

DESCRIPTION

CYLINDER LUBRICATING OIL COMPOSITION FOR CROSSHEAD DIESEL ENGINE

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TECHNICAL FIELD

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

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BACKGROUND ART

[0002] Cylinder oil for lubricating between the cylinder and piston and system oil responsible 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 detergency. 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 also needs to have the functions of neutralizing acidic components such as generated sulfuric acid and of preventing corrosion.

[0003] The base oils used in conventional lubricating oil are mainly manufactured by separating gasoline or a light oil component from crude oil by distillation, further subjecting the resulting atmospheric distillation residue to reduced-pressure distillation, bringing out the necessary viscosity fraction, and refining the result. These base oils are classified in group I under the API base oil categorization.

[0004] Since the sulfur content and the aromatic content included in the base oil adversely affect the oxidative stability of the base oil, the above-mentioned residue has in recent years started to be subjected to hydrocracking to manufacture a base oil with an extremely small sulfur content and aromatic content.

[0005] Petroleum-based wax, which is a by-product when manufacturing

wax or base oil manufactured by the Fischer-Tropsch process or the like, is also subjected to hydrocracking to manufacture base oils with an extremely high viscosity index. These base oils manufactured by hydrocracking are classified in group II or III under the API base oil categorization.

5 [0006] During the refining process of the former base oils (group I), many processes are used to employ a solvent such as furfural, phenol, methylpyrrolidone, or the like to selectively extract and remove unstable compounds centering on the aromatic content. By contrast, in the manufacturing method of the latter base oils, the aromatic content in the base
10 oils is extremely low, and there is nearly no need to undergo the above-described solvent refining processes. Therefore, the relative amount of base oil manufactured by undergoing a solvent refining process is declining.

[0007] When using heavy fuel, a polycyclic aromatic such as asphaltene is included in the heavy fuel, and in the case of internal combustion, the
15 polycyclic aromatic mixes into the lubricating oil as a portion of non-combusted material. This non-combusted material dissolves relatively easily in group I base oil yet has poor solubility in group II base oil and group III base oil. Therefore, the non-combusted material accumulates in the lubricating oil channel and the lubricated portion and also tends to suffer
20 oxidation degradation, thus forming deposits even more easily.

[0008] Furthermore, during manufacturing of group I base oil, the residue after reduced-pressure distillation of the atmospheric distillation residue is also subjected to solvent extraction to manufacture base oil. This base oil is generally referred to as bright stock, and while properties vary by process,
25 bright stock has at least a kinematic viscosity at 100°C of 15 mm²/s or more and is essential for manufacturing of high viscosity oil. As described above, however, manufacturing devices for group I base oil have decreased relatively in number, and the amount of production of bright stock is also declining.

30 CITATION LIST

Patent Literature

[0009] PTL 1: JP 2002-275491 A

PTL 2: JP 2002-515933 A

PTL 3: JP 2002-501974 A

PTL 4: JP 2002-500262 A

PTL 5: JP 2002-241780 A

SUMMARY OF INVENTION

5 (Technical Problem)

[0010] Based on these circumstances, as a cylinder lubricating oil composition for crosshead diesel engines that use heavy fuel, the present invention provides a cylinder lubricating oil composition for crosshead diesel engines that generates few deposits even when using a group II or group III
10 base oil.

[0011] As there is also demand for a cylinder lubricating oil composition for crosshead diesel engines to have high base oil viscosity, conventionally bright stock has been used in a portion of the base oil. As described above, however, the amount of production of bright stock is declining. Therefore, the
15 present invention also provides a cylinder lubricating oil composition for crosshead diesel engines that does not use such bright stock.

(Solution to Problem)

[0012] As a result of intensive research in order to resolve the above problems, the inventors discovered that adding an extract that is a by-product
20 yielded during solvent refining to a group II and/or group III base oil and furthermore using a specific synthetic oil as a substitute that provides the same level of viscosity as bright stock can contribute to resolving the above problems, thereby completing the present invention.

[0013] A cylinder lubricating oil composition for a crosshead diesel
25 engine according to the present invention comprises:

a base oil including

(A) a mineral lubricating base oil with a saturated hydrocarbon content of 90% by mass or more, a sulfur content of 0.03% by mass or less in terms of element content, a viscosity index of 80 or more, and a kinematic
30 viscosity at 100°C of 10 mm²/s to 20 mm²/s;

(B) 3% by mass or more, in terms of total content of the base oil, of an extract yielded as a by-product during solvent refining in a mineral lubricating base oil manufacturing process, the extract containing 15% or more of aromatic hydrocarbon compounds (%C_A) according to a composition

analysis method stipulated in ASTM D2140; and

(C) a high molecular weight compound based synthetic oil that is an olefin polymer having a carbon number of 4 or more or is a hydride thereof and that has a kinematic viscosity at 100°C of 20 mm²/s to 400 mm²/s,

5 the base oil being compounded with:

(D) a metallic detergent; and

(E) an ashless dispersant.

[0014] In the cylinder lubricating oil composition for a crosshead diesel engine according to the present invention, component (B) is preferably an
10 extract with a PCA content of less than 3% by mass.

[0015] In the cylinder lubricating oil composition for a crosshead diesel engine according to the present invention, component (B) is preferably an extract with an MI value of less than 1.0, a benzo[a]pyrene content of 1 mg/kg or less, and a particular aromatic compound (PAH) content of 10 mg/kg or
15 less.

[0016] In the cylinder lubricating oil composition for a crosshead diesel engine according to the present invention, component (C) is preferably a polybutene-based synthetic oil and/or a poly- α -olefin-based synthetic oil.

[0017] In the cylinder lubricating oil composition for a crosshead diesel
20 engine according to the present invention, kinematic viscosity at 100°C is preferably 12.5 mm²/s to 21.9 mm²/s, and a base number is preferably 20 mg KOH/g to 100 mg KOH/g (perchloric acid method).

(Advantageous Effect of Invention)

[0018] According to the present invention, as a cylinder lubricating oil
25 composition for crosshead diesel engines that use heavy fuel, it is possible to provide a cylinder lubricating oil composition for crosshead diesel engines that generates few deposits even when using a group II or group III base oil.

[0019] According to the present invention, it is also possible to provide a cylinder lubricating oil composition for crosshead diesel engines that does not
30 use bright stock.

DESCRIPTION OF EMBODIMENTS

[0020] The present invention is described below in detail. The base oil in a cylinder lubricating oil composition for a crosshead diesel engine according to

the present invention (also referred to below simply as a lubricating oil composition) includes the following:

(A) a mineral lubricating base oil with a saturated hydrocarbon content of 90% by mass or more, a sulfur content of 0.03% by mass or less in terms of
5 element content, a viscosity index of 80 or more, and a kinematic viscosity at 100°C of 10 mm²/s to 20 mm²/s;

(B) 3% by mass or more, in terms of total content of the base oil, of an extract yielded as a by-product during solvent refining in a mineral lubricating base oil manufacturing process, the extract containing 15% or more of
10 aromatic hydrocarbon compounds (%C_A) according to a composition analysis method prescribed in ASTM D2140; and

(C) a high molecular weight compound based synthetic oil that is an olefin polymer having a carbon number of 4 or more or is a hydride thereof and that has a kinematic viscosity at 100°C of 20 mm²/s to 400 mm²/s.

15 **[0021]** Component (A) is a mineral lubricating base oil with a saturated hydrocarbon content of 90% by mass or more, a sulfur content of 0.03% by mass or less in terms of element content, a viscosity index of 80 or more, and a kinematic viscosity at 100°C of 10 mm²/s to 20 mm²/s, and is classified as group II or group III in accordance with base oil classification by the
20 American Petroleum Institute (API). In the present invention, the saturated hydrocarbon content denotes the value measured by ASTM D-2007.

[0022] The manufacturing method of the above mineral lubricating base oil is not particularly limited, yet typically, the atmospheric residual oil yielded by subjecting crude oil to atmospheric distillation is subjected to
25 desulfurization and hydrocracking, and then to fractional distillation to a set viscosity grade. Alternatively, the residual oil is subjected to solvent dewaxing or catalytic dewaxing, and as necessary, further subjected to solvent extraction and hydrogenated to yield the base oil.

[0023] Component (A) also includes the case of a petroleum wax
30 isomerization lubricating base oil yielded by hydroisomerization of petroleum wax that is a by-product yielded during a dewaxing process in a process for manufacturing base oil performed in recent years, whereby the atmospheric distillation residual oil is further subjected to reduced-pressure distillation and to fractional distillation to the necessary viscosity grade, and then after

undergoing processes such as solvent refining, hydrotreating, and the like, the result is subjected to solvent dewaxing. Additionally, component (A) includes the case of a GTL-based wax isomerization lubricating base oil manufactured by a method to isomerize GTL WAX (gas-to-liquid wax) manufactured by a process such as a Fischer-Tropsch process, and the like. The method of manufacturing the wax isomerization lubricating base oil in this case has the same basic manufacturing process as the manufacturing process for hydrocracked base oil.

[0024] The total aromatic content in the mineral lubricating base oil in component (A) is not particularly limited, yet the total aromatic content is 3% by mass or less in one embodiment, 1% by mass or less in another embodiment, and 0.5% by mass or less in yet another embodiment. As the total aromatic content in the mineral lubricating base oil is smaller, i.e. as aromaticity is lower, the problem of solubility of sludge occurs more easily. Note that the above total aromatic content denotes the aromatic fraction content measured in conformity with ASTM D2549.

[0025] The sulfur content of the mineral lubricating base oil that is component (A) is 0.03% by mass or less. In one embodiment, the sulfur content is 0.01% by mass or less, and in another embodiment, the mineral lubricating base oil substantially does not include sulfur. A lower sulfur content means a higher degree of refinement, making the problem of solubility of sludge occur more easily.

[0026] The kinematic viscosity at 100°C of the mineral lubricating base oil that is component (A) is 10 mm²/s to 20 mm²/s, preferably 10 mm²/s to 16 mm²/s, and particularly preferably 10 mm²/s to 15 mm²/s. When the kinematic viscosity at 100°C of the mineral lubricating base oil exceeds 20 mm²/s, the low temperature viscosity characteristics worsen, whereas when the kinematic viscosity is less than 10 mm²/s, oil film formation is insufficient at the lubrication spot, causing lubricity to deteriorate and loss of lubricating base oil by evaporation to increase. Note that in the present invention, the kinematic viscosity at 100°C refers to the kinematic viscosity at 100°C as prescribed by ASTM D-445.

[0027] The viscosity index of the mineral lubricating base oil that is component (A) is 80 or more. The viscosity index is 95 or more in one

embodiment and is 105 or more in another embodiment. As the viscosity index of the mineral lubricating base oil is higher, the problem of solubility of sludge occurs more easily. Note that in the present invention, the viscosity index denotes the viscosity index measured in conformity with JIS

5 K2283-2000.

[0028] On the other hand, no particular restriction is placed on the upper limit of the viscosity index of the mineral lubricating base oil, and a base oil with a viscosity index of approximately 125 to 170 may be used, such as normal paraffin, slack wax, GTL wax, or the like, or an isoparaffinic mineral
10 oil in which these are isomerized. With respect to low-temperature fluidity, however, the viscosity index of the mineral lubricating base oil is preferably 160 or less.

[0029] The content of the mineral lubricating base oil that is component (A) is preferably 65% by mass or more in terms of total content of the base oil,
15 more preferably 70% by mass or more, and even more preferably 75% by mass or more. Furthermore, the content is preferably 85% by mass or less and more preferably 80% by mass or less.

[0030] The base oil in the cylinder lubricating oil composition for crosshead diesel engines according to the present invention includes (B) 3%
20 by mass or more, in terms of total content of the base oil, of an extract yielded as a by-product during solvent refining in a mineral lubricating base oil manufacturing process.

[0031] The extract yielded as a by-product during solvent refining contains 70% to 99% aromatic compounds by column chromatography,
25 includes 15% or more of aromatic hydrocarbon compounds (%C_A) according to a composition analysis method stipulated in ASTM D2140, and includes 5% to 25% by mass of Polycyclic Aromatic (PCA) compounds extracted by dimethyl sulfoxide (DMSO) according to the IP 346 method prescribed by the Institute of Petroleum.

30 [0032] The method of manufacturing the extract yielded as a by-product during solvent refining is not particularly limited, yet one example thereof is to use oil obtained as follows: the lubricating oil fraction and reduced-pressure distillation residual oil obtained by reduced-pressure distillation of crude oil are subjected to deasphalting and subsequently to

dewaxing and hydrorefining as necessary, and then the oil is subjected to a solvent extraction process with a solvent having affinity for aromatic hydrocarbons.

[0033] The above solvent extraction process refers to an operation using a solvent to separate the oil into a raffinate with little aromatic content and an extract with a high aromatic content. As the solvent, furfural, phenol, cresol, sulfolane, N-methylpyrrolidone, dimethyl sulfoxide, formylmorpholine, a glycol-based solvent, or the like is used.

[0034] In recent years, however, importance has been placed on the carcinogenicity of Polycyclic Aromatic (PCA) compounds. In Europe, an indication of toxicity is required for oils and the like that include 3% by mass or more of PCA, and action is being taken to restrict their usage. Accordingly, the extract that is component (B) preferably has a PCA content of less than 3% by mass, i.e. the Polycyclic Aromatic (PCA) compound content extracted by dimethyl sulfoxide (DMSO) according to the IP 346 method prescribed by the Institute of Petroleum is preferably less than 3% by mass.

[0035] The content of PCA in the extract varies according to the separation capacity during the solvent extraction process, the solvent that is used, the stock oil / solvent ratio, the reaction temperature, and the like. Accordingly, by appropriately changing these conditions, the PCA content can be controlled to be 3% by mass or less. Furthermore, in order to control the PCA content of the extract to be 3% by mass or less, a hydrocracking process is preferably used.

[0036] The method of manufacturing the extract as component (B) with a PCA content of less than 3% by mass is not limited, yet the following method of manufacturing is provided as an example.

[0037] JP H6-505524 A discloses a process to manufacture process oil with the PCA content reduced to less than 3% by mass by subjecting reduced-pressure distillation residue to deasphalting and dewaxing the resulting oil. JP H7-501346 A discloses a non-carcinogenic bright stock extract as well as a deasphalted oil with a low PCA content and a production process thereof, and discloses an oil obtained by deasphalting residue in a vacuum distillation column, an oil with reduced aromatic compounds via an extraction process on deasphalted oil, and an oil obtained by the deasphalting

process.

[0038] JP H11-80751 A discloses a method of manufacturing that, by solvent extraction, uses a countercurrent extraction column to perform extraction under specific conditions to obtain, from a mineral-based hydrocarbon mixture, an extracted oil with a polycyclic aromatic compound content of less than 1.6% by mass by the IP 346 test method, and then by second-stage solvent extraction, obtains a mineral-based aromatic hydrocarbon oil, as an extracted oil, with a polycyclic aromatic compound content of less than 3% by mass by the IP 346 test method.

10 [0039] Furthermore, JP 2000-80208 A discloses a method of manufacturing rubber process oil including a raw material adjustment step to adjust stock oil selected from the group consisting of lubricating oil fraction by reduced-pressure distillation of crude oil and deasphalted oil by deasphalting reduced-pressure distillation residue of crude oil, and a solvent extraction step to perform solvent extraction on the stock oil with a solvent having selective affinity for aromatic hydrocarbons, wherein extraction conditions are set so that the polycyclic aromatic compound content of the extract determined in accordance with the IP 346 method is less than 3% by mass, and the aniline point is 80°C or less.

20 [0040] The extract that is component (B) preferably has low carcinogenicity due to PCA, as described above, and preferably has a mutagenicity index MI of less than 1.0. Of course, the extract more preferably has PCA of less than 3% by mass and a mutagenicity index MI of less than 1.0. The extract even more preferably has PCA of less than 3% by mass and a mutagenicity index MI of less than 0.4.

[0041] The mutagenicity index MI is the mutagenicity index MI as stipulated in conformity with the "Standard Test Method for Determining Carcinogenic Potential of Virgin Base Oils in Metalworking Fluids", stipulated in ASTM-E-1687-10.

30 [0042] The method of manufacturing the extract that is component (B) with a mutagenicity index MI of less than 1.0 is not particularly limited, yet as an example, process oil is disclosed in JP 3624646 B2.

[0043] Furthermore, the extract that is component (B) preferably has a benzo[a]pyrene (BaP) content of 1 mg/kg or less and a particular aromatic

compound (PAH) content of 10 mg/kg or less, since at these values, there is no risk of carcinogenicity. Here, a particular aromatic compound (PAH) denotes the aromatic compounds (PAH) 1) to 8) below.

- 1) Benzo[a]pyrene (BaP)
- 5 2) Benzo[e]pyrene (BeP)
- 3) Benzo[a]anthracene (BaA)
- 4) Chrysene (CHR)
- 5) Benzo[b]fluoranthene (BbFA)
- 6) Benzo[j]fluoranthene (BjFA)
- 10 7) Benzo[k]fluoranthene (BkFA)
- 8) Dibenzo[a,h]anthracene (DBAhA)

Note that quantitative analysis by GC-MS analysis can be performed for these particular aromatic compounds on test material prepared by separating and concentrating the target component and then adding an internal standard
15 material.

[0044] The method of manufacturing the extract for which the benzo[a]pyrene (BaP) content is 1 mg/kg or less and the particular aromatic compound (PAH) content is 10 mg/kg or less is not limited. For example, JP 2010-229314 A discloses a method of manufacturing an extract for which
20 the %C_A by ASTM D3238 is 25 to 45, the benzo[a]pyrene (BaP) content is 1 mg/kg or less, and the particular aromatic compound (PAH) content is 10 mg/kg or less.

[0045] The extract that is component (B) preferably has a bay proton concentration (%H_{Bay}) of less than 0.35%. Here, bay protons refer to the ratio
25 of hydrogen atoms in a portion called the "Bay region", surrounded by condensed benzene rings, as measured by ¹H-NMR. The bay proton concentration is used to judge the carcinogenicity due to the structure of an aromatic compound. The measurement method is ISO 21461, "Rubber-Determination of the aromaticity of oil in vulcanized rubber
30 compound". It is said that carcinogenicity is higher as the bay proton concentration is higher, and a bay proton concentration of less than 0.35% is preferable.

[0046] The extract that is component (B) particularly preferably has a benzo[a]pyrene (BaP) content of 1 mg/kg or less, a particular aromatic

compound (PAH) content of 10 mg/kg or less, a bay proton concentration (%H_{Bay}) of less than 0.35%, and a mutagenicity index MI of less than 1.0.

[0047] In the present invention, the kinematic viscosity at 100°C of the extract that is component (B) is preferably 5 mm²/s to 100 mm²/s. If the
5 kinematic viscosity at 100°C exceeds 100 mm²/s, workability decreases. On the other hand, if the kinematic viscosity at 100°C is less than 5 mm²/s, it becomes extremely difficult to ensure sufficient aromaticity, which may prevent the effects of the present invention from being achieved. Furthermore, the kinematic viscosity at 100°C is preferably 50 mm²/s or less and preferably
10 20 mm²/s or more. If the kinematic viscosity at 100°C is 50 mm²/s or less, the high temperature detergency is high. The high temperature detergency is also high if the kinematic viscosity at 100°C is 20 mm²/s or more.

[0048] When the %C_A (ASTM D2140) of the extract that is component (B) is less than 15%, the solubility might not be sufficient. On the other hand,
15 a %C_A (ASTM D2140) of the extract that exceeds 50% is not preferable, since it becomes extremely difficult to set the DMSO extractable portion to less than 3%, thus worsening the economic efficiency of the manufacturing process.

[0049] The aniline point of the extract that is component (B) is preferably
20 90°C or less. An aniline point of the extract that exceeds 90°C is not preferable, since the solubility decreases.

[0050] If the aromatic content by column chromatography of the extract that is component (B) is less than 60%, the solubility may decrease. On the other hand, an aromatic content by column chromatography of the extract that
25 exceeds 95% is not preferable, since it becomes extremely difficult to set the DMSO extractable portion to less than 3%, worsening the economic efficiency of the manufacturing process.

[0051] The content of the extract that is component (B) is 3% by mass or more, preferably 5% by mass or more, and more preferably 10% by mass or
30 more in terms of total content of the base oil. The content of the extract is preferably 90% by mass or less and more preferably 80% by mass or less in terms of total content of the base oil. If the content of the extract that is component (B) is less than 3% by mass, the piston detergency worsens, whereas upon exceeding 90% by mass, the viscosity index decreases, yielding

a larger increase in viscosity at low temperatures. Therefore, contents of less than 3% by mass and more than 90% by mass are not preferable.

[0052] The base oil in the cylinder lubricating oil composition for crosshead diesel engines according to the present invention includes, as
5 component (C), a high molecular weight compound based synthetic oil that is an olefin polymer having a carbon number of 4 or more or is a hydride thereof and that has a kinematic viscosity at 100°C of 20 mm²/s to 400 mm²/s. As described above, one of the objectives of the component (C) is to raise the viscosity of the base oil. Accordingly, a kinematic viscosity at 100°C of the
10 component (C) of less than 20 mm²/s is not preferable, since the viscosity of the base oil does not rise sufficiently, preventing sufficient lubricity of the engine. On the other hand, a kinematic viscosity at 100°C of the component (C) of more than 400 mm²/s is not preferable, because the piston detergency worsens, and because there is a risk of the amount of exhaust-related carbon
15 sediment increasing.

[0053] Component (C) is not particularly limited, as long as it is a high molecular weight compound based synthetic oil that is an olefin polymer having a carbon number of 4 or more or is a hydride thereof and that has a kinematic viscosity at 100°C of 20 mm²/s to 400 mm²/s. However, a
20 polybutene-based synthetic oil, a poly- α -olefin-based synthetic oil (PAO), or a hydride of these oils is preferable, and polybutene is particularly preferable. Polybutene is a polymer of butene, which is an olefin having a carbon number of 4.

[0054] The polybutene-based synthetic oil or hydride thereof that is
25 component (C) normally refers to a copolymeric substance, or the hydrogenated and saturated double bond of a copolymeric substance, obtained by cationic polymerization, using a catalyst such as aluminum chloride or the like, of the remnant after extracting butadiene from the C₄ fraction generated when producing ethylene or propylene by cracking naphtha, i.e. the
30 butane-butene fraction. Here, the term "butane-butene fraction" includes isobutane, n-butane, isobutylene, 1-butene, trans-2-butene, cis-2-butene, and the like.

[0055] The kinematic viscosity at 100°C of the polybutene-based synthetic oil or hydride thereof is preferably 60 mm²/s or more and more preferably 100

mm²/s or more, and is preferably 350 mm²/s or less and more preferably 250 mm²/s or less. When the kinematic viscosity at 100°C of the polybutene-based synthetic oil or hydride thereof is 60 mm²/s or more, the viscosity of the base oil rises sufficiently, thus achieving sufficient engine lubricity. When the
5 kinematic viscosity is 250 mm²/s or less, the piston detergency is good, and the increase in the amount of exhaust-related carbon sediment can be suppressed.

[0056] The polybutene-based synthetic oil or hydride thereof preferably has a number average molecular weight of 500 or more and less than 1500.
10 The number average molecular weight is more preferably 1300 or less, even more preferably 1000 or less, and particularly preferably from 700 to 1000. When the number average molecular weight of the polybutene-based synthetic oil or hydride thereof is 500 or more, the viscosity of the base oil rises sufficiently, thus achieving sufficient engine lubricity. When the number
15 average molecular weight is less than 1500, the piston detergency is good, and the increase in the amount of exhaust-related carbon sediment can be suppressed.

[0057] The poly- α -olefin-based synthetic oil (PAO) or hydride thereof that is the component (C) is an oligomer or co-oligomer of an α -olefin with a
20 carbon number of 8 to 14, or a hydride thereof. Examples of an α -olefin with a carbon number of 8 to 14 include 1-octene, 1-decene, 1-dodecene, and the like.

[0058] The method of manufacturing the poly- α -olefin-based synthetic oil is not particularly limited, yet an example is a method to polymerize α -olefin
25 in the presence of polymerization catalysts such as aluminum trichloride or borontrifluoride, water, and alcohol (ethanol, propanol, butanol, or the like).

[0059] The kinematic viscosity at 100°C of the poly- α -olefin-based synthetic oil or hydride thereof is 20 mm²/s to 400 mm²/s, preferably 30 mm²/s or more, and more preferably 35 mm²/s or more. The kinematic
30 viscosity is also preferably 200 mm²/s or less and more preferably 160 mm²/s or less. A kinematic viscosity at 100°C of the poly- α -olefin-based synthetic oil or hydride thereof of less than 20 mm²/s is not preferable, since the viscosity does not rise sufficiently, preventing sufficient lubricity of the engine. On the other hand, when the kinematic viscosity at 100°C of the

poly- α -olefin-based synthetic oil or hydride thereof is 200 mm²/s or less, the piston detergency is good, and the increase in the amount of exhaust-related carbon sediment can be suppressed.

[0060] The content of the component (C), i.e. the high molecular weight compound based synthetic oil that is an olefin polymer having a carbon number of 4 or more or is a hydride thereof and that has a kinematic viscosity at 100°C of 20 mm²/s to 400 mm²/s, is preferably in a range of 5% to 60% by mass, more preferably 50% by mass or less, even more preferably 40% by mass or less, and most preferably 30% by mass or less in terms of total content of the base oil. If the content of the component (C) is less than 5% by mass, it becomes difficult to ensure the minimum viscosity for cylinder oil, whereas if the content exceeds 60% by mass, viscosity is too high, which conversely leads to the risk of lubrication problems.

[0061] A synthetic oil-based base oil that does not fall under the component (C) may be mixed into the base oil of the lubricating oil composition according to the present invention. Specifically, examples of such a synthetic oil-based base oil include an oligomer of isobutene with a kinematic viscosity at 100°C of 3 mm²/s or more and less than 25 mm²/s, or a poly- α -olefin, or hydride thereof, that is an oligomer of an α -olefin with a carbon number of 8 to 14, representative examples of which include a homooligomer and/or a co-oligomer of 1-octene, 1-decene, and 1-dodecene; 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 a carbon number of 2 to 30; aromatic synthetic oils such as alkyl naphthalene, alkyl benzene, and aromatic esters, or mixtures thereof; and the like. Among these, a preferable synthetic oil-based base oil is an oligomer of an α -olefin with a carbon number of 8 to 14, called a poly- α -olefin, with a kinematic viscosity at 100°C of 4 mm²/s or more and less than 20 mm²/s.

[0062] In the lubricating oil composition according to the present invention, the kinematic viscosity at 100°C of the base oil that includes the mineral lubricating base oil that is component (A), the extract that is

component (B), and the high molecular weight compound based synthetic oil that is component (C) is preferably in a range of 10 mm²/s to 20 mm²/s, is more preferably 12 mm²/s or more, and is even more preferably 15 mm²/s or more. The kinematic viscosity is also preferably 19 mm²/s or less and more preferably 18 mm²/s or less. If the kinematic viscosity at 100°C of the base oil is less than 10 mm²/s, there is a risk of lubricity deteriorating since the oil film formation is insufficient at the lubrication spot, and of an increase in the loss of base oil by evaporation. If the kinematic viscosity at 100°C of the base oil exceeds 20 mm²/s, there is a risk of a problem occurring in fluidity at low temperatures.

[0063] The %C_A by n-d-m ring analysis (ASTM D3238) of the base oil component having the component (A) and the component (B) mixed therein, multiplied by the content ratio of the component (A) and the component (B) in the total base oil, is preferably a value of 1% or more. This value is more preferably 2% or more, preferably 20% or less, and more preferably 17% or less. A value of less than 1% is not preferable since solubility and detergency worsen, whereas a value exceeding 20% is not preferable, since the viscosity index worsens.

[0064] In the base oil that includes the component (A), the component (B), and the component (C), the aromatic content by alumina silica chromatographic analysis is preferably 4% by mass or more, more preferably 7% by mass or more, preferably 60% by mass or less, and more preferably 40% by mass or less. An aromatic content of the base oil of less than 4% is not preferable since solubility and detergency worsen, whereas an aromatic content exceeding 60% is not preferable, since the viscosity index worsens.

[0065] In the base oil that includes the component (A), the component (B), and the component (C), the %C_A by n-d-m ring analysis (ASTM D3238) of the base oil component having the component (A) and the component (B) mixed therein, multiplied by the content ratio of the component (A) and the component (B) in the total base oil, is preferably a value of 1% or more and 20% or less, and the aromatic content by alumina silica chromatographic analysis is preferably 4% by mass or more and 60% by mass or less.

Furthermore, in the base oil that includes the component (A), the component (B), and the component (C), the %C_A by n-d-m ring analysis

(ASTM D3238) of the base oil component having the component (A) and the component (B) mixed therein, multiplied by the content ratio in the total base oil of the component (A) and the component (B), is particularly preferably a value of 2% or more and 17% or less, and the aromatic content by alumina
5 silica chromatographic analysis is particularly preferably 7% by mass or more and 40% by mass or less.

[0066] The amount of loss by evaporation of the base oil of the lubricating oil composition according to the present invention is preferably a NOACK evaporation amount of 20% by mass or less, more preferably 16% by mass or
10 less, and particularly preferably 10% by mass or less. A NOACK evaporation amount of the base oil that exceeds 20% by mass is not preferable, since the evaporation loss of the lubricating oil composition grows large, causing an increase in viscosity and the like. The NOACK evaporation loss referred to here is a measurement of the evaporation loss of base oil measured in
15 conformity with ASTM D5800.

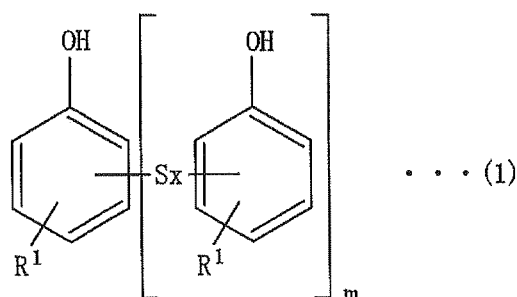
[0067] The cylinder lubricating oil composition for crosshead diesel engines according to the present invention includes (D) a metallic detergent (also referred to below as component (D)) as an essential component.

[0068] Any compound normally used in lubricating oil can be used as the
20 metallic detergent of the component (D). 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.

[0069] Examples of a sulfonate detergent that can be used include an
25 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 alkaline earth metal include sodium, potassium, magnesium, barium, and calcium. Magnesium and calcium are
30 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. The synthetic sulfonic acid may, for example, be the result of sulfonating an alkyl benzene having a straight-chain or branched alkyl group obtained as a by-product from a plant for producing alkyl benzene used as the raw material for a detergent or
 5 obtained by an alkylation of a polyolefin in benzene. 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.

10 [0070] 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 (1) may be used. Examples of the alkali metal or alkaline earth metal include sodium, potassium, magnesium, barium, and calcium. Magnesium and calcium are preferable, with calcium being
 15 particularly preferable.



[0071] In the formula (1), R¹ 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 represents elemental sulfur, and x represents an integer from 1 to 3.

[0072] The carbon number of the alkyl group or alkenyl group in the formula (1) is preferably from 9 to 18 and more preferably from 9 to 15. When
 25 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.

[0073] The phenate metal detergent preferably includes an alkylphenol sulfide metal salt for which the degree of polymerization m in the formula (1)

is 4 or more, particularly 4 to 5, since the resulting heat resistance is excellent.

[0074] Examples of the above salicylate detergent include an alkali metal, alkaline earth metal salicylate, or (overbased) basic salt thereof having one hydrocarbon group with a carbon number of 1 to 19; an alkali metal, alkaline earth metal salicylate, or (overbased) basic salt thereof having one hydrocarbon group with a carbon number of 20 to 40; and an alkali metal, alkaline 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, alkaline 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 alkaline earth metal include sodium, potassium, magnesium, barium, and calcium. Magnesium and/or calcium are preferable, with use of calcium being particularly preferable.

[0075] The base number of the component (D) 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 exceeding 500 mg KOH/g, problems may occur with solubility.

[0076] The metal ratio of the component (D) is not particularly limited, yet it is preferable to use a component (D) having a metal ratio with a lower limit preferably of 1 or more, more preferably 2 or more, and even more preferably 2.5 or more, and an upper limit of preferably 20 or less, more preferably 19 or less, and even more preferably 18 or less. 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 (D). Furthermore, the metal element refers to calcium, magnesium, or the like, and the soap group refers to a sulfonic acid group, phenol group, salicylic acid group, or the like.

[0077] In the lubricating oil composition according to the present invention, a single component (D) 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 / overbased Ca sulfonate, (2) overbased Ca phenate / overbased Ca salicylate, and (3) overbased Ca phenate / overbased Ca sulfonate / overbased Ca salicylate.

5 [0078] The preferable ratio for (1) overbased Ca phenate / overbased Ca sulfonate and (2) overbased Ca phenate / overbased Ca salicylate is 0.1 or more as a weight ratio of the additive blend, with 0.2 or more being more preferable and 0.3 or more being most preferable. The reason is that when the ratio is less than 0.1, heat resistance worsens. A ratio of 9 or less is preferable, with 7 or less being more preferable, and 5 or less being most preferable. The reason is that if the ratio exceeds 9, the height in the TGA burning test is insufficient, and the deposits on the piston top land are not sufficiently reduced.

10 [0079] 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 0.1 or more is preferable, with 0.2 or more being more preferable, and 0.3 or more 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 9 or less is preferable, with 7 or less being more preferable, and 5 or less being most preferable. A weight ratio exceeding 9 causes the detergency to decrease.

20 [0080] The content by percentage of the component (D) 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 the component (D) is less than 3% by mass, the necessary detergency 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.

30 [0081] The metal element content based on the component (D) 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 particularly preferably 1.4% to 2.7% by mass. When the metal element content based on the component (D) is less
5 than 0.7% by mass, the necessary detergency 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.

[0082] The cylinder lubricating oil composition for crosshead diesel
10 engines according to the present invention includes (E) an ashless dispersant (also referred to below as component (E)) as an essential component.

[0083] Any ashless dispersant used in lubricating oil may be used as the component (E). Examples include a nitrogen-containing compound or a derivative thereof having in the molecule at least one straight-chain or
15 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.

[0084] When the carbon number of the alkyl group or alkenyl group in the
20 nitrogen-containing compound or derivative thereof 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
25 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.

[0085] Examples of the component (E) include a single type, or two or more types, selected from among components (E-1) through (E-3) below.

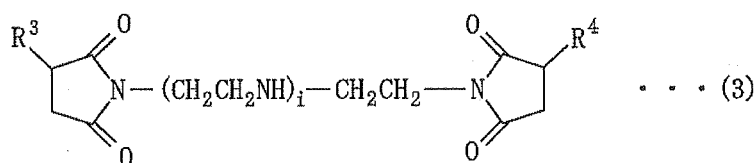
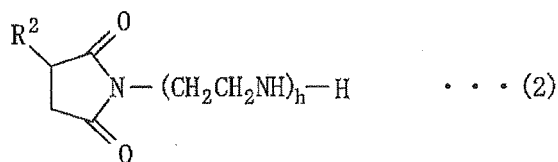
30 (E-1): succinimide, or a derivative thereof, containing at least one alkyl group or alkenyl group with a carbon number of 40 to 400 in the molecule;

(E-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

(E-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.

[0086] Examples of component (E-1) above include the compounds shown in the following formulas (2) and (3).

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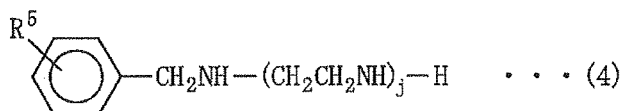
[0087] In the formula (2), R² represents an alkyl group or alkenyl group with a carbon number of 40 to 400, preferably 60 to 350, and h represents an integer from 1 to 5, preferably from 2 to 4.

[0088] In the formula (3), R³ and R⁴ 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.

15 [0089] Component (E-1) includes a so-called monotype succinimide
represented by the formula (2), in which succinic anhydride is attached to one
end of a polyamine, and a so-called bis-type succinimide represented by the
formula (3), in which succinic anhydride is attached to both ends of a
polyamine. Either, or a mixture of both, may be included in the composition
20 according to the present invention.

[0090] The method of manufacturing the succinimide in component (E-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.

[0091] Examples of component (E-2) above include the compound shown in the following formula (4).

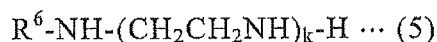


5

[0092] In the formula (4), R^5 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.

[0093] The method of manufacturing the benzylamine in component (E-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.

[0094] Examples of component (E-3) above include the compound shown in the following formula (5).



[0095] In the formula (5), R^6 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.

[0096] The method of manufacturing the polyamine in component (E-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, tetraethylenepentamine, or pentaethylenehexamine.

[0097] Examples of the derivative of a nitrogen-containing compound listed as an example of the component (E) include a so-called denatured compound from an oxygen-containing organic compound, in which a 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

30

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 nitrogen-containing compound, and a portion or the entirety of the remaining
5 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 so-called phosphoric acid denatured compound in which phosphoric acid is
10 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 compound; and a denatured compound in which the above-described
15 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 succinimide, in particular a boric acid denatured compound of a bis-type
20 alkenyl succinimide, can further enhance heat resistance by being used along with the above-described component (A).

[0098] The content by percentage of the component (E) in the lubricating oil composition according to the present invention is, in terms of total content of the composition, preferably 0.1% to 3.0% by mass, more preferably 0.2% to
25 2.5% by mass, and even more preferably 0.3% to 2.0% by mass. The content by percentage of the component (E) 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
30 boron-containing ashless dispersant as the component (E), the mass ratio 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 anti-scuffing performance, yet a ratio exceeding 1 leads to concerns about safety. When

using a boron-containing ashless dispersant, the content by percentage is not 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.

[0099] The component (E) in the lubricating oil composition of the present 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 bis-type boron-containing succinimide-based ashless dispersant is most preferably included. Note that the boron-containing ashless dispersant with 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.

[0100] The number average molecular weight (M_n) of the ashless dispersant of component (E) in the lubricating oil composition according to the present invention is preferably 2500 or more, more preferably 3000 or more, even more preferably 4000 or more, and most preferably 5000 or more. Furthermore, the number average molecular weight (M_n) is preferably 10000 or less. If the number average molecular weight of the ashless dispersant is less than 2500, dispersibility may be insufficient. 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.

[0101] In the present invention, the content and effective concentration of the ashless dispersant of component (E) are preferably such that the product of the number average molecular weight (M_n), the content, and the effective concentration of the ashless dispersant is 9000 or more. The effective concentration of the ashless dispersant of component (E) (the ratio of the mass remaining in the rubber membrane to the amount of the initially collected sample) is preferably in a range from 0.30 to 0.70, and the concentration in the composition of the ashless dispersant of component (E) (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 lubricating oil composition.

[0102] 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
5 include dihydrocarbyl polysulfide, sulfurized fatty acid, sulfurized olefin, sulfurized ester, sulfurized fat, sulfurized mineral oil, a thiazole compound, a thiadiazole compound, and an alkyl thiocarbamate compound.

[0103] The lubricating oil composition according to the present invention preferably includes an organic molybdenum compound. Examples of the
10 organic molybdenum compound include an organic molybdenum compound 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
15 sulfurized (poly)molybdic acid; a metal salt of these molybdic acids, or a 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
20 halogenated molybdenum such as molybdenum chloride) and a 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
25 sulfur-containing molybdenum compound, such as the above molybdenum sulfide and sulfurized molybdenum acid, and alkenyl succinimide.

[0104] Furthermore, as an antiwear agent, the lubricating oil composition according to the present invention preferably includes a zinc dithiophosphate (ZnDTP). Examples of the zinc dithiophosphate include zinc
30 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.

5 [0105] 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 may accordingly further include any additives that are typically used in a lubricating oil. Examples of such additives include antioxidants, ashless
10 friction modifiers, corrosion inhibitors, rust inhibitors, demulsifiers, metal deactivators, anti-foaming agents, and dyes.

[0106] Examples of the antioxidant include phenol-based or amine-based ashless antioxidants; and metallic antioxidants such as zinc-based, copper-based, and molybdenum-based antioxidants. When included, the
15 content of the antioxidant in terms of total content of the composition is normally 0.1% to 5% by mass.

[0107] 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%
20 to 5% by mass.

[0108] Examples of the corrosion inhibitor include benzotriazole-based, tolyltriazole-based, thiadiazole-based, and imidazole-based compounds.

[0109] Examples of the rust inhibitor include petroleum sulfonates, alkyl benzene sulfonates, dinonylnaphthalene sulfonates, alkenyl succinic acid
25 esters, and polyhydric alcohol esters.

[0110] 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.

[0111] Examples of the metal deactivator include imidazolines,
30 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.

[0112] 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.

[0113] When these additives are included in the lubricating oil composition according to the present invention, the content in terms of total
5 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.

[0114] The cylinder lubricating oil composition for crosshead diesel engines according to the present invention preferably has a kinematic
10 viscosity at 100°C of 12.5 mm²/s to 21.9 mm²/s. If the kinematic viscosity at 100°C of the lubricating oil composition is 12.5 mm²/s or more, the oil film forming ability is sufficient, and the occurrence of scuffing or the occurrence of excessive wear can be suppressed. Furthermore, if the kinematic viscosity is 21.9 mm²/s or less, sufficient lubricating performance that exhibits good
15 spread through the piston liner can be maintained.

[0115] In the cylinder lubricating oil composition for crosshead diesel engines according to the present invention, the base number is preferably 20 mg KOH/g (perchloric acid method) or more, more preferably 30 mg KOH/g or more, and even more preferably 40 mg KOH/g or more. Furthermore, the
20 base number is preferably 100 mg KOH/g (perchloric acid method) or less, more preferably 80 mg KOH/g or less, and even more preferably 70 mg KOH/g or less. If the base number of the lubricating oil composition is less than 20 mg KOH/g, the piston detergency is insufficient. Furthermore, a base number of the lubricating oil composition that exceeds 100 mg KOH/g yields
25 an excessive base number, i.e. metal carbonate forms deposits, leading to wear and to the piston ring sticking. In the present invention, the base number denotes the base number measured by a perchloric acid method in conformity with section 7 of JIS K2501, "Petroleum products and lubricants - Determination of neutralization number".

30 [0116] When both high sulfur fuel and low sulfur fuel are used, the base number is preferably 50 mg KOH/g or more, more preferably 60 mg KOH/g or more, and even more preferably 70 mg KOH/g or more. 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.

[0117] When only low sulfur fuel or gas fuel is used, the base number is preferably 60 mg KOH/g or less, more preferably 50 KOH/g or less, and even more preferably 45 mg KOH/g or less. If the base number exceeds 60 mg
5 KOH/g, then when using low sulfur fuel or gas fuel, there is a higher chance that the excessive base number, i.e. deposits forming due to metal carbonate, will lead to wear and to the piston ring sticking. In this case, the lower limit is as described above.

[0118] Note that "high sulfur fuel" as used herein refers to fuel with a
10 sulfur content of 3.5% by mass or more, and "low sulfur fuel" refers to fuel with a sulfur content of less than 1.0% by mass. Fuel with a sulfur content of 1.0% by mass or more 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 0.1% or less.

15 EXAMPLES

[0119] 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.

[0120] (Examples 1 to 15, Comparative Examples 1 to 6)

20 Lubricating oil compositions with the formulations shown in Tables 1 and 2 were prepared, and a hot tube test was performed in conformity with JPI-5S-55-99. Tables 1 and 2 list the results. Note that in Tables 1 and 2, the amount of the base oil is the content in terms of total content of the base oil, whereas the amount of the additives is the content in terms of total content of
25 the composition.

[0121] <Hot tube test>

In conformity with JPI-5S-55-99, a hot tube test was performed at 320°C and at 325°C, and assessment was performed by rating the depth of hue of the discolored portion in the test tube after the test (from 0 points (black) to 10
30 points (transparent = best)). A higher rating indicates better high temperature detergency.

[0122] [Table 1]

	Ex. 10	Ex. 11	Ex. 12	Ex. 13
5	75	70	70	
5	20	20		
			20	
				10
10				
	5	10		
4.9	1.6	4.1	2.5	
4.6	4.4	8.8	23.7	
4.6	1.4	2.8	13.2	
2.5	1.8	3.6	7.7	
4	1.2	2.4	2.8	
5.0	15.0	15.0	15.0	
0	5.0	5.0	5.0	
0.6	0.6	0.6	0.6	
0.5	0.5	0.5	0.5	
8.2	228.5	253.7	242.7	
0.2	20.2	21.1	20.6	
0.5	69.6	69.9	69.5	
0.1	102	98	99	
			7.5	
0.5	6.5	7.0	2.0	

ral base oil + extract) in the base oil

			Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
Base oil	Mineral base oil 1	% by mass	70	65	50	57	49	31	25	19
	Mineral base oil 2	% by mass			31					
	Synthetic oil 1	% by mass	25	25	9	23	21	19	15	11
	Synthetic oil 2	% by mass								
	Synthetic oil 3	% by mass								
	Synthetic oil 4	% by mass								
	Synthetic oil 5	% by mass								
	Extract 1	% by mass	5	10	10	20	30	50	60	70
	Extract 2	% by mass								
	Extract 3	% by mass								
%C _A in base oil *		%C _A	1.1	2.5	2.4	5.8	8.0	12.4	14.7	17.0
Aromatic content in base oil	Total aromatic content	% by mass	4.0	7.9	7.9	15.8	23.7	39.6	47.5	55.4
	Monocyclic aromatic	% by mass	2.2	4.4	4.4	8.8	13.2	22.0	26.4	30.8
	Bicyclic aromatic	% by mass	1.3	2.6	2.6	5.1	7.7	12.8	15.4	17.9
	Tricyclic or higher aromatic	% by mass	0.5	0.9	0.9	1.9	2.8	4.7	5.6	6.6
Additive	(D) Ca sulfonate	% by mass	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
	(D) Ca phenate	% by mass	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	(E) Dispersant	% by mass	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
	(F) Antioxidant	% by mass	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Kinematic viscosity of composition	40°C	mm ² /s	239.6	247.4	243.5	253.5	265.5	296.5	291.4	283.7
	100°C	mm ² /s	20.7	21.0	21.0	20.9	21.2	21.8	20.9	20.3
Base number of composition (perchloric acid method)		mg KOH/g	69.5	69.7	69.5	69.6	69.8	69.5	69.5	69.6
Viscosity index of composition			101	100	102	97	95	89	84	82
Hot tube test	Rating (320°C)									
	Rating (325°C)		7.0	7.5	7.5	7.5	7.5	8.0	8.5	8.5

* value for %C_A (ASTM D3238) in the (mineral base oil + extract) calculated by a formula for m-d-i analysis, multiplied by the conte

[0123] [Table 2]

Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
74	81	55	50
25			
	9		
		35	30
1	10	10	20
0.2	2.3	2.6	5.6
0.8	7.9	7.9	15.8
0.4	4.4	4.4	8.8
0.3	2.6	2.6	5.1
0.1	0.9	0.9	1.9
5.0	15.0	15.0	15.0
5.0	5.0	5.0	5.0
0.6	0.6	0.6	0.6
0.5	0.5	0.5	0.5
34.8	242.0	217.4	218.9
0.7	21.9	21.8	21.5
9.5	69.6	69.8	69.5
03	109	121	117
	7.5	8.0	
0.0	0.0	0.0	0.0

n-d-i analysis, multiplied by the

			Ex. 14	Ex. 15	Comp Ex. 1
Base oil	Mineral base oil 1	% by mass	50	60	75
	Mineral base oil 2	% by mass			
	Synthetic oil 1	% by mass			25
	Synthetic oil 2	% by mass			
	Synthetic oil 3	% by mass			
	Synthetic oil 4	% by mass			
	Synthetic oil 5	% by mass	40	30	
	Extract 1	% by mass	10		
	Extract 2	% by mass			
	Extract 3	% by mass		10	
%C _A in base oil *		%C _A	2.7	4.2	0.0
Aromatic content in base oil	Total aromatic content	% by mass	7.9	8.8	0.0
	Monocyclic aromatic	% by mass	4.4	2.8	0.0
	Bicyclic aromatic	% by mass	2.6	3.6	0.0
	Tricyclic or higher aromatic	% by mass	0.9	2.4	0.0
Additive	(D) Ca sulfonate	% by mass	15.0	15.0	15.0
	(D) Ca phenate	% by mass	5.0	5.0	5.0
	(E) Dispersant	% by mass	0.6	0.6	0.6
	(F) Antioxidant	% by mass	0.5	0.5	0.5
Kinematic viscosity of composition	40°C	mm ² /s	210.9	216.9	231.7
	100°C	mm ² /s	21.9	21.56	20.6
Base number of composition (perchloric acid method)		mg KOH/g	69.6	69.8	69.6
Viscosity index of composition			125	119	104
Hot tube test	Rating (320°C)		8.0		6.0
	Rating (325°C)		8.0	7.5	0.0

* value for %C_A (ASTM D3238) in the (mineral base oil + extract) calculated
content ratio of (mineral base oil + extract) in the base oil

[0124] Mineral base oil 1: group II base oil, kinematic viscosity at 40°C =
93.9 mm²/s, kinematic viscosity at 100°C = 10.7 mm²/s, viscosity index =
97, %C_A = 0, %C_N = 33.9, %C_P = 66.1, nitrogen content = less than 3 ppm,
sulfur content = 0.01% by mass, saturated hydrocarbon content = 98.9% by
mass

Mineral base oil 2: group II base oil, kinematic viscosity at 40°C = 387.3
mm²/s, kinematic viscosity at 100°C = 29.4 mm²/s, viscosity index =

105, %C_A = 0, %C_N = 28.8, %C_P = 71.2, nitrogen content = less than 0.01% by mass, sulfur content = 4 mass ppm, saturated hydrocarbon content = 99.1% by mass

[0125] Synthetic oil 1: polybutene, kinematic viscosity at 40°C = 3450 mm²/s, kinematic viscosity at 100°C = 110 mm²/s, viscosity index = 98, number average molecular weight = 800

Synthetic oil 2: polybutene, kinematic viscosity at 40°C = 9500 mm²/s, kinematic viscosity at 100°C = 220 mm²/s, viscosity index = 107, number average molecular weight = 980

10 Synthetic oil 3: polybutene, kinematic viscosity at 40°C = 160000 mm²/s, kinematic viscosity at 100°C = 3710 mm²/s, viscosity index = 257, number average molecular weight = 2900

Synthetic oil 4: ethylene and co-oligomer of α-olefin, kinematic viscosity at 40°C = 400 mm²/s, kinematic viscosity at 100°C = 40 mm²/s, viscosity index = 150, number average molecular weight = 1000

Synthetic oil 5: poly-α-olefin (PAO), α-olefin polymers with carbon numbers of 8, 10, and 12, kinematic viscosity at 40°C = 396 mm²/s, kinematic viscosity at 100°C = 39 mm²/s, viscosity index = 147, number average molecular weight = 2000

20 [0126] Extract 1: TDAE, kinematic viscosity at 40°C = 274.8 mm²/s, kinematic viscosity at 100°C = 14.8 mm²/s, viscosity index = 11, %C_A = 24.2, %C_N = 22.3, %C_P = 53.5, nitrogen content = 370 ppm, sulfur content = 3.3% by mass, DMSO extraction PCA amount = 2.7% by mass

25 Extract 2: TDAE, kinematic viscosity at 40°C = 1185 mm²/s, kinematic viscosity at 100°C = 34.1 mm²/s, viscosity index = 14, %C_A = 29.5, %C_N = 16.3, %C_P = 54.2, nitrogen content = 870 ppm, sulfur content = 3.8% by mass, DMSO extraction PCA amount = 2.8% by mass

30 Extract 3: RAE, kinematic viscosity at 40°C = 3739 mm²/s, kinematic viscosity at 100°C = 70.5 mm²/s, viscosity index = 36, %C_A = 33.8, %C_N = 7.2, %C_P = 59.0, nitrogen content = 1500 ppm, sulfur content = 3.7% by mass, benzo[a]pyrene content = less than 0.5 mg/kg, 8 types of PAH (* (1) benzo[a]anthracene, (2) benzo[b]fluoranthene, (3) benzo[j]fluoranthene, (4) benzo[k]fluoranthene, (5) benzo[a]pyrene, (6) dibenzo[a,h]anthracene, (7) triphenylene, (8) chrysene)) = less than 1.6 mg/kg, MI value = less than 0.4

[0127] Ca sulfonate: 400 mg KOH/g

Ca phenate: 150 mg KOH/g

Dispersant: boronated alkenylsuccinimide, boron content = 1.9% by mass

5 Antioxidant: zinc-based antioxidant, amine-based antioxidant

[0128] The results for Examples 1 to 13 and Comparative Examples 1 and 2 show that as compared to the test oils with a base oil structure combining only polybutene with a group II type mineral base oil (Comparative Examples 1 and 2), the test oils that further combined an extract and added aromatic
10 content (Examples 1 to 13) exhibited excellent high temperature detergency.

[0129] Furthermore, the results for Examples 2 and 13 and Comparative Example 4 show that in the test oils with a base oil structure combining polybutene and an extract with a group II type mineral base oil, the high temperature detergency differs depending on the kinematic viscosity at 100°C
15 and the number average molecular weight of the polybutene, with excellent high temperature detergency being expressed when the polybutene has a kinematic viscosity at 100°C of 400 mm²/s or less and a number average molecular weight of 1000 or less.

[0130] Furthermore, the results for Examples 14 and 15 indicate good high
20 temperature detergency even when using poly- α -olefin (PAO) as a high viscosity base material in combination with a group II type mineral base oil and adding an extract.

[0131] The above results show that by combining a high molecular weight compound that is an olefin polymer with a carbon number of 4 or more, or a
25 hydride thereof, and an extract with a group II and/or group III type mineral base oil, it is possible to provide a cylinder oil having a proper amount of aromatic component content and excellent high temperature detergency, while maintaining an appropriate viscosity.

CLAIMS

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

5 a base oil including

(A) a mineral lubricating base oil with a saturated hydrocarbon content of 90% by mass or more, a sulfur content of 0.03% by mass or less in terms of element content, a viscosity index of 80 or more, and a kinematic viscosity at 100°C of 10 mm²/s to 20 mm²/s;

10 (B) 3% by mass or more, in terms of total content of the base oil, of an extract yielded as a by-product during solvent refining in a mineral lubricating base oil manufacturing process, the extract containing 15% or more of aromatic hydrocarbon compounds (%C_A) according to a composition analysis method stipulated in ASTM D2140; and

15 (C) a high molecular weight compound based synthetic oil that is an olefin polymer having a carbon number of 4 or more or is a hydride thereof and that has a kinematic viscosity at 100°C of 20 mm²/s to 400 mm²/s,

the base oil being compounded with:

(D) a metallic detergent; and

20 (E) an ashless dispersant.

2. The cylinder lubricating oil composition for a crosshead diesel engine according to claim 1, wherein component (B) is an extract with a PCA content of less than 3% by mass.

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3. The cylinder lubricating oil composition for a crosshead diesel engine according to claim 1 or 2, wherein component (B) is an extract with an MI value of less than 1.0, a benzo[a]pyrene content of 1 mg/kg or less, and a particular aromatic compound (PAH) content of 10 mg/kg or less.

30

4. The cylinder lubricating oil composition for a crosshead diesel engine according to any one of claims 1 to 3, wherein component (C) is a polybutene-based synthetic oil and/or a poly- α -olefin-based synthetic oil.

5. The cylinder lubricating oil composition for a crosshead diesel engine according to any one of claims 1 to 4, wherein kinematic viscosity at 100°C is 12.5 mm²/s to 21.9 mm²/s, and a base number is 20 mg KOH/g to 100 mg
- 5 KOH/g (perchloric acid method).