a phosphorus content of a zinc dithiophosphate as an extreme-pressure agent with respect to a total amount thereof.

Fig. 1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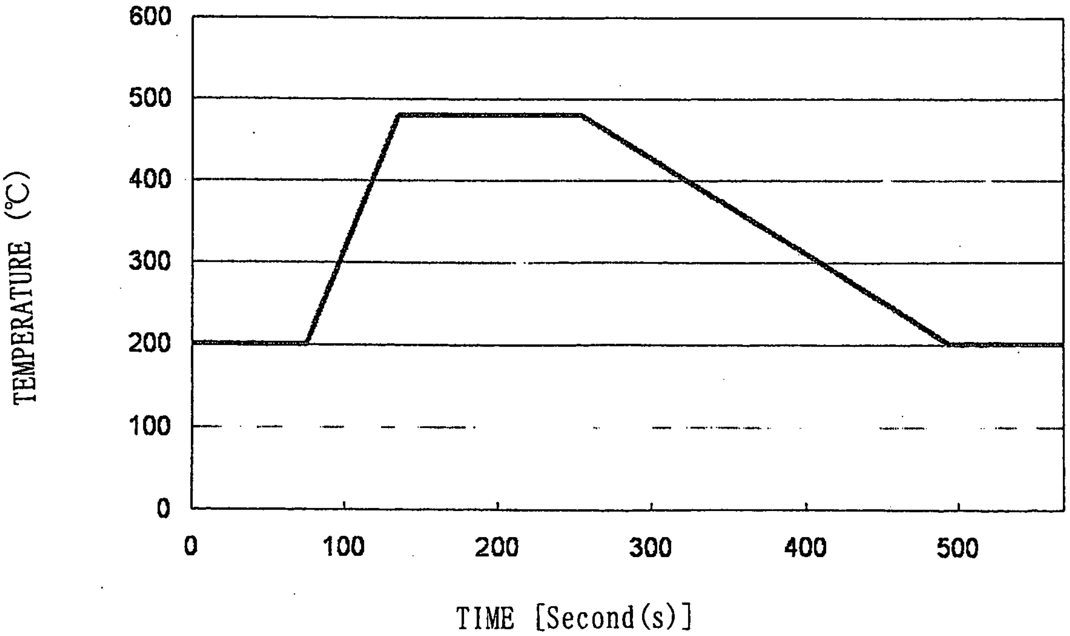
2
1
N_2O GAS
AIR
3
4

Fig. 2


600
500
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TEMPERATURE (℃)
0
100
200
300
400
500
TIME [Second(s)]

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/068747

A. CLASSIFICATION OF SUBJECT MATTER
C10M141/10(2006.01)i, *C10M135/18*(2006.01)n, *C10M137/10*(2006.01)n, *C10M139/00*(2006.01)n, *C10N10/12*(2006.01)n, *C10N20/02*(2006.01)n, *C10N30/06*(2006.01)n, *C10N30/08*(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)
C10M141/10, C10M135/18, C10M137/10, C10M139/00, C10N10/12, C10N20/02, C10N30/06, C10N30/08, C10N40/25

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	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

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.
Y	JP 2001-131570 A (Cosmo Oil Lubricants Co., Ltd.), 15 May 2001 (15.05.2001), claims; paragraph [0027]; example 1 (Family: none)	1-5
Y	JP 2008-303241 A (Japan Energy Corp.), 18 December 2008 (18.12.2008), claims; paragraph [0025] & CN 101319163 A	1-5
Y	JP 2004-277712 A (Nippon Oil Corp.), 07 October 2004 (07.10.2004), claims; paragraphs [0042], [0047], [0055], [0076], [0078], [0091]; example 1 & CN 1524933 A & CN 101629124 A & JP 2010-255009 A	1-5

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

* Special categories of cited documents:
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 01 November, 2011 (01.11.11)	Date of mailing of the international search report 15 November, 2011 (15.11.11)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/068747

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2006-348223 A (Idemitsu Kosan Co., Ltd.), 28 December 2006 (28.12.2006), claims; paragraphs [0003], [0028] & EP 1734105 A2 & US 2006/0287203 A1	1-5
E,X	JP 2011-184566 A (JX Nippon Oil & Energy Corp.), 22 September 2011 (22.09.2011), claims; examples 1 to 8 (Family: none)	1-5
A	JP 2010-180420 A (JX Nippon Oil & Energy Corp.), 19 August 2010 (19.08.2010), claims; paragraphs [0018], [0062]; examples 1 to 5 (Family: none)	1-5

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

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- JP 59122595 A **[0005]**
- JP 9328694 A **[0005]**
- JP 5062639 B **[0011]**
- JP 4030959 B **[0011]**