

DESCRIPTION

CYLINDER LUBRICATING OIL COMPOSITION FOR CROSSHEAD DIESEL ENGINE

5

TECHNICAL FIELD

[0001] The present invention relates to a cylinder lubricating oil composition for crosshead diesel engines.

10

BACKGROUND ART

[0002] Cylinder oil for lubricating between the cylinder and piston and system oil for lubricating and cooling other parts are used in crosshead diesel engines. In order to lubricate between the cylinder and piston (piston ring), the cylinder oil needs to have an appropriate viscosity, and in order for the piston and piston ring to move appropriately, the cylinder oil needs to have a function of preserving necessary cleanliness. Furthermore, in crosshead diesel engines, high sulfur fuel is normally used for its economic efficiency, leading to the problem of cylinder corrosion due to acidic components such as sulfuric acid generated by fuel combustion. In order to resolve this problem, the cylinder oil needs to have the functions of neutralizing acidic components such as generated sulfuric acid and of preventing corrosion.

[0003] On the other hand, for enhanced performance, crosshead diesel engines of recent years tend to have a larger cylinder diameter (for example, a bore size of 70 cm or greater), an increased piston stroke (for example, an exceedingly long stroke such that the average piston speed is 8 m/s or more), and increased combustion pressure (for example, a Brake Mean Effective Pressure (BMEP) of 1.8 MPa or more). Increased combustion pressure leads to a higher dew point for sulfuric acid, thus yielding conditions in which sulfuric acid corrosion of the cylinder occurs even more easily. One measure for preventing sulfuric acid corrosion is to raise the wall temperature of the cylinder (for example, to a cylinder wall temperature of 250°C or more). Moreover, for economic efficiency, the amount of lubricating oil fed into the cylinder is being reduced. The environment surrounding cylinder lubrication is thus becoming increasingly severe.

[0004] Furthermore, in recent years, the International Maritime Organization (IMO) has started to regulate gas emissions from ships engines and has restricted the sulfur level in fuel in order to decrease the emission of sulfur dioxide. Currently, in public waters, even high sulfur fuel is required
5 to be fuel with a sulfur content of 4.5% or less by mass, and in restricted areas, focusing on the North Sea, low sulfur fuel with a sulfur content of 1% or less by mass must be used.

[0005] When using high sulfur fuel, cylinder oil with a high base number (generally 70 mg KOH/g) needs to be used to neutralize acidic components
10 generated by fuel combustion, whereas when using low sulfur fuel, it is necessary to switch to cylinder oil with a low base number (generally 40 mg KOH/g). This is because if low sulfur fuel (sulfur content of 1% or less by mass) were to be used while still using cylinder oil with a high base number (70 mg KOH/g), the excessively basic component in the high base number
15 cylinder oil would accumulate as hard ash on the piston top land, and polishing of the cylinder liner may cause excessive wear. Conversely, if high sulfur fuel were to be used while still using cylinder oil with a low base number (40 mg KOH/g), neutralization of sulfuric acid generated by fuel combustion would be insufficient, leading to wear due to corrosion.

20 [0006] An expansion in restricted waters is expected in the future, and therefore it is predicted that the frequency with which cylinder oil is switched along with a switch in fuel oil while at sea will increase. In order to simplify this complicated switching operation, it would be preferable to use a single cylinder oil that is compatible with both high sulfur fuel and low sulfur fuel.

25 [0007] On the other hand, gas fuel is being studied. In the case of gas fuel, the amount of sulfur in the fuel is low, yet from the perspective of guaranteeing cleanliness, cylinder oil with a base number of 40 mg KOH/g or more is preferable. In this case, however, even at 40 mg KOH/g the base number is excessive. For stable operation of a gas-fueled engine,
30 suppression of deposits of excessively basic components on the piston top land becomes an issue. Accordingly, if the same cylinder oil as for liquid fuel can also be used with gas fuel without problems, then complications at the providing end can be mitigated and costs reduced.

[0008] Conventional cylinder oil is often low cost and maintains corrosion

and wear resistance by using, as the main component in the base oil, an overbased sulfonate-type metallic detergent, yet recently, a variety of types of metallic detergents are being used as the main component, such as salicylate-types, phenate-types, complex detergents, and the like. Oils
5 containing extreme pressure agents and dispersants are also being developed (see PTL 1 through 5).

CITATION LIST

Patent Literature

- 10 [0009] PTL 1: JP2002-275491A
PTL 2: JP2002-515933A
PTL 3: JP2002-501974A
PTL 4: JP2002-500262A
PTL 5: JP2002-241780A

15

SUMMARY OF INVENTION

(Technical Problem)

- [0010] Based on these circumstances, it is an object of the present invention to provide, as a cylinder lubricating oil composition for crosshead
20 diesel engines, a cylinder lubricating oil that in addition to having conventional characteristics such as heat resistance, cleanliness, wear resistance, and the like, can be used with fuel of any sulfur content and that suppresses the amount of piston deposit even when the base number is excessive.

25 (Solution to Problem)

- [0011] As a result of intensive research in order to achieve the above object, the inventors discovered that a cylinder lubricating oil composition for crosshead diesel engines that includes an ashless dispersant and a metallic detergent, the product of the number average molecular weight, the content,
30 and the effective concentration of the ashless dispersant being at least a specific value, and the endothermic peak temperature of the metallic detergent being at most a specific value, can contribute to achieving the above object, thereby completing the present invention.

[0012] Namely, according to the present invention, a cylinder lubricating

oil composition for a crosshead diesel engine includes an ashless dispersant (B) and a metallic detergent (C) in a lubricant base oil (A), a product of a number average molecular weight, a content, and an effective concentration of the ashless dispersant (B) being at least 9000, and an endothermic peak
5 temperature of the metallic detergent (C) as measured by DSC at a rate of temperature increase of 50°C/min being at most 460°C.

[0013] Furthermore, in the cylinder lubricating oil composition for a crosshead diesel engine, the number average molecular weight of the ashless dispersant (B) is at least 2,500.

10 (Advantageous Effect of Invention)

[0014] By softening cylinder oil ash that accumulates on the piston top land so as to allow for easy breakage, the accumulation of deposits on the land portion can be suppressed, and as a result, the cylinder lubricating oil composition for crosshead diesel engines according to the present invention
15 can be used with low sulfur fuel and in gas-fired engines despite being a high base number cylinder oil.

BRIEF DESCRIPTION OF DRAWING

[0015] FIG. 1 is a photograph showing the height of a burned product
20 (ash).

DESCRIPTION OF EMBODIMENTS

[0016] The following describes the present invention in detail. In the cylinder lubricating oil composition for crosshead diesel engines according to
25 the present invention (hereinafter also simply referred to as a lubricating oil composition), the lubricant base oil (A) is not particularly limited, and a mineral base oil and/or a synthetic base oil normally used in lubricating oil may be used.

[0017] Examples of a mineral base oil include an oil manufactured by
30 applying one or more of solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, catalytic dewaxing, hydrotreating, and the like to lubricating oil distillate yielded by reduced-pressure distillation of atmospheric residue obtained through atmospheric distillation of crude oil, as well as wax isomerized mineral oil, lubricant base oil manufactured by a

method for isomerization of GTL WAX (gas-to-liquid wax) manufactured by a process such as a Fischer-Tropsch process, and the like.

[0018] The total aromatic content of the mineral base oil is not particularly limited yet is preferably at most 40% by mass and more preferably at most 30% by mass. The total aromatic content of the mineral base oil may be 0% by mass, yet from the perspective of solubility of additives, the total aromatic content is preferably at least 1% by mass, more preferably at least 5% by mass, even more preferably at least 10% by mass, and still more preferably at least 20% by mass. A total aromatic content of the base oil exceeding 40% is not preferable, since the oxidative stability worsens.

[0019] Note that the above "total aromatic content" indicates the aromatic fraction content measured in conformity with ASTM D2549. Normally, in addition to alkyl benzene and alkyl naphthalene, the aromatic fraction includes anthracene, phenanthrene, an alkylation of the above, a compound in which four or more benzene rings are condensed, heteroaromatic compounds such as pyridines, quinolines, phenols, or naphthols, and the like.

[0020] The sulfur content in the mineral base oil is not particularly limited, yet is preferably at most 1% by mass and more preferably at most 0.5% by mass. The sulfur content in the mineral base oil may be 0% by mass, yet is preferably at least 0.1% by mass and more preferably at least 0.2% by mass. Including a certain degree of sulfur content in the mineral base oil can greatly improve the solubility of additives.

[0021] Examples of the synthetic base oil include polybutene or hydrogenated compounds thereof; poly- α -olefins, or hydrogenated compounds thereof, which are a polymer with a carbon number of 8 to 14, representative examples being 1-octene oligomer and 1-decene oligomer; diesters such as ditridecyl glutarate, di-2-ethyl hexyl adipate, diisodecyl adipate, ditridecyl adipate, and di-2-ethyl hexyl sebacate; polyol esters such as trimethylol propane caprylate, trimethylol propane pelargonate, pentaerythritol-2-ethyl hexanoate, and pentaerythritol pelargonate; copolymers of a dicarboxylic acid such as dibutyl maleate and an α -olefin with 2 to 30 carbons; aromatic synthetic oils such as alkyl naphthalene, alkyl benzene, and aromatic esters, or mixtures thereof; and the like. Among these, the most preferable

synthetic base oil is an oligomer with a carbon number of 8 to 14, called a polyalphaolefin, the kinematic viscosity thereof at 100°C being from 4 mm²/s to 150 mm²/s.

5 [0022] A mineral base oil, a synthetic base oil, any mixture of two or more base oils selected from mineral base oils and synthetic base oils, or the like may be used as the lubricant base oil (A) in the present invention. Examples include one or more mineral base oils, one or more synthetic base oils, a mixture of one or more mineral base oils and one or more synthetic base oils, and the like.

10 [0023] The kinematic viscosity of the lubricant base oil that is used is not particularly limited, yet at 100°C, the kinematic viscosity is preferably from 4 mm²/s to 50 mm²/s, more preferably from 6 mm²/s to 40 mm²/s, and even more preferably from 8 mm²/s to 35 mm²/s. When the kinematic viscosity of the lubricant base oil at 100°C exceeds 50 mm²/s, the low temperature viscosity
15 characteristics worsen, whereas when the kinematic viscosity is less than 4 mm²/s, oil film formation is insufficient at the lubrication spot, causing lubricity to deteriorate and loss of lubricant base oil by evaporation to increase. Hence, both of these ranges are undesirable.

[0024] The lubricating oil composition according to the present invention
20 preferably includes, as the lubricant base oil, a lubricant base oil having a kinematic viscosity at 100°C of 4 mm²/s to less than 17 mm²/s and/or a kinematic viscosity at 100°C of 17 mm²/s to 150 mm²/s. Examples of the lubricant base oil having a kinematic viscosity at 100°C of 4 mm²/s to less than 17 mm²/s include an SAE 10 to 40 mineral base oil or synthetic base oil.
25 The kinematic viscosity thereof is preferably at least 5.6 mm²/s, more preferably at least 9.3 mm²/s, preferably at most 14 mm²/s, and more preferably at most 12.5 mm²/s. Examples of the lubricant base oil having a kinematic viscosity at 100°C of 17 mm²/s to 50 mm²/s include an SAE 50 bright stock or other mineral base oil or synthetic base oil. The kinematic
30 viscosity thereof is preferably at least 20 mm²/s, more preferably at least 25 mm²/s, preferably at most 40 mm²/s, and more preferably at most 35 mm²/s. Furthermore, a synthetic base oil corresponds to a lubricant base oil having a kinematic viscosity at 100°C of 50 mm²/s to 150 mm²/s.

[0025] The amount of loss of lubricant base oil by evaporation is, in terms

of NOACK evaporation, preferably at most 20% by mass, more preferably at most 16% by mass, and even more preferably at most 10% by mass. If the NOACK evaporation of the lubricant base oil exceeds 20% by mass, the evaporation loss of the lubricating oil becomes great, leading to increased viscosity and the like, and hence such a value is not desirable. Note that the NOACK evaporation is measured as the amount of evaporation of the lubricating oil measured with ASTM D5800.

[0026] The viscosity index of the lubricant base oil that is used is not particularly limited, yet in order to obtain excellent viscosity characteristics from a low temperature to a high temperature, the value thereof is preferably at least 80, more preferably at least 90, and even more preferably at least 100. No particular restriction is placed on the upper limit of the viscosity index of the lubricant base oil, and a base oil with a viscosity index of approximately 135 to 180 may be used, such as normal paraffin, slack wax, GTL wax, or the like, or an isoparaffinic mineral oil in which these are isomerized. A complex ester base oil or HVI-PAO base oil with a viscosity index of approximately 150 to 250 may also be used. From the perspective of solubility and storage stability of additives, however, the viscosity index is preferably at most 120 and more preferably at most 110.

[0027] The cylinder lubricating oil composition for crosshead diesel engines according to the present invention includes an ashless dispersant (B) (hereinafter also referred to as component (B)) as an essential component.

[0028] Any ashless dispersant used in lubricating oil may be used as component (B). Examples include a nitrogen-containing compound or a derivative thereof having in the molecule at least one straight-chain or branched alkyl group or alkenyl group with a carbon number of 40 to 400, preferably 60 to 350, a Mannich base dispersant, or a denatured alkenyl succinimide. Any single type, or two or more types, selected from the above may be blended and used.

[0029] In the nitrogen-containing compound or a derivative thereof, when the carbon number of the alkyl group or alkenyl group is less than 40, the solubility in the lubricant base oil may decrease, whereas when the carbon number exceeds 400, the low-temperature fluidity of the lubricating oil composition according to the present invention may worsen. The alkyl group

or alkenyl group may be straight-chain or branched, and preferable examples include a branched alkyl group or branched alkenyl group derived from olefin oligomers such as propylene, 1-butene, isobutylene, and the like, or from a co-oligomer of ethylene and propylene.

- 5 [0030] Examples of the component (B) include a single type, or two or more types, selected from among components (B-1) through (B-3) below.

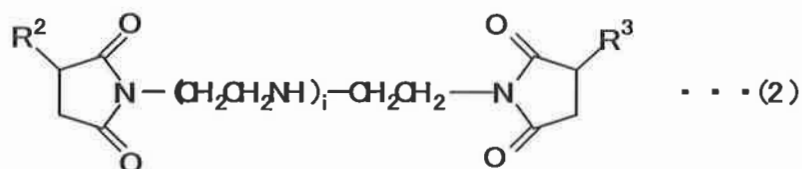
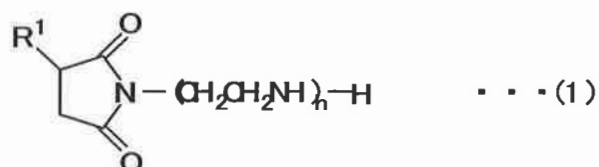
(B-1): succinimide, or a derivative thereof, containing at least one alkyl group or alkenyl group with a carbon number of 40 to 400 in the molecule;

- 10 (B-2): benzylamine, or a derivative thereof, containing at least one alkyl group or alkenyl group with a carbon number of 40 to 400 in the molecule; and

- (B-3): polyamine, or a derivative thereof, containing at least one alkyl group or alkenyl group with a carbon number of 40 to 400 in the molecule.

[0031] Examples of component (B-1) above include the compounds shown in the following formulas (1) and (2).

[Chem. 1]



- 20 [0032] In the formula (1), R¹ represents an alkyl group or alkenyl group with a carbon number of 40 to 400, preferably 60 to 350, and h represents an integer from 1 to 5, preferably from 2 to 4.

- [0033] In the formula (2), R² and R³ independently represent an alkyl group or alkenyl group with a carbon number of 40 to 400, preferably 60 to 350, and more preferably represent a polybutenyl group. Furthermore, i represents an integer from 0 to 4, preferably from 1 to 3.

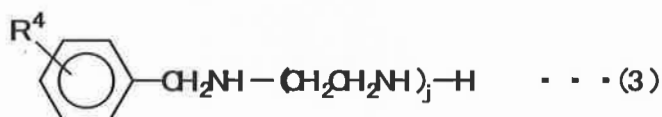
[0034] Component (B-1) includes a so-called monotype succinimide

represented by the formula (1), in which succinic anhydride is attached to one end of a polyamine, and a so-called bis-type succinimide represented by the formula (2), in which succinic anhydride is attached to both ends of a polyamine. Either, or a mixture of both, may be included in the composition according to the present invention.

[0035] The method of manufacturing the succinimide in component (B-1) is not particularly limited. For example, the succinimide may be obtained by reacting a compound having an alkyl group or alkenyl group with a carbon number of 40 to 400 with maleic anhydride at 100°C to 200°C, and reacting the resulting alkyl succinic acid or alkenyl succinic acid with polyamine. Examples of polyamine include diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and pentaethylenehexamine.

[0036] Examples of component (B-2) above include the compound shown in the following formula (3).

[Chem. 2]



[0037] In the formula (3), R⁴ represents an alkyl group or alkenyl group with a carbon number of 40 to 400, preferably 60 to 350, and j represents an integer from 1 to 5, preferably from 2 to 4.

[0038] The method of manufacturing the benzylamine in component (B-2) is not particularly limited. Examples include a method to react a polyolefin, such as a propylene oligomer, polybutene, or ethylene-α-olefin copolymer, with a phenol to yield alkyl phenol, and then to react the alkyl phenol with formaldehyde and with a polyamine such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, or pentaethylenehexamine via a Mannich reaction.

[0039] Examples of component (B-3) above include the compound shown in the following formula (4).



[0040] In the formula (4), R⁵ represents an alkyl group or alkenyl group with a carbon number of 40 to 400, preferably 60 to 350, and k represents an integer from 1 to 5, preferably from 2 to 4.

[0041] The method of manufacturing the polyamine in component (B-3) is not particularly limited. Examples include a method to chlorinate a polyolefin, such as a propylene oligomer, polybutene, or ethylene- α -olefin copolymer and then to react the result with ammonia and a polyamine such as ethylenediamine, diethylenetriamine, triethylenetetramine, 5 tetraethylenepentamine, or pentaethylenehexamine.

[0042] Examples of the derivative of a nitrogen-containing compound listed as an example of the component (B) include a so-called denatured compound from an oxygen-containing organic compound, in which a 10 monocarboxylic acid, such as a fatty acid, with a carbon number of 1 to 30, or a polycarboxylic acid, such as oxalic acid, phthalic acid, trimellitic acid, or pyromellitic acid, with a carbon number of 2 to 30, or anhydride of these acids, or an ester compound, an alkylene oxide with a carbon number of 2 to 6, or hydroxy(poly)oxyalkylene carbonate is caused to act on the above-described 15 nitrogen-containing compound, and a portion or the entirety of the remaining amino group and/or imino group is neutralized or amidated; a so-called boron denatured compound in which boric acid is caused to act on the above-described nitrogen-containing compound, and a portion or the entirety of the remaining amino group and/or imino group is neutralized or amidated; a 20 so-called phosphoric acid denatured compound in which phosphoric acid is caused to act on the above-described nitrogen-containing compound, and a portion or the entirety of the remaining amino group and/or imino group is neutralized or amidated; a sulfur denatured compound in which a sulfur compound is caused to act on the above-described nitrogen-containing 25 compound; and a denatured compound in which the above-described nitrogen-containing compound is combined with two or more denatured components selected from among a denatured oxygen-containing organic compound, denatured boron, denatured phosphoric acid, and denatured sulfur. Among these derivatives, a boric acid denatured compound of alkenyl 30 succinimide, in particular a boric acid denatured compound of a bis-type alkenyl succinimide, can further enhance heat resistance by being used along with the above-described component (A).

[0043] The content by percentage of component (B) in the lubricating oil composition according to the present invention is, as nitrogen content in terms

of total content of the composition, normally 0.005% to 0.4% by mass, preferably 0.01% to 0.2% by mass, more preferably 0.01% to 0.1% by mass, and even more preferably 0.02% to 0.05% by mass. Furthermore, when using a boron-containing ashless dispersant as component (B), the mass ratio
5 of the boron content to the nitrogen content (B/N ratio) is not particularly limited yet is preferably from 0.5 to 1 and more preferably from 0.7 to 0.9. A higher B/N ratio makes it easier to enhance the wear resistance and burn resistance, yet a ratio exceeding 1 leads to concerns about safety. When using a boron-containing ashless dispersant, the content by percentage is not
10 particularly limited, yet the boron content in terms of total content of the composition is preferably from 0.001% to 0.1% by mass, more preferably from 0.005% to 0.05% by mass, and even more preferably from 0.01% to 0.04% by mass.

[0044] The component (B) in the lubricating oil composition of the present
15 invention is preferably a boron-containing ashless dispersant with a boron content of at least 0.5% by mass, more preferably at least 1.0% by mass, even more preferably at least 1.5% by mass, and still more preferably 1.8% by mass. In particular, a boron-containing succinimide-based ashless dispersant is most preferably included. Note that the boron-containing ashless dispersant with
20 a boron content of at least 0.5% by mass as described herein may include a diluent oil, such as a mineral oil or a synthetic oil, accounting for 10% to 90% by mass, preferably 30% to 70% by mass, and the boron content normally refers to the boron content in a state including the diluent oil.

[0045] The number average molecular weight (M_n) of component (B) in
25 the present invention is measured by removing the diluent oil by rubber membrane separation from a sample and analyzing the result with Gel Permeation Chromatography (GPC).

[0046] The procedure for rubber membrane dialysis separation is as follows.

- 30
- (i) Collect an approximately 5 g sample from the rubber membrane.
 - (ii) Tie the rubber membrane with a thread and insert the rubber membrane into an extraction thimble.
 - (iii) Place the extraction thimble into a Soxhlet extractor.
 - (iv) Pour 100 ml of petroleum ether into a flat-bottom flask, and

attach the Soxhlet extractor to the top thereof.

(v) Heat the flat-bottom flask (70°C) in a water bath, and cool the Soxhlet extractor with an attached condenser.

(vi) Heat to reflux for two days.

5 (vii) Transfer the dialysis residue in the rubber membrane to a beaker, and wash the rubber membrane deposit in the beaker with petroleum ether. Heat the petroleum ether with a water bath and remove, determine the rubber membrane residue.

10 (viii) Heat the petroleum ether of the dialysis portion in the flat-bottom flask with a water bath and remove, determine the rubber membrane dialysis portion.

[0047] The analysis conditions for GPC are as follows.

Device: Waters Alliance 2695

Column: Tosoh GMHHR-M

15 Mobile phase: tetrahydrofuran

Solvent dilute concentration of sample: 1% by mass (solvent: tetrahydrofuran)

Temperature: 23°C

Flow rate: 1 ml/min

20 Sample amount: 100 µl

Detector: RI

Molecular weight: by molecular weight of polystyrene

[0048] In the present invention, the effective concentration of the ashless dispersant in component (B) is determined from the results of the
25 above-described rubber membrane dialysis separation. In other words, the effective concentration was calculated as the ratio of the remaining mass in the rubber membrane with respect to the amount (approximately 5 g) initially collected as the sample.

[0049] In the present invention, the ashless dispersant (B) needs to be
30 added so that the product of the number average molecular weight (M_n), the content, and the effective concentration thereof is at least 9000. The product is preferably at least 10000, more preferably at least 12000, even more preferably at least 15000, and most preferably at least 20000. The product is also preferably at most 50000. When the product is less than 9000, the ease

of breakage of deposits, which is the objective of the present invention, is insufficient. This not only causes the deposits to increase but also has a larger adverse impact on wear. Conversely, when the product exceeds 50000, viscosity is too high, making fluidity insufficient and leading to an increase in deposits.

[0050] The ease of breakage of deposits referred to here is measured by the height of a product yielded by burning the cylinder lubricating oil composition in a Thermo Gravimetry Analyzer (TGA). Specifically, the cylinder lubricating oil composition is collected in a hermetic pan of a TGA and burned, and the height of the product from the cylinder lubricating oil composition, which rises from the hermetic pan like a cupcake, as illustrated in FIG. 1, is measured. The higher the deposit forms, the greater the breakability. Details are listed in the section on Examples.

[0051] The number average molecular weight (M_n) of the ashless dispersant (B) in the present invention is preferably at least 2500, more preferably at least 3000, even more preferably at least 4000, and most preferably at least 5000. Furthermore, the number average molecular weight (M_n) is preferably at most 10000. If the number average molecular weight of the ashless dispersant is less than 2500, the ease of breakage of deposits, which is the objective of the present invention, is insufficient. This not only causes the deposits to increase but also has a larger adverse impact on wear. Conversely, if the number average molecular weight of the ashless dispersant exceeds 10000, viscosity is too high, making fluidity insufficient and leading to an increase in deposits.

[0052] In the present invention, as long as the product of the number average molecular weight (M_n), the content, and the effective concentration of the ashless dispersant is at least 9000, the content and effective concentration of the ashless dispersant (B) are not particularly limited. The effective concentration of the ashless dispersant (B) (the ratio of the mass remaining in the rubber membrane to the amount of the initially collected sample), however, is preferably in a range from 0.30 to 0.70, and the concentration in the composition of the ashless dispersant (B) (the product of the content and the effective concentration) is preferably in a range from 0.9% to 14% by mass in terms of total content of the composition.

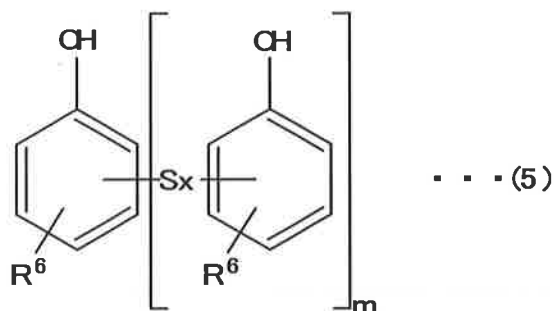
[0053] The cylinder lubricating oil composition for crosshead diesel engines according to the present invention includes a metallic detergent (C) (hereinafter also referred to as component (C)) as an essential component.

[0054] Any compound normally used in lubricating oil can be used as the metallic detergent (C). Examples include sulfonate detergents, phenate detergents, salicylate detergents, naphthenate detergents, and the like. A single type of the above metallic detergents may be used, or two or more types may be used in combination.

[0055] Examples of a sulfonate detergent that can be used include an alkali metal salt, alkaline-earth metal salt, or (overbased) basic salt of alkyl aromatic sulfonic acid obtained by sulfonation of an alkyl aromatic compound with a weight-average molecular weight of 400 to 1500, preferably 700 to 1300. Examples of the alkali metal or alkali earth metal include sodium, potassium, magnesium, barium, and calcium. Magnesium or calcium are preferable, with calcium being particularly preferable. Examples of the alkyl aromatic sulfonic acid include so-called petroleum sulfonic acid and synthetic sulfonic acid. Examples of the petroleum sulfonic acid referred to here generally include the result of sulfonating an alkyl aromatic compound of lubricating oil distillate in mineral oil, as well as so-called mahogany acid, which is a by-product when manufacturing white oil. As the synthetic sulfonic acid, for example the result of sulfonating an alkyl benzene, which is the raw material for the detergent, having a straight-chain or branched alkyl group obtained as a by-product from an alkyl benzene manufacturing plant or by an alkylation of a polyolefin in benzene may be used. The result of sulfonating an alkyl naphthalene, such as dinonylnaphthalene, may also be used. The sulfonating agent when sulfonating these alkyl aromatic compounds is not particularly limited, yet typically fuming sulfuric acid or sulfuric anhydride is used.

[0056] As the above phenate detergent, an alkylphenol sulfide alkali metal salt, alkaline-earth metal salt, or (overbased) basic salt having the structure shown in the following formula (5) may be used. Examples of the alkali metal or alkali earth metal include sodium, potassium, magnesium, barium, and calcium. Magnesium or calcium are preferable, with calcium being particularly preferable.

[Chem. 3]



[0057] In the formula (5), R^6 represents a straight-chain or branched, saturated or unsaturated alkyl group or alkenyl group with a carbon number of 6 to 21, m represents the degree of polymerization and is an integer from 1 to 10, S represent elemental sulfur, and x represents an integer from 1 to 3.

[0058] The carbon number of the alkyl group or alkenyl group in the formula (5) is preferably from 9 to 18 and more preferably from 9 to 15.

When the carbon number is less than 6, the solubility in the base oil may decrease, whereas when the carbon number exceeds 21, production becomes difficult, and heat resistance may worsen.

[0059] The phenate metal detergent preferably includes an alkylphenol sulfide metal salt for which the degree of polymerization m in the formula (5) is at least 4, particularly 4 to 5, since the resulting heat resistance is excellent.

[0060] Examples of the above salicylate detergent include an alkali metal, alkali earth metal salicylate, or (overbased) basic salt thereof having one hydrocarbon group with a carbon number of 1 to 19; an alkali metal, alkali earth metal salicylate, or (overbased) basic salt thereof having one hydrocarbon group with a carbon number of 20 to 40; and an alkali metal, alkali earth metal salicylate, or (overbased) basic salt thereof having two or more hydrocarbon groups with a carbon number of 1 to 40. These hydrocarbon groups may be the same or different. Among these, use of an alkali metal, alkali earth metal salicylate, or (overbased) basic salt thereof having one hydrocarbon group with a carbon number of 8 to 19 is preferable, since low-temperature fluidity is excellent. Examples of the alkali metal or alkali earth metal include sodium, potassium, magnesium, barium, and calcium. Magnesium and/or calcium are preferable, with use of calcium being particularly preferable.

[0061] The base number of the component (C) is preferably in a range

from 50 mg KOH/g to 500 mg KOH/g, with a range from 100 mg KOH/g to 450 mg KOH/g being more preferable, and a range from 120 mg KOH/g to 400 mg KOH/g being even more preferable. When the base number is less than 50 mg KOH/g, corrosion and wear may greatly increase, whereas when
5 exceeding 500 mg KOH/g, problems may occur with solubility.

[0062] The metal ratio of the component (C) is not particularly limited, yet it is preferable to use a component (C) having a metal ratio with a lower limit preferably of at least 1, more preferably at least 2, and even more preferably at least 2.5, and an upper limit of preferably at most 20, more
10 preferably at most 19, and even more preferably at most 18. Note that the metal ratio referred to here is expressed as the valence of the metal element $\times$ the content of the metal element (mol %) / soap group content (mol %) in the component (C). Furthermore, the metal element refers to calcium, magnesium, or the like, and the soap group refers to a sulfonic acid group,
15 phenol group, salicylic acid group, or the like.

[0063] In the lubricating oil composition according to the present invention, a single component (C) may be used, yet two or more types are preferably used in combination. When used in combination, one of the following combinations is particularly preferable: (1) overbased Ca phenate /
20 overbased Ca sulfonate, (2) overbased Ca phenate / overbased Ca salicylate, and (3) overbased Ca phenate / overbased Ca sulfonate / overbased Ca salicylate.

[0064] The preferable ratio for (1) overbased Ca phenate / overbased Ca sulfonate and (2) overbased Ca phenate / overbased Ca salicylate is at least 0.1 as a weight ratio of the additive blend, with at least 0.2 being more
25 preferable and at least 0.3 being most preferable. The reason is that when the ratio is less than 0.1, heat resistance worsens. A ratio of at most 9 is preferable, with at most 7 being more preferable, and at most 5 being most preferable. The reason is that when the ratio exceeds 9, the height in the
30 TGA burning test is insufficient, and the deposits on the piston top land are not sufficiently reduced.

[0065] In the case of (3) overbased Ca phenate / overbased Ca sulfonate / overbased Ca salicylate, the ratio of the sum of overbased Ca sulfonate and overbased Ca salicylate to overbased Ca phenate is preferably the

above-indicated ratio. In this case, the weight ratio of the content of overbased Ca sulfonate / overbased Ca salicylate is not limited, yet a value of at least 0.1 is preferable, with at least 0.2 being more preferable, and at least 0.3 being most preferable. The reason is that if the weight ratio is less than 0.1, deposits may end up increasing in conditions greatly exceeding 300°C. A weight ratio of at most 9 is preferable, with at most 7 being more preferable, and at most 5 being most preferable. A weight ratio exceeding 9 causes the cleanliness to decrease.

[0066] The content by percentage of component (C) in the lubricating oil composition according to the present invention is, in terms of total content of the composition, preferably 3% to 30% by mass, more preferably 6% to 25% by mass, and even more preferably 8% to 20% by mass. When the content by percentage of component (C) is less than 3% by mass, the necessary cleanliness and acid neutralization characteristics might not be obtained, whereas when exceeding 30% by mass, an excessive metallic component may form a deposit on the piston.

[0067] The metal component content based on the component (C) in the lubricating oil composition according to the present invention is, in terms of total content of the composition, preferably 0.35% to 3.6% by mass, more preferably 1.0% to 2.9% by mass, and even more preferably 1.4% to 2.7% by mass. When the metal component content based on the component (C) is less than 0.7% by mass, the necessary cleanliness and acid neutralization characteristics might not be obtained, whereas when exceeding 3.6% by mass, excessive ash may form a deposit on the piston top land, which may lead to scuffing or bore polishing of the liner.

[0068] For the component (C) in the present invention, the endothermic peak temperature measured by a differential scanning calorimeter (DSC) needs to be at most 460°C.

[0069] Note that the measurement conditions for DSC are as follows.

Device: TA instrument DSC2920

Sample collection pan: hermetic pan

Sample amount: 30 mg

Atmosphere: nitrogen (flow rate: 50 ml/min)

Rate of temperature increase: 50°C/min

Endothermic peak temperature: endothermic peak temperature after evaporation of diluent oil in additive

[0070] When the endothermic peak temperature exceeds 460°C, the effect of softening the deposits is not sufficiently obtained. Of course, if no
5 endothermic peak exists between the endothermic peak due to evaporation of the diluent oil and 460°C, then no effect of softening the deposits is obtained. Conversely, the lower limit on the endothermic peak temperature of the metallic detergent (C) is not particularly limited, yet a temperature of at least 350°C is preferable. At a lower temperature, the compound becomes
10 unstable, and heat resistance may become insufficient.

[0071] The lubricating oil composition according to the present invention preferably includes a sulfur-based extreme pressure agent as an additional component. Preferable examples of the sulfur-based extreme pressure agent include dihydrocarvyl polysulfide, sulfurized fatty acid, sulfurized olefin,
15 sulfurized ester, sulfurized fat, sulfurized mineral oil, a thiazole compound, a thiadiazole compound, and an alkyl thiocarbamate compound.

[0072] The lubricating oil composition according to the present invention preferably includes an organic molybdenum compound. Examples of the organic molybdenum compound include an organic molybdenum compound
20 that includes sulfur, such as molybdenum dithiophosphate and molybdenum dithiocarbamate (MoDTC); a complex of a molybdenum compound (for example, molybdenum oxide such as molybdenum dioxide or molybdenum trioxide; a molybdic acid such as orthomolybdic acid, paramolybdic acid, and sulfurized (poly)molybdic acid; a metal salt of these molybdic acids, or a
25 molybdic acid salt such as an ammonium salt of these molybdic acids; molybdenum sulfide such as molybdenum disulfide, molybdenum trisulfide, molybdenum pentasulfide, or molybdenum polysulfide; sulfurized molybdenum acid, metal or amine salt of sulfurized molybdenum acid, or halogenated molybdenum such as molybdenum chloride) and a
30 sulfur-containing organic compound (for example, alkyl(thio)xanthate, thiaziazole, mercaptothiadiazole, thiocarbonate, tetrahydrocarbyl thiuram disulfide, bis(di(thio)hydrocarbyl dithiophosphonate)disulfide, organic (poly) sulfide, and sulfurized ester) or other organic compound; or a complex of a sulfur-containing molybdenum compound, such as the above molybdenum

sulfide and sulfurized molybdenum acid, and alkenyl succinimide.

[0073] Furthermore, as an antiwear agent, the lubricating oil composition according to the present invention preferably includes zinc dithiophosphates (ZnDTP) (hereinafter also referred to as component (E)). Examples of the zinc dithiophosphate include zinc dialkyldithiophosphate that includes a straight-chain or branched (primary, secondary, or tertiary, with primary or secondary being preferable) alkyl group with a carbon number of 3 to 18, preferably 3 to 10, such as dipropyl zinc dithiophosphate, dibutyl zinc dithiophosphate, dipentyl zinc dithiophosphate, dihexyl zinc dithiophosphate, diheptyl zinc dithiophosphate, or dioctyl zinc dithiophosphate; and di((alkyl)aryl)zinc dithiophosphate having an aryl group or alkylaryl group with a carbon number of 6 to 18, preferably 6 to 10, such as diphenyl zinc dithiophosphate or ditolyl zinc dithiophosphate, or a mixture of two or more of these.

[0074] In addition to the above structural components, in order to further improve the properties of the lubricating oil composition of the present invention or to add other required properties, the lubricating oil composition according to the present invention may, for this purpose, further include any additives that are typically used in a lubricating oil. Examples of such additives include antioxidants, ashless friction modifiers, corrosion inhibitors, rust inhibitors, demulsifiers, metal deactivators, anti-foaming agents, and dyes.

[0075] Examples of the antioxidant include phenol-based or amine-based ashless antioxidants; and metallic antioxidants such as copper and molybdenum antioxidants. When included, the content of the antioxidant in terms of total content of the composition is normally 0.1% to 5% by mass.

[0076] Examples of the ashless friction modifier include fatty acid esters, aliphatic amines, and fatty acid amides. When included, the content of the friction modifier in terms of total content of the composition is normally 0.1% to 5% by mass.

[0077] Examples of the corrosion inhibitor include benzotriazole-based, tolyltriazole-based, thiadiazole-based, and imidazole-based compounds.

[0078] Examples of the rust inhibitor include petroleum sulfonates, alkyl benzene sulfonates, dinonylnaphthalene sulfonates, alkenyl succinic acid

esters, and polyhydric alcohol esters.

[0079] Examples of the demulsifier include polyalkylene glycol-based non-ionic surfactants such as polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, and polyoxyethylene alkyl naphthyl ethers.

5 [0080] Examples of the metal deactivator include imidazolines, pyrimidine derivatives, alkyl thiadiazoles, mercaptobenzothiazoles, benzotriazoles and derivatives thereof, 1,3,4-thiadiazole polysulfide, 1,3,4-thiadiazolyl-2,5-bisdialkyl dithiocarbamate, 2-(alkyldithio) benzoimidazole, and β -(o-carboxybenzylthio) propionitrile.

10 [0081] Examples of the anti-foaming agent include silicone oil, alkenylsuccinic acid derivatives, and the like with a kinematic viscosity at 25°C of 0.1 mm²/s to less than 100 mm²/s.

[0082] When these additives are included in the lubricating oil composition according to the present invention, the content in terms of total
15 content of the composition is normally selected from a range of 0.005% to 5% by mass, and the anti-foaming agent is normally selected from a range of 0.0005% to 1% by mass.

[0083] In the cylinder lubricating oil composition for crosshead diesel engines according to the present invention, the base number is preferably at
20 least 10 mg KOH/g, more preferably at least 20 mg KOH/g, even more preferably at least 25 mg KOH/g, and still more preferably at least 40 mg KOH/g. Furthermore, the base number is preferably at most 100 mg KOH/g, more preferably at most 85 mg KOH/g, and even more preferably at most 75 mg KOH/g. When the base number is less than 10 mg KOH/g, the piston
25 cleanliness is insufficient. Furthermore, when the base number exceeds 100 mg KOH/g, the excessive base number, i.e. metal carbonate, forms deposits, leading to wear and to the piston ring sticking.

[0084] When both high sulfur fuel and low sulfur fuel are used, the base number is preferably at least 50 mg KOH/g, more preferably at least 60 mg
30 KOH/g, and even more preferably at least 70 mg KOH/g. If the base number is less than 50 mg KOH/g, then when using high sulfur fuel, the ability to neutralize generated acid material is insufficient, and corrosion and wear cannot be controlled. In this case, the upper limit is as described above.

[0085] When only low sulfur fuel or gas fuel is used, the base number is

preferably at most 60 mg KOH/g, more preferably at most 50 KOH/g, and even more preferably at most 45 mg KOH/g. If the base number exceeds 60 mg KOH/g, then when using low sulfur fuel or gas fuel, there is a higher chance of wear and of the piston ring sticking as a result of formation of deposits due to the excessive base number, i.e. metal carbonate. In this case, the lower limit is as described above.

[0086] Note that "high sulfur fuel" as used herein refers to fuel with a sulfur content of at least 3.5% by mass, and "low sulfur fuel" refers to fuel with a sulfur content of less than 1.0% by mass. Fuel with a sulfur content of at least 1.0% by mass and less than 3.5% by mass may be treated as either high sulfur fuel or low sulfur fuel. Note that the sulfur content of gas is at most 0.1% by mass.

EXAMPLES

[0087] The present invention will be described in more detail with reference to the following Examples and Comparative Examples, yet the present invention is not limited thereto.

[0088] (Examples 1 to 14, Comparative Examples 1 to 8)
Lubricating oil compositions with the formulations shown in Table 1 were prepared, and as described above, the ease of breakage of formed deposits was measured with a TGA. The test conditions are as follows.

Device: TA instrument TGA2950
Sample collection pan: hermetic pan
Sample amount: 30 mg
Atmosphere: nitrogen (flow rate: 50 ml/min)
Rate of temperature increase: 50°C/min
Ease of breakage of deposits: measured as height of ash after being raised from room temperature to 600°C and, after reaching 600°C, being maintained for 30 min

An example is illustrated in FIG. 1.

[0089] A test with a Ricardo WD300 engine was conducting under the following conditions on the prepared lubricating oil compositions.

Device: Ricardo WD300 engine (number of cylinders: 1; displacement: 2.2 L; piston bore: 135 mm)

Brake mean effective pressure: 20 bar

Frequency of rotation: 1200 rpm

Fuel: diesel oil (sulfur content of less than 10 ppm)

Coolant outlet temperature: 85°C

Lubricating oil temperature: 80°C

- 5 Method of evaluating piston top land: merit rating according to Japan Petroleum Institute method (JPI-5S-15) (a higher rating indicates less deposit)

[0090] [Table 1]

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Base oil		residue	residue	residue	residue	residue	residue	residue	residue	residue	residue	residue	residue	residue	residue	residue	residue	residue	residue	residue	residue	residue	residue
Additive																							
ashless dispersant 1	mass %																5						
ashless dispersant 2	mass %							10										5					
ashless dispersant 3	mass %	5																					
ashless dispersant 4	mass %		5																				
ashless dispersant 5	mass %			5																			
ashless dispersant 6	mass %				3	5	10		5	5	5	5	5	5	5				2.1	5	5	5	5
metallic detergent 1	mass %										6.3	12.5	21.9		19.5								
metallic detergent 2	mass %	17.5	17.5	17.5	17.5	17.5	17.5	17.5	5	10				15.6		17.5	17.5	17.5	17.5				
metallic detergent 3	mass %																			17.5			
metallic detergent 4	mass %																				17.5		
metallic detergent 5	mass %																					17.5	
metallic detergent 6	mass %																						17.5
metallic detergent 7	mass %														5	5							
Base number of composition (perchloric acid method)	mg KOH/g	70	70	70	70	70	70	70	20	40	20	40	70	70	70	70	70	70	70	70	70	70	70
Number average molecular weight Mn of ashless dispersant		3180	4460	4770	7630	7630	7630	2660	7630	7630	7630	7630	7630	7630	7630		2390	2660	7630	7630	7630	7630	7630
Effective concentration of ashless dispersant	mass ratio	0.60	0.50	0.60	0.45	0.45	0.45	0.50	0.45	0.45	0.45	0.45	0.45	0.45	0.45		0.40	0.50	0.50	0.45	0.45	0.45	0.45
Mn x content x effective concentration of ashless dispersant		9540	11150	14310	10301	17168	34335	13300	17168	17168	17168	17168	17168	17168	17168	0	4780	6650	8012	17168	17168	17168	17168
Concentration of ashless dispersant in composition (content x effective concentration)	mass %	3	2.5	3	1.35	2.25	4.5	5	2.25	2.25	2.25	2.25	2.25	2.25	2.25	0	2	2.5	1.05	2.25	2.25	2.25	2.25
Height of ash from composition via TGA burning test	mm	2	2.5	2.7	2.2	3	4	2.6	2.8	2.9	2.6	2.7	2.8	2.9	2.8	0	0.4	0.6	1.1	0.2	0.7	0	0.2
Top land deposit in WD300 engine test	rating	3.8	4			4.5	5.5	4.1	4.4		4.2		4.4	4.5		2		2.6	2.9	2	2.6	2	

[0091] Base oil: as a fraction of the base oil, solvent-refined base oil SAE 30 altered to 44 to 69 parts by mass, bright stock altered to 31 to 56 parts by mass, and kinematic viscosity of lubricating oil composition (100°C) adjusted to 20.0 mm²/s to 21.0 mm²/s

5 * Solvent-refined base oil SAE 30: kinematic viscosity (40°C) 94.33 mm²/s, kinematic viscosity (100°C) 10.79 mm²/s

 ** Bright stock: kinematic viscosity (40°C) 466.6 mm²/s, kinematic viscosity (100°C) 31.57 mm²/s

[0092] Ashless dispersant 1: polybutenyl succinimide, Mn 2390 (effective
10 concentration 40% by mass, ratio of mass remaining in rubber membrane to the amount of collected sample = 0.4), endothermic peak temperature in DSC of 442°C

Ashless dispersant 2: polybutenyl succinimide, Mn 2660 (effective concentration 50% by mass, ratio of mass remaining in rubber membrane to
15 the amount of collected sample = 0.5), endothermic peak temperature in DSC of 447°C

Ashless dispersant 3: polybutenyl succinimide, Mn 3180 (effective concentration 60% by mass, ratio of mass remaining in rubber membrane to the amount of collected sample = 0.6), endothermic peak temperature in DSC
20 of 456°C

Ashless dispersant 4: polybutenyl succinimide, Mn 4460 (effective concentration 50% by mass, ratio of mass remaining in rubber membrane to the amount of collected sample = 0.5), endothermic peak temperature in DSC of 442°C

25 Ashless dispersant 5: polybutenyl succinimide, Mn 4770 (effective concentration 60% by mass, ratio of mass remaining in rubber membrane to the amount of collected sample = 0.6), endothermic peak temperature in DSC of 450°C

Ashless dispersant 6: polybutenyl succinimide, Mn 7630 (effective
30 concentration 45% by mass, ratio of mass remaining in rubber membrane to the amount of collected sample = 0.45), endothermic peak temperature in DSC of 453°C

[0093] Metallic detergent 1: overbased calcium salicylate, base number of 320 mg KOH/g, endothermic peak temperature in DSC of 403°C

Metallic detergent 2: overbased calcium sulfonate, base number of 400 mg KOH/g, endothermic peak temperature in DSC of 449°C

Metallic detergent 3: overbased calcium sulfonate, base number of 400 mg KOH/g, endothermic peak temperature in DSC of 470°C

5 Metallic detergent 4: overbased calcium sulfonate, base number of 400 mg KOH/g, endothermic peak temperature in DSC of 481°C

Metallic detergent 5: overbased calcium sulfonate, base number of 400 mg KOH/g, endothermic peak temperature in DSC of 498°C

10 Metallic detergent 6: overbased calcium sulfonate, base number of 400 mg KOH/g, endothermic peak temperature in DSC of 512°C

Metallic detergent 7: overbased calcium phenate, base number of 150 mg KOH/g, endothermic peak temperature in DSC of 484°C

[0094] As illustrated in Table 1, the height of the ash showed an excellent correlation with the piston top land rating in the Ricardo WD300 engine test.
15 In other words, when the height of the ash exceeded 2 mm, the deposit rating exceeded 3.5, indicating little presence of deposits.

[0095] Furthermore, whereas the ash height and the piston top land rating were both high for the cylinder lubricating oil composition in the Examples, the ash height and the piston top land rating were both low for the cylinder
20 lubricating oil composition in Comparative Examples 2 to 4, in which the product of the number average molecular weight, the content, and the effective concentration of the ashless dispersant is less than 9000, and for the cylinder lubricating oil composition in Comparative Examples 5 to 8, which do not include a metallic detergent with an endothermic peak temperature of
25 less than 460°C.

CLAIMS

1. A cylinder lubricating oil composition for a crosshead diesel engine, comprising an ashless dispersant (B) and a metallic detergent (C) in a
5 lubricant base oil (A), wherein

a product of a number average molecular weight, a content, and an effective concentration of the ashless dispersant (B) is at least 9000, and
an endothermic peak temperature of the metallic detergent (C) as measured by DSC at a rate of temperature increase of 50°C/min is at most
10 460°C.

2. The cylinder lubricating oil composition for a crosshead diesel engine according to claim 1, wherein the number average molecular weight of the ashless dispersant (B) is at least 2500.

15