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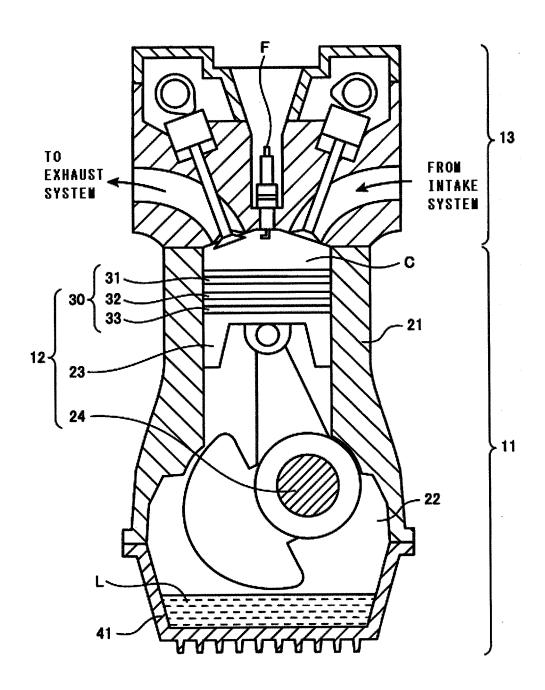
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(54) LUBRICATING OIL COMPOSITION FOR SPARK-IGNITION INTERNAL COMBUSTION ENGINE

(57) The lubricating oil composition for spark-ignition internal combustion engine according to the present invention is a lubricating oil composition to be used for a spark-ignition internal combustion engine including a piston having a piston ring, in which a total tension per piston of tensions applied to the piston ring is 30 N or less, the lubricating oil composition being a lubricating oil composition comprising a base oil, (A) an organic metal-based additive containing an alkali metal and/or an alkaline earth metal, and (B) an organic zinc-based additive, wherein a concentration of the component (A) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a metal content; a concentration of the component (B) on a basis of the total amount of the lubricating oil composition is 0.15%

by mass or less as converted into a zinc content; the product of the concentration (% by mass) of the component (A) and a base number (mgKOH/g) of the lubricating oil composition is 1.3 or less; the product of the concentration (% by mass) of the component (B) and an acid number (mgKOH/g) of the lubricating oil composition is 1.2 or less; and the lubricating oil composition has a Noack evaporation loss of 10% by mass or more and a kinematic viscosity at 100°C of 9.3 mm²/s or less. The lubricating oil composition for spark-ignition internal combustion engine according to the present invention is capable of preventing a deterioration of the combustion state of a spark-ignition internal combustion engine.

[FIG. 1]



Description

Technical Field

[0001] The present invention relates to a lubricating oil composition to be used for a spark-ignition internal combustion engine including a piston having a piston ring, in which a total tension per piston of tensions applied to the piston ring is 30 N or less.

Background Art

[0002] In view of increasing awareness of environmental issues, an improvement of fuel consumption performance of automobiles having an internal combustion engine, or the like is being demanded. As an example of the improvement of fuel consumption performance, there is known a method of reducing a friction loss to be caused due to friction between a piston ring and a cylinder inner wall of an internal combustion engine (see PTL 1). According to this method, the friction loss is reduced by reducing a tension applied to the piston ring.

[0003] Meanwhile, the fuel consumption performance can also be improved by setting a viscosity of a lubricating oil composition to be used for an internal combustion engine low.

Citation List

Patent Literature

[0004] PTL 1: JP 2012-215238A

25 Summary of Invention

Technical Problem

[0005] However, if the piston ring tension is excessively reduced, so-called oil loss through piston, in which the lubricating oil composition invades into a combustion chamber, is liable to be generated. Even in the case of using a lowviscosity lubricating oil composition, similarly in view of the facts that a flow resistance is small and that a permeation amount in an oil ring increases, oil loss through piston is liable to be generated.

[0006] In an internal combustion engine provided with a reciprocating piston, a mixed gas composed of a fuel and an oxidizing agent is compressed by the piston in a cylinder interior, whereby the temperature and pressure increase. At this time, before original ignition accompanied by definite heat generation is generated, the mixed gas ignites itself due to the compression, thereby causing combustion. This is called low-temperature autoignition. The low-temperature autoignition includes a stage at which a low-temperature flame called a cool flame or a blue flame reveals, and an active chemical species is produced, leading to generation and propagation of a hot flame accompanied by abrupt heat generation.

[0007] In a spark-ignition internal combustion engine, an active chemical species is forcedly provided by an ignition source, such as an electric spark, etc., leading to generation and propagation of a hot flame. For this reason, in the case where the progress of a low-temperature autoignition reaction is faster than the generation and propagation of a hot flame originated from the ignition, a deterioration of the combustion state or abrupt pressure vibration which will cause knocking is generated.

[0008] The lubricating oil composition which has invaded into the combustion chamber due to the oil loss through piston is exposed to high heat, a base oil evaporates, and a metal-based additive is concentrated. It may be considered that the concentrated metal-based additive causes a deterioration of the combustion state.

[0009] For this reason, from the viewpoint of preventing the oil loss through piston, in the case of reducing a piston ring tension, it may be considered to set a viscosity of the lubricating oil composition high, whereas in the case of setting the viscosity of the lubricating oil composition low, it may be considered to set the piston ring tension high.

[0010] In the light of the above, since there is a problem of antinomy between the improvement of fuel consumption performance and the deterioration of combustion state, a lubricating oil composition for internal combustion engine capable of solving this problem and improving the fuel consumption performance has been demanded.

[0011] Then, an object of the present invention is to provide a lubricating oil composition for internal combustion engine capable of delaying a generation timing of a cool flame, namely making it close to the general spark discharge timing, even in a spark-ignition internal combustion engine in which the oil loss through piston is liable to be generated.

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Solution to Problem

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[0012] The present inventors obtained such a finding that the metal-based additive which has invaded into the combustion chamber and been concentrated hastens the generation timing of a cool flame, promotes the autoignition, and increases the knock intensity.

[0013] Then, it has been found that by adding a specified additive in the lubricating oil composition and further adjusting its content, even if the oil loss through piston is generated, the generation timing of a cool flame can be delayed, namely it can be made close to a timing of general spark discharge.

[0014] The present invention provides the following.

- [1] A lubricating oil composition for spark-ignition internal combustion engine that is a lubricating oil composition to be used for a spark-ignition internal combustion engine including a piston having a piston ring, in which a total tension per piston of tensions applied to the piston ring is 30 N or less, the lubricating oil composition being a lubricating oil composition containing a base oil, (A) an organic metal-based additive containing an alkali metal and/or an alkaline earth metal, and (B) an organic zinc-based additive, wherein a concentration of the component (A) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a metal content; a concentration of the component (B) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a zinc content; the product of the concentration (% by mass) of the component (A) and a base number (mgKOH/g) of the lubricating oil composition is 1.3 or less; the product of the concentration (% by mass) of the component (B) and an acid number (mgKOH/g) of the lubricating oil composition is 1.2 or less; and the lubricating oil composition has a Noack evaporation loss of 10% by mass or more and a kinematic viscosity at 100°C of 9.3 mm²/s or less.
- [2] The lubricating oil composition for spark-ignition internal combustion engine as set forth above in [1], comprising an ashless base number improver having a base number of 1 mgKOH/g or more and 200 mgKOH/g or less on a basis of the total amount of the lubricating oil composition in an amount of 0.01% by mass or more as converted into a nitrogen content.
- [3] The lubricating oil composition for spark-ignition internal combustion engine as set forth above in [1] or [2], wherein the component (A) is a metal-based detergent having a base number of 10 mgKOH/g or more and 600 mgKOH/g or less.
- [4] The lubricating oil composition for spark-ignition internal combustion engine as set forth above in any of [1] to [3], wherein the component (B) is a zinc dialkyldithiophosphate and/or a zinc dialkyldioxyphosphate.
- [5] The lubricating oil composition for spark-ignition internal combustion engine as set forth above in any of [1] to [4], further comprising an organic molybdenum-based additive, a content of the organic molybdenum-based additive on a basis of the total amount of the lubricating oil composition being 0.01% by mass or more and 0.07% by mass or less as converted into a molybdenum content.
- [6] The lubricating oil composition for spark-ignition internal combustion engine as set forth above in any of [1] to [5], wherein the spark-ignition internal combustion engine is a gasoline engine.
- [7] A method for producing a lubricating oil composition for spark-ignition internal combustion engine that is a lubricating oil composition to be used for a spark-ignition internal combustion engine comprising a piston having a piston ring, in which a total tension per piston of tensions applied to the piston ring is 30 N or less, the method comprising blending a base oil with (A) an organic metal-based additive containing an alkali metal and/or an alkaline earth metal and (B) an organic zinc-based additive in such a manner that a concentration of the component (A) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a metal content; a concentration of the component (B) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a zinc content; the product of the concentration (% by mass) of the component (A) and a base number (mgKOH/g) of the lubricating oil composition is 1.3 or less; the product of the concentration (% by mass) of the component (B) and an acid number (mgKOH/g) of the lubricating oil composition is 1.2 or less; and the lubricating oil composition has a Noack evaporation loss of 10% by mass or more and a kinematic viscosity at 100°C of 9.3 mm²/s or less.
- [8] A spark-ignition internal combustion engine including a piston having a piston ring constituted of plural rings including an oil ring, in which a total tension per piston of tensions applied to the piston ring is 30 N or less, the spark-ignition internal combustion engine being lubricated by a lubricating oil composition, wherein the lubricating oil composition contains a base oil, (A) an organic metal-based additive containing an alkali metal and/or an alkaline earth metal, and (B) an organic zinc-based additive; a concentration of the component (A) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a metal content; a concentration of the component (B) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a zinc content; the product of the concentration (% by mass) of the component (A) and a base number (mgKOH/g) of the lubricating oil composition is 1.3 or less; the product of the concentration (% by mass) of the

component (B) and an acid number (mgKOH/g) of the lubricating oil composition is 1.2 or less; and the lubricating oil composition has a Noack evaporation loss of 10% by mass or more and a kinematic viscosity at 100° C of 9.3 mm²/s or less.

[9] A method for lubricating a spark-ignition internal combustion engine including a piston having a piston ring constituted of plural rings including an oil ring, in which a total tension per piston of tensions applied to the piston ring is 30 N or less, with a lubricating oil composition, wherein the lubricating oil composition contains a base oil, (A) an organic metal-based additive containing an alkali metal and/or an alkaline earth metal, and (B) an organic zinc-based additive; a concentration of the component (A) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a metal content; a concentration of the component (B) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a zinc content; the product of the concentration (% by mass) of the component (A) and a base number (mgKOH/g) of the lubricating oil composition is 1.3 or less; the product of the concentration (% by mass) of the component (B) and an acid number (mgKOH/g) of the lubricating oil composition is 1.2 or less; and the lubricating oil composition has a Noack evaporation loss of 10% by mass or more and a kinematic viscosity at 100°C of 9.3 mm²/s or less.

Advantageous Effects of Invention

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[0015] In accordance with the present invention, it is possible to provide a lubricating oil composition for internal combustion engine, which is capable of preventing a deterioration of the combustion state of a spark-ignition internal combustion engine.

Brief description of Drawing

[0016] FIG. 1 is a constitutional view of a spark-ignition internal combustion engine 1 according to an embodiment of the present invention.

Description of Embodiments

[0017] The present invention is hereunder described in more detail.

[Lubricating Oil Composition for Spark-Ignition Internal Combustion Engine]

[0018] The lubricating oil composition for spark-ignition internal combustion engine according to an embodiment of the present invention is a lubricating oil composition to be used for a spark-ignition internal combustion engine including a piston having a piston ring, in which a total tension per piston of tensions applied to the piston ring is 30 N or less, the lubricating oil composition being a lubricating oil composition including a base oil, (A) an organic metal-based additive containing an alkali metal and/or an alkaline earth metal, and (B) an organic zinc-based additive, wherein a concentration of the component (A) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a metal content; a concentration of the component (B) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a zinc content; the product of the concentration (% by mass) of the component (A) and a base number (mgKOH/g) of the lubricating oil composition is 1.3 or less; the product of the concentration (% by mass) of the component (B) and an acid number (mgKOH/g) of the lubricating oil composition is 1.2 or less; and the lubricating oil composition has a Noack evaporation loss of 10% by mass or more and a kinematic viscosity at 100°C of 9.3 mm²/s or less.

[0019] It is to be noted that the concentration of the component (A) referred to hereunder is expressed by "% by mass" (the same is also applied to the component (B)).

<Properties of Lubricating Oil Composition for Spark-Ignition Internal Combustion Engine>

[0020] The present invention is to solve the problems of a low-viscosity lubricating oil composition, and the lubricating oil composition for spark-ignition internal combustion engine according to the embodiment of the present invention has a Noack evaporation loss of 10% by mass or more and a kinematic viscosity at 100°C of 9.3 mm²/s or less.

[0021] When the Noack evaporation loss of the lubricating oil composition for spark-ignition internal combustion engine is less than 10% by mass, a low viscosity sufficient for contributing to the low fuel consumption performance may not be achieved. On the other hand, in order to inhibit excessive oil loss through piston, the Noack evaporation loss may be controlled to 15% by mass or less.

[0022] When the kinematic viscosity at 100°C of the lubricating oil composition for spark-ignition internal combustion engine is more than 9.3 mm²/s, a sufficient low fuel consumption performance is not obtained. On the other hand, in

order to inhibit excessive oil loss through piston, the kinematic viscosity at 100°C may be controlled to 5.6 mm²/s or more. **[0023]** In the case where the lubricating oil composition in which the Noack evaporation loss and the kinematic viscosity at 100°C fall within the foregoing ranges is used for a spark-ignition internal combustion engine in which a total tension per piston of tensions applied to the piston ring is 30 N or less, the oil loss through piston is liable to be generated.

[0024] It is to be noted that the kinematic viscosity at 100°C is a value as measured in accordance with "Testing methods for kinematic viscosity of petroleum products" as prescribed in JIS K2283, and the Noack evaporation loss is a value as measured in accordance with JPI-5S-41-2004.

<Base Oil>

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[0025] With respect to the base oil of the lubricating oil composition for spark-ignition internal combustion engine of the present invention, an arbitrary material may be properly selected and used among mineral oils and synthetic oils which have been conventionally used as the base oil of lubricating oil for internal combustion engine.

[0026] Examples of the mineral oil may include distillates obtained through atmospheric distillation of paraffin-based crude oil, intermediate-base crude oil, or naphthene-base crude oil, or distillates obtaining through vacuum distillation of a residual oil of atmospheric distillation, or refined oils obtained through refining of such a distillate according to a conventional method, for example, solvent refined oil, hydrogenated refined oil, dewaxing treated oil, white clay treated oil, etc.

[0027] Examples of the synthetic oil include poly- α -olefins that are an α -olefin oligomer having 8 to 14 carbon atoms, polybutene, various esters (for example, polyol esters, dibasic acid esters, phosphate esters, etc.), various ethers (for example, polyphenyl ethers, etc.), polyglycols, alkylbenzenes, alkylnaphthalenes, and the like.

[0028] In the present invention, as the base oil, a single kind of each of the aforementioned mineral oils and synthetic oils may be used, or a combination of two or more kinds thereof may be used. A mixture of the mineral oil and the synthetic oil may be used.

[0029] Although a viscosity of the base oil may be properly determined depending upon an application of the lubricating oil composition, the kinematic viscosity at 100°C is generally 2 mm²/s or more and 30 mm²/s or less, preferably 2 mm²/s or more and 15 mm²/s or less, and more preferably 2 mm²/s or more and 10 mm²/s or less. When the kinematic viscosity at 100°C is 2 mm²/s or more, an evaporation loss is small; whereas when it is 30 mm²/s or less, a power loss to be caused due to viscous resistance is not so large, and hence, a fuel consumption improving effect is obtained.

[0030] As for the base oil, its viscosity index is generally 80 or more, preferably 100 or more, and more preferably 120 or more. The base oil having a viscosity index of 80 or more is small in a change of viscosity to be caused due to a change of temperature, and hence, it is preferred.

[0031] In the case of using, as the base oil, a mixture of mineral oils, a mixture of synthetic oils, or a mixture of a mineral oil and a synthetic oil, the viscosity after mixing has only to fall within the foregoing range. As an example, the base oil containing a poly- α -olefin or a mineral oil having a viscosity index of 120 or more which is corresponding to Group 3 of the API classification, may be used.

[0032] It is to be noted that a content of the base oil on a basis of the total amount of the lubricating oil composition for spark-ignition internal combustion engine is preferably 70% by mass or more and 90% by mass or less.

<(A) Organic Metal-Based Additive>

[0033] The component (A) in the lubricating oil composition for spark-ignition internal combustion engine of the present invention is an organic metal-based additive containing an alkali metal and/or an alkaline earth metal. It is to be noted that zinc is not included in the metal as referred to herein.

[0034] As the component (A), an arbitrary metal-based detergent which is used for lubricating oils may be used. As the metal-based detergent, an alkaline earth metal-based detergent may be used, and examples thereof include an alkaline earth metal sulfonate, an alkaline earth metal salicylate, an alkaline earth metal phenate, and a mixture of two or more selected from those materials, and the like.

[0035] Examples of the alkaline earth metal phenate include alkaline earth metal salts, especially magnesium salts and/or calcium salts, of an alkylphenol, an alkylphenol sulfide, or a Mannich reaction product of an alkylphenol, and the like. Among those, calcium salts are especially preferably used.

[0036] Examples of the alkaline earth metal sulfonate include alkaline earth metal salts, especially magnesium salts and/or calcium salts, of an alkyl aromatic sulfonic acid obtained by sulfonating an alkyl aromatic compound having a molecular weight of 300 or more and 1,500 or less, and preferably 400 or more and 700 or less. Among those, calcium salts are preferably used.

[0037] Examples of the alkaline earth metal salicylate include alkaline earth metal salts, especially magnesium salts and/or calcium salts, of an alkyl salicylic acid. Among those, calcium salts are preferably used.

[0038] The alkyl group constituting the alkaline earth metal-based detergent is an alkyl group having preferably 4 to

30 carbon atoms, and more preferably 6 to 18 carbon atoms, and the alkyl group may be either linear or branched. The alkyl group may be a primary alkyl group, a secondary alkyl group, or a tertiary alkyl group.

[0039] The alkaline earth metal sulfonate, the alkaline earth metal phenate, and the alkaline earth metal salicylate include not only a neutral alkaline earth metal sulfonate, a neutral alkaline metal phenate, and a neutral alkaline earth salicylate, each of which is obtained by allowing the aforementioned alkyl aromatic sulfonic acid, alkylphenol, alkylphenol sulfide, Mannich reaction product of an alkylphenol, or alkylsalicylic acid, or the like to react directly with an alkaline earth metal base, such as an oxide or hydroxide, etc., of an alkaline earth metal of magnesium and/or calcium, or once forming into an alkali metal salt, such as a sodium salt, a potassium salt, etc., and then substituting with an alkaline earth metal salt, or other means; but also a basic alkaline earth metal sulfonate, a basic alkaline earth metal phenate, and a basic alkaline earth metal salicylate, each of which is obtained by heating a neutral alkaline earth metal sulfonate, a neutral alkaline earth metal base in the presence of water as well as a overbased alkaline earth metal sulfonate, a overbased alkaline earth metal phenate, and a overbased alkaline earth metal salicylate, each of which is obtained by allowing a neutral alkaline earth metal sulfonate, or a neutral alkaline earth metal sulfonate or borate of an alkaline earth metal in the presence of a carbon dioxide gas.

[0040] As for a metal ratio of the organic metal-based additive which is used in the present invention, a material having a metal ratio of generally 20 or less may be used alone or in admixture of two or more thereof. The use of a metal-based detergent having a metal ratio of preferably 3 or less, more preferably 1.5 or less, and especially preferably 1.2 or less is especially preferred because it is more excellent in oxidation stability, base number retention, high-temperature detergency, and the like.

[0041] It is to be noted that the metal ratio as referred to herein is expressed by (valence of metal element) x (metal element content (mol%))/(soap group content (mol%)) in the metal-based detergent; the metal element as referred to herein means calcium, magnesium, or the like; and the soap group as referred to herein means a sulfonic acid group, a phenol group, a salicylic acid group, or the like.

[0042] In the lubricating oil composition for spark-ignition internal combustion engine of the present invention, from the viewpoints of piston detergency and acid neutralization performance, a Ca salt of sulfonate, salicylate, or phenate is preferably used, and a Ca salt of salicylate is especially preferably used.

[0043] A concentration of the organic metal-based additive (A) which may be used in the present embodiment on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a metal content. [0044] When the concentration of the component (A) is more than 0.15% by mass as converted into a metal content, the generation of a cool flame, acceleration of autoignition, and an increase of the knock intensity are problematic. From this viewpoint, the concentration of the component (A) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less, preferably 0.11% by mass or less, and more preferably 0.06% by mass or less as converted

into a metal content.

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[0045] It is to be noted that from the viewpoints that when the concentration of the component (A) is 0.02% by mass or less, a degree of improvement of the combustion state is low, and the piston detergency and the acid neutralization performance may not be maintained, a lower limit thereof is 0.02% by mass.

[0046] From the viewpoints of piston detergency and acid neutralization performance, a base number of the organic metal-based additive (A) which may be used in the present embodiment is preferably 10 mgKOH/g or more and 600 mgKOH/g or less. Furthermore, from the standpoint that a lubricating oil composition in which the product of the concentration of the component (A) and the base number of the lubricating oil composition is 1.3 or less is liable to be obtained, the base number of the organic metal-based additive (A) is more preferably 50 mgKOH/g or more and 300 mgKOH/g or less, and still more preferably 100 mgKOH/g or more and 250 mgKOH/g or less.

[0047] Furthermore, from the standpoint of making it easy to control the generation of a cool flame and acceleration of autoignition, an acid number of the organic metal-based additive (A) which may be used in the present embodiment is preferably 0.5 mgKOH/g or more and 100 mgKOH/g or less, more preferably 1 mgKOH/g or more and 50 mgKOH/g or less, and still more preferably 5 mgKOH/g or more and 20 mgKOH/g or less.

[0048] It is to be noted that the base number as referred to herein means a base number as measured by the hydrochloric acid method in accordance with JIS K2501, the 7th section of "Petroleum products and lubricating oils-neutralization number test method", and the acid number as referred to herein means an acid number as measured by the potentiometric titration method in accordance with JIS K2501, "Petroleum products and lubricating oils-neutralization number test method".

<(B) Organic Zinc-Based Additive>

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[0049] The lubricating oil composition for spark-ignition internal combustion engine of the present invention contains (B) an organic zinc-based additive, and a concentration of the component (B) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a zinc content.

[0050] When the concentration of the component (B) is more than 0.15% by mass as converted into a zinc content, the generation of a cool flame, acceleration of autoignition, and an increase of the knock intensity are problematic.

[0051] From this viewpoint, the concentration of the component (B) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less, preferably 0.10% by mass or less, and more preferably 0.05% by mass or less as converted into a zinc content.

[0052] It is to be noted that from the viewpoints that when the concentration of the component (B) is 0.01% by mass or less, a degree of improvement of the combustion state is low, and the wear resistant properties may not be maintained, a lower limit thereof is 0.01% by mass.

[0053] From the standpoint that a lubricating oil composition in which the product of the concentration of the component (B) and the acid number of the lubricating oil composition is 1.2 or less is liable to be obtained, an acid number of the organic zinc-based additive (B) which may be used in the present embodiment is preferably 0.1 mgKOH/g or more and 30 mgKOH/g or less, more preferably 0.5 mgKOH/g or more and 20 mgKOH/g or less, and still more preferably 1 mgKOH/g or more and 10 mgKOH/g or less.

[0054] Furthermore, from the standpoint of making it easy to control the generation of a cool flame and acceleration of autoignition, a base number of the organic zinc-based additive (B) which may be used in the present embodiment is preferably 5 mgKOH/g or more and 400 mgKOH/g or less, more preferably 10 mgKOH/g or more and 300 mgKOH/g or less, and still more preferably 50 mgKOH/g or more and 200 mgKOH/g or less.

[0055] As the component (B), a zinc dialkyldithiophosphate and/or a zinc dialkyldioxyphosphate represented by the following general formula (I) may be used.

 $\begin{bmatrix} R^1 & X & X \\ R^2 & X & Z_n \end{bmatrix}_2$ (I)

In the formula, each of Xs is independently either O or S, and at least two of Xs are the same element; and each of R¹ and R² independently represents a primary or secondary alkyl group having 3 to 22 carbon atoms or an alkylaryl group substituted with an alkyl group having 3 to 18 carbon atoms.

[0056] Here, examples of the primary or secondary alkyl group having 3 to 22 carbon atoms include a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, a dodecyl group, a tetradecyl group, a hexadecyl group, an octadecyl group, and an eicosyl group, each of which is primary or secondary, and the like. Examples of the alkylaryl group substituted with an alkyl group having 3 to 18 carbon atoms include a propylphenyl group, a pentylphenyl group, an octylphenyl group, a nonylphenyl group, a dodecylphenyl group, and the like.

[0057] In the lubricating oil composition for spark-ignition internal combustion engine of the present invention, as the component (B), the aforementioned zinc dithiophosphate may be used alone or in combination of two or more thereof; however, from the standpoint of enhancing the wear resistant properties, it is especially preferred to use a material containing, as a main component, a zinc dialkyldithiophosphate of a secondary alkyl group.

[0058] <-Contents of Component (A) and Component (B)>

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[0059] It may be considered that in the lubricating oil composition which has invaded into the combustion chamber, the base oil evaporates to cause concentration of the metal-based additive, thereby lowering the combustion performance.

[0060] The present inventors have found that when the organic metal-based additive component originated from the lubricating oil is present within the combustion chamber, the generation of a cool flame is excessively accelerated. It is known that a part of organic metal-based additives largely contributes to the acid number or base number of a lubricating oil. The present inventors have found that among organic metal-based additives, an additive which largely contributes to the acid number or base number of the lubricating oil composition is high especially in the effect for accelerating the generation timing of a cool flame.

[0061] Accordingly, in order to inhibit the acceleration of the generation timing of a cool flame, it is necessary to not only reduce the content of such a metal-based additive but also reduce the acid number and the base number originated from such a metal-based additive. In the lubricating oil composition, from the standpoint that the acceleration of the generation timing of a cool flame may be inhibited, it is preferred to reduce the product of the concentration of the additive and the acid number or the base number.

[0062] From the aforementioned viewpoints, in the lubricating oil composition for spark-ignition internal combustion engine of the present invention, it is required that the product of the concentration of the component (A) and the base number of the lubricating oil composition is 1.3 or less; and that the product of the concentration of the component (B)

and the acid number of the lubricating oil composition is 1.2 or less.

[0063] When the product of the concentration of the component (A) and the base number of the lubricating oil composition is more than 1.3, the generation of a cool flame and the autoignition are accelerated, so that the knocking is liable to be generated. From this viewpoint, the product of the concentration of the component (A) and the base number of the lubricating oil composition is preferably 1.0 or less, more preferably 0.7 or less, and still more preferably 0.4 or less. **[0064]** When the product of the concentration of the component (B) and the acid number of the lubricating oil composition is more than 1.2, the generation of a cool flame and the autoignition are accelerated, so that the knocking is liable to be generated. From this viewpoint, the product of the concentration of the component (B) and the acid number of the lubricating oil composition is preferably 0.8 or less, more preferably 0.4 or less, and still more preferably 0.2 or less.

[0065] From the viewpoint that the piston detergency and the acid neutralization performance may not be maintained, a lower limit of the product of the concentration of the component (A) and the base number of the lubricating oil composition is preferably set to 0.1. From the viewpoint that the wear resistant properties may not be maintained, a lower limit of the product of the concentration of the component (B) and the acid number of the lubricating oil composition is preferably set to 0.05.

[0066] It is to be noted that in the present embodiment, the product of the concentration of the component (A) and the base number of the lubricating oil composition and the product of the concentration of the component (B) and the acid number of the lubricating oil composition are each expressed by rounding to the second decimal place.

<Ashless Base Number Improver>

[0067] The lubricating oil composition for spark-ignition internal combustion engine of the present invention not only reduces the contents of the organic metal-based additive and the organic zinc-based additive but also reduces the acid number and the base number originated from these metal-based additives and reduces the product of the concentration of the additive and the acid number or base number, and hence, the acceleration of the general timing of a cool flame may be inhibited.

[0068] In the lubricating oil composition for spark-ignition internal combustion engine of the present invention, an ashless base number improver may be contained. By containing the ashless base number improver in the lubricating oil composition for spark-ignition internal combustion engine of the present invention, the base number originated from the metal-based additive as the lubricating oil composition may be lowered without impairing the performance as the lubricating oil. For that reason, not only the lubricating oil composition for spark-ignition internal combustion engine of the present invention may avoid a lowering of the performance as the lubricating oil, but also even in the case where the lubricating oil composition for spark-ignition internal combustion engine is concentrated within the combustion chamber, it does not cause acceleration of the generation timing of a cool flame.

[0069] It is preferred that the lubricating oil composition for spark-ignition internal combustion engine according to the embodiment of the present invention contains an ashless base number improver having a base number of 1 mgKOH/g or more and 200 mgKOH/g or less in an amount of 0.01% by mass or less as converted into a nitrogen content on a basis of the total amount of the lubricating oil composition.

[0070] Examples of the ashless base number improver include nitrogen-containing compounds, such as amines, imides, etc. Examples thereof include nitrogen-containing compounds, such as dispersants, e.g., a polybutenylsuccinimide, etc., or boron-modified products thereof, a hindered amine, etc. Among those, it is preferred to use a hindered amine from the standpoint of making it easy to lower the base number as the lubricating oil composition without impairing the performance as the lubricating oil.

[0071] As the imide-based nitrogen-containing compound, a boronated imide-based dispersant and if desired, a non-boronated imide-based dispersant may be used. The non-boronated imide-based dispersant is generally called an imide-based dispersant. As such an imide-based dispersant, it is suitable to use a polybutenylsuccinimide. Examples of the polybutenylsuccinimide include compounds represented by the following general formulae (1) and (2).

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[0072] In the foregoing general formulae (1) and (2), PIB represents a polybutenyl group, and its number average molecular weight is generally 900 or more and 3,500 or less, and preferably 1,000 or more and 2,000 or less. When the number average molecular weight is 900 or more, there is no concern that the dispersibility is inferior, and when it is 3,500 or less, there is no concern that the storage stability is inferior. In the foregoing general formulae (1) and (2), n is generally an integer of 1 to 5, and more preferably an integer of 2 to 4.

[0073] Although a production method of the polybutenylsuccinimide is not particularly limited, the polybutenylsuccinimide may be produced by a known method. For example, the polybutenylsuccinimide may be obtained by allowing a polybutenylsuccinic acid obtained through a reaction between polybutene and maleic anhydride at 100°C or higher and 200°C or lower to react with a polyamine, such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, etc.

[0074] As the boronated imide-based dispersant, it is preferred to use a boronated polybutenylsuccinimide obtained by allowing a boron compound to act on the non-borated imide-based dispersant exemplified by the foregoing general formula (1) or (2).

[0075] Examples of the born compound include boric acid, a boric acid salt, a boric acid ester, and the like. Examples of the boric acid include orthoboric acid, metaboric acid, paraboric acid, and the like. Suitable examples of the boric acid salt include ammonium salts, such as ammonium borates, for example, ammonium metaborate, ammonium tetraborate, ammonium pentaborate, ammonium octaborate, etc., and the like. Suitable examples of the boric acid ester include esters between boric acid and an alkyl alcohol (desirably having 1 to 6 carbon atoms), such as monomethyl borate, dimethyl borate, trimethyl borate, monoethyl borate, diethyl borate, triethyl borate, monopropyl borate, dipropyl borate, tripropyl borate, monobutyl borate, dibutyl borate, tributyl borate, etc.

[0076] It is to be noted that a weight ratio B/N of a boron content B to a nitrogen content N in the boronated polybute-nylsuccinimide is generally 0.1 to 3, and preferably 0.2 to 1.

[0077] As the amine-based nitrogen-containing compound, compounds represented by the following general formulae (3) and (4) are preferred,

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[0078] R³ represents a linear or branched alkyl group having 7 to 17 carbon atoms; and n represents 6 to 18. The alkyl group is, for example, an alkyl group having 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, or 17 carbon atoms. n is preferably 6, 8, 10, 12, 14, 16, or 18.

[0079] The aforementioned heterocyclic compounds can be produced by a well-known method. Examples of the heterocyclic compound include a 2,2,6,6-tetramethylpiperidino-4-ol ester of an aliphatic carboxylic acid, and esters of lauric acid or stearic acid. As the heterocyclic compound (B), hindered amines represented by the following formulae are preferred.

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[0080] A preferred content of the ashless base number improver is 0.01% by mass or more, preferably 0.05% by mass or more, and more preferably 0.1% by mass or more as converted into a nitrogen content on a basis of the total amount of the composition. It is to be noted that its upper limit is 0.5% by mass.

[0081] The base number of the ashless base number improver which may be used in the present embodiment varies with the content of the ashless base number improver; however, from the standpoint of making it easy to lower the base number of the lubricating oil composition without imparting the performance of the lubricating oil, the base number of the ashless base number improver is preferably 10 mgKOH/g or more, more preferably 50 mgKOH/g or more, and still more preferably 100 mgKOH/g or more.

<Organic Molybdenum-Based Additive>

[0082] In the lubricating oil composition for spark-ignition internal combustion engine according to the present embodiment, an organic molybdenum-based additive may be contained, and a content of the organic molybdenum-based additive on a basis of the total amount of the lubricating oil composition is preferably 0.01% by mass or more and 0.07% by mass or less as converted into a molybdenum content. From the viewpoint of maintaining the wear resistant properties, the content of the organic molybdenum-based additive is more preferably 0.04% by mass or more and 0.07% by mass or less. From the viewpoint of antioxidative properties, the content of the organic molybdenum-based additive is more preferably 0.01% by mass or more and 0.02% by mass or less.

[0083] As the organic molybdenum-based additive, a molybdenum-based friction modifier and a molybdenum-based antioxidant may be used.

[0084] As the molybdenum-based friction modifier, all of arbitrary compounds which are generally used as a friction modifier of lubricating oil for internal combustion engine may be used. For example, there is exemplified at least one selected from a molybdenum amine complex and/or oxymolybdenum dithiocarbamate sulfide, a trinuclear molybdenum-sulfur compound, and molybdenum dithiophosphate. More specifically, at least one selected from molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate (also referred to MoDTP), and an amine salt of molybdic acid may be used.

[0085] As the molybdenum-based antioxidant, there is preferably exemplified a molybdenum amine complex. As the molybdenum amine complex, hexavalent molybdenum compounds, specifically those obtained through a reaction between molybdenum trioxide and/or molybdic acid and an amine compound, for example, compounds obtained by the production method described in JP 2003-252887A, may be used.

[0086] As for a reaction ratio between the hexavalent molybdenum compound and the amine compound, a molar ratio of the Mo atom of the molybdenum compound is preferably 0.7 to 5, more preferably 0.8 to 4, and still more preferably 1 to 2.5 relative to one mole of the amine compound. As for a reaction method, a conventionally known method, for example, a method described in JP 2003-252887A, may be adopted.

[0087] In the present invention, as the molybdenum-based antioxidant, besides the aforementioned molybdenum amine complex, a sulfur-containing molybdenum complex of succinimide, as described in JP 3-22438B, JP 2004-2866A, etc., may also be used.

<Other Additives>

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[0088] In the lubricating oil composition for spark-ignition internal combustion engine according to the embodiment of the present invention, it is preferred to further contain at least one selected from a viscosity index improver, an antioxidant, and a friction modifier.

[0089] Examples of the viscosity index improver include a polymethacrylate, a dispersion type polymethacrylate, an olefin-based copolymer (for example, an ethylene-propylene copolymer, etc.), a dispersion type olefin-based copolymer" a styrene-based copolymer (for example, a styrene-diene copolymer, a styrene-isoprene copolymer, etc.), and the like.

[0090] From the standpoint of a blending effect, a blending amount of such a viscosity index improver is generally 0.5% by mass or more and 15% by mass or less, and preferably 1% by mass or more and 10% by mass or less on a basis of the lubricating oil composition.

[0091] As the antioxidant, a phenol-based antioxidant, an amine-based antioxidant, and the like may be used.

[0092] As the phenol-based antioxidant, an arbitrary material may be properly selected and used among known phenol-based antioxidants which have been conventionally used as the antioxidant of lubricating oil for internal combustion engine. Specifically, for example, there may be preferably exemplified 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butylphenol, 2,6-di-tert-butylphenol, 2,6-di-tert-butylphenol, 2,6-di-tert-butylphenol, 2,6-di-tert-butylphenol, 2,6-di-tert-butylphenol, 2,6-di-tert-butylphenol, 2,6-di-tert-butylphenol, 2,2'-methylenebis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-isopropylidenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-nonylphenol), 2,2'-isobutylidenebis(4,6-dimethylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 2,2'-isobutylidenebis(2-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), 2,2'-thio-diethylenebis(3-methyl-4-hydroxy-5-tert-butylbenzyl)sulfide, bis(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, pentaerythrityl-tetrrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, and the like.

[0093] As the amine-based antioxidant, an arbitrary material may be properly selected and used among known amine-based antioxidants which have been conventionally used as the antioxidant of lubricating oil for internal combustion engine. Examples of the amine-based antioxidant include diphenylamine-based antioxidants, specifically diphenylamine and alkylated diphenylamines having an alkyl group having 3 to 20 carbon atoms, such as monooctyldiphenylamine, monononyldiphenylamine, 4,4'-dibutyldiphenylamine, 4,4'-dihexyldiphenylamine, 4,4'-dioctyldiphenylamine, 4,4'-dinonyldiphenylamine, tetrabutyldiphenylamine, tetrahexyldiphenylamine, tetraoctyldiphenylamine, tetranonyldiphenylamine, etc.; naphthylamine-based antioxidants, specifically α -naphthylamine, phenyl- α -naphthylamine, and phenyl- α -naphthylamines substituted with an alkyl group having 3 to 20 carbon atoms, such as butylphenyl- α -naphthylamine, hexylphenyl- α -naphthylamine, octylphenyl- α -naphthylamine, nonylphenyl- α -naphthylamine, etc.; and the like. Among those, from the standpoint of effects, diphenylamine-based antioxidants are preferred, and in particular, alkylated diphenylamines having an alkyl group having 3 to 20 carbon atoms, especially 4,4'-di(C3 to C20 alkyl)diphenylamines are suitable.

[0094] In the lubricating oil composition for spark-ignition internal combustion engine of the present invention, the aforementioned antioxidant may be used alone-or in combination of two or more thereof.

[0095] From the standpoints of a balance between effects and economy, and the like, a blending amount of the antioxidant is selected within the range of preferably 0.05% by mass or more and 7% by mass or less, and more preferably 0.05% by mass or more and 5% by mass or less on a basis of the total amount of the lubricating oil composition.

[0096] In the lubricating oil composition for spark-ignition internal combustion engine of the present invention, other additive(s) may be further blended within the range where the purpose of the present invention is not impaired, as the need arises.

[0097] Examples of the other additive may include a metal-based detergent other than the aforementioned component (A); an extreme pressure agent, such as a sulfur-based extreme pressure agent (e.g., sulfides, sulfoxides, sulfoxides, sulfones, thiophosphinates, etc.), a halogen-based extreme pressure agent (e.g., chlorinated hydrocarbons, etc.), an organic metal-based extreme pressure agent, etc.; an ashless dispersant, such as a boron-containing ashless dispersant, a combination of a boron-containing ashless dispersant and a boron-free ashless dispersant, etc.; a rust inhibitor, such as a petroleum sulfonate, an alkylbenzene sulfonate, dinonylnaphthalene sulfonate, an alkenyl succinate ester, a polyhydric alcohol ester, e.g.; an anticorrosive agent; an anti-wear agent, such as a sulfur-containing anti-wear agent, a phosphorus-containing anti-wear agent, an ashless friction modifier, e.g., an aliphatic amine, a fatty acid ester, a fatty acid amide, a fatty acid, an aliphatic alcohol, or an aliphatic ether each having at least one an alkyl group or an alkenyl group having 6 to 30 carbon atoms, especially a linear alkyl group or a linear alkenyl group having 6 to 30 carbon atoms, etc.; a defoaming agent, such as a silicone,

a fluorosilicone, a fluoroalkyl ether, etc.; a surfactant, such as a polyalkylene glycol-based nonionic surfactant, e.g., a polyoxyethylene alkyl ether, a polyoxyethylene alkylphenyl ether, a polyoxyethylene alkylnaphthyl ether, etc.; a metal deactivator, such as a benzotriazole-based compound, a tolyltriazole-based compound, a thiadiazole-based compound, an imidazole-based compound, etc.; a pour point depressant, such as an ethylene-vinyl acetate copolymer, a condensate of a chlorinated paraffin and naphthalene, a condensate of a chlorinated paraffin and phenol, a polymethacrylate, a polyalkylstyrene, etc.; and the like.

[0098] In the lubricating oil composition, the aforementioned other additive(s) may be properly blended in an amount falling within the range where the purpose of the present invention is not impaired.

<Production Method of Lubricating Oil Composition for Spark-Ignition Internal Combustion Engine>

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[0099] The production method of a lubricating oil composition according to the embodiment of the present invention is concerned with a method for producing a lubricating oil composition to be used for a spark-ignition internal combustion engine comprising a piston having a piston ring, in which a total tension per piston of tensions applied to the piston ring is 30 N or less, the method including blending a base oil with (A) an organic metal-based additive containing an alkali metal and/or an alkaline earth metal and (B) an organic zinc-based additive in such a manner that a concentration of the component (A) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a metal content; a concentration of the component (B) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a zinc content; the product of the concentration (% by mass) of the component (A) and a base number (mgKOH/g) of the lubricating oil composition is 1.3 or less; the product of the concentration (% by mass) of the component (B) and an acid number (mgKOH/g) of the lubricating oil composition is 1.2 or less; and the lubricating oil composition has a Noack evaporation loss of 10% by mass or more and a kinematic viscosity at 100°C of 9.3 mm²/s or less.

[0100] In producing the lubricating oil composition for spark-ignition internal combustion engine, at least the aforementioned component (A) and component (B) have only to have the aforementioned blending, and other additive(s) may be blended within the range where the effects of the present invention are not impaired. After separately mixing the component (A) and the component (B) and optionally other additive(s), the resulting mixture may be introduced into the base oil, or the component (A) and the component (B) and optionally other additive(s) may be added to and mixed with the base oil one after another. It is to be noted that the addition order does not matter.

<Spark-Ignition Internal Combustion Engine and Lubricating Method of the Spark-Ignition Internal Combustion Engine>

[0101] A spark-ignition internal combustion engine 1 according to the present embodiment is described by reference to FIG. 1.

[0102] The spark-ignition internal combustion engine 1 in the present embodiment includes a gasoline engine. Examples of a fuel which is used for the spark-ignition internal combustion engine include, in addition to a fuel oil classified into Class I petroleums, petroleum, biomass ethanol, an alcohol fuel, a liquefied petroleum gas, a natural gas, a synthetic gas, a hydrogen fuel, a bi-fuel, and the like.

[0103] The spark-ignition internal combustion engine 1 includes a cylinder block 11, a piston crank mechanism 12 installed in the cylinder block 11, and a valve mechanism 13 undergoing intake of an air-fuel mixture into the cylinder block 11 and exhaust of a combustion gas.

[0104] The cylinder block 11 is provided with a cylinder 21 and a crank case 22. The spark-ignition internal combustion engine 1 includes a spark plug F in an upper portion of the cylinder 21. The piston crank mechanism 12 includes a piston 23 and a crank shaft 24. In the piston 23, a piston ring 30 is disposed. The piston ring 30 is constituted of a top ring 31, a second ring 32, and an oil ring 33. In the spark-ignition internal combustion engine 1, a total tension per piston of tensions applied to the piston ring 30 is set to 30 N or less.

[0105] The total tension per piston of tensions applied to the piston ring 30 is a sum total of tensions applied to each of the plural rings. For example, in the spark-ignition internal combustion engine 1 shown in FIG. 1, the total tension is a sum total of tensions (n) applied to the each piston ring of the top ring 31, the second ring 32, and the oil ring 33.

[0106] The spark-ignition internal combustion engine 1 has a lubricating oil composition L. The lubricating oil composition L is stored in an oil pan 41 within the crank case 22 or an oil tank (not shown), and following the operation of the spark-ignition internal combustion engine 1, the lubricating oil composition L is circulated in the piston crank mechanism 12, the valve mechanism 13, and the like and lubricates and cools each of these parts. In the spark-ignition internal combustion engine 1, the aforementioned lubricating oil composition for spark-ignition internal combustion engine is applied as the lubricating oil composition L.

[0107] That is, the method for lubricating the spark-ignition internal combustion engine 1, in which a total tension per piston of tensions applied to the piston ring 30 is 30 N or less, with the aforementioned lubricating oil composition for spark-ignition internal combustion engine is included in the present invention.

[0108] As mentioned above, in the spark-ignition internal combustion engine in the present embodiment, the total tension per piston of tensions applied to the piston ring 30 is 30 N or less. In such a low-tension internal combustion engine, the oil loss through piston from the crank case 22 into a combustion chamber C is liable to be generated. On the other hand, in the lubricating oil composition for spark-ignition internal combustion engine according to the present embodiment, even when the oil loss through piston is generated, the generation timing of a cool flame may be delayed. For this reason, the lubricating oil composition for spark-ignition internal combustion engine according to the present embodiment may be preferably used for a low-tension spark-ignition internal combustion engine, in which a total tension per piston of tensions applied to the piston ring 30 is 20 N or less, and moreover 15 N or less.

[0109] So long as the total tension per piston of tensions applied to the piston ring of the spark-ignition internal combustion engine can be lowered, in the case where the spark-ignition internal combustion engine is mounted in an automobile, it is possible to contemplate to improve the fuel consumption performance of the automobile.

Examples

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[0110] Next, the present invention is specifically described by reference to Examples, but it should be construed that the present invention is not limited by these Examples at all. In the following Examples and so on, measurement of properties and performance evaluation of lubricating oil compositions were carried out in the following manners.

[Evaluation Methods]

- <Properties of Lubricating Oil Composition>
- [0111] Respective properties of a base oil, an additive, and a lubrication oil composition were measured in the following methods.
- (1) Kinematic Viscosity:
- **[0112]** The kinematic viscosity was measured in accordance with "Testing methods for kinematic viscosity of petroleum products" as prescribed in JIS K2283.
- (2) Noack Evaporation Loss of Lubricating Oil Composition:
- [0113] The Noack evaporation loss was measured in accordance with JPI-5S-41-2004.
- 35 (3) Base Number:
 - **[0114]** The base number was measured by the hydrochloric acid method in accordance with JIS K2501, "Petroleum products and lubricating oils-neutralization value test method".
- 40 (4) Acid Number:
 - **[0115]** The acid number was measured by the potentiometric titration method in accordance with JIS K2501, "Petroleum products and lubricating oils-neutralization value test method".
- 45 (5) Molybdenum Content:
 - [0116] The molybdenum content was measured in accordance with JPI-5S-38-92.
 - (6) Amounts of Calcium, Zinc, Molybdenum, and Phosphorus:
 - [0117] The amounts of calcium, zinc, molybdenum, and phosphorus were measured in accordance with JPI-5S-38-92.
 - <Combustibility Test>
- ⁵⁵ **[0118]** The specification and operating condition of a spark-ignition internal combustion engine used in the combustibility test are shown below.
 - (1) Bore diameter: 85 mm

(2) Stroke length: 70 mm
(3) Displacement: 397 cm²
(4) Compression ratio: 8/1

(5) Number of revolution of engine: 1,400 rpm(6) Air-fuel ratio: Theoretical air-fuel ratio

(7) Ignition timing: -5° aTDC

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[0119] In the aforementioned engine, a small-sized quartz window was provided in a cylinder head, and a light from a xenon light source was transmitted through a right end portion of a combustion chamber, thereby carrying out light absorption measurement in the end portion. The xenon light having been transmitted through the combustion chamber was introduced into a spectroscope by optical fibers and spectrally separated in a wavelength of 293.1 nm. This wavelength is a wavelength at which strong absorption occurs in formaldehyde. The formaldehyde is an important chemical species such that it is produced at the time of generation of a cool flame and abruptly reduced with the movement into a blue flame and the generation of a hot flame. The spectrally separated light was converted into an electric signal by a photomultiplier tube, and by using a transmission light intensity E0 in a state where no reaction takes place and a transmission light intensity E1 at an arbitrary crank angle, an absorbance was defined as (E0 - E1)/E0 and calculated. A timing at which an increase of this absorbance started was defined as a generation timing of a cool flame, and a timing at which the absorbance abruptly decreased was defined as an autoignition timing. In addition, a pressure sensor was provided within the combustion chamber, and an amplitude of pressure vibration generated at the time of knocking was measured and defined as an index of the knock intensity. After the engine was subjected to a warming up operation to set a spark plug washer temperature to 450 to 470K, each of the samples shown in Table 1 was introduced by the following method, followed by carrying out the tests.

[0120] In the case where a total tension per piston of tensions applied to the piston ring is 30 N or less, and a lubricating oil composition has a kinematic viscosity at 100°C of 9.3 mm²/s or less and a Noack evaporation loss of 10% by mass or more, oil loss through piston from a crank chamber is liable to be generated; however, it is difficult to quantitatively control the oil loss through piston from the crank chamber. An amount of the lubricating oil composition which invades into the combustion chamber from the crank chamber due to oil loss through piston is not constant but is largely dominated by the probability. On the occasion when a large amount of the lubricating oil composition accidentally invades into the combustion chamber, and droplets of the lubricating oil composition itself are scattered into the interior of the combustion chamber, the influence which the lubricating oil composition gives to the combustion becomes maximum. For that reason, by forcedly scattering the droplets having specified properties into the interior of the combustion chamber to analyze the combustion state, the maximum influence which the composition may give can be evaluated.

[0121] Then, in the present combustibility test, assuming the case where in a low-tension spark-ignition internal combustion engine, in which a total tension per piston of tensions applied to the piston ring is 30 N or less, the lubricating oil composition invaded into the combustion chamber, the sample was forcedly introduced into the combustion chamber. [0122] It is to be noted that in the spark-ignition internal combustion engine used for the combustibility test, a general lubricating oil composition is filled in the crank chamber and the like; however, since the invasion of the lubricating oil composition from the crank chamber into the combustion chamber is restricted, it is not necessary to consider the influence against the results of the present test.

[0123] A fuel oil was replaced in each of the samples shown in Table 1, and the sample was introduced into the combustion chamber through a fuel injector and combusted. Since a lubricant base oil is high in viscosity as compared with the fuel oil, it is difficult to spray a lubricating oil composition by a fuel injector. Then, an additive was mixed in PRF50 that is a fuel oil having an octane number of 50 in place of the lubricant base oil, thereby preparing a sample shown in Table 1.

[0124] According to this, it becomes possible to achieve a test assuming the situation of invasion of the lubricating oil composition into the combustion chamber, which is possibly generated in a low-tension spark-ignition internal combustion engine, in which a total tension per piston of tensions applied to the piston ring is 30 N or less. It is to be noted that in view of the fact that both the lubricant base oil and the fuel oil are a hydrocarbon, it may be considered that a difference in reactivity with the additive is small.

[0125] It may be considered that the influence which droplets of a fuel oil containing a certain concentration of an organic metal-based additive give to the combustion is close to that in the case where droplets of a lubricant base oil containing the foregoing additive are scattered within the combustion chamber. For that reason, as a result of the test, so far as the fuel oil containing a prescribed additive does not influence the combustion, even in the case where the lubricating oil composition similarly containing the foregoing prescribed additive invaded into the combustion chamber, it may be judged that the combustion is not influenced. Conversely, so far as the combustion is influenced, when the lubricating oil composition invades into the combustion chamber in the actual equipment, it may be judged that there is a possibility that the combustion is influenced.

[0126] The results of the combustion test are shown in Tables 1 and 2.

[0127] Table 1 shows the presence or absence of acceleration of the generation timing of a cool flame and a value of pressure vibration when the content of the component (A) was changed. In addition, Table 2 shows the presence or absence of acceleration of the generation timing of a cool flame and a value of pressure vibration when the component (B) and the organic molybdenum-based additive were contained.

[0128] The comprehensive evaluation was made according to the following criteria. In the case where the evaluation is A and B, the generation timing of a cool flame is equal or close to the timing of usual spark discharge, and the value of pressure vibration is low, and hence, it may be said that the deterioration of the combustion state was inhibited, and the knocking was inhibited. On the other hand, in the case where the evaluation is C, the generation timing of a flame is faster than the timing of usual spark discharge, and the value of pressure vibration is high, and hence, it may be said that the combustion state was deteriorated, and the knocking was promoted.

<Criteria of Comprehensive Evaluation>

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- A: As compared with a standard sample, the generation timing of a cool flame is not accelerated, and an increase of the pressure vibration is 0.04 or less in terms of a ratio to the standard.
- B: As compared with a standard sample, the generation timing of a cool flame is accelerated, but an increase of the pressure vibration is 0.04 or less in terms of a ratio to the standard.
- C: As compared with a standard sample, the generation timing of a cool flame is accelerated, and an increase of the pressure vibration is more than 0.04 in terms of a ratio to the standard.

Table 1

		'	able 1			
		Test Example 1	Test Example 2	Test Example 3	Test Example 4	Test Example 5
	Fuel oil	Whole amount	Remainder	Remainder	Remainder	Remainder
Sample composition	Addition amount of component (A) (% by volume)	-	2.00	1.00	0.50	0.10
	Addition amount of component (B) (% by volume)	-	-	-	-	-
	Addition amount of component (C) (% by volume)	-	-	-	-	-
	Ca (% by mass) = [A]	-	0.22	0.11	0.06	0.01
	Zn (% by mass) = [B]	-	-	-	-	-
Characteristic values	Mo (% by mass)	-	-	-	-	-
	Acid number (mgKOH/g) = AN	0.0	0.5	0.2	0.1	0.0
	Base number (HCI) (mgKOH/g) = BN	0.0	6.3	3.2	1.6	0.3
	Product of [A] and BN	0.0	1.4	0.4	0.1	0.0
	Product of [B] and AN	0.0	0.0	0.0	0.0	0.0

(continued)

Test Test Test Test Test Example Example 2 Example 5 Example 3 Example 4 1 Acceleration of generation timing of Standard Yes Yes Yes No Measurement cool flame results Pressure vibration 0.017 0.061 0.024 0.037 0.013 [MPa] С В Comprehensive evaluation Α В Α

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Table 2

			Test Example 6	Test Example 7	Test Example 8
		Fuel oil	Whole amount	Remainder	Remainder
20	0	Addition amount of component (A) (% by volume)	-	-	-
	Sample composition	Addition amount of component (B) (% by volume)	-	0.70	-
25	25	Addition amount of component (C) (% by volume)	-	-	0.50
30	Characteristic values	Ca (% by mass) = [A]	-	-	-
		Zn (% by mass) [B]	-	0.10	-
		Mo (% by mass)	-	-	0.07
		Acid number (mgKOH/g) = AN	0.0	1.6	0.0
35		Base number (HCI) (mgKOH/g) = BN	0.0	0.1	0.0
		Product of [A] and BN	0.0	0.0	0.0
		Product of [B] and AN	0.0	0.2	0.0
40	Measurement results	Acceleration of generation timing of cool flame	Standard	Yes	No
		Pressure vibration [MPa]	0.010	0.040	0.010
	Comprehensive evaluation		А	В	А

[0130] In Tables 1 and 2, the calcium content (% by mass) in the sample composition is expressed as [A], and the zinc content (% by mass) in the sample composition is expressed as [B]. In addition, the acid number (mgKOH/g) is expressed as AN, and the base number (HCl) (mgKOH/g) is expressed as BN.

[0131] It is to be noted that the various additives as used are as follows.

Fuel oil:

[0132] Mixture of equal parts of normal-heptane and isooctane (PRF50)

• Component (A):

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[0133] Calcium-based detergent: Ca salicylate (Ca content: 7.8% by mass, base number: 225, acid number: 16.1)

· Component (B):

[0134] Zinc dialkyldithiophosphate (Zn content: 8.9% by mass, phosphorus content: 7.4% by mass, sulfur content: 15.0% by mass)

• Component (C):

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[0135] Molybdenum dithiocarbamate (Mo content: 1.0% by mass)

[0136] From the results of Table 1, it can be understood that the higher the content of the component (A), the faster the generation timing of a cool flame and the autoignition timing, and the more increased the value of pressure vibration.

[0137] From the results of Table 2, it can be understood that in the case where a prescribed amount of the component (B) is contained, though the generation timing of a cool flame is hastened, the value of pressure vibration is low.

[0138] In addition, even when the organic molybdenum-based additive is contained in an amount of 0.07% by mass which may be contained as a lubricating oil composition, all of the generation timing of a cool flame and the pressure vibration did not substantially change. For this reason, it can be understood that even in metal-based additives, the Mobased additive not substantially having a base number and an acid number does not influence the generation timing of a cool flame and the like.

[0139] The results of Tables 1 and 2 demonstrate that among the lubricating oil compositions having invaded into the combustion chamber, when the concentration of the aforementioned metal-based additive (A) having a base number or the aforementioned metal-based additive (B) having an acid number is made lower, the generation timing of a cool flame can be delayed, and the pressure vibration can be attenuated. In addition, it is suggested that even by reducing the base number or the acid number originated from the metal-based additive, the generation timing of a cool flame and the autoignition timing can be delayered, and the pressure vibration can be attenuated. As for this, the product of the metal quantity and the base number originated from the aforementioned component (A) and the product of the metal quantity and the acid number originated from the aforementioned component (B) can be made as an index.

[0140] A lubricating oil composition capable of solving the problem of the present invention was prepared on the basis of the aforementioned combustibility test. The results are shown in Table 3.

Table 3

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Formulation (% by mass)	
Base oil	Remainder
Component (A)	1.4
Component (B)	1.1
Component (C)	0.5
Viscosity index improver	Adjusted
Polymeric alkyl succinimide	6.0
Boron-modified alkyl succinimide	2.0
Hindered amine	1.0
Other additives	2.0
Properties/performance	
Kinematic viscosity at 40°C (mm²/s)	33.9
Kinematic viscosity at 100°C (mm²/s)	7.7
Acid number (mgKOH/q) = AN	2.0
Base number (HCI) (mgKOH/g) = BN	5.6
Ca (% by mass) = [A]	0.11
Zn (% by mass) = [B]	0.10
Mo (% by mass)	0.05
Product of [A] and BN	0.6
Product of [B] and AN	0.2

(continued)

Formulation (% by mass)

Noack evaporation loss (%) ≥10

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[0141] In Tables 1 and 2, the calcium content (% by mass) in the sample composition is expressed as [A], and the zinc content (% by mass) in the sample composition is expressed as [B]. In addition, the acid number (mgKOH/g) is expressed as AN, and the base number (HCI) (mgKOH/g) is expressed as BN.

[0142] It is to be noted that the various additives as used are as follows.

- · Base oil:
- **[0143]** A mixture of a paraffin-based mineral oil having a kinematic viscosity at 100° C of 4.1 mm^2 /s and a kinematic viscosity at 40° C of 17.8 mm^2 /s and a poly- α -olefin having a kinematic viscosity at 100° C of 5.1 mm^2 /s and a kinematic viscosity at 40° C of 25.3 mm^2 /s in a mass ratio of 7/1
 - · Component (A):
- [0144] Calcium-based detergent: Ca salicylate (Ca content: 7.8% by mass, base number: 225, acid number: 16.1 mgKOH/g)
 - · Component (B):
- [0145] Zinc dithiophosphate (Zn content: 8.9% by mass, phosphorus content: 7.4% by mass, sulfur content: 15.0% by mass)
 - · Component (C):
- 30 [0146] Molybdenum dithiocarbamate (Mo content: 1.0% by mass)
 - Viscosity index improver:

[0147] Polymethacrylate (weight average molecular weight: 400,000). A blending amount was set to an amount at which an HTHS viscosity at 150°C of the lubricating oil composition was 2.6 mPa·s.

Ashless base number improver:

[0148]

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Polymeric alkyl succinimide: Base number: 24

Boron-modified alkyl succinimide: Base number:25, B content: 1.3% by mass

Hindered amine: Base number: 164

Other additives:

[0149] Diphenylamine, alkylphenol, copper deactivator, silicone-based defoaming agent, polymethacrylate-based pour point depressant

[0150] From the results of Tables 1 and 2, it was understood that even when the oil loss through piston is generated, even at the highest estimate, even in the case where the additives are contained in the quantities shown in Table 1 or 2 in the combustion chamber of the cylinder, the deterioration of the combustion state does not take place.

[0151] In view of this fact, the lubricating oil composition shown in Table 3 can be prepared.

[0152] According to the lubricating oil composition shown in Table 3, since the lubricating oil composition contains a base oil, (A) an organic metal-based additive containing an alkali metal and/or an alkaline earth metal, and (B) an organic zinc-based additive, wherein a concentration of the component (A) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a metal content; a concentration of the component (B) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a zinc content; the product of the concentration (% by mass) of the component (A) and a base number (mgKOH/g) of the lubricating oil

composition is 1.3 or less; and the product of the concentration (% by mass) of the component (B) and an acid number (mgKOH/g) of the lubricating oil composition is 1.2 or less, even if the oil loss through piston takes place, the deterioration of the combustion state does not take place.

5 Reference Signs List

[0153]

- 1: Spark-ignition internal combustion engine
- 10 11: Cylinder block
 - 12: Piston crank mechanism
 - 13: Valve mechanism
 - 21: Cylinder
 - 22: Crank case
- 15 23: Piston
 - 24: Crank shaft
 - 30: Piston ring
 - 31: Top ring
 - 32: Second ring
- 20 33: Oil ring
 - 41: Oil pan
 - C: Combustion chamber
 - F: Spark plug
 - L: Lubricating oil composition

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- Claims
- 1. A lubricating oil composition for spark-ignition internal combustion engine that is a lubricating oil composition to be used for a spark-ignition internal combustion engine comprising a piston having a piston ring, in which a total tension per piston of tensions applied to the piston ring is 30 N or less, the lubricating oil composition being a lubricating oil composition comprising a base oil,
 - (A) an organic metal-based additive containing an alkali metal and/or an alkaline earth metal, and
 - (B) an organic zinc-based additive, wherein

a concentration of the component (A) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a metal content;

- a concentration of the component (B) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a zinc content;
- the product of the concentration (% by mass) of the component (A) and a base number (mgKOH/g) of the lubricating oil composition is 1.3 or less;
- the product of the concentration (% by mass) of the component (B) and an acid number (mgKOH/g) of the lubricating oil composition is 1.2 or less; and
- the lubricating oil composition has a Noack evaporation loss of 10% by mass or more and a kinematic viscosity at 100°C of 9.3 mm²/s or less.
- 2. The lubricating oil composition for spark-ignition internal combustion engine according to claim 1, comprising an ashless base number improver having a base number of 1 mgKOH/g or more and 200 mgKOH/g or less on a basis of the total amount of the lubricating oil composition in an amount of 0.01% by mass or more as converted into a nitrogen content.
 - 3. The lubricating oil composition for spark-ignition internal combustion engine according to claim 1 or 2, wherein the component (A) is a metal-based detergent having a base number of 10 mgKOH/g or more and 600 mgKOH/g or less.
 - **4.** The lubricating oil composition for spark-ignition internal combustion engine according to any of claims 1 to 3, wherein the component (B) is a zinc dialkyldithiophosphate and/or a zinc dialkyldioxyphosphate.

- 5. The lubricating oil composition for spark-ignition internal combustion engine according to any of claims 1 to 4, further comprising an organic molybdenum-based additive, a content of the organic molybdenum-based additive on a basis of the total amount of the lubricating oil composition being 0.01% by mass or more and 0.07% by mass or less as converted into a molybdenum content.
- **6.** The lubricating oil composition for spark-ignition internal combustion engine according to any of claims 1 to 5, wherein the spark-ignition internal combustion engine is a gasoline engine.
- 7. A method for producing a lubricating oil composition for spark-ignition internal combustion engine that is a lubricating oil composition to be used for a spark-ignition internal combustion engine comprising a piston having a piston ring, in which a total tension per piston of tensions applied to the piston ring is 30 N or less, the method comprising blending a base oil with
 - (A) an organic metal-based additive containing an alkali metal and/or an alkaline earth metal and
 - (B) an organic zinc-based additive in such a manner that

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a concentration of the component (A) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a metal content;

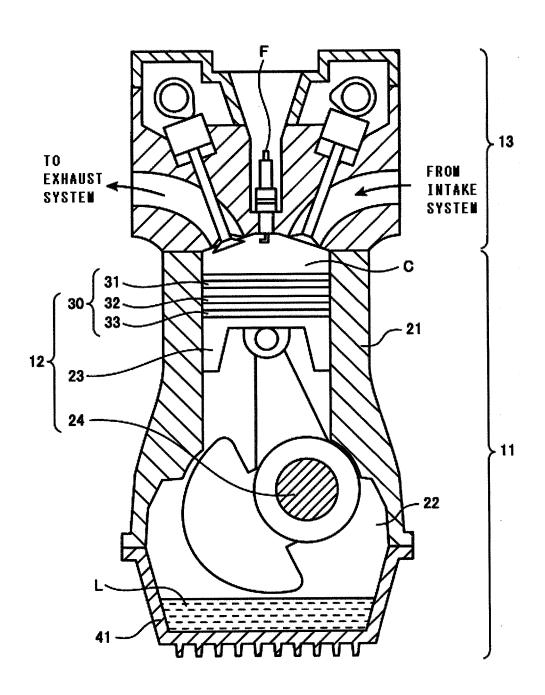
a concentration of the component (B) on a basis of the total amount of the lubricating oil composition is 0.15% by mass or less as converted into a zinc content;

the product of the concentration (% by mass) of the component (A) and a base number (mgKOH/g) of the lubricating oil composition is 1.3 or less;

the product of the concentration (% by mass) of the component (B) and an acid number (mgKOH/g) of the lubricating oil composition is 1.2 or less; and

the lubricating oil composition has a Noack evaporation loss of 10% by mass or more and a kinematic viscosity at 100°C of 9.3 mm²/s or less.

[FIG. 1]



INTERNATIONAL SEARCH REPORT International application No. PCT/JP2014/081125 A. CLASSIFICATION OF SUBJECT MATTER C10M171/00(2006.01)i, C10M137/10(2006.01)i, C10M139/00(2006.01)i, 5 C10M141/12(2006.01)i, C10N10/02(2006.01)n, C10N10/04(2006.01)n, C10N10/12(2006.01)n, C10N20/00(2006.01)n, C10N20/02(2006.01)n, According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) 10 C10M171/00, C10M137/10, C10M139/00, C10M141/12, C10N10/02, C10N10/04, C10N10/12, C10N20/00, C10N20/02, C10N30/00, 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 1996-2015 15 Kokai Jitsuyo Shinan Koho 1971-2015 Toroku Jitsuyo Shinan Koho 1994-2015 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DOCUMENTS CONSIDERED TO BE RELEVANT 20 Relevant to claim No. Category* Citation of document, with indication, where appropriate, of the relevant passages JP 2013-199595 A (JX Nippon Oil & Energy 1-7 Α Corp.), 03 October 2013 (03.10.2013), 25 claims 1 to 7; examples 1 to 3; table 1 (Family: none) JP 2008-239775 A (Nippon Oil Corp.), 1 - 7Α 09 October 2008 (09.10.2008), claims 1 to 7; examples 1 to 9; tables 1, 2 30 (Family: none) JP 2005-162968 A (Cosmo Oil Lubricants Co., Α 1 - 7Ltd.), 23 June 2005 (23.06.2005), claims 1 to 4; examples 1 to 10 35 (Family: none) X Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents: later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date document which may throw doubts on priority claim(s) or which is 45 cited to establish the publication date of another citation or other special reason (as specified) document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination document referring to an oral disclosure, use, exhibition or other means "O" being obvious to a person skilled in the art document published prior to the international filing date but later than the priority date claimed document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 50 03 March 2015 (03.03.15) 10 March 2015 (10.03.15) Name and mailing address of the ISA/ Authorized officer Japan Patent Office $3-\bar{4}-3$, Kasumigaseki, Chiyoda-ku, 55 Tokyo 100-8915, Japan Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/081125

	C (Continuation)	. DOCUMENTS CONSIDERED TO BE RELEVANT	101/0120	014/001123
5	Category*	Citation of document, with indication, where appropriate, of the relevan	t passages	Relevant to claim No.
10	A	JP 2012-215238 A (Nippon Piston Ring Co., Ltd.), 08 November 2012 (08.11.2012), claims 1 to 5; examples 1, 2 (Family: none)		1-7
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INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2014/081125

5	Continuation of A. CLASSIFICATION OF SUBJECT MATTER (International Patent Classification (IPC))
	C10N30/00(2006.01)n, C10N40/25(2006.01)n
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/081125

Range to be covered by this search:

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Claim 1 is an invention relating to "a lubricating oil composition which contains (A) an organometallic additive containing an alkali metal and/or alkaline-earth metal and (B) an organozinc additive". However, the modes disclosed in the meaning of PCT Article 5 are limited to the case where calcium salicylate is used as the (A) and a zinc dialkyldithiophosphate is used as the (B), as described in the examples of the description. Claim 1 hence lacks a support in the meaning of PCT Article 6.

Therefore, a search was made mainly for the range disclosed in the description wherein the "organometallic additive (A) containing an alkali metal and/or alkaline-earth metal" mentioned in claim 1 is calcium salicylate and a zinc dialkyldithiophosphate is used as the "organozinc additive (B)" mentioned in claim 1.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2012215238 A **[0004]**
- JP 2003252887 A [0085] [0086]

- JP 3022438 B [0087]
- JP 2004002866 A [0087]