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(54) LUBRICATING OIL COMPOSITION

(57) The lubricating oil composition of the present invention contains, along with a base oil, (A) an olefin oligomer having a mass average molecular weight of 500 or more and 5,000 or less, (B) an antioxidant containing (B-1) a phenol-based antioxidant and (B-2) an amine-based antioxidant, and (C) an alkaline earth metal-based detergent, wherein the content of the alkaline earth metal-based detergent (C) is 1,700 ppm by mass or more and 2,700 ppm by mass or less in terms of an alkaline earth metal atom thereof based on the total amount of the lubricating oil composition, and the kinematic viscosity at 100°C of the lubricating oil composition is 4.0 mm^2/s or more and 6.0 mm^2/s or less.

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Description

Technical Field

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

Background Art

[0002] The present invention relates to a lubricating oil composition, and, for example, relates to a lubricating oil composition favorably used for transmissions.

[0003] Recently, from the viewpoint of reducing carbon dioxide gas emission and reducing fossil-fuel consumption, fuel saving for automobiles is strongly desired. For example, in lubricating oil for automotive gears, viscosity reduction is promoted for reducing resistance to stirring. However, viscosity reduction in lubricating oil may lower oil film strength in a high-temperature region, and there will be fears of reduction in seizure resistance, anti-wear performance and fatigue resistance. Against this, it is effective to keep a high viscosity of lubricating oil in a high-temperature region and to lower the viscosity thereof in a normal-temperature region. Specifically, it is effective to increase the viscosity index of lubricating oil.

[0004] However, for increasing the viscosity index of lubricating oil, a viscosity index improver such as polymer will have to be added to lubricating oil. The polymer receives shear in use to reduce the viscosity of lubricating oil. Consequently, in the case where a viscosity index improver is blended in lubricating oil, the viscosity lowering in actual vehicle driving will have to be taken into consideration.

[0005] Down-sizing and weight-saving is under way in planning transmissions. Owing to down-sizing and weight-saving of transmissions, the mechanical load to a lubrication part increases, and therefore further improved lubrication performance is desired for the lubricating oil to be loaded. In addition, thermal load also increases, and therefore further more improved heat resistance and oxidation stability is desired for lubricating oil.

[0006] When heat resistance and oxidation stability of lubricating oil worsens, sludge may form, and when adhering to lubrication sites, it may cause lubrication failure. For example, sludge adhesion may cause operation failure of bearings, etc. In addition, especially in manual transmissions, sludge adhesion in the synchromesh mechanism that takes care of variable speed level change may cause reduction in shift feeling owing to reduction in friction performance and may further cause driving failure owing to synchronizer ring immobilization.

[0007] In PTLs 1 and 2, a viscosity index improver excellent in shear stability is blended in a low-viscosity base oil to further lower the viscosity of lubricating oil (kinematic viscosity at 100°C: at least 6.2 mm^2/s). However, it is impossible to completely prevent viscosity lowering of lubricating oil in actual vehicle driving, and therefore viscosity reduction in fresh oil is limited.

[0008] In PTL 3, viscosity reduction of lubricating oil is tried, not adding a polymethacrylate compound thereto (kinematic viscosity at 100°C: about 6.0 mm^2/s or more in Examples), and with that, a molybdenum compound is blended in the lubricating oil to prevent synchromesh abrasion to thereby maintain friction characteristics.

Citation List

Patent Literature

[0009]

PTL 1: JP 2012-193255 A
PTL 2: JP 2014-177605 A
PTL 3: JP 2014-98090 A

Summary of Invention

Technical Problem

[0010] The techniques described in PTLs 1 to 3 are not to solve the concerns accompanied by viscosity reduction of lubricating oil. In addition, these could not sufficiently satisfy the requirements of improving heat resistance and oxidation stability accompanied by down-sizing and weight-saving of devices.

[0011] The present invention has been made in consideration of the above-mentioned situation. Specifically, an object of the present invention is to provide a lubricating oil composition capable of attaining viscosity reduction and preventing viscosity lowering in actual vehicle driving, and capable of improving heat resistance and oxidation resistance.

Solution to Problem

[0012] As a result of assiduous studies, the present inventors have found that a lubricating oil composition containing, along with a base oil, specific components (A) to (C) as indispensable components can solve the above-mentioned problems.

[0013] Specifically, the present invention provides the following [1] to [5]:

[1] A lubricating oil composition containing, along with a base oil,

(A) an olefin oligomer having a mass average molecular weight of 500 or more and 5,000 or less,
(B) an antioxidant containing (B-1) a phenol-based antioxidant and (B-2) an amine-based antioxidant, and
(C) an alkaline earth metal-based detergent,

wherein the content of the alkaline earth metal-based detergent (C) is 1,700 ppm by mass or more and 2,700 ppm by mass or less in terms of an alkaline earth metal atom thereof based on the total amount of the lubricating oil composition, and
the kinematic viscosity at 100°C of the lubricating oil composition is 4.0 mm^2/s or more and 6.0 mm^2/s or less.
[2] A transmission loaded with the lubricating oil composition of the above [1].
[3] A lubrication method including using the lubricating oil composition of the above [1].
[4] A use method, including using the lubricating oil composition of the above [1] in transmissions.
[5] A method for producing a lubricating oil composition, including blending (A) an olefin oligomer having a mass average molecular weight of 500 or more and 5,000 or less, (B) an antioxidant containing (B-1) a phenol-based antioxidant and (B-2) an amine-based antioxidant, and (C) an alkaline earth metal-based detergent, in a base oil, the alkaline earth metal-based detergent (C) being blended such that the content of the alkaline earth metal-based detergent (C) is 1,700 ppm by mass or more and 2,700 ppm by mass or less in terms of an alkaline earth metal atom thereof based on the total amount of the lubricating oil composition.

Advantageous Effects of Invention

[0014] According to the present invention, there can be provided a lubricating oil composition capable of attaining viscosity reduction and preventing viscosity lowering in actual vehicle driving, and capable of improving heat resistance and oxidation resistance.

Description of Embodiments

[0015] One embodiment of the present invention is described in detail hereinunder. In the present invention, the "kinematic viscosity at 100°C" and the "kinematic viscosity at 40°C" of the base oil or the lubricating oil composition mean values measured according to the method described in JIS K2283:2000.

[0016] In the present invention, the content of the alkaline earth metal atom in the lubricating oil composition means a value measured according to JPI-5S-38-92.

[0017] In the present invention, the "alkaline earth metal atom" indicates a beryllium atom, a magnesium atom, a calcium atom, a strontium atom, and a barium atom.

[0018] The lubricating oil composition of this embodiment contains, along with a base oil, (A) an olefin oligomer having a mass average molecular weight of 500 or more and 5,000 or less, (B) an antioxidant containing (B-1) a phenol-based antioxidant and (B-2) an amine-based antioxidant, and (C) an alkaline earth metal-based detergent, wherein the content of the alkaline earth metal-based detergent (C) is 1,700 ppm by mass or more and 2,700 ppm by mass or less in terms of an alkaline earth metal atom thereof based on the total amount of the lubricating oil composition, and the kinematic viscosity at 100°C of the lubricating oil composition is 4.0 mm^2/s or more and 6.0 mm^2/s or less.

[0019] In the lubricating oil composition of one embodiment of the present invention, the total content of the base oil, the olefin oligomer (A), the antioxidant (B) and the alkaline earth metal-based detergent (C) is, based on the total amount of the lubricating oil composition (100% by mass), preferably 70% by mass or more, more preferably 75% by mass or more, even more preferably 80% by mass or more, further more preferably 85% by mass or more, and still further more preferably 90% by mass or more, and is generally 100% by mass or less, preferably 99.9% by mass or less, more preferably 99% by mass or less.

[0020] Each component to be blended in the lubricating oil composition of this embodiment is described below.

<Olefin oligomer (A)>

[0021] The lubricating oil composition of this embodiment contains an olefin oligomer (A), and the mass average molecular weight of the olefin oligomer (A) is needed to be 500 or more and 5,000 or less.

[0022] The olefin oligomer (A) has fluidity in a high-temperature region of a device, for example, a transmission, and has an effect of washing out formed sludge. When the molecular weight thereof is less than 500, the olefin oligomer evaporates in a high-temperature region and could not sufficient exhibit the washing effect. When the molecular weight thereof is more than 5,000, the olefin oligomer (A) could not keep fluidity in a high-temperature region and could not sufficiently exhibit the effect of washing out sludge.

[0023] The mass average molecular weight of the olefin oligomer (A) is preferably 600 or more and 4,500 or less, more preferably 700 or more and 4,000 or less, even more preferably 800 or more and 3,000 or less.

[0024] Not specifically limited, the olefin oligomer (A) may be any one having a polyolefin skeleton and having a molecular weight of 500 or more and 5,000 or less. The olefin oligomer (A) preferably contains a structural unit derived from an unsaturated hydrocarbon monomer having 2 or more and 5 or less carbon atoms, and examples thereof include an olefin oligomer such as a propylene oligomer, an isobutylene oligomer, a polybutene, a polyisobutylene, an octene oligomer, a decene oligomer, and an ethylene-propylene oligomer. Above all, a polybutene-1 is preferably used.

[0025] One kind of the olefin oligomer (A) may be used alone or two or more kinds thereof may be used in combination.

[0026] The olefin oligomer (A) is blended such that the kinematic viscosity at 100°C of the lubricating oil composition of this embodiment falls within a range of 4.0 mm^2/s or more and 6.0 mm^2/s or less. Specifically, the content of the olefin oligomer (A) having a mass average molecular weight of 500 or more and 5,000 or less in the lubricating oil composition of this embodiment is, based on the total amount of the lubricating oil composition, preferably 0.8% by mass or more and 4.5% by mass or less, more preferably 1% by mass or more and 4% by mass or less, even more preferably 1.2% by mass or more and 2.5% by mass or less.

<Antioxidant (B)>

[0027] The lubricating oil composition of this embodiment contains an antioxidant (B), and the antioxidant (B) contains a phenol-based antioxidant (B-1) and an amine-based antioxidant (B-2). In this embodiment, the antioxidant (B) is needed to contain both the phenol-based antioxidant (B-1) and the amine-based antioxidant (B-2), and the use of either one alone fails to attain a sufficient antioxidation performance.

[0028] Not specifically limited, the phenol-based antioxidant (B-1) may be any compound having a phenol structure and having an effect of preventing oxidation of the lubricating oil composition.

[0029] Examples of the phenol-based antioxidant (B-1) include 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4,6-tri-tert-butylphenol, 2,6-di-tert-butyl-4-hydroxymethylphenol, 2,6-di-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert-butyl-4-(N,N'-dimethylaminomethyl)phenol, 2,6-di-tert-amyl-4-methylphenol, 2,6-di-tert-amyl-p-cresol, 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-nonylphenol), 2,2'-isobutylidenebis(4,6-dimethylphenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,4-dimethyl-6-tert-butylphenol, 4,4'-thiobis(2-methyl-6-tert-butylphenol), 4,4'-thiobis(3-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)sulfide, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, 2,2'-thio-diethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], tridecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], octyl-3-(3,5-d-tert-butyl-4-hydroxyphenyl)propionate, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, and octyl-3-(3-methyl-5-tert-butyl-4-hydroxyphenyl)propionate.

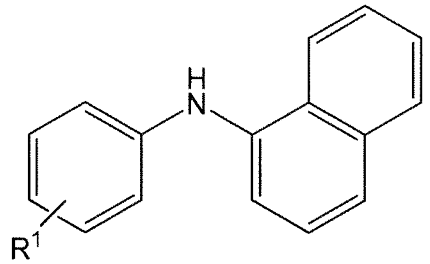
[0030] In this embodiment, one kind of the phenol-based antioxidant (B-1) may be used alone or two or more kinds thereof may be used in combination.

[0031] The amine-based antioxidant (B-2) usable in this embodiment is not specifically limited. Examples thereof include compounds represented by the following general formula (B-2-1).

$$Ar^1\text{-NH-}Ar^2 \qquad \text{(B-2-1)}$$

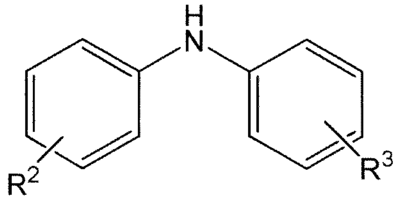
[0032] In the formula, Ar^1 and Ar^2 each independently represent an aryl group having 6 to 24 carbon atoms selected from a phenyl group, a phenyl group substituted with an alkyl group, a phenyl group substituted with an aralkyl group, a naphthyl group, and a naphthyl group substituted with an alkyl group.

[0033] More specifically, the amine-based antioxidant (B-2) is preferably selected from phenyl-α-naphthylamines represented by the following general formula (B-2-2) and diphenylamines represented by the following general formula (B-2-3).



(B-2-2)

In the formula, R^1 represents a hydrogen atom, or an alkyl group having 1 to 18 carbon atoms.



(B-2-3)

In the formula, R^2 and R^3 each independently represent a hydrogen atom, an alkyl group having 1 to 18 carbon atoms, or an aralkyl group having 7 to 18 carbon atoms.

[0034] Specific examples of the amine-based antioxidant (B-2) include monoalkyldiphenylamines such as monooctyldiphenylamine, and monononyldiphenylamine; dialkyldiphenylamines such as 4,4'-dibutyldiphenylamine, 4,4'-dipentyldiphenylamine, 4,4'-dihexyldiphenylamine, 4,4'-diheptyldiphenylamine, 4,4'-dioctyldiphenylamine, and 4,4'-dinonyldiphenylamine; polyalkyldiphenylamines such as tetrabutyldiphenylamine, tetrahexyldiphenylamine, tetraoctyldiphenylamine, and tetranonyldiphenylamine; naphthylamines such as α-naphthylamine, and phenyl-α-naphthylamine; alkyl-substituted phenyl-α-naphthylamines such as butylphenyl-α-naphthylamine, pentylphenyl-α-naphthylamine, hexylphenyl-α-naphthylamine, heptylphenyl-α-naphthylamine, octylphenyl-α-naphthylamine, and nonylphenyl-α-naphthylamine; and diphenylamine, monobutylphenylmonooctylphenylamine, N-p-t-octylphenyl-1-naphthylamine, and 4,4'-bis(α,α-dimethylbenzyl)diphenylamine.

[0035] In this embodiment, one kind of the amine-based antioxidant (B-2) may be used alone or two or more kinds thereof may be used in combination.

[0036] Specific examples of the phenol-based antioxidant (B-1) and the amine-based antioxidant (B-2) to be used in combination for the antioxidant (B) include arbitrary combinations of pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] or octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (B-1), and monobutylphenylmonooctylphenylamine or N-p-t-octylphenyl-1-naphthylamine (B-2).

[0037] In this embodiment, the content of the antioxidant (B) containing the phenol-based antioxidant (B-1) and the amine-based antioxidant (B-2) is, based on the total amount of the lubricating oil composition, preferably 0.5% by mass or more and 3.0% by mass or less, more preferably 0.5% by mass or more and 2.0% by mass or less, even more preferably 1% by mass or more and 2% by mass or less. Here, the content of the antioxidant (B) means the total amount of the phenol-based antioxidant (B-1) and the amine-based antioxidant (B-2).

[0038] When the content of the antioxidant (B) is 0.5% by mass or more, the antioxidation effect can be sufficiently exhibited. From the viewpoint of the antioxidation effect, the upper limit of the content of the antioxidant (B) may be well 3.0% by mass.

[0039] Though not specifically limited, the ratio by mass of the amine-based antioxidant (B-2) to the phenol-based antioxidant (B-1) [(B-2)/(B-1)] is preferably 1/3 to 3/1 or so, more preferably 1/2 to 2/1 or so.

[0040] Further, in this embodiment, the total content of the phenol-based antioxidant (B-1) and the amine-based antioxidant (B-2) in the antioxidant (B) is, based on the total amount of the antioxidant (B), preferably 60% by mass or more and 100% by mass or less, more preferably 70% by mass or more and 100% by mass or less, even more preferably 80% by mass or more and 100% by mass or less, further more preferably 90% by mass or more and 100% by mass or less, still further more preferably 99% by mass or more and 100% by mass or less.

[0041] As described above, in this embodiment, using the phenol-based antioxidant (B-1) and the amine-based antioxidant (B-2) in combination as the antioxidant (B) is indispensable, but does not exclude containing any other antioxidant within a range not detracting from the advantageous effects of the present invention. Examples of the other antioxidant include a molybdenum amine complex-based antioxidant.

[0042] The molybdenum amine complex-based antioxidant includes hexavalent molybdenum compounds, specifically those produced by reacting molybdenum trioxide and/or molybdic acid and an amine compound, for example, the compounds obtained according to the production method described in JP 2003-252887 A.

<Alkaline earth metal-based detergent (C)>

[0043] The lubricating oil composition of this embodiment contains an alkaline earth metal-based detergent (C), and the content of the alkaline earth metal-based detergent (C) is 1,700 ppm by mass or more and 2,700 ppm by mass or less in terms of an alkaline earth metal atom thereof based on the total amount of the lubricating oil composition.

[0044] The alkaline earth metal-based detergent (C) prevents sludge formation owing to the acid neutralization effect for the degraded components formed in oil, and has a detergent effect for sludge dispersion.

[0045] When the content of the alkaline earth metal-based detergent (C) is less than 1,700 ppm by mass in terms of an alkaline earth metal atom thereof based on the total amount of the lubricating oil composition, the above-mentioned neutralization effect could not be sufficiently exhibited and therefore the composition is poor in oxidation stability and heat resistance. When the content of the alkaline earth metal-based detergent (C) is more than 2,700 ppm by mass in terms of an alkaline earth metal atom thereof, the metal amount in the composition may increase to form nuclei for sludge formation, and the composition is poor in heat resistance. The content of the alkaline earth metal-based detergent (C) is, in terms of an alkaline earth metal atom thereof based on the total amount of the lubricating oil composition, preferably 1,800 ppm by mass or more and 2,600 ppm by mass or less, more preferably 1,900 ppm by mass or more and 2,500 ppm by mass or less, even more preferably 2,000 ppm by mass or more and 2,500 ppm by mass or less.

[0046] As the alkaline earth metal-based detergent (C), at least one selected from the group consisting of alkaline earth metal sulfonates, alkaline earth metal phenates and alkaline earth metal salicylates to be mentioned below may be used, and a mixture of two or more of them may also be used. Above all, alkaline earth metal sulfonates are preferred from the viewpoint of heat resistance.

[0047] The alkaline earth metal sulfonate includes alkaline earth metal salts, especially magnesium salts and/or calcium salts of alkylaromatic sulfonic acids obtained by sulfonating an alkylaromatic compound having a molecular weight of 300 to 1,500, preferably 400 to 700. Above all, using calcium salts is preferred. The alkaline earth metal phenate includes alkaline earth metal salts, especially magnesium salts and/or calcium salts of an alkylphenol, an alkylphenol sulfide or a Mannich reaction product of an alkylphenol, and above all, calcium salts are especially preferred. The alkaline earth metal salicylate includes alkaline earth metal salts, especially magnesium salts and/or calcium salts of an alkylsalicylic acid, and above all, calcium salts are preferred.

[0048] The carbon number of the alkyl group constituting the alkaline earth metal-based detergent (C) is preferably 4 to 30, more preferably 6 to 18, and the alkyl group may be linear or branched. The alkyl group may be any of a primary alkyl group, a secondary alkyl group or a tertiary alkyl group.

[0049] The alkaline earth metal sulfonate, the alkaline earth metal phenate and the alkaline earth metal salicylate may be any of neutral, basic or overbased ones. Examples of the neutral alkaline earth metal salts include neutral alkaline earth metal sulfonates, neutral alkaline earth metal phenates and neutral alkaline earth metal salicylates to be obtained by directly reacting the above-mentioned alkylaromatic sulfonic acid, alkylphenol, alkylphenol sulfide, Mannich reaction product of an alkylphenol, or an alkylsalicylic acid with an alkaline earth metal base such as an oxide or hydroxide of an alkaline earth metal of magnesium and/or calcium, or once converting into an alkali metal salt, such as a sodium salt and a potassium salt, and then substituting with an alkaline earth metal salt. Examples of the basic alkaline earth metal salt include basic alkaline earth metal sulfonates, basic alkaline earth metal phenates and basic alkaline earth metal salicylates to be obtained by heating the above-mentioned neutral alkaline earth metal sulfonate, neutral alkaline earth metal phenate or neutral alkaline earth metal salicylate with an excessive amount of an alkaline earth metal salt or an alkaline earth metal base in the presence of water. Examples of the overbased alkaline earth metal salt include overbased alkaline earth metal sulfonates, overbased alkaline earth metal phenates and overbased alkaline earth metal salicylates to be obtained by reacting the above-mentioned neutral alkaline earth metal sulfonate, neutral alkaline earth metal phenate or neutral alkaline earth metal salicylate with an alkaline earth metal carbonate or borate in the presence of carbon dioxide. The alkaline earth metal-based detergent (C) is generally sold on the market in a form thereof diluted with a light lubricant base oil or the like and is therefore available, and in general, those having a metal content of 1.0 to 20% by mass, preferably 2.0 to 16% by mass are preferred.

[0050] The metal ratio in the alkaline earth metal-based detergent (C) in this embodiment is not specifically limited, and one or more having a metal ratio of 20 or less may be used singly or in combination. The metal ratio is preferably 3 or less, more preferably 1.5 or less, even more preferably 1.2 or less from the viewpoint of securing excellent oxidation stability, base number retention and heat resistance at high temperatures.

[0051] The metal ratio as referred to herein is represented by [valence of metal element × metal element content (mol%)/soap group content (mol%)] in a metal-based detergent, and the metal element includes calcium and magnesium, the soap group includes a sulfonic acid group, a phenol group and a salicylic acid group.

[0052] The alkaline earth metal-based detergent (C) may be any of the above-mentioned neutral, basic or overbased ones, and examples thereof include an alkaline earth metal-based detergent (C) generally having a base number of 10 mgKOH/g or more and 500 mgKOH/g or less, preferably 15 mgKOH/g or more and 450 mgKOH/g or less, and one or more of these may be used singly or in combination. In this embodiment, basic or overbased ones are more preferred, and those having a base number of 150 mgKOH/or or more and 450 mgKOH/g or less are preferred. Those having a base number of 150 mgKOH/or or more and 450 mgKOH/g or less can exhibit more excellent oxidation stability and are also excellent in heat resistance. The base number of the alkaline earth metal-based detergent (C) as referred to in this description is one measured according to the perchloric acid method of JIS K2501:2003. The base number of the alkaline earth metal-based detergent (C) is more preferably 200 mgKOH/or or more and 450 mgKOH/g or less, even more preferably 250 mgKOH/or or more and 400 mgKOH/g or less.

[0053] The alkaline earth metal atom contained in the alkaline earth metal-based detergent (C) is one or more selected from a beryllium atom, a magnesium atom, a calcium atom, a strontium atom and a barium atom, and from the viewpoint of high-temperature heat resistance, calcium, magnesium or barium is preferred, calcium or magnesium is more preferred, and calcium is even more preferred. As the alkaline earth metal-based detergent (C), a calcium sulfonate is preferably used.

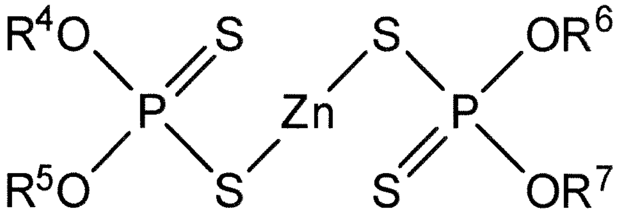
<Polymer (D) having mass average molecular weight of more than 5,000>

[0054] The lubricating oil composition of this embodiment may contain a polymer (D) having a mass average molecular weight of more than 5,000. However, in the case where the composition contains the polymer (D), the content of the polymer (D) is preferably less than 50 parts by mass relative to 100 parts by mass of the olefin oligomer (A). When the proportion to 100 parts by mass of the olefin oligomer (A) falls within the above range, the composition can maintain heat resistance in, for example, high-temperature parts of transmissions. In addition, when the amount of the polymer (D) falls within the above range, viscosity lowering in actual vehicle driving owing to shear of the polymer compound can be suppressed as much as possible. The content of the polymer (D) is more preferably less than 30 parts by mass relative to 100 parts by mass of the olefin oligomer (A), even more preferably less than 20 parts by mass. The mass average molecular weight of the polymer (D) is preferably 120,000 or less, more preferably 50,000 or less, even more preferably 40,000 or less.

[0055] The polymer (D) is not specifically limited, and any polymethacrylates and the like generally usable as a pour point depressant can be used. Even though not containing a viscosity index improver, the lubricating oil composition of this embodiment can still maintain a stable oil film strength even at high temperatures though, and therefore the composition is not needed to contain a viscosity index improver. Even in the case where the polymer (D) grouped in the category of a viscosity index improver is contained, the lubricating oil composition can still realize excellent shear stability when the content of the polymer falls within the above-mentioned mass ratio.

<Zinc dithiophosphate (E)>

[0056] The lubricating oil composition of this embodiment may contain a zinc dithiophosphate (E). As the zinc dithiophosphate (E), those represented by the following general formula (E-1) are usable.



(E-1)

In the formula, R^4 to R^7 each independently represent a group selected from a linear, branched or cyclic alkyl group having 1 to 24 carbon atoms, and a linear, branched or cyclic alkenyl group having 1 to 24 carbon atoms.

[0057] In the general formula (E-1), R^4 to R^7 each independently represent a linear, branched or cyclic alkyl group having 1 to 24 carbon atoms, or a linear, branched or cyclic alkenyl group having 1 to 24 carbon atoms, and they may be the same as or different from each other, but from the viewpoint of easiness in production, they are preferably the same.

[0058] R^4 to R^7 are preferably linear, and R^4 to R^7 each are preferably an alkyl group.

[0059] The alkyl group for R^4 to R^7 includes 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 nonyl 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, an octadecyl group, a nonadecyl group, an eicosyl group, a heneicosyl group, a docosyl group, a tricosyl group and a tetracosyl group, and these may be linear, branched or cyclic. The alkenyl group includes a vinyl group, a propenyl group, a butenyl group, a pentenyl group, a hexenyl group, a heptenyl group, an octenyl group, a nonenyl group, a decenyl group, an undecenyl group, a dodecenyl group, a tridecenyl group, a tetradecenyl group, a pentadecenyl group, a hexadecenyl group, a heptadecenyl group, an octadecenyl group, a nonadecenyl group, an eicosenyl group, a heneicosenyl group, a docosenyl group, a tricosenyl group, and a tetracosenyl group, and these may be linear, branched or cyclic, and in these, the double bond may be at any position.

[0060] In the case where the lubricating oil composition of the present invention contains the zinc dithiophosphate (E), the content thereof is, based on the total amount of the lubricating oil composition, generally 0.05% by mass or more and 5% by mass or less, preferably 0.1% by mass or more and 3% by mass or less, more preferably 1% by mass or more and 2.5% by mass or less. When the content of the zinc dithiophosphate (E) falls within the above range, and for example, when the composition is used for MTF (manual transmission fluid), the friction coefficient (μ) may be improved in gear change to better shift feeling.

<Base oil>

[0061] The base oil for use in this embodiment may be any of a mineral oil or a synthetic oil, and a mixed oil of a mineral oil and a synthetic oil may also be used.

[0062] Examples of the mineral oil include topped crudes obtained through atmospheric distillation of crude oils such as paraffin base crude oils, mixed crude oils, and naphthene base crude oils; distillates obtained through vacuum distillation of such topped crudes; purified oils obtained by purifying the distillates through one or more purification treatments of solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, catalytic dewaxing or hydrorefining, and waxes.

[0063] In this embodiment, from the viewpoint of preventing sludge formation, mineral oils grouped in Group 2 or 3 in the base oil category of API (American Petroleum Institute) are preferred. In addition, for further bettering oxidation stability, those grouped in Group 3 are more preferred. The base oil grouped in Group 2 has a saturation content of 90% or more, a sulfur content of 0.03% or less, and a viscosity index of from 80 to less than 120. The base oil grouped in Group 3 has a saturation content of 90% or more, a sulfur content of 0.03% or less, and a viscosity index of 120 or more.

[0064] The sulfur content is a value measured according to JIS K2541-6:2013; the saturation content is a value measured according to ASTM D 2007. Further, the viscosity index is a value measured according to JIS K 2283:2000.

[0065] The synthetic oil includes various esters such as polyol esters, dibasic acid esters (for example, ditridecyl glutarate), tribasic acid esters (for example, 2-ethylhexyl trimellitate), and phosphates; various ethers such as polyphenyl ethers; polyalkylene glycols; alkylbenzenes; alkylnaphthalenes; and synthetic oils obtained through isomerization of wax (GTL (gas-to-liquid wax)) produced in Fischer-Tropsch synthesis.

[0066] In this embodiment, one of these base oils may be used alone or two or more kinds thereof may be used in combination. The kinematic viscosity at 100°C of the base oil for use in this embodiment is preferably 2.0 mm^2/s or more and 30 mm^2/s or less, more preferably 2.5 mm^2/s or more and 25 mm^2/s or less, even more preferably 3.0 mm^2/s or more and 20 mm^2/s or less.

[0067] The viscosity index of the base oil for use in this embodiment is, from the viewpoint of providing a lubricating oil composition capable of preventing viscosity change with temperature change and capable of improving fuel saving performance, preferably 80 or more, more preferably 90 or more, even more preferably 120 or more.

[0068] In the case where a mixed oil prepared by mixing two or more kinds of base oils is used, preferably, the kinematic viscosity and the viscosity index of the mixed oil each fall within the above-mentioned range.

[0069] In this embodiment, the content of the base oil is, based on the total amount of the composition, preferably 75% by mass or more, more preferably 80% by mass or more, even more preferably 85% by mass or more, and is preferably 97% by mass or less, more preferably 95% by mass or less.

<Other additives>

[0070] The lubricating oil composition for transmissions of this embodiment may contain additives such as a friction modifier, a dispersant and an anti-foaming agent. However, a pour point depressant is grouped in the polymer (D) having a mass average molecular weight of more than 5,000, and is not included in the other additives.

[0071] The amount of the additive to be blended is, based on the total amount of the composition, preferably 10% by mass or less, more preferably 7.5% by mass or less, even more preferably 5.0% by mass or less.

<Physical properties of lubricating oil composition>

[0072] The kinematic viscosity at 100°C of the lubricating oil composition of this embodiment is 4.0 mm^2/s or more and 6.0 mm^2/s or less. When the kinematic viscosity at 100°C is less than 4.0 mm^2/s, the oil film strength lowers therefore resulting in lowering of seizure resistance, wear resistance and fatigue resistance. When the kinematic viscosity at 100°C is more than 6.0 mm^2/s, resistance to stirring increases, which is unfavorable in point of fuel saving performance.

[0073] The kinematic viscosity at 100°C of the lubricating oil composition of this embodiment is more preferably 4.5 mm^2/s or more and 5.8 mm^2/s or less, even more preferably 4.6 mm^2/s or more and 5.5 mm^2/s or less

<Use, lubrication method, transmission>

[0074] The lubricating oil composition of this embodiment can be favorably used for transmissions.

[0075] The lubricating oil composition of this embodiment has a low viscosity, therefore preventing viscosity lowering in actual vehicle driving, and is excellent in heat resistance and oxidation stability. Consequently, in down-sized and weight-reduced transmissions, for example, the composition can prevent sludge adhesion to a synchromesh mechanism, therefore securing good shift feeling. In addition, the composition can keep good synchronizer ring operation. Accordingly, this embodiment also provides a lubrication method using the lubricating oil composition mentioned above and a use method for the composition.

[0076] In addition, this embodiment can provide a transmission loaded with the lubricating oil composition.

<Production method for lubricating oil composition>

[0077] The lubricating oil composition of this embodiment can be produced by blending (A) an olefin oligomer having a mass average molecular weight of 500 or more and 5,000 or less, (B) an antioxidant containing (B-1) a phenol-based antioxidant and (B-2) an amine-based antioxidant, and (C) an alkaline earth metal-based detergent, in a base oil, wherein the alkaline earth metal-based detergent (C) is blended such that the content of the alkaline earth metal-based detergent (C) is 1,700 ppm by mass or more and 2,700 ppm by mass or less in terms of an alkaline earth metal atom thereof based on the total amount of the lubricating oil composition.

Examples

[0078] Next, this embodiment is described more specifically with reference to Examples, but this embodiment is not whatsoever restricted by these Examples.

<Measurement methods>

(1) Mass average molecular weight (Mw)

[0079] Measured through GPC (gel permeation chromatography) in terms of a standard polystyrene. Specifically, it was measured using the following apparatus under the following condition.
GPC apparatus: Waters 1515 Isocratic HPLC Pump + Waters 2414 Refractive Index Detector (all by Waters Corporation)
Columns: Two columns of "TSKgel Super Multipore HZ-M" (by Tosoh Corporation) were connected.
Column temperature: 40°C
Eluent: tetrahydrofuran
Flow rate: 0.35 mL/min
Detector: refractive index detector

(2) Kinematic viscosity

[0080] The kinematic viscosity at different temperatures was measured according to JIS K2283:2000.

(3) Calcium atom content, nitrogen atom content, phosphorus atom content and sulfur atom content in lubricating oil composition

[0081] The content of each component was measured according to the following methods.

(3-1) Calcium atom (Ca) content and phosphorus atom (P) content

[0082] Measured according to JPI-5S-38-92.

(3-2) Nitrogen atom (N) content

[0083] Measured according to JIS K2609:1998.

(3-3) Sulfur atom (S) content

[0084] Measured according to JIS K2541-6:2013.

<Evaluation methods>

(I) Panel coking test

[0085] According to Federal test method 791B·3462, each sample was tested under the condition of a panel temperature of 300°C and an oil temperature of 100°C, in a cycle of a splashing time of 15 seconds and a stop time of 45 seconds for 3 hours. After the test, the weight of coke having adhered to the panel (mg) was measured.

(II) Oxidation stability

[0086] In an ISOT test (165.5°C) according to JIS K2514-1:2013, a test oil (lubricating oil composition) and a copper piece and an iron piece as catalyst were put in a vessel, and the test oil was forcedly degraded therein. The base number (according to a perchloric acid method) after 96 hours was measured. A higher value of the base number after the test means higher base number retention, and a test oil having a higher value thereof means a long drain oil durable for long-term use. After the ISOT test, the n-pentane insoluble content (method A) was measured.

(III) Shear stability

[0087] According to JIS K2283:2000, the kinematic viscosity at 100°C before and after a shear test was measured, and the shear stability was calculated according to the following equation. The shear test was carried out based on the ultrasonic method A (JPI-5S-29-06) under the condition of an ultrasonic irradiation time of 60 minutes, at room temperature and an oil amount of 30 cc. The output voltage for ultrasonic waves in the shear stability test was controlled such that, after 30 cc of a standard oil was irradiated with ultrasonic waves for 10 minutes, the kinematic viscosity reduction at 100°C was 25%.

$$\text{Shear stability (\%)} = \{([\text{kinematic viscosity before test}] - [\text{kinematic viscosity after test}])/[\text{kinematic viscosity before test}]\} \times 100$$

Examples 1 to 6, and Comparative Examples 1 to 7

[0088] The components shown in Tables 1 and 2 were blended to prepare lubricating oil compositions. The lubricating oil compositions prepared in Examples and Comparative Examples were analyzed to determine the acid value, the 40°C kinematic viscosity, the 100°C kinematic viscosity, the calcium content, the nitrogen content, the phosphorus content and the sulfur content before the test, and then these compositions were tested as in the above-mentioned (I) to (III). All the results are shown in Tables.

Table 1

			Unit	Example					
				1	2	3	4	5	6
Base Oil	Gr. III			balance	balance	balance	balance	balance	balance
Component (A)	Oligomer 1	Mw: 940	wt%	1.25	2	2		2	2
	Oligomer 2	Mw: 2300	wt%				2		
Component (D)	Oligomer 3	Mw: 10000	wt%						
	Oligomer 4	Mw: 12000	wt%						
	Oligomer 5	Mw: 17000	wt%						
Component (B-1)	Antioxidant (B-1-A)	phenol-based	wt%	0.5	0.5	1	0.5		0.5
	Antioxidant (B-1-B)	phenol-based	wt%					0.5	
Component (B-2)	Antioxidant (B-2-C)	amine-based	wt%	0.5	0.5	1	0.5	0.5	
	Antioxidant (B-2-D)	amine-based	wt%						0.5
Component (C)	Alkaline Earth Metal-Based Detergent		wt%	1.4	1.4	1.4	1.4	1.4	1.4
Component (E)	ZnDTP		wt%	1.5	1.5	1.5	1.5	1.5	1.5
Other Additives			wt%	4.1	4.1	4.1	4.1	4.1	4.1
Total			wt%	100.0	100.0	100.0	100.0	100.0	100.0
Properties of Composition	Kinematic Viscosity at 40°C		mm^2/s	22.9	24.0	23.7	27.2	24.0	24.1
	Kinematic Viscosity at 100°C		mm^2/s	4.75	4.90	4.88	5.49	4.90	4.91
	Ca		ppm	2200	2200	2200	2200	2200	2200
	N		wt%	420	420	620	420	420	390
	P		ppm	1100	1100	1100	1100	1100	1100
	S		wt%	0.4	0.4	0.4	0.4	0.4	0.4

(continued)

			Unit	Example					
				1	2	3	4	5	6
Evaluation Items	Panel Coking	sludge amount	mg	18	16	15	20	19	18
	Oxidation Stability	base number after ISOT test	mgKOH/g	0.04	0.04	0.06	0.03	0.04	0.06
		n-P insoluble content after ISOT test	wt%	0	0	0	0	0	0
	Shear Stability	viscosity reduction percentage	%	0.5	0.9	0.9	1.1	0.9	0.9

Table 2

				Comparative Example						
				1	2	3	4	5	6	7
Base Oil	Gr. III			balance	balance	balance	balance	balance	balance	balance
Component (A)	Oligomer 1	Mw: 940	wt%	2	2				2	2
	Oligomer 2	Mw: 2300	wt%							
Component (D)	Oligomer 3	Mw: 10000	wt%			2				
	Oligomer 4	Mw: 12000	wt%				2			
	Oligomer 5	Mw: 17000	wt%					2		
Component (B-1)	Antioxidant (B-1-A)	phenol-based	wt%	0.5	0.5	0.5	0.5	0.5		0.5
	Antioxidant (B-2-B)	phenol-based	wt%							
Component (B-2)	Antioxidant (B-2-C)	amine-based	wt%	0.5	0.5	0.5	0.5	0.5	0.5	
	Antioxidant (B-2-D)	amine-based	wt%							
Component (C)	Alkaline Earth Metal-Based Detergent		wt%	1	1.8	1.4	1.4	1.4	1.4	1.4
Component (E)	ZnDTP		wt%	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Other Additives			wt%	4.8	4.1	4.1	4.1	4.1	4.1	4.1
Total			wt%	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Properties of Composition	Kinematic Viscosity at 40°C		mm^2/s	20.8	23.8	25.6	28.0	33.1	24.3	24.3
	Kinematic Viscosity at 100°C		mm^2/s	4.56	5.03	5.27	5.66	6.47	4.96	4.96
	Ca		ppm	1600	2800	2200	2200	2200	2200	2200
	N		wt%	420	420	420	420	420	420	210
	P		ppm	1100	1100	1100	1100	1100	1100	1100
	s		wt%	0.4	0.4	0.4	0.4	0.4	0.4	0.4

(continued)

				Comparative Example						
				1	2	3	4	5	6	7
Evaluation Items	Panel Coking	sludge amount	mg	14	33	35	35	41	30	43
	Oxidation Stability	base number after ISOT test	mgKOH/g	0.00	0.41	0.03	-	-	-	-
		n-P insoluble content after ISOT test	wt%	0.08	0	0	-	-	-	-
	Shear Stability	viscosity reduction percentage	%	-	-	-	-	2.8	-	-

[0089] The blended materials in Examples and Comparative Examples are as follows.

<Blended materials>

(1) Base oil

[0090] Mineral oil grouped in Group III in API base oil category (kinematic viscosity at 40°C: 18.9 mm^2/s, kinematic viscosity at 100°C: 4.2 mm^2/s, viscosity index: 128)

(2) Olefin oligomer

Component (A)

[0091]

Oligomer 1: polybutene-1 having a mass average molecular weight (Mw) of 940
Oligomer 2: polybutene-1 having a mass average molecular weight (Mw) of 2300 Olefin oligomers except for the component (A)
Oligomer 3: decene oligomer having a mass average molecular weight (Mw) of 10000
Oligomer 4: ethylene-propylene having a mass average molecular weight (Mw) of 12000
Oligomer 5: ethylene-propylene having a mass average molecular weight (Mw) of 17000

(3) Antioxidant (B)

Phenol-based antioxidant (B-1)

[0092] Antioxidant (B-1-A): octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate Antioxidant (B-1-B): pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] Amine-based antioxidant (B-2) Antioxidant (B-2-C): monobutylphenylmonooctylphenylamine Antioxidant (B-2-D): N-p-t-octylphenyl-1-naphthylamine

(4) Alkaline earth metal-based detergent (C)

[0093] Overbased calcium sulfonate (base number: 400 mgKOH/g, measured according to the perchloric acid method of JIS K2501:2003)

(5) Zinc dithiophosphate (E)

[0094] Zinc dihexyldithiophosphate (n-hexyl group)

(6) Other additives; sulfur-based extreme-pressure agent, dispersant, ash-free friction modifier and anti-foaming agent

[0095] From Table 1, it is known that the lubricating oil compositions of Examples 1 to 6 have a low kinematic viscosity at 100°C and are excellent in heat resistance and oxidation stability. In addition, since these compositions do not require a polymer having a high molecular weight such as a viscosity index improver to cause viscosity reduction by shearing, the viscosity lowering percentage thereof is low even after a shear test, and it is known that the compositions can sufficiently prevent viscosity reduction in actual vehicle driving.

[0096] On the other hand, from Table 2, the following are known. From Comparative Example 1, it is known that, when the content of the component (C) in terms of a calcium atom based on the total amount of the lubricating oil composition does not satisfy this embodiment, oxidation stability is poor. As in Comparative Example 2, it is known that, when the content of the component (C) in terms of a calcium atom based on the total amount of the lubricating oil composition is too high, sludge formation increases and heat resistance is poor. As in Comparative Examples 3 to 5, it is known that, when an olefin oligomer whose mass average molecular weight does not fall within the scope in the present invention, heat resistance is poor. In particular, in Comparative Example 5, an oligomer having a mass average molecular weight of 17,000 is used, and therefore shear stability is poor. From Comparative Examples 6 and 7, it is known that, when a phenol-based antioxidant and an amine-based antioxidant are not used in combination as the antioxidant (B), heat resistance is also poor.

Industrial Applicability

[0097] According to the present invention, there can be provided a lubricating oil composition capable of attaining viscosity reduction and capable of preventing viscosity lowering in actual vehicle driving, and capable of attaining improved heat resistance and oxidation stability accompanied by down-sizing and weight-saving of devices.

Claims

1. A lubricating oil composition comprising, along with a base oil,

   (A) an olefin oligomer having a mass average molecular weight of 500 or more and 5,000 or less,
   (B) an antioxidant containing (B-1) a phenol-based antioxidant and (B-2) an amine-based antioxidant, and
   (C) an alkaline earth metal-based detergent,

   wherein the content of the alkaline earth metal-based detergent (C) is 1,700 ppm by mass or more and 2,700 ppm by mass or less in terms of an alkaline earth metal atom thereof based on the total amount of the lubricating oil composition, and the kinematic viscosity at 100°C of the lubricating oil composition is 4.0 mm^2/s or more and 6.0 mm^2/s or less.

2. The lubricating oil composition according to claim 1, wherein the content of the olefin oligomer (A) is 0.8% by mass or more and 4.5% by mass or less based on the total amount of the lubricating oil composition.

3. The lubricating oil composition according to claim 1 or 2, wherein the olefin oligomer (A) contains a structural unit derived from an unsaturated hydrocarbon monomer having 2 or more and 5 or less carbon atoms.

4. The lubricating oil composition according to any one of claims 1 to 3, wherein the olefin oligomer (A) is a polybutene.

5. The lubricating oil composition according to any one of claims 1 to 4, wherein the alkaline earth metal-based detergent (C) is an alkaline earth metal salt having a base number of 150 mgKOH/g or more and 450 mgKOH/g or less.

6. The lubricating oil composition according to any one of claims 1 to 5, wherein the alkaline earth metal-based detergent (C) is at least one selected from the group consisting of an alkaline earth metal sulfonate, an alkaline earth metal phenate and an alkaline earth metal salicylate.

7. The lubricating oil composition according to any one of claims 1 to 6, wherein the alkaline earth metal atom of the alkaline earth metal-based detergent (C) is a calcium atom or a magnesium atom.

8. The lubricating oil composition according to any one of claims 1 to 7, wherein the content of the antioxidant (B) is 0.5% by mass or more and 3.0% by mass or lessbased on the total amount of the lubricating oil composition.

9. The lubricating oil composition according to any one of claims 1 to 8, further comprising (E) a zinc dithiophosphate.

10. The lubricating oil composition according to any one of claims 1 to 9, which is for transmissions.

11. A transmission loaded with the lubricating oil composition of any one of claims 1 to 9.

12. A lubrication method, comprising using the lubricating oil composition of any one of claims 1 to 9.

13. A use method, comprising using the lubricating oil composition of any one of claims 1 to 9 for transmissions.

14. A method for producing a lubricating oil composition, comprising blending (A) an olefin oligomer having a mass average molecular weight of 500 or more and 5,000 or less, (B) an antioxidant comprising (B-1) a phenol-based antioxidant and (B-2) an amine-based antioxidant, and (C) an alkaline earth metal-based detergent, in a base oil, the alkaline earth metal-based detergent (C) being blended such that the content of the alkaline earth metal-based detergent (C) is 1,700 ppm by mass or more and 2,700 ppm by mass or less in terms of an alkaline earth metal atom thereof based on the total amount of the lubricating oil composition.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/008496

A. CLASSIFICATION OF SUBJECT MATTER
See extra sheet.

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)
C10M169/04, C10M129/10, C10M133/12, C10M137/10, C10M143/00, C10M143/06, C10M159/22, C10M159/24, C10M163/00, C10N10/04, C10N20/00, C10N20/02, C10N20/04, C10N30/02, C10N30/08, C10N30/10, C10N40/04

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	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

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.
A	JP 2015-502446 A (Showa Shell Sekiyu Kabushiki Kaisha), 22 January 2015 (22.01.2015), & WO 2013/093103 A1	1-14
A	JP 2014-25004 A (JX Nippon Oil & Energy Corp.), 06 February 2014 (06.02.2014), & US 2015/0203780 A1 & WO 2014/017182 A1 & EP 2878653 A1 & CA 2880179 A & CN 104662138 A	1-14
A	WO 2004/069967 A1 (Nippon Oil Corp.), 19 August 2004 (19.08.2004), (Family: none)	1-14

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

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

Date of the actual completion of the international search 17 March 2017 (17.03.17)	Date of mailing of the international search report 28 March 2017 (28.03.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/008496

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2007/058213 A1 (Idemitsu Kosan Co., Ltd.), 24 May 2007 (24.05.2007), & US 2010/0062954 A1 & EP 1950277 A1 & KR 10-2008-0069181 A	1-14
A	JP 2012-107142 A (Idemitsu Kosan Co., Ltd.), 07 June 2012 (07.06.2012), (Family: none)	1-14
A	WO 2008/016038 A1 (Idemitsu Kosan Co., Ltd.), 07 February 2008 (07.02.2008), & JP 2008-37963 A & US 2009/0312211 A1 & EP 2053117 A1 & KR 10-2009-0050051 A & CN 101495607 A	1-14
A	JP 4-202398 A (Tonen Corp.), 23 July 1992 (23.07.1992), (Family: none)	1-14

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

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PCT/JP2017/008496

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

C10M169/04(2006.01)i, *C10M129/10*(2006.01)i, *C10M133/12*(2006.01)i, *C10M137/10*(2006.01)i, *C10M143/00*(2006.01)i, *C10M143/06*(2006.01)i, *C10M159/22*(2006.01)i, *C10M159/24*(2006.01)i, *C10M163/00*(2006.01)i, *C10N10/04*(2006.01)n, *C10N20/00*(2006.01)n, *C10N20/02*(2006.01)n, *C10N20/04*(2006.01)n, *C10N30/02*(2006.01)n, *C10N30/08*(2006.01)n, *C10N30/10*(2006.01)n, *C10N40/04*(2006.01)n

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2012193255 A **[0009]**
- JP 2014177605 A **[0009]**
- JP 2014098090 A **[0009]**
- JP 2003252887 A **[0042]**