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(54) LUBRICATING OIL COMPOSITION FOR AUTOMATIC TRANSMISSION

(57) A lubricating oil composition for automatic transmissions wherein the mass ratio of phosphorus : calcium : boron : sulfur determined by elemental analysis is 1 : (0.1 to 2) : (0.06 to 2) : (0.2 to 20), the concentration of phosphorus is from 0.01 to 0.06 percent by mass, the concentration of the sulfur derived from a base oil is from 0 to 0.1 percent by mass, and the concentration of the sulfur derived from sulfur-based additives is from 0.01 to 0.15 percent by mass, based on the total amount of the composition. The lubricating oil composition can prevent the occurrence of scratch phenomenon even over a long period of time when used in a metal belt type continuously variable automatic transmission.

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Description

[Technical Field]

[0001] The present invention relates to lubricating oil compositions for automatic transmissions and more particularly to those advantageously applicable to belt type continuously variable transmissions for automobiles, which compositions are capable of preventing the occurrence of scratch noise by making the friction material of such an automatic transmission exhibit the μ-V characteristics of a positive gradient and of maintaining the positive gradient μ-V characteristics for a longer period of time.

[Background Art]

[0002] Automatic transmissions widely used for modern automobiles are those comprising a gear-shifting unit which is the combination of a torque converter equipped with a lock-up clutch, a wet clutch, and a planetary gear set, and a hydraulic control unit. However, such automatic transmissions have defects that they are poor in fuel efficiency and make a driver feel uncomfortableness caused by shifting shock due to the stepped gear-shifting. Continuously variable transmissions (belt type CVT) transmitting a power via a metal belt and effecting gear-shifting in a stepless manner have been put in use as those for compensating these defects.

[0003] A belt type CVT comprises a driving pulley, a driven pulley, and a belt for transmitting a power which belt is composed of a plurality of elements and a belt (steel belt) connecting the elements together. Automatic transmission fluids (ATF) conventionally used in stepped type automatic transmissions have also been used widely in such a belt type CVT because the ATFs have cooling, lubricating, and anti-abrasion properties and many common parts are used in stepped type automatic transmissions and CVTs. However, it has been found in recent years that automobiles with certain types of belt type CVTs encounter a phenomenon that noises (scratch noises) are made particularly when the automobiles are put into the garage or started, a so-called "scratch phenomenon".

[0004] It has already been found that this scratch phenomenon is caused by tooth hit noise of the gears arranged behind the CVTs and resulting from a fluctuation in the rotation of the driven pulley. Furthermore, it has also been found that such a fluctuation occurs when the change in the friction coefficient (μ) of the belt and elements over that in the slipping velocity (V) is in a negative gradient, as disclosed in Japanese Patent Laid-Open Publication No. 9-263782. ATFs which have been conventionally used in belt type CVT are not always excellent in μ-V characteristics and large in change thereof when used in a long period of time, leading to a failure of complete prevention of the occurrence of scratch noise. As a result, the scratch phenomenon frequently occurs.

[0005] In order to prevent the scratch phenomenon completely with the use of such conventional ATFs, it is necessary to develop a blend technique for an ATF which can always make friction materials exhibit Positive gradient μ-V characteristics. Furthermore, an ATF must meet such requisite performances not only when it is fresh but also after it is used for a certain period of running time and maintain such performances for a long period of time. It is now found that a lubricating oil after a certain period of running progresses to oxidation deterioration and particularly a lubricating oil containing a relatively large amount of sulfur is susceptible to a decrease in μ-V characteristics.

[0006] Therefore, the object of the present invention is to provide a lubricating oil composition for automatic transmissions which composition is suitable for belt type CVTs and capable of preventing the occurrence of scratch noise by making friction materials exhibit the μ-V characteristics of a positive gradient and of maintaining the positive gradient μ-V characteristics for a longer period of time.

[Disclosures of the Invention]

[0007] After extensive researches and studies conducted by the inventors of the present invention, the present invention was made based on the finding that the above object was able to be achieved with a composition wherein specific additives are blended so as to be at specific elemental ratios.

[0008] According to the present invention, there is provided a lubricating oil composition for automatic transmissions wherein the mass ratio of phosphorus : calcium : boron : sulfur determined by elemental analysis is 1 : (0.1 to 2) : (0.06 to 2) : (0.2 to 20), the concentration of phosphorus is from 0.01 to 0.06 percent by mass, the concentration of the sulfur derived from a base oil is from 0 to 0.1 percent by mass, and the concentration of the sulfur derived from sulfur-based additives is from 0.01 to 0.15 percent by mass, based on the total amount of the composition.

[0009] The lubricating oil compositions according to the present invention are preferably those wherein the mass ratio of phosphorus : calcium : boron : sulfur determined by elemental analysis is 1 : (0.1 to 1) : (0.1 to 0.8) : (0.4 to 5), the concentration of phosphorus is from 0.02 to 0.05 percent by mass, the concentration of the sulfur derived from a base oil is from 0 to 0.1 percent by mass, and the concentration of the sulfur derived from sulfur-based additives is from 0.01 to 0.15 percent by mass, based on the total amount of the composition.

[0010] Sulfur-based additives contained in a lubricating oil composition according to the present invention are at least one compound selected from the group consisting of (A) thiadiazoles and/or benzothiazoles, (B) dithiocarbamates, (C) dithiophosphates, (D) trithiophosphites, (E) polysulfides, and derivatives of (A) though (E).

[0011] The present invention will be described in more detail below.

[0012] The lubricating oil compositions of the present invention comprise, phosphorus, calcium, boron, and sulfur in addition to a lubricating base oil. Among these elements, sulfur is derived from the base oil or additives such as sulfur-based additives and/or calcium-based detergents such as calcium sulfonate and calcium phenate. Phosphorus is derived from phosphorus-based additives and a part of sulfur-based additives. Calcium is derived from calcium-based detergents. Boron is derived from various additives such as boric acid-modified succinimides and/or alkali metal borates or hydrates thereof. Each of components of the lubricating oil composition of the present invention will be described in order below.

(1) Base oil

[0013] Lubricating base oils which may be used for the lubricating oil compositions of the present invention may be any mineral base oils and/or synthetic base oils which are conventionally used as base oils for a lubricating oil.

[0014] Examples of such mineral base oil include paraffinic or naphthenic oils which can be obtained by subjecting a lubricating oil fraction produced by atmospheric- or vacuum-distilling a crude oil, to one or more refining processes such as solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, catalytic dewaxing, hydrorefining, washing with sulfuric acid, and clay treatment; and n-paraffines.

[0015] Examples of synthetic base oils include poly-α -olefins such as 1-octene oligomer, 1-decene oligomer, and ethylene-propylene oligomer, and hydrides thereof; isobutene oligomer and hydrides thereof; isoparaffines; alkylbenzenes; alkylnaphthalenes; diesters such as ditridecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate, and di-2-ethylhexyl cebacate; polyol esters such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol-2-ethyl hexanoate, and pentaerythritol pelargonate; polyoxyalkylene glycols; dialkyldiphenyl ethers; and polyphenyl ethers.

[0016] No particular limitation is imposed on the kinematic viscosity of the lubricating base oil. However, the kinematic viscosity at 100 °C of the lubricating base oil is preferably from 1 to 10 mm^2/s, and more preferably from 2 to 8 mm^2/s.

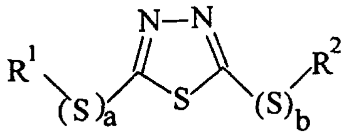
[0017] The concentration of the sulfur derived from the base oil is 0.1 percent by mass or less, preferably 0.05 percent by mass or less, and more preferably 0.005 percent by mass or less. A sulfur concentration in excess of 0.1 percent by mass makes it difficult to maintain stable μ-V characteristics over a long time.

(2) Sulfur-based additives

[0018] Sulfur-based additives which may be used in the present invention are any compounds (A) through (E) described below.

(A) Thiadiazoles and/or benzothiazoles

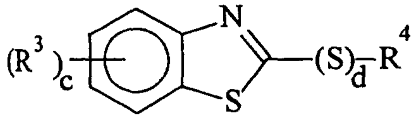
[0019] Specific examples of thiadiazoles include compounds represented by the formula



(1)

[0020] In formula (1), R^1 is a straight-chain or branched alkyl group having 1 to 30, preferably 6 to 24 carbon atoms, R^2 is hydrogen or a straight-chain or branched alkyl group having 1 to 30 carbon atoms, preferably hydrogen or a straight-chain or branched alkyl group having 1 to 24 carbon atoms, and a and b are each independently 1, 2 or 3, preferably 1 or 2.

[0021] Specific examples of benzothiazole include compounds represented by the formula

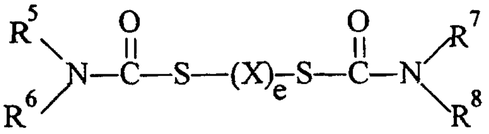

(2)

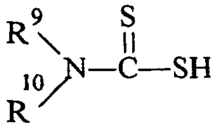
[0022] In formula (2), R^3 is a straight-chain or branched alkyl group having 1 to 4 carbon atoms, preferably methyl and ethyl groups, R^4 is a straight-chain or branched alkyl group having 1 to 30, preferably 6 to 24 carbon atoms, c is an integer of 0 to 3, preferably 0 or 1, and d is an integer from 1 to 3, preferably 1 or 2.

[0023] When Component (A) is blended in a lubricating oil composition according to the present invention, one compound selected from those of formulas (1) and (2) may be used or alternatively two or more compounds having different structures selected from those of formulas (1) and (2) may be used.

(B) Dithiocarbamates

[0024] Although any dithiocarbamates may be used, preferred examples thereof include compounds represented by formula (3) or (4):


(3)


(4)

[0025] In formulas (3) and (4), R^5, R^6, R^7, R^8, R^9, and R^{10} are each independently a hydrocarbon group having 1 to 30, preferably 1 to 20 carbon atoms, X is sulfur or methylene ($-CH_2-$), and e is an integer of 0 to 6.

[0026] Examples of hydrocarbon groups having 1 to 30 carbon atoms for R^5 through R^{10} include alkyl, cycloalkyl, alkylcycloalkyl, alkenyl, aryl, alkylaryl, and arylalkyl groups.

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

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

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

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

[0031] Specific examples of aryl groups include phenyl and naphtyl groups.

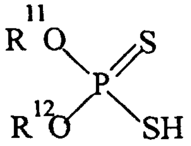
[0032] Examples of alkylaryl groups include those having 7 to 18 carbon atoms, such as tolyl, xylyl, ethylphenyl, propylphenyl, butylphenyl, pentylphenyl, hexylphenyl, heptylphenyl, octylphenyl, nonylphenyl, decylphenyl, undecylphenyl, and dodecylphenyl groups, of which the alkyl group may be straight-chain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

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

[0034] One or more Components (B) may be arbitrary blended.

(C) Dithiophosphates

[0035] Examples of dithiophosphates include one dialkyldithiophosphate and mixtures of two or more dialkyldithiophosphates selected from compounds represented by the formula



(5)

[0036] In formula (5), R^{11} and R^{12} are each independently a hydrocarbon group having 2 to 30, preferably 3 to 20 carbon atoms. Examples of hydrocarbon groups having 2 to 30 carbon atoms for R^{11} and R^{12} are the same as those as described with respect to R^5 through R^8 in formula (3).

(D) Trithiophosphites

[0037] Examples of trithiophosphites include trithiophosphite compounds having a hydrocarbon group having 2 to 30, preferably 3 to 20 carbon atoms. Examples of hydrocarbon group having 2 to 30 carbon atoms are the same as those as described with respect to R^5 through R^8 in formula (3).

(E) Polysulfides

[0038] Polysulfides are sulfur-based compounds generally referred to dihydrocarbylsulfides or olefin sulfides and represented by the formula

$$R^{13} - S_f - R^{14} \tag{6}$$

[0039] In formula (6), R^{13} and R^{14} are each independently a straight-chain or branched alkyl group having 3 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, an alkylaryl group having 6 to 20 carbon atoms, or an arylalkyl group having 6 to 20 carbon atoms, and f is an integer of 2 to 6, preferably 2 to 5.

[0040] Examples of alkyl groups for R^{13} and R^{19} include n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, straight-chain or branched pentyl, straight-chain or branched hexyl, straight-chain or branched heptyl, straight-chain or branched octyl, straight-chain or branched nonyl, straight-chain or branched decyl, straight-chain or branched undecyl, straight-chain or branched dodecyl, straight-chain or branched tridecyl, straight-chain or branched tetradecyl, straight-chain or branched pentadecyl, straight-chain or branched hexadecyl, straight-chain or branched heptadecyl, straight-chain or branched octadecyl, straight-chain or branched nonadecyl, and straight-chain or branched eicosyl groups.

[0041] Examples of aryl groups for R^{13} and R^{14} include phenyl and naphthyl groups.

[0042] Examples of alkylaryl groups for R^{13} and R^{14} include tolyl (inclusive all structural isomers), ethylphenyl (inclusive all structural isomers), straight-chain or branched propylphenyl (inclusive all structural isomers), straight-chain or branched butylphenyl (inclusive all structural isomers), straight-chain or branched pentylphenyl(inclusive all structural isomers), straight-chain or branched hexylphenyl (inclusive all structural isomers), straight-chain or branched heptylphenyl (inclusive all structural isomers), straight-chain or branched octylphenyl (inclusive all structural isomers), straight-chain or branched nonylphenyl (inclusive all structural isomers), straight-chain or branched decylphenyl (inclusive all structural isomers), straight-chain or branched undecylphenyl (inclusive all structural isomers), straight-chain or branched dodecylphenyl (inclusive all structural isomers), xylyl (inclusive all structural isomers), ethylmethylphenyl group (inclusive all structural isomers), diethylphenyl (inclusive all structural isomers), di(straight-chain or branched) propylphenyl (inclusive all structural isomers), di (straight-chain or branched)butylphenyl (inclusive all structural isomers), methylnaphtyl (inclusive all structural isomers), ethylnaphtyl (inclusive all structural isomers), straight-chain or branched propylnaphtyl (inclusive all structural isomers), straight-chain or branched butylnaphtyl (inclusive all structural isomers), dimethylnaphtyl (inclusive all structural isomers), ethylmethylnaphtyl (inclusive all structural isomers), diethylnaphtyl (inclusive all structural isomers), di(straight-chain or branched)propylnaphtyl (inclusive all structural isomers), and di(straight-chain or branched)butylnaphtyl groups (inclusive all structural isomers).

[0043] Examples of arylalkyl groups for R^{13} and R^{14} include benzyl, phenylethyl(inclusive all isomers), and phenylpropyl (inclusive all isomers).

[0044] R^{13} and R^{14} each are preferably an alkyl group having 3 to 18 carbon atoms derived from propylene, 1-butene, or isobutylene, an aryl group having 6 to 8 carbon atoms, an alkylaryl group having 7 or 8 carbon atoms, or an arylalkyl group having 7 or 8 carbon atoms.

[0045] Specific examples of such an alkyl group include isopropyl, branched hexyl derived from a propylene dimmer (inclusive all branched isomers), branched nonyl derived from a propylene trimer (inclusive all branched isomers), branched dodecyl derived from a propylene tetramer (inclusive all branched isomers), branched pentadecyl derived from a propylene pentamer (inclusive all branched isomers), branched octadecyl derived from a propylene hexamer (inclusive all branched isomers), sec-butyl, tert-butyl, branched octyl derived from a 1-butene dimmer (inclusive all branched isomers), branched octyl derived from an isobutylene dimmer (inclusive all branched isomers), branched dodecyl derived from a 1-butene trimer (inclusive all branched isomers), branched dodecyl derived from an isobutylene trimer (inclusive all branched isomers), branched hexadecyl derived from a 1-butene tetramer (inclusive all branched isomers), and branched hexadecyl derived from an isobutylene tetramer (inclusive all branched isomers). Specific examples of such an aryl groups include phenyl group. Specific examples of such alkylaryl groups are tolyl (inclusive all structural isomers), ethylphenyl (inclusive all structural isomers), and xylyl (inclusive all structural isomers). Specific examples of such arylalkyl groups are benzyl and phenetyl (inclusive all structural isomers).

[0046] One or more compounds selected from the above described sulfur-containing additive, i.e., Components (A) through (E) and derivatives thereof may be used in the lubricating oil composition of the present invention. In the present invention, the content of the sulfur-based additives is in such a range that the total sulfur concentration of the sulfur derived from Components (A) through (E) and derivatives thereof and the sulfur derived from other additives is from 0.01 to 0.15 percent by mass, based on the total amount of the composition and the total phosphorus concentration of the phosphorus derived from Components (A) through (E) and derivatives thereof and the phosphorus derived from the phosphorus-based additives is from 0.01 to 0.06 percent by mass, based on the total amount of the composition. When the sulfur-based additives are contained in an amount of less than 0.01 percent by mass in terms of sulfur or in an amount of less than 0.01 percent by mass in terms of phosphorus, they are less in effect to improve the μ-V characteristics. When the sulfur-based additives are contained in an amount exceeding 0.15 percent by mass in terms of sulfur or in an amount exceeding 0.06 percent by mass in terms of phosphorus, they deteriorate the oxidation stability of the resulting lubricating oil composition.

[0047] In order to further improve the μ-V characteristics, the content of the sulfur-based additives is preferably in such a range that the total sulfur concentration of the sulfur derived from Components (A) through (E) and derivatives thereof and the sulfur derived from the other additives is from 0.01 to 0.15 percent by mass, based on the total amount of the composition and the total phosphorus concentration of the phosphorus derived from Components (A) through (E) and derivatives thereof and the phosphorus derived from the phosphorus-based additives is from 0.02 to 0.05 percent by mass, based on the total amount of the composition.

(3) (F) Phosphorus-based additives

[0048] Examples of phosphorus-based additives, hereinafter referred to as Component (F) which may be used in the present invention are monophosphates, diphosphates, triphosphates, monophosphites, diphosphites, triphosphites, salts of phosphates and phosphites, phosphoric acid, phosphorous acid, zinc alkyldithiophosphates and mixtures thereof. Among these components (Component (F)), those other than phosphoric acid and phosphorus acid are compounds containing a hydrocarbon group having 2 to 30, preferably 3 to 20 carbon atoms.

[0049] Examples of hydrocarbon groups having 2 to 30 carbon atoms include alkyl, cycloalkyl, alkylcycloalkyl, alkenyl, aryl, alkylaryl, and arylalkyl groups.

[0050] Examples of alkyl groups include ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl groups, all of which may be straight-chain or branched.

[0051] Examples of cycloalkyl groups include those having 5 to 7 carbon atoms, such as cyclopentyl, cyclohexyl, and cycloheptyl groups.

[0052] Examples of alkylcycloalkyl groups include those having 6 to 11 carbon atoms, of which the cycloalkyl group may possess an alkyl substituent at any position, such as methylcyclopentyl, dimethylcyclopentyl, methylethylcyclopentyl, diethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, methylethylcyclohexyl, diethylcyclohexyl, methylcycloheptyl, dimethylcycloheptyl, methylethylcycloheptyl and diethylcycloheptyl groups.

[0053] Examples of alkenyl groups include butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl and octadecenyl groups, all of which may be straight-chain or branched and the position of which the double bond may vary.

[0054] Examples of aryl groups include those having 6 to 18 carbon atoms such as phenyl and naphthyl.

[0055] Examples of alkylaryl groups include those having 7 to 18 carbon atoms, such as tolyl, xylyl, ethylphenyl, propylphenyl, butylphenyl, pentylphenyl, hexylphenyl, heptylphenyl, octylphenyl, nonylphenyl, decylphenyl, undecylphenyl, and dodecylphenyl groups, all of which the alkyl group may be straight-chain or branched and may bond to any position of the aryl group.

[0056] Examples of arylalkyl groups include those having 7 to 12 carbon atoms, such as benzyl, phenylethyl, phenylpropyl, phenylbutyl, phenylpentyl and phenylhexyl groups, all of which may be straight-chain or branched.

[0057] Preferred compounds as Component (F) are phosphoric acid; phosphorus acid; zinc alkyldithiophosphates, of which the alkyl group may be straight-chain or branched, such as zinc dipropyldithiophosphate, zinc dibutyldithiophosphate, zinc dipentyldithiophosphate, zinc dihexyldithiophosphate, zinc diheptyldithiophosphate, and zinc dioctyldithiophosphate; monoalkyl phosphates, of which the alkyl group may be straight-chain or branched, such as monopropyl phosphate, monobutyl phosphate, monopentyl phosphate, monohexyl phosphate, monoheptyl phosphate and monooctyl phosphate; mono(alkyl)aryl phosphates such as monophenyl phosphate and monocresyl phosphate; dialkyl phosphates, of which the alkyl group may be straight-chain or branched, such as dipropyl phosphate, dibutyl phosphate, dipentyl phosphate, dihexyl phosphate, diheptyl phosphate and dioctyl phosphate; di(alkyl)aryl phosphates such as diphenyl phosphate and dicresyl phospahte; trialkyl phosphates, of which the alkyl group may be straight-chain or branched, such as tripropyl phosphate, tributyl phosphate, tripentyl phosphate, trihexyl phosphate, triheptyl phosphate and trioctyl phosphate; tri(alkyl)aryl phosphates such as triphenyl phosphate and tricresyl phosphate; monoalkyl phosphites, of which the alkyl group may be straight-chain or branched, such as monopropyl phosphite, monobutyl phosphite, monopentyl phosphite, monohexyl phosphite, monoheptyl phosphite and monooctyl phosphite; mono(alkyl)aryl phosphites such as monophenyl phosphite and monocresyl phosphite; dialkyl phosphites, of which the alkyl group may be straight-chain or branched, such as dipropyl phosphite, dibutyl phosphite, dipentyl phosphite, dihexyl phosphite, diheptyl phosphite and dioctyl phosphite; di(alkyl)aryl phosphites such as diphenyl phosphite and dicresyl phosphite; trialkyl phosphites, of which the alkyl group may be straight-chain or branched, such as tripropyl phosphite, tributyl phosphite, tripentyl phosphite, trihexyl phosphite, triheptyl phosphite and trioctyl phosphite; tri(alkyl)aryl phosphites, of which the alkyl group may be straight-chain or branched, such as triphenyl phosphite and tricresyl phosphite; and mixtures thereof.

[0058] Specific examples of salts of phosphates and phosphites include those obtained by allowing monophosphate, diphosphate, monophosphite, or diphosphite to react with a nitrogen-containing compound such as ammonia or an amine compound having in its molecules only a hydrocarbon group or hydroxyl-containing hydrocarbon group having 1 to 8 carbon atoms so as to neutralize the whole or part of the remaining acid hydrogen.

[0059] Specific examples of nitrogen-containing compound include ammonia; alkylamines, of which the alkyl group may be straight-chain or branched, such as monomethylamine, monoethylamine, monopropylamine, monobutylamine, monopentylamine, monohexylamine, monoheptylamine, monooctylamine, dimethylamine, methylethylamine, diethylamine, methylpropylamine, ethylpropylamine, dipropylamine, methylbutylamine, ethylbutylamine, propylbutylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine and dioctylamine; alkanolamines, of which the alkanol group may be straight-chain or branched, such as monomethanolamine, monoethanolamine, monopropanolamine, monobutanolamine, monopentanolamine, monohexanolamine, monoheptanolamine, monooctanolamine, monononanolamine, dimethanolamine, methanolethanolamine, diethanolamine, methanolpropanolamine, ethanolpropanolamine, dipropanolamine, methanolbutanolamine, ethanolbutanolamine, propanolbutanolamine, dibutanolamine, dipentanolamine, dihexanolamine, diheptanolamine, and dioctanolamine; and mixtures thereof.

[0060] The lubricating oil compositions of the present invention contain Component (F) in such an amount that the total phosphorus concentration of the phosphorus derived from Component (F) and the phosphorus derived from the other additives is from 0.01 to 0.06 percent by mass, based on the total amount of the composition. A phosphorus concentration of less than 0.01 percent by mass is not preferred because the resulting composition would be less effective in anti-abrasion properties, while a phosphorus concentration in excess of 0.06 percent by mass is not also preferred because the resulting composition would be deteriorated in oxidation stability. In order to further improve the μ-V characteristics, Component (F) is preferably contained in such an amount that the total phosphorus concentration of the phosphorus derived from Components (F) and the phosphorus derived from the other additives is from 0.02 to 0.05 percent by mass, based on the total amount of the composition.

(4) (G) Calcium-based detergents

[0061] Examples of calcium-based detergents, hereinafter referred to as Component (G) which may be used in the present invention include basic calcium-based detergents having a total base number of generally 20 to 450 mgKOH/g, preferably 50 to 400 mgKOH/g. The term "total base number" used herein denotes a total base number measured by the perchloric acid potentiometric titration method in accordance with section 7 of JIS K2501 (1992) "Petroleum products and lubricants-Determination of neutralization number".

[0062] Specific examples of Component (G) include one or more calcium-based detergents selected from the following compounds:

(G-1) calcium sulfonate having a total base number of 20 to 450 mgKOH/g;
(G-2) calcium phenate having a total base number of 20 to 450 mgKOH/g; and
(G-3) calcium salicylate having a total base number of 20 to 450 mgKOH/g.

[0063] Specifically, Component (G-1), i.e., calcium sulfonate may be a calcium salt of an alkyl aromatic sulfonic acid obtained by sulfonating an alkyl aromatic compound having a molecular weight of 100 to 1,500 and preferably 200 to 700. Specific examples of alkyl aromatic sulfonic acids are petroleum sulfonic acids and synthetic sulfonic acids.

[0064] Petroleum sulfonic acids may be those obtained by sulfonating the alkyl aromatic compound contained in the lubricant fraction of a mineral oil or mahogany acid by-produced upon production of white oil. Synthetic sulfonic acids may be those obtained by sulfonating an alkyl benzene having a straight-chain or branched alkyl group, which may be by-produced from a plant for producing an alkyl benzene used as materials of detergents or obtained by alkylating a polyolefin to benzene or sulfonating dinonylnaphthalene. Although not restricted, there may be used fuming sulfuric acids and sulfuric acid as a sulfonating agent.

[0065] Specifically, Component (G-2),i.e., calcium phenate may be a calcium salt of an alkylphenol having at least one straight-chain or branched alkyl group having 4 to 30, preferably 6 to 18 carbon atoms; a calcium salt of an alkylphenolsulfide obtained by reacting such an alkylphenol with sulfur; or a calcium salt of a Mannich reaction product of an alkylphenol obtained by reacting an alkylphenol with formaldehyde.

[0066] Specifically, Component (G-3),i.e., calcium salicylate may be a calcium salt of an alkyl salicylic acid having at least one straight-chain or branched alkyl group having 4 to 30, preferably 6 to 18 carbon atoms.

[0067] As long as Component (G), i.e., the above described calcium sulfonate, calcium phenate, or calcium salicylate has a total base number within a range of 20 to 450 mgKOH/g, it may be a neutral (normal) salt obtained by reacting an alkylaromatic sulfonic acid, an alkylphenol, an alkylphenolsulfide, a Mannich reaction product of an alkylphenol or an alkyl salicylic acid directly with calcium oxide or calcium hydroxide or by substituting an alkylaromatic sulfonic acid, an alkylphenol, an alkylphenolsulfide, a Mannich reaction product of an alkylphenol or an alkyl salicylic acid which has been converted to an alkali metal salt such as a sodium salt or a potassium salt, with a calcium salt. Alternatively, Component (G) may be a basic calcium salt obtained by heating a normal salt as described above with an excess amount of a calcium salt or calcium hydroxide in the presence of water. Further alternatively, Component (G) may be an overbased calcium salt obtained by reacting a normal salt as described above with a basic calcium salt as described above in the presence of carbonic acid gas. These reactions are conducted in a solvent, for example, an aliphatic hydrocarbon solvent such as hexane, an aromatic hydrocarbon solvent such as xylene, or a light fraction lubricating base oil.

[0068] Metallic detergents are commercially available in the form of being diluted with a light fraction lubricating base oil. It is preferred to use metallic detergents whose metal content is within the range of 1.0 to 20 percent by mass, preferably 2.0 to 16 percent by mass.

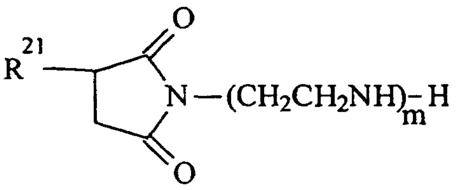
[0069] No particular limitation is imposed on the content of Component (G). However, Component (G) is contained in an amount of preferably 0.01 to 5.0 percent by mass, more preferably 0.05 to 4.0 percent by mass, based on the total amount of the composition. Component (G) of less than 0.01 percent by mass would be less effective in suppressing a wet clutch from being decreased in strength against repeating compression applied thereto, while Component (G) in excess of 5.0 percent by mass would decrease the oxidation stability of the resulting composition.

(5) (H) Boric acid-modified succinimides

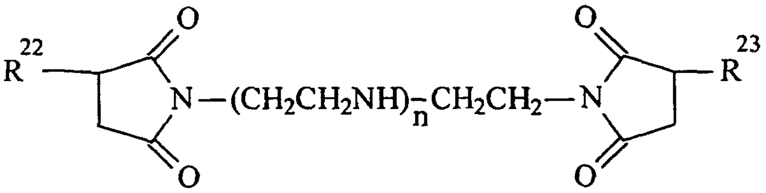
[0070] Examples of boric acid-modified succinimides, hereinafter referred to as Component (H), which may be used in the present invention include those obtained by modifying an alkenyl succinimide having in its molecules at least one alkyl or alkenyl group having 40 to 400 carbon atoms, with boric acid. One or more of such succinimides may be blended in the lubricating oil compositions of the present invention.

[0071] The carbon number of the alkyl or alkenyl group is from 40 to 400, preferably from 60 to 350. An alkyl or alkenyl group having less than 40 carbon atoms would decrease the solubility of Component (H) in a lubricating base oil, while an alkyl or alkenyl group having more than 400 carbon atoms would deteriorate the low temperature fluidity.

[0072] Specific examples of succinimides which may be used in the present invention include compounds represented by formula (7) or (8):


(7)

wherein R^{21} is an alkyl or alkenyl having 40 to 400, preferably 60 to 350 carbon atoms, and m is an integer from 1 to 5, preferably from 2 to 4; or


(8)

wherein R^{22} and R^{23} are each independently an alkyl or alkenyl group having 40 to 400, preferably 60 to 350 carbon atoms, and n is an integer of 0 to 4, preferably 1 to 3.

[0073] The succinimides are classified into mono-type succinimides wherein a succinic anhydride is added to one end of a polyamine as represented by formula (7) and bis-type succinimides wherein a succinic anhydride is added to both ends of a polyamine as represented by formula (8). In the present invention, both types of the succinimides and mixtures thereof can be used as Component (H). The boric acid-modified succinimides used herein are boron-modified compounds obtained by bringing the above-described succinimide into the reaction with boric acid so as to neutralize or amidize the whole or part of the remaining amino and/or imino groups.

[0074] When the lubricating oil composition of the present invention contains Component (H), the content thereof is generally from 0.01 to 10.0 percent by mass, preferably from 0.1 to 7.0 percent by mass, based on the total mass of the composition. Component (H) of less than 0.01 percent by mass would fail to obtain a sufficient detergency effect, while Component (H) in excess of 10.0 percent by mass would deteriorate extremely the low temperature fluidity of the resulting composition.

(6) (I) Alkali metal borates and hydrides thereof

[0075] Examples of Components (I), i.e., alkali metal borate and hydrides thereof include lithium borate hydride, sodium borate hydride, potassium borate hydride, rubidium borate hydride, and cesium borate hydride. Particularly preferred is potassium borate hydride.

[0076] These alkali metal borates may be obtained by dissolving potassium hydroxide or sodium hydroxide and boric acid in water such that the atomic ratio of boric acid to an alkali metal (potassium/sodium) falls within the range of 2.0 to 4.5 (boron/alkali metal); adding the solution in an oily solution containing a neutral alkaline earth metal sulfonate or a succinimide-based ashless dispersant, followed by vigorous stirring so as to produce a water in oil emulsion; and dehydrating the emulsion so as to obtain a dispersant of fine particles of a potassium borate hydride or a sodium borate hydride.

[0077] In the lubricating oil composition, the blend ratio of one or more Components (I) is arbitrarily selected but is preferably 0.002 percent by mass or more, preferably 0.005 percent by mass or more and 0.1 percent by mass or less, preferably 0.06 percent by mass or less, in terms of boron, based on the total amount of the composition. Component (I) of less than 0. 002 percent by mass in terms of boron would make Component (A) less effective in providing the resulting composition with enhanced friction properties between metal parts, while Component (I) in excess of 0.1 percent by mass in terms of boron would decrease the storage stability of the resulting oil composition.

(7) Other additives

[0078] The lubricating oil compositions of the present invention may be used in combination with various known additives in order to further enhance the scratch preventing properties and other properties as a lubricating oil. Such additives may be ashless dispersants, metal detergents other than Components (G), friction modifiers, oxidation inhibitors, viscosity index improvers, antifoamers, and abrasion inhibitors.

(J) Ashless dispersants

[0079] Ashless dispersants which may be used in combination with the lubricating oil compositions of the present invention may be any compounds which are usually used as ashless dispersants in a lubricating oil. For example, there may be used nitrogen-containing compounds having in the molecules at least one alkyl or alkenyl group having 40 to 400 carbon atoms, such as those having an amino or imino group or derivatives thereof, or the modified products of alkenyl succinimides.

[0080] The alkyl or alkenyl group may be straight-chain or branched and is preferably a branched alkyl or alkenyl group derived from an oligomer of an olefin such as propylene, 1-butene, and isobutylene or a cooligomer of ethylene and propylene. The alkyl or alkenyl group has 40 to 400, preferably 60 to 350 carbon atoms. An alkyl or alkenyl group having less than 40 carbon atoms would adversely affect the solubility of the compound in a base oil, while an alkyl or alkenyl group having more than 400 carbon atoms would deteriorate the low-temperature fluidity of the resulting lubricating oil composition.

[0081] Specific examples of the derivatives of nitrogen-containing compounds include oxygen-modified compounds obtained by bringing a nitrogen-containing compound into a reaction with a monocarboxylic acid having 2 to 30 carbon atoms, such as fatty acid or a polycarboxylic acid having 2 to 30 carbon atoms, such as oxalic acid, phthalic acid, trimellitic acid, and pyromellitic acid so as to neutralize or amidize the whole or part of the remaining amino and/or imino groups; sulfur-modified compounds obtained by bringing a nitrogen-containing compound into a reaction with a sulfuric compound; and modified products obtained by bringing the nitrogen-containing compound into a combination of two or more modifications selected from the oxygen modification and sulfur modification.

[0082] Although in the present invention, one or more compounds selected from the above-described ashless dispersants may be blended in an arbitrary ratio, the content of the ashless dispersants is generally within the range of 0.1 to 10 percent by mass, based on the lubricating oil composition.

(K) Metal detergents

[0083] Metal detergents, other than Component (G), which may be used in combination with the lubricating oil compositions of the present invention may be any compounds which are usually used as metal detergents in a lubricating oil. For example, there may be used alkali metal or alkaline earth metal sulfonates, alkali metal or alkaline earth metal pehnates, alkali metal or alkaline earth metal salicylates, and alkali metal or alkaline earth metal naphthenates. One or more these compounds may be used in combination. Examples of alkali metals are sodium and potassium, while example of alkaline earth metal is magnesium. Specific preferred examples of the metal detergents are magnesium sulfonate, magnesium phenate, and magnesium salicylate. The total base value and blend amount of these metal detergents are arbitrarily selected depending on the requisite performance characteristics of a lubricating oil.

[0084] Although in the present invention, one or more compounds selected from the above-described metal detergents may be blended in an arbitrary ratio, the content of thereof is generally within the range of 0.01 to 5 percent by mass, based on the lubricating oil composition.

(L) Friction modifiers

[0085] Friction modifiers which may be used in combination with the lubricating oil compositions of the present invention may be any compounds which are usually used as friction modifiers in a lubricating oil. For example, there may be used amine compounds, fatty acid esters, fatty acid amides, and fatty acid metal salts, all having in the molecules at least one alkyl or alkenyl group having 6 to 30 carbon atoms, preferably at least one straight-chain alkyl or alkenyl group having 6 to 30 carbon atoms.

[0086] Examples of amine compounds include straight-chain or branched, preferably straight-chain aliphatic monoamines having 6 to 30 carbon atoms, straight-chain or branched, preferably straight-chain aliphatic polyamines having 6 to 30 carbon atoms, and alkyleneoxide adducts of these aliphatic amines. Examples of fatty acid esters include esters of straight-chain or branched, preferably straight-chain fatty acids having 7 to 31 carbon atoms and aliphatic monohydric alcohols or aliphatic polyhydric alcohols. Examples of fatty acid amides include amides of straight-chain or branched, preferably straight-chain fatty acids having 7 to 31 carbon atoms and aliphatic monoamines or aliphatic polyamines. Examples of fatty acid metal salts include alkaline earth metal salts (magnesium salts and calcium salts) or zinc salts of straight-chain or branched, preferably straight-chain fatty acids having 7 to 31 carbon atoms.

[0087] Although in the present invention, one or more compounds selected from the above-described friction modifiers may be blended in an arbitrary ratio, the content of thereof is generally within the range of 0.01 to 5.0 percent by mass, preferably 0.03 to 3.0 percent by mass, based on the total amount of the lubricating oil composition.

(M) Oxidation inhibitors

[0088] Oxidation inhibitors which may be used in combination with the lubricating oil compositions of the present invention may be any conventional ones such as phenol-based compounds or amine-based compounds which are usually used as oxidation inhibitors in a lubricating oil.

[0089] Specific examples of oxidation inhibitors are alkylphenols such as 2-6-di-tert-butyl-4-methylphenol, bisphenols such as methylene-4,4-bisphenol(2,6-di-tert-butyl-4-methylphenol), naphtylamines such as phenyl-α -naphtylamine, dialkyldiphenylamines, zinc dialkyldithiophosphates such as zinc di-2-ethylhexyldithiophosphate, and esters of (3, 5-di-tert-butyl-4-hydroxyphenyl) fatty acid such as propionic acid and monohydric or polyhydric alcohols such as methanol, octadecanol, 1,6-hexanediol, neopentyl glycol, thiodiethylene glycol, triethylene glycol, and pentaerythritol.

[0090] Although in the present invention, one or more compounds selected from the above-described oxidation inhibitors may be blended in an arbitrary ratio, the content of thereof is generally within the range of 0.01 to 5.0 percent by mass, based on the total amount of the lubricating oil composition.

(N) Viscosity index improvers

[0091] Viscosity index improvers which may be used in combination with the lubricating oil compositions of the present invention may be non-dispersion type viscosity index improvers such as polymers or copolymers of one or more monomers selected from various methacrylates or hydrides thereof and dispersion type viscosity index improvers such as copolymers of various methacrylates further containing nitrogen compounds. Another examples of viscosity index improvers are non-dispersion- or dispersion-type ethylene-α-olefin copolymers wherein the α-olefin may be propylene, 1-butene, or 1-pentene, or the hydrides thereof, polyisobutylenes or the hydrogenated products thereof, styrene-diene hydrogenated copolymers, styrene-maleate anhydride copolymers, and polyalkylstyrenes.

[0092] It is necessary to select the molecular weight of these viscosity index improvers considering the shear stability thereof. Specifically, the number-average molecular weight of non-dispersion or dispersion type polymethacrylates is preferably from 5,000 to 150, 000, and more preferably from 5,000 to 35,000. The number-average molecular weight of polyisobutylenes or hydrides thereof is from 800 to 5,000, preferably from 1,000 to 4,000. Ethylene-α-olefin copolymers and hydrides thereof have a number-average molecular weight of from 800 to 150,000, preferably from 3,000 to 12,000.

[0093] Among these viscosity index improvers, the use of ethylene-α-olefin copolymers or hydrides thereof is contributive to the production of a lubricating oil composition which is excellent in particularly shear stability.

[0094] Although in the present invention, one or more compounds selected from the above-described viscosity index improvers may be blended in an arbitrary ratio, the content of thereof is generally within the range of 0.1 to 40.0 percent by mass, based on the total amount of the lubricating oil composition.

(O) Anti-foamers

[0095] Anti-foamers which may be used in combination with the lubricating oil compositions of the present invention may be any conventional ones which are usually used as anti-foamers in a lubricating oil. Specific examples of anti-foamers include silicones such as dimethylsilicone and fluorosilicone. Although in the present invention, one or more compounds selected from the above-described anti-foamers may be blended in an arbitrary ratio, the content of thereof is generally within the range of 0.001 to 0.05 percent by mass, based on the total amount of the lubricating oil composition.

(P) Corrosion inhibitors

[0096] Corrosion inhibitors which may be used in combination with the lubricating oil composition of the present invention may be any conventional ones which are usually used as corrosion inhibitors for a lubricating oil. Examples of corrosion inhibitors include benzotriazole-, tolyltriazole-, and imidazole-based compounds. Although in the present invention, one or more compounds selected from the above-described corrosion inhibitors may be blended in an arbitrary ratio, the content of thereof is generally within the range of 0.01 to 3.0 percent by mass, based on the total amount of the lubricating oil composition.

[0097] The lubricating oil compositions of the present invention contain phosphorus, calcium, boron and sulfur in a mass ratio of 1 : (0.1-2) : (0.06-2) : (0.2-20), determined by elemental analysis, based on the total amount of the composition. The mass ratio is preferably 1 : (0.1-1.0) : (0.1-0.8) : (0.4-5.0).

[0098] The lubricating oil compositions contain phosphorus at a concentration of from 0.01 to 0.06 percent by mass, preferably from 0.02 to 0.05 percent by mass, based on the total amount of the composition.

[0099] The lubricating oil compositions contain the sulfur derived from the base oil at a concentration of from 0 to 0.1 percent by mass and the sulfur derived from the sulfur-based additives at a concentration of from 0.01 to 0.01 to 0.15. When the above-described elemental mass ratio and concentrations of the phosphorus and the sulfur in the base oil and the sulfur-based additives deviate the above-described ranges, respectively, the resulting lubricating oil composition would be deteriorates in μ-V characteristics and thus scratch phenomenon frequently occurs.

[Applicabilities in the Industry]

[0100] The use of the lubricating oil compositions of the present invention can prevent the occurrence of scratch phenomenon by making the belt and elements in an automatic transmission exhibit the μ-V characteristics of a positive gradient and can maintain the positive gradient μ-V characteristics for a long period of time. Therefore, the lubricating oil compositions of the present invention are suitable for continuously variable transmissions such as belt type CVTs. The lubricating oil compositions can be also suitably used step type automatic transmission and final reduction drive gears equipped with a limited-slip differential.

[Best Modes for Carrying out the Invention]

[0101] The present invention will de described in more detail with reference to the following Inventive and Comparative Examples but are not limited thereto.

<u>Inventive Examples 1 to 8 and Comparative Examples 1 to 5</u>

[0102] Lubricating oil compositions of Inventive Examples 1 to 8 and Comparative Examples 1 to 5 were prepared in accordance with the formulations set forth in Tables 1 to 3 below. Each of the compositions was subjected to the following μ-V characteristics test.

(μ-V characteristics test)

[0103] μ-V characteristics were evaluated by the following friction test.

Apparatus : Falex No. 6 friction wear tester
Surface pressure : 3 Mpa
Oil temperature : 80°C

[0104] μ-V characteristics evaluation : a friction coefficient at a slipping velocity of 0.020 m/s and a friction coefficient at a slipping velocity of 0.005 m/s are measured and the ratio (gradient) therebetween is calculated. There is a correlation between whether the gradient is positive or negative and whether scratch phenomenon occurs or not. When the gradient is positive, scratch phenomenon does not occur, while the gradient is negative, scratch phenomenon possibly occurs.

[0105] As apparent from the test results shown in Tables 1 to 3, all the lubricating oil compositions of the present invention (Inventive Examples 1 to 8) exhibited positive-gradient μ-V characteristics. However, the lubricating oil compositions of Comparative Examples 1 to 5 wherein the elemental ratio (mass ratio) of phosphorus, calcium, boron, and sulfur deviated from the range defined by the present invention failed to exhibit positive-gradient μ-V characteristics.

Table 1

			Example 1	Example 2	Example 3	Example 4
Base Oil	Hydrocracking Mineral Oil A 1)	mass%				
	Hydrocracking Mineral Oil B 2)	mass%	100	100	100	100
	Solvent Refining Mineral Oil A 3)	mass%				
Base Oil Viscosity (100°C)		mm^2/s	4.1	4.1	4.1	4.1
Concentration of Sulfur derived from Base Oil		mass%	0.000	0.000	0.000	0.000
Polyalkylmethacrylate A 4)		mass%	6	6	6	6
Polyalkytmethacrylate B 5)		mass%				
ATF Additive Package 6)			8	8	8	8
Ashless Dispersant A 7)			1.5	1.5	1.5	1.5
Calcium Sulfonate 8)		mass%	0.09	0.09	0.09	0.09
Sulfur-based Additives	Thiadiazole 9)	mass%	0.05	0.2		
	Dithiocarbamate 10)	mass%			0.2	
	Dithiophosphate 11)	mass%				0.2
	Trithiophosphite 12)	mass%				
	Polysulfide A 13)	mass%				
	Polysulfide B 14)	mass%				
Element Concentration	Phosphorus	mass%	0.030	0.030	0.030	0.048
	Calcium	mass%	0.011	0.011	0.011	0.011
	Boron	mass%	0.007	0.007	0.007	0.007
	Sulfur	mass%	0.019	0.073	0.061	0.036
Element Ratio	Phosphorus		1.00	1.00	1.00	1.00
	Calcium		0.36	0.36	0.36	0.23
	Boron		0.23	0.23	0.23	0.14
	Sulfur		0.65	2.45	2.05	0.76

1) Hydrocracking Mineral Oil A: Base Oil Viscosity (100°C) 3.1mm^2/s, Sulfur Content: <0.001 mass%

2) Hydrocracking Mineral Oil B: Base Oil Viscosity (100°C) 4.1mm^2/s, Sulfur Content: <0.001mass%

3) Solvent Refining Mineral Oil A: Base Oil Viscosity (100°C) 2.1mm^2/s. Sulfur Content: 0.09mass%

4) Dispersion Type Polymethacrylate

5) Non-dispertion Type Polymethacrylate

6) Containing Ashless Dispersant, Phosphorus-based Additive, Oxidation Inhibitor, Diluted Oil, and the like
Phosphorus Content and Boron Content in ATF Additive Package: 0.38mass%, 0.013mass%

7) Boric Acid-modified Polybutenyl Succinimide. Boron Content: about 0.5mass%

8) Total Base Value: 300mgKOH/g, Calcium Content: about 12mass%

9) Sulfur Content: 36mass%

10) Sulfur Content: 30mass%

11) Sulfur Content: 8.8mass%, Phosphorus Content: 8.8mass%

12) Sulfur Content: 15mass%, Phosphorus Content: 4mass%

13) Sulfur Content: 10mass%

14) Sulfur Content: 43mass%

Table 1 (continued)

			Example 1	Example 2	Example 3	Example 4
μ-V Gradient 15)			0.002	0.004	0.004	0.003

15) Falex No.6 friction wear tester Oil Temperature 80°C, Surface Pressure 3MPa, Gradient Value between Slipping Velocity of 0.005-0.020m/s

Table 2

			Example 5	Example 6	Example 7	Example 8
Base Oil	Hydrocracking Hydrocracking Mineral Oil A 1)	mass%				60
	Hydrocracking Mineral Oil B 2)	mass%	100	100	100	
	Solvent Refining Mineral Oil A 3)	mass%				40
Base Oil Viscosity (100°C)		mm^2/s	4.1	4.1	4.1	2.8
Concentration of Sulfur derived from Base Oil		mass%	0.000	0.000	0.000	0.027
Polyalkylmethacrylate A 4)		mass%	6	6	6	
Polyalkylmethacrylate B 5)		mass%				10
ATF Additive Package 6)			8	8	8	8
Ashless Dispersant A 7)			1.5	1.5	1.5	1.5
Calcium Sulfonate 8)		mass%	0.09	0.09	0.09	0.09
Sulfur-based Additives	Thiadiazole 9)	mass%				0.05
	Dithiocarbamate 10)	mass%				
	Dithiophosphate 11)	mass%				
	Trithiophosphite 12)	mass%	0.23			
	Polysulfide A 13)	mass%		0.3		
	Polysulfide B 14)	mass%			0.07	
Element Concentration	Phosphorus	mass%	0.040	0.030	0.030	0.030
	Calcium	mass%	0.011	0.011	0.011	0.011
	Boron	mass%	0.007	0.007	0.007	0.007
	Sulfur	mass%	0.036	0.033	0.031	0.047
Element Ratio	Phosphorus		1.00	1.00	1.00	1.00
	Calcium		0.27	0.36	0.36	0.36
	Boron		0.17	0.23	0.23	0.23
	Sulfur		0.90	1.10	1.05	1.55
μ-V Gradient 15)			0.005	0.006	0.002	0.004
1)-15) are the same as those in Table 1						

Table 3

			Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Base Oil	Hydrocracking Mineral Oil A 1)	mass%					60
	Hydrocracking Mineral Oil B 2)	mass%	100	100	100	100	
	Solvent Refining Mineral Oil A 3)	mass% mass%					40
Base Oil Viscosity (100°C)		mm²/s	4.1	4.1	4.1	4.1	2.8
Concentration of Sulfur derived from Base Oil		mass% mass%	0.000	0.000	0.000	0.000	0.027
Polyalkylmethacrylate A 4)		mass%	6	6	6	6	
Polyalkylmethacrylate B 5)		mass%					12
ATF Additive Package 6)			8	8	8	8	8
Ashless Dispersant A 7)				1.5		1.5	
Calcium Sulfonate 8)		mass%			0.09	0.09	
Sulfur-based Additives	Thiadiazole 9)	mass%		0.05	0.05		
	Dithiocarbamate 10)	mass%					
	Dithiophosphate 11)	mass%					
	Trithiophosphite 12)	mass%					
	Polysulfide A 13)	mass%					
	Polysulfide B 14)	mass%					
Element Concentration	Phosphorus	mass%	0.030	0.030	0.030	0.030	0.030
	Calcium	mass%	0.000	0.000	0.011	0.011	0.000
	Boron	mass%	0.001	0.007	0.001	0.007	0.001
	Sulfur	mass%	0.000	0.018	0.019	0.001	0.027

Table 3 (continued)

			Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Element Ratio	Phosphorus		1.00	1.00	1.00	1.00	1.00
	Calcium		0.00	0.00	0.36	0.36	0.00
	Boron		0.04	0.23	0.04	0.23	0.04
	Sulfur		0.00	0.80	0.65	0.05	0.91
μ-V Gradient 15)			-0.0087	-0.0072	-0.0029	-0.0022	-0.0091
1)-15) are the same as those in Table 1							

Comparative Examples 6 and 7

[0106] For the purpose of comparison, lubricating oil compositions of Comparative Examples 6 and 7 were prepared in accordance with the formulations set forth in Table 4. The resulting compositions and the composition of Inventive Example 1 were evaluated in μ-V characteristics prior to and after running for a certain period of time, i.e., prior to and after they were deteriorated by oxidation. Each of the compositions was deteriorated in accordance with ISOT under test conditions of an oil temperature of 1.65.5°C and a test time of 150 hours to evaluate the oxidation stability in a manner prescribed by JIS K2514 (Test for Oxidation Stability of Lubricating Oil for Internal Combustion Engine). The results are also shown in Table 4.

[0107] As apparent from the results shown in Table 4, the composition of Inventive Example 1 maintained positive gradient μ-V characteristics even after it was deteriorated by oxidation. Whereas, the compositions of Comparative Examples 6 and 7 wherein the concentration of the sulfur derived from the base oil was high and wherein the same derived from the additives was high were deteriorated in μ-V characteristics and exhibited negative gradient μ-V characteristics.

Table 4

			Example 1	Comparative Example 6	Comparative Example 7
Base Oil	Hydrocracking Mineral Oil B 1)	mass%	100		100
	Solvent Refining Mineral Oil A2)	mass%			
	Solvent Refining Mineral Oil B 3)	mass%		100	
Base Oil Viscosity (100°C)		mm^2/s	4.1	4.1	4.1
Concentration of Sulfur derived from Base Oil		mass%	0.000	0.150	0.000
Polyalkylmethacrylate A 4)		mass%	6	6	6
Polyalkylmethacrylate B 5)		mass%			
ATF Additive Package 6)			8	8	8
Ashless Dispersant A 7)			1.5	1.5	1.5
Calcium Sulfonate 8)		mass%	0.09	0.09	0.09

1) Hydrocracking Mineral Oil B: Base Oil Viscosity (100°C) 4.1mm^2/s. Sulfur Content <0.001mass%

2) Solvent Refining Mineral Oil A: Base Oil Viscosity (100°C) 2.1mm^2/s, Sulfur Content: 0.09mass%

3) Solvent Refining Mineral Oil B: Base Oil Viscosity (100°C) 4.1mm^2/s. Sulfur Content 0.16mass%

4) Dispersion Type Polymethacrylate

5) Non-dispertion Type Polymethacrylate

6) Containing Ashless Dispersant, Phosphorus-based Additive. Oxidation Inhibitor. Diluted Oil, and the like Phosphorus Content and Boron Content in ATF Additive Package: 0.38mass%. 0.013mass%

7) Boric Acid-modified Polybutenyl Succinimide, Boron Content about 0.5mass%

8) Total Base Value: 300mgKOH/g, Calcium Content about 12mass%

Table 4 (continued)

			Example 1	Comparative Example 6	Comparative Example 7
Sulfur-based Additives	Thiadiazole 9)	mass%	0.05	0.05	0.4
	Dithiocarbamate 10)	mass%			
	Dithiophosphate 11)	mass%			
	Trithiophosphite 12)	mass%			
	Polysulfide A 13)	mass%			
	Polysulfide B 14)	mass%			
Element Concentration	Phosphorus	mass%	0.030	0.030	0.030
	Calcium	mass%	0.011	0.011	0.011
	Boron	mass%	0.007	0.007	0.007
	Sulfur	mass%	0.019	0.169	0.145
Element Ratio	Phosphorus		1.00	.1.00	1.00
	Calcium		0.36	0.36	0.36
	Boron		0.23	0.23	0.23
	Sulfur		0.65	5.65	4.85
μ-V Gradient 15)			0.002	0.003	0.002
μ-V Gradient after ISOT 16)			0.002	-0.004	-0.002

9) Sulfur Content 36mass%

10) Sulfur Content 30mass%

11) Sulfur Content 8.8mass%. Phosphorus Content 8.8mass%

12) Sulfur Content 15mass%. Phosphorus Content 4mass%

13) Sulfur Content 10mass%

14) Sulfur Content 43mass%

15) Falex No.6 friction wear tester Oil Temperature 80°C. Surface Pressure 3MPa. Gradient Value between Slipping Velocity of 0.005-0.020m/s

16) Falex No.6 friction wear tester Oil Temperature 80°C, Surface Pressure 3MPa, Gradient Value between Slipping Velocity of 0.005-0.020m/s evaluated after ISOT treatment (165.5°C. 150h)

Claims

1. A lubricating oil composition for automatic transmissions wherein the mass ratio of phosphorus : calcium : boron : sulfur determined by elemental analysis is 1 : (0.1 to 2) : (0.06 to 2) : (0.2 to 20), the concentration of phosphorus is from 0.01 to 0.06 percent by mass, the concentration of the sulfur derived from a base oil is from 0 to 0.1 percent by mass, and the concentration of the sulfur derived from sulfur-based additives is from 0.01 to 0.15 percent by mass, based on the total amount of the composition and.

2. The lubricating oil composition according to claim 1 wherein the mass ratio of phosphorus : calcium : boron : sulfur determined by elemental analysis is 1 : (0.1 to 1) : (0.1 to 0.8) : (0.4 to 5), the concentration of phosphorus is from 0.02 to 0.05 percent by mass, the concentration of the sulfur derived from a base oil is from 0 to 0.1 percent by mass, and the concentration of the sulfur derived from sulfur-based additives is from 0.01 to 0.15 percent by mass, based on the total amount of the composition.

3. The lubricating oil composition according to claim 1 or 2 wherein said sulfur-based additive is at least one compound selected from the group consisting of (A) thiadiazoles and/or benzothiazoles, (B) dithiocarbamates, (C) dithiophosphates, (D) trithiophosphites, (E) polysulfides, and derivatives of (A) though (E).

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP02/07207

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C10M171/00, 135/18, 135/20, 135/36, 137/02, 137/10//
C10N10:04, 40:04

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)
Int.Cl^7 C10M171/00, 125/06, 125/22-125/26, 135/00-139/00,
151/00-153/04, 155/04, 159/20-159/24, C10N10:04, 40:04

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

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Kokai Jitsuyo Shinan Koho	1971-2002	Jitsuyo Shinan Toroku Koho	1996-2002

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	WO 00/29523 A1 (Japan Energy Corp.), 25 May, 2000 (25.05.00), Claims: examples & EP 1055722 A1	1-3
X	EP 770669 A2 (The Lubrizol Corp.), 02 May, 1997 (02.05.97), Claims; examples & AU 9665820 A & US 5635459 A & CA 2188362 A1 & JP 9-165592 A	1-3
X	EP 798367 A2 (Idemitsu Kosan Co., Ltd.), 01 October, 1997 (01.10.97), Claims; examples & JP 9-263782 A & US 6051536 A	1-3

☒ 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 document 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 04 October, 2002 (04.10.02)	Date of mailing of the international search report 29 October, 2002 (29.10.02)
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP02/07207

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 218086 A2 (Idemitsu Kosan Co., Ltd.), 15 April, 1987 (15.04.87), Claims; examples & JP 62-53398 A & US 4704215 A & CA 1267134 A & KR 9000896 B1 & DE 3687106 T2	1-3
X	JP 2001-89779 A (Idemitsu Kosan Co., Ltd.), 03 April, 2001 (03.04.01), Claims; examples (Family: none)	1-3

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