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(54) CYLINDER LUBRICATING OIL COMPOSITION FOR SCRUBBER-EQUIPPED CROSSHEAD DIESEL ENGINES

(57) A cylinder lubricating oil composition for a crosshead diesel engine equipped with a scrubber, including: a base oil; and (A) a metallic detergent, wherein the lubricating oil composition has a base number of 15 to 125 mgKOH/g, and a kinematic viscosity at 100°C of 10 to 30 mm^2/s; and the lubricating oil composition satisfies the following requirement (i) or (ii): (i) the lubricating oil composition includes: (B) a demulsifier in an amount of 0.02 to 5.0 mass% on the basis of the total mass of the composition; (ii) the lubricating oil composition includes, as the component (A), (A1) a Ca phenate detergent; and (A2) a metallic detergent other than any Ca phenate detergent; the lubricating oil composition optionally includes: (C-1') a succinimide having at least one alkyl or alkenyl group in a molecule thereof, or a borated derivative thereof, in an amount of no more than 0.015 mass% in terms of nitrogen on the basis of the total mass of the composition; and the Ph value represented by the following formula (1) is no more than 20×10^{-3}:

$$\text{Ph value} = C_{Ca} \times 2/(r_M \times 40.08) \qquad \cdots (1)$$

(in the formula (1), C_{Ca} represents calcium content (mass%) derived from the component (A1), and r_M represents a metal ratio of the component (A1).).

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Description

TECHNICAL FIELD

[0001] The present invention relates to a cylinder lubricating oil composition for a crosshead diesel engine equipped with a scrubber, and specifically relates to a cylinder lubricating oil composition suitable for use in a crosshead diesel engine equipped with a scrubber.

BACKGROUND

[0002] Crosshead diesel engines are used a lot for main engines of large ships. Thus, it can be said that large part of the effect of ship operations on the environment is from emission matter of crosshead diesel engines.

[0003] Interests in environmental problems have been increased, and attentions are also given to nitrogen oxides (NOx) and sulfur oxides (SOx) contained in exhaust gases emitted from ships to the air. Regarding NO_x regulations, International Maritime Organization (IMO) decided to put Tier III into effect in Emission Control Area from 2016. Regarding SO_x regulations, discussed is to reduce the sulfur components in fuels used in General Sea Area into no more than 0.5 %, from 2020 or 2025.

[0004] As a technique to reduce the concentrations of SO_x and NO_x in exhausted gases from ships, applications of scrubber techniques are focused on. As a NO_x reduction technique conforming to IMO Tier III, EGR (Exhaust Gas Recirculation) scrubbers (Patent Literatures 1 to 4) are focused on. As options to reduce SO_x emission amount, considered are to reduce the sulfur components in fuels (use of low-sulfur fuels), and to make the amounts of sulfur oxide emitted from conventional high-sulfur fuels same as the amounts of sulfur oxide emitted from low-sulfur fuels of no more than 0.5 % in sulfur component, by means of exhaust gas aftertreatment apparatuses. The latter option is more focused on because low-sulfur fuels are expensive. There is a suggestion of a de-SO_x treatment by means of a scrubber as an exhaust gas aftertreatment apparatus (Patent Literature 5).

[0005] A scrubber (scrubbing dust collector) generally means a device to separate harmful substances (e.g. harmful gases and dusts) in exhaust gases, by collecting the harmful substances into liquid drops and liquid films of absorption liquids (e.g. water). For example, separation of SO_x by absorbing it into an aqueous solution such as sodium hydroxide aqueous solution and separation of soot by density difference after the soot is collected in water phase are considered.

[0006] In order to efficiently collect harmful substances by scrubber, the gases and the absorption liquid need to sufficiently contact with each other. Thus, scrubbers are well made to increase the efficiency of gas-liquid mixing. However, exhaust gases from diesel engines include hydrocarbon-based substances such as unburnt fuel and lubricant mist. Such hydrocarbon-based substances do not dissolve in water, and may emulsify by strong mixing with water. If these hydrocarbon-substances and water are emulsified, the soot component in the exhaust gases are wrapped inside the emulsion to form scums, and the scums accumulate at the upper portion of the absorption liquid, as a result, the separation becomes difficult.

[0007] Among engine oils used for diesel engines, system oils for crosshead diesel engines and engine oils for four-cycle trunk piston diesel engines are purified by centrifugal purifiers and repeatedly used for lubrication. In order to keep the cleaning effect by centrifugal purifier, water separation property is required of these lubricating oils. Cylinder oils for crosshead diesel engines are once-through type lubricating oils, that is, they are not cleaned by centrifugal purifiers or repeatedly used, and do not contact with water in centrifugal purifiers. Therefore, water separation property was not previously required of cylinder oils for crosshead diesel engines.

Citation List

Patent Literature

[0008]

Patent Literature 1: JP 2011-157959 A
Patent Literature 2: JP 2011-157960 A
Patent Literature 3: JP 2012-137092 A
Patent Literature 4: JP H8-511074 T
Patent Literature 5: JP 2011-185275 A

Summary of Invention

Technical Problem

[0009] An object of the present invention is to provide a cylinder lubricating oil composition for a crosshead diesel engine equipped with a scrubber, by which it is possible to improve water separation property and to reduce or inhibit generation of scums from hydrocarbon-based substances, soots and moisture in the scrubber.

Solution to Problem

[0010] A first aspect of the present invention is A cylinder lubricating oil composition for a crosshead diesel engine equipped with a scrubber, including:

a base oil; and

(A) a metallic detergent,

wherein the lubricating oil composition has a base number of 15 to 125 mgKOH/g, and a kinematic viscosity at 100°C of 10 to 30 mm2/s; and
the lubricating oil composition satisfies the following requirement (i) or (ii):

(i) the lubricating oil composition comprises:

(B) a demulsifier in an amount of 0.02 to 5.0 mass% on the basis of the total mass of the composition;

(ii) the lubricating oil composition comprises, as the component (A),

(A1) a Ca phenate detergent; and
(A2) a metallic detergent other than any Ca phenate detergent;
the lubricating oil composition optionally comprises:

(C-1') a succinimide having at least one alkyl or alkenyl group in a molecule thereof, or a borated derivative thereof, in an amount of no more than 0.015 mass% in terms of nitrogen on the basis of the total mass of the composition; and
the Ph value represented by the following formula (1) is no more than 20 × 10^{-3}:

$$\text{Ph value} = C_{Ca} \times 2 / (r_M \times 40.08) \qquad \cdots (1)$$

(in the formula (1), C_{Ca} represents calcium content (mass%) derived from the component (A1), and r_M represents a metal ratio of the component (A1).).

[0011] In the present description, "crosshead diesel engine equipped with a scrubber" means a crosshead diesel engine provided with a structure of purifying gases emitted from cylinders by at least one scrubber. The scrubber may be an EGR scrubber with which the gases that passed through the scrubber are guided to the inlet side of the cylinders (for example see Patent Literatures 1 to 4), and may be an exhaust gas scrubber with which the gases that passed through the scrubber are not guided to the inlet side of the cylinders (for example see Patent Literature 5). "Crosshead diesel engine" is typically a two-stroke crosshead diesel engine.
[0012] A first embodiment of the first aspect of the present invention is a cylinder lubricating oil composition for a crosshead diesel engine equipped with a scrubber, including:

a base oil;

(A) a metallic detergent; and
(B) a demulsifier in an amount of 0.02 to 5.0 mass% on the basis of the total mass of the composition;

wherein the lubricating oil composition has a base number of 15 to 125 mgKOH/g, and a kinematic viscosity at

100°C of 10 to 30 mm^2/s.

[0013] As a preferable embodiment of the first embodiment, a configuration in which the lubricating oil composition includes (C) a nitrogen-containing ashless dispersant may be given for example.
[0014] As a preferable embodiment of the fist embodiment, a configuration in which the lubricating oil composition optionally includes:

(C) a nitrogen-containing ashless dispersant in an amount of no more than 0.2 mass% in terms of nitrogen on the basis of the total mass of the composition may be given for example.

[0015] As a preferable embodiment of the first embodiment, a configuration in which the component (B) is one or more polyether compound may be given for example. In such a configuration, it is preferable that the number average molecular weight of the component (B) is no less than 500. It is noted that, in the present invention, "polyether compound" means a compound having a polyether part, and the polyether part may be further modified by an ester bond and the like for example.
[0016] As a preferable embodiment of the first embodiment, a configuration in which the component (A) is a Ca phenate may be given for example.
[0017] A second embodiment of the first aspect of the present invention is A cylinder lubricating oil composition for a crosshead diesel engine equipped with a scrubber, including:

a base oil;
(A1) a Ca phenate detergent; and
(A2) a metallic detergent other than any Ca phenate detergent,

wherein

the lubricating oil composition optionally includes:

(C-1) a succinimide having at least one alkyl or alkenyl group in a molecule thereof, or a borated derivative thereof, in an amount of no more than 0.015 mass% in terms of nitrogen on the basis of the total mass of the composition,

the lubricating oil composition has a base number of 15 to 125 mgKOH/g, and a kinematic viscosity at 100°C of 10 to 30 mm^2/s,

and

the Ph value represented by the following formula (1) is no more than 20×10^{-3}:

$$\text{Ph value} = C_{Ca} \times 2 / (r_M \times 40.08) \qquad \cdots (1)$$

(in the formula (1), C_{Ca} represents calcium content (mass%) derived from the component (A1), and r_M represents a metal ratio of the component (A1).).

[0018] As a preferable embodiment of the second embodiment, a configuration in which the lubricating oil composition includes the component (C) in an amount of greater than 0 mass% and no more than 0.015 mass% in terms of nitrogen on the basis of the total mass of the composition may be given for example.
[0019] As a preferable embodiment of the second embodiment, a configuration in which the component (A2) is a Ca sulfonate and/or a Ca salicylate may be given for example.
[0020] A second aspect of the present invention is a method of lubricating a cylinder of a crosshead diesel engine equipped with a scrubber, including:

operating the crosshead diesel engine while supplying the lubricating oil composition according to the first aspect of the present invention to the cylinder of the crosshead diesel engine equipped with the scrubber; and
purifying at least a part of gas exhausted from the cylinder in the scrubber.

[0021] In the second aspect of the present invention, the purifying in the scrubber may include contacting the gas introduced into the scrubber with water and/or a basic aqueous solution.

Advantageous Effects of Invention

[0022] According to the first aspect of the present invention, it is possible to provide a cylinder oil for a crosshead diesel engine equipped with a scrubber, by which it is possible to reduce or inhibit generation of scums from hydrocarbon-based substances, soots and moisture in the scrubber.

[0023] According to the method of lubricating a cylinder of a crosshead diesel engine equipped with a scrubber of the second aspect of the present invention, it is possible to reduce or inhibit generation of scums from hydrocarbon-based substances, soots and moisture in the scrubber, in purification of gases emitted from the cylinder in the scrubber.

DESCRIPTION OF EMBODIMENTS

[0024] Hereinafter, the present invention will be described in detail. It should be noted that, unless otherwise mentioned, "A to B" regarding numerical values A and B means "A or more and B or less". When the unit of the numerical value A is omitted, the unit given to the numerical value B is applied as the unit of the numerical value A.

<Lubricating Base Oil>

[0025] As the base oil in the present invention, at least one selected from the group consisting of mineral oils and synthetic oils may be used.

[0026] The mineral oil is not particularly limited. General examples of the mineral oil include: a product made by fractional distillation of an atmospheric residue obtained by atmospheric distillation of a crude oil, by carrying out desulfuration and hydrogenolysis to have a desirable viscosity grade; and a product made by solvent dewaxing or contact dewaxing of the above-described atmospheric residue, on which a solvent extraction and hydrogenation are further carried out if necessary.

[0027] Further, as the mineral oil: an isomerized petroleum wax lubricating base oil made by hydroisomerizing a petroleum wax, which is a by-product in a dewaxing process in producing a base oil produced by carrying out a fraction distillation on an atmospheric distillation residual under reduced pressure to have a desirable viscosity grade, thereafter carrying out processes of solvent refining, hydrorefining, and the like, thereafter carrying out a solvent dewaxing; and an isomerized GTL wax lubricating base oil produced by a method of isomerizing GTL WAX (Gas To Liquid Wax) produced by a method of fisher-tropsh process may also be used. The basic production process of these isomerized wax lubricating base oils are the same as the production process of a hydrogenolysis base oil.

[0028] As the synthetic oil, synthetic oils used as general lubricating base oils may be used without particular limitations. Specific examples include: polybutenes and hydrides thereof; oligomers such as 1-octene, 1-decene and dodecene, and poly α-olefines and hydrides thereof which are oligomers and the like of mixtures of the above-mentioned oligomers; diesters such as ditridecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate, di-2-ethylhexyl sebacate; polyolesters such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythrytol-2-ethylhexanoate, pentaerythritol pelargonate; copolymers of dicarboxylic acids such as dibutyl maleate and C_2 to C_{30} α-olefines; aromatic-based synthetic oils such as alkylnaphthalene, alkylbenzene, and aromatic esters; and mixtures thereof.

[0029] The kinematic viscosity at 100°C of the base oil is preferably no less than 10 mm^2/s, more preferably no less than 14 mm^2/s, and preferably no more than 25 mm^2/s and more preferably no more than 20 mm^2/s. By having such lower limit values or more of the kinematic viscosity at 100 ° C of the base oil, sufficient oil films may be formed at the lubricating points, and good lubricity may be obtained. By having such upper limit values or less of the kinematic viscosity at 100 ° C of the base oil, good fluidity at a low temperature may be obtained. In the present invention, the kinematic viscosity at 100°C means a kinematic viscosity at 100°C defined in ASTM D-445.

[0030] Examples of a preferable embodiment of the base oil include a mixture base oil of a base oil having a kinematic viscosity at 100°C of 10 to 14 mm^2/s and a base oil having a kinematic viscosity at 100 ° C of 20 to 40 mm^2/s.

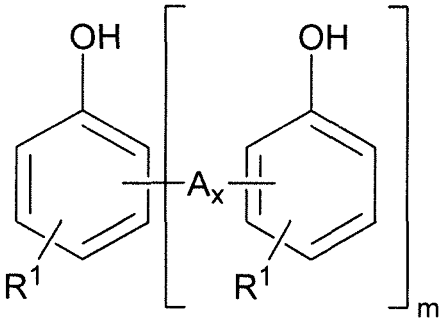
[0031] The viscosity index of the base oil is preferably no less than 85, more preferably no less than 90, and especially preferably no less than 95. By having such lower limit values or more of the viscosity index of the base oil, the viscosity at a low temperature may be held down, and good startability may be obtained. In the present invention, the viscosity index means a viscosity index measured in conformity with JISK2283-1993.

[0032] The content of saturated component of the base oil based on the total amount of the base oil is preferably no less than 50 mass%, more preferably no less than 55 mass%, and preferably no more than 90 mass% and more preferably no more than 75 mass%. By having such lower limit values or more of the saturated component, good oxidation stability may be obtained. By having such upper limit values or less of the saturated component, sufficient solubility of asphaltene and deteriorated substances may be obtained, whereby good cleanliness is obtained. In the present description, the saturated component means a saturated component measured by the method described in ASTM D 2007-93.

<(A) Metallic Detergent (1)>

[0033] In the first embodiment of the lubricating oil composition of the present invention, (A) metallic detergent (hereinafter referred to as "component (A)") is a so-called metallic detergent generally used in lubricating oils. Examples of the component (A) include phenate detergents, sulfonate detergents, and salicylate detergents. These metallic detergents may be used alone or in combination.

[0034] As the component (A), phenate detergents may be especially preferably used. Preferable examples of the phenate detergents include alkaline earth metal salts of compounds having a structure represented by the following formula (1), basic salts thereof, and overbased salts thereof. Examples of the alkaline earth metal salts include magnesium, barium, and calcium. Among them, magnesium and calcium are preferable, and calcium is especially preferable. The component (A) may be used alone or in combination.



(1)

[0035] In the formula (1), R^1 is a linear or branched, saturated or unsaturated C_6-C_{21} alkyl or alkenyl group, m is a polymerization degree shown by an integer of 1 to 10, A is a sulfide (-S-) group or methylene (-CH_2-) group, x is an integer of 1 to 3. R^1 may be a combination of two or more different groups.

[0036] The carbon number of R^1 in the formula (1) is preferably 9 to 18, and more preferably 9 to 15. If the carbon number of R^1 is less than 6, the solubility to the base oil may degrade. If the carbon number of R^1 is more than 21, manufacturing is difficult, and the heat resistance may degrade.

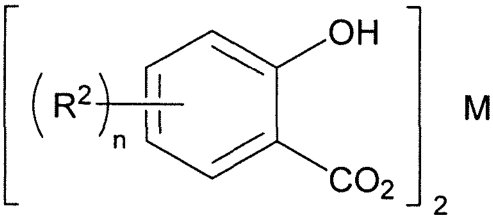
[0037] The polymerization degree m in the formula (1) is preferably 1 to 4. By having the polymerization degree m within this range, the heat resistance may be improved.

[0038] The base number of the phenate detergent is preferably no less than 60 mg KOH/g, and more preferably no less than 100 mg KOH/g, and preferably no more than 350 mg KOH/g, and more preferably no more than 300 mg KOH/g. By having such lower limit values or more of the base number, good acid neutralizing property may be obtained, and by having such upper limit values or less of the base number, good detergent property may be obtained. In the present invention, the base number is measured by perchloric acid method.

[0039] Preferable examples of the sulfonate detergent include alkaline earth metal salts of alkyl aromatic sulfonc acids obtained by sulfonation of alkyl aromatic compounds, basic salts thereof, and overbased salts thereof. The weight average molecular weight of the alkyl aromatic compound is preferably 400 to 1500, and more preferably 700 to 1300. Examples of alkaline earth metal include magnesium, barium, and calcium. Magnesium and calcium are preferable, and calcium is especially preferable. Examples of the alkyl aromatic sulfonic acid include a so-called petroleum sulfonic acid and synthetic sulfonic acid. As the petroleum sulfonic acid mentioned here, a sulfonated alkyl aromatic compound of lubricating oil distillate of a mineral oil, and a so-called mahogany acid which is a by-product of white oil manufacturing may be given for example. As an example of the synthetic sulfonic acid, sulfonated alkylbenzene having a linear or brunched alkyl group, obtained by recovery of by-product in alkylbenzene manufacturing plant, the alkylbenzene being a raw material of cleansers, or by alkylation of benzene with polyolefin, may be given. As another example of the synthetic sulfonic acid, sulfonated alkylnaphthalenes such as sulfonated dinonylnaphthalene may be given. The sulfonating agent used in sulfonation of these alkyl aromatic compounds is not particularly limited, and fuming sulfuric acid and anhydrous sulfate may be used for example.

[0040] The base number of the sulfonate detergent is preferably no less than 10 mgKOH/g, more preferably no less than 150 mgKOH/g, and more preferably no less than 250 mgKOH/g, and preferably no more than 500 mgKOH/g, and more preferably no more than 450 mgKOH/g. By having such lower limit values or more of the base number, good acid neutralizing property may be obtained. By having such upper limit values or less of the base number, good detergent property may be obtained.

[0041] Preferable examples of the salicylate detergent include metal salicylates, basic salts thereof, and overbased salts thereof. As the metal salicylate mentioned herein, a compound represented by the following formula (2) may be given for example.



(2)

[0042] In the above formula (2), R^2 independently is a C_{14}-C_{30} alkyl or alkenyl group, M is an alkaline earth metal, and n is 1 or 2. M is preferably calcium or magnesium, and especially preferably calcium. Preferably, n is 1. When n = 2, R^2 may be a combination of different groups.

[0043] Examples of a preferable embodiment of the salicylate detergent include an alkaline earth metal salicylate represented by the above formula (2) wherein n = 1, basic salt thereof, and overbased salt thereof.

[0044] The method for manufacturing the alkaline earth metal salicylate is not particularly limited, and a known method for manufacturing a mono alkyl salicylate may be employed. For example, the alkaline earth metal salicylate may be obtained by reacting monoalkyl salicylic acid and the like with metal base such as oxides and hydroxides of alkaline earth metals, or by once changing the monoalkyl salicylic acid and the like to be alkaline metal salts such as sodium salts and potassium salts, then metal-exchanging them with alkaline earth metal salts. The monoalkyl salicylic acid and the like are obtained from phenol as a starting raw material, by carrying out an alkylation on the phenol with olefin thereafter carrying out a carboxylation with carbon dioxide, or from salicylic acid as a starting raw material, by carrying out an alkylation on the salicylic acid with the olefin.

[0045] The method for obtaining a basic salt of the alkaline earth metal salicylate is not particularly limited. For example, the basic salt may be obtained by heating the alkaline earth metal salicylate and excess alkaline earth metal salt or excess alkaline earth metal basic salt (hydroxide or oxide of alkaline earth metal) in presence of water. The method for obtaining an overbased salt of the alkaline earth metal salicylate is not particularly limited. For example, the overbased salt may be obtained by reaction of the alkaline earth metal salicylate and the base of the hydroxide of the alkaline earth metal and the like, in presence of carbon dioxide, boric acid, or borate salt.

[0046] The base number of the salicylate detergent is preferably no less than 60 mgKOH/g, more preferably no less than 100 mgKOH/g, and preferably no more than 350 mgKOH/g, and more preferably no more than 300 mgKOH/g. By having such lower limit values or more of the base number, good acid neutralizing property may be obtained. By having such upper limit values or less of the base number, good detergency may be obtained.

[0047] The metal ratio of the component (A) is a value calculated according to the following formula, and preferably no less than 1, more preferably no less than 3, and preferably no more than 50 and more preferably no more than 30.

Metal ratio of component (A) = metal content of component (A) (mol) / soap base content of component (A) (mol)

[0048] When the component (A) includes two or more metals, "metal content of the component (A) (mol)" is the total of the mol amounts of all metals included in the component (A). When the component (A) includes two or more soap bases, "soap base content of the component (A) (mol)" is the total of mol amounts of all soap bases included in the component (A).

[0049] In the first embodiment of the lubricating oil composition of the present invention, as the component (A), one or more calcium detergent selected from the group consisting of Ca phenate detergents, Ca sulfonate detergents, and Ca salicylate detergents may be preferably used.

[0050] The Ca phenate detergents are the above-described phenate detergents in which calcium is used as the alkaline earth metal. That is, the Ca phenate detergent means a calcium salt, basic salt, or overbased salt of alkylphenol sulfide.

[0051] The Ca sulfonate detergents are the above-described detergents in which calcium is used as the alkaline earth metal. That is, the Ca sulfonate detergent means a calcium salt, basic salt, or overbased salt of an alkyl aromatic sulfonic acid.

[0052] The Ca salicylate detergents are the above-described salicylate detergents in which calcium is used as the metal. That is, the Ca salicylate detergent means calcium salicylate, or, a basic salt or overbased salt thereof. When a calcium detergent is used as the component (A), the content thereof is preferably 0.50 to 4.3 mass% in terms of calcium on the basis of the total mass of the lubricating oil composition.

<(A) Metallic Detergent (2)>

[0053] The second embodiment of the lubricating oil composition of the present invention includes, as the component (A), (A1) a Ca phenate detergent and (A2) a metallic detergent other than any Ca phenate detergent.

((A1) Ca phenate detergent)

[0054] As (A1) Ca phenate detergent (hereinafter referred to as "component (A1)"), a calcium salt, basic salt, or overbased salt of a compound having a structure represented by the above formula (1) may be given. For the component (A1), one kind may be used alone, or two or more kinds may also be used in combination. A preferable embodiment of the component (A1) is as described above regarding the phenate detergent.

((A2) Metallic detergent other than any Ca phenate detergent)

[0055] (A2) Metallic detergent other than any Ca phenate detergent (hereinafter referred to as "component (A2)") is preferably a metallic detergent other than any phenate detergent. Examples of such a metallic detergent include sulfonate detergents and salicylate detergents. These metallic detergents may be used alone or in combination.

[0056] As the sulfonate detergent, the above-described sulfonate detergents may be used. The preferable embodiment of the sulfonate detergent is as described above.

[0057] As the salicylate detergent, the above-described salicylate detergent may be used. The preferable embodiment of the salicylate detergent is as described above.

[0058] In one preferable embodiment, the component (A2) is a Ca sulfonate detergent and/or a Ca salicylate detergent. The base number of the Ca sulfonate detergent is preferably no less than 10 mgKOH/g, more preferably no less than 150 mgKOH/g, and further preferably no less than 250 mgKOH/g, and preferably no more than 500 mgKOH/g, and more preferably no more than 450mgKOH/g. By having such lower limit values or more of the base number, good acid neutralizing property may be obtained. By having such upper limit values or less of the base number, good detergent property may be obtained. The base number of the Ca salicylate detergent is preferably no less than 60 mgKOH/g, and more preferably no less than 100 mgKOH/g, and preferably no more than 350 mgKOH/g, and more preferably 300 mgKOH/g. By having such lower limit values or more of the base number, good acid neutralizing property may be obtained. By having such upper limit values or less of the base number, good detergent property may be obtained.

<(B) Demulsifier>

[0059] As the (B) demulsifier (hereinafter referred to as "component (B)") in the first embodiment of the lubricating oil composition of the present invention, so-called demulsifiers which are commercially available may be used without particular limitations. Among them, polyether compounds may be preferably used.

[0060] As the polyether compound that may be preferably used as the component (B), one or more polyether compound selected from the group consisting of: polyoxypropylene glycol monoalkyl ethers such as polypropylene glycol butyl ether and polypropylene glycol stearyl ether; polyoxyethylene polyoxypropylene alkyl ether (ethylene oxide-propylene oxide copolymer); polyoxyethylene alkyl ether; polyethylene glycol fatty acid ester; polyoxyethylene glycerin fatty acid ester; polyoxyethylene sorbit fatty acid ester; and polyoxyethylene sorbitan fatty acid ester may be given. They may be used alone or in combination.

[0061] Among these polyether compounds, polyether compounds including propylene oxide unit are especially preferable, such as: polyoxypropylene glycol monoalkyl ethers such as polypropylene glycol butyl ether and polypropylene glycol stearyl ether; and polyoxyethylene polyoxypropylene alkyl ether (ethylene oxide-propylene oxide copolymer).

[0062] The molecular weight of the component (B) is not particularly limited, and preferably no less than 350, more preferably no less than 500, and further preferably no less than 1000, and preferably no more than 30000, more preferably no more than 10000, and further preferably no more than 5000, by number average molecular weight. By having such lower limit values or more of the number average molecular weight of the component (B), good demulsibility may be obtained.

[0063] The HLB (hydrophile-lipophile balance) value of the component (B) is not particularly limited as long as it shows demulsification function (emulsion destabilization function), and preferably no less than 13, and more preferably no less than 14.5. The HLB value must be no more than 20 by definition, and preferably no more than 19.5 in view of affinity with the base oil.

[0064] The content of the component (B) in the first embodiment of the lubricating oil composition of the present invention is 0.02 to 5 mass% on the basis of the total mass of the composition. The content is preferably no less than 0.03 mass%, more preferably no less than 0.04 mass%, and preferably no more than 4 mass%, and more preferably no more than 3 mass%. By having such lower limit values or more of the content of the component (B), good demulsibility may be obtained.

<(C) Nitrogen-containing ashless dispersant (1)>

[0065] The first embodiment of the lubricating oil composition of the present invention may include (C) a nitrogen-containing ashless dispersant (hereinafter referred to as "component (C)").

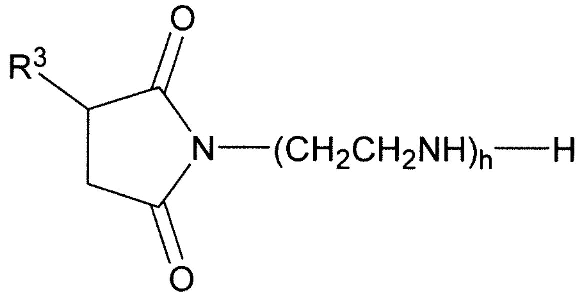
[0066] As the component (C), for example one or more compound selected from the following (C-1) to (C-3) may be used.

[0067] (C-1) a succinimide having at least one alkyl or alkenyl group in a molecule thereof, or a derivative thereof (hereinafter referred to as "component (C-1)");

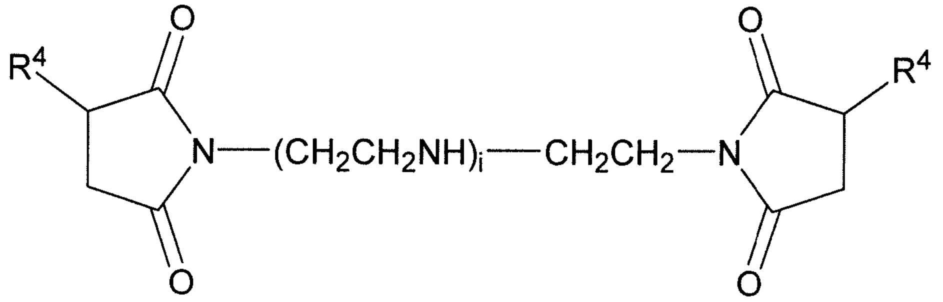
[0068] (C-2) a benzylamine having at least one alkyl or alkenyl group in a molecule thereof, or a derivative thereof (hereinafter referred to as "component (C-2)"); and

[0069] (C-3) a polyamine having at least one alkyl or alkenyl group in a molecule thereof, or a derivative thereof (hereinafter referred to as "component (C-3)").

[0070] As the component (C), the component (C-1) may be especially preferably used. Examples of the succinimide having at least one alkyl group or alkenyl group in a molecule thereof of the component (C-1) include a compound represented by the following formula (3) or (4).



(3)



(4)

[0071] In the formula (3), R^3 is a C_{40}-C_{400} alkyl or alkenyl group, h is an integer of 1 to 5, preferably 2 to 4. The carbon number of R^3 is preferably no less than 60 and preferably no more than 350.

[0072] In the formula (4), R^4, independently, same or different, is a C_{40}-C_{400} alkyl or alkenyl group. R^4 is especially preferably a polybutenyl group. i is an integer of 0 to 4, preferably of 1 to 3. The carbon number of R^4 is preferably no less than 60 and preferably no more than 350.

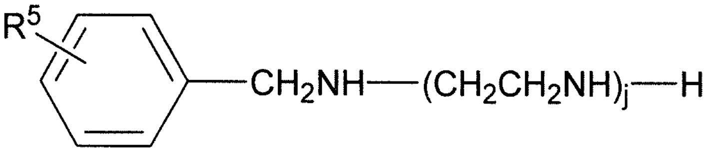
[0073] By having the above-described lower limit values or more of the carbon numbers of R^3 and R^4 in the formulas (3) and (4), it is possible to obtain good solubility to the lubricating base oil. By having the above-described upper limit values or less of the carbon numbers of R^3 and R^4, it is possible to increase the low-temperature fluidity of the lubricating oil composition.

[0074] The alkyl or alkenyl group (R^3, R^4) in the formulas (3) and (4) may be linear or branched. Preferable examples thereof include oligomers of olefins such as propylene, 1-butene and isobutene, and a branched alkyl or alkenyl group derived from a co-oligomer of ethylene and propylene. Among them, a branched alkyl or alkenyl group derived from an oligomer of isobutene idiomatically called as polyisobutylene, and a polybutenyl group are most preferable. A preferable weight-average molecular weight of the alkyl or alkenyl group (R^3, R^4) in the formulas (3) and (4) is 800 to 3500.

[0075] The succinimide having at least one alkyl or alkenyl group in a molecule thereof includes a so-called mono-type succinimide represented by the formula (3), in which succinic anhydride is added only to one end of the polyamine chain, and a so-called bis-type succinimide represented by the formula (4), in which succinic anhydride is added to both ends of the polyamine chain. The lubricating oil composition of the present invention may include either one of the mono-type succinimide and the bis-type succinimide, and may include a mixture of the mono-type and bis-type succinimides.

[0076] The production method of the succinimide having at least one alkyl or alkenyl group in a molecule thereof is not particularly limited. For example, it may be obtained by reaction of polyamine and an alkyl or alkenyl succinic acid obtained by reaction of a compound having a C_{40}-C_{400} alkyl or alkenyl group and maleic anhydride at 100 to 200°C. Here, examples of the polyamine include diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine.

[0077] Examples of the benzylamine having at least one alkyl or alkenyl group in a molecule thereof of the component (C-2) include a compound represented by the following formula (5).



(5)

[0078] In the formula (5), R^5 is a C_{40} to C_{400} alkyl or alkenyl group, j is an integer of 1 to 5, preferably 2 to 4. The carbon number of R^5 is preferably no less than 60 and preferably no more than 350.

[0079] The production method of the component (C-2) is not particularly limited. For example, the method of reacting a propylene oligomer, polybutene or polyolefin such as ethylene-α-olefin copolymer with phenol to make an alkylphenol, thereafter reacting the alkylphenol with formaldehyde and a polyamine such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and pentaethylenehexamine by Mannich reaction may be given.

[0080] Examples of the polyamine having at least one alkyl or alkenyl group in a molecule thereof of the component (C-3) include a compound represented by the following formula (6).

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

[0081] In the formula (6), R^6 is a C_{40} to C_{400} alkyl or alkenyl group, and k is an integer of 1 to 5, preferably 2 to 4. The carbon number of R^6 is preferably no less than 60 and preferably no more than 350.

[0082] The production method of the component (C-3) is not particularly limited. For example, a method of: chlorinating a propylene oligomer, polybutene or polyolefin such as ethylene-α-olefin copolymer; thereafter reacting the chlorinated product with a polyamine such as ammonia, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and pentaethylenehexamine may be given.

[0083] As the derivative in the components (C-1) to (C-3), for example, (i) a modified compound by an oxygen-containing organic compound, in which some or all of the remaining amino group and/or imino group is neutralized or amidated by a function of C_1-C_{30} monocarboxylic acid such as fatty acid, C_2-C_{30} polycarboxylic acid (e.g. oxalic acid, phthalic acid, trimellitic acid, and pyromellitic acid), anhydrides or ester compounds thereof, C_2-C_6 polyalkylene oxide, or hydroxyl(poly)oxyalkylenecarbonate to the above-described succinimide having at least one alkyl or alkenyl group in a molecule thereof (hereinafter referred to as "above-described nitrogen-containing compound"); (ii) a boron modified compound in which some or all of the remaining amino group and/or imino group is neutralized or amidated by a function of boric acid to the above-described nitrogen-containing compound; (iii) a phosphoric-acid modified compound in which some or all of the remaining amino group and/or imino group is neutralized or amidated by a function of phosphoric acid to the above-described nitrogen-containing compound; (iv) a sulfur modified compound obtained by a function of a sulfur compound to the above-described nitrogen-containing compound; and (v) a modified compound obtained by carrying out two or more modifications in combination selected from a modification by an oxygen-containing organic compound, boron modification, phosphoric acid modification, and sulfur modification, to the above-described nitrogen-containing compound may be given. Among the derivatives of (i) to (v), by using a boron modified compound of alkenyl succinimide, especially a boron modified compound of a bis-type alkenyl succinimide, it is possible to further improve the heat resistance of the lubricating oil composition.

[0084] The molecular weight of the component (C) is not particularly limited, and a preferable weight-average molecular weight the component (C) is from 1000 to 8000. In the first embodiment of the lubricating oil composition of the present invention, the content of the component (C) when contained is preferably no less than 0.02 mass%, more preferably no less than 0.04 mass%, and further preferably no less than 0.07 mass%, and preferably no more than 0.2 mass% and more preferably no more than 0.12 mass%, in terms of nitrogen on the basis of the total mass of the lubricating oil composition. By having the above-described lower limit values or more of the content of the component (C), it is possible to sufficiently improve the coking resistance (heat resistance) of the lubricating oil composition. By having the above-described upper limit values or less of the content of the component (C), it is possible to obtain good separation property of impurities in a centrifugal cleaner and to improve water separation property to inhibit the scum generation in the scrubber.

<(C) Nitrogen-containing ashless dispersant (2)>

[0085] The second embodiment of the lubricating oil composition of the present invention optionally includes (C-1') a succinimide having at least one alkyl or alkenyl group in a molecule thereof, or a borated derivative thereof (hereinafter may be referred to as "component (C-1')"). However, when the second embodiment of the lubricating oil composition of the present invention includes the component (C-1'), the content of the component (C-1') has to be no more than 0.015 mass% in terms of nitrogen on the basis of the total mass of the composition. By having the content of the component (C-1') of no more than 0.015 mass% in terms of nitrogen, good demulsibility may be obtained and the generation of scum in the scrubber may be inhibited.

[0086] Examples of the succinimide having at least one alkyl or alkenyl group in a molecule thereof include the compounds represented by the above formulas (3) or (4) described above regarding the component (C-1) in the first embodiment. The preferable embodiments of these compounds are as described above.

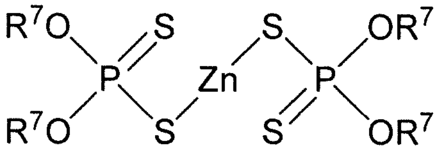
[0087] Examples of the borated derivative of the succinimide having at least one alkyl or alkenyl group in a molecule thereof include a so-called boron modified compound in which some or all of the remaining amino group and/or imino group is neutralized or amidated by reaction of boric acid with the above-described succinimide having at least one alkyl or alkenyl group in a molecule thereof.

[0088] The molecular weight of the component (C-1') is not particularly limited, and a preferable weight-average molecular weight thereof is from 1000 to 8000.

<Other additive>

[0089] The lubricating oil composition of the present invention may further contain any additives generally used in lubricating oils, depending on the intended use. Examples of such additives include zinc dithiophosphates, antioxidants, defoaming agents, pour point depressants, metal inactivators, and extreme pressure agents.

[0090] As the zinc dithiophosphate (ZnDTP), a compound represented by the following formula (7) may be preferably used.



(7)

[0091] In the formula (7), R^7 independently, the same or different, is a C_1-C_{24} hydrocarbon group. Preferable examples of the C_1-C_{24} hydrocarbon group include a linear or branched C_1-C_{24} alkyl group. The carbon number of R^7 is preferably no less than 3, and preferably no more than 12, and more preferably no more than 8. The alkyl group as R^7 may be any one of a primary alkyl group, a secondary alkyl group, and a tertiary alkyl group. The alkyl group as R^7 is preferably a primary alkyl group or a secondary alkyl group or a mixture thereof, and most preferably a primary alkyl group.

[0092] Examples of the above zinc dithiophosphate include: zinc dialkyldithiophosphates having a linear or branched C_3-C_{18}, preferably C_3-C_{10} alkyl group (primary, secondary or tertiary, preferably primary or secondary), such as zinc dipropyl dithiophosphate, zinc dibutyl dithiophosphate, zinc dipentyl dithiophosphate, zinc dihexyl dithiophosphate, zinc diheptyl dithiophosphate, and zinc dioctyl dithiophosphate; zinc di((alkyl)aryl)dithiophosphates having a C_6-C_{18}, preferably C_6-C_{10} aryl or alkyaryl group, such as zinc diphenyl dithiophosphate and zinc ditolyl dithiophosphate; and a mixture of two or more thereof.

[0093] The production method of the above zinc dithiophosphate is not particularly limited. For example, it may be synthesized by making a reaction of an alcohol having an alkyl group corresponding to R^7 with phosphorus pentasulfide to synthesize a dithiophosphoric acid, and neutralizing the dithiophosphoric acid by zinc oxide.

[0094] In the lubricating oil composition of the present invention, the content of the zinc dithiophosphate is preferably 0.03 to 1.0 mass%, more preferably 0.05 to 0.5 mass%, and especially preferably 0.01 to 0.3 mass% on the basis of the total mass of the composition. The zinc dithiophosphate is desirably contained in such a manner that the phosphorus component in the lubricating oil composition is preferably 25 to 700 mass ppm, more preferably no less than 40 mass ppm, further preferably no less than 50 mass ppm, and especially preferably no less than 80 mass ppm, and more preferably no more than 500 mass ppm, further preferably no more than 300 mass ppm, and especially preferably no more than 250 mass ppm. If the phosphorus component derived from the zinc dithiophosphate in the lubricating oil composition is no less than 25 mass ppm, it is possible to secure necessary oxidation stability, and if it is no more than 700 mass ppm, it is possible to prevent the base number from lowering due to hydrolysis of the zinc dithiophosphate.

[0095] Examples of the antioxidant include ashless antioxidants such as phenol-based antioxidants, amine-based antioxidants, and metallic antioxidants. Among them, phenol-based antioxidants and/or amine-based antioxidants are preferably used, in view of maintaining high temperature detergent performance. When an antioxidant is contained in the lubricating oil composition of the present invention, the content thereof is preferably no less than 0.05 mass%, and more preferably no less than 0.1 mass%, on the basis of the total mass of the composition, and when the antioxidant is an amine-based antioxidant, the content is especially preferably no less than 0.3 mass%, and when the antioxidant is a phenol-based antioxidant, the content is especially preferably no less than 0.15 mass%, on the basis of the total mass of the composition. The upper limit of the content of the antioxidant is not particularly limited, and preferably no more than 5 mass% and more preferably no more than 2 mass% on the basis of the total mass of the composition.

[0096] Examples of the defoaming agent include silicone oils, derivatives of alkenyl succinic acid, esters of aliphatic polyhydroxy alcohol and a long-chain fatty acid, methyl salicylate and o-hydroxybenzyl alcohol, aluminum stearate, potassium oleate, N-dialkyl-allylaminenitroaminoalkanol, aromatic amine salts of isoamyl octyl phosphate, alkylalkylenediphosphate, metal derivatives of thioethers, metal derivatives of disulfides, fluorine compounds of aliphatic hydrocarbons, triethylsilane, dichlorosilane, alkylphenyl polyethylene glycol ethersulfide, and fluoroalkylether. When a defoaming agent is contained in the lubricating oil composition of the present invention, the content thereof is normally 0.0005 to 1 mass% on the basis of the total mass of the composition. When the defoaming agent includes silicon, the defoaming agent is preferably included in such a manner that the Si component in the lubricating oil composition is 5 to 50 mass ppm.

[0097] Examples of the pour point depressant include polymethacrylate-based polymers that conform to the lubricating base oil to be used. When a pour point depressant is contained in the lubricating oil composition of the present invention, the content thereof may be normally 0.005 to 5 mass% on the basis of the total mass of the composition.

[0098] Examples of the metal deactivator include imidazoline, pyrimidine derivatives, alkylthiadiazole, mercaptobenzothiazole, benzotriazole or derivatives thereof, 1,3,4-thiadiazolepolysulfide, 1,3,4-thiadiazolyl-2,5-bisdialkyldithiocarbamate, 2-(alkyldithio)benzoimidazole, and β-(o-carboxybenzylthio)propionitrile. When a metal deactivator is contained in the lubricating oil composition of the present invention, the content thereof is normally 0.005 to 1 mass% on the basis of the total mass of the composition.

[0099] Examples of the extreme-pressure agent include sulfur-based, phosphorus-based, and sulfur-phosphorus-based extreme-pressure agents. Specific examples thereof include phosphorous esters, thiophosphorous esters, dithiophosphorous esters, trithiophosphorous esters, phosphate esters, thiophosphate esters, dithiophosphate esters, trithiophosphate esters, amine salts thereof, metallic salts thereof, derivatives thereof, dithiocarbamate, zinc dithiocarbamate, molybdenum dithiocarbamate, disulfides, polysulfides, olefin sulfides, and sulfurized oils and fats. When an extreme-pressure agent is contained in the lubricating oil composition of the present invention, the content thereof is not particularly limited, and normally 0.01 to 5 mass% on the basis of the total mass of the composition.

<Lubricating oil composition>

[0100] The base number of the lubricating oil composition of the present invention is 15 to 125 mgKOH/g, preferably no less than 20 mgKOH/g, more preferably no less than 30 mgKOH/g, and further preferably no less than 40 mgKOH/g, and preferably no more than 120 mgKOH/g, more preferably no more than 105 mgKOH/g, and further preferably no more than 100 mgKOH/g. If the base number of the lubricating oil composition is less than 15 mgKOH/g, the detergency might be insufficient. If the base number of the lubricating oil composition is more than 125 mgKOH/g, excessive base components accumulate on the piston to obstruct formation of oil film, which results in a potential bore polish and scuffing. Therefore it is not preferable that the base number of the lubricating oil composition is less than 15 mgKOH/g or more than 125 mgKOH/g.

[0101] The kinematic viscosity at 100°C of the lubricating oil composition of the present invention is 10 to 30 mm^2/s, preferably no less than 12 mm^2/s, more preferably no less than 12.5 mm^2/s, further preferably no less than 16.3 mm^2/s, and especially preferably no less than 18.0 mm^2/s, and preferably no more than 27 mm^2/s, more preferably no more than 26.1 mm^2/s, further preferably no more than 21.9 mm^2/s, and especially preferably no more than 21.0 mm^2/s. If the kinematic viscosity at 100°C of the lubricating oil composition is less than 10 mm^2/s, the performance of oil formation is insufficient, which might results in searing of ring and liner. Therefore, it is not preferable that the kinematic viscosity at 100°C of the lubricating oil composition of the present invention is less than 10 mm^2/s. If the kinematic viscosity at 100°C of the lubricating oil composition is more than 30 mm^2/s, which is a high viscosity, the starting performance might degrade. Therefore it is not preferable that the kinematic viscosity at 100°C of the lubricating oil composition of the present invention is more than 30 mm^2/s.

[0102] In the second embodiment of the lubricating oil composition of the present invention, the Ph value represented by the following formula (1) is no more than 20×10^{-3}, preferably no more than 19×10^{-3}, and more preferably no more than 18×10^{-3}. By having such an upper limit value or less of the Ph value, the demulsibility improves, and it is possible to inhibit generation of scum in the scrubber.

$$\text{Ph value} = C_{Ca} \times 2 / (r_M \times 40.08) \ldots (1)$$

(in the formula (1), C_{Ca} represents calcium content (mass%) derived from the component (A1), and r_M represents a metal ratio of the component (A1).)

[0103] The calcium content (mass%) derived from the component (A1) mentioned here means a value of the content of calcium derived from the Ca phenate detergent of the component (A1) in the lubricating oil composition of the present invention, show by mass% on the basis of the total mass of the lubricating oil composition. The metal ratio of the component (A1) mentioned here is a value calculated according to the following formula, regarding the Ca phenate detergent which is the component (A1).

[0104] Metal ratio of component (A1) = calcium content (mass%) in Ca phenate detergent which is component (A1) / calcium content (mass%) derived from soap base in Ca phenate detergent which is component (A1)

<Method of lubricating cylinder>

[0105] The method of lubricating a cylinder of a crosshead diesel engine equipped with a scrubber according to the second aspect of the present invention includes: (i) operating the crosshead diesel engine while supplying the lubricating oil composition according to the first aspect of the present invention to the cylinder of the crosshead diesel engine equipped with a scrubber; and (ii) purifying at least a part of gas exhausted from the cylinder in the scrubber.

[0106] As the crosshead diesel engine equipped with a scrubber, known crosshead diesel engines equipped with scrubbers may be used without particular limitations (for example, see Patent Literatures 1 to 5). The method of supplying the lubricating oil composition according to the first aspect of the present invention to the crosshead diesel engine is not particularly limited, and known methods for supplying lubricating oils to crosshead diesel engines may be used. The scrubber may be an EGR scrubber, may be a scrubber that does not send back the gases that passed through the scrubber to the inlet side but releases them to the environment, and may be a combination thereof. However, considering that the demulsibility improved in the lubricating oil composition according to the first aspect of the present invention advantageously functions, a scrubber that purifies gasses guided in the scrubber by making the gasses into contact with water and/or a basic aqueous solution is preferable. As the basic aqueous solution, an aqueous solution in which salts such as alkali metal hydroxides and alkali metal carbonates are dissolved may be used for example, and seawater may be preferably used.

Examples

[0107] Hereinafter, the present invention will be explained further in detail based on Examples and Comparative Examples. However, the present invention is not limited to these Examples.

<Examples 1 to 11, Comparative Examples 1 to 7>

[0108] Regarding the first embodiment of the lubricating oil composition, lubricating oil compositions of compounding formulations shown in Tables 1 and 2 were prepared and a high-speed emulsification test was carried out thereon. The results are shown in Tables 1 and 2. In Tables 1 and 2, the amounts of the base oils are the contents on the basis of the total amount of the base oils, and the amounts of additives are the contents on the basis of the total amount of the composition.

(Commercially available cylinder oil)

[0109] A commercially available cylinder oil containing: mineral base oil in an amount of 81 mass%; a Ca phenate detergent of the above formula (1) wherein R^1 is a C_{12} alkyl or alkenyl group; a carbonic Ca sulfonate detergent (C_{20}, C_{22} and C_{24} hydrocarbon groups are bonded to an aromatic six-membered ring); a polybutenyl succinimide of the above formula (4) wherein R^4 is a polybutenyl group; alkyldiphenylamine (carbon numbers of the alkyl groups are 4 and 8); alkylphenol; and a Si compound. The calcium content of the commercially available cylinder oil was 2.60 mass% in terms of calcium on the basis of the total mass of the commercially available cylinder oil. The nitrogen content of the commercially available cylinder oil was 0.03 mass% in terms of nitrogen on the basis of the total mass of the commercially available cylinder oil.

(Base oil)

[0110]

Base oil 1: solvent refining oil, 500 N, kinematic viscosity at 100°C 10.8 mm^2/s, content of saturated component 62 mass%
Base oil 2; solvent refining oil, Bright Stock, kinematic viscosity at 100°C 31.8 mm^2/s, content of saturated component 46 mass%

(Metallic detergent)

[0111]

Ca phenate: a Ca phenate of the above formula (1) wherein A is a sulfide group, x = 1 to 2, m = 1 to 2, base number 250 mgKOH/g, Ca content 8.9 mass%, metal ratio 4.5, sulfur component 3.5 mass%
Ca sulfonate: base number 400 mgKOH/g, Ca content 15.5 mass%, metal ratio 20

(Nitorogen-containing ashless dispersant)

[0112] Nitrogen-containing ashless dispersant: a polyisobutenyl succinimide of the above formula (4) wherein R^4 is a polybutenyl group, n = 5, N content 1.1 mass%, Mw = 2490, weight average molecular weight of the part of the polybutenyl group Mw = 1000

(Demulsifier)

[0113]

B-1: polypropylene glycol stearyl ether, Mw = 1600
B-2: polypropylene glycol butyl ether ("NEWPOL LB-285" manufactured by Sanyo Chemical Industries, Ltd.), Mn = 1170
B-3: polypropylene glycol butyl ether ("NEWPOL LB-1715" manufactured by Sanyo Chemical Industries, Ltd.), Mn = 2390
B-4: ethylene oxide-propylene oxide copolymer, Mw = 4840
Solbitan monooleate: HLB4.3

<Evaluation method>

(High-speed emulsification test)

[0114] This test was a model examination simulating a process of oil-water separation after stirring in a scrubber. In a 100 ml measuring cylinder, 40 g of a sodium hydroxide aqueous solution (pH = 12) and 10 g of the sample oil were collected. The measuring cylinder was set on a homogenizer (POLYTRON PT10-35, generator shaft PT36/4K manufactured by KINEMATICA), and stirred for 5 minutes at 15,000 rpm. After that, the homogenizer was pulled upward from the measuring cylinder and allowed to stand for 5 minutes, to collect the wet, oil and emulsion attached to the homogenizer to the measuring cylinder. The measuring cylinder after the test was allowed to stand for 1 week at a room temperature. From the separated oil amount, the separation performance was judged as follows.

Separated oil amount of 10 ml: mark 3,
Separated oil amount of no less than 7.5 ml and less than 10 ml: mark 2.5,
Separated oil amount of no less than 5 ml and less than 7.5 ml: mark 2,
Separated oil amount of no less than 1 ml and less than 5 ml: mark 1, and
Separated oil amount of less than 1 ml: mark 0
Oils of mark no less than 2 were acceptable and no more than 1 were rejected.

<Evaluation result>

[0115] The lubricating oil compositions of Examples 1 to 11 showed good separation performances on the high-speed emulsification test (Table 1). The compositions of Comparative Examples 1 and 5 to 7 that did not include the component

(B), the composition of Comparative Example 2 including the component (B) by less than 0.02 mass%, and the compositions of Comparative Examples 3 and 4 including surfactants that did not have demulsification function instead of the component (B) each got mark 0 (rejected) in the high-speed emulsification test, which meant they were inferior in separation performance (Table 2). It is noted, when the composition of Comparative Example 1 (that is, the commercially available cylinder oil itself), which marked 0 on the high-speed emulsification test, was used as a cylinder lubricating oil to operate a crosshead diesel engine, and when the exhaust gas was cleaned by a scrubber, scums were generated in the scrubber.

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11
Commercially available cylinder oil	mass%	99.95	99.9	99.5	99	98	99.5	99.5	99.5	-	-	-
Base oil 1	mass%									41.2	39.3	43.2
Base oil 2	mass%									40.5	34.9	21.3
Ca phenate	mass%									14	14	20
Ca sulfonate	mass%									1.3	8.8	12.5
Nitrogen-containing ashless dispersant	mass%									2.7	2.7	2.7
B-1	mass%	0.05	0.1	0.5	1	2						0.3
B-2	mass%						0.5			0.3		
B-3	mass%							0.5			0.3	
B-4	mass%								0.5			
Solbitan monooleate	mass%											
Methyloleate	mass%											
Kinematic viscosity of composition (100°C)	mm^2/s	20.7	20.7	20.7	20.7	20.7	20.7	20.7	20.7	20.5	20.5	20.5
Base number of composition	mgKOH/g	70	70	70	70	70	70	70	70	40	70	100
Ca content in composition	mass%	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	1.4	2.6	3.7
Nitrogen content in composition	mass%	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03

(continued)

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11
High-speed demulsification test	Mark	3	3	3	3	3	2.5	3	3	3	3	3

[Table 2]

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7
Commercially available cylinder oil	mass%	100	99.99	99.5	99.5	-	-	-
Base oil 1	mass%					41	39.5	43.4
Base oil 2	mass%					41	35	21.4
Ca phenate	mass%					14	14	20
Ca sulfonate	mass%					1.3	8.8	12.5
Nitrogen-containing ashless dispersant	mass%					2.7	2.7	2.7
B-1	mass%		0.01					
B-2	mass%							
B-3	mass%							
B-4	mass%							
Solbitan monooleate	mass%			0.5				
Methyl oleate	mass%				0.5			
Kinematic viscosity of composition (100°C)	mm^2/s	20.7	20.7	20.7	20.7	20.5	20.5	20.5
Base number of composition	mgKOH/g	70	70	70	70	40	70	100
Ca content in composition	mass%	2.60	2.60	2.60	2.60	1.4	2.6	3.7
Nitrogen content in composition	mass%	0.03	0.03	0.03	0.03	0.03	0.03	0.03

(continued)

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7
High-speed emulsification test	Mark	0	0	0	0	0	0	0

<Examples 12 to 26, Comparative Examples 8 to 13>

[0116] Regarding the second embodiment of the lubricating oil composition of the present invention, lubricating oil compositions of the compounding formulations shown in Tables 3 to 5 were prepared, and a high-speed emulsification test was carried out in the same way as above. The results are shown in Tales 3 to 5. In Tables 3 to 5, the amounts of the base oils are the contents on the basis of the total amount of the base oils, and the amounts of additives are the contents on the basis of the total amount of the composition.

(Base oil)

[0117]

Base oil 1: solvent refining base oil, 500 N, kinematic viscosity at 100°C 10.8 mm^2/s, content of saturated component 62 mass%
Base oil 2: solvent refining base oil, Bright Stock, kinematic viscosity at 100°C 31.8 mm^2/s, content of saturated component 46 mass%

(Component (A1))

[0118]

(A1)-1: a Ca phenate of the above formula (1) wherein A is a sulfide group, x = 1 to 2, and m = 1 to 2, base number 250 mgKOH/g, Ca content 8.9 mass%, metal ratio 4.5, sulfur content 3.5 mass%
(A1)-2: a Ca phenate of the above formula (1) wherein A is a sulfide group, x = 1 to 3, and m = 1 to 4, base number 150 mgKOH/g, Ca content 5.4 mass%, metal ratio 2.7, sulfur content 4.1 mass%
(A1)-3: a Ca phenate of the above formula (1) wherein A is a methylene group, x = 1 to 3, and m = 1 to 4, base number 70 mgKOH/g, Ca content 2.5 mass%, metal ratio 1.3

(Component (A2))

[0119]

(A2)-1: a Ca sulfonate, base number 400 mgKOH/g, Ca content 15.5 mass%, metal ratio 20
(A2)-2: a Ca salicylate of the above formula (2) wherein M is calcium, R^2 is a C_{14}-C_{18} alkyl group derived from α olefin, and n = 1 to 2, base number 225 mgKOH/g, Ca content 8.2 mass%, metal ratio 3.1

(Component (C-1'))

[0120]

(C-1')-1: a polyisobutenyl succinimide of the above formula (4) wherein R^4 is a polybutenyl group and n = 5, bis-type, N content 1.1 mass%, Mw = 2490, weight average molecular weight of the part of the polybutenyl group Mw = 1000
(C-1')-2: a polyisobutenyl succinimide of the above formula (3) wherein R^3 is a polybutenyl group, and n = 4, mono-type, N content 2.0 mass%, Mw = 1000

<Evaluation result>

[0121] The lubricating oil compositions of Examples 12 to 26 showed good separation property at the high-speed emulsification test (Tables 1 and 2). The lubricating oil compositions of Examples 24 to 26 showed sufficient demulsification property even though each composition contained the component (C), which functioned as a dispersant, in an amount of no more than 0.015 mass% in terms of nitrogen on the basis of the total mass of the composition. The compositions of Comparative Examples 8 to 10, whose Ph value was over 20×10^{-3} , each marked 0 (rejected) at the high-speed emulsification test, which meant they were inferior in separation property. The compositions of Comparative Examples 11 to 13, whose content of the component (C) was over 0.015 mass% in terms of nitrogen on the basis of the total mass of the composition, each marked 0 (rejected) at the high-speed emulsification test even though the Ph value was no more than 20×10^{-3}, which meant they were inferior in separation property.

[Table 3]

		Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Examnle 18
Base oil 1	mass%	46.6	48.2	49.8	51.4	53.0	46.5	49.4
Base oil 2	mass%	53.4	51.8	50.2	48.6	47.0	53.5	50.6
(A1)-1	mass%	2.8	5.6	8.4	11.2	14.0		
(A1)-2	mass%						3.5	10.3
(A1)-3	mass%							
(A2)-1	mass%	15.8	14.0	12.3	10.5	8.8	16.2	13.7
(A2)-2	mass%							
(C-1')-1	mass%							
(C-1')-2	mass%							
Lubricating oil composition								
Base number	mgKOH/g	70	70	70	70	70	70	70
Kinematic viscosity (100°C)	mm^2/s	20.5	20.5	20.5	20.5	20.5	20.5	20.5
Ca component	mass%	2.70	2.67	2.65	2.62	2.61	2.70	2.68
Cacomponent derivent from Ca phenate	mass%	0.250	0.500	0.750	1.000	1.250	0.189	0.556
Nitrogen component derived from component (C-1')	mass%	0	0	0	0	0	0	0
Ph value$\times 10^3$		2.763	5.527	8.290	11.053	13.817	3.493	10.279
High-speed emulsification test	Mark	2	3	3	3	3	2	3

[Table 4]

		Example 19	Example 20	Example 21	Example 22	Example 23	Example 24	Example 25	Example 26
Base oil 1	mass%	52.2	51.6	56.0	53.0	49.4	49.8	49.8	49.8
Base oil 2	mass%	47.8	48.4	44.0	47.0	50.6	50.2	50.2	50.2
(A1)-1	mass%				14.0		8.4	8.4	8.4
(A1)-2	mass%	16.9				10.3			
(A1)-3	mass%		9.0	15.0					
(A2)-1	mass%	11.2	16.0	15.0		7.5	12.3	12.3	12.3
(A2)-2	mass%				15.6	11.0			
(C-1')-1	mass%						0.5	1.0	
(C-1')-2	mass%								0.5
Lubricating oil composition									
Base number	mgKOH/g	70	70	70	70	70	70	70	70
Kinematic viscosity (100°C)	mm^2/s	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5
Ca component	mass%	2.65	2.71	2.70	2.53	2.62	2.65	2.65	2.65
Ca component derived from Ca phenate	mass%	0.913	0.230	0.380	1.250	0.556	0.750	0.750	0.750
Nitrogen component derived from component (C-1')	mass%	0.000	0.000	0.000	0.000	0.000	0.005	0.011	0.010
Ph value $\times 10^3$		16.866	8.637	14.394	13.817	10.279	8.290	8.290	8.290
High-speed emulsification test	Mark	3	3	3	3	3	3	2	2

[Table 5]

		Comparative Example 8	Comparative Example 9	Comparative Example 10	Comparative Example 11	Comparative Example 12	Comparative Example 13
Base oil 1	mass%	57.0	56.9	61.5	49.8	49.8	49.8
Base oil 2	mass%	43.0	43.1	38.5	50.2	50.2	50.2
(A1)-1	mass%	21.0			8.4	8.4	8.4
(A1)-2	mass%		28.0				
(A1)-3	mass%			22.5			
(A2)-1	mass%	4.4	7.0	13.8	12.3	12.3	12.3
(A2)-2	mass%						
(C-1')-1	mass%				1.5		
(C-1')-2	mass%					1.0	1.5
Lubricating oil composition							
Base number	mgKOH/g	70	70	70	70	70	70
Kinematic viscosity (100°C)	mm^2/s	20.5	20.5	20.5	20.5	20.5	20.5
Ca component	mass%	2.55	2.60	2.70	2.65	2.65	2.65
Ca component derived from Ca phenate	mass%	1.87	1.51	0.563	0.750	0.750	0.750
Nitrogen component derived from component (C-1')	mass%	0.000	0.000	0.000	0.016	0.020	0.030
Ph value $\times 10^3$		20.725	27.944	21.591	8.290	8.290	8.290
Emulsification test	Mark	0	0	0	0	0	0

Claims

1. A cylinder lubricating oil composition for a crosshead diesel engine equipped with a scrubber, comprising:

    a base oil; and

    (A) a metallic detergent,
    wherein the lubricating oil composition has a base number of 15 to 125 mgKOH/g, and a kinematic viscosity at 100°C of 10 to 30 mm^2/s; and
    the lubricating oil composition satisfies the following requirement (i) or (ii):

    (i) the lubricating oil composition comprises:

    (B) a demulsifier in an amount of 0.02 to 5.0 mass% on the basis of the total mass of the composition;

    (ii) the lubricating oil composition comprises, as the component (A),

    (A1) a Ca phenate detergent; and
    (A2) a metallic detergent other than any Ca phenate detergent;

    the lubricating oil composition optionally comprises:

    (C-1') a succinimide having at least one alkyl or alkenyl group in a molecule thereof, or a borated derivative thereof, in an amount of no more than 0.015 mass% in terms of nitrogen on the basis of the total mass of the composition; and
    a Ph value represented by the following formula (1) is no more than 20×10^{-3}:

$$\text{Ph value} = C_{Ca} \times 2/(r_M \times 40.08) \qquad \cdots (1)$$

    (in the formula (1), C_{Ca} represents calcium content (mass%) derived from the component (A1), and r_M represents a metal ratio of the component (A1).).

2. The cylinder lubricating oil composition for the crosshead diesel engine equipped with the scrubber according to claim 1,
wherein the lubricating oil composition satisfies the requirement (i); and
the lubricating oil composition comprises:

    (C) a nitrogen-containing ashless dispersant.

3. The cylinder lubricating oil composition for the crosshead diesel engine equipped with the scrubber according to claim 1,
wherein the lubricating oil composition satisfies the requirement (i); and
the lubricating oil composition optionally comprises:

    (C) a nitrogen-containing ashless dispersant in an amount of no more than 0.2 mass% in terms of nitrogen on the basis of the total mass of the composition.

4. The cylinder lubricating oil composition for the crosshead diesel engine equipped with the scrubber according to any one of claims 1 to 3,
wherein the lubricating oil composition satisfies the requirement (i); and
the component (B) is one or more polyether compound.

5. The cylinder lubricating oil composition for the crosshead diesel engine equipped with the scrubber according to claim 4,
wherein a number average molecular weight of the component (B) is no less than 500.

6. The cylinder lubricating oil composition for the crosshead diesel engine equipped with the scrubber according to any one of claims 1 to 5,
wherein the lubricating oil composition satisfies the requirement (i); and
the component (A) is a Ca phenate.

7. The cylinder lubricating oil composition for the crosshead diesel engine equipped with the scrubber according to claim 1,
wherein the lubricating oil composition satisfies the requirement (ii); and
the lubricating oil composition comprises the component (C-1') in an amount of greater than 0 mass% and no more than 0.015 mass% in terms of nitrogen on the basis of the total mass of the composition.

8. The cylinder lubricating oil composition for the crosshead diesel engine equipped with the scrubber according to claim 1 or 7,
wherein the lubricating oil composition satisfies the requirement (ii); and
the component (A2) is a Ca sulfonate and/or a Ca salicylate.

9. A method of lubricating a cylinder of a crosshead diesel engine equipped with a scrubber, comprising:

> operating the crosshead diesel engine while supplying the lubricating oil composition as in any one of claims 1 to 8 to the cylinder of the crosshead diesel engine equipped with the scrubber; and
> purifying at least a part of gas exhausted from the cylinder in the scrubber.

10. The method of lubricating the cylinder of the crosshead diesel engine equipped with the scrubber according to claim 9, wherein the purifying in the scrubber comprises contacting the gas introduced into the scrubber with water and/or a basic aqueous solution.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/082411

A. CLASSIFICATION OF SUBJECT MATTER

C10M171/02(2006.01)i, *C10M145/24*(2006.01)i, *C10M159/22*(2006.01)i, *C10M163/00*(2006.01)i, *C10M133/16*(2006.01)n, *C10N10/04*(2006.01)n, *C10N20/00*(2006.01)n, *C10N20/02*(2006.01)n, *C10N20/04*(2006.01)n,

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M171/02, C10M145/24, C10M159/22, C10M163/00, C10M133/16, C10N10/04, C10N20/00, C10N20/02, C10N20/04, C10N30/00, C10N40/25

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2015
Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus/JST7580/JSTChina(JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of Box C.
☐ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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Date of the actual completion of the international search 04 December 2015 (04.12.15)	Date of mailing of the international search report 15 December 2015 (15.12.15)
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/JP2015/082411

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

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

C10N30/00(2006.01)n, *C10N40/25*(2006.01)n

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

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

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