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(54) ## LUBRICATING OIL COMPOSITION

(57) Provided is a lubricating oil composition for use in internal-combustion engines, containing a base oil (A), an ashless dispersant (B) containing a non-boronated alkenylsuccinic acid imide (B1) and a boronated alkenylsuccinic acid imide (B2), a thiadiazole compound (C), and an aromatic carboxylate (D) having one or more hydroxy groups, wherein the content of the component (C) is 0.2 to 1.2% by mass based on the total amount of the lubricating oil composition, the content of a zinc dithiophosphate is, as calculated in terms of zinc atoms, less than 500 ppm by mass based on the total amount of the lubricating oil composition, and the content of a metal-based detergent is, as calculated in terms of metal atoms, less than 600 ppm by mass based on the total amount of the lubricating oil composition.

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Description

Technical Field

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

Background Art

[0002] Recently, for car engines, high-power engines and also tightening of emission control regulations have become desired, and a development of post-treatment devises for emission gas has been made.
[0003] For such post-treatment devices for emission gas, an oxidation catalyst for cleaning exhaust gas, or a ternary catalyst, DPF (diesel particulate filter) or the like is employed.
[0004] However, it is reported that a phosphorus component in an engine oil poisons the active point of a catalyst to lower the catalyst function, or an ash derived from a metal component therein deposits on DPF to cause reduction in lifetime. In addition, the metal component-derived ash also deposits on the upper portion of a piston to be a cause of accelerating contamination of a spark-ignition plug.
[0005] Consequently, the tendency is toward requiring an engine oil for automobiles, in which the blending amounts of a phosphorus-containing anti-wear agent and a metal-based additive that have heretofore been used are reduced.
[0006] In addition, a gas engine oil is also required, in which the blending amounts of these are reduced and further the phosphorus content and the sulfated ash content are also reduced.
[0007] A gas engine uses a natural gas, a liquefied petroleum gas (LPG) or an autogas as a fuel, and has a good combustion quality, and as compared with that of a gasoline engine and a diesel engine, the combustion temperature thereof is high. Consequently, an engine oil for use in a gas engine is used under a high load condition and is therefore readily degraded to often cause a problem in lifetime.
[0008] In addition, in a gas engine to be driven under a high load condition, various additives used in the engine oil are readily decomposed, and the decomposition products of the additives may often cause corrosion of copper contained in the members that constitute an engine.
[0009] Consequently, an engine oil for use in a gas engine is required to have metal corrosion resistance along with degradation control, and various engine oils are developed.
[0010] For example, PTL 1 discloses an engine oil composition containing a base oil, a polyoxyethylene alkyl ether having an HLB value of 8 to 11, and a predetermined amount of an organic molybdenum complex, for the purpose of providing an engine oil composition for gas engines excellent in metal corrosion resistance such as copper corrosion resistance for bearing members of a gas engine, and having a long lifetime.

Citation List

Patent Literature

[0011] PTL 1: JP 2010-209182 A

Summary of Invention

Technical Problem

[0012] Recently, high-powered car engines and gas engines have become popular year by year. In high-powered car engines and gas engines, bearings such as piston-pin bearings as well as slide members are subjected to high temperatures, and therefore an engine oil for lubricating those members is desired to maintain various performances in use in a high-temperature environment higher than 160°C of a higher temperature than before. In a high-temperature environment higher than 160°C, an engine oil is more readily degraded by oxidation, and reduction in heat resistance thereof is a serious problem.
[0013] By blending a metal-based detergent therein, an engine oil may be prevented from being oxidatively degraded. However, the present inventors' investigations have revealed that blending of a metal-based detergent may cause reduction in wear resistance.
[0014] In addition, metal parts to constitute bearings such as piston-pin bearings and slide members that high-powered car engines and gas engines have are more readily corroded in a high-temperature environment higher than 160°C.
[0015] In particular, in the case where an engine oil contains zinc dithiophosphate (ZnDTP) as an anti-wear agent, zinc dithiophosphate may be more readily decomposed in such a high-temperature environment higher than 160°C to often produce sulfuric acid or phosphoric acid, which may be a factor to accelerate corrosion of metal parts.

[0016] Also in PTL 1, investigation of metal corrosion resistance for engine oil is made, in which, however, the ambient temperature is 135°C, and no investigation to simulate use in such a high-temperature environment higher than 160°C is made.
[0017] The present inventors' investigations have revealed that the engine oil disclosed as a specific example in PTL 1 is problematic in metal corrosion resistance in a high-temperature environment higher than 160°C.
[0018] As described above, car engines and gas engines have been high-powered, and supercharged engines are being promoted. Use of a laser ignition plug in an internal-combustion engine is being attempted, since ignition under high pressure is easy as compared with ignition by a heretofore-known spark-ignition plug. However, metal component-derived ash may also be a factor to accelerate contamination of a laser ignition plug not limited to a heretofore-known spark-ignition plug.
[0019] The present invention has been made in consideration of the above-mentioned problems, and its object is to provide a lubricating oil composition having excellent wear resistance, and in addition, even in use in a high-temperature environment higher than 160°C, capable of expressing excellent metal corrosion resistance and heat resistance.

Solution to Problem

[0020] The present inventors have found that a lubricating oil composition, which contains an ashless dispersant containing a non-boronated alkenyl succinic acid imide and a boronated alkenylsuccinic acid imide, a thiadiazole compound, and an aromatic carboxylate having one or more hydroxy groups, and in which the content of the thiadiazole compound is controlled to fall within a predetermined range, and the content of a zinc dithiophosphate and that of a metal-based detergent each are controlled to be a predetermined amount or less, can solve the above-mentioned problems, and have completed the present invention.
[0021] Specifically, the present invention provides the following [1].

[1] A lubricating oil composition for use in internal-combustion engines, containing:

a base oil (A),
an ashless dispersant (B) containing a non-boronated alkenylsuccinic acid imide (B1) and a boronated alkenylsuccinic acid imide (B2),
a thiadiazole compound (C), and
an aromatic carboxylate (D) having one or more hydroxy groups, wherein:

the content of the component (C) is 0.2 to 1.2% by mass based on the total amount of the lubricating oil composition,
the content of a zinc dithiophosphate is, as calculated in terms of zinc atoms, less than 500 ppm by mass based on the total amount of the lubricating oil composition, and
the content of a metal-based detergent is, as calculated in terms of metal atoms, less than 600 ppm by mass based on the total amount of the lubricating oil composition.

Advantageous Effects of Invention

[0022] The lubricating oil composition of the present invention has excellent wear resistance and, even in use in a high-temperature environment higher than 160°C, capable of expressing excellent metal corrosion resistance and heat resistance.

Description of Embodiments

[0023] In this description, the contents of a boron atom, a phosphorus atom, a calcium atom, a zinc atom and a molybdenum atom are values measured according to JPI-5S-38-03.
[0024] The content of a nitrogen atom is a value measured according to JIS K2609:1998.
[0025] The content of a sulfur atom is a value measured according to JIS K2541-6:2013.

[Lubricating Oil Composition]

[0026] The lubricating oil composition of the present invention contains a base oil (A), an ashless dispersant (B) containing a non-boronated alkenylsuccinic acid imide (B1) and a boronated alkenylsuccinic acid imide (B2), a thiadiazole compound (C), and an aromatic carboxylate (D) having one or more hydroxy groups, and is used in internal-combustion engines.

[0027] In this description, the base oil (A), the ashless dispersant (B), the thiadiazole compound (C), and the aromatic carboxylate having one or more hydroxy groups may be referred to as "component (A)", "component (B)", "component (C)" and "component (D)", respectively.

[0028] The non-boronated alkenylsuccinic acid imide (B1) and the boronated alkenylsuccinic acid imide (B2) may be referred to as "component (B1)" and "component (B2)", respectively.

[0029] The lubricating oil composition of one embodiment of the present invention may contain any other additive for lubricating oil not corresponding to the above-mentioned components, within a range not detracting from the advantageous effects of the present invention.

[0030] In the lubricating oil composition of one embodiment of the present invention, the total content of the component (A), the component (B), the component (C), and the component (D) is, based on the total amount (100% by mass) of the lubricating oil composition, preferably 60% by mass or more, more preferably 70% by mass or more, even more preferably 75% by mass or more, further more preferably 80% by mass or more, and is generally 100% by mass or less, preferably 99.5% by mass or less, more preferably 99.0% by mass or less.

[0031] Hereinunder the components contained in the lubricating oil composition of one embodiment of the present invention are described.

<Base Oil (A)>

[0032] The base oil (A) to be contained in the lubricating oil composition of the present invention may be any one containing one or more selected from a mineral oil and a synthetic oil.

[0033] Examples of the mineral oil include an atmospheric residue given by atmospheric distillation of a crude oil such as a paraffinic crude oil, an intermediate base crude oil, or a naphthenic crude oil; a distillate given by reduced-pressure distillation of such an atmospheric residue; a mineral oil refined by subjecting the distillate to one or more treatments of solvent deasphalting, solvent extraction, hydro-cracking, solvent dewaxing, catalytic dewaxing, or hydrorefining; and a mineral oil (GTL) produced by isomerizing a wax (GTL wax, gas-to-liquid wax) produced from a natural gas by a Fischer-Tropsch process.

[0034] The mineral oil for use in one embodiment of the present invention is preferably a mineral oil grouped in Group 2 or 3 in the base oil category by API (American Petroleum Institute), and is more preferably a mineral oil grouped in Group 3 thereof.

[0035] Examples of the synthetic oil include poly-α-olefins, such as α-olefin homopolymers or α-olefin copolymers (e.g., α-olefin copolymers having 8 to 14 carbon atoms such as ethylene-α-olefin copolymers); isoparaffin; various esters such as polyol esters and dibasic acid esters; various ethers such as polyphenyl ethers; polyalkylene glycols; alkylbenzenes; and alkylnaphthalenes.

[0036] The kinematic viscosity at 40°C of the base oil (A) is preferably 10 to 150 mm^2/s, more preferably 12 to 120 mm^2/s, even more preferably 15 to 100 mm^2/s.

[0037] The viscosity index of the base oil (A) is preferably 80 or more, more preferably 90 or more, even more preferably 100 or more, further more preferably 105 or more.

[0038] In this description, the kinematic viscosity and the viscosity index are values measured or calculated according to JIS K 2283:2000.

[0039] In the case where the base oil (A) is a mixed base oil of two or more selected from a mineral oil and a synthetic oil, the kinematic viscosity and the viscosity index of the mixed base oil each may fall within the above-mentioned range.

[0040] In the lubricating oil composition of one embodiment of the present invention, the content of the base oil (A) is, based on the total amount (100% by mass) of the lubricating oil composition, generally 55% by mass or more, preferably 60% by mass or more, more preferably 65% by mass or more, even more preferably 70% by mass or more, further more preferably 75% by mass or more, and is preferably 98% by mass or less, more preferably 97% by mass or less, even more preferably 95% by mass or less, further more preferably 93% by mass or less.

<Ashless Dispersant (B)>

[0041] The lubricating oil composition of the present invention contains an ashless dispersant (B) containing a non-boronated alkenylsuccinic acid imide (B1) and a boronated alkenylsuccinic acid imide (B2).

[0042] By the use of both the component (B1) and the component (B2), the dispersibility of the components (C) and (D) can be improved, and even in use in a high-temperature environment higher than 160°C, the lubricating oil composition can express excellent metal corrosion resistance and heat resistance.

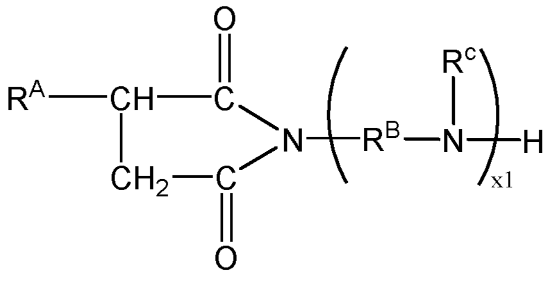
[0043] From the above-mentioned viewpoint, the content ratio of the boron atom to the nitrogen atom [B/N] in the component (B) is, as a ratio by mass, preferably 0.10 to 1.30, more preferably 0.20 to 1.20, even more preferably 0.20 to 1.10, further more preferably 0.30 to 1.10, further more preferably 0.70 to 1.05.

[0044] The content ratio of the component (B1) to the component (B2) [(B1)/(B2)] is, as a ratio by mass, preferably

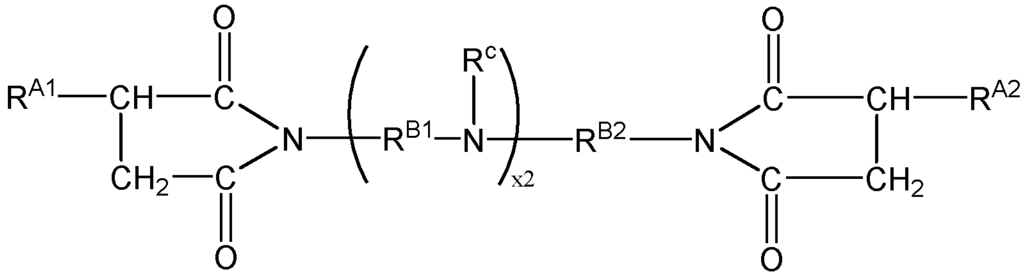
0.01 to 6.00, more preferably 0.05 to 4.00, even more preferably 0.10 to 2.00, further more preferably 0.15 to 1.50, further more preferably 0.20 to 0.95.

(Non-boronated Alkenylsuccinic Acid Imide (B1))

[0045] The non-boronated alkenylsuccinic acid imide (B1) includes an alkenylsuccinic acid monoimide represented by the following general formula (b-1) or an alkenylsuccinic acid bisimide represented by the following general formula (b-2).



(b-1)



(b-2)

[0046] In the above-mentioned general formulae (b-1) and (b-2), R^A, R^{A1} and R^{A2} each independently represent an alkenyl group having a number-average molecular weight (Mn) of 500 to 3000 (preferably 1000 to 3000, more preferably 1500 to 2500).

[0047] Examples of the alkenyl group include a polybutenyl group, a polyisobutenyl group and an ethylene-propylene copolymer, and among these, a polybutenyl group or a polyisobutenyl group is preferred.

[0048] R^B, R^{B1} and R^{B2} each independently represent an alkylene group having 2 to 5 carbon atoms.

[0049] R^C represents a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, or a group represented by $-(AO)_n-H$ (wherein A represents an alkylene group having 2 to 4 carbon atoms, and n represents an integer of 1 to 10).

[0050] x1 represents an integer of 1 to 10, preferably an integer of 2 to 5, more preferably 3 or 4.

[0051] x2 represents an integer of 0 to 10, preferably an integer of 1 to 4, more preferably 2 or 3.

[0052] The component (B1) can be produced, for example, by reaction of an alkenylsuccinic anhydride to be prepared by reaction of a polyolefin and a maleic anhydride, and a polyamine.

[0053] Examples of the polyolefin include a polymer to be prepared by polymerization of one or more selected from an α-olefin having 2 to 8 carbon atoms, and a copolymer of isobutene and 1-butene is preferred.

[0054] Examples of the polyamine include monodiamines such as ethylenediamine, propylenediamine, butylenediamine and pentylenediamine; polyalkylenepolyamines such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, di(methylethylene)triamine, dibutylenetriamine, tributylenetetramine and pentapentylenehexamine; and piperazine derivatives such as aminoethylpiperazine.

[0055] The component (B1) used in one embodiment of the present invention may also be a modified alkenylsuccinic acid imide prepared by reaction of a compound represented by the above-mentioned general formula (b-1) or (b-2) and a boron-free compound such as an alcohol, an aldehyde, a ketone, an alkylphenol, a cyclic carbonate, an epoxy compound or an organic acid.

[0056] In the lubricating oil composition of one embodiment of the present invention, the content of the component (B1) is, as calculated in terms of nitrogen atoms and based on the total amount (100% by mass) of the lubricating oil composition, preferably 400 to 3000 ppm by mass, more preferably 420 to 2500 ppm by mass, even more preferably 450 to 2200 ppm by mass, further more preferably 480 to 2000 ppm by mass, further more preferably 500 to 1500 ppm by mass.

[0057] In the lubricating oil composition of one embodiment of the present invention, the content of the component (B1) as calculated in terms of nitrogen atoms may be controlled to fall within the above-mentioned range, and based on the total amount (100% by mass) of the lubricating oil composition, the content is preferably 0.1 to 8.0% by mass, more preferably 0.2 to 6.0% by mass, even more preferably 0.3 to 4.0% by mass.

(Boronated Alkenylsuccinic Acid Imide (B2))

[0058] The boronated alkenylsuccinic acid imide (B2) includes a boron-modified derivative of an alkenylsuccinic acid imide represented by the above-mentioned general formula (b-1) or (b-2).
[0059] The boronated alkenylsuccinic acid imide (B2) can be produced, for example, by reaction of an alkenylsuccinic anhydride to be prepared by reaction of a polyolefin and a maleic anhydride, and the above-mentioned polyamine and a boron compound.
[0060] Examples of the boron compound include boron oxide, boron halides, boric acid, boric anhydride, borates, and ammonium salts of boric acid.
[0061] The content ratio of the boron atom to the nitrogen atom in the component (B2) to be used in one embodiment of the present invention [B/N] is, as a ratio by mass, preferably 0.3 to 2.5, more preferably 0.5 to 2.0, even more preferably 0.7 to 1.5.
[0062] In the lubricating oil composition of one embodiment of the present invention, the content of the component (B2) is, as calculated in terms of boron atoms and based on the total amount (100% by mass) of the lubricating oil composition, preferably 200 to 3000 ppm by mass, more preferably 400 to 2800 ppm by mass, even more preferably 600 to 2700 ppm by mass, further more preferably 700 to 2600 ppm by mass, further more preferably 1100 to 2500 ppm by mass.
[0063] In the lubricating oil composition of one embodiment of the present invention, the content of the component (B2) is, as calculated in terms of nitrogen atoms and based on the total amount (100% by mass) of the lubricating oil composition, preferably 250 to 3500 ppm by mass, more preferably 300 to 3200 ppm by mass, even more preferably 350 to 2800 ppm by mass, further more preferably 400 to 2500 ppm by mass.
[0064] In the lubricating oil composition of one embodiment of the present invention, the content of the component (B2) as calculated in terms of boron atoms and in terms of nitrogen atoms may be controlled to fall within the above-mentioned range, and based on the total amount (100% by mass) of the lubricating oil composition, the content is preferably 0.1 to 15.0% by mass, more preferably 0.5 to 13.0% by mass, even more preferably 1.0 to 11.0% by mass.
[0065] The lubricating oil composition of one embodiment of the present invention may contain any other ashless dispersant than the components (B1) and (B2) as the component (B) within a range not detracting from the advantageous effects of the present invention.
[0066] Examples of the ashless dispersant include benzylamines, boron-containing benzylamines, succinates, and mono or dicarboxylic acid amides typified by fatty acids or succinic acid.
[0067] However, in the lubricating oil composition of one embodiment of the present invention, the total content ratio of the components (B1) and (B2) in the ashless dispersant (B) is, based on the total amount (100% by mass) of the ashless dispersant (B) contained in the lubricating oil composition, preferably 70 to 100% by mass, more preferably 80 to 100% by mass, even more preferably 90 to 100% by mass, further more preferably 95 to 100% by mass.
[0068] In the lubricating oil composition of one embodiment of the present invention, the content of the component (B) is, as calculated in terms of nitrogen atoms and based on the total amount (100% by mass) of the lubricating oil composition, preferably 600 to 6500 ppm by mass, more preferably 700 to 5200 ppm by mass, even more preferably 800 to 4000 ppm by mass, further more preferably 850 to 3500 ppm by mass.
[0069] In the lubricating oil composition of one embodiment of the present invention, the content of the component (B) is, based on the total amount (100% by mass) of the lubricating oil composition, preferably 0.2 to 30.0% by mass, more preferably 0.7 to 27% by mass, even more preferably 1.5 to 25.0% by mass, further more preferably 3.0 to 15.0% by mass.

<Thiadiazole Compound (C)>

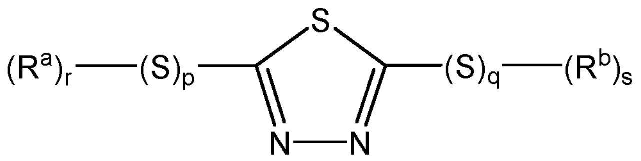
[0070] The lubricating oil composition of the present invention contains a thiadiazole compound (C), and the content of the component (C) therein is 0.2 to 1.2% by mass based on the total amount (100% by mass) of the lubricating oil composition.
[0071] The lubricating oil composition where the content of the component (C) therein is less than 0.2% by mass could hardly express a friction-reducing effect and is problematic in point of wear resistance.
[0072] On the other hand, the lubricating oil composition where the content of the component (C) therein is more than 1.2% by mass often causes corrosion of metal parts when used in a high-temperature environment higher than 160°C, and is problematic in point of metal corrosion resistance. In addition, in use in the environment, the composition often causes oxidative degradation and is problematic also in point of heat resistance.
[0073] In the lubricating oil composition of one embodiment of the present invention, the content of the component

(C) is, based on the total amount (100% by mass) of the lubricating oil composition and from the viewpoint of improving wear resistance, preferably 0.22% by mass or more, more preferably 0.25% by mass or more, even more preferably 0.30% by mass or more, further more preferably 0.35% by mass or more, further more preferably 0.40% by mass or more, and is, from the viewpoint of improving metal corrosion resistance and heat resistance, preferably 1.15% by mass or less, more preferably 1.10% by mass or less, even more preferably 1.00% by mass or less, further more preferably 0.90% by mass or less.

[0074] In the lubricating oil composition of one embodiment of the present invention, the content of the component (C) is, as calculated in terms of sulfur atoms and based on the total amount (100% by mass) of the lubricating oil composition and from the viewpoint of improving wear resistance, preferably 500 ppm by mass or more, more preferably 700 ppm by mass or more, even more preferably 900 ppm by mass or more, further more preferably 1200 ppm by mass or more, and is, from the viewpoint of improving metal corrosion resistance and heat resistance, preferably 4000 ppm by mass or less, more preferably 3800 ppm by mass or less, even more preferably 3600 ppm by mass or less, further more preferably 3000 ppm by mass or less.

[0075] The thiadiazole compound (C) for use in one embodiment of the present invention may be any compound having a thiadiazole ring, but from the viewpoint of providing a lubricating oil composition excellent in wear resistance, a compound having a 1,3,4-thiadiazole ring is preferred, and a compound represented by the following general formula (c-1) is more preferred.

[0076] One alone or two or more kinds of compounds for the component (C) may be used either singly or as combined.



(c-1)

[0077] In the general formula (c-1), p and q each independently represent an integer of 0 to 5 (preferably an integer of 1 to 5, more preferably 1 or 2, even more preferably 2), and p + q is 1 or more.

[0078] In one embodiment of the present invention, preferably, p = q.

[0079] On the other hand, r and s each independently represent an integer of 1 to 5 (preferably 1 or 2, more preferably 1).

[0080] R^a and R^b each independently represent a hydrogen atom, a hydrocarbon group, or a hetero atom-containing group that contains one or more of an oxygen atom, a nitrogen atom and a sulfur atom, but preferably a hydrocarbon group.

[0081] Examples of the hydrocarbon group that is selectable for R^a and R^b include a linear or branched alkyl group such as a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a 1,1-dimethylhexyl group, a 2-ethylhexyl group, a nonyl group, a 1,1-dimethylheptyl group, a decyl group, an undecyl group, a dodecyl group, a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group, or an octadecyl group; a linear or branched alkenyl group such as an octenyl group, a nonenyl group, a decenyl group, an undecenyl group, a dodecenyl group, a tridecenyl group, a tetradecenyl group, or a pentadecenyl group; a cycloalkyl group such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a dimethylcyclohexyl group, an ethylcyclohexyl group, a methylcyclohexylmethyl group, a cyclohexylethyl group, a propylcyclohexyl group, a butylcyclohexyl group, or a heptylcyclohexyl group; an aryl group such as a phenyl group, a naphthyl group, an anthracenyl group, a biphenyl group, or a terphenyl group; an alkylaryl group such as a tolyl group, a dimethylphenyl group, a butylphenyl group, a nonylphenyl group, a methylbenzyl group, or a dimethylnaphthyl group; and an arylalkyl group such as a phenylmethyl group, a phenylethyl group, or a diphenylmethyl group.

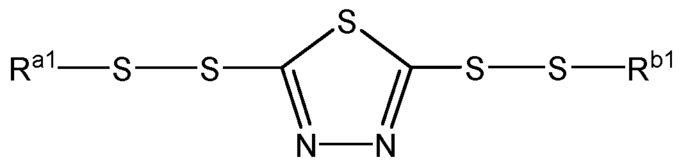
[0082] Among these, the hydrocarbon group selectable for R^a and R^b is preferably an alkyl group. The alkyl group may be a linear alkyl group, or may be a branched alkyl group.

[0083] The carbon number of the hydrocarbon group is preferably 1 to 30, more preferably 1 to 24, even more preferably 4 to 16, further more preferably 6 to 12.

[0084] Examples of the hetero atom-containing group selectable for R^a and R^b include a hydroxy group, an amino group, a nitro group, a carboxy group, a sulfo group, or a group represented by -COOR (where R represents the above-mentioned hydrocarbon group), and a hydrocarbon group substituted with any of these groups.

[0085] Among these, the hetero atom-containing group is preferably an alkyl group having 1 to 30 carbon atoms and substituted with a hydroxy group, or a group represented by -COOR (where R represents the above-mentioned hydrocarbon group and is preferably an alkyl group having 1 to 30 carbon atoms).

[0086] Preferably, the component (C) for use in one embodiment of the present invention is a compound of the general formula (c-1) where p and q each are independently 1 or 2, r and s are 1, and R^a and R^b each are independently a linear or branched alkyl group having 1 to 30 carbon atoms, more preferably a compound represented by the following general formula (c-11), even more preferably a compound represented by the following general formula (c-12).



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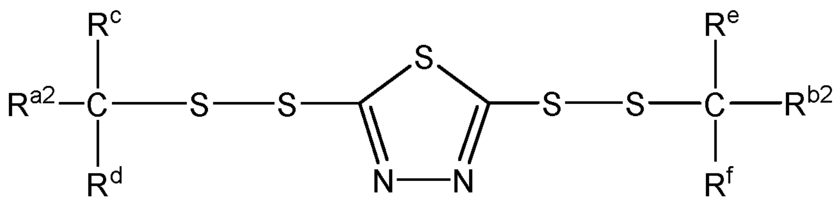


(c-12)

[0087] In the general formula (c-11), R^{a1} and R^{b1} each independently represent a linear or branched alkyl group having 1 to 30 carbon atoms, preferably a branched alkyl group having 4 to 16 carbon atoms, more preferably a branched alkyl group having 6 to 12 carbon atoms.

[0088] In the general formula (c-12), R^{a2} and R^{b2} each independently represent a linear or branched alkyl group having 1 to 16 carbon atoms, preferably a linear alkyl group having 1 to 16 carbon atoms, more preferably a linear alkyl group having 4 to 12 carbon atoms.

[0089] R^c, R^d, R^e and R^f each independently represent a hydrogen atom, or an alkyl group having 1 to 6 carbon atoms, and at least one of R^c and R^d and at least one of R^e and R^f each are an alkyl group having 1 to 6 carbon atoms.

[0090] Preferably, R^c, R^d, R^e and R^f each are independently an alkyl group having 1 to 3 carbon atoms, more preferably a methyl group or an ethyl group, even more preferably a methyl group.

<Aromatic Carboxylate (D) having one or more hydroxy groups>

[0091] The lubricating oil composition of the present invention contains an aromatic carboxylate (D) having one or more hydroxy groups.

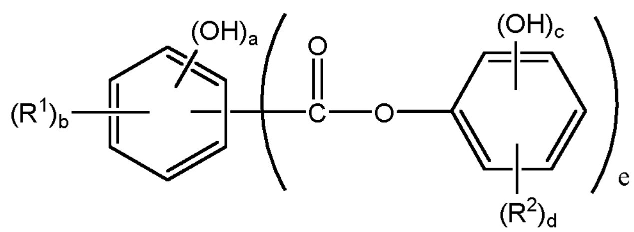
[0092] One alone or two or more kinds of the component (D) may be used either singly or as combined.

[0093] As containing the component (D), the lubricating oil composition of the present invention can express excellent heat resistance even when used in a high-temperature environment higher than 160°C.

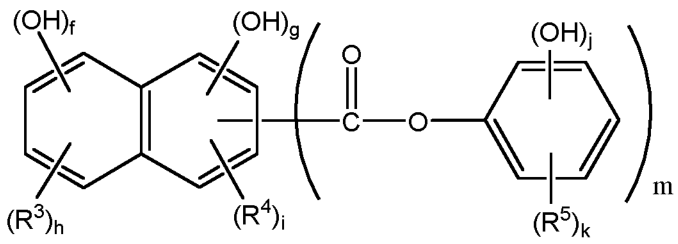
[0094] In particular, in the lubricating oil composition of the present invention, the component (D) can readily disperse owing to the existence of the component (B2), and the property that the component (D) has can be more remarkably expressed, and consequently, the lubricating oil composition can express excellent heat resistance even in use in a high-temperature environment higher than 160°C.

[0095] From the above-mentioned viewpoints, in the lubricating oil composition of one embodiment of the present invention, the content ratio of the component (D) to the component (B2) [(D)/(B2)] is, as a ratio by mass, preferably 0.1 to 5.0, more preferably 0.15 to 4.0, even more preferably 0.2 to 3.0, further more preferably 0.3 to 2.0.

[0096] The aromatic carboxylate (D) having one or more hydroxy groups for use in one embodiment of the present invention is preferably one or more selected from a compound (D1) represented by the following general formula (d-1) and a compound (D2) represented by the following general formula (d-2), and more preferably contains at least a compound (D1).



(d-1)



(d-2)

[0097] In the general formulae (d-1) and (d-2), R^1 to R^5 each independently represent a hydrocarbon group having 1 to 50 carbon atoms.

[0098] The carbon number of the hydrocarbon is preferably 1 to 50, more preferably 4 to 40, even more preferably 6 to 30, further more preferably 8 to 20.

[0099] As the hydrocarbon group, there are mentioned the same ones as those of the hydrocarbon group selectable for R^a and R^b in the general formula (c-1), and an alkyl group or an alkenyl group is preferred, and an alkyl group is more preferred.

[0100] The alkyl group and the alkenyl group may be linear or branched.

[0101] In the general formula (d-1), a represents an integer of 1 to 3 (preferably 1), b represents an integer of 1 to 3 (preferably 1), c represents an integer of 0 to 3 (preferably 0 or 1, more preferably 0), d represents an integer of 1 to 3 (preferably 1), e represents an integer of 1 to 3 (preferably 1), a + b+ e is an integer of 3 to 6, and c + d is an integer of 1 to 5.

[0102] In the general formula (d-2), f represents an integer of 0 to 3, g represents an integer of 0 to 3, and f + g is an integer of 1 to 3.

[0103] h represents an integer of 0 to 4, i represents an integer of 0 to 3, and h + i is an integer of 1 to 6.

[0104] j represents an integer of 0 to 3, k represents an integer of 1 to 3, and j + k is an integer of 1 to 5.

[0105] m represents an integer of 1 to 3, and f + g + h + i + m is an integer of 3 to 8.

[0106] In the lubricating oil composition of one embodiment of the present invention, the content of the component (D) is, based on the total amount (100% by mass) of the lubricating oil composition and from the viewpoint of providing a lubricating oil composition having excellent heat resistance even in use in a high-temperature environment higher than 160°C, preferably 0.5 to 15.0% by mass, more preferably 0.7 to 13.0% by mass, even more preferably 1.0 to 12.0% by mass, further more preferably 2.0 to 10.0% by mass.

<Zinc Dithiophosphate>

[0107] The lubricating oil composition of the present invention may contain a zinc dithiophosphate (ZnDTP), and the content of the zinc dithiophosphate therein is, as calculated in terms of zinc atoms, limited to less than 500 ppm by mass based on the total amount (100% by mass) of the lubricating oil composition.

[0108] A lubricating oil composition in which the content of a zinc dithiophosphate is more than 500 ppm by mass is problematic in point of metal corrosion resistance.

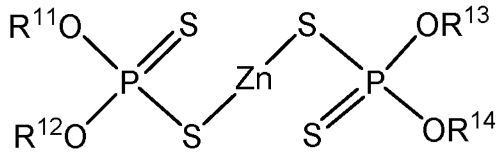
[0109] As described above, decomposition of ZnDTP is more accelerated in a high-temperature environment higher than 160°C to often generate sulfuric acid and phosphoric acid to be a factor of accelerating corrosion of metal parts.

[0110] However, the lubricating oil composition of the present invention contains the components (B) to (D) and can suppress in some degree decomposition of ZnDTP even in a high-temperature environment higher than 160°C. Consequently, so far as the content of ZnDTP therein is less than 500 ppm by mass, the lubricating oil composition can maintain good metal corrosion resistance and can improve wear resistance by the presence of ZnDTP.

[0111] From the above-mentioned viewpoint, in the lubricating oil composition of one embodiment of the present invention, the content of zinc dithiophosphate is, as calculated in terms of zinc atoms, preferably less than 400 ppm by mass based on the total amount (100% by mass) of the lubricating oil composition, more preferably less than 350 ppm by mass, even more preferably less than 300 ppm by mass, further more preferably less than 280 ppm by mass. From the viewpoint of improving wear resistance, the content is preferably 100 ppm by mass or more.

[0112] In the lubricating oil composition of one embodiment of the present invention, the content of zinc dithiophosphate may be controlled to fall within the above-mentioned range as calculated in terms of zinc atoms, but is preferably less than 0.50% by mass or less based on the total amount (100% by mass) of the lubricating oil composition, more preferably less than 0.40% by mass, even more preferably less than 0.30% by mass, and from the viewpoint of improving wear resistance, the content is preferably 0.10% by mass or more.

[0113] The zinc dithiophosphate for use in one embodiment of the present invention includes a compound represented by the following general formula (e-1).



(e-1)

[0114] In the above formula (e-1), R^{11} to R^{14} each independently represent a hydrocarbon group.
[0115] Examples of the hydrocarbon group may be the same as those of the hydrocarbon group selectable for R^a and R^b in the above-mentioned general formula (c-1), and an alkyl group is preferred.
[0116] The alkyl group may be a linear alkyl group, or may be a branched alkyl group, but is preferably a branched alkyl group.
[0117] The carbon number of the hydrocarbon group selectable for R^{11} to R^{14} is preferably 1 to 20, more preferably 3 to 16, even more preferably 4 to 12, further more preferably 5 to 10.

<Metal-based Detergent>

[0118] The lubricating oil composition of the present invention may contain a metal-based detergent, and the content of the metal-based detergent therein is, as calculated in terms of metal atoms, limited to less than 600 pm by mass based on the total amount (100% by mass) of the lubricating oil composition.
[0119] A lubricating oil composition in which the content is 600 ppm by mass or more tends to be poor in wear resistance.
[0120] However, the lubricating oil composition of the present invention contains the component (D) and therefore can suppress in some degree reduction in wear resistance so far as the content of the metal-based detergent therein is less than 600 ppm by mass, and owing to the presence of the metal-based detergent, the heat resistance of the composition can be improved more.
[0121] In the lubricating oil composition of one embodiment of the present invention, the content of the metal-based detergent is, as calculated in terms of metal atoms and based on the total amount (100% by mass) of the lubricating oil composition, and from the viewpoint of maintaining good wear resistance, preferably less than 550 ppm by mass, more preferably less than 500 ppm by mass, even more preferably less than 470 ppm by mass, further more preferably less than 300 ppm by mass.
[0122] Examples of the metal-based detergent include organic acid metal salt compounds containing a metal atom selected from an alkali metal and an alkaline earth metal, specifically, metal salicylates, metal phenates and metal sulfonates containing a metal atom selected from an alkali metal and an alkaline earth metal.
[0123] The metal atom contained in the metal-based detergent is, from the viewpoint of improving heat resistance, preferably sodium, calcium, magnesium or barium, more preferably calcium.
[0124] Namely, the metal-based detergent for use in one embodiment of the present invention is preferably one or more selected from calcium salicylate, calcium phenate and calcium sulfonate.
[0125] In one embodiment of the present invention, the metal-based detergent may be any of a neutral salt, a basic salt, an overbased salt, and a mixture of these.
[0126] The total base number of the metal-based detergent is preferably 0 to 600 mgKOH/g.
[0127] In one embodiment of the present invention, where the metal-based detergent is a basic salt or an overbased salt, the total base number of the metal-based detergent is preferably 10 to 600 mgKOH/g, more preferably 20 to 500 mgKOH/g.
[0128] In this description, "base number" means a base number determined through the perchloric acid method in accordance with JIS K 2501 7:2003 "Petroleum products and lubricating oils - neutralization value test method".

<Other Additives for Lubricating Oil>

[0129] The lubricating oil composition of one embodiment of the present invention may contain any other additives for lubricating oil than the above-mentioned components, within a range not detracting from the advantageous effects of the present invention. In the following description, the other additive for lubricating oil is referred to as "component (E)".
[0130] Examples of the other additives for lubricating oil include an antioxidant, a viscosity index improver, a pour point depressant, an anti-wear agent, an extreme pressure agent, a metal-based friction regulator, a rust inhibitor, a metal deactivator, an anti-emulsifying agent, and an anti-foaming agent.
[0131] One alone or two or more kinds of these additives for lubricating oil may be used either singly or as combined.
[0132] Each content of the additives for lubricating oil can be appropriately controlled within a range not detracting from the advantageous effects of the present invention, and is, based on the total amount (100% by mass) of the lubricating oil composition, generally 0.001 to 15% by mass, preferably 0.005 to 10% by mass, more preferably 0.01 to 5% by mass, even more preferably 0.03 to 2% by mass.

[0133] In this description, additives such as a viscosity index improver and an anti-foaming agent may be blended with the other component in the form of a solution diluted and dissolved in a part of the above-mentioned base oil (A), in consideration of the handleability and the solubility thereof in the base oil (A). In such a case, in this description, the content of the additive such as an anti-foaming agent and a viscosity index improver means a content thereof as calculated in terms of active ingredient (in terms of resin fraction) excluding the diluting oil.

[0134] Examples of the antioxidant include an amine-based antioxidant, a phenol-based antioxidant, a molybdenum-based antioxidant, a sulfur-based antioxidant, and a phosphorus-based antioxidant.

[0135] Among these, one or more selected from an amine-based antioxidant and a phenol-based antioxidant are preferred, and combined use of an amine-based antioxidant and a phenol-based antioxidant is more preferred.

[0136] Examples of the viscosity index improver include polymers such as a non-dispersant-type polymethacrylate, a dispersant-type polymethacrylate, an olefinic copolymer (e.g., ethylene-propylene copolymer), a dispersant-type olefinic copolymer, and a styrenic copolymer (e.g., styrene-diene copolymer, styrene-isoprene copolymer).

[0137] The weight-average molecular weight (Mw) of the viscosity index improver is generally 3,000 to 1,000,000, preferably 5,000 to 800,000, more preferably 10,000 to 700,000, and may be appropriately preset in accordance with the type of the polymer.

[0138] Examples of the pour point depressant include an ethylene-vinyl acetate copolymer, a condensate of a chloroparaffin and naphthalene, a condensate of a chloroparaffin and phenol, a polymethacrylate, and a polyalkylstyrene.

[0139] Examples of the anti-wear agent or the extreme pressure agent include sulfur-containing compounds such as molybdenum dithiocarbamate, molybdenum dithiophosphate, disulfides, olefin sulfides, sulfurized oils and fats, sulfurized esters, thiocarbonates, thiocarbamates, and polysulfides; phosphorus-containing compounds such as phosphites, phosphates, phosphonates, and amine salts or metal salts thereof; and sulfur and phosphorus-containing compounds such as thiophosphites, thiophosphates, thiophosphonates, and amine salts or metal salts thereof.

[0140] Examples of the metal-based friction regulator include molybdenum-based friction regulators such as molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate (MoDTP), and amine salts of molybdic acid.

[0141] Examples of the rust inhibitor include fatty acids, alkenylsuccinic acid half esters, fatty acid soaps, alkylsulfonates, polyalcohol fatty acid esters, aliphatic acid amines, paraffin oxides, and alkyl polyoxyethylene ethers.

[0142] Examples of the metal deactivator include benzotriazole compounds, tolyltriazole compounds, thiadiazole compounds, imidazole compounds, and pyrimidine compounds.

[0143] Examples of the anti-emulsifying agent include anionic surfactants such as castor oil sulfate salts, and petroleum sulfonate salts; cationic surfactants such as quaternary ammonium salts, and imidazolines; polyoxyalkylene polyglycols and dicarboxylic acid esters thereof; and alkylene oxide adducts such as alkylphenol-formaldehyde polycondensates.

[0144] Examples of the anti-foaming agent include silicone oils, fluorosilicone oils, and fluoroalkyl ethers.

[0145] In the lubricating oil composition of one embodiment of the present invention, the content of a molybdenum compound to be blended as an additive is preferably as small as possible from the viewpoint of reducing metal-derived ash.

[0146] Specifically, the content of the molybdenum compound, as calculated in terms of molybdenum, is preferably less than 100 ppm by mass based on the total amount (100% by mass) of the lubricating oil composition, more preferably less than 50 ppm by mass, even more preferably less than 10 ppm by mass.

[Production Method for Lubricating Oil Composition]

[0147] A method for producing the lubricating oil composition of the present invention is not specifically limited, but may be, for example, a production method including the following step (I).

Step (I): a step of blending an ashless dispersant (B) containing a non-boronated alkenylsuccinic acid imide (B1) and a boronated alkenylsuccinic acid imide (B2), a thiadiazole compound (C), and an aromatic carboxylate (D) having one or more hydroxy groups, in a base oil (A).

[0148] In the step (I), a component (E) may be blended along with the components (A) to (D).

[0149] However, in the step (I), the components are so blended that the content of the metal-based detergent therein, as calculated in terms of metal atoms, could be less than 600 ppm by mass based on the total amount of the lubricating oil composition.

[0150] In this step, the components to be blended are as mentioned above, and the kind of a preferred component and the content of each component are also as mentioned above.

[0151] The components to be blended in the step (I) may be blended in a form of a solution (dispersion) added with a diluent oil or the like. After the components have been blended, preferably, they are uniformly dispersed by stirring.

(Various Properties of Lubricating Oil Composition)

[0152] The kinematic viscosity at 100°C of the lubricating oil composition of one embodiment of the present invention is preferably 8.0 to 20.0 mm^2/s, more preferably 9.3 to 18.0 mm^2/s, even more preferably 9.3 to 16.3 mm^2/s.

[0153] Also preferably, the kinematic viscosity at 100°C is 8.0 to 20 mm^2/s, more preferably 8.0 to 16.3 mm^2/s, even more preferably 8.0 to 12.5 mm^2/s.

[0154] The viscosity index of the lubricating oil composition of one embodiment of the present invention is preferably 100 or more, more preferably 110 or more, even more preferably 120 or more.

[0155] In the lubricating oil composition of one embodiment of the present invention, the content of the phosphorus atom is, based on the total amount (100% by mass) of the lubricating oil composition and from the viewpoint of reducing the load to an emission gas post-treatment device, preferably less than 400 ppm by mass, more preferably less than 350 ppm by mass, even more preferably less than 300 ppm by mass, further more preferably less than 250 ppm by mass.

[0156] In the lubricating oil composition of one embodiment of the present invention, the content of the sulfur atom is, based on the total amount (100% by mass) of the lubricating oil composition, preferably 500 to 5000 ppm by mass, more preferably 700 to 4500 ppm by mass, even more preferably 900 to 4000 ppm by mass, further more preferably 1050 to 3500 ppm by mass.

[0157] In the lubricating oil composition of one embodiment of the present invention, the sulfated ash content is, based on the total amount (100% by mass) of the lubricating oil composition, preferably less than 0.30% by mass, more preferably less than 0.25% by mass, even more preferably less than 0.20% by mass, further more preferably less than 0.05% by mass.

[0158] When the sulfated ash content is less than 0.30% by mass, functional depression of a catalyst attached to a post-treatment device for emission gas can be prevented, and a metal-derived ash can be prevented from depositing on DPF.

[0159] In this description, the sulfated ash content means a value measured according to JIS K2272:1998.

[0160] When the lubricating oil composition of one embodiment of the present invention is tested in a metal corrosion test according to a test tube method of JIS K2513:2000 under a temperature condition of 100°C, the specified discoloration number is preferably 1 or 2, more preferably 1.

[0161] When the lubricating oil composition of one embodiment of the present invention is tested according to a test tube method of JIS K2513:2000 under a temperature condition of 165.5°C, the specified discoloration number is preferably 1 or 2.

[0162] In this description, detailed conditions for the test according to a test tube method of JIS K2513:2000 are as described in the section of Examples to be given below.

[0163] A value of a wear track diameter of the lubricating oil composition of one embodiment of the present invention, as measured according to the method and the condition described in the section of Examples given below, is preferably 450 pm or less, more preferably 440 pm or less, even more preferably 435 pm or less, further more preferably 430 pm or less.

[0164] When the lubricating oil composition of one embodiment of the present invention is tested in a hot tube test according to JPI-5S-55-99 under a temperature condition of 280°C, the specified merit score is preferably 8.0 or more, more preferably 8.5 or more, even more preferably 9.0 or more, further more preferably 9.5 or more.

[0165] When the lubricating oil composition of one embodiment of the present invention is tested in an ISOT test according to JIS K 2514-1:2013 at 165.5°C for 72 hours and when the resultant degraded oil is tested in a hot tube test according to JPI-5S-55-99 under a temperature condition of 280°C, the specified merit score is preferably 7.0 or more, more preferably 7.5 or more, even more preferably 8.0 or more, further more preferably 8.5 or more.

[0166] In the present invention, detailed conditions for the hot tube test, and detailed conditions for the ISOT test according to JIS K 2514-1:2013 are as described in the section of Examples given below.

[Use of Lubricating Oil Composition]

[0167] The lubricating oil composition of the present invention has excellent wear resistance and, in addition, can express excellent metal corrosion resistance and heat resistance even in use in a high-temperature environment higher than 160°C.

[0168] The lubricating oil composition of the present invention can be used in internal-combustion engines, and are especially preferably used in internal-combustion engines equipped with components that are subjected to a maximum temperature of higher than 160°C.

[0169] Examples of the internal-combustion engines include gasoline engines, diesel engines and gas engines to be mounted in two-wheel vehicles, four-wheel vehicles, electric generators, and ships.

[0170] In the lubricating oil composition of the present invention, the metal content is reduced, and therefore the lubricating oil composition is also favorably used in internal-combustion engines equipped with an emission gas post-treatment device, or spark-ignition internal-combustion engines equipped with a spark-ignition plug, or laser-ignition internal-combustion engines equipped with a laser-ignition plug.

[0171] Also the present invention can provide an internal-combustion engine according to the following [1], and a use method according to the following [2].

[1] An internal-combustion engine using a lubricating oil composition that contains:
a base oil (A), an ashless dispersant (B) containing a non-boronated alkenylsuccinic acid imide (B1) and a boronated alkenylsuccinic acid imide (B2), a thiadiazole compound (C), and an aromatic carboxylate (D) having one or more hydroxy groups, wherein:

the content of the component (C) is 0.2 to 1.2% by mass,
the content of a zinc dithiophosphate is, as calculated in terms of zinc atoms, less than 500 ppm by mass, and
the content of a metal-based detergent is, as calculated in terms of metal atoms, less than 600 ppm by mass.

[2] A method of using a lubricating oil composition in an internal-combustion engine, the lubricating oil composition containing:
a base oil (A), an ashless dispersant (B) containing a non-boronated alkenylsuccinic acid imide (B1) and a boronated alkenylsuccinic acid imide (B2), a thiadiazole compound (C), and an aromatic carboxylate (D) having one or more hydroxy groups, wherein:

the content of the component (C) is 0.2 to 1.2% by mass,
the content of a zinc dithiophosphate is, as calculated in terms of zinc atoms, less than 500 ppm by mass, and
the content of a metal-based detergent is, as calculated in terms of metal atoms, less than 600 ppm by mass.

[0172] Regarding the lubricating oil composition for use in the above [1] and [2], preferred embodiments of the constituent components and preferred properties of the lubricating oil composition are as described above.
[0173] The internal-combustion engine in the above [1] and [2] is preferably an internal-combustion engine equipped with a component that is subjected to a maximum temperature of higher than 160°C, and more preferably an internal-combustion engine equipped with a component that is subjected to a maximum temperature of higher than 160°C and further equipped with an emission gas post-treatment device. Also preferred is a spark-ignition internal-combustion engine equipped with a spark-ignition plug, as well as a laser-ignition internal-combustion engine equipped with a laser-ignition plug.

Examples

[0174] Next, the present invention is described in more detail with reference to Examples, but the present invention is not whatsoever restricted by these Examples. Various properties of the components used in Examples and Comparative Examples and the lubricating oil compositions obtained therein were measured according to the methods mentioned below.

<Kinematic Viscosity, Viscosity Index>

[0175] Measured or calculated according to JIS K 2283:2000.

<Content of boron atom, phosphorus atom, calcium atom, zinc atom, and molybdenum atom>

[0176] Measured according to JPI-5S-38-03.

<Content of nitrogen atom>

[0177] Measured according to JIS K2609:1998.

<Content of sulfur atom>

[0178] Measured according to JIS K2541-6:2013.

<Sulfated Ash Content>

[0179] Measured according to JIS K2272:1998.

Examples 1 to 12, Comparative Examples 1 to 8

[0180] A base oil and various additives shown below were blended in a blending ratio shown in Tables 1 to 3, and

well mixed to prepare lubricating oil compositions having a kinematic viscosity at 100°C of 12.0 to 13.0 mm^2/s.
[0181] Details of the base oil and various additives used in Examples and Comparative Examples are as shown below.

(Component (A))

[0182] "Base oil (a)": Hydrorefined 500N mineral oil grouped in Group 2 in the base oil category by API, 40°C kinematic viscosity = 89.3 mm^2/s, 100°C kinematic viscosity = 10.9 mm^2/s, viscosity index = 107.

(Component (B1))

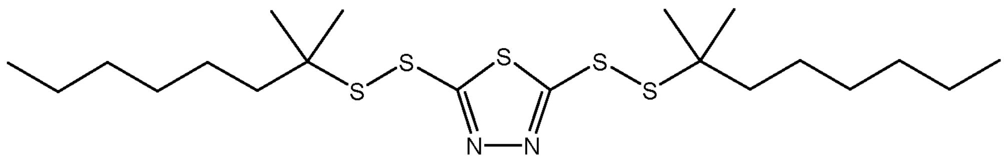
[0183] "Non-boronated alkenylsuccinic acid monoimide (b1)": alkenylsuccinic acid monoimide represented by the general formula (b-1), wherein R^A is a polybutenyl group having a number-average molecular weight (Mn) of 1000, nitrogen atom content = 2.0% by mass.

(Component (B2))

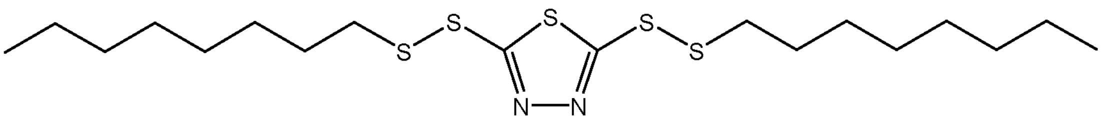
[0184] "Boronated alkenylsuccinic acid monoimide (b2-1)": boron-modified derivative of alkenylsuccinic acid monoimide represented by the general formula (b-1), wherein R^A is a polybutenyl group having a number-average molecular weight (Mn) of 1000, nitrogen atom content = 1.8% by mass, boron atom content = 2.0% by mass, B/N = 1.11.
[0185] "Boronated alkenylsuccinic acid monoimide (b2-2)": boron-modified derivative of alkenylsuccinic acid monoimide represented by the general formula (b-1), wherein R^A is a polybutenyl group having a number-average molecular weight (Mn) of 1000, nitrogen atom content = 1.2% by mass, boron atom content = 1.3% by mass, B/N = 1.08.

(Component (C))

[0186] Thiadiazole compound (c1): compound represented by the following formula (c-i), sulfur atom content = 35.0% by mass.
[0187] Thiadiazole compound (c2): compound represented by the following formula (c-ii), sulfur atom content = 33.6% by mass.



(c-i)



(c-ii)

(Component (D))

[0188] Aromatic carboxylate (d1): dodecylphenyl dodecylsalicylate, a compound of the general formula (d-1) where R^1 and R^2 each are a dodecyl group ($-C_{12}H_{25}$), a=b=d=e=1, and c=0.

(Other Components)

[0189] ZnDTP: zinc dithiophosphate, a compound of the general formula (e-1) where R^{11} to R^{14} each are a 2-ethylhexyl group, phosphorus atom content = 8.2% by mass, zinc atom content = 9.0% by mass, sulfur atom content = 17.1% by mass.
[0190] Ca-based detergent: Ca phenate, calcium atom content = 9.25% by mass.
[0191] Antioxidant: mixture of amine-based antioxidant and phenol-based antioxidant.
[0192] Mixed additive: mixed additive containing an anti-foaming agent and pour point depressant.
[0193] The prepared lubricating oil compositions were tested in (1) to (3) in that order. The results are shown in Tables 1 to 3.
[0194] A sample which failed in the metal corrosion test (1) was no more tested in the subsequent wear resistance test (2) and the hot tube test (3). A sample which failed in the wear resistance test (2) was no more tested in the hot tube test (3).

[(1) Metal Corrosion Test]

[0195] Samples were tested according to a test tube method of JIS K2513:2000, at a preset temperature condition of 100°C and 165.5°C.

[0196] After the test, the copper plate was taken out, and the discoloration degree of the copper plate was evaluated according to the copper plate evaluation method stipulated in JIS K2513:2000 to specify the discoloration number at each temperature condition. Discoloration numbers are 1 to 4 in 4 ranks, and a smaller numerical value means that the discoloration of the sample was suppressed more, that is, the sample can be said to have a higher metal corrosion-resistant effect.

[0197] At each temperature condition 100°C and 165.5°C, a sample given a discoloration number 1 or 2 was considered to have good metal corrosion resistance. Only the lubricating oil compositions whose metal corrosion resistance was evaluated as good were tested in the next wear resistance test (2).

[(2) Wear Resistance Test]

[0198] Using a high-speed reciprocating wear resistance tester TE77 (from Phoenix Tribology Limited), a lubricating oil composition was introduced into the space between a test plate and a test ball, and under the condition mentioned below, the test ball was moved to carry out the test. After the test, the wear track diameter of the test ball was measured.

Test plate, material: SUJ2, shape: 58 mm in length × 38 mm in width × 3.9 mm in thickness
Test ball, material: SUJ2, diameter 10 mm
Oiling condition: oil bath, oil amount 3 mL
Load: 50 N (5 min) → 100 N (5 min) → 150 N (5 min) → 200 N (5 min)
Temperature: 100°C
Frequency: 10 Hz

[0199] A sample having a smaller value of the wear track diameter can be said to be a lubricating oil composition excellent in wear resistance.

[0200] A sample whose wear track diameter value is 450 pm or less was evaluated to have good wear resistance. Only the lubricating oil composition that had been evaluated to have good wear resistance was tested in the next hot tube test (3).

[(3) Hot Tube Test]

[0201] The prepared lubricating oil composition was taken in a glass tube, and tested in a hot tube test according to JPI-5S-55-99, at a test temperature of 280°C. The glass tube after the test was evaluated from a score 0 point (black) to 10 point (colorless) at intervals of 0.5 point, and the score of the fresh oil in 21 ranks was determined. A sample having a higher score number has better high-temperature detergency.

[0202] A copper piece and an iron piece as a catalyst was put into the test oil (lubricating oil composition), and the oil was tested in an ISOT test according to JIS K 2514-1:2013, at 165.5°C for 72 hours and was thus forcedly degraded to be a degraded oil. The degraded oil was tested in a hot tube test under the same condition as above, and was evaluated.

[0203] A sample given a score of 8.0 point or more as a fresh oil, and given a score of 7.0 or more as a degraded oil was evaluated to have good heat resistance.

Table 1

				Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Composition	Component (A)	Base Oil (a)	mass%	86.50	86.47	86.00	86.70	86.50	88.50	81.50
	Component (B1)	Non-boronated Alkenylsuccinic Acid Monoimide (b1)	mass%	3.00	3.00	3.00	3.00	3.00	3.00	3.00
	Component (B2)	Boronated Alkenylsuccinic Acid Monoimide (b2-1)	mass%	5.00	5.00	5.00	5.00		3.00	10.00
		Boronated Alkenylsuccinic Acid Monoimide (b2-2)	mass%	-	-	-	-	5.00	-	-
	Component (C)	Thiadiazole Compound (c1)	mass%	0.50		1.00	0.30	0.50	0.50	0.50
		Thiadiazole Compound (c2)	mass%	-	0.53	-	-	-	-	-
	Component (D)	Aromatic Carboxylate (d1)	mass%	3.00	3.00	3.00	3.00	3.00	3.00	3.00
	Other Components	ZnDTP	mass%	-	-	-	-	-	-	-
		Ca-based Detergent	mass%	-	-	-	-	-	-	-
		Antioxidant	mass%	1.00	1.00	1.00	1.00	1.00	1.00	1.00
		Mixed Additive	mass%	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	-	Total	mass%	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Content of ZnDTP in terms of zinc atoms			mass ppm	0	0	0	0	0	0	0
Content of Ca-based detergent in terms of Ca atoms			-	0	0	0	0	0	0	0
Content Ratio of Component (D) to Component (B2) [(D)/(B2)] (mass ratio)			-	0.60	0.60	0.60	0.60	0.60	1.00	0.30
Content of component (B1) in terms of nitrogen atoms			mass ppm	600	600	600	600	600	600	600
Content of component (B2) in terms of boron atoms			mass ppm	1000	1000	1000	1000	650	600	2000

(continued)

			Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Content of component (B2) in terms of nitrogen atoms		mass ppm	900	900	900	900	600	540	1800
Ratio of boron atom to nitrogen atom in component (B) [B/N]		-	0.67	0.67	0.67	0.67	0.54	0.53	0.83
Content of component (C) in terms of sulfur atoms		mass ppm	1750	1781	3500	1050	1750	1750	1750
Properties of Lubricating Oil Composition	Phosphorus Atom Content	mass ppm	0	0	0	0	0	0	0
	Sulfur Atom Content	mass ppm	1750	1781	3500	1050	1750	1750	1750
	Molybdenum Atom Content	mass ppm	0	0	0	0	0	0	0
	Sulfated Ash Content	mass%	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Test Items	(1) Metal Corrosion Test, Discoloration Number (100°C)	-	1	1	1	1	1	1	1
	(1) Metal Corrosion Test, Discoloration Number (165.5°C)	-	2	2	2	2	2	2	2
	(2) Wear Resistance Test, wear track diameter	pm	430	422	421	438	427	434	422
	(3) Hot Tube Test, score (fresh oil)	-	9.5	9.5	9.0	10.0	9.5	9.0	10.0
	(3) Hot Tube Test, score (degraded oil)	-	8.5	8.5	8.0	9.0	8.5	8.0	9.0

Table 2

				Example 8	Example 9	Example 10	Example 11	Example 12
Composition	Component (A)	Base Oil (a)	mass%	88.50	79.50	86.20	86.00	87.50
	Component (B1)	Non-boronated Alkenylsuccinic Acid Monoimide (b 1)	mass%	3.00	3.00	3.00	3.00	3.00
	Component (B2)	Boronated Alkenylsuccinic Acid Monoimide (b2-1)	mass%	5.00	5.00	5.00	5.00	5.00
		Boronated Alkenylsuccinic Acid Monoimide (b2-2)	mass%	-	-	-	-	-
	Component (C)	Thiadiazole Compound (c1)	mass%	0.50	0.50	0.50	0.50	0.50
		Thiadiazole Compound (c2)	mass%	-	-	-	-	-
	Component (D)	Aromatic Carboxylate (d1)	mass%	1.00	10.00	3.00	3.00	3.00
	Other Components	ZnDTP	mass%	-	-	0.30	-	-
		Ca-based Detergent	mass%	-	-	-	0.50	-
		Antioxidant	mass%	1.00	1.00	1.00	1.00	
		Mixed Additive	mass%	1.00	1.00	1.00	1.00	1.00
	-	Total	mass%	100.00	100.00	100.00	100.00	100.00
Content of ZnDTP in terms of zinc atoms			mass ppm	0	0	270	0	0
Content of Ca-based detergent in terms of Ca atoms			-	0	0	0	463	0
Content Ratio of Component (D) to Component (B2) [(D)/(B2)] (mass ratio)			-	0.20	2.00	0.60	0.60	0.60
Content of component (B1) in terms of nitrogen atoms			mass ppm	600	600	600	600	600
Content of component (B2) in terms of boron atoms			mass ppm	1000	1000	1000	1000	1000
Content of component (B2) in terms of nitrogen atoms			mass ppm	900	900	900	900	900
Ratio of boron atom to nitrogen atom in component (B) [B/N]			-	0.67	0.67	0.67	0.67	0.67
Content of component (C) in terms of sulfur atoms			mass ppm	1750	1750	1750	1750	1750

(continued)

			Example 8	Example 9	Example 10	Example 11	Example 12
Properties of Lubricating Oil Composition	Phosphorus Atom Content	mass ppm	0	0	246	0	0
	Sulfur Atom Content	mass ppm	1750	1750	2263	1750	1750
	Molybdenum Atom Content	mass ppm	0	0	0	0	0
	Sulfated Ash Content	mass%	<0.05	<0.05	0.13	0.22	<0.05
Test Items	(1) Metal Corrosion Test, Discoloration Number (100°C)	-	1	1	1	1	1
	(1) Metal Corrosion Test, Discoloration Number (165.5°C)	-	2	2	2	2	2
	(2) Wear Resistance Test, wear track diameter	μm	430	432	418	435	428
	(3) Hot Tube Test, score (fresh oil)	-	9.0	10.0	9.0	10.0	9.0
	(3) Hot Tube Test, score (degraded oil)	-	8.0	8.5	8.5	8.5	8.0

Table 3

				Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Composition	Component (A)	Base Oil (a)	mass %	89.50	95.70	95.47	95.42	85.90	85.70	85.70	86.90
	Component (B1)	Non-boronated Alkenylsuccinic Acid Monoimide (b1)	mass %	3.00	-	-	-	3.00	3.00	3.00	3.00
	Component (B2)	Boronated Alkenylsuccinic Acid Monoimide (b2-1)	mass %	5.00	4.00	4.00	4.00	5.00	5.00	5.00	5.00
		Boronated Alkenylsuccinic Acid Monoimide (b2-2)	mass %	-	-	-	-	-	-	-	-
	Component (C)	Thiadiazole Compound (c1)	mass %	0.50	-	-	-	0.50	0.50	1.30	0.10
		Thiadiazole Compound (c2)	mass %	-	0.30	0.53	-	-	-	-	-
	Component (D)	Aromatic Carboxylate (d1)	mass %	-	-	-	-	3.00	3.00	3.00	3.00
	Other Components	ZnDTP	mass %	-	-	-	0.58	0.60	-	-	-
		Ca-based Detergent	mass %	-	-	-	-		0.80	-	-
		Antioxidant	mass %	1.00	-	-	-	1.00	1.00	1.00	1.00
		Mixed Additive	mass %	1.00	-	-	-	1.00	1.00	1.00	1.00
	-	Total	mass %	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

(continued)

			Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Content of ZnDTP in terms of zinc atoms		mass ppm	0	0	0	522	540	0	0	0
Content of Ca-based detergent in terms of Ca atoms		-	0	0	0	0	0	740	0	0
Content Ratio of Component (D) to Component (B2) [(D)/(B2)] (mass ratio)		-	-	-	-	-	0.60	0.60	0.60	0.60
Content of component (B1) in terms of nitrogen atoms		mass ppm	600	-	-	-	600	600	600	600
Content of component (B2) in terms of boron atoms		mass ppm	1000	800	800	800	1000	1000	1000	1000
Content of component (B2) in terms of nitrogen atoms		mass ppm	900	720	720	720	900	900	900	900
Ratio of boron atom to nitrogen atom in component (B) [B/N]		-	0.67	1.11	1.11	1.11	0.67	0.67	0.67	0.67
Content of component (C) in terms of sulfur atoms		mass ppm	1750	1008	1781	0	1750	1750	4550	350
Properties of Lubricating Oil Composition	Phosphorus Atom Content	mass ppm	0	0	0	476	492	0	0	0
	Sulfur Atom Content	mass ppm	1750	1008	1781	992	2776	1750	4550	350
	Molybdenum Atom Content	mass ppm	0	0	0	0	0	0	0	0
	Sulfated Ash Content	mass %	<0.05	<0.05	<0.05	0.17	0.19	0.31	<0.05	<0.05

(continued)

			Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Test Items	(1) Metal Corrosion Test, Discoloration Number (100°C)	-	1	1	1	1	1	1	1	1
	(1) Metal Corrosion Test, Discoloration Number (165.5°C)	-	2	3	3	4	4	2	3	2
	(2) Wear Resistance Test, wear track diameter	μm	427	(*1)	(*1)	(*1)	(*1)	456	(*1)	458
	(3) Hot Tube Test, score (fresh oil)	-	7.5					(*2)		(*2)
	(3) Hot Tube Test, score (degraded oil)	-	6.5							

(*1): Since the results of the metal corrosion test (1) were not good, the wear resistance test (2) and the hot tube test (3) were not carried out.
(*2): Since the results of the wear resistance test (2) were not good, the hot tube test (3) was not carried out.

[0204] The results are that the lubricating oil compositions prepared in Examples 1 to 12 had excellent wear resistance and exhibited excellent metal corrosion resistance and heat resistance even in use in a high-temperature environment higher than 160°C.

[0205] On the other hand, the results are that the lubricating oil compositions prepared in Comparative Examples 2 to 5 and 7 were not good in the metal corrosion test in which use in a high-temperature environment higher than 160°C was simulated, and were therefore poor in metal corrosion resistance.

[0206] Also the results are that the lubricating oil compositions prepared in Comparative Examples 6 and 8 were good in metal corrosion resistance but were poor in wear resistance.

[0207] Further, the results are that the lubricating oil composition prepared in Comparative Example 1 was given a low score point in the hot tube test and was therefore problematic in terms of heat resistance.

Claims

1. A lubricating oil composition for use in internal-combustion engines, comprising:

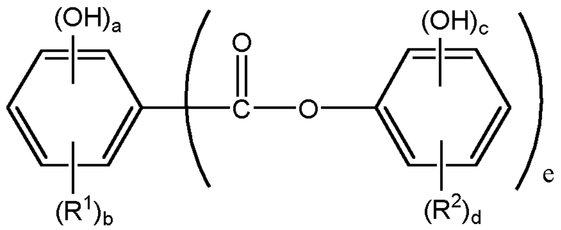
   a base oil (A),
   an ashless dispersant (B) containing a non-boronated alkenylsuccinic acid imide (B1) and a boronated alkenylsuccinic acid imide (B2),
   a thiadiazole compound (C), and
   an aromatic carboxylate (D) having one or more hydroxy groups, wherein:

      the content of the component (C) is 0.2 to 1.2% by mass based on the total amount of the lubricating oil composition,
      the content of a zinc dithiophosphate is, as calculated in terms of zinc atoms, less than 500 ppm by mass based on the total amount of the lubricating oil composition, and
      the content of a metal-based detergent is, as calculated in terms of metal atoms, less than 600 ppm by mass based on the total amount of the lubricating oil composition.

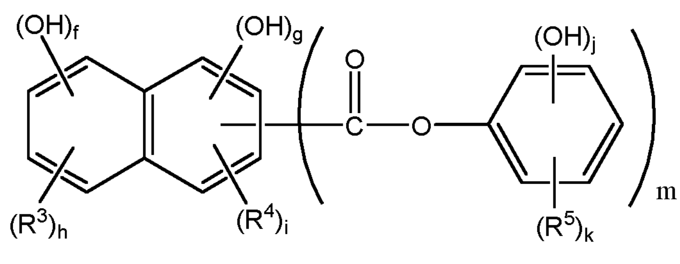
2. The lubricating oil composition according to claim 1, wherein the content ratio of the component (D) to the component (B2) [(D)/(B2)] is, as a ratio by mass, 0.1 to 5.0.

3. The lubricating oil composition according to claim 1 or 2, wherein the content of the component (D) is, based on the total amount of the lubricating oil composition, 0.5 to 15.0% by mass.

4. The lubricating oil composition according to any one of claims 1 to 3, wherein the component (D) is one or more selected from a compound (D1) represented by the following general formula (d-1) and a compound (D2) represented by the following general formula (d-2):



(d-1)



(d-2)

   wherein R^1 to R^5 each independently represent a hydrocarbon group having 1 to 50 carbon atoms;

a represents an integer of 1 to 3, b represents an integer of 1 to 3, c represents an integer of 0 to 3, d represents an integer of 1 to 3, e represents an integer of 1 to 3, a + b+ e is an integer of 3 to 6, and c + d is an integer of 1 to 5; f represents an integer of 0 to 3, g represents an integer of 0 to 3, and f + g is an integer of 1 to 3; h represents an integer of 0 to 4, i represents an integer of 0 to 3, and h + i is an integer of 1 to 6; j represents an integer of 0 to 3, k represents an integer of 1 to 3, and j + k is an integer of 1 to 5; m represents an integer of 1 to 3, and f + g + h + i + m is an integer of 3 to 8.

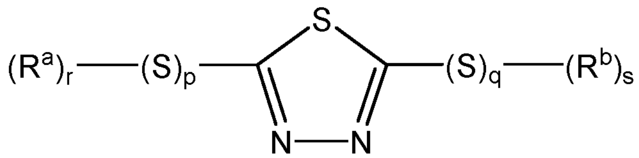
5. The lubricating oil composition according to any one of claims 1 to 4, wherein the content of the component (B2) is, as calculated in terms of boron atoms and based on the total amount of the lubricating oil composition, 200 to 3000 ppm by mass.

6. The lubricating oil composition according to any one of claims 1 to 5, wherein the content ratio of the boron atom to the nitrogen atom in the component (B2) [B/N] is, as a ratio by mass, 0.3 to 2.5.

7. The lubricating oil composition according to any one of claims 1 to 6, wherein the content of the component (B1) is, as calculated in terms of nitrogen atoms and based on the total amount of the lubricating oil composition, 400 to 3000 ppm by mass.

8. The lubricating oil composition according to any one of claims 1 to 7, wherein the content ratio of the boron atom to the nitrogen atom in the component (B) [B/N] is, as a ratio by mass, 0.10 to 1.30.

9. The lubricating oil composition according to any one of claims 1 to 8, wherein the component (C) is a compound represented by the following general formula (c-1):



(c-1)

wherein p and q each independently represent an integer of 0 to 5, p + q is 1 or more, and r and s each independently represent an integer of 1 to 5;
R^a and R^b each independently represent a hydrogen atom, a hydrocarbon group, or a hetero atom-containing group that contains one or more of an oxygen atom, a nitrogen atom and a sulfur atom.

10. The lubricating oil composition according to any one of claims 1 to 9, wherein the content of the molybdenum compound is, as calculated in terms of molybdenum and based on the total amount of the lubricating oil composition, less than 100 ppm by mass.

11. The lubricating oil composition according to any one of claims 1 to 10, wherein the phosphorus atom content is, based on the total amount of the lubricating oil composition, less than 400 ppm by mass.

12. The lubricating oil composition according to any one of claims 1 to 11, wherein the sulfated ash content is, based on the total amount of the lubricating oil composition, less than 0.30% by mass.

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2019/010695

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C10M141/08(2006.01)i, C10M129/74(2006.01)n, C10M129/76(2006.01)n, C10M133/16(2006.01)n, C10M133/56(2006.01)n, C10M135/36(2006.01)n, C10N30/06(2006.01)n, C10N30/08(2006.01)n, C10N30/12(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)
Int.Cl. C10M141/08, C10M129/74, C10M129/76, C10M133/16, C10M133/56, C10M135/36, C10N30/06, C10N30/08, C10N30/12, C10N40/25

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus/JMEDPlus/JST7580 (JDreamI II)キーワード：エンジン油，チアジアゾール，芳香族カルボン酸エステル及び それに類する用語

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2013/141077 A1 (IDEMITSU KOSAN CO., LTD.) 26 September 2013, claims, paragraphs [0010]-[0096], tables 1, 5, examples A, C, etc. & US 2015/0072907 A1 claims, paragraphs [0014]-[0169], tables 1, 5, examples A, C, etc. & EP 2829592 A1 & CN 104204164 A	1-12
Y	JP 2001-226381 A (IDEMITSU KOSAN CO., LTD.) 21 August 2001, claims, paragraphs [0051]-[0053], table 1, examples, etc. & US 2003/0018198 A1 claims, paragraphs [0194]-[0196], table 1, examples, etc. & WO 2001/048055 A1 & EP 1243609 A1	1-12

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 May 2019 (08.05.2019)	21 May 2019 (21.05.2019)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/010695

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 2000-226593 A (IDEMITSU KOSAN CO., LTD.) 15 August 2000, claims, paragraphs [0036]-[0048], table 1, examples, etc. (Family: none)	1-12
Y	WO 2014/189057 A1 (IDEMITSU KOSAN CO., LTD.) 27 November 2014, claims, paragraphs [0083]-[0091], tables 1-4, examples, etc. & US 2016/0115419 A1 claims, paragraphs [0114]-[0125], tables 1-4, examples, etc. & EP 3000866 A1 & CN 105229128 A	1-12
A	WO 2017/057361 A1 (JX ENERGY CORPORATION) 06 April 2017, claims, examples, etc. & US 2018/0346842 A1 claims, examples, etc. & EP 3357993 A1 & CN 108026474 A	1-12
A	WO 2014/156307 A1 (JX NIPPON OIL & ENERGY CORPORATION) 02 October 2014, claims, examples, etc. & US 2016/0075964 A1 claims, examples, etc. & CN 105073963 A	1-12
A	JP 2009-108157 A (NIPPON OIL CORPORATION) 21 May 2009, claims, examples, etc. (Family: none)	1-12
A	JP 11-246883 A (COSMO SOGO KENKYUSHO KK) 14 September 1999, claims, examples, etc. (Family: none)	1-12
A	JP 11-269476 A (COSMO SOGO KENKYUSHO KK) 05 October 1999, claims, examples, etc. (Family: none)	1-12

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REFERENCES CITED IN THE DESCRIPTION

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