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(54) LUBRICATING OIL COMPOSITION FOR INTERNAL COMBUSTION ENGINE

(57) A lubricating oil composition for an internal combustion engine, which includes a base oil, (A) at least one member selected from the group consisting of disulfide compounds represented by the general formula (I):

$$R^1OOC\text{-}A^1\text{-}S\text{-}S\text{-}A^2\text{-}COOR^2 \quad (I)$$

and disulfide compounds represented by the general formula (II):

$$R^7OOC\text{-}CR^9R^{10}\text{-}CR^{11}(COOR^8)\text{-}S\text{-}S\text{-}CR^{16}(OOR^{13})\text{-}CR^{14}R^{15}COOR^{12} \quad (II),$$

and (B) at least one member selected from the group consisting of alkali metal-based detergents and alkaline earth metal-based detergents, the component (B) being present in an amount of 10 to 2,000 ppm by mass in terms of metal content.

The lubricating oil composition has a low ash content, a low phosphorous content and a low sulfur content. But, Nonetheless, it can maintain wear resistance, has excellent heat resistance, can extend the lubricating oil change interval and has a long service life.

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Description

[Technical Field]

[0001] The present invention relates to a lubricating oil composition for an internal combustion, particularly to a lubricating oil composition suitable for use in an internal combustion engine such as a gasoline engine, a diesel engine or a gas engine. More specifically, the present invention is directed to a lubricating oil composition which, despite its low ash content, low phosphorus content and low sulfur content, can maintain excellent wear resistance, exhibits excellent heat resistance, can extend the lubricating oil change interval and has a long service life.

[Background Art]

[0002] A lubricating oil for an internal combustion engine mainly functions to lubricate various sliding portions such as piston rings, cylinder liners, crankshafts, connecting rods and a valve-operating mechanism including a cam and a valve-lifter. In addition, the lubricating oil functions to cool the inside of the engine and to disperse sludge and uncombusted resides of the fuel.
Thus, lubricating oils for internal combustion engines are required to have various properties. Further, in recent years, lubricating oils are required to exhibit high performance, since internal combustion engines have been improved in their performance and output and since the operation conditions thereof have become more severe. In order to satisfy the required performance, various additives such as an wear inhibitor, a metal detergent, an ashless dispersant and an antioxidant are compounded in the lubricating oils.

[0003] As a part of the improvement of the service life of lubricating oils, studies have been made on the development of more effective antioxidants and combination thereof. Among others, as an extreme-pressune additive, a zinc alkyldithiophosphate (ZnDTP) has been used a lot. The ZnDTP does not only function as an antioxidant but also has a significant effect to prevent wear and corrosion and, therefore, has been widely used in engine oils, in particular.
Recent tightening of automobile exhaust gas emission regulations requires mounting of an exhaust gas cleaning device for gasoline engines. In order to prevent poisoning of a three-way catalyst, lead-free gasoline and low-phosphorus engine oils begin to be used. For this reason, the use of ZnDTP begins to be subjected to restrictions. Thus, it is essential to develop an extreme-pressure antiwear agent, which is free of phosphorus.

[0004] In diesel engines, since fine particulate matters contained in combustion gases exhausted from the diesel cars cause a problem, it is obliged to mount a diesel particulate filter (hereinafter referred to as "DPF" for brevity) on the diesel cars. When ZnDTP is used as an extreme-pressure additive in the same manner as above, the zinc component contained in ZnDTP deposits on DPF may cause clogging of the filter. In this circumstance, there is a demand for the development of a substitute for ZnDTP.
From the viewpoint of catalyst poisoning, it is desired to reduce a phosphorus component contained in ZnDTP.

[0005] Patent Document 1 discloses a lubricating oil composition which contains a metal salt or amine salt of a thiophosphate or of a phosphate and which is alleged to have a reduced sulfur content and excellent properties to maintain its base number. Though the composition can reduce the sulfur content as a replacement for ZnDTP, reduction of a phosphorus component and a zinc (ash) component is not achieved. Thus, problems of catalyst poisoning and clogging of DPF remain unsolved. Namely, the composition is still unsatisfactory as a lubricating oil composition.
As described above, it is difficult to decrease a zinc component, a phosphorus component and a sulfur component without reducing the wear resistance and antioxidizing properties of an extreme-pressure additive. Yet, reduction of such components is desired in order to minimize adverse influence upon post-treatment systems for automobiles, such as an exhaust gas treatment device and DPF, as much as possible.

[0006] It is conventionally well known that a combination of a sulfur-based antioxidant with a phenol-type antioxidant gives a synergetic effect. As the sulfur-based antioxidant, mainly known is one which has a monosulfide structure. Such a sulfur-based antioxidant, however, has a problem because it causes an increase of the acid value by hydrolysis. Sulfur-based compounds having a polysulfide (tri- or higher polysulfide) structure has a problem that it is highly corrosive to non-iron metals.

[0007]

[Patent Document 1] Publication No. 2002-924721

[Disclosure of the Invention]

[Problem to be Solved by the Invention]

[0008] Under the above-mentioned circumstance, an object of the present invention is to provide a lubricating oil

composition which, despite its low ash content, low phosphorous content and low sulfur content, can maintain excellent wear resistance, exhibits excellent heat resistance, can extend the lubricating oil change interval and has a long service life.

[Means for Solving the Problem]

[0009] The present inventors have made an earnest study with a view toward developing a lubricating oil composition for internal combustion engines having the above-described suitable properties and have found that a combination of a disulfide compound having a specific structure with a specific amount of a detergent can accomplish the above object. The present invention has been completed based on the above finding.
That is, the present invention provides:

(1) A lubricating oil composition for an internal combustion engine, including a base oil; (A) at least one member selected from the group consisting of disulfide compounds represented by the general formula (I):

$$R^1OOC\text{-}A^1\text{-}S\text{-}S\text{-}A^2\text{-}COOR^2 \qquad (I)$$

(wherein R^1 and R^2 each independently represent a C_1 to C_{30} hydrocarbyl group which may contain an oxygen atom, a sulfur atom or a nitrogen atom, and A^1 and A^2 each independently represent a group expressed by CR^3R^4 $CR^3R^4\text{-}CR^5R^6$ where R^3 to R^6 each independently represent a hydrogen atom or a C_1 to C_{20} hydrocarbyl group), and disulfide compounds represented by the general formula (II):

$$R^7OOC\text{-}CR^9R^{10}\text{-}CR^{11}(COOR^8)\text{-}S\text{-}S\text{-}CR^{16}(COOR^{13})\text{-}CR^{14}R^{15}\text{-}COOR^{12} \qquad (II)$$

(wherein R^7, R^8, R^{12} and R^{13} each independently represent a C_1 to C_{30} hydrocarbyl group which may contain an oxygen atom, a sulfur atom or a nitrogen atom and R^9 to R^{11} and R^{14} to R^{16} each independently represent a hydrogen atom or C_1 to C_5 hydrocarbyl group), and (B) at least one member selected from the group consisting of alkali metal-based detergents and alkaline earth metal-based detergents, the component (B) being present in an amount of 10 to 2,000 ppm by mass in terms of metal content;
(2) The lubricating oil composition for an internal combustion engine as defined above (1), wherein the component (A) being at least one member selected from the disulfide compounds is present in an amount of 0.01 to 0.50% by mass in terms of sulfur content;
(3) The lubricating oil composition for an internal combustion engine as defined in above (1) or (2), wherein the alkali metal-based or alkaline earth metal-based detergent of the component (B) is a salicylate and/or a sulfonate; and
(4) The lubricating oil composition for an internal combustion engine as defined in any one of above (1) to (3), wherein the metal of the component (B) is Ca or Mg.

[Effect of the Invention]

[0010] According to the present invention, a lubricating oil composition for internal combustion engines, which, despite its low ash content, low phosphorus content and low sulfur content, can maintain excellent wear resistance, exhibits excellent heart resistance, can extend the lubricating oil change interval and has long service life can be provided.

[Best Mode for Carrying Out the Invention]

[0011] A lubricating oil composition for internal combustion engines of the present invention (hereinafter occasionally referred to simply as "lubricating oil composition") contains a base oil which may be a mineral oil or a synthetic oil. Various types of mineral oils and synthetic oils are available, and a suitable oil can be suitably selected in accordance with the intended use. Examples of the mineral oil include paraffinic mineral oils, naphthenic mineral oils and intermediate mineral oils. Specific examples of the mineral oil include light neutral oil, intermediate neutral oil, heavy neutral oil and bright stock. which are obtained by solvent refining or purification by hydrorefining.
Examples of the synthetic oil include poly-α-olefins, α-olefin copolymers, polybutene, alkylbenzenes, polyol esters, esters of dibasic acids, polyhydric alcohol esters, polyoxyalkylene glycols, polyoxyalkylene glycol esters, polyoxyalkylene glycol ethers and cycloalkane compounds. These lube base oils may be used singly or in combination of two or more thereof. A combination of a mineral oil with a synthetic oil may be also used.
[0012] The compound of the general formula (I) used as the component (A) of the lubricating oil of the present invention has the following structure:

$$R^1OOC\text{-}A^1\text{-}S\text{-}S\text{-}A^2\text{-}COOR^2 \quad (I)$$

In the general formula (I), R^1 and R^2 each independently represent a C_1 to C_{30} hydrocarbyl group (which may contain an oxygen atom, a sulfur atom or a nitrogen atom), preferably a C_1 to C_{20}, more preferably C_2 to C_{18}, particularly preferably C_3 to C_{18} hydrocarbyl group. The hydrocarbyl group may be straight chained, branched or cyclic. R^1 and R^2 may be the same or different but are preferably the same for reasons of easy production.

Next, A^1 and A^2 each independently represent a group expressed by CR^3R^4 or $CR^3R^4\text{-}CR^5R^6$ where R^3 to R^6 each independently represent a hydrogen atom or a C_1 to C_{20} hydrocarbyl group- The hydrocarbyl group is preferably a C_1 to C_{12}, more preferably C_1 to C_8 hydrocarbyl group. A^1 and A^2 may be the same or different but are preferably the same for reasons of easy production.

[0013] In the lubricating oil composition of the present intention, it is preferred that the content of tri- or higher poly-sulfides (namely $-S_x-$ where x is 3 or more; namely -S-S-S- or higher sulfide bonds) in the general formula (I) be 30% by mass or less based on a total amount of the disulfide compound. When the polysulfide content is 30% by mass or less, corrosiveness to non-iron metals may be suppressed. The content of tri- or higher poly-sulfide is more preferably 10% by mass or less, particularly preferably 5% by mass or less.

Thus, it is important that the disulfide compound represented by the above general formula (I) should be produced by a method in which the amount of tri- or higher polysulfide compounds by-produced is within the above range. In the present invention, the disulfide compound may be preferably produced by the following method.

[0014] Namely, an ester of a mercaptoalkanecarboxylic acid represented by the following general formula (III) and/or general formula (IV) as a raw material is subjected to oxidative coupling:

$$R^1OOC\text{-}A^1\text{-}SH \quad (III)$$

$$R^2OOC\text{-}A^2\text{-}SH \quad (IV)$$

(wherein R^1, R^2, A^1 and A^2 are as defined above).

With the above production method, tri- or higher poly-sulfide compounds are substantially not by-produced. Specifically produced are $R^1OOC\text{-}A^1\text{-}S\text{-}S\text{-}A^2\text{-}COOR^2$, $R^1OOC\text{-}A^1\text{-}S\text{-}S\text{-}A^1\text{-}COOR^1$ and $R^2OOC\text{-}A^2\text{-}S\text{-}S\text{-}A^2\text{-}COOR^2$.

As an oxidizing agent for oxidizing an α-mercaptocarboxylic acid ester for the production of the corresponding disulfide, there may be used an oxidizing agent used for producing a disulfide from mercaptan. Examples of such an oxidizing agent include oxygen, hydrogen peroxide, a halogen (such as iodine or bromine), a hypohalous acid and a salt thereof, a sulfoxide (such as dimethyl sulfoxide or diisopropyl sulfoxide) and manganese (IV) oxide. Among these oxidizing agents, oxygen, hydrogen peroxide and dimethyl sulfoxide are preferred because they are inexpensive and make it easy to produce a disulfide.

[0015] Specific examples of the disulfide compound represented by the general formula (I) include bis(methoxycarbonylmethyl) disulfide, bis(ethoxycarbonylmethyl) disulfide, bis (n-propoxycarbonylmethyl) disulfide, bis(isopropoxycarbonylmethyl) disulfide, bis(n-butoxycarbonylmethyl) disulfide, bis(n-octoxycarbonylmethyl) disulfide, bis(n-dodecyloxycarbonylmethyl) disulfide, bis(cyclopropoxycarbonylmethyl) disulfide, 1,1-bis(1-methoxycarbonylethyl) disulfide, 1,1-bis (1-methoxycarbonyl-n-propyl) disulfide, 1,1-bis(1- methoxycarbonyl-n-butyl) disulfide, 1,1-bis(1-methoxycarbonyl-n-hexyl) disulfide, 1,1-bis(1-methoxycarbonyl-n-octyl) disulfide, 1,1-bis(1-methoxycarbonyl-n-dodecyl) disulfide, 2,2-bis (2-methoxycarbonyl-n-propyl) disulfide, α,α-bis(α-methoxycarbonylbenzyl) disulfide, 1,1-bis(2-methoxycarbonylethyl) disulfide, 1,1-bis(2-ethoxycarbonylethyl) disulfide, 1,1-bis(2-n-propoxycarbonylethyl) disulfide, 1,1-bis(2-isopropoxycarbonylethyl) disulfide, 1,1-bis(2-cyclopropoxycarbonylethyl) disulfide, 1,1-bis(2-methoxycarbonyl-n-propyl) disulfide, 1,1-bis(2-methoxycarbonyl-n-butyl) disulfide, 1,1-bis(2-methoxycarbonyl-n-hexyl) disulfide, 1,1-bis(2-methoxycarbonyl-n-propyl) disulfide, 2,2-bis(3-methoxycarbonyl-n-pentyl) disulfide and 1,1-bis(2-methoxycarbonyl-1-phenethyl) disulfide,

[0016] The compound of the general formula (II) used as the component (A) of the lubricating oil composition of the present invention has the following structure:

$$R^7OOC\text{-}CR^9R^{10}\text{-}CR^{11}(COOR^8)\text{-}S\text{-}S\text{-}CR^{16}(COOR^{13})\text{-}CR^{14}R^{15}\text{-}COOR^{12} \quad (II).$$

In the general formula (II), R^7, R^8, R^{12} and R^{13} each independently represent a C_1 to C_{30} hydrocarbyl group (which may contain an oxygen atom, a sulfur atom or a nitrogen atom), preferably a C_1 to C_{20}, more preferably C_2 to C_{18}, particularly preferably C_3 to C_{18} hydrocarbyl group. The hydrocarbyl group may be straight chained, branched or cyclic. R^7, R^8, R^{12} and R^{13} may be the same or different but are preferably the same for reasons of easy production.

Next, R^9 to R^{11} and R^{14} to R^{16} each independently represent a hydrogen atom or C_1 to C_5 hydrocarbyl group. For reasons of easy material availability, a hydrogen atom is preferred.

[0017] The above disulfide compound is preferably produced by, for example, the following two method. In the first production method, a diester of a mercaptoalkanedicarboxylic acid represented by the following general formula (V)

and/or general formula (VI) as a raw material is subjected to oxidative coupling:

$$R^7OOC\text{-}CR^9R^{10}\text{-}CR^{11}(COOR^8)\text{-}SH \quad (V)$$

$$R^{12}OOC\text{-}CR^{15}R^{14}\text{-}CR^{16}(COOR^{13})\text{-}SH \quad (VI)$$

wherein R^7 to R^{16} are as defined above.

[0018] Specifically produced are $R^7OOC\text{-}CR^9R^{10}\text{-}CR^{11}(COOR^8)\text{-}S\text{-}S\text{-}CR^{16}(COOR^{13})\text{-}CR^{14}CR^{15}\text{-}COOR^{12}$, $R^7OOC\text{-}CR^9R^{10}\text{-}CR^{11}(COOR^8)\text{-}S\text{-}S\text{-}R^{11}(COOR^8)\text{-}CR^{10}CR^9\text{-}COOR^7$ and $R^{12}OOC\text{-}CR^{15}R^{14}\text{-}CR^{16}(COOR^{13})\text{-}S\text{-}S\text{-}CR^{16}(COOR^{13})\text{-}CR^{14}CR^{15}\text{-}COOR^{12}$.

As an oxidizing agent, there may be mentioned oxygen, hydrogen peroxide, a halogen (such as iodine or bromine), a hypohalous acid and a salt thereof, a sulfoxide (such as dimethyl sulfoxide or diisopropyl sulfoxide) and manganese (IV) oxide. Among these oxidizing agents, oxygen, hydrogen peroxide and dimethyl sulfoxide are preferred because they are inexpensive and make it easy to produce a disulfide.

[0019] In the second production method, a mercaptoalkanedicarboxylic acid represented by the following general formula (VII) and/or general formula (VIII) as a raw material is subjected to oxidative coupling:

$$HOOC\text{-}CR^9R^{10}\text{-}CR^{11}(COOH)\text{-}SH \quad (VII)$$

$$HOOC\text{-}CR^{14}R^{15}\text{-}CR^{16}(COOH)\text{-}SH \quad (VIII)$$

wherein R^9 to R^{11} and R^{14} to R^{16} are as defined above. The product is then esterified with a monohydric alcohol having a C_1 to C_{30} hydrocarbyl group which may contain an oxygen atom, a sulfur atom or a nitrogen atom. Specifically produced by the oxidative coupling are:

$HOOC\text{-}CR^9R^{10}\text{-}CR^{11}(COOH)\text{-}S\text{-}S\text{-}CR^{16}(COOH)\text{-}CR^{15}R^{14}\text{-}COOH$,
$HOOC\text{-}CR^9R^{10}\text{-}CR^{11}(COOH)\text{-}S\text{-}S\text{-}CR^{11}(COOH)\text{-}CR^{10}R^9\text{-}COOH$, and
$HOOC\text{-}CR^{14}R^{15}\text{-}CR^{16}(COCH)\text{-}S\text{-}S\text{-}CR^{16}(COOH)\text{-}CR^{15}R^{14}\text{-}COOH$

As an oxidizing agent, there may be used the above-described oxidizing agent.

[0020] The oxidative coupling is followed by the esterification with an alcohol represented by the following general formula (IX):

$$R^{17}\text{-}OH \quad (IX)$$

wherein R^{17} is the same as the above R^7. The esterification may be carried out by an ordinary method using an acid catalyst. Specifically produced by the above method are:

R^{17} $OOC\text{-}CR^9R^{10}\text{-}CR^{11}(COOR^{17})\text{-}S\text{-}S\text{-}CR^{16}(COOR^{17})\text{-}CR^{15}R^{14}\text{-}COOR^{17}$,
$R^{17}OOC\text{-}CR^9R^{10}\text{-}CR^{11}(COOR^{17})\text{-}S\text{-}S\text{-}CR^{11}(COOR^{17})\text{-}CR^{10}R^{11}\text{-}COOR^{17}$ and
$R^{17}OOC\text{-}CR^{14}R^{15}\text{-}CR^{16}(COOR^{17})\text{-}S\text{-}S\text{-}CR^{16}(COOR^{17})\text{-}CR^{15}R^{14}\text{-}COOR^{17}$.

[0021] Specific examples of the disulfide compound represented by the general formula (II) include tetramethyl dithiomalate, tetraethyl dithiomalate, tetra-1-propyl dithiomalate, tetra-2-propyl dithiomalate, tetra-1-butyl dithiomalate, tetra-2-butyl dithiomalate, tetraisobutyl dithiomalate, tetra-1-hexyl dithiomalate, tetra-1-octyl dithiomalate, tetra-1-(2-ethyl) hexyl dithiomalate, tetra-1-(3,5,5-trimethyl)hexyl dithiomalate, tetra-1-decyl dithiomalate, tetra-1-dodecyl dithiomalate, tetra-1-hexadecyl dithiomalate, tetra-1-octadecyl dithiomalate, tetrabenzyl dithiomalate, tetra-α-(methyl)benzyl dithiomalate, tetra-α,α-dimethylbenzyl dithiomalate, tetra-1-(2-methoxy)ethyl dithiomalate, tetra-1-(2-ethoxy)ethyl dithiomalate, tetra-1-(2-butoxy)ethyl dithiomalate, tetra-1-(2-ethoxy)ethyl dithiomalate, tetra-1-(2-butoxy)ethyl dithiomalate, tetra-1-(2-ethoxy)ethyl dithiomalate, tetra-1-(2-butoxybutoxy)ethyl dithiomalate and tetra-1-(2-phenoxy)ethyl dithiomalate.

[0022] The disulfide compounds represented by the above general formulas (I) and (II) have excellent load-carrying capacity and wear resistance as a sulfur-based extreme-pressure additive and is used as an additive for the lubricating oil composition.

In the lubricating oil composition of the present invention, one of or two or more of the disulfide compounds represented by the above general formula (I) may be used as the component (A). Also, one of or two or more of the disulfide compounds represented by the above general formula (II) may be used as the component (A).

Further, a mixture of at least one of the disulfide compounds represented by the above general formula (I) and at least one of the disulfide compounds represented by the above general formula (II) may be used.

[0023] The content of the component (A), the disulfide compound, in the lubricating oil composition of the present invention may be suitably determined in view of the intended use and using conditions of the composition but is generally preferably 0.01 to 0.50% by mass, more preferably 0.01 to 0.30% by mass, in terms of sulfur content.

[0024] It is necessary that the lubricating oil composition of the present invention should contain 10 to 2,000 ppm by mass, in terms of metal, of at least one member selected from alkali metal-based detergents and alkaline earth metal-based detergents, as component (B). The content of the component (B) is preferably 100 to 2,000 ppm by mass, more preferably 200 to 2,000 ppm by mass.

When the content, in terms of metal, of the component (B) is within the above range, an increase of the ash content can be prevented without reducing the acid neutralisation power, so that the clogging of DPF can be prevented. Additionally, formation of deposits can be prevented, and lubricating oil change interval can be extended.

[0025] The alkali metal-based or alkaline earth metal-based detergent of the component (B) (hereinafter occasionally referred to as "metal-based detergent" for brevity) is preferably used to improve the acid neutralization power, high-temperature detergency, wear preventing property, etc. The metal-based detergent is not specifically limited, i.e. any metal-based detergent commonly used for lubricating oils may be used. Specific examples of the metal-based detergent include at least one metal-based detergent selected from alkali metal sulfonates, alkaline earth metal sulfonates, alkali metal phenates, alkaline earth metal phenates, alkali metal salicylates and alkaline earth metal salicylates. As the alkali metal, there may be mentioned sodium and potassium. As the alkaline earth metal, there may be mentioned magnesium, calcium and barium. Especially preferably used is magnesium or calcium of an alkaline earth metal.

In the present invention, it is preferred that an alkali metal sulfonate and/or an alkaline earth metal salicylate be used for reasons of obtaining a composition having improved base number maintaining property, high-temperature detergency and wear preventing property. The metal-based detergent preferably has a total base number of 20 to 600 mg KOH/g (JIS K2501; perchloric acid method). A total base number of the above range can ensure the ability to neutralize acidic components farmed by oxidation, can suppress an increase of ash in the lubricating oil and can prevent the formation of a large amount of deposits during a long-term use.

[0026] The alkaline earth metal sulfonate, which is an alkaline earth metal salt of any of various sulfonic acids, may be generally obtained by carbonating an alkaline earth metal salt of any of various sulfonic acids. As the sulfonic acid, there may be mentioned an aromatic petroleum sulfonic acid alkylsulfonic acid, an arylsulfonic acid and an alkylarylsulfonic acid. Specific examples include dodecylbenzenesulfonic acid, dilaurylcetylbenzenesulfonic acid, paraffin wax-substituted benzenesulfonic acid, polyolefin-substituted benzenesulfonic acid, polyisobutylene-substituted benzenesulfonic acid and naphthalenesulfonic acid.

[0027] The alkaline earth metal salicylate, which is an alkaline earth metal salt of an alkylsalicylic acid, may be generally produced by a method in which phenol is alkylated with a C_8 to C_{18} α-olefin, the resulting product being then successively subjected to the Kolbe-Schmitt reaction for introducing a carboxyl group, to double-decomposition and to carbonation. Specific examples of the alkylsalicylic acid include dodecylsalicylic acid, dodecylmethylsalicylic acid, tetradecylsalicylic acid, hexadecylsalicylic acid, octadecylsalicylic acid and dioctylsalicylic acid.

[0028] The lubricating oil composition of the present invention may contain, depending upon its intended use, a variety of additives such as a friction modifier other than the above-mentioned, an antiwear agent, an ashless dispersant, a viscosity index improver, a pour-point depressant, a rust preventive agent, a metal corrosion inhibitor, an antifoaming agent, a surfactant and an antioxidant.

As the friction modifier and antiwear agent, there may be mentioned, for example, sulfur-based compounds such as sulfurized olefins, dialkyl polysulfides, diarylalkyl polysulfides and diaryl polysulfides; phosphorus-based compounds such as esters of phosphoric acid, esters of thiophosphoric acid, esters of phosphorous acid, alkyl hydrogenphosphites, amine salts of esters of phosphoric acid and amine salts of esters of phosphorous acid; chlorine-based compounds such as chlorinated fats and oils, chlorinated paraffins, chlorinated fatty acid esters and chlorinated fatty acids; ester-based compounds such as esters of alkylmaleic acids and alkenylmaleic acids and esters of alkylsuccinic acids and alkenylsuccinic acids; organic acid-based compounds such as alkylmaleic acids, alkenylmaleic acids, alkylsuccinic acids and alkenylsuccinic acids; and organometallic compounds such as salts of naphthenic acid, zinc dithiophosphate (ZnDTP), zinc dithiocarbamate (ZnDTC), sulfurized oxymolybdenum organophosphoro dithioate (MoDTP) and sulfurized oxymolybdenum dithiocarbamate (MoDTC).

[0029] As the ashless dispersant there may be mentioned, for example, succinimides, succinimides containing boron, benzylamines, benzylamines containing boron, esters of succinic acid and amides of monobasic or dibasic carboxylic acids typically examples, which include fatty acids and succinic acid.

As the viscosity index improver, there may be mentioned polymethacrylates, dispersion type polymethacrylates, olefin-based copolymers such as ethylene-propylene copolymers, dispersion type olefin-based copolymers and styrene-based copolymer such as styrene-diene copolymers. As the pour point depressant, there may be mentioned, for example, polymethacrylates.

As the rust preventive agent, there may be mentioned, for example, alkenylsuccinic acid and martial esters thereof. As the metal corrosion inhibitor, there may be mentioned, for example, benzotriazole-based agents, benzimidazole-based

agents, benzothiazole-based agents and thiadiazole-based agents. As the defoaming agent, there may be mentioned, for example, dimethylpolysiloxane and polyacrylates. As the surfactant, there may be mentioned, for example, polyoxyethylene alkylphenyl ethers.

[0030] As the antioxidant, there may be mentioned, for example, amine-based antioxidants such as alkylated diphenylamines, phenyl-α-naphthylamine and alkylated naphthylamines, and phenol-based antioxidants such as 2,6-di-t-butyl-cresol and 4,4'-methylenebis(2,6-di-t-butylphenol).

The lubricating oil composition of the present invention is, despite its low ash content, low phosphorus content and low sulfur content, excellent in wear resistance and in heat resistance, can extend the lubricating oil change interval and has a long service life. Thus, the lubricating oil composition is mainly used as the lubricating oil for internal engines. Further, the lubricating oil composition is used as automobile lube oils for driving instruments such as automatic transmissions, shock absorbers and power steerings, and for gears; as metal working oils for metal working such as cutting, grinding and deformation processing, and as hydraulic oils, being power transmission fluids, for transmission of power, power control and shock absorbing in hydraulic systems such as hydraulic apparatuses and instruments.

[Examples]

[0031] The present invention will be next described in further detail by way of Examples but is not limited to these Examples in any way.

The analysis and evaluation of the lubricating oil compositions prepared using the compounding formulations shown in Table 1 were determined by the following methods.

(1) Measurement of phosphorus concentration

Sample is subjected to emission spectral analysis by ICP (Inductively Coupled Plasma) analysis (apparatus: IRIS Advantage manufactured by JARRELL ASH Inc.) to determine the content (% by mass) of phosphorus in the sample. The results of the measurement are shown in Table 1.

(2) Measurement of sulfur concentration

Sulfur concentration was measured in accordance with ASTM D-1552.

(3) Sulfate ash

Sulfate ash was determined in accordance with JIS K2272, "Crude oil and Petroleum Products; Testing Method for Ash and Sulfated Ash".

(4) Base number (hydrochloric acid method)

Base number was measured by the potentiometric titration method (base number; hydrochloric acid method) in accordance with JIS K2501 "Petroleum products and lubricants; Testing Method for Neutralization Numbed".

(5) Hot tube test

Through a glass tube having an inner diameter of 2 mm, a sample oil and air were allowed to continuously flow at rates of 0.3 ml/hr and 10 ml/min, respectively, for 16 hours, while maintaining the temperature of the glass tube at a predetermined evaluation temperature (280 to 310˚C). Next, the color of a lacquer deposited onto the glass tube was compared to a color specimen and was rated on the basis of standards in which transparency was rated as 10 points and black as 0 point. The higher the rating is, the better is the performance.

(6) LFW-1 friction test

The friction test was performed using LFW-1 friction tester as a testing machine to measure a width of wear scar on a tested block under the following conditions:

Block material: H-60
Ring material: S-10
Revolution speed: 1,400 rpm
Oil temperature: 80˚C
Load: 30 Lbs
Time: 30 minutes

(7) ISOT test (oxidation stability test)

ISOT test was performed in accordance with JIS K-2514 "Lubricating oil; Oxidation Stability Test". Thus, an iron-cropper plate was immersed in an oil sample while stirring the oil at 165.5˚C for 96 hours. Then, a total base number was measured in accordance with JIS K-2501 (hydrochloric acid method).

Preparation Example 1

Preparation of bis(n-octoxycarbonylmethyl) disulfide

[0032] Octyl ester of mercaptoacetic acid was subjected to oxidative coupling according to the production method for the compound represented by the above general formula (I) to obtain bis(n-octoxycarbonylmethyl) disulfide. No tri- or higher polysulfides were detected in the obtained disulfide compound. A sulfur content was found to be 15.8% by mass. Namely, into a 100 ml recovery flask, 40.8 g of octyl ester of mercaptoacetic acid and 30.8 g of dimethyl sulfoxide were placed, and the resultant mixture was heated in an oil bath at 120˚C for 8 hours. After having been cooled, the obtained reaction mixture was dissolved into 100 ml of toluene and washed ten times to remove unreacted dimethyl sulfoxide. Toluene was then removed by distillation under a reduced pressure to obtain 30.5 g of bis(n-octoxycarbonylmethyl) disulfide.

Preparation Example 2

Composition containing oil-soluble molybdenum

[0033] Bis-succinimde was synthesized by reacting a mixture of polybutenyl (molecular weight: 1,000) succinic anhydride (PIBSA) and a polyethylene polyamine oligomer (commercially available as Polyethyleneamine E-100 from Huntsman Chemical Company) with a molar ratio of the amine to PIBSA of 0.5:1. The produced bis-succinimde (250 g) and 162.5 g of neutral oil were placed in a glass reactor equipped with a thermoregulator, a mechanical agitator and a water-cooling unit. The mixture was heated to 70˚C being a reaction temperature for forming a molybdic acid salt. Then, 26.6 g of molybdenum oxide and 45.8 g of water were added to the reactor while maintaining the reaction temperature unchanged. The temperature of the reactor was then maintained at 70˚C for 28 hours. After the salt forming reaction of molybdic acid had been completed, the product was distilled for 30 minutes at a temperature of 99˚C and a pressure of 25 mmHg (absolute) or lower for about 30 minutes to remove the water. The product was found to contain 4.01% by mass of molybdenum and 1.98% by mass of nitrogen.

Examples 1 to 3 and Comparative Example 1

[0034] Lubricating oil compositions having compounding formulations shown in Table 1 were prepared.
The obtained lubricating oil compositions were each measured for their phosphorus concentrations, sulfur concentrations and sulfated ash and subjected to the hot tube test, LFW-1 friction test and ISOT test. The results of the measurement and evaluation are shown in Table 1.

[0035] [Table 1]

Table 1

		Example 1	Example 2	Example 3	Example 1
100N Mineral oil *1	% by mass	balance	balance	balance	balance
500N Mineral oil *1	% by mass	15.00	15.00	15.00	15.00
Viscosity index improver*3	% by mass	6.00	6.00	6.00	6.00
Pour-point depronsant*4	% by mass	0.20	0.20	0.20	0.20
ZnDTP:(as P)	ppm by mass	--	--	--	740
Disulfide *5	% by mass	0.13	0.06	0.06	--
Ca-based detergent *6: (as Ca)	ppm by mass	1100	1100	1600	1100
Hindered phenol-basad antioxidant *7	% by mass	0.50	0.50	0.50	0.50
Amine-based antioxidant*8	% by mass	0.60	0.60	0.60	0.60
Mo-based antioxidant *91(as Mo)	ppm by mass	100	100	100	100
Polybutenylsuccinimide *101 (as N)	ppm by mass	200	200	200	200
Boron-modified polybutanylouccinimide*11: (as B)	ppm by mass	400	400	400	400

(continued)

		Example 1	Example 2	Example 3	Example 1
Copper deactivating agent*12	% by mass	0.10	0.10	0.10	0.10
Antifoaming agent*13	% by mass	0.10	0.10	0.10	0.10
Total		100.00	100.00	100.00	100.00
P content	% by mass	0.00	0.00	0.00	0.08
S content	% by mass	0.15	0.08	0.09	0.17
Sulfated ash	% by mass	0.43	0.43	0.59	0.59
Hot tube test 280 ˚C merit grade	-	10	10	10	8.5
Hot tube test 300 ˚C merit grade	-	8.5	9.0	10	6.0
Hot tube test 310 ˚C merit grade	-	3.0	7.5	9.0	0.0
LFW-1 wear scar width 1400 rpm,30 Lbs,30 min, 80 ˚C	mm	0.45	0.50	0.49	0.51
Base number (hydrochloric acid) after ISOT after 96 hr at 165.5˚C	mgKOH/g	0.38	0.40	1.44	0.36

Remarks:
*1: 100N Mineral oil: hydrorefined mineral oil, kinematic viscosity at 100˚C of 4.5 mm^2/s, sulfur content of 0.01% by mass or below
*2: 500N Mineral oil: hydrorefined mineral oil, kinematic viscosity at 100˚C of 10.9 mm^2/s, sulfur content of 0.01% by mass or below
*3: Viscosity index improver: polymethacrylate (weight average molecular weight of 90,000)
*4: Pour-point depressant: polyalkyl methacrylate (weight average molecular weight of 69,000)
*5: Disulfide: bis(n-octoxycarbonylmethyl) disulfide, sulfur content of 15.8% by mass (prepared in Preparation Example 1)
*6: Metal-based detergent: calcium sulfonate (base number of 300 mgKOH/g, calcium content of 12% by mass)
*7: Hindered phenol-based antioxidant: 4,4'-methylenebis(2,6-di-t-butylphenol)
*8: Amine-based antioxidant: dialkyldiphenylamine (alkyl group is a fixture of butyl and octyl groups)
*9: Molybdenum-based antioxidant: oil-soluble molybdenum-containing composition prepared in Preparation Example 2
*10: Aashless dispersant: polybutenylsuccinimide (nitrogen content of 0.7% by mass)
*11: Ashless dispersant: boron-modified polybutenylsuccinimide (boron content of 0.2% by mass, nitrogen content of 2.1% by mass)
*12: Copper deactivating agent: benzotriazole
*13: Antifoaming agent: silicone oil

[0036] The results shown in Table 1 indicate as follows:

The compositions of Example 1 is the same as that of Comparative Example except for using a disulfide compound according to the present invention in place of ZnDTP in an amount corresponding to the sulfur content of ZnDTP. It is seen that heat resistance (hot tube test) of Example 1 is superior to that of Comparative Example, while the wear resistance of Example 1 is comparable to that of Comparative Example.

The composition of Example 2 is the same as that of Comparative Example except for using a disulfide compound according to the present invention in place of ZnDTP in a reduced amount relative to the sulfur content of ZnDTP. It is seen that heat resistance of Example 2 is superior to that of Comparative Example, while the wear resistance and basle umber maintaining property of Example 2 are comparable to those of Comparative Example.

The composition of Example 3 is the same as that of Comparative Example except for using a disulfide compound according to the present invention in place of ZnDTP in a reduced amount relative to the sulfur content of ZnDTP and for adjusting the sulfated ash to 0.6% by mass or less (by increasing the amount of Ca-based detergent). It is

seen that heat resistance and base number maintaining property of Example 3 are superior to those of Comparative Example, while the wear resistance of Example 3 is comparable to that of Comparative Example.

[0037] The compositions of Examples 1 to 3 do not contain phosphorus that would cause catalyst poisoning. Further, as seen in Examples 2 and 3, it is possible to reduce, without adversely affecting the wear resistance, the content of sulfur which would also cause catalyst poisoning. In general, there is a specified upper limit (API standard, JASO standard, etc.) for sulfated ash which represents a total content of metals which would cause clogging of DPF. From the standpoint of influence on DPF, therefore, the lubricating oil composition of the present invention, in which the disulfide compound is substituted for ZnDTP as shown in Example 3, is of significance in that it can improve the heat resistance (hot tube test) and base number maintaining property after the ISOT test without adversely affecting the wear resistance.

[Industrial Applicability]

[0038] The lubricating oil composition of the present invention can, despite its low ash content, low phosphorus content and low sulfur content, maintain wear resistance and is excellent in heat resistance and has merits that it can extend the lubricating oil change interval. Thus, the lubricating oil composition is used not only as the lubricating oil for internal engines but also as automobile lube oils for driving instruments such as automatic transmissions, shock absorbers and power steering, and for gears; as metal working oils for metal working such as cutting, grinding and deformation processing, and as hydraulic oils, being power transmission fluids, for transmission of power, power control and shock absorbing in hydraulic systems such as hydraulic apparatuses and instruments.

Claims

1. A lubricating oil composition for an internal combustion engine, includes a base oil; (A) at least one member selected from the group consisting of disulfide compounds represented by the general formula (I):

$$R^1OOC\text{-}A^1\text{-}S\text{-}S\text{-}A^2\text{-}COOR^2 \qquad (I)$$

(wherein R^1 and R^2 each independently represent a C_1 to C_{30} hydrocarbyl group which may contain an oxygen atom, a sulfur atom or a nitrogen atom, and A^1 and A^2 each independently represent a group expressed by CR^3R^4 or $CR^3R^4\text{-}CR^5R^6$ where R^3 to R^6 each independently represent a hydrogen atom or C_1 to C_{20} hydrocarbyl group), and disulfide compounds represented by the general formula (II):

$$R^7OOC\text{-}CR^9R^{10}\text{-}CR^{11}(CDDR^8)\text{-}S\text{-}S\text{-}CR^{16}(COOR^{13})\text{-}CR^{14}R^{15}\text{-}COOR^{12} \qquad (II)$$

(wherein R^7, R^8, R^{12} and R^{13} each independently represent a C_1 to C_{30} hydrocarbyl group which may contain an oxygen atom, a sulfur atom or a nitrogen atom and R^9 to R^{11} and R^{14} to R^{16} each independently represent a hydrogen atom or C_1 to C_5 hydrocarbyl group), and (B) at least one member selected from the group consisting of alkali metal-based detergents and alkaline earth metal-based detergents, the component (B) being present in an amount of 10 to 2,000 ppm by mass in terms of metal content.

2. The lubricating oil composition for an internal combustion engine as defined in claim 1, wherein the component (A) being at least one member selected from the disulfide compounds is present in an amount of 0.01 to 0.50% by mass in terms of sulfur content.

3. The lubricating oil composition for an internal combustion engine as defined in claim 1, wherein the alkali metal-based or alkaline earth metal-based detergent of the component (B) is a salicylate and/or a sulfonate.

4. The lubricating oil composition for an internal combustion engine as defined in claim 1, wherein the metal of the component (B) is Ca or Mg.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/070547

A. CLASSIFICATION OF SUBJECT MATTER
C10M169/04(2006.01)i, *C10M129/10*(2006.01)i, *C10M129/54*(2006.01)i, *C10M135/10*(2006.01)i, *C10M135/26*(2006.01)i, *C10M159/22*(2006.01)i, *C10M159/24*(2006.01)i, *C10N10/02*(2006.01)n, *C10N10/04*(2006.01)n,
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M169/04, C10M129/10, C10M129/54, C10M135/10, C10M135/26, C10M159/22, C10M159/24, C10N10/02, C10N10/04, C10N30/06, C10N30/08, C10N40/04, C10N40/08, C10N40/24, C10N40/25

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2007
Kokai Jitsuyo Shinan Koho 1971-2007 Toroku Jitsuyo Shinan Koho 1994-2007

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2006/013946 A1 (Idemitsu Kosan Co., Ltd.), 09 February, 2006 (09.02.06), Claims; Par. Nos. [0012], [0019], [0021], [0023]; examples & EP 1785469 A1	1-4
Y	WO 2004/069966 A1 (Idemitsu Kosan Co., Ltd.), 19 August, 2004 (19.08.04), Claims; page 4, line 23 to page 5, line 4; page 15, lines 7 to 14; page 16, lines 9 to 20; page 17, lines 14 to 19; examples & EP 1602709 A1 & US 2006/148663 A1	1-4

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

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Date of the actual completion of the international search	Date of mailing of the international search report
21 December, 2007 (21.12.07)	15 January, 2008 (15.01.08)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/070547

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2005-146010 A (Nippon Oil Corp.), 09 June, 2005 (09.06.05), Claims; Par. Nos. [0001], [0032] to [0034], [0038] (Family: none)	1-4
Y	WO 02/16532 A1 (Idemitsu Kosan Co., Ltd.), 28 February, 2002 (28.02.02), Claims; page 8, line 21 to page 9, line 4; page 10, lines 2 to 18 & US 2003/182847 A1 & EP 1362905 A1	1-4

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INTERNATIONAL SEARCH REPORT

International application No.
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Continuation of A. CLASSIFICATION OF SUBJECT MATTER
(International Patent Classification (IPC))

C10N30/06(2006.01)n, *C10N30/08*(2006.01)n, *C10N40/04*(2006.01)n,
C10N40/08(2006.01)n, *C10N40/24*(2006.01)n, *C10N40/25*(2006.01)n

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Patent documents cited in the description

- WO 2002924721 A **[0007]**