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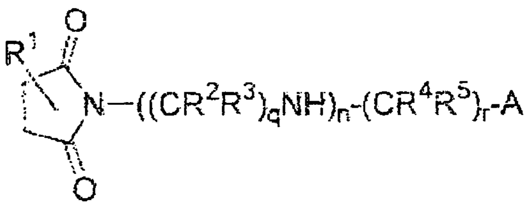
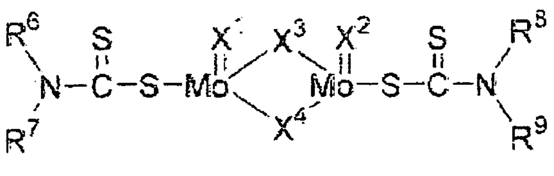
(54) Lubricating oil composition for internal combustion engine

(57) A lubricating oil composition for internal combustion engines contains: base oil; (A) a boronated product of a polyalkenyl succinimide compound; (B) molybdenum dithiocarbamate; and (C) zinc dialkyldithiophosphate.
The component (A) is a boronated product of a succinimide compound represented by the following formula (1), and the succinimide compound is obtained by reacting (a) a succinic acid or its anhydride substituted by a polyalkenyl group with (b) polyalkylene polyamine of which 5 mol% or more of the entirety has a ring structure at its terminal. B/N ratio thereof is 0.5 or more, and a content of the component (A) is 0.01 to 0.1 mass% of the total amount of the composition in terms of boron.



(1)

The component (B) is MoDTC represented by the following formula (2), and a content of the component (B) is 0.01 to 0.08 mass% of the total amount of the composition in terms of Mo. A content of the component (C) is 0.01 to 0.09 mass% of the total amount of the composition in terms of phosphorus.



(2)

Each symbol in the above formulae means the same as described in the description.

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Description

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

[0001] The present invention relates to a lubricating oil composition used in an internal combustion engine such as a diesel engine or a gasoline engine.

2. DESCRIPTION OF RELATED ART

[0002] These days, environmental regulations are being increasingly tightened on a global scale, among which fuel efficiency regulations and exhaust emission regulations for automobiles are especially being further tightened. Demands for tightening of the regulations are derived from environmental issues such as global warming and resource conservation due to a concern for depletion of petroleum resources. For the reasons stated above, it is estimated that automobiles are further advanced to consume less fuel.

[0003] An important problem in diesel engines has been how to reduce environment pollution caused by such emission gas components as particulate matters (PM) and NO_x. An effective solution is to mount such an exhaust purifying device as a particulate filter or an exhaust purifying catalyst (oxidization or reduction catalyst) on an automobile. On the other hand, when conventional lubricating oil is used in an engine of an automobile on which such an exhaust purifying device is mounted, soot adhered to the particulate filter can be eliminated by oxidation or combustion. However, the filter may be clogged by metal oxides, phosphoric salts, sulfate salts, carboxylate salts and the like that are generated by combustion. Further, the used engine oil is partially combusted to be exhausted as exhaust gas. Accordingly, the less metal components and sulfur components are contained in the lubricating oil, the more preferable the lubricating oil becomes. In order to prevent degradation of catalysts, phosphorus components and sulfur components in the lubricating oil are required to be reduced.

[0004] Under the above circumstances, there have been developments on lubricating oil compositions for use in diesel engines with diesel particulate filters (DPF), so as to provide lubricating oil compositions capable of reducing clogging of DPF with ash contents, capable of stably combusting PM at lower temperatures by enhancing combustibility of PM captured by DPF and capable of contributing to higher efficiency of elimination of PM and longer lifetime of DPF. For instance, according to a proposed lubricating oil composition for use in diesel engines with eliminators of diesel particulate (diesel soots), the content of sulfate ash content is 1.0 weight% or less, the content of sulfur content is 0.3 weight% or less and the content of molybdenum is 100 ppm or more (see, for instance, document 1: JP-A-2002-060776).

[0005] In order to reduce fuel consumption of automobiles, it is important not only to improve the automobiles themselves, for instance, by reducing size and weight of the automobiles and by improving the engines, but also to improve engine oil, for instance, by lowering viscosity of engine oil so as to prevent friction loss of the engine and by adding favorable friction modifiers.

[0006] On the other hand, the lowering of the viscosity of the engine oil may cause portions of the engine to be more easily worn. In view of the above, additives such as friction modifiers and extreme pressure agents are added to the engine oil so as to reduce friction damages and wear of the engine entailed by lowered viscosity of the engine oil. The extreme pressure agents typically used are phosphorus-containing compounds. However, since the phosphorus-containing compounds are known to degrade the catalysts for purifying exhaust gas, the content of the phosphorus-containing compounds in the engine oil is preferably reduced as much as possible. When this is applied, however, it may become difficult to maintain the wear prevention of the engines for a long time, so that a method of maintaining the wear prevention is required.

[0007] One possible method, which is frequently relied upon, is to add molybdenum-containing friction modifiers and amine-based or ester-based ashless friction modifiers. These friction modifiers, though capable of greatly reducing friction, may be exhausted at a higher speed due to oxidation degradation, depending on combinations with other additives and the additive amount. Thus, it may not be possible to expect these friction modifiers to maintain the performance of the engine oil for a long time.

[0008] According to a proposal on the solution, engine oil compositions are formed by adding mineral oil or synthetic oil with boron compound derivatives of alkenylsuccinimide, organic molybdenum compounds, specific alkylthiadiazole and specific fatty acid ester (see, for instance, document 2: JP-A-11-269476).

[0009] Alternatively, in engine oil compositions according to another proposal, sulfurized mixture of alkaline earth metal salts of hydroxybenzoic acid and alkylphenol is added with the specific proportion in place of the specific alkylthiadiazole and specific fatty acid ester (see, for instance, document 3: JP-A-11-269477).

[0010] Further alternatively, according to still another proposal, succinimide having a specific structure is used as ashless dispersants in place of or in combination with metal-based detergents (see, for instance, document 4: JP-A-

2001-226381, document 5: JP-A-2001-247623). Such ashless dispersants can finely disperse the diesel soots generated during the combustion and sludge generated by oxidation degradation of the engine oil and can prevent these diesel soots and sludge from adhering to the engine parts, thereby enhancing detergency for the pistons.

[0011] However, such conventional lubricating oil as disclosed in Documents 1 to 5 may hardly maintain the practically sufficient level of friction modification capability for a long time while suppressing the metal contents and phosphorus contents to lower levels. Additionally, in practice, such conventional lubricating oil is yet to provide sufficient friction modification under incorporation of diesel soots.

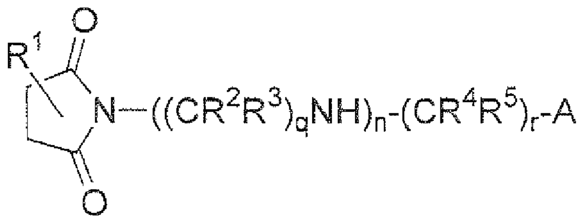
SUMMARY OF THE INVENTION

[0012] An object of the invention is to provide a lubricating oil composition for use in internal combustion engines such as gasoline engines, diesel engines and gas engines, the lubricating oil composition capable of maintaining such a high level of friction modification as exhibited when the composition is new oil for a long time even when contents of metal contents and phosphorus contents are suppressed to lower levels, and also capable of maintaining such friction modification even when diesel soots are mixed in a diesel engine.

[0013] In order to solve the above-mentioned problems, according to an aspect of the present invention, lubricating oil compositions for internal combustion engines as follows are provided:

[1] a lubricating oil composition for internal combustion engines, containing: base oil formed of mineral oil and/or synthetic oil; (A) a boronated product of polyalkenyl succinimide compound; (B) molybdenum dithiocarbamate; and (C) zinc dialkyldithiophosphate, in which

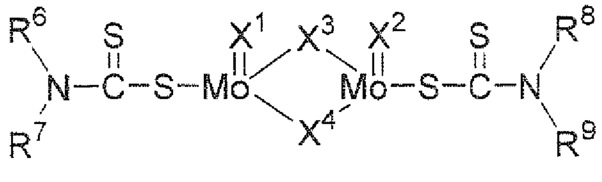
the component (A) is a boronated product of a polyalkenyl succinimide compound obtained by reacting (a) a succinic acid or its anhydride substituted by a polyalkenyl group having a number average molecular weight of 500 to 5000 with (b) polyalkylene polyamine of which 5 mol% or more of the entirety has a ring structure at its terminal, the polyalkenyl succinimide compound being represented by a formula (1) as follows, a mass ratio of boron to nitrogen (B/N ratio) being 0.5 or more, a content of the component (A) being 0.01 to 0.1 mass% of the total amount of the composition in terms of boron,



(1)

where: R^1 represents a polyalkenyl group having a number average molecular weight of 500 to 5000; R^2, R^3, R^4 and R^5 each independently represent hydrogen or an alkyl group having 1 to 3 carbon atoms; q represents an integer of 2 to 4; n represents an integer of 0 to 3; r represents an integer of 2 to 4; and A represents an amino group or a group having the same ring structure as the terminal of the polyalkylene polyamine,

the components (B) is molybdenum dithiocarbamate represented by a formula (2) as follows, a content of the component (B) being 0.01 to 0.08 mass% of the total amount of the composition in terms of molybdenum,



(2)

where: R^6 to R^9 each independently represent a hydrocarbyl group having 4 to 22 carbon atoms; and X^1 to X^4 each represent a sulfur atom or an oxygen atom, and

a content of the component (C) is 0.01 to 0.09 mass% of the total amount of the composition in terms of phosphorus; and

[2] the lubricating oil composition for internal combustion engines as recited in [1], in which a sulfur content is 0.3 mass% or less of the total amount of the composition while a sulfate ash content is 0.8 mass% or less of the total amount of the composition.

[0014] Since containing a boronated product of the polyalkenyl succinimide compound having the specific structure and molybdenum dithiocarbamate, the lubricating oil composition for internal combustion engines according to the aspect of the invention is capable of suppressing contents of metal contents and phosphorus contents to lower levels on one hand and providing excellent friction modification as new oil on the other hand. In addition, the lubricating oil composition is capable of maintaining such a high level of friction modification as exhibited when the composition is new oil for a long time, and also capable of maintaining such friction modification even when diesel soots are mixed. In other words, the lubricating oil composition, which contains less ash content and less phosphorus, is favorably applicable to internal combustion engines such as gasoline engines, diesel engines and gas engines as a lubricating oil composition in compliance with environmental regulations.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT(S)

[0015] The lubricating oil composition for internal combustion engines according to the aspect of the invention (hereinafter may be abbreviated as "composition") contains: base oil; (A) a boronated product of a succinimide compound; (B) molybdenum dithiocarbamate (hereinafter may also be referred to as "MoDTC"); and (C) zinc dialkyldithiophosphate (hereinafter may also be referred to as "ZnDTP"). The base oil and components of each additive will be described in detail below.

[Base Oil]

[0016] For the base oil of the composition, mineral oil and/or synthetic oil is used. The mineral oil and synthetic oil are not particularly limited but may be suitably selected from any mineral oil and synthetic oil that have been conventionally used as base oil of the lubricating oil for internal combustion engines.

[0017] Examples of the mineral oil are mineral oil refined by processing lubricating oil fractions by at least one of solvent-deasphalting, solvent-extracting, hydrocracking, solvent-dewaxing, catalytic-dewaxing and hydrorefining (the lubricating oil fractions are obtained by vacuum-distilling atmospheric residual oil obtained by atmospherically distilling crude oil) and mineral oil manufactured by isomerizing wax and GTL (gas-to-liquid) WAX.

[0018] On the other hand, examples of the synthetic oil are polybutene, polyolefin (α-olefin homopolymer or copolymer such as ethylene-α-olefin copolymer), various esters (such as polyol ester, diacid ester and phosphoric ester), various ethers (such as polyphenylether), polyglycol, alkylbenzene, alkyl naphthalene and the like. Among the above, polyolefin and polyol ester are particularly preferable in perspective of viscosity characteristics, solubility of additives and compatibility with seal rubber.

[0019] In the aspect of the invention, one of the above mineral oil may be singularly used or a combination of two or more thereof may be used as the base oil. In addition, one of the above synthetic oil may be singularly used or a combination of two or more thereof may be used. Further, a combination of at least one of the above mineral oil and at least one of the above synthetic oil may be used.

[0020] While viscosity of the base oil is subject to no specific limitation and the viscosity varies depending on usage of the lubricating oil composition, kinematic viscosity of base oil at 100 degrees C is preferably 2 to 30 mm^2/s, more preferably 3 to 15 mm^2/s, further more preferably 4 to 10 mm^2/s. When the kinematic viscosity at 100 degrees C is 2 mm^2/s or more, evaporation loss is small. When the kinematic viscosity at 100 degrees C is 30 mm^2/s or less, power loss due to viscosity resistance is not so large, thereby improving fuel efficiency.

[0021] As the base oil, oil whose %CA measured by a ring analysis is 3.0 or less and whose sulfur content is 50 ppm by mass or less is preferably usable. The %CA measured by the ring analysis means a proportion (percentage) of aromatic content calculated by the n-d-M ring analysis method. The sulfur content is measured based on Japanese Industrial Standard (hereinafter referred to as JIS) K 2541.

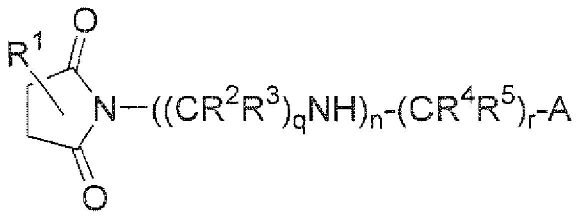
[0022] The base oil whose %CA is 3.0 or less and whose sulfur content is 50 ppm by mass or less exhibits favorable oxidation stability. Such base oil can restrict an increase of acid number and a generation of sludge, thereby providing a lubricating oil composition that is less corrosive to metal.

[0023] The %CA is more preferably 1.0 or less, much more preferably 0.5 or less while the sulfur content is more preferably 30 ppm by mass or less.

[0024] In addition, viscosity index of the base oil is preferably 70 or more, more preferably 100 or more, much more preferably 120 or more. In the base oil whose viscosity index is 120 or more, a viscosity change due to temperature change is small.

[Component (A)]

[0025] The component (A) used in the aspect of the invention is a boronated product of a polyalkenyl succinimide compound represented by the following formula (1). The polyalkenyl succinimide compound is obtained by reacting (a) succinimide or its anhydride substituted by a polyalkenyl group having a number average molecular weight of 500 to 5000 with (b) polyalkylene polyamine of which 5 mol% or more of the entirety contains a ring structure at its terminal.



(1)

In the formula: R^1 represents a polyalkenyl group having a number average molecular weight of 500 to 5000; R^2, R^3, R^4 and R^5 each independently represent hydrogen or an alkyl group having 1 to 3 carbon atoms; q represents an integer of 2 to 4; n represents an integer of 0 to 3; r represents an integer of 2 to 4; and A represents an amino group or a group having the same ring structure as the terminal of the polyalkylene polyamine.

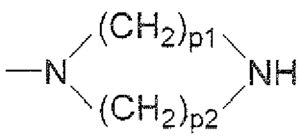
[0026] When the number average molecular weight of the polyalkenyl group is less than 500 in the component (a), the boronated product of the succinimide compound represented by the formula (1) may not be sufficiently soluble in the base oil of the lubricating oil. On the other hand, when the number average molecular weight of the polyalkenyl group is more than 5000, the polyalkenyl succinimide compound may have high viscosity, thereby deteriorating the handleability. Accordingly, the number average molecular weight of the polyalkenyl group is preferably 500 to 5000, more preferably 800 to 3000.

[0027] As the polyalkenyl group having such a molecular weight, a polymer or a copolymer of monoolefin and diolefin having 2 to 16 carbon atoms is typically used. Examples of the monoolefin are ethylene, propylene, butene, butadiene, decene, dodecene, hexadecene and the like. Among the above-listed monoolefin, butene is particularly preferable in the aspect of the invention because of its enhanced high-temperature detergency for the engine parts and its easy availability. A polybutenyl group (a polymer of the butene) are also preferable.

[0028] The polyalkenyl-substituted succinic acid or its anhydride is obtainable by reacting a substance such as polybutene having the molecular weight equivalent to that of the polyalkenyl group with a substance such as maleic anhydride by a known method.

[0029] The polyalkylene polyamine as the component (b) may be polyalkylene polyamine entirely having a ring structure at its terminal, or may alternatively be a mixture of polyalkylene polyamine having a ring structure at its terminal and polyalkylene polyamine having no ring structure at its terminal. However, when the content of the polyalkylene polyamine having a ring structure at its terminal is less than 5 mol%, the high-temperature detergency and oxidation stability may become insufficient. When the content is 10 mol% or more or 20 mol% or more, the high-temperature detergency and oxidation stability are enhanced. In the aspect of the invention, the upper limit on the content of the polyalkylene polyamine having a ring structure at its terminal is preferably 95 mol% or less, more preferably 90 mol% or less. When the content exceeds 95 mol%, the manufactured boronated succinimide compound may become so highly viscous as to impair manufacturing efficiency of the compound and solubility of the product in the base oil of the lubricating oil may be deteriorated. Accordingly, the content of the polyalkylene polyamine having a ring structure at its terminal is preferably 5 to 95 mol%, more preferably 10 to 90 mol%.

[0030] The terminal ring structure of the polyalkylene polyamine having a ring structure at its terminal is preferably represented by a formula (1') as follows.



(1')

[0031] In the formula (1'), p1 and p2 each represent an integer of 2 to 4. Particularly, a group where both p1 and p2 are 2, i.e., piperazinyl group is preferable. A representative example of the polyalkylene polyamine having a ring structure at its terminal is aminoalkyl piperazine having a piperazinyl structure at its terminal such as aminoethyl piperazine, aminopropyl piperazine, aminobutyl piperazine, amino(diethylenediamino) piperazine, amino(dipropyldiamino) piperazine and the like. Among the above, aminoethyl piperazine is particularly preferable in view of its easy availability.

[0032] On the other hand, the polyalkylene polyamine having no ring structure at its terminal means polyalkylene polyamine having no ring structure or polyalkylene polyamine having a ring structure at any site other than its terminal.

[0033] Representative examples of the polyalkylene polyamine having no ring structure are polyethylene polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine, propylenediamine, dibutylenetriamine, tributylenetriamine and the like. A representative example of the polyalkylene polyamine having a ring structure at any site other than its terminal is di(aminoalkyl) piperazine such as di(aminoethyl) piperazine.

[0034] Among the above listed polyalkylene polyamine that may have a ring structure, a mixture of polyalkylene polyamine and polyethylene polyamine such as triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine is particularly preferable because of its enhanced high-temperature detergency for engine-parts and its easy availability.

[0035] The component (A) according to the aspect of the invention is a boronated product of the polyalkenyl succinimide compound obtained from the above-described component (a) and component (b). The boronated product is obtainable by reacting the polyalkenyl succinimide compound obtained from the component (a) and component (b) with a boron compound (component (c)). Examples of the boron compound are boracic acid, boric anhydride, borate ester, boric oxide and boron halogenide. Among the above, boracic acid is particularly preferable.

[0036] Without special limitations, any known methods of reacting can be used. For instance, by reacting the materials by the following manner, the target substance can be obtained. The components (a) and (b) are initially reacted with each other, then its reaction product is reacted with the component (c). A mixing ratio of the components (a) to (b) in the reaction of the components (a) and (b) is preferably 0.1-to-10 to 1 (mole ratio), more preferably 0.5-to-2 to 1 (mole ratio). A reaction temperature of the components (a) and (b) is preferably approximately 80 to 250 degrees C, more preferably approximately 100 to 200 degrees C. At the time of reacting, depending on the materials, or in order to adjust the reaction, solvents such as an organic solvent exemplified by hydrocarbon oil may be used as necessary.

[0037] The reaction product of the components (a) and (b) obtained as described above is reacted with the component (c). A mixing ratio of polyalkylene polyamine to the boron compound as the component (c) is typically 1 to 0.05-to-10, preferably 1 to 0.5-to-5 (mole ratio). A reaction temperature thereof is preferably approximately 50 to 250 degrees C, more preferably 100 to 200 degrees C.

[0038] At the time of reacting, as in the reaction of the materials (a) and (b), depending on the materials or in order to adjust the reaction, solvents such as an organic solvent exemplified by hydrocarbon oil may be used for the reaction product.

[0039] As a product of the above reaction, a boronated product of the succinimide compound substituted by the polyalkenyl group having a number average molecular weight of 200 to 5000 (i.e., the component(A)) is obtained. In the aspect of the invention, one of the components (A) may be singularly used or a combination of two or more thereof may be used.

[0040] The component (A), which is a boronated product of the polyalkenyl succinimide compound having the structure represented by the formula (1) as described above, may be used together with a non-boron-containing polyalkenyl succinimide compound. The polyalkenyl succinimide compound used at this time may be monoimide or bisimide. In perspective of low corrosivity to metal materials, enhancement of compatibility with seal rubber and oxidation stability, polybutenyl succinic acid bisimide, which is a polybutene of an alkenyl group having a number average molecular weight of 1500 to 3000, is particularly preferable.

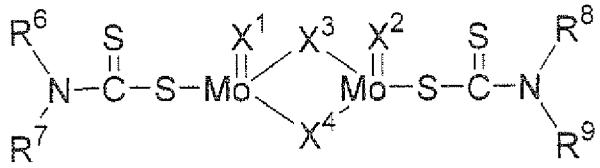
[0041] The content of the component (A) contained in the composition is preferably 0.01 to 0.1 mass% of the total amount of the composition in terms of boron (atoms), more preferably 0.01 to 0.05 mass%, much more preferably 0.01 to 0.03 mass%. Since a predetermined amount or more of boron is contained in the component (A), pistons can be favorably cleaned in the high-temperature internal combustion engine. When the content of boron is less than 0.01 mass%, sufficient high-temperature detergency is not obtained. When the content of boron exceeds 0.1 mass%, no further improvement is made on the high-temperature detergency, which is of little practical use.

[0042] A mass ratio (B/N) of boron (B) to nitrogen (N) contained in the component (A) is preferably 0.5 or more, more preferably 0.6 or more, much more preferably 0.8 or more. When B/N is 0.5 or more, high-temperature detergency for engine parts is greatly enhanced.

[0043] While a boronated product of the succinimide compound is obtainable by initially reacting the materials (a) and (b) and subsequently reacting the reaction product thereof with the material (c), the reaction order may be changed such that the materials (a) and (c) are initially reacted and the reaction product thereof is subsequently reacted with the material (b). With this reaction order, the target boronated product of the polyalkenyl succinimide compound may also be likewise obtained.

[Component (B)]

[0044] The component (B) contained in the composition is molybdenum dithiocarbamate (MoDTC) represented by the following formula (2).



(2)

In the formula: R^6 to R^9 each independently represent a hydrocarbyl group having 4 to 22 carbon atoms; and X^1 to X^4 each represent a sulfur atom or an oxygen atom.

[0045] In the formula (2), R^6 to R^9 each preferably represent a hydrocarbon group having 4 to 22 carbon atoms, examples of which are an alkyl group, alkenyl group, alkylaryl group, cycloalkyl group and cycloalkenyl group. Among the above, R^6 to R^9 each preferably represent a branched or linear alkyl group or alkenyl group having 4 to 18 carbon atoms, more preferably an alkyl group having 8 to 13 carbon atoms. Examples thereof are n-octyl group, 2-ethylhexyl group, isononyl group, n-decyl group, isodecyl group, dodecyl group, tridecyl group and isotridecyl group. This is because oil solubility may be deteriorated when the number of carbon atoms contained therein is too small. On the other hand, when the number of carbon atoms is too large, the melt point may be heightened, thereby deteriorating the handleability and the activity. R^6 to R^9 may be mutually the same or different, but the solubility in the base oil, storage stability and duration of friction modification can be enhanced when R^6 and R^7 and R^8 and R^9 represent different alkyl groups.

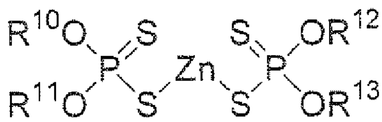
[0046] In the above formula (2), X^1 to X^4 each represent a sulfur atom or an oxygen atom. All of X^1 to X^4 may be sulfur atoms or oxygen atoms. A ratio of sulfur atoms to oxygen atoms (sulfur atom/oxygen atom) is preferably 1/3 to 3/1, more preferably 1.5/2.5 to 3/1 because the corrosion resistance and solubility in the base oil can be enhanced.

[0047] In the aspect of the invention, one of the components (B) may be singularly used or a combination of two or more thereof may be used.

[0048] The lubricating oil composition is prepared such that the content of the component (B) in the lubricating oil composition is 0.01 to 0.08 mass% of the total amount of the composition in terms of molybdenum, preferably 0.03 to 0.08 mass%. When the content is less than 0.01 mass%, sufficient friction modification is not obtained. When the content is more than 0.08 mass%, the solubility in the base oil and the corrosion resistance may be deteriorated.

[Component (C)]

[0049] The composition further contains zinc dialkyldithiophosphate (ZnDTP) as the component (C). The structure of ZnDTP is exemplarily represented by the following formula (3).



(3)

[0050] In the formula (3), R^{10}, R^{11}, R^{12} and R^{13} each represent a primary or secondary alkyl group having 3 to 22 carbon atoms or a substituent selected from alkylaryl groups substituted by an alkyl group having 3 to 18 carbon atoms. R^{10}, R^{11}, R^{12} and R^{13} may be mutually the same or different.

[0051] According to the aspect of the invention, one of the ZnDTP may be singularly used or two or more thereof may be used in combination. Particularly, ZnDTP containing zinc dithiophosphate of a secondary alkyl group as the main component is preferable for enhancing wear resistance.

[0052] Examples of the ZnDTP are zinc dipropyl dithiophosphate, zinc dibutyl dithiophosphate, zinc dipentyl dithiophosphate, zinc dihexyl dithiophosphate, zinc diisopentyl dithiophosphate, zinc diethylhexyl dithiophosphate, zinc dioctyl dithiophosphate, zinc dinonyl dithiophosphate, zinc didecyl dithiophosphate, zinc didodecyl dithiophosphate, zinc dipropylphenyl dithiophosphate, zinc dipentylphenyl dithiophosphate, zinc dipropylmethylphenyl dithiophosphate, zinc dinonylphenyl dithiophosphate, zinc didodecylphenyl dithiophosphate and zinc didodecylphenyl dithiophosphate.

[0053] The content of the ZnDTP as the component (C) in the lubricating oil composition according to the aspect of the invention is preferably 0.01 to 0.09 mass% of the total amount of the composition in terms of phosphorus, more preferably 0.02 to 0.08 mass%. When the content of phosphorus in the composition is less than 0.01 mass%, the wear resistance is not sufficient, and MoDTC of the component (B) cannot sufficiently provide the friction modification. On the other hand, when the content of phosphorus exceeds 0.09 mass%, poisoning on the purifying catalysts for exhaust gas becomes unfavorably worsened.

[0054] The composition is preferably further added with a phenol-based antioxidant and/or an amine-based antioxidant.

[0055] Examples of the phenol-based antioxidant are: octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate; 4,4'-methylenebis(2,6-di-butylphenol); 4,4'-bis(2,6-di-t-butylphenol); 4,4'-bis(2-methyl-6-t-butylphenol); 2,2'-methylenebis(4-ethyl-6-t-butylphenol); 2,2'-methylenebis(4-methyl-6-t-butylphenol); 4,4'-butylidenebis(3-methyl-6-t-butylphenol); 4,4'-isopropylidenebis(2,6-di-t-butylphenol); 2,2'-methylenebis(4-methyl-6-nonylphenol); 2,2'-isobutylidenebis(4,6-dimethylphenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol); 2,6-di-t-butyl-4-methylphenol; 2,6-di-t-butyl-4-ethylphenol; 2,4-dimethyl-6-t-butylphenol; 2,6-di-t-amyl-p-cresol; 2,6-di-t-butyl-4-(N,N'-dimethylaminomethylphenol); 4,4'-thiobis(2-methyl-6-t-butylphenol); 4,4'-thiobis(3-methyl-6-t-butylphenol); 2,2'-thiobis(4-methyl-6-t-butylphenol); bis(3-methyl-4-hydroxy-5-t-butylbenzyl)sulfide; bis(3,5-di-t-butyl-4-hydroxybenzyl)sulfide; n-octyl-3-(4-hydroxy-3,5-di-t-butylphenyl)propionate; n-octadecyl-3-(4-hydroxy-3,5-di-t-butylphenyl)propionate; 2,2'-thio[diethyl-bis-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] and the like. Among the above, bisphenyl-based antioxidant and ester group-containing phenol-based antioxidant are preferable.

[0056] Examples of the amine-based antioxidant are: an antioxidant based on monoalkyl diphenylamine such as monooctyl diphenylamine and monononyl diphenylamine; an antioxidant based on dialkyl diphenylamine such as 4,4-dibutyl diphenylamine, 4,4'-dipentyl diphenylamine, 4,4'-dihexyl diphenylamine, 4,4'-diheptyl diphenylamine, 4,4'-dioctyl diphenylamine and 4,4'-dinonyl diphenylamine; an antioxidant based on polyalkyl diphenylamine such as tetrabutyl diphenylamine, tetrahexyl diphenylamine, tetraoctyl diphenylamine and tetranonyl diphenylamine; and an antioxidant based on naphthylamine, specifically alkyl-substituted phenyl-a-naphthylamine such as α-naphthylamine, phenyl-α-naphthylamine, butylphenyl-α-naphthylamine, penylphenyl-α-naphthylamine, hexylphenyl-α-naphthylamine, heptylphenyl-α-naphthylamine, octylphenyl-α-naphthylamine and nonylphenyl-α-naphthylamine. Among the above, the diphenylamine-based antioxidants are preferred to the naphthylamine-based antioxidants in perspective of antioxidant capabilities.

[0057] According to the aspect of the invention, the composition may be further added with a molybdenum-amine-based antioxidant as another oxidant. As the molybdenum-amine-based antioxidant, a hexahydric Molybdenum compound, an example of which is a reaction product obtained by reacting molybdenum trioxide and/or molybdenum acid with an amine compound, may be used. The reaction product may be, for example, a compound obtained by the manufacturing method disclosed in JP-A-2003-252887. The anime compound to be reacted with the hexahydric molybdenum compound is subject to no particular limitation, and examples thereof are monoamine, diamine, polyamine and alkanolamine. Specifically, examples of the amine compound are: alkyl amine having an alkyl group of 1 to 30 carbon atoms (the alkyl group may be linear or branched), exemplified by methylamine, ethylamine, dimethylamine, diethylamine, methylethylamine, methylpropylamine and the like; alkenyl amine having an alkenyl group of 2 to 30 carbon atoms (the alkenyl group may be linear or branched), exemplified by ethenylamine, propenylamine, butenylamine, octenylamine and oleylamine; alkanol amine having an alkanol group of 1 to 30 carbon atoms (the alkanol group may be linear or branched), exemplified by methanolamine, ethanolamine, methanolethanolamine and methanolpropanolamine; alkylenediamine having an alkylene group of 1 to 30 carbon atoms, exemplified by methylenediamine, ethylenediamine, propylenediamine and butylenediamine; polyamine such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine; a heterocyclic compound obtained by reacting monoamine, diamine and polyamine with a compound having an alkyl or alkenyl group of 8 to 20 carbon atoms or imidazoline, the monoamine, diamine and polyamine being exemplified by undecyldiethylamine, undecyidiethanolamine, dodecyldipropanolamine, oleyldiethanolamine, oleylpropylenediamine and stearyltetraethylenepentamine; an alkylene-oxide adduct of the above compounds; and a mixture thereof. In addition, sulfur-containing molybdenum complexes of succinimide as disclosed in JP-B-03-22438 and JP-A-2004-2866 may be used.

[0058] A content of the antioxidant is preferably 0.3 mass% or more of the total amount of the composition, more preferably 0.5 mass% or more. On the other hand, when the content exceeds 2 mass%, the antioxidant may not be dissolved in the base oil of the lubricating oil. Accordingly, the contents of the antioxidant is preferably in a range from 0.3 to 2 mass% of the total amount of the composition.

[0059] The lubricating oil composition for internal combustion engines according to the aspect of the invention may be added as necessary with other additives such as a viscosity index improver, a metal-based detergent, an ashless friction modifier (friction modifier), a pour point depressant, a rust inhibitor, a metal deactivator, a surfactant and anti-foaming agent as long as advantages of the invention are not hampered.

[0060] Examples of the viscosity index improver are polymethacrylate, dispersed polymethacrylate, an olefin-based copolymer (such as an ethylene-propylene copolymer), a dispersed olefin-based copolymer, a styrene-based copolymer (such as a styrene-diene copolymer and a styrene-isoprene copolymer) and the like. In view of blending effects, a content of the viscosity index improver is approximately 0.5 to 15 mass% of the total amount of the composition, preferably I to 10 mass%.

[0061] The metal-based detergent may be any alkyl earth metal-based detergent usable in the lubricating oil. For example, any one of alkaline earth metal sulfonate, alkaline earth metal phenate and alkaline earth metal salicylate and a mixture of two or more selected therefrom are usable. An example of the alkaline earth metal sulfonate is alkaline earth metal salt of alkyl aromatic sulfonic acid obtained by sulfonating an alkyl aromatic compound having a molecular weight of 300 to 1500 (preferably 400 to 700). The alkaline earth metal salt is exemplified by magnesium salt and/or calcium salt and the like, among which calcium salt is preferably used. An example of alkaline earth metal phenate is alkaline earth metal salt of alkylphenol, alkylphenol sulfide and a Mannich reaction product of alkylphenol. The alkaline earth metal salt is exemplified by magnesium salt and/or calcium salt and the like, among which calcium salt is preferably used. An example of alkaline earth metal salicylate is alkaline earth metal salt of alkyl salicylic acid. The alkaline earth metal salt is exemplified by magnesium salt and/or calcium salt and the like, among which calcium salt is preferably used. An alkyl group for forming the alkaline earth metal-based detergent preferably has 4 to 30 carbon atoms. The alkyl group is more preferably a linear or branched alkyl group having 6 to 18 carbon atoms, in which 6 to 18 carbon atoms may be in a linear chain or in a branched chain. The alkyl group may be a primary alkyl group, a secondary alkyl group or a tertiary alkyl group. In addition, alkaline earth metal sulfonate, alkaline earth metal phenate and alkaline earth metal salicylate may be neutral alkaline earth metal sulfonate, neutral alkaline earth metal phenate and neutral alkaline earth metal salicylate obtained by: directly reacting the above-described alkyl aromatic sulfonic acid, alkylphenol, alkylphenol sulfide, a Mannich reaction product of alkylphenol, alkyl salicylic acid or the like with alkaline earth metal base exemplified by an oxide or a hydroxide of alkaline earth metal such as magnesium and/or calcium; or converting the above-described substance into alkali metal salt such as sodium salt or potassium salt and subsequently substituting the alkali metal salt with alkaline earth metal salt. Alternatively, alkaline earth metal sulfonate, alkaline earth metal phenate and alkaline earth metal salicylate may be: basic alkaline earth metal sulfonate, basic alkaline earth metal phenate and basic alkaline earth metal salicylate obtained by heating neutral alkaline earth metal sulfonate, neutral alkaline earth metal phenate and neutral alkaline earth metal salicylate with excess alkaline earth metal salt or alkaline earth metal base under the presence of water; or overbased alkaline earth metal sulfonate, overbased alkaline earth metal phenate and overbased alkaline earth metal salicylate obtained by reacting neutral alkaline earth metal sulfonate, neutral alkaline earth metal phenate and neutral alkaline earth metal salicylate with carbonate or borate of alkaline earth metal under the presence of carbon dioxide gas.

[0062] In the aspect of the invention, the metal-based detergent may be the neutral salt, the basic salt, the overbased salt or a mixture thereof. Particularly, a mixture of at least one of the overbased salicylate, the overbased phenate and the overbased sulfonate with the neutral sulfonate is preferable in terms of detergency for the interior of the engines and wear resistance.

[0063] The metal-based detergent, which is diluted with light lubricant base oil and the like to be commercially available, preferably has a metal content of 1.0 to 20 mass%, more preferably 2.0 to 16 mass%.

[0064] In the aspect of the invention, the total base number of the metal-based detergent is typically 10 to 500 mg KOH/g, preferably 15 to 450 mg KOH/g. One or two selected therefrom is usable. The total base number herein means the total base number measured by potentiometer titration (base number· perchloric acid method) based on the item 7 of "Petroleum Products and Lubricating Oil - Examining Method of Neutralization Value" of JIS K2501.

[0065] The metal-based detergent in the aspect of the invention, of which metal ratio is subject to no particular limitation, is typically one of or a mixture of two or more of detergents having the metal ratio of 20 or less. In terms of oxidation stability, base number maintainability and high-temperature detergency, the metal-based detergent especially preferably contains as the main component a metal-based detergent that has the metal ratio of 3 or less, more preferably the metal ratio of 1.5 or less, particularly preferably the metal ratio of 1.2 or less. The metal ratio herein is represented by (valence of metal element in the metal-based detergent) $\times$ (content of metal element (mol%)) / (content of soap base (mol%)), and the metal element means calcium, magnesium and the like while the soap base means a sulfonate group, phenol group, salicylic acid group and the like.

[0066] In the aspect of the invention, the content of the metal-based detergent is 1 mass% or less of the total amount of the composition in terms of metal element, more preferably 0.5 mass% or less. Further, in order to reduce the sulfate ash content of the composition down to 0.8 mass% or less, the content of the metal-based detergent is preferably 0.2 mass% or less. On the other hand, the content of the metal-based detergent is preferably 0.005 mass% or more in terms of metal element, more preferably 0.01 mass% or more. In order to further enhance oxidation stability, base number maintainability and high-temperature detergency, the content of the metal-based detergent is further preferably 0.05 mass% or more. Particularly when the content of the metal-based detergent is 0.08 mass% or more, the obtained compound can favorably maintain the base number and the high-temperature detergency for a long time. The sulfate ash content herein refers to a value measured by a method defined in "Experiment Method of Sulfate Ash", Item 5 of JIS K2272. The sulfate ash content is mainly originated from metal-containing additives.

[0067] As the ashless friction modifier, any compounds generally used as the ashless friction modifier for lubricating oil may be used, examples of which are fatty acid, aliphatic alcohol, aliphatic ether, aliphatic ester, aliphatic amine and aliphatic amide that have at least one alkyl or alkenyl group of 6 to 30 carbon atoms in the molecule.

[0068] In terms of anticorrosion effect and friction modification effect on metal materials, the additive amount of the ashless friction modifier is preferably 0.2 to 1.0 mass%, more preferably 0.25 to 0.8 mass%, further preferably 0.3 to 0.6mass%. When the additive amount is less than 0.2 mass%, the friction modification is not sufficiently provided. Even when the additive amount exceeds 1.0 mass%, no incremental friction modification comparative thereto is additionally provided.

[0069] Examples of the pour point depressant are a copolymer of ethylene and vinyl acetate, a condensation product of paraffin chloride with naphthalene, a condensation product of paraffin chloride with phenol, polymethacrylate, poly-alkylstyrene and the like. Among the above, polymethacrylate having a mass-average molecular weight of approximately 5,000 to 50,000 is preferable. The pour point depressant is contained with a content of 0.1 to 5 mass% of the total amount of the composition.

[0070] Examples of the rust inhibitor are petroleum sulfonate, alkylbenzene sulfonate, dinonylnaphthalene sulfonate, alkenyl succinic ester, multivalent alcohol ester and the like. In view of blending effects, a content of the viscosity index improver is approximately 0.01 to 1 mass% of the total amount of the composition, preferably 0.05 to 0.5 mass%.

[0071] Examples of the metal deactivator (copper corrosion inhibitor) are benzotriazole-based compounds, tolyltriazole-based compounds, thiadiazole-based compounds and imidazole-based compounds. Among the above, the benzotriazole-based compounds are preferable. By adding the metal deactivator, the engine parts can be prevented from being metallically corroded and degraded due to oxidation. In view of blending effects, a content of the metal deactivator is preferably 0.01 to 0.1 mass% of the total amount of the composition, more preferably 0.03 to 0.05 mass%.

[0072] Examples of the antifoaming agent are silicone oil, fluorosilicone oil, fluoroalkylether and the like. In view of a balance between antifoaming effects and economics, a content of the antifoaming agent is preferably approximately 0.005 to 0.1 mass% of the total amount of the compound.

[0073] Sulfur content of the lubricating oil composition according to the aspect of the invention is preferably 0.3 mass% or less of the total amount of the composition, more preferably 0.2 mass% or less, much more preferably 0.1 mass% or less. When the sulfur content is 0.3 mass% or less, deterioration of the catalyst performance for purifying exhaust gas can be effectively prevented.

[0074] Sulfate ash content of the lubricating oil composition according to the aspect of the invention is preferably 0.8 mass% or less, more preferably 0.6 mass% or less. When the sulfate ash content is 0.8 mass% or less, a smaller amount of the ash content is accumulated on the filter of the DPF in diesel engines, thereby preventing the filter clogging due to the ash content and contributing to a longer life of the DPF. The sulfate ash content means ash content obtained by adding sulfuric acid to carbonized residue generated by combustion of samples for heating so that the residue has a constant mass. The sulfate ash is generally used for knowing a rough amount of metal-based additives contained in the lubricating oil composition. Specifically, the sulfate ash is measured by a method defined in "5. Experiment Method of Sulfate Ash" of JIS K 2272.

[0075] The lubricating oil composition for internal combustion engines according to the aspect of the invention can maintain such a high level of friction modification as exhibited when the composition is new oil for a long time. Thus, the lubrication oil composition is favorably applicable to internal combustion engines such as gasoline engines, diesel engines and gas engines. Further, even when diesel soots are mixed, the lubricating oil composition can maintain the above effects, which is particularly preferable in diesel engines.

[Examples]

[0076] Next, the invention will be further described in detail based on Examples, which by no means limit the present invention.

[Examples 1, 2 and Comparatives 1 to 4]

[0077] Lubricating oil compositions composed as in Table 1 were prepared, and then the friction coefficients of the compositions when being new oil and the friction coefficients of the compositions after NOx degradation were measured. In accordance with the results, the compositions were evaluated in terms of performance as the lubricating oil for internal combustion engines.

[0078] The characteristics and properties of the base oil, additives and compositions (sample oil) were measured in the following manner.

(1) Kinematic Viscosity of Base Oil and Lubricating Oil Compositions

[0079] Measurement was conducted based on "Examining Method of Kinematic Viscosity of Petroleum Products" defined in JIS K2283.

(2) Viscosity Index of Base Oil

[0080] Measurement was conducted based on "Examining Method of Kinematic Viscosity of Petroleum Products" defined in JIS K2283.

(3) Sulfur Content of Base Oil and Lubricating Oil Compositions

[0081] Measurement was conducted based on JIS K2541.

(4) %CA of Base Oil

[0082] A proportion (percentage) of aromatic content was calculated by the n-d-M ring analysis method.

(5) NOACK Evaporation Amount of Base Oil

[0083] Measurement was conducted based on JPI (Japan Petroleum Institute)-5S-41-2004.

(5) Boron Content

[0084] Measurement was conducted based on JPI-5S-38-92.

(6) Nitrogen Content

[0085] Measurement was conducted based on JIS K2609.

(7) Molybdenum and Phosphorus Content

[0086] Measurement was conducted based on JPI-5S-38-92.

(8) Sulfate Ash Content

[0087] Measurement was conducted based on JIS K2272.

(9) NOx Degradation Test

[0088] With use of a testing machine for ISOT test (JIS K2514), nitrogen gas containing 8000 volume ppm of NO and air were blown to the sample oil under the presence of copper and iron catalysts, respectively at flow rate of 100 mL/minite, and NOx degradation test was conducted. The test temperature was 140 degrees C and testing time was 24 hours.

(10) Friction Coefficient (SRV, 80°C)

[0089] The following four sample oils were prepared, and friction coefficients thereof were measured:

[1] new oil (compositions composed as in Table 1);
[2] compositions after NOx degradation test was conducted on the new oil;
[3] compositions prepared by adding 0.5 mass% of carbon black to the new oil; and
[4] compositions prepared by adding 0.5 mass% of carbon black to the compositions [2];

[0090] The friction coefficients were measured with an SRV testing machine (manufactured by Optimol Ltd.) under the following conditions.

Testing piece: (a) disk: SUJ-2 material, (b) cylinder: SUJ-2 material
Amplitude: 1.5 mm

Frequency: 50 Hz
Load: 400N
Temperature: 80 degrees C

[0091] The components used for preparing the lubricating oil compositions are as follows.

(1) Base Oil: hydrorefined base oil: kinematic viscosity of 21 mm^2/s at 40 degrees C; Kinematic viscosity of 4.5 mm^2/s at 100 degrees C; viscosity index of 127; %CA of 0.1 or less; sulfur content of less than 20 mass ppm; and NOACK evaporation amount of 13.3 mass%.

(2) Boronated Polybutenyl Succinic Monoimide A: number average molecular weight of the polybutenyl group being 980; nitrogen content of 1.76 mass%; boron content of 2.1 mass%; B/N ratio of 1.19; and chlorine content of 0.01 mass% or less.

The above boronated polybutenyl succinic monoimide A was manufactured by the following method.

550 g of polybutene (Mn: 980), 1.5 g (0.005 mol) of cetyl bromide and 59 g (0.6 mol) of maleic acid anhydride were put into an autoclave of 1 litter, which were then subjected to nitrogen substitution and reacted with one another at 240 degrees C for five hours. After the temperature was lowered to 215 degrees C, unreacted maleic acid anhydride and unreacted cetyl bromide were distilled away therefrom under a low pressure. After the temperature was further lowered to 140 degrees C, filtration was conducted. An yield of obtained polybutenyl succicic anhydride was 550 g and its saponification number was 86 mg KOH/g. 500 g of the obtained polybutenyl succicic anhydride, 17.4 g (0.135 mol) of aminoethyl piperazine (AEP), 10.3 g (0.10 mol) of diethylene triamine (DETA), 14.6 g (0.10 mol) of triethylene tetramine (TETA) and 250 g of mineral oil were put into a separable flask of 1 litter and reacted with one another in nitrogen gas stream at 150 degrees C for two hours. After the temperature was raised to 200 degrees C, unreacted AEP, DETA and TETA and generated water were distilled away therefrom under a low pressure. An yield of the obtained polybutenyl succinimide was 750 g and its base number was 51 mg KOH/g (by a perchloric acid method). 150 g of the obtained polybutenyl succinimide and 20 g of boric acid were put into a separable flask of 500 milliliter and reacted with each other in nitrogen gas stream at 150 degrees C for four hours. After generated water was distilled away therefrom under a low pressure at 150 degrees C, the temperature was lowered to 140 degrees C and filtration was conducted. An yield of the generated boronated polybutenyl succinic monoimide A was 165 g and its boron content was 2.1 mass%. Polyalkylene polyamine having a ring structure at its terminal was approximately 40 mol% of the total polyalkylene polyamine.

(3)Boronated Polybutenyl Succinic Monoimide B: number average molecular weight of the polybutenyl group being 980; nitrogen content of 1.90 mass%; boron content of 0.8 mass%; B/N ratio of 0.42; and chlorine content of 0.01 mass% or less.

The boronated polybutenyl succinic monoimide B was manufactured through the same reactions as the boronated polybutenyl succinic monoimide A, except that the additive amount of boric acid was 13 g. An yield of the generated boronated polybutenyl succinic monoimide B was 161 g. Polyalkylene polyamine having a ring structure at its terminal was approximately 40 mol% of the total polyalkylene polyamine.

(4) Boronated Polybutenyl Succinic Monoimide C: number average molecular weight of the polybutenyl group being 980; nitrogen content of 2.30 mass%; boron content of 1.90 mass%; B/N ratio of 0.83; and chlorine content of 0.01 mass% or less.

The boronated polybutenyl succinic monoimide C was manufactured through the same reactions as the boronated polybutenyl succinic monoimide A, except that 18 g (0.17 mol) of diethylene triamine (DETA) and 25 g (0.17 mol) of triethylene tetramine (TETA) were used without use of aminoethyl piperazine (AEP). An yield of the generated boronated polybutenyl succinic monoimide C was 165g. No polyalkylene polyamine having a ring structure at its terminal was contained therein.

(5) Boronated Polybutenyl Succinic Monoimide D: number average molecular weight of the polybutenyl group being 980; nitrogen content of 1.95 mass%; boron content of 0.67 mass%; B/N ratio of 0.34; and chlorine content of 0.01 mass% or less.

The boronated polybutenyl succinic monoimide D was manufactured through the same reactions as the boronated polybutenyl succinic monoimide A, except that 18 g (0.17 mol) of diethylene triamine (DETA) and 25 g (0.17 mol) of triethylene tetramine (TETA) were used without use of aminoethyl piperazine (AEP) and that the additive amount of boric acid was 13 g. An yield of the generated boronated polybutenyl succinic monoimide D was 161g. No polyalkylene polyamine having a ring structure at its terminal was contained therein.

(6) Molybdenum Dithiocarbamate (MoDTC): SAKURA-LUBE 515 (manufactured by ADEKA Corporation); Mo content of 10.0 mass%; and sulfur content of 11.5 mass%.

(7) Phenol-Based Antioxidant: octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate.

(8) Amine-Based Antioxidant: dialkyl diphenylamine; nitrogen content of 4.6 mass%.

(9) Zinc Dialkyldithiophosphate (ZnDTP): Zn content of 9.0 mass%; phosphorus content of 8.2 mass%: sulfur content of 17.1 mass%; and the alkyl group being a mixture of a secondary butyl group and a secondary hexyl group.

(10) Viscosity Index Improver: styrene-isobutylene copolymer; mass average molecular weight of 584,000; and resin content of 10 mass%.

(11) Metal-Based Detergent A: overbased calcium phenate; base number of 225 mg KOH/g (perchloric acid method); calcium content of 9.3 mass%; and sulfur content of 3.0 mass%.

(12) Metal-Based Detergent B: calcium sulfonate; base number of 17 mg KOH/g (perchloric acid method); calcium content of 2.4 mass%; and sulfur content of 2.8 mass%.

(13) Polybutenyl Succinic Bisimide: number average molecular weight of the polybutenyl group being 2000; nitrogen content of 2.10 mass%; and chlorine content of 0.01 mass% or less.

(14) Molybdenum-Based Antioxidant: SAKURA-LUBE S-710 (manufactured by ADEKA Corporation), Mo content of 10 mass%.

(15) Ester-Based Friction Modifier: glycerin monooleate.

(16) Other Additives: a metal deactivator, pour point depressant and antifoaming agent.

[Table 1]

				Example		Comparative			
				1	2	1	2	3	4
Composition (mass%)	Base Oil			Remnant	Remnant	Remnant	Remnant	Remnant	Remnant
	Additives	(A)	Boronated Polybutenyl Succinic Monoimide A (B/N=1.19)	1.00	1.50	-	-	-	1.00
			Boronated Polybutenyl Succinic Monoimide B (B/N=0.42)	-	-	2.50	-	-	-
			Boronated Polybutenyl Succinic Monoimide C (B/N=0.83)	-	-	-	1.05	-	-
			Boronated Polybutenyl Succinic Bisimide D (B/N=0.34)	-	-	-	-	3.00	-
		(B)	MoDTC	0.35	0.35	4.35	0.35	0.35	-
		(C)	ZnDTP	0.92	0.36	0.92	0.92	0.92	0.92
		Others	Amine-Based Antioxidant	0.30	0.30	0.30	0.30	0.30	0.30
			Phenol-Based Antioxidant	0.30	0.30	0.30	0.30	0.30	0.30
			Viscosity Index Improver	6.50	6.50	6.50	6.54	6.50	6.50
			Metal-Based Detergent A	1.00	1.00	1.00	1.00	1.00	1.00
			Metal-Based Detergent B	0.40	0.40	0.40	0.40	0.40	0.40
			Polybutenyl Succinic Bisimide	5.00	5.00	5.00	5.00	5.00	5.00

(continued)

	Base Oil			Remnant	Remnant	Remnant	Remnant	Remnant	Remnant
			Molybdenum-Based Antioxidant	0.10	0.10	0.10	0.10	0.10	0.10
			Ester-Based Friction Modifier	0.30	0.30	0.30	0.30	0.30	0.30
			Other Additives	0.60	0.60	0.60	0.60	0.60	0.60
Composition Properties	Boron Content (mass%)			0.021	0.032	0.020	0.020	0.020	0.020
	MoDTC Content (Mo Quantity) (mass%)			0.035	0.035	0.035	0.035	0.035	0.000
	Phosphorus Content (mass%)			0.075	0.030	0.075	0.075	0.075	0.075
	Sulfur Content (mass%)			0.25	0.15	0.25	0.25	0.25	0.25
	Sulfate Ash Content (mass%)			0.55	0.45	0.55	0.55	0.55	0.53
SRV Friction Coefficient	New Oil			0.045	0.050	0.048	0.050	0.050	0.155
	Oil After NOx Degradation Test			0.055	0.063	0.068	0.072	0.104	0.163
	New Oil + Addition of 0.5 mass% of Carbon Black			0.095	0.098	0.102	0.098	0.125	0.156
	Oil After NOx Degradation Test + Addition of 0.5 mass% of Carbon Black			0.100	0.105	0.135	0.143	0.155	0.156

[Evaluation Results]

[0092] As understandable from Table 1, in Examples 1 and 2, in each of which the lubricating oil composition according to the aspect of the invention was used, all of the new oil, the oil after NOx degradation test and the oil added with carbon black had lower SRV friction coefficients and provided excellent friction modification, irrespective of their small phosphorus content and sulfate ash content.

[0093] On the other hand, in the sample oil of Comparative 1, which was blended with the boronated polybutenyl succinic monoimide B, the oil added with carbon black after the NOx degradation test had a higher SRV friction coefficient, because the B/N ratio of the boronated polybutenyl succinic monoimide B was as low as 0.42. In the sample oil of Comparative 2, which was blended with the boronated polybutenyl succinic monoimide C, the oil after the NOx degradation test and the oil added with carbon black after the NOx degradation test had higher SRV friction coefficients, because the boronated polybutenyl succinic monoimide C did not contain polyalkylene polyamine having a ring structure at its terminal. In the sample oil of Comparative 3, which was blended with the boronated polybutenyl succinic monoimide D, the oil after the NOx degradation test, the oil added with carbon black and the oil added with carbon black after the NOx degradation test had higher SRV friction coefficients, because the boronated polybutenyl succinic monoimide D did not contain polyalkylene polyamine having a ring structure at its terminal and its B/N ratio was as low as 0.34. Comparative 4, in which no MoDTC was blended, had a high SRV friction coefficient, and no friction modification was provided.

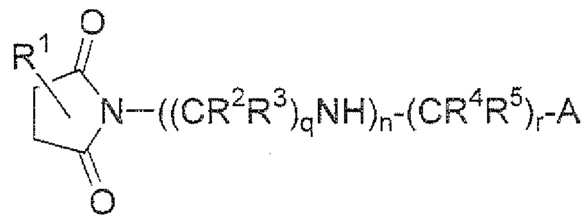
Claims

1. A lubricating oil composition for internal combustion engines, comprising:

base oil formed of mineral oil and/or synthetic oil;

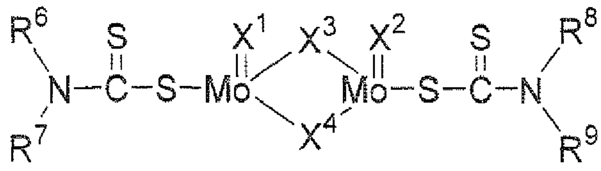
(A) a boronated product of polyalkenyl succinimide compound;
(B) molybdenum dithiocarbamate; and
(C) zinc dialkyldithiophosphate, wherein

the component (A) is a boronated product of a polyalkenyl succinimide compound obtained by reacting (a) a succinic acid or its anhydride substituted by a polyalkenyl group having a number average molecular weight of 500 to 5000 with (b) polyalkylene polyamine of which 5 mol% or more of the entirety has a ring structure at its terminal, the polyalkenyl succinimide compound being represented by a formula (1) as follows, a mass ratio of boron to nitrogen (B/N ratio) being 0.5 or more, a content of the component (A) being 0.01 to 0.1 mass% of the total amount of the composition in terms of boron,



(1)

where: R^1 represents a polyalkenyl group having a number average molecular weight of 500 to 5000; R^2, R^3, R^4 and R^5 each independently represent hydrogen or an alkyl group having 1 to 3 carbon atoms; q represents an integer of 2 to 4; n represents an integer of 0 to 3; r represents an integer of 2 to 4; and A represents an amino group or a group having the same ring structure as the terminal of the polyalkylene polyamine,
the component (B) is molybdenum dithiocarbamate represented by a formula (2) as follows, a content of the component (B) being 0.01 to 0.08 mass% of the total amount of the composition in terms of molybdenum,



(2)

where: R^6 to R^9 each independently represent a hydrocarbyl group having 4 to 22 carbon atoms; and X^1 to X^4 each represent a sulfur atom or an oxygen atom, and
a content of the component (C) is 0.01 to 0.09 mass% of the total amount of the composition in terms of phosphorus.

2. The lubricating oil composition according to claim 1, wherein a sulfur content is 0.3 mass% or less of the total amount of the composition while a sulfate ash content is 0.8 mass% or less of the total amount of the composition.

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EUROPEAN SEARCH REPORT

Application Number
EP 09 16 2272

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	28 July 2009	Greß, Tobias

CATEGORY OF CITED DOCUMENTS

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