

SYSTEM LUBRICATING OIL COMPOSITION FOR CROSSHEAD-TYPE  
DIESEL ENGINE

**Technical Field**

[0001] The present invention relates to a system lubricating oil composition for a crosshead-type diesel engine.

**Background Art**

[0002] For a crosshead-type diesel engine, a cylinder oil for lubricating the friction point between the cylinders and pistons, and a system oil for lubricating and cooling other portions have been used. The cylinder oil is required to have a suitable viscosity needed to lubricate a friction portion between a cylinder and a piston (piston ring) and a function to maintain detergency needed to allow a piston and a piston ring to move appropriately. Furthermore, since for this engine, a high-sulfur content fuel is generally used for the economy reason, it has a problem that acidic components such as sulfuric acid generated by the combustion of the fuel corrode a cylinder. In order to avoid this problem, the cylinder oil is required to have a function to neutralize the acidic components such as sulfuric acid so as to prevent corrosion.

Whereas, the system oil does not contact combustion gas unlike the usual diesel engine oil and is a lubricating oil which is stored in a tank and supplied to bearings with a circulation pump for lubrication and cooling and is thus required to maintain a suitable viscosity for a long period of time because it is used for a long time unlike the cylinder oil (see, for example, Patent Literature 1 below). However, a crosshead-type engine for ships has a problem that the system oil is eventually increased in viscosity by being mixed with a drip oil, and how such viscosity increase should be suppressed has become a longstanding problem. In particular, due to the recent growing environment issue, emphasis has been on avoidance of a deterioration in fuel efficiency resulting from the increased friction loss at bearings involving the viscosity increase or of a decrease in the heat-exchange efficiency at piston surfaces to be cooled.

#### **Citation List**

##### **Patent Literature**

[0003] Patent Literature 1: Japanese Patent  
Laid-Open Publication No. 2002-275491

##### **Summary of Invention**

##### **Technical Problem**

[0004] The present invention has an object to provide a system lubricating oil composition for a crosshead-type diesel engine, which can prevent fuel efficiency deterioration by suppressing the viscosity increase.

#### **Solution to Problem**

[0005] As the results of extensive study and research, the present invention was accomplished on the basis of the finding that a lubricating oil composition containing a specific polymer can balance a viscosity increase caused by being mixed with a drip oil and a viscosity decrease due to thermal decomposition of a polymer and thus is an advantageously effective system lubricating oil composition for a crosshead-type diesel engine.

Specifically, a system oil comprising a lubricating base oil blended with a star polymer having a vinyl aromatic hydrocarbon structure in the molecule and/or an olefin copolymer, which have characteristics that are excellent in shear stability but likely to decompose with heat makes it possible to decrease the viscosity of the system oil by the decomposition of the polymer at piston surfaces to be cooled and thus balance out the viscosity increase caused by being mixed with a cylinder drip oil thereby suppressing fuel efficiency

deterioration.

[0006] That is, the present invention relates to a system lubricating oil composition for a crosshead-type diesel engine comprising a mineral base oil and/or a synthetic base oil, and (A) (a-1) a star polymer having a vinyl aromatic hydrocarbon structure in the molecule and/or (a-2) an ethylene- $\alpha$ -olefin copolymer or a hydrogenated compound thereof, and having a base number of 4 to 20 mgKOH/g and a 100°C kinematic viscosity of 7.5 to 15.0 mm<sup>2</sup>/s.

[0007] The present invention also relates to the foregoing system lubricating oil composition for a crosshead-type diesel engine wherein Component (a-1) is a compound having a structure wherein the polymer or copolymer of a diene extends radially from the core of the vinyl aromatic hydrocarbon located in the center of the molecule.

The present invention also relates to the foregoing system lubricating oil composition for a crosshead-type diesel engine wherein the vinyl aromatic hydrocarbon is divinylbenzene.

The present invention also relates to the foregoing system lubricating oil composition for a crosshead-type diesel engine wherein the polymer or copolymer of a diene is polyisoprene or an

isoprene-styrene copolymer.

[0008] The present invention also relates to the foregoing system lubricating oil composition for a crosshead-type diesel engine further comprising at least one type selected from the group consisting of (B) metal detergents, (C) zinc dialkyldithiophosphates, (D) rust inhibitors and (E) ashless dispersants.

The present invention also relates to the foregoing system lubricating oil composition for a crosshead-type diesel engine wherein the base oil has a 100°C kinematic viscosity of 3.5 to 9.3 mm<sup>2</sup>/s.

#### **Advantageous Effects of Invention**

[0009] The use of the system lubricating oil composition for a crosshead-type diesel engine of the present invention makes it possible to suppress the viscosity from increasing, resulting in inhibition of fuel efficiency deterioration.

#### **Description of Embodiments**

[0010] The present invention will be described in details below.

No particular limitation is imposed on the type of lubricating base oil to be used in the system lubricating oil composition for a crosshead-type diesel engine of the present invention (hereinafter merely referred to as "the lubricating oil composition

of the present invention"), which may be a mineral oil, a synthetic oil, or a mixture thereof.

[0011] Specific examples of the mineral base oil include those which can be produced by subjecting a lubricating oil fraction produced by vacuum-distilling an atmospheric distillation bottom oil resulting from atmospheric distillation of a crude oil, to any one or more treatments selected from solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, and hydrorefining; wax-isomerized mineral oils; and those produced by isomerizing GTL WAX (Gas to Liquid Wax) produced through Fischer-Tropsch process.

[0012] Specific examples of the synthetic base oil include polybutenes and hydrogenated compounds thereof; poly- $\alpha$ -olefins such as 1-octene oligomer and 1-decene oligomer, and hydrogenated compounds thereof; copolymers of ethylene having a weight average molecular weight of 8,000 or less and  $\alpha$ -olefins having 3 to 30 carbon atoms; diesters such as ditridecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate and di-2-ethylhexyl sebacate; polyol esters such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol 2-ethylhexanoate and pentaerythritol pelargonate; copolymers of dicarboxylic acids such as

dibutyl maleate and  $\alpha$ -olefins having 2 to 30 carbon atoms; aromatic synthetic oils such as alkylnaphthalenes, alkylbenzenes, and aromatic esters; and mixtures of the foregoing.

[0013] The lubricating base oil used in the lubricating oil composition of the present invention may be any one or more type of the mineral base oils or synthetic base oils or a mixture of one or more of the mineral base oils and one or more of the synthetic base oils.

[0014] The 100°C kinematic viscosity of the lubricating base oil used in the present invention is preferably 9.3 mm<sup>2</sup>/s or lower, more preferably 8.5 mm<sup>2</sup>/s or lower, more preferably 8.0 mm<sup>2</sup>/s or lower. Whereas, the 100°C kinematic viscosity is preferably 3.5 mm<sup>2</sup>/s or higher, more preferably 3.8 mm<sup>2</sup>/s or higher, more preferably 4.0 mm<sup>2</sup>/s or higher. The 100°C kinematic viscosity referred herein denotes one defined by ASTM D-445. If the 100°C kinematic viscosity is higher than 9.3 mm<sup>2</sup>/s, the resulting composition would be less in viscosity decrease and thus could not exhibit the effect of suppressing the viscosity increase when mixed with a cylinder drip oil. If the 100°C kinematic viscosity is lower than 3.5 mm<sup>2</sup>/s, the resulting composition would be decreased in viscosity too much

and thus could be deteriorated in oil film formation capability at bearings, possibly causing seizure.

[0015] No particular limitation is imposed on the 40°C kinematic viscosity of the lubricating base oil used in the present invention, which is, however, preferably 150 mm<sup>2</sup>/s or lower, more preferably 120 mm<sup>2</sup>/s or lower, more preferably 90 mm<sup>2</sup>/s or lower. Whereas, the 40°C kinematic viscosity is preferably 15 mm<sup>2</sup>/s or higher, more preferably 20 mm<sup>2</sup>/s or higher, more preferably 25 mm<sup>2</sup>/s or higher. If the 40°C kinematic viscosity is higher than 200 mm<sup>2</sup>/s, the resulting composition would be less in viscosity decrease and thus could not exhibit the effect of suppressing the viscosity increase when mixed with a cylinder drip oil. If the 40°C kinematic viscosity is lower than 50 mm<sup>2</sup>/s, the resulting composition would be decreased in viscosity too much and thus could be deteriorated in oil film formation capability at bearings, possibly causing seizure.

[0016] The viscosity index of the lubricating base oil used in the present invention is preferably 85 or greater, more preferably 90 or greater, more preferably 95 or greater. No particular limitation is imposed on the upper limit of the viscosity index. Normal paraffin, slack wax or GTL wax or isoparaffinic mineral

oils produced by isomerizing the foregoing may also be used.

The viscosity index referred herein denotes one measured in accordance with JIS K 2283-1993.

[0017] The lubricating oil composition of the present invention contains necessarily (a-1) a star polymer having a vinyl aromatic hydrocarbon structure in the molecule and/or (a-2) an ethylene- $\alpha$ -olefin copolymer or a hydrogenated compound thereof, as Component (A).

[0018] The star polymer having a vinyl aromatic hydrocarbon structure in the molecule that is Component (a-1) is a compound having a structure wherein the arms of polymers or copolymers of a number of (two or more) dienes extend radially from the core of the vinyl aromatic hydrocarbon located in the center of the molecule.

[0019] Examples of the vinyl aromatic hydrocarbon located in the center of the molecule include divinylbenzene, trivinylbenzene, tetravinylbenzene, divinylortho-, divinylmetha- or divinylpara-xylene, trivinylortho-, trivinylmetha- or trivinylpara-xylene, tetravinylortho-, tetravinylmetha- or tetravinylpara-xylene, divinyl naphthalene, divinylethylbenzene, divinylbiphenyl,

diisobutenylbenzene, diisopropenylbenzene, and diisopropenylbiphenyl. Among these compounds, preferred is divinylbenzene.

[0020] The diene monomer constituting the polymer or copolymer of dienes has preferably 4 to 12 carbon atoms. Specific examples include 1,3-butadiene, isoprene, piperylene, methylpentadiene, phenylbutadiene, 3,4-dimethyl-1,3-hexadiene, and 4,5-diethyl-1,3-octadiene. Preferred are 1,3-butadiene and isoprene.

Examples of the polymer or copolymer of dienes that will be a star polymer include homopolymers of diene such as polyisoprene and copolymers of diene such as isoprene-butadiene copolymer. Alternatively, copolymers of diene and other monomer that is not diene (for example, isoprene-styrene copolymer) may be used. The copolymer may be a random copolymer or a block copolymer.

[0021] Component (a-1) that is a star polymer having a vinyl aromatic hydrocarbon structure in the molecule used as Component (A) in the present invention has a weight average molecular weight (Mw) of preferably 10,000 or greater, more preferably 50,000 or greater, more preferably 100,000 or greater and preferably 1,000,000 or less, more preferably 800,000 or less,

more preferably 500,000 or less. If the weight average molecular weight is less than 10,000, the resulting composition could not exhibit sufficiently an viscosity adjustment effect but also the production cost could be increased. If the weight average molecular weight is greater than 1,000,000, the resulting composition could be poor in shear stability and could not exhibit an viscosity adjustment effect as well.

[0022] The PSSI (permanent shear stability index) of (a-1) the star polymer having a vinyl aromatic hydrocarbon structure in the molecule used in the present invention is preferably from 1 to 40, more preferably from 1 to 35, more preferably 1 to 30, particularly preferably from 1 to 25. If the PSSI is greater than 40, the resulting composition is poor in shear stability and thus could not exhibit sufficiently an viscosity adjustment effect. If the PSSI is less than 1, the resulting composition could not exhibit sufficiently an viscosity adjustment effect as well.

The term "PSSI" used herein denotes the permanent shear stability index of a polymer calculated on the basis of the data measured with ASTM D 6278-02 (Test Method for Shear Stability of Polymer Containing Fluids Using a European Diesel Injector Apparatus) in

conformity with ASTM D 6022-01 (Standard Practice for Calculation of Permanent Shear Stability Index).

[0023] The ethylene- $\alpha$ -olefin copolymer or a hydrogenated compound thereof that is Component (a-2) is a copolymer of ethylene and an  $\alpha$ -olefin or a compound produced by hydrogenating the copolymer. Specific examples of the  $\alpha$ -olefin include propylene, isobutylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, and 1-dodecene. The ethylene- $\alpha$ -olefin copolymer may be one consisting of hydrocarbons that is of non-dispersant type or one produced by reacting a copolymer with a polar compound such as a nitrogen-containing compound that is a dispersant-type ethylene- $\alpha$ -olefin copolymer. Among these compounds, the most preferred is an ethylene- $\alpha$ -propylene copolymer.

[0024] The ethylene- $\alpha$ -olefin copolymer or a hydrogenated compound thereof that is (a-2) used as Component (A) in the present invention has a weight average molecular weight (Mw) of preferably 10,000 or greater, more preferably 20,000 or greater, more preferably 50,000 and preferably 500,000 or less, more preferably 400,000 or less, more preferably 300,000. If the weight average molecular weight is less than 10,000, the resulting composition could not exhibit

sufficiently an viscosity adjustment effect but also the production cost could be increased. If the weight average molecular weight is greater than 500,000, the resulting composition could be poor in shear stability and thus could not exhibit an viscosity adjustment effect as well.

[0025] The PSSI (permanent shear stability index) of (a-2) the ethylene- $\alpha$ -olefin copolymer or a hydrogenated compound thereof is preferably from 1 to 75, more preferably from 3 to 50, more preferably from 5 to 30, particularly preferably from 10 to 28. If the PSSI is greater than 75, Component (a-2) would be poor in shear stability and thus could not exhibit a viscosity adjustment effect when added to a system oil. If the PSSI is less than 1, the resulting composition could not exhibit a viscosity adjustment effect as well.

[0026] The content of Component (A) in the lubricating oil composition of the present invention is preferably from 1 to 20 percent by mass, more preferably from 2 to 15 percent by mass, more preferably from 3 to 12 percent by mass, most preferably from 4 to 10 percent by mass on the basis of the total mass of the composition. If the content is less than 1 percent by mass, the resulting composition could not

exhibit sufficiently a viscosity adjustment effect. If the content is more than 20 percent by mass, the resulting composition could be poor in handling properties, possibly causing adverse affects on the production of the composition and also could be deteriorated in detergency due to the generation of deposit caused by the degradation of the polymer.

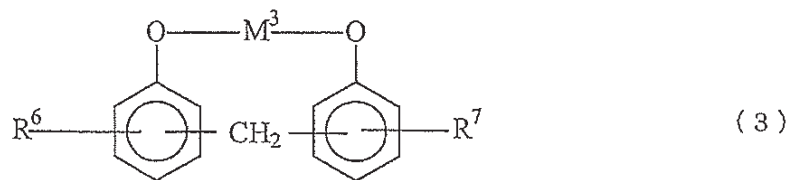
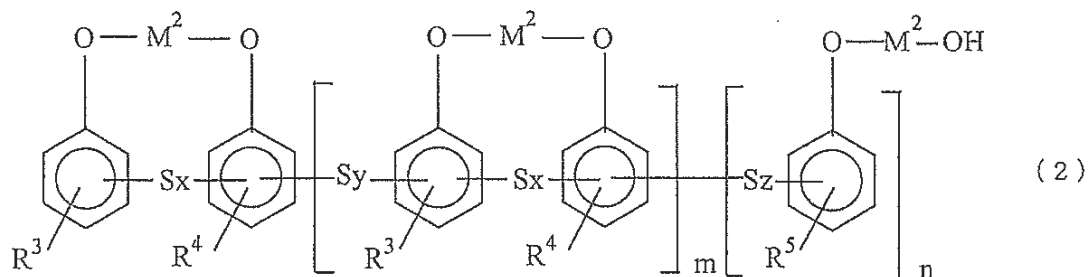
The ethylene- $\alpha$ -olefin copolymer or hydrogenated compound thereof is provided in a state wherein it is diluted with 1 to 90 percent by mass of a mineral oil.

[0027] The lubricating oil composition of the present invention contains preferably at least one type selected from the group consisting of (B) metal detergents, (C) zinc dialkyldithiophosphates, (D) rust inhibitors and (D) ashless dispersants.

[0028] Component (B) that is a metal detergent may be one or more metal detergents selected from phenate detergents, sulfonate detergents, salicylate detergents, carboxylate detergents and phosphonate detergents.

[0029] The phenate metal detergent is a phenate metal detergent containing an alkaline earth metal salt of an alkylphenol, an alkylphenolsulfide or a Mannich reaction product of an alkylphenol represented by

Examples of the alkaline earth metal include magnesium, barium, and calcium. Preferred are magnesium and calcium, and particularly preferred is calcium.

$$\begin{array}{c} \text{O} \quad \text{M}^1 \quad \text{O} \\ | \quad \quad | \\ \text{R}^1 \text{---} \text{C}_6\text{H}_4 \quad \text{C}_6\text{H}_4 \text{---} \text{R}^2 \end{array} \quad (1)$$


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alkyl group having 4 to 30 carbon atoms, preferably 6 to 18 carbon atoms. If the carbon number is fewer than 4, Component (B) would be poor in dissolubility in the lubricating base oil. If the carbon number is more than 30, Component (B) would be difficult to produce and poor in heat resistance. Specific examples of the alkyl group for  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ , and  $R^7$  are butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, and triacontyl groups. These alkyl groups may be straight-chain or branched and may be of primary, secondary, or tertiary.

$M^1$ ,  $M^2$  and  $M^3$  are each independently an alkaline earth metal, preferably calcium and/or magnesium, x, y and z are each independently an integer of 1 to 3, m is 0, 1 or 2, and n is 0 or 1.

[0032] The sulfonate detergent may be an alkali metal salt or alkaline earth metal salt of an alkyl aromatic sulfonic acid produced by sulfonating an alkyl aromatic compound having a molecular weight of 300 or more, preferably 400 to 700 and/or an (overbased) basic salt of the alkali metal salt or alkaline earth metal salt. Examples of the alkali metal or alkaline earth

metal include sodium, potassium, magnesium, barium and calcium. Preferred are magnesium and/or calcium. Particularly preferred is calcium.

[0033] Specific examples of the alkyl aromatic sulfonic acid include petroleum sulfonic acids and synthetic sulfonic acids. The petroleum sulfonic acids may be those produced by sulfonating an alkyl aromatic compound contained in the lubricant fraction of a mineral oil or may be mahogany acid by-produced upon production of white oil. The synthetic sulfonic acids may be those produced by sulfonating an alkyl benzene having a straight-chain or branched alkyl group, produced as a by-product from a plant for producing an alkyl benzene used as the raw material of a detergent or produced by alkylating polyolefin to benzene, or those produced by sulfonating alkylnaphthalenes such as dinonylnaphthalene. No particular limitation is imposed on the sulfonating agent used for sulfonating these alkyl aromatic compounds. In general, fuming sulfuric acids or sulfuric acid may be used.

[0034] The salicylate detergent may be an alkali metal or alkaline earth metal salicylate having one hydrocarbon group having 1 to 19 carbon atoms and/or an (overbased) basic salt thereof; an alkali metal or alkaline earth metal salicylate having one hydrocarbon

group having 20 to 40 carbon atoms and/or an (overbased) basic salt thereof; or an alkali metal or alkaline earth metal salicylate having two or more hydrocarbon groups having 1 to 40 carbon atoms and/or an (overbased) basic salt thereof (these alkyl groups may be the same or different). Among these compounds, preferred are alkali metal or alkaline earth metal salicylates having one hydrocarbon group having 8 to 19 carbon atoms and/or (overbased) basic salts thereof because they are excellent in low-temperature flowability. Examples of the alkali metal or alkaline earth metal include sodium, potassium, magnesium, barium, and calcium. Preferred are magnesium and/or calcium. Particularly preferred is calcium.

[0035] The base number of Component (B) that is a metal detergent used in the present invention is preferably from 50 to 500 mgKOH/g, more preferably from 100 to 450 mgKOH/g, more preferably from 150 to 350 mgKOH/g. If the base number is less than 100 mgKOH/g, corrosive wear could be increased because the resulting composition could be insufficient in acid neutralization properties. If the base number is greater than 500 mgKOH/g, a problem regarding dissolubility would arise.

The term "base number" used herein denotes

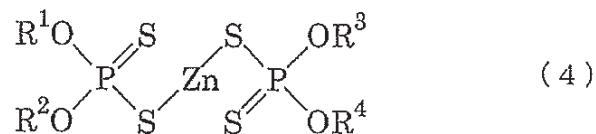
one measured by the perchloric acid potentiometric titration method in accordance with section 7 of JIS K2501 "Petroleum products and lubricants-Determination of neutralization number".

[0036] No particular limitation is imposed on the metal ratio of (B) the metal detergent. The lower limit is, however, 1 or greater, preferably 2 or greater, particularly preferably 2.5 or greater while the upper limit is 20 or less, preferably 15 or less, more preferably 10 or less.

The term "metal ratio" used herein is represented by "valence of metal element x metal element content (mole%) / soap group content (mole%)" in (B) the metal detergent". The metal element denotes an alkaline earth metal such as calcium and magnesium. The soap group denotes phenol group.

[0037] The content of (B) the metal detergent if contained in the composition of the present invention is usually from 0.5 to 15 percent by mass, preferably from 1 to 12 percent by mass, particularly preferably from 1.5 to 10 percent by mass.

[0038] The lubricating oil composition of the present invention contains preferably (C) zinc dialkyldithiophosphates represented by formula (4):



[0039] In formula (4), R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> may be the same or different from each other and are each independently an alkyl group having 1 to 30 carbon atoms, which may be straight-chain or branched and of primary, secondary, or an alkylaryl group having 7 to 30 carbon atoms.

[0040] No particular limitation is imposed on the method for producing zinc dithiophosphates that is Component (C) since any conventional method may be used. For example, an alcohol having alkyl groups corresponding to R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> above is reacted with phosphorus pentasulfide to produce dithiophosphoric acid, which is then neutralized with zinc oxide thereby synthesizing zinc dithiophosphate.

[0041] The content of (C) the zinc dithiophosphate if contained in the lubricating oil composition of the present invention is preferably from 0.005 to 0.12 percent by mass, more preferably from 0.01 to 0.10 percent by mass, more preferably from 0.02 to 0.08 percent by mass on the basis of phosphorus of the total mass of the composition. If the content is less than

0.005 percent by mass, the resulting composition would fail to obtain extreme pressure properties or gear characteristics required for a system oil. If the content is more than 0.12 percent by mass, the resulting composition could corrodes bearings, seal rings in a staffing box or oil scraper rings.

[0042] The lubricating oil composition of the present invention contains preferably (D) rust inhibitors. Examples of the rust inhibitors include sulfonic acid salts (salts of sodium, calcium or barium), succinic acid derivatives, organic acid esters such as fatty acid esters and sorbitan acid esters, carboxylic acid salts (sodium, magnesium, barium and zinc salts of stearic acid or naphthenic acid), polyhydric alcohol partial esters such as sorbitan monoester and pentaerythritol monoester, oxidized paraffin (oxidized wax), carboxylic acid, and phosphoric acid esters. Preferred are sulfonates.

[0043] The content of (D) the rust inhibitor if contained in the lubricating oil composition of the present invention is preferably from 0.005 to 5 percent by mass on the basis of the total mass of the composition.

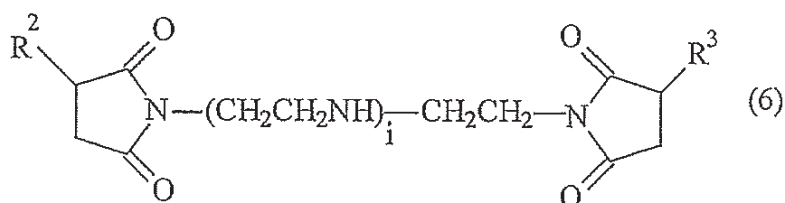
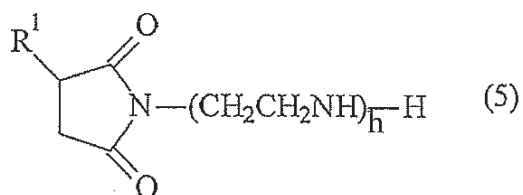
[0044] The lubricating oil composition of the present invention contains preferably (E) ashless

dispersants.

The ashless dispersant may be any ashless dispersant that has been used in a lubricating oil. The ashless dispersant may be succinic acid imide, benzylamine, or polyamine having in their molecules at least one straight-chain or branched alkyl or alkenyl group having 40 to 400, preferably 60 to 350 carbon atoms, or modified products thereof.

The alkyl or alkenyl group may be straight-chain or branched but is preferably a branched alkyl or alkenyl group derived from oligomers of olefins such as propylene, 1-butene or isobutylene or a cooligomer of ethylene and propylene.

[0045] Among these compounds, preferred are succinimide or products modified with boron represented by the following formulas:



[0046] In formula (5), R<sup>1</sup> is an alkyl or alkenyl

group having 40 to 400, preferably 60 to 350, and h is an integer of 1 to 5, preferably 2 to 4. In formula (6),  $R^2$  and  $R^3$  are each independently an alkyl or alkenyl group having 40 to 400, preferably 60 to 350 carbon atoms, and particularly preferably polybutenyl group, and i is an integer of 0 to 4, preferably 1 to 3.

[0047] The content of the ashless dispersant if contained in the lubricating oil composition of the present invention is preferably from 1 to 8 percent by mass on the basis of the total mass of the composition.

[0048] In addition to the above-described components in order to further improve the properties of the lubricating oil composition of the present invention or add other required properties thereto, any additives that have been conventionally used in a lubricating oil may be added in accordance with the purposes. Examples of such additives include antioxidants, extreme pressure additives, corrosion inhibitors, demulsifiers, metal deactivators, pour point depressants, and anti-foaming agents.

[0049] Examples of the antioxidants include phenolic antioxidants such as DBPC, bisphenol, and hindered phenols, aminic antioxidants such as diphenylamine and N-phenyl- $\alpha$ -naphthylamine, and metal antioxidants such copper and molybdenum antioxidants.

The content of the antioxidant if contained in the lubricating oil composition is preferably from 0.05 to 5 percent by mass on the basis of the total mass of the composition.

[0050] Eligible extreme pressure additives are any extreme pressure additives and anti-wear agents that have been used in a lubricating oil. For example, sulfuric-, phosphoric- and sulfuric-phosphoric extreme pressure additives may be used. Specific examples include phosphorus acid esters, thiophosphorus acid esters, dithiophosphorus acid esters, trithiophosphorus acid esters, phosphoric acid esters, thiophosphoric acid esters, dithiophosphoric acid esters, trithiophosphoric acid esters, amine salts, metal salts or derivatives thereof, dithiocarbamates, zinc dithiocarbamates, molybdenum dithiocarbamates, disulfides, polysulfides, sulfurized olefins, and sulfurized fats and oils.

The content of the extreme pressure additive if contained in the lubricating oil composition of the present invention is preferably from 0.05 to 5 percent by mass on the basis of the total mass of the composition.

[0051] Examples of the corrosion inhibitor include benzotriazole-, tolyltriazole-, thiadiazole-, and

imidazole-types compounds.

[0052] Examples of the demulsifier include polyalkylene glycol-based non-ionic surfactants such as polyoxyethylenealkyl ethers, polyoxyethylenealkylphenyl ethers, and polyoxyethylenealkylnaphthyl ethers.

[0053] Examples of the metal deactivator include imidazolines, pyrimidine derivatives, alkylthiadiazoles, mercaptobenzothiazoles, benzotriazoles and derivatives thereof, 1,3,4-thiadiazolepolysulfide, 1,3,4-thiadiazolyl-2,5-bisdialkyldithiocarbamate, 2-(alkyldithio)benzoimidazole, and  $\beta$ -(o-carboxybenzylthio)propionitrile.

[0054] The pour point depressant may be a polymethacrylate polymer that is suitable for a lubricating base oil to be used.

[0055] Examples of the anti-foaming agent include silicone oil with a 25°C kinematic viscosity of 100 to 100,000 mm<sup>2</sup>/s, alkenylsuccinic acid derivatives, esters of polyhydroxy aliphatic alcohols and long-chain fatty acids, aromatic amine salts of methylsalicylate and o-hydroxybenzyl alcohol, aluminum stearate, potassium oleate, N-dialkyl-allylamine nitroaminoalkanol, and

isoamylloctylphosphate, alkylalkylenediphosphates, metal derivatives of thioethers, metal derivatives of disulfides, fluorine compounds of aliphatic hydrocarbons, triethylsilane, dichlorosilane, alkylphenyl polyethylene glycol ether sulfide, and fluoroalkyl ethers.

[0056] When these additives are contained in the lubricating oil composition of the present invention, the corrosion inhibitor, rust inhibitor and demulsifier are each contained in an amount of usually 0.005 to 5 percent by mass, the metal deactivator is usually contained in an amount of usually 0.005 to 1 percent by mass, and the anti-foaming agent is usually contained in an amount of usually 0.0005 to 1 percent by mass, all on the basis of the total mass of the composition.

[0057] The kinematic viscosity at 100°C of the lubricating oil composition of the present invention is necessarily 7.5 mm<sup>2</sup>/s or higher, preferably 9.3 mm<sup>2</sup>/s or higher, more preferably 10 mm<sup>2</sup>/s or higher. The kinematic viscosity at 100°C is necessarily 15.0 mm<sup>2</sup>/s or lower, preferably 14.5 mm<sup>2</sup>/s or lower, more preferably 12.5 mm<sup>2</sup>/s or lower. If the 100°C kinematic viscosity is lower than 7.5 mm<sup>2</sup>/s, the resulting composition would be poor in film formation capability

and thus could cause seizure at bearings. If the 100°C kinematic viscosity is higher than 15.0 mm<sup>2</sup>/s, the resulting composition could not sufficiently cool piston surfaces to be cooled, causing burn of pistons and also could deteriorate fuel efficiency due to the increased friction loss.

[0058] The base number of the lubricating oil composition of the present invention is necessarily from 4 to 20 mgKOH/g. The lower limit is preferably 5 mgKOH/g or greater, more preferably 5.5 mgKOH/g or greater while the upper limit is preferably 15 mgKOH/g or less, more preferably 10 mgKOH/g or less. If the base number is less than 4 mgKOH/g, the resulting composition could be poor in detergency. If the base number is greater than 20 mgKOH/g, the composition could be less likely to remove mixed foreign substances in a purifier.

[0059] The lubricating oil composition of the present invention is not only suitably applicable as a system oil for a crosshead-type diesel engine but also can be used for trunk-piston-type diesel engines as well as gasoline, diesel and gas engines of motorcycles, automobiles, power generators and cogeneration units.

#### **Examples**

[0060] The present invention will be described in

more detail with reference to the following Examples and Comparative Examples but are not limited thereto.

[0061] (Examples 1 to 18, and Comparative Examples 1 to 4)

Lubricating oil compositions of the present invention (Examples 1 to 18) and those for comparison (Comparative Examples 1 to 4) as set forth in Tables 1 and 2 were prepared. Each of the resulting compositions was subjected to a hot tube test, and the results thereof are also set forth in Tables 1 and 2. For Examples 1 to 7 and 10 to 16 and Comparative Examples 1, 3 and 4, the content of the polymer compound and the ratio of the base oil were adjusted so that the 100°C kinematic viscosity of each composition mixed with additives was 11.5 mm<sup>2</sup>/s.

[0062] (Base Oil)

Base Oil A: 100 neutral (kinematic viscosity at 100°C: 4.42 mm<sup>2</sup>/s)

Base Oil B: 250 neutral (kinematic viscosity at 100°C: 7.12 mm<sup>2</sup>/s)

Base Oil C: 500 neutral (kinematic viscosity at 100°C: 10.8 mm<sup>2</sup>/s)

Base Oil D: 150 bright stock (kinematic viscosity at 100°C: 31.7 mm<sup>2</sup>/s)

(Additive)

(1) Polymer Compound

A-1: Polyisoprene star polymer (polymer wherein polyisoprene bonds as arms to dibinylbenzene, PSSI=2)

A-2: Polyisoprene-polystyrene star polymer (polymer wherein an isoprene-styrene copolymer bonds as arms to dibinylbenzene, PSSI=25)

A-3: Ethylene-propylene copolymer (PSSI=25)

PMA: Polymethacrylate (PSSI=5)

PB: Polybutene (molecular weight: 800)

(2) Additives other than the polymer compounds

B-1: Metal Detergent (overbased basic calcium phenate, base number: 255 mgKOH/g, Ca content: 9.25 mass%)

B-2: Metal Detergent (overbased calcium salicylate, base number: 170 mgKOH/g, Ca content: 6.2 mass%)

Zinc dialkyldithiophosphate: Primary zinc dialkyldithiophosphate (alkyl=2-ethylhexyl, P content: 7.4 mass%)

Rust Inhibitor: Neutral calcium sulfonate (base number: 20 mgKOH/g, Ca content: 2.35 percent by mass)

Ashless Dispersant: alkenyl succinimide  
(bis-type, nitrogen content: 1 mass%)

Other Additives (antioxidant, extreme  
pressure additive, pour point depressant, anti-foaming  
agent)

[0063] (Hot Tube Test)

This test was carried out in accordance with  
JPI-5S-55-99. At a test temperature of 250°C, each oil  
flowing out from a glass tube is collected, and the  
viscosity of the oil was measured with an automatic  
capillary viscometer (CACV) manufactured by Canon Inc.  
Six types of sample oils were tested for the following  
two cases.

A) Fresh Oil 100%

B) Mixture of 85% fresh oil and 15 mass% of  
cylinder drip oil collected from a crosshead-type  
diesel engine mounted on VLCC (Middle East to Japan),  
properties of the cylinder drip oil are as follows:  
kinematic viscosity (100°C): 28.1 mm<sup>2</sup>/s, acid number:  
7.5 mgKOH/g, base number (perchloric acid method): 24.1  
mgKOH/g, pentane insoluble (A method): 6.0 mass%

[0064]

[Table 1]

|                                                                    | Example 1 | Example 2 | Example 3 | Example 4 | Example 5 | Example 6 | Example 7 | Example 8 | Example 9 | Comparative Example 1 | Comparative Example 2 | Comparative Example 3 | Comparative Example 4 |
|--------------------------------------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------------------|-----------------------|-----------------------|-----------------------|
| Base Oil Composition                                               | mass%     |           |           |           |           |           |           |           |           |                       |                       |                       |                       |
| Base Oil A ( 100 neutral )                                         |           | 100       | 100       | 100       | 100       | 100       | 100       | 100       |           |                       |                       |                       |                       |
| Base Oil B ( 250 neutral )                                         | 100       |           |           |           |           |           |           |           |           |                       | 100                   | 100                   | 100                   |
| Base Oil C ( 500neutral )                                          |           |           |           |           |           |           |           |           |           | 92                    |                       |                       |                       |
| Base Oil D ( 150 bright stock )                                    |           |           |           |           |           |           |           |           |           | 8                     |                       |                       |                       |
| Polymer Compounds                                                  |           |           |           |           |           |           |           |           |           |                       |                       |                       |                       |
| A-1 ( Polyisoprene star polymer )                                  | 4.0       | 8.5       |           |           |           |           |           |           |           |                       |                       |                       |                       |
| A-2 ( Polyisoprene-polystyrene star polymer )                      |           |           | 9.0       | 9.5       | 8.7       | 8.4       | 8.9       | 6.5       | 10.7      |                       |                       |                       |                       |
| PMA ( Polymethacrylate )                                           |           |           |           |           |           |           |           |           |           |                       |                       | 4.5                   |                       |
| PB ( Polybutene )                                                  |           |           |           |           |           |           |           |           |           |                       |                       |                       | 19.0                  |
| Additives other than polymer compounds                             |           |           |           |           |           |           |           |           |           |                       |                       |                       |                       |
| B-1 ( Metal Detergent )                                            | 2.35      | 2.35      | 2.35      |           | 3.60      | 5.00      | 2.50      | 2.35      | 2.35      | 2.35                  | 2.35                  | 2.35                  | 2.35                  |
| B-2 ( Metal Detergent )                                            |           |           |           | 3.65      |           |           | 3.70      |           |           |                       |                       |                       |                       |
| Zinc dialkyldithiophosphate                                        | 0.55      | 0.55      | 0.55      | 0.55      | 0.55      | 0.55      | 0.55      | 0.55      | 0.55      | 0.55                  | 0.55                  | 0.55                  | 0.55                  |
| Rust inhibitor                                                     | 1.25      | 1.25      | 1.25      | 1.25      | 1.25      | 1.25      | 1.25      | 1.25      | 1.25      | 1.25                  | 1.25                  | 1.25                  | 1.25                  |
| Ashless Dispersant                                                 |           |           |           |           | 1.00      | 1.00      | 1.00      |           |           |                       |                       |                       |                       |
| Other Additives                                                    | 0.45      | 0.45      | 0.45      | 0.45      | 0.45      | 0.45      | 0.45      | 0.45      | 0.45      | 0.45                  | 0.45                  | 0.45                  | 0.45                  |
| Properties of composition                                          |           |           |           |           |           |           |           |           |           |                       |                       |                       |                       |
| Kinematic Viscosity at 100°C                                       | 11.5      | 11.5      | 11.5      | 11.5      | 11.5      | 11.5      | 11.5      | 10.0      | 12.5      | 11.5                  | 7.4                   | 11.5                  | 11.5                  |
| Base Number                                                        | 5.9       | 5.9       | 5.9       | 6.2       | 9.0       | 12.5      | 12.5      | 5.9       | 5.9       | 5.9                   | 5.9                   | 5.9                   | 5.9                   |
| Hot Tube Test Results ( 100°C kinematic viscosity )                |           |           |           |           |           |           |           |           |           |                       |                       |                       |                       |
| Evaluation 1                                                       |           |           |           |           |           |           |           |           |           |                       |                       |                       |                       |
| Before Test : Fresh Oil 100%                                       | 11.5      | 11.5      | 11.5      | 11.5      | 11.5      | 11.5      | 11.5      | 10.0      | 12.5      | 11.5                  | 7.4                   | 11.5                  | 11.5                  |
| Oil collected through Hot Tube Test                                | 11.4      | 11.1      | 11.0      | 11.0      | 11.3      | 11.2      | 11.2      | 9.8       | 12.2      | 11.6                  | 7.3                   | 11.3                  | 11.3                  |
| Evaluation 2                                                       |           |           |           |           |           |           |           |           |           |                       |                       |                       |                       |
| Before Test : Mixed Oil of 85% Fresh Oil and 15% Cylinder Drip Oil | 13.3      | 13.3      | 13.3      | 13.2      | 13.4      | 13.3      | 13.3      | 11.9      | 14.4      | 13.4                  | 8.7                   | 13.5                  | 13.5                  |
| Oil collected through Hot Tube Test                                | 12.4      | 11.5      | 11.4      | 11.3      | 11.4      | 11.6      | 11.5      | 10.5      | 12.1      | 13.3                  | 8.8                   | 13.2                  | 13.6                  |

[Table 2]

|                                                                    | Example 10         | Example 11 | Example 12 | Example 13 | Example 14 | Example 15 | Example 16 | Example 17 | Example 18 | Comparative Example 1 | Comparative Example 2 | Comparative Example 3 |
|--------------------------------------------------------------------|--------------------|------------|------------|------------|------------|------------|------------|------------|------------|-----------------------|-----------------------|-----------------------|
| Base Oil Composition                                               | mass%              |            |            |            |            |            |            |            |            |                       |                       |                       |
| Base Oil A ( 100 neutral )                                         |                    | 100        |            | 100        | 100        | 100        | 100        | 100        | 100        |                       |                       |                       |
| Base Oil B ( 250 neutral )                                         | 100                |            | 100        |            |            |            |            |            |            |                       | 100                   | 100                   |
| Base Oil C ( 500neutral )                                          |                    |            |            |            |            |            |            |            |            | 92                    |                       |                       |
| Base Oil D ( 150 bright stock )                                    |                    |            |            |            |            |            |            |            |            | 8                     |                       |                       |
| Polymer Compounds                                                  |                    |            |            |            |            |            |            |            |            |                       |                       |                       |
| A-3 (Ethylene-propylene copolymer                                  | inmass%            | 8.5        | 4.5        | 9.0        | 8.2        | 7.9        | 8.5        | 6.0        | 10.2       |                       |                       |                       |
| PMA ( Polymethacrylate )                                           | inmass%            |            |            |            |            |            |            |            |            |                       |                       | 4.5                   |
| Additives other than polymer compounds                             |                    |            |            |            |            |            |            |            |            |                       |                       |                       |
| B-1 ( Metal Detergent )                                            | inmass%            | 2.35       |            |            | 3.80       | 5.00       | 2.50       | 2.35       | 2.35       | 2.35                  | 2.35                  | 2.35                  |
| B-2 (Metal Detergent )                                             | inmass%            |            | 3.65       | 3.65       |            |            | 3.70       |            |            |                       |                       |                       |
| Zinc dialkyl/dithiophosphate                                       | inmass%            | 0.55       | 0.55       | 0.55       | 0.55       | 0.55       | 0.55       | 0.55       | 0.55       | 0.55                  | 0.55                  | 0.55                  |
| Rust inhibitor                                                     | inmass%            | 1.25       | 1.25       | 1.25       | 1.25       | 1.25       | 1.25       | 1.25       | 1.25       | 1.25                  | 1.25                  | 1.25                  |
| Ashless Dispersant                                                 | inmass%            |            |            |            | 1.00       | 1.00       | 1.00       | 1.00       | 1.00       |                       |                       |                       |
| Other Additives                                                    | inmass%            | 0.45       | 0.45       | 0.45       | 0.45       | 0.45       | 0.45       | 0.45       | 0.45       | 0.45                  | 0.45                  | 0.45                  |
| Properties of composition                                          |                    |            |            |            |            |            |            |            |            |                       |                       |                       |
| Kinematic Viscosity at 100°C                                       | mm <sup>2</sup> /s | 11.5       | 11.5       | 11.5       | 11.5       | 11.5       | 11.5       | 10.0       | 12.5       | 11.5                  | 7.4                   | 11.5                  |
| Base Number                                                        | mgKOH/g            | 5.9        | 6.2        | 6.2        | 9.0        | 12.5       | 12.5       | 5.9        | 5.9        | 5.9                   | 5.9                   | 5.9                   |
| Hot Tube Test Results ( 100°C kinematic viscosity )                |                    |            |            |            |            |            |            |            |            |                       |                       |                       |
| Evaluation 1                                                       |                    |            |            |            |            |            |            |            |            |                       |                       |                       |
| Before Test : Fresh Oil 100%                                       | mm <sup>2</sup> /s | 11.5       | 11.5       | 11.5       | 11.5       | 11.5       | 11.5       | 10.0       | 12.5       | 11.5                  | 7.4                   | 11.5                  |
| Oil collected through Hot Tube Test                                | mm <sup>2</sup> /s | 11.4       | 11.3       | 11.2       | 11.3       | 11.2       | 11.2       | 9.8        | 12.3       | 11.6                  | 7.3                   | 11.3                  |
| Evaluation 2                                                       |                    |            |            |            |            |            |            |            |            |                       |                       |                       |
| Before Test : Mixed Oil of 85% Fresh Oil and 15% Cylinder Drip Oil | mm <sup>2</sup> /s | 13.4       | 13.3       | 13.2       | 13.4       | 13.3       | 13.3       | 11.8       | 14.5       | 13.4                  | 8.7                   | 13.5                  |
| Oil collected through Hot Tube Test                                | mm <sup>2</sup> /s | 12.8       | 11.9       | 12.7       | 11.8       | 12.1       | 12.0       | 10.8       | 12.8       | 13.3                  | 8.8                   | 13.2                  |

[0065] As apparent from the results set forth in Tables 1 and 2, the lubricating oil compositions of the present invention has no difference in viscosity change over those of Comparative Examples when tested by 100% fresh oils but are smaller in viscosity increase than the comparative oils when mixed with a cylinder drip oil.

#### **Industrial Applicability**

[0066] The lubricating oil composition of the present invention is smaller in viscosity increase even when mixed with a cylinder drip oil and thus excellent in fuel efficiency and exhibits excellent effects in particular as a system lubricating oil for a crosshead-type diesel engine.

## CLAIMS

[Claim 1] A system lubricating oil composition for a crosshead-type diesel engine comprising:

a mineral base oil and/or a synthetic base oil;

(A) (a-1) a star polymer having a vinyl aromatic hydrocarbon structure in the molecule and/or (a-2) an ethylene- $\alpha$ -olefin copolymer or a hydrogenated compound thereof,

and having a base number of 4 to 20 mgKOH/g and a 100°C kinematic viscosity of 7.5 to 15.0 mm<sup>2</sup>/s.

[Claim 2] The system lubricating oil composition for a crosshead-type diesel engine according to claim 1 wherein Component (a-1) is a compound having a structure wherein the polymer or copolymer of a diene extends radially from the core of the vinyl aromatic hydrocarbon located in the center of the molecule.

[Claim 3] The system lubricating oil composition for a crosshead-type diesel engine according to claim 1 or 2 wherein the vinyl aromatic hydrocarbon is divinylbenzene.

[Claim 4] The system lubricating oil composition for a crosshead-type diesel engine according to any one of claims 1 to 3 wherein the polymer or copolymer of

a diene is polyisoprene or an isoprene-styrene copolymer.

[Claim 5]           The system lubricating oil composition for a crosshead-type diesel engine according to any one of claims 1 to 4 wherein Component (A) is contained in an amount of 2 to 15 percent by mass on the basis of the total mass of the composition.

[Claim 6]           The system lubricating oil composition for a crosshead-type diesel engine according to any one of claims 1 to 5 further comprising at least one type selected from the group consisting of (B) metal detergents, (C) zinc dialkyldithiophosphates, (D) rust inhibitors and (E) ashless dispersants.

[Claim 7]           The system lubricating oil composition for a crosshead-type diesel engine according to any one of claims 1 to 6 wherein the base oil has a 100°C kinematic viscosity of 3.5 to 9.3 mm<sup>2</sup>/s.