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**(54) LUBRICATING OIL COMPOSITION**

(57) A lubricating oil composition is provided, which can reduce friction even when the viscosity is lowered.

A lubricating oil composition comprising a lubricating base oil, (A) a cleaning agent containing magnesium, and (B) a zinc dialkyl dithiophosphate, wherein the amount of component (A) in terms of ppm by weight of magnesium ([Mg]) based on the total weight of the lubricating oil composition is in a range of 200 to 1200 ppm by weight; the amount of component (B) in terms of ppm by weight of phosphorus ([P]) based on the total weight of the lubricating oil composition is in a range of 300 to 1000 ppm by weight; wherein component (B) comprises (B-1) a zinc dialkyl dithiophosphate having a primary alkyl group, and the proportion of the weight of component (B-1) to the total weight of component (B) is 30 weight% or more; and wherein the concentration of boron [B] in terms of ppm by weight of boron based on the total weight of the lubricating oil composition is less than 100 ppm by weight.

**Description**

## [Field]

5 [0001] The present invention relates to a lubricating oil composition, specifically to a lubricating oil composition for an internal combustion engine, and particularly to a lubricating oil composition for a gasoline engine.

## [Background]

10 [0002] A lubricating oil composition is widely used in the automotive field, for example, for an internal combustion engine, an automatic transmission, a gear oil, and the like. In recent years, it has been demanded to lower the viscosity in order to improve the fuel economy, but as the viscosity becomes lower, the oil film also becomes thinner and the friction cannot be reduced adequately. Therefore, molybdenum dithiocarbamate (MoDTC) capable of reducing the friction by generating molybdenum disulfide under a boundary lubrication condition has been conventionally used. In such a 15 case, it is usual to use a calcium type cleaning agent in combination (for example, Japanese Unexamined Patent Publication (Kokai) No. 2013-199594). However, with this combination, there is a limit in the reduction of friction, and the fuel economy cannot be improved sufficiently.

20 [0003] It has been also known to use a magnesium type cleaning agent as a cleaning agent (for example, Japanese Unexamined Patent Publication (Kokai) No. 2011-184566, and Japanese Unexamined Patent Publication (Kokai) No. 2006-328265). Although the use of a magnesium type cleaning agent can reduce friction better than a calcium type 25 cleaning agent, there is a drawback in that wear is apt to occur. For example, International Publication No. 2016/159258 discloses a lubricating oil composition containing a base oil, a calcium type cleaning agent, a magnesium type cleaning agent, molybdenum dithiocarbamate, a boron-free succinimide, a boron-containing succinimide, and a viscosity index improver, and that the lubricating oil composition is excellent in fuel consumption reduction, and such fuel consumption reduction effect can be obtained in a short time owing to the friction reducing effect. Meanwhile, the present applicant has found that the friction can be reduced by using a specific amount of a boron-containing succinimide, as well as a primary alkyl group-containing zinc dialkyl dithiophosphate and a secondary alkyl group-containing zinc dialkyl dithiophosphate at a specific ratio, and has already filed a patent application (Japanese Patent Application No. 2016-152180).

## 30 [Citation List]

## [Patent Literature]

**[0004]**

35 [PTL 1] Japanese Unexamined Patent Publication (Kokai) No. 2013-199594  
 [PTL 2] Japanese Unexamined Patent Publication (Kokai) No. 2011-184566  
 [PTL 3] Japanese Unexamined Patent Publication (Kokai) No. 2006-328265  
 40 [PTL 4] International Publication No. WO 2016/159258  
 [PTL 5] Japanese Patent Application No. 2016-152180

## [Summary]

## [Technical Problem]

45 [0005] In order to further improve the fuel economy of a gasoline engine vehicle, further lower viscosity of a lubricating oil composition is required. In the invention described in Japanese Patent Application No. 2016-152180 (PTL 5), for purpose of securing antiwear performance and decreasing friction with a lubricating oil composition having preferably a kinematic viscosity at 100°C of less than 9.3 mm<sup>2</sup>/s, the amount of boron-containing succinimide, and the blend ratio 50 of a zinc dialkyl dithiophosphate having a primary alkyl group to a zinc dialkyl dithiophosphate having a secondary alkyl group were optimized. The present invention aims at a viscosity still lower than the lubricating oil composition described in the above PTL 5. When the viscosity of a lubricating oil composition is further reduced, the thickness of the oil film decreases, and the lubricating condition becomes even more severe. An object of the present invention is to provide a lubricating oil composition which can reduce friction even under such conditions.

55 [0006] As described above, when the viscosity of the lubricating oil decreases, the oil film thickness becomes thinner, and therefore the lubrication condition becomes more severe than before to promote formation of a reaction film on the sliding surface. For the present invention, optimization of the composition of an additive having an effect on formation of a reaction film (the ratio of primary to secondary of ZnDTP, and a boron type dispersant) has been studied for purpose

of controlling the formation rate and the properties of a reaction film. More specifically, an object is (1) to form a uniform reaction film slowly by decreasing the formation rate of a reaction film reaction film, so as to acquire viscosity lowering capability, and (2) to lower the friction of the formed reaction film itself, with a lubricating oil having a lower viscosity than in the past.

5 [0007] In other words, an object of the present invention is to reduce friction, even when the viscosity of a lubricating oil composition is further reduced compared to a conventional lubricating oil composition, especially when the kinematic viscosity is less than 6.1 mm<sup>2</sup>/s at 100°C, and the high temperature high shear viscosity (HTHS viscosity) at 150°C is not less than 1.3 but less than 2.3 mPa · s. Another object is to provide a lubricating oil composition for an internal combustion engine as a more preferable embodiment, and more preferably a lubricating oil composition for a supercharged gasoline engine.

10 [Solution to Problem]

15 [0008] Increase of the proportion of a zinc dialkyl dithiophosphate having a primary alkyl group as a means to lower the rate of formation of a reaction film was investigated. With respect to a zinc dialkyl dithiophosphate, a zinc dialkyl dithiophosphate having a secondary alkyl group has higher reactivity than a zinc dialkyl dithiophosphate having a primary alkyl group. Therefore, by increasing the proportion of a zinc dialkyl dithiophosphate having a primary alkyl group, it can be expected that the formation rate of a reaction film can be retarded. By retarding the formation rate of a reaction film, a homogeneous reaction film is formed slowly, and it can be anticipated that the orientation and coverage of the reaction film is improved, and furthermore, reduction of the friction of the reaction film itself can be also achieved.

20 [0009] As a means for reducing the friction of a reaction film itself, reduction of the content of a boron-containing dispersant was investigated. Comparing the friction coefficients of a boron-containing reaction film and a boron-free reaction film, the boron-containing reaction film exhibits a higher friction. Therefore, heretofore an expensive boron-containing reaction film was formed to obtain a low friction in order to prevent abrasion of the reaction film by a magnesium type cleaning agent. However, since the lubrication conditions become more severe as a consequence of viscosity reduction of a lubricating oil, a reaction film is now formed faster than before. Under such circumstances, it was anticipated that friction could be reduced by a boron-free reaction film.

25 [0010] The present inventors have investigated the optimal balance of (1) the proportion of a zinc dialkyl dithiophosphate having a primary alkyl group, and (2) reduction of the amount of boron-containing dispersant, to find that a friction reducing effect can be achieved with a lubricating oil composition having further lower viscosity characteristics (in particular, kinematic viscosity at 100°C of less than 6.1 mm<sup>2</sup>/s, and high temperature high shear viscosity (HTHS viscosity) at 150°C of not less than 1.3 but less than 2.3 mPa · s) by specifying the contents including mandatorily a zinc dialkyl dithiophosphate having a primary alkyl group, and limiting the content of boron in the composition less than a specific value.

30 [0011] In other words, the present inventors have found that the above object is achieved with a lubricating oil composition comprising a lubricating base oil, a cleaning agent containing magnesium, and a zinc dialkyl dithiophosphate, by limiting the boron content in the composition to a specified amount or less, and specifying the proportion of a zinc dialkyl dithiophosphate having a primary alkyl group.

35 [0012] The present invention is a lubricating oil composition comprising a lubricating base oil, (A) a cleaning agent containing magnesium, and (B) a zinc dialkyl dithiophosphate, wherein the amount of component (A) in terms of ppm by weight of magnesium ([Mg]) based on the total weight of the lubricating oil composition is in a range of 200 to 1200 ppm by weight; the amount of component (B) in terms of ppm by weight of phosphorus ([P]) based on the total weight of the lubricating oil composition is in a range of 300 to 1000 ppm by weight; wherein component (B) comprises (B-1) a zinc dialkyl dithiophosphate having a primary alkyl group, and the proportion of the weight of component (B-1) to the total weight of component (B) is 30 weight% or more, and wherein the concentration of boron [B] in terms of ppm by weight of boron based on the total weight of the lubricating oil composition is less than 100 ppm by weight.

40 [0013] In a preferable embodiment of the present invention, the lubricating oil composition has additionally at least one of features (1) to (9) described below.

45 (1) The lubricating oil composition further comprises (C) a dispersant, and the amount of component (C) is 0.1 to 8 weight% based on the total weight of the lubricating oil composition.

50 (2) The lubricating oil composition further comprises (A') a cleaning agent containing calcium, and  $\{[Mg]/([Mg] + [Ca])\} \times 100 \geq 5$ , wherein [Ca] represents the concentration of calcium in terms of ppm by weight based on the weight of the lubricating oil composition, is satisfied.

55 (3) The lubricating oil composition further comprises a friction modifier containing molybdenum, and the concentration [Mo] of molybdenum in terms of ppm by weight based on the weight of the lubricating oil composition is from 200 to 1400 ppm by weight.

(4) The lubricating oil composition further comprises a viscosity index improver, and the amount of the viscosity index improver in terms of the amount of polymer contained in the viscosity index improver based on the total weight

of the lubricating oil composition is 1 weight% or less.

(5) The CCS viscosity at -35°C is 6.2 Pa · s or less.

(6) The high temperature high shear viscosity (HTHS viscosity) at 150°C is not less than 1.3 mPa · s but less than 2.3 mPa · s.

5 (7) The kinematic viscosity at 100°C is less than 6.1 mm<sup>2</sup>/s.

(8) The lubricating oil composition is for an internal combustion engine.

(9) The lubricating oil composition is for a supercharged gasoline engine.

10 [0014] Further, the present invention is related to a method of reducing friction by using the lubricating oil composition or the lubricating oil composition according to any one of above embodiments (1) to (9).

[Advantageous Effects of Invention]

15 [0015] The low viscosity condition of a lubricating oil composition targeted by the present invention is as described above, in particular, the kinematic viscosity at 100°C is less than 6.1 mm<sup>2</sup>/s, and the high temperature high shear viscosity (HTHS viscosity) at 150°C is not less than 1.3 mPa · s but less than 2.3 mPa · s. The above targets a lubricating oil composition aiming at a viscosity lower than the viscosity, which the prior invention of the present invention, namely the invention described in Japanese Patent Application No. 2016-152180 (PTL 5), aimed at. In PTL 5, the antiwear performance was secured and the friction was reduced successfully with a low viscosity lubricating oil composition exhibiting a 20 kinematic viscosity at 100°C of less than 9.3 mm<sup>2</sup>/s, particularly not less than 6.1 mm<sup>2</sup>/s but less than 9.3 mm<sup>2</sup>/s, and a high temperature high shear viscosity(HTHS viscosity) at 150°C of particularly 2.3 to 2.9 mPa · s, by including a boron-containing compound in an amount in a range of 100 to 300 ppm by weight in terms of the weight of boron contained in the composition, and including mandatorily a zinc dialkyl dithiophosphate having a secondary alkyl group.

25 [0016] The present inventors have found that a friction reducing effect can be achieved based on a lubricating oil composition exhibiting viscosity characteristics lower than before (in particular, the kinematic viscosity at 100°C of less than 6.1 mm<sup>2</sup>/s, and the high temperature high shear viscosity (HTHS viscosity) at 150°C of not less than 1.3 mPa · s but less than 2.3 mPa · s), by regulating the concentration of boron [B] in terms of ppm by weight of boron based on the total weight of the lubricating oil composition to less than 100 ppm by weight, and by including mandatorily a zinc dialkyl dithiophosphate having a primary alkyl group at a specified content. In other words, by lowering the targeted viscosity 30 further, a relationship different from the optimum condition found in the prior invention has been found.

35 [0017] For the sake of further clarification of the particulars, based on a lubricating oil composition exhibiting a high temperature high shear viscosity at 150°C (HTHS 150) of 2.3 mPa · s, and a lubricating oil composition exhibiting a HTHS 150 of 1.7 mPa · s, graphs representing the respective average friction coefficients are represented in FIGs. 1 and 2. FIG. 1 is a graph representing the average friction coefficient at each time point measured with a MTM traction machine in a medium speed range (20 to 300 mm/s) with respect to a lubricating oil composition exhibiting a HTHS 150 of 2.3 mPa · s. FIG. 2 is a graph representing the average friction coefficient at each time point measured with a MTM traction machine in a medium speed range (20 to 300 mm/s) with respect to a lubricating oil composition exhibiting a HTHS 150 of 1.7 mPa · s. In each of FIGs. 1 and 2, with respect to a lubricating oil composition in which the weight ratio of a zinc dialkyl dithiophosphate having a primary alkyl group to a zinc dialkyl dithiophosphate having a secondary alkyl group is 40/60, the dotted line represents the friction coefficient of the composition in which the concentration of boron [B] in terms of ppm by weight of boron based on the total weight of the lubricating oil composition is 0 ppm, and the solid line represents the friction coefficient of the composition in which the concentration of boron [B] in terms of ppm by weight of boron based on the total weight of the lubricating oil composition is 200 ppm. As represented in FIGs. 1 and 2, by 40 lowering the targeted viscosity, the relationship between the optimal amount of boron for reducing the friction and the zinc dialkyl dithiophosphate composition has been changed from the past.

45 [0018] With a lubricating oil composition according to the present invention, the friction can be decreased, even when the viscosity is lowered as compared with the conventional one. In particular, the friction can be reduced even at a low viscosity of less than 6.1 mm<sup>2</sup>/s in terms of kinematic viscosity at 100°C. The lubricating oil composition may be used more preferably as a lubricating oil composition for an internal combustion engine, or further preferably as a lubricating oil composition for a supercharged gasoline engine favorably.

[Brief Description of Drawings]

55 [0019]

[Fig. 1]

FIG. 1 is a graph representing the average friction coefficient of a lubricating oil composition having a HTHS 150 of 2.3 mPa · s.

[Fig. 2]

FIG. 2 is a graph representing the average friction coefficient of a lubricating oil composition having a HTHS 150 of 1.7 mPa · s.

[Fig. 3]

5 FIG. 3 is a schematic view illustrating a mode of a ball-on-disk friction test.

[Description of Embodiments]

10 [0020] A lubricating oil composition according to the present invention is characterized in that the amount of boron contained in the composition is less than 100 ppm by weight in terms of ppm by weight of boron [B] based on the total weight of the composition. The boron content is preferably less than 80 ppm by weight, more preferably less than 50 ppm by weight, further preferably less than 20 ppm by weight, and most preferably 0 ppm by weight. In the present invention, it is preferable that the amount of boron contained in the composition is as small as possible. By doing so, a uniform reaction film may be formed, and the friction coefficient may be reduced. The boron to be added to a lubricating oil composition is derived from a conventionally known additive, provided that its origin is not particularly limited. In particular, it is derived from a boron-containing ashless dispersant, which is an optional component (C) described later.

15 [0021] The lubricating oil composition according to the present invention will be described in more detail below.

Lubricating base oil

20 [0022] There is no particular restriction on a lubricating base oil according to the present invention. Any of mineral oils and synthetic oils may be used, and these may be used singly or in mixture.

25 [0023] Examples of a mineral oil include an oil obtained by distilling a crude oil under an atmospheric pressure to obtain an atmospheric residue, vacuum-distilling the atmospheric residue to obtain a lubricating oil fraction, and then refining the lubricating oil fraction by one or more treatments selected from solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, hydrofining, and the like; a wax isomerized mineral oil; a GTL (Gas to Liquid) base oil; an ATL (Asphalt to Liquid) base oil; a vegetable oil type base oil; and a mixed base oil thereof.

30 [0024] Examples of a synthetic oil include polybutene or a hydrogenated product thereof; a poly( $\alpha$ -olefin), such as 1-octene oligomer, and 1-decene oligomer, or a hydrogenated product thereof; a monoester, such as 2-ethylhexyl laurate, 2-ethylhexyl palmitate, and 2-ethylhexyl stearate; a diester, such as ditridecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate, and di-2-ethylhexyl sebacate; a polyol ester, such as neopentyl glycol di-2-ethylhexanoate, neopentyl glycol di-*n*-octanoate, neopentyl glycol di-*n*-decanoate, trimethylolpropane tri-*n*-octanoate, trimethylolpropane tri-*n*-decanoate, pentaerythritol tetra-*n*-pentanoate, pentaerythritol tetra-*n*-hexanoate, and pentaerythritol tetra-2-ethylhexanoate; and an aromatic synthetic oil, such as alkylnaphthalene, alkylbenzene, and an aromatic ester; as well as a mixture thereof.

35 [0025] There is no particular restriction on the kinematic viscosity (mm<sup>2</sup>/s) at 100°C of a lubricating base oil, and it is preferably 2 to 10 mm<sup>2</sup>/s, more preferably 2 to 8 mm<sup>2</sup>/s, further preferably 2 to 6 mm<sup>2</sup>/s, and most preferably 3 to 5 mm<sup>2</sup>/s. In such a case it is possible to obtain a lubricating oil composition, which is capable of forming an oil film adequately, is excellent in lubricity, and able to make the evaporation loss low.

40 [0026] There is no particular restriction on the viscosity index (VI) of a lubricating base oil, and it is preferably 100 or more, more preferably 120 or more, and most preferably 125 or more. In such a case it is possible to reduce the viscosity at low temperature, while securing an oil film at high temperature.

(A) Magnesium type cleaning agent

45 [0027] A cleaning agent containing magnesium (hereinafter referred to as "magnesium type cleaning agent") is mandatory for a lubricating oil composition according to the present invention. The magnesium type cleaning agent is a compound containing magnesium, and those conventionally used as a metal type cleaning agent for a lubricating oil composition may be used without any particular limitation. Examples thereof include magnesium sulfonate, magnesium phenate, and magnesium salicylate. Among them, magnesium salicylate, or magnesium sulfonate is particularly preferable. The magnesium type cleaning agents may be used singly, or in mixture of two or more kinds thereof.

50 [0028] By including a magnesium type cleaning agent as component (A), the high temperature cleaning performance and the antirust performance required as a lubricating oil may be secured. In addition, the friction can be reduced. This is advantageous particularly in terms of fuel consumption characteristics.

55 [0029] A magnesium type cleaning agent is added in such an amount that the concentration [Mg] in terms of ppm by weight of magnesium based on the total weight of the lubricating oil composition is in a range of 200 to 1200 ppm by weight, preferably 300 to 1100 ppm by weight, and more preferably 400 to 1000 ppm by weight. When the amount of a magnesium type cleaning agent exceeds the upper limit, the wear becomes too large, and when it is below the lower

limit, the friction reduction effect is low.

[0030] A magnesium type cleaning agent is especially preferably overbasic. In such a case, it is possible to secure acid neutralization performance, which is necessary for a lubricating oil. In a case where an overbasic magnesium type cleaning agent is used, a neutral magnesium type or calcium type cleaning agent may be admixed.

[0031] Although there is no particular restriction on the total base number of a magnesium type cleaning agent, it is preferably 20 to 600 mg KOH/g, more preferably 50 to 500 mg KOH/g, and most preferably 100 to 450 mg KOH/g. In such a case, it is possible to secure acid neutralization performance, high temperature cleaning performance and antirust performance necessary for a lubricating oil. When two or more kinds of metal cleaning agents are used in mixture, the base number obtained from the mixture is preferably in the above-mentioned range.

[0032] Although the magnesium content in a magnesium type cleaning agent is preferably 0.5 to 20 weight%, more preferably 1 to 16 weight%, and most preferably 2 to 14 weight%, it is acceptable so long as magnesium is added so that the lubricating oil composition comes to contain it in the above described range.

[0033] A lubricating oil composition according to the present invention may contain another metal type cleaning agent in addition to the above described magnesium type cleaning agent. The metal type cleaning agent may be a common one used in the conventional lubricating oil composition. Preferably, a cleaning agent containing calcium (A') (hereinafter referred to as "calcium type cleaning agent") is used together. When a lubricating oil composition further contains a calcium type cleaning agent, it is possible to further secure the high temperature cleaning performance and antirust performance required for a lubricating oil.

[0034] A calcium type cleaning agent (A') is a compound containing calcium, and it is possible to use the one used as a metal type cleaning agent in the conventional lubricating oil composition without any particularly restriction. Examples thereof include calcium sulfonate, calcium phenate, and calcium salicylate. The calcium type cleaning agents may be used singly, or in mixture of two or more kinds thereof.

[0035] The amount of the component (A') preferably satisfies following formula (1).

$$\{[Mg]/([Mg] + [Ca])\} \times 100 \geq 5 \quad (1)$$

wherein [Ca] represents the concentration of calcium in terms of ppm by weight of calcium based on the weight of the lubricating oil composition.

[0036] The value of  $\{[Mg]/([Mg] + [Ca])\} \times 100$  is preferably 10 or more, more preferably 15 or more, and especially preferably 20 or more. When the value is less than the lower limit, the friction reducing effect is small. The upper limit of  $\{[Mg]/([Mg] + [Ca])\} \times 100$  is preferably 100, more preferably 80, further preferably 60, especially preferably 50, and most preferably 40.

[0037] A calcium type cleaning agent (A') is preferably overbasic. In such a case, it is possible to secure acid neutralization performance necessary for the lubricating oil. When an overbasic calcium-containing cleaning agent is used, a neutral calcium type cleaning agent may be used together.

[0038] Although there is no particular restriction on the total base number of a calcium type cleaning agent (A'), it is preferably 20 to 500 mg KOH/g, more preferably 50 to 400 mg KOH/g, and most preferably 100 to 350 mg KOH/g. In such a case, it is possible to secure acid neutralization performance, high temperature cleaning performance, and antirust performance necessary for a lubricating oil. When two or more kinds of metal cleaning agents are used in mixture, it is preferable that the resultant base number of the mixture falls within the above range.

[0039] The calcium content in a calcium type cleaning agent (A') is preferably 0.5 to 20 weight%, more preferably 1 to 16 weight%, and most preferably 2 to 14 weight%.

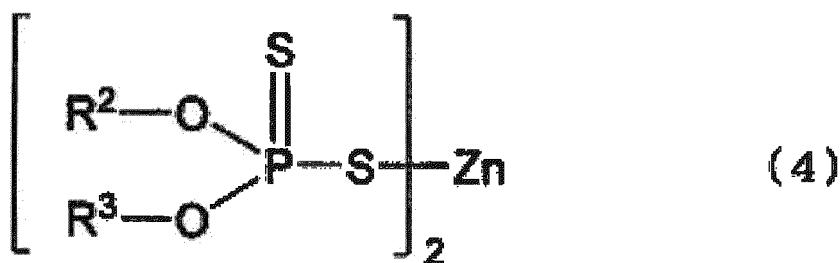
[0040] A lubricating oil composition according to the present invention may also comprise a sodium type cleaning agent as a metal type cleaning agent other than the above to the extent that the advantageous effect of the present invention is not impaired. A sodium type cleaning agent is a compound having sodium, and for example sodium sulfonate, sodium phenate, and sodium salicylate are preferable. The sodium type cleaning agents may be used singly, or in mixture of two or more kinds thereof. When a sodium type cleaning agent is included, high temperature cleaning performance and antirust performance required for a lubricating oil may be secured. A sodium type cleaning agent may be used in combination with the magnesium type cleaning agent and with an optional calcium type cleaning agent.

[0041] There is no particular restriction on the total amount of the metal type cleaning agents in a lubricating oil composition according to the present invention, insofar as the magnesium amount contained in the composition satisfies the above specified range. Depending on the amount of magnesium type cleaning agent, the addition amounts of a calcium type cleaning agent and a sodium type cleaning agent may be limited.

(B) Zinc dialkyl dithiophosphate

**[0042]** A lubricating oil composition according to the present invention comprises a zinc dialkyl dithiophosphate (ZnDTP) (also referred to as ZDDP)). The zinc dialkyl dithiophosphate functions as an antiwear agent. According to the present invention, the zinc dialkyl dithiophosphate necessarily includes (B-1) a zinc dialkyl dithiophosphate having a primary alkyl group. If a zinc dialkyl dithiophosphate having a primary alkyl group is not included, it is not possible to ensure adequate antiwear performance in a low viscosity lubricating oil composition. Accordingly, the content of (B-1) a zinc dialkyl dithiophosphate having a primary alkyl group in a lubricating oil composition according to the present invention is 30 weight% or more based on the total amount of component (B). It is preferably 40 weight% or more, more preferably 50 weight% or more, further preferably 60 weight% or more, especially preferably 80 weight% or more, and most preferably 100 weight%.

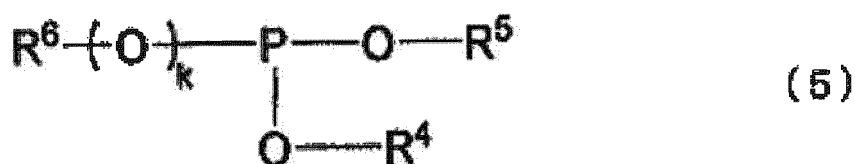
**[0043]** A zinc dialkyl dithiophosphate is a compound represented by following formula (4).



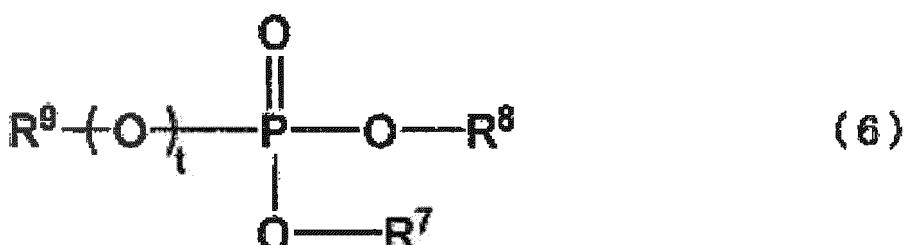
**[0047]** In the present invention, the composition is optimized in order to reduce friction while ensuring the antiwear performance in a lubricating oil composition having a lower viscosity. The viscosity of a lubricating oil composition required according to the present invention will be described later. According to the present invention, the relationship (combination) between the amount of boron contained in a lubricating oil composition and the content of (B-1) a zinc dialkyl dithiophosphate having a primary alkyl group is adjusted to improve the friction reducing effect. The effect can be maintained under the low viscosity condition described later. The combination may be adjusted to the extent that the amount of boron based on the total amount of the composition is less than 100 ppm by weight, preferably less than 80 ppm by weight, more preferably less than 50 ppm by weight, especially preferably less than 20 ppm by weight, and most preferably 0 ppm; and the content of (B-1) a zinc dialkyl dithiophosphate having a primary alkyl group based on the total amount of the component (B) is 30 weight% or more, preferably 40 weight% or more, more preferably 50 weight% or more, further preferably 60 weight% or more, especially preferably 80 weight% or more, and most preferably 100 weight%. Particularly, the composition of a zinc dialkyl dithiophosphate, namely the weight ratio of the component (B-1) to the component (B-2) satisfies 99:1 to 30:70, preferably 95:5 to 35:65, more preferably 90:10 to 40:60, especially preferably 85:15 to 45:55, and most preferably 80:20 to 50:50. In this regard, the total amount of a zinc dialkyl dithiophosphate is acceptable insofar as the total weight (ppm) of phosphorus satisfies the above-mentioned range. A lubricating oil composition to be obtained under the above conditions is able to secure both friction preventing performance and antiwear performance even when the viscosity is further reduced compared to the conventional lubricating oil composition.

**[0048]** A lubricating oil composition according to the present invention may further comprise an antiwear agent other than a zinc dialkyl dithiophosphate. Examples thereof include a compound represented by the above formula, wherein R<sup>2</sup> and R<sup>3</sup> are independently a hydrogen atom, or a monovalent hydrocarbon group, which is not an alkyl group, and has 1 to 26 carbon atoms. Examples of the monovalent hydrocarbon group include an alkenyl group having 2 to 26 carbon atoms; a cycloalkyl group having 6 to 26 carbon atoms; an aryl group, alkylaryl group, or arylalkyl group having 6 to 26 carbon atoms; and a hydrocarbon group having an ester bond, an ether bond, an alcohol group, or a carboxyl group. R<sup>2</sup> and R<sup>3</sup>, which may be the same or different, are preferably a cycloalkyl group having 8 to 18 carbon atoms, or an alkylaryl group having 8 to 18 carbon atoms. In addition, zinc dithiocarbamate (ZnDTC) may be used in combination.

**[0049]** Further, at least one compound selected from phosphorus compounds, such as a phosphite, or a phosphate, represented by following formulas (5) and (6), and metal salts and amine salts thereof may be used in combination.



35 **[0050]** In formula (5), R<sup>6</sup> is a monovalent hydrocarbon group having 1 to 30 carbon atoms, R<sup>4</sup> and R<sup>5</sup> are independently a hydrogen atom, or a monovalent hydrocarbon group having 1 to 30 carbon atoms, and k is 0 or 1.



45 **[0051]** In formula (6), R<sup>9</sup> is a monovalent hydrocarbon group having 1 to 30 carbon atoms, R<sup>7</sup> and R<sup>8</sup> are independently a hydrogen atom, or a monovalent hydrocarbon group having 1 to 30 carbon atoms, and t is 0 or 1.

50 **[0052]** Examples of the monovalent hydrocarbon group having 1 to 30 carbon atoms represented by R<sup>4</sup> to R<sup>9</sup> in formulas (5) and (6) include an alkyl group, a cycloalkyl group, an alkenyl group, an alkyl-substituted cycloalkyl group, an aryl group, an alkyl-substituted aryl group, and an arylalkyl group. In particular, an alkyl group having 1 to 30 carbon atoms, or an aryl group having 6 to 24 carbon atoms is preferable, an alkyl group having 3 to 18 carbon atoms is more preferable, and an alkyl group having 4 to 15 carbon atoms is most preferable.

55 **[0053]** Examples of the phosphorus compound represented by formulas (5) and (6) include a phosphorous acid monoester having a hydrocarbon group having 1 to 30 carbon atoms, and hydrocarbyl phosphorous acid, a phosphonic acid monoester, and an acidic phosphoric acid monoester; a phosphorous acid diester, monothiophosphorous acid diester, phosphonic acid diester, acidic phosphoric acid diester, and hydrocarbyl phosphorous acid monoester, having

two hydrocarbon groups having 1 to 30 carbon atoms; and a phosphorous acid trister, and hydrocarbyl phosphorous acid diester, having three hydrocarbon groups having 1 to 30 carbon atoms; as well as mixtures thereof.

**[0054]** A metal salt or amine salt of a phosphorus compound represented by Formula (5) or (6) can be obtained by making a metallic base, such as a metal oxide, a metal hydroxide, a metal carbonate, and a metal chloride, or a nitrogen compound, such as ammonia, an amine compound having in the molecule only a hydrocarbon group having 1 to 30 carbon atoms, or a hydroxyl group-containing hydrocarbon group, react with the phosphorus compound represented by formula (5) or (6) to neutralize part or all of remaining acidic hydrogens. Examples of the metal in the metallic base include alkali metals, such as lithium, sodium, potassium, and cesium; alkaline earth metals, such as calcium, magnesium, and barium; heavy metals, such as zinc, copper, iron, lead, nickel, silver, and manganese (provided that molybdenum is excluded). Among these, alkaline earth metals, such as calcium, and magnesium, and zinc are preferable, and zinc is especially preferable.

**[0055]** As for the addition amount of a zinc dialkyl dithiophosphate, it may be added as described above such that the phosphorus content derived from the zinc dialkyl dithiophosphate falls within the above specified range. In a case where another antiwear agent is contained, the total amount of antiwear agents including the zinc dialkyl dithiophosphate to be added in a lubricating oil composition is ordinarily 0.1 to 5 weight%, and preferably 0.2 to 3 weight%.

(C) Dispersant

**[0056]** A lubricating oil composition according to the present invention preferably comprises a dispersant. The dispersant may be any of known dispersants conventionally added in a lubricating oil composition. A typical dispersant is an ashless dispersant. As an ashless dispersant either of a boron-containing dispersant, and a boron-free dispersant may be used, or both of them may be used in combination. Preferably, a boron-free ashless dispersant is used singly. The addition amount of a dispersant based on the total amount of the composition is 0.1 to 8 weight%, preferably 0.5 to 5.5 weight%, especially preferably 1.0 to 5.0 weight%, and most preferably 2.5 to 4.0 weight%.

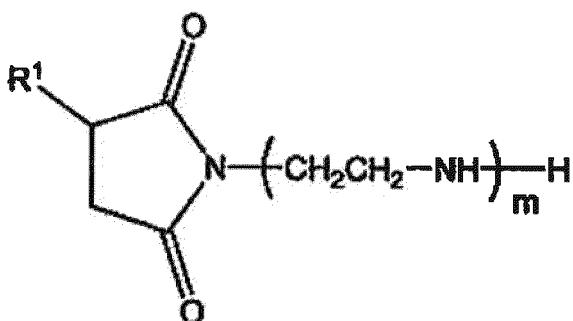
**[0057]** Examples of a known ashless dispersant include a nitrogen-containing compound having at least one linear or branched alkyl group or alkenyl group having 40 to 500 carbon atoms, preferably 60 to 350 carbon atoms in the molecule, or a derivative thereof, a Mannich dispersant, a mono-type or bis-type derivative of succinimide (for example, a compound having a structure of alkenylsuccinimide), a benzylamine having at least one alkyl group or alkenyl group having 40 to 500 carbon atoms in the molecule, and a polyamine having at least one alkyl group or alkenyl group having 40 to 400 carbon atoms in the molecule, as well as modified products thereof with a boron compound, a carboxylic acid, phosphoric acid, or the like. One kind or two or more kinds optionally selected from the above may be added. A boron-containing ashless dispersant is a compound obtained by modifying any of the above-mentioned compounds with a boron compound. Particularly a mono-type or bis-type derivative of a succinimide is preferable, and further a compound obtained by modifying (boronating) an alkenylsuccinimide compound with a boron compound, such as boric acid or a borate, is more preferable.

**[0058]** When a boron-containing ashless dispersant is used, it is blended in such an amount that the amount of boron to be contained in the composition satisfies the above-described range. When a boron-containing ashless dispersant and another boron-containing compound are used in combination, the total amount of boron contained in the composition is adjusted so as to satisfy the above-mentioned range. Particularly, the content of a boron-containing ashless dispersant is 0 to 1.5 weight% based on the total amount of the composition, preferably 0.001 to 1.0 weight%, more preferably 0.01 to 0.75 weight%, and especially preferably 0.1 to 0.5 weight%, although it depends on the boron content in the boron-containing ashless dispersant.

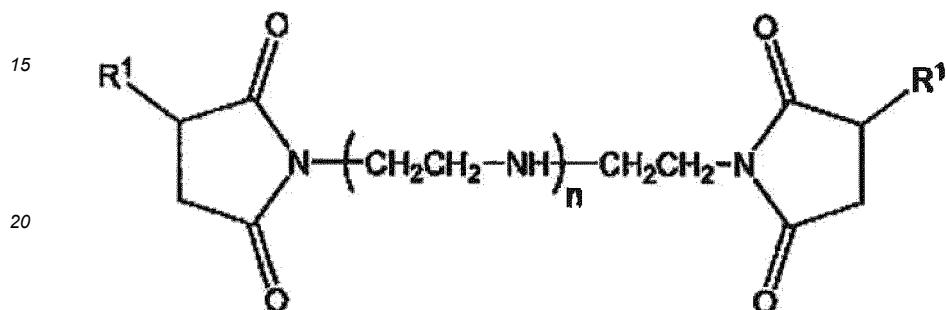
**[0059]** A boronated succinimide derivative is one produced by a known method and there is no particular restriction. For example, a mono-type or bis-type succinimide derivative is obtained by reacting a compound having an alkyl group or an alkenyl group having 40 to 500 carbon atoms with maleic anhydride between 100 and 200°C to produce an alkylsuccinic acid or alkenylsuccinic acid, and reacting the alkylsuccinic acid or alkenylsuccinic acid with a polyamine. In this regard, examples of the polyamine include diethylene triamine, triethylene tetramine, tetraethylene pentamine, and pentaethylene hexamine. A mono-type succinimide derivative may be represented, for example, by following formula (a). A bis-type succinimide derivative may be represented, for example, by following formula (b).

50

55



(a)



(b)

25 [0060] In the above formulas, R<sup>1</sup> is independently an alkyl group or alkenyl group having 40 to 400 carbon atoms, m is an integer of 1 to 20, and n is an integer of 0 to 20. A bis-type succinimide compound is particularly preferable. A succinimide derivative may be a combination of a mono-type and a bis-type, a combination of two or more kinds of monotypes, or a combination of two or more kinds of bis-types.

30 [0061] By reacting the succinimide derivative with a boron compound, a boronated succinimide derivative may be obtained. A boron compound includes boric acid, boric anhydride, boric acid ester, boron oxide, boron halide, and the like. Boronated succinimide derivatives may be used singly or in combination of two or more kinds thereof.

35 [0062] A derivative of a nitrogen-containing compound is known as another ashless dispersant. Examples thereof include a compound modified with a so-called oxygen-containing organic compound, for which the above described nitrogen-containing compound (that is, a nitrogen-containing compound having at least one linear or branched alkyl group or alkenyl group having 40 to 500, preferably 60 to 350 carbon atoms in the molecule) is reacted with a mono-carboxylic acid having 1 to 30 carbon atoms such as a fatty acid, or a polycarboxylic acid having 2 to 30 carbon atoms such as oxalic acid, phthalic acid, trimellitic acid, or pyromellitic acid, or an anhydride, or an ester compound thereof; an alkylene oxide having 2 to 6 carbon atoms, or hydroxy(poly)oxyalkylene carbonate, to neutralize or amide part or all of remaining amino groups and/or imino groups; a so-called boron-modified compound, for which the above described nitrogen-containing compound is reacted with boric acid to neutralize or amide part or all of remaining amino groups and/or imino groups; a so-called phosphoric acid-modified compound, for which the above described nitrogen-containing compound is reacted with phosphoric acid to neutralize or amide part or all of remaining amino groups and/or imino groups; a sulfur-modified compound, for which the above described nitrogen-containing compound is reacted with a sulfur compound; and a modified compound, for which the above described nitrogen-containing compound is subjected to a combination of two or more kinds of modifications selected from modification with an oxygen-containing organic compound, boron modification, phosphoric acid modification, and sulfur modification.

40 [0063] In a case where a boron-containing ashless dispersant is contained, among the above described boron-containing ashless dispersants, specifically a boric acid-modified compound of the alkenylsuccinimide derivative, particularly a boric acid-modified compound of the bis-type alkenylsuccinimide derivative is preferable, because it can further improve the heat resistance by combination with the base oil described above.

45 [0064] The number average molecular weight (Mn) of an ashless dispersant is preferably, but not restrictively, 2000 or more, more preferably 2500 or more, further preferably 3000 or more, and most preferably 5000 or more. Further, it is preferably 15,000 or less. When the number average molecular weight of an ashless dispersant is less than the lower limit value, the dispersibility may not be sufficient. On the other hand, when the number average molecular weight of an ashless dispersant exceeds the upper limit value, the viscosity becomes too high, and deposits are liable to increase due to insufficient fluidity.

50 [0065] As another boron-containing compound, an alkali borate type additive may be added. An alkali borate type additive contains an alkali metal borate hydrate, and may be expressed by the following general formula.



**[0066]** In the above formula, M is an alkali metal, x is 2.5 to 4.5, and y is 1.0 to 4.8. Examples thereof include lithium borate hydrate, sodium borate hydrate, potassium borate hydrate, rubidium borate hydrate, and cesium borate hydrate, and potassium borate hydrate and sodium borate hydrate are preferable, and potassium borate hydrate is particularly preferable. The average particle size of particles of the alkali metal borate hydrate is generally 1  $\mu\text{m}$  or less. The ratio of boron to an alkali metal in an alkali metal borate hydrate used according to the present invention is preferably in a range of about 2.5:1 to 4.5:1. The addition amount of the alkali borate type additive in terms of the boron amount together with the boron of the above boron-containing ashless dispersant based on the total amount of a lubricating oil composition is preferably not less than 0 ppm by weight but less than 100 ppm by weight.

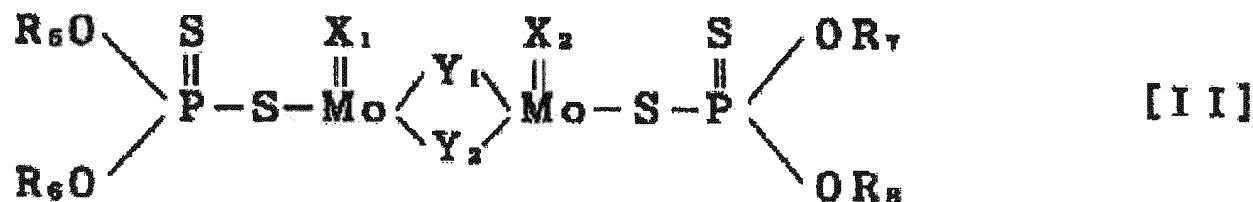
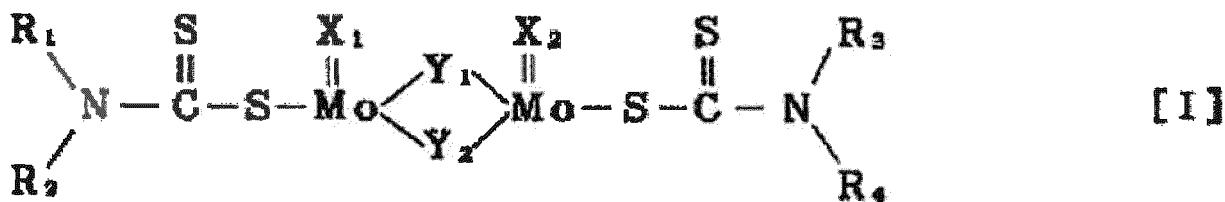
**[0067]** Examples of other boron-containing compounds include a potassium borate, such as potassium metaborate, potassium tetraborate, potassium pentaborate, potassium hexaborate, and potassium octaborate, calcium borate sulfonate, calcium borate salicylate, and tributyl borate.

**[0068]** A lubricating oil composition according to the present invention may comprise, in addition to the above components, various conventionally known additives as optional components. For example, it may comprise a molybdenum type friction modifier, or a viscosity index improver.

(D) Molybdenum type friction modifier

**[0069]** There is no particular restriction on a friction modifier containing molybdenum (hereinafter referred to as "molybdenum type friction modifier"), and a conventionally known friction modifier may be used. A molybdenum type friction modifier is a compound containing molybdenum, and examples thereof include a sulfur-containing organic molybdenum compound, such as molybdenum dithiophosphate (MoDTP), and molybdenum dithiocarbamate (MoDTC), a complex of a molybdenum compound with a sulfur-containing organic compound or another organic compound, and a complex of a sulfur-containing molybdenum compound, such as molybdenum sulfide and sulfurized molybdic acid, with an alkenylsuccinimide. Examples of the molybdenum compound include a molybdenum oxide, such as molybdenum dioxide and molybdenum trioxide; a molybdic acid, such as orthomolybdic acid, paramolybdic acid, and (poly)sulfurized molybdic acid; metal salts or ammonium salts of the molybdic acids; a sulfurized molybdenum, such as molybdenum sulfide, molybdenum disulfide, molybdenum trisulfide, molybdenum pentasulfide, and molybdenum polysulfide; sulfurized molybdic acid, and a metal salt or an amine salt of sulfurized molybdic acid; and a molybdenum halide, such as molybdenum chloride. Examples of the sulfur-containing organic compound include alkyl (thio)xanthate, thiadiazole, mercaptothiadiazole, thiocarbonate, tetrahydrocarbyl thiuram disulfide, bis[di(thio)hydrocarbyl dithiophosphonate] disulfide, an organic (poly)sulfide, and a sulfurized ester. In particular, an organic molybdenum compound, such as molybdenum dithiophosphate (MoDTP), and molybdenum dithiocarbamate (MoDTC), is preferable.

**[0070]** Molybdenum dithiocarbamate (MoDTC) is a compound expressed by following formula [I], and molybdenum dithiophosphate (MoDTP) is a compound expressed by following formula [II]:



**[0071]** In formulas [I] and [II], R<sub>1</sub> to R<sub>8</sub> may be the same or different, and are monovalent hydrocarbon groups having 1 to 30 carbon atoms. The hydrocarbon group may be linear or branched. Examples of the monovalent hydrocarbon group include a linear or branched alkyl group having 1 to 30 carbon atoms; an alkenyl group having 2 to 30 carbon atoms; a cycloalkyl group having 4 to 30 carbon atoms; an aryl group, alkylaryl group, or arylalkyl group having 6 to 30

carbon atoms. In the arylalkyl group, the bonding position of the alkyl group is arbitrary. More specifically, examples of the alkyl group include a methyl group, an ethyl group, 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 undecyl group, a dodecyl group, a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group, and an octadecyl group, as well as branched alkyl groups thereof. Especially, an alkyl group having 3 to 8 carbon atoms is preferable.  $X_1$  and  $X_2$  are an oxygen atom or a sulfur atom, and  $Y_1$  and  $Y_2$  are an oxygen atom or a sulfur atom.

**[0072]** As a friction modifier, a sulfur-free organic molybdenum compound may also be used. Examples of such a compound include a molybdenum-amine complex, a molybdenum-succinimide complex, a molybdenum salt of an organic acid, and a molybdenum salt of an alcohol.

**[0073]** Furthermore, as a friction modifier according to the present invention, a trinuclear molybdenum compound described in US Patent No. 5,906,968 may be used.

**[0074]** A friction modifier is added in such an amount that the concentration of molybdenum [Mo] in terms of ppm by weight based on the total weight of a lubricating oil composition falls within a range of 200 to 1400 ppm by weight, preferably 300 to 1200 ppm by weight, more preferably 400 to 1000 ppm by weight, and most preferably 500 to 900 ppm by weight. When the amount of a friction modifier exceeds the upper limit, the cleaning performance may be deteriorated, meanwhile when it is less than the lower limit, the friction may not be sufficiently reduced, or the cleaning performance may be deteriorated.

**[0075]** A friction modifier is preferably contained in an amount satisfying following formula (2):

$$[Mg]/[Mo] < 2.5 \quad (2)$$

**[0076]** [Mo] is the concentration of molybdenum in terms of ppm by weight based on the weight of a lubricating oil composition.

**[0077]** The value of [Mg]/[Mo] is more preferably 2.0 or less, further preferably 1.8 or less, and still further preferably 1.5 or less. The lower limit of [Mg]/[Mo] is preferably 0.1, more preferably 0.2, and further preferably 0.3.

(E) Viscosity index improver

**[0078]** Examples of a viscosity index improver include those containing polymethacrylate, dispersed polymethacrylate, an olefin copolymer (polyisobutylene, and an ethylene/propylene copolymer), a dispersed olefin copolymer, polyalkyl-styrene, a hydrogenated styrene/butadiene copolymer, a styrene/maleic anhydride ester copolymer, or a star-shaped isoprene. Further, it is also possible to use a comb-shaped polymer containing, in the main chain, at least a repeating unit based on a polyolefin macromer and a repeating unit based on an alkyl (meth)acrylate having an alkyl group having 1 to 30 carbon atoms.

**[0079]** A viscosity index improver usually comprises the above described polymer and a diluent oil. The content of a viscosity index improver in terms of the polymer amount contained in the viscosity index improver based on the total massweight of the composition is preferably 1.0 weight% or less, more preferably 0.5 weight% or less, further preferably 0.2 weight% or less, and especially preferably 0.1 weight% or less. In order to further lower the viscosity of a lubricating oil composition, it is preferable that the content of a viscosity index improver is as small as possible, and most preferable that the viscosity index improver is not contained at all (0 weight% in terms of the polymer amount).

**[0080]** In order to improve its performance, a lubricating oil composition according to the present invention may further comprise another additive depending on the object. As other additives, those commonly used for a lubricating oil composition may be used, and examples thereof include an antioxidant, a friction modifier other than the above, an anticorrosive agent, an antirust agent, a pour-point depressant, a demulsifying agent, a metal deactivator, and an antifoaming agent.

**[0081]** Examples of an antioxidant include an ashless antioxidant, such as a phenol type and an amine type, and a metallic antioxidant, such as a copper type and a molybdenum type. Examples of the phenol type ashless antioxidant include 4,4'-methylene-bis(2,6-di-*tert*-butylphenol), 4,4'-bis(2,6-di-*tert*-butylphenol), and isooctyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate. Examples of an amine type ashless antioxidants include phenyl- $\alpha$ -naphthylamine, an alkyl-phenyl- $\alpha$ -naphthylamine, and a dialkyldiphenylamine. An antioxidant is usually blended in a lubricating oil composition at 0.1 to 5 weight%.

**[0082]** Examples of a friction modifier other than the above include an ester, an amine, an amide, and a sulfurized ester. The friction modifier is usually blended in a lubricating oil composition at 0.01 to 3 weight%.

**[0083]** Examples of the anticorrosive agent include a benzotriazole type, a tolyltriazole type, a thiadiazole type, and an imidazole type compounds. Examples of the antirust agent include petroleum sulfonate, an alkylbenzene sulfonate, dinonylnaphthalene sulfonate, an alkenylsuccinate, and a polyhydric alcohol ester. The anticorrosive agent and the

antirust agent are usually blended in a lubricating oil composition each at 0.01 to 5 weight%.

[0084] As the pour-point depressant, for example, a polymethacrylate type polymer compatible with a used lubricating base oil may be used. The pour-point depressant is usually blended in a lubricating oil composition at 0.01 to 3 weight%.

[0085] Examples of the demulsifying agent include a polyalkylene glycol nonionic surfactant, such as a polyoxyethylene alkyl ether, a polyoxyethylene alkylphenyl ether, and a polyoxyethylene alkylnaphthyl ether. The demulsifying agent is usually blended in a lubricating oil composition at 0.01 to 5 weight%.

[0086] Examples of the metal deactivator include imidazoline, a pyrimidine derivative, an alkylthiadiazole, mercapto-benzothiazole, benzotriazole or a derivative thereof, 1,3,4-thiadiazole polysulfide, 1,3,4-thiadiazolyl-2,5-bis(dialkyldithiocarbamate), 2-(alkyldithio)benzimidazole, and  $\beta$ -(*o*-carboxybenzylthio)propionitrile. The metal deactivator is usually blended in a lubricating oil composition at 0.01 to 3 weight%.

[0087] Examples of the antifoaming agent include a silicone oil having a kinematic viscosity at 25°C of 1000 to 100,000 mm<sup>2</sup>/s, an alkenylsuccinic acid derivative, an esters between a polyhydroxy aliphatic alcohol and a long-chain fatty acid, and methyl salicylate and *o*-hydroxybenzyl alcohol. The antifoaming agent is usually blended in a lubricating oil composition at 0.001 to 1 weight%.

[0088] Although there is no particular restriction on the CCS viscosity at -35°C of a lubricating oil composition according to the present invention, it is preferably 6.2 Pa · s or less, more preferably 5.0 Pa · s or less, further preferably 4.0 Pa · s or less, especially preferably 3.0 Pa · s or less, and most preferably 2.6 Pa · s or less.

[0089] In a case where a lubricating oil composition according to the present invention contains molybdenum, the amount of molybdenum contained in the lubricating oil composition and the CCS viscosity at -35°C preferably satisfies following formula (7).

$$[\text{CCS viscosity}]/[\text{Mo}] \leq 0.01 \quad (7)$$

[0090] [CCS viscosity] represents the value of CCS viscosity (Pa · s) at -35°C of a lubricating oil composition, and [Mo] represents the concentration in terms of ppm by weight of molybdenum based on the weight of the lubricating oil composition.

[0091] The value of [CCS viscosity]/[Mo] is more preferably 0.008 or less, and further preferably 0.005 or less. When this value exceeds 0.01, the torque reduction rate may become small, or the cleaning performance is liable to be deteriorated. Although the lower limit value of [CCS viscosity]/[Mo] is not limited, it is preferably 0.002, and more preferably 0.003.

[0092] Although there is no particular restriction on the high temperature high shear viscosity (HTHS viscosity) at 150°C of a lubricating oil composition according to the present invention, it is not less than 1.3 mPa · s but less than 2.3 mPa · s, preferably not less than 1.5 mPa · s but less than 2.0 mPa · s, and more preferably from 1.6 to 1.9 mPa · s.

[0093] Although there is no particular restriction on the kinematic viscosity at 100°C of a lubricating oil composition according to the present invention, it is preferably less than 6.1 mm<sup>2</sup>/s, more preferably less than 5.8 mm<sup>2</sup>/s, and further preferably less than 5.4 mm<sup>2</sup>/s. The lower limit value is preferably 3.0 mm<sup>2</sup>/s, more preferably 3.5 mm<sup>2</sup>/s, further preferably 3.8 mm<sup>2</sup>/s, and most preferably 4.0 mm<sup>2</sup>/s.

[0094] According to the present invention, a lubricating oil composition which is reduced in viscosity as described above can still have sufficient friction characteristics. A lubricating oil composition according to the present invention can be suitably used for an internal combustion engine, and further for a supercharged gasoline engine.

#### [Examples]

[0095] The present invention will be described below in more detail by way of Examples and Comparative Examples, provided that the present invention is not limited to the following Examples.

[0096] Materials used in Examples and Comparative Examples are as follows.

#### Lubricating base oil

[0097] Base oil originated from GTL (kinematic viscosity at 100°C = 3.9 mm<sup>2</sup>/s, VI = 127)

(A) Magnesium type cleaning agent

[0098] Magnesium sulfonate (total base number: 400 mg KOH/g, magnesium content: 9.4 weight%)

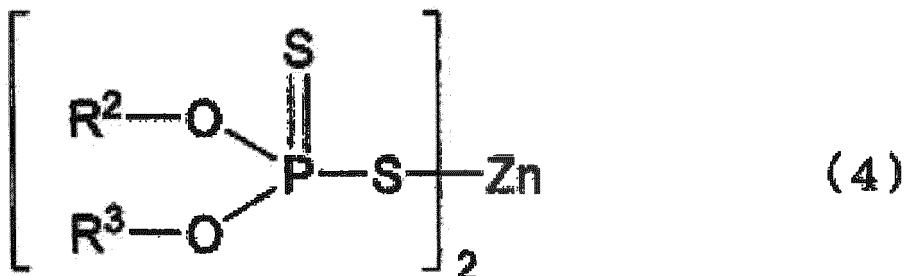
(A') Calcium type cleaning agent

[0099] Calcium salicylate (total base number: 146 mg KOH/g, calcium content: 5.2 weight%)

5 (B) Zinc dialkyl thiophosphate (antiwear agent)

(B-1) Antiwear agent 1:

10 [0100] Pri-ZnDTP (the compound represented by following formula (4), in which R<sup>2</sup> and R<sup>3</sup> are both primary alkyl group having 8 carbon atoms)



(B-2) Antiwear agent 2:

25 [0101] Sec-ZnDTP (the compound represented by above formula (4), in which R<sup>2</sup> is secondary alkyl group having 4 carbon atoms, and R<sup>3</sup> is a secondary alkyl group having 6 carbon atoms)

(C) Ashless dispersant

30 (C-1) Ashless dispersant containing boron

35 [0102] Boronated succinimide compound (the mixture represented by above formula (b), wherein R<sup>1</sup> is polybutenyl, n is 4 to 12, the boron content is 0.7 weight%, and the nitrogen content is 2 weight%),

(C-2) Ashless dispersant not containing boron

40 [0103] Succinimide compound (the mixture represented by above formula (b), wherein R<sup>1</sup> is polybutenyl, n is 4 to 12, and the nitrogen content is 1 weight%).

(D) Friction modifier

45 [0104] Molybdenum type friction modifier: MoDTP (molybdenum content: 10 weight%)

(E) Viscosity index improver

50 [0105] Polymethacrylate (Mw = 350,000)

Other additives

[0106]

55 Antioxidant: phenol type antioxidant

Antifoaming agent: dimethyl silicone

Examples 1 to 9 and Comparative Examples 1 to 8

55 [0107] A lubricating oil composition was prepared by mixing the respective components in the amounts set forth in Table 1 or 3. The parts by weight described in the table are parts by weight based on the total amount (100 parts by weight) of the lubricating oil composition. The amounts of the magnesium type cleaning agent, the calcium type cleaning

agent, and the molybdenum type friction modifier described in the tables are the respective contents of magnesium, calcium, and molybdenum in terms of ppm by weight ([Mg], [Ca], and [Mo] in the order) based on the total amount of the lubricating oil composition. The amount of B described in the Table is the weight of boron in terms of ppm by weight based on the total amount of the lubricating oil composition. An antiwear agent (B) was blended in total 1 part by weight based on the total amount (100 parts by weight) of the lubricating oil composition. The weight ratio ((B-1)/(B-2)) of an antiwear agent (B-1) (zinc dialkyl dithiophosphate having a primary alkyl group) to an antiwear agent (B-2) (zinc dialkyl dithiophosphate having a secondary alkyl group) in the 1 part by weight was described in the Table. Meanwhile, in Example 7, the used amount of an antiwear agent was 0.5 parts by weight in total based on the total amount (100 parts by weight) of the lubricating oil composition, and the weight ratio ((B-1)/(B-2)) of an antiwear agent (B-1) (zinc dialkyl dithiophosphate having a primary alkyl group) to an antiwear agent (B-2) (zinc dialkyl dithiophosphate having a secondary alkyl group) in the 0.5 parts by weight was described in the Table. In addition, the amount of P described in the Table is the weight of phosphorus in terms of ppm by weight based on the total amount of the lubricating oil composition.

**[0108]** In this regard, the amounts of a magnesium type cleaning agent and a calcium type cleaning agent were regulated such that the total molar amount of magnesium and calcium contained in these cleaning agent became identical as possible in all of Examples and Comparative Examples.

**[0109]** The following tests were conducted on the obtained compositions. The results are described in Tables 2 and 4.

(1) High temperature high shear viscosity at 150°C (HTHS 150)

**[0110]** Measured according to ASTM D4683.

(2) CCS viscosity at -35°C (CCS viscosity)

**[0111]** Measured according to ASTM D5293.

(3) Kinematic viscosity at 100°C (KV 100)

**[0112]** Measured at 100°C according to ASTM D445.

(4) Friction coefficient

**[0113]** A friction coefficient was measured according to the following method. FIG. 3 illustrates a schematic diagram representing a mode of the measurement.

**[0114]** A ball-on-disk friction test was carried out on each lubricating oil composition (reference numeral 4 in FIG. 3) using a standard test piece according to PCS Instruments (reference numeral 3 in FIG. 3) as a plate test piece (material: AISI 52100 steel), and a standard test piece according to PCS Instruments (reference numeral 2 in FIG. 3) as an opponent ball test piece (material: AISI 52100 steel) with a diameter of 0.75 inches. A ball-on-disk friction test was performed for 2 hours under a test load (reference numeral 1 in FIG. 3) of 37 N, a slip ratio of 50%, and an oil temperature of 60°C (constant), and the friction coefficient after an elapse of 2 hours was defined as the friction coefficient in this test. Those having a friction coefficient of 0.038 or less were accepted.

(5) Hot tube test (Evaluation of high temperature cleaning performance)

**[0115]** Through a glass tube having an inner diameter of 2 mm, a lubricating oil composition was sent to flow at a rate of 0.3 mL/hour together with air at a rate of 10 mL/sec for 16 hours, while maintaining the temperature of the glass tube at 280°C. A lacquer having adhered to the glass tube was compared with the color samples and scored, wherein transparency scored 10, and black scored 0. The higher score means that the high temperature cleaning performance is higher. Those having a score of 5.5 or higher were accepted.

Table 1

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Lubricating base oil		balance	balance	balance	balance	balance	balance	balance	balance	balance
[A]	(A) Metal cleaning agent 1	Amount of Mg	ppm by weight	470	470	470	470	300	470	470
	(A') Metal cleaning agent 2	Amount of Ca	ppm by weight	1400	1400	1400	1400	1500	1400	1400
[B]	(B-1) Antiwear agent 1 (Pri)	part by weight	0.4	0.4	1.0	0.6	1.0	0.4	0.4	0.3
	(B-2) Antiwear agent 2 (Sec)	part by weight	0.6	0.6	0	0.4	0	0.6	0.6	0.7
Primary/Secondary (weight ratio)		40/60	40/60	100/0	60/40	100/0	40/60	40/60	40/60	30/70
Total amount of P		ppm by weight	800	800	800	800	800	400	800	800
[C]	(C-1) Ashless dispersant	Addition amount	0	0.75	0	0	0.75	0	0.75	0
		Amount of B	ppm by weight	0	50	0	0	50	0	0
[D]	(C-2) Ashless dispersant	Addition amount	3.50	2.75	3.50	3.50	2.75	3.50	2.75	3.50
	Friction modifier	Amount of Mo	ppm by weight	800	800	800	800	800	800	800
[E]	Viscosity index improver (net polymer)	part by weight	0	0	0	0	0	0	0	0
	Other additive	part by weight	2	2	2	2	2	2	2	2
[[Mg]/([Mg] + [Ca])] × 100		25	25	25	25	17	25	25	25	25
[Mg]/[Mo]		0.59	0.59	0.59	0.59	0.38	0.59	0.59	0.59	0.59

Table 2

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Evaluation	CCS viscosity (Pa·s)	2.5	2.5	2.5	2.5	2.5	2.5	2.4	2.6	2.5
	HTHS 150 (mPa·s)	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.8	1.7
	KV 100 (mm <sup>2</sup> /s)	4.8	4.8	4.8	4.8	4.8	4.8	4.7	5.0	4.8
	[CCS viscosity]/[Mo]	0.0032	0.0031	0.0032	0.0031	0.0032	0.0031	0.0030	0.0031	0.0031
	Friction coefficient	0.038	0.038	0.037	0.038	0.038	0.038	0.038	0.038	0.038
	HTT	6.0	6.5	7.0	6.5	8.5	6.0	7.0	5.5	6.0

Table 3

Composition		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Lubricating base oil		balance							
[A]	(A) Metal cleaning agent 1	Amount of Mg	ppm by weight	470	470	470	470	470	470
	(A') Metal cleaning agent 2	Amount of Ca	ppm by weight	1400	1400	1400	1400	1400	1400
	(B-1) Antiwear agent 1	part by weight	0.4	0.2	0	0	0.4	0.4	0.6
[B]	(B-2) Antiwear agent 2	part by weight	0.6	0.8	1.0	1.0	0.6	0.6	0.4
	Primary/Secondary (weight ratio)	40/60	20/80	0/100	0/100	40/60	40/60	100/0	60/40
	Total amount of P	ppm by weight	800	800	800	800	800	800	800
[C]	(C-1)Ashless dispersant	Addition amount	part by weight	3	0	0	6	0	3
	(C-2)Ashless dispersant	Addition amount	part by weight	0.5	3.5	0	3.5	3.5	0.5
[D]	Friction modifier	Amount of Mo	ppm by weight	800	800	800	800	100	800
[E]	Viscosity index improver (net polymer)	part by weight	0	0	0	0	0	0	0
	Other additive	part by weight	2	2	2	2	2	2	2
	$[\text{Mg}]/([\text{Mg}] + [\text{Ca}]) \times 100$		25	25	25	88	25	25	25
	$[\text{Mg}]/[\text{Mo}]$		0.59	0.59	0.59	1.75	4.70	0.59	0.59

Table 4

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Evaluation	CCS viscosity (Pa·s)	2.5	2.5	2.5	3.0	2.5	2.5	2.5	2.5
	HTHS 150 (mPa·s)	1.7	1.7	1.7	1.9	1.7	1.7	1.7	1.7
	KV 100 (m <sup>2</sup> /s)	4.8	4.8	4.8	5.4	4.8	4.8	4.8	4.8
	[CCS viscosity]/[Mo]	0.0032	0.0031	0.0031	0.0038	0.0031	0.0250	0.0031	0.0031
	Friction coefficient	0.039	0.041	0.039	0.041	0.045<	0.05<	0.039	0.039
	HTT	7.5	5.5	4.5	7.5	<4.0	-	5.5<	5.5<

[0116] As described in Table 2, a lubricating oil composition according to the present invention can reduce friction even at low viscosity less than 6.1 mm<sup>2</sup>/s in terms of kinematic viscosity at 100°C, and at the same time the high temperature cleaning performance can be high.

5 [Industrial Applicability]

[0117] The lubricating oil composition according to the present invention exerts an effect of reducing friction even when the viscosity is lowered, and its preferable embodiment is suitable for a lubricating oil composition for an internal combustion engine, and further for a lubricating oil composition for a supercharged gasoline engine.

10 [Reference Signs List]

[0118]

15 1. Load  
2. Ball test piece  
3. Plate test piece  
4. Lubricating oil composition

20 **Claims**

1. A lubricating oil composition comprising a lubricating base oil, (A) a cleaning agent containing magnesium, and (B) a zinc dialkyl dithiophosphate, wherein the amount of component (A) in terms of ppm by weight of magnesium ([Mg]) based on the total weight of the lubricating oil composition is in a range of 200 to 1200 ppm by weight; the amount of component (B) in terms of ppm by weight of phosphorus ([P]) based on the total weight of the lubricating oil composition is in a range of 300 to 1000 ppm by weight; wherein component (B) comprises (B-1) a zinc dialkyl dithiophosphate having a primary alkyl group, and the proportion of the weight of component (B-1) to the total weight of component (B) is 30 weight% or more; and wherein the concentration of boron [B] in terms of ppm by weight of boron based on the total weight of the lubricating oil composition is less than 100 ppm by weight.

2. The lubricating oil composition according to claim 1, further comprising (C) a dispersant, wherein the amount of component (C) is 0.1 to 8 weight% based on the total weight of the lubricating oil composition.

3. The lubricating oil composition according to claim 1 or 2, which further comprises (A') a cleaning agent containing calcium, and satisfies following formula (1):

$$40 \quad \{[Mg]/([Mg] + [Ca])\} \times 100 \geq 5 \quad (1)$$

wherein [Ca] represents the weight of calcium in terms of ppm based on the weight of the lubricating oil composition.

45 4. The lubricating oil composition according to any one of claims 1 to 3, further comprising (D) a friction modifier containing molybdenum, wherein the amount of component (D) is in a range of 200 to 1400 ppm by weight in terms of the ppm by weight of molybdenum ([Mo]) based on the total weight of the lubricating oil composition.

50 5. The lubricating oil composition of any one of claims 1 to 4, further comprising a viscosity index improver, wherein the amount of the viscosity index improver in terms of the weight of polymer contained in the viscosity index improver based on the total weight of the lubricating oil composition is 1 weight% or less.

55 6. The lubricating oil composition according to any one of claims 1 to 5, having a CCS viscosity at -35°C of 6.2 Pa · s or less.

7. The lubricating oil composition according to any one of claims 1 to 6, having a high temperature high shear viscosity (HTHS viscosity) at 150°C of not less than 1.3 mPa · s but less than 2.3 mPa · s.

8. The lubricating oil composition according to any one of claims 1 to 7, having a kinematic viscosity at 100°C of less than 6.1 mm<sup>2</sup>/s.
9. The lubricating oil composition according to any one of claims 1 to 8, which is for an internal combustion engine.
- 5 10. The lubricating oil composition according to any one of claims 1 to 9, which is for a supercharged gasoline engine.

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FIG. 1

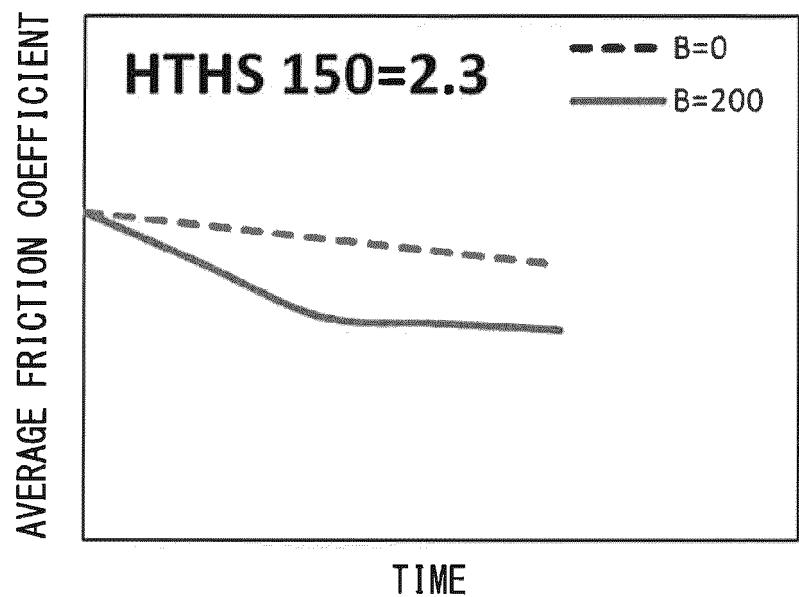


FIG. 2

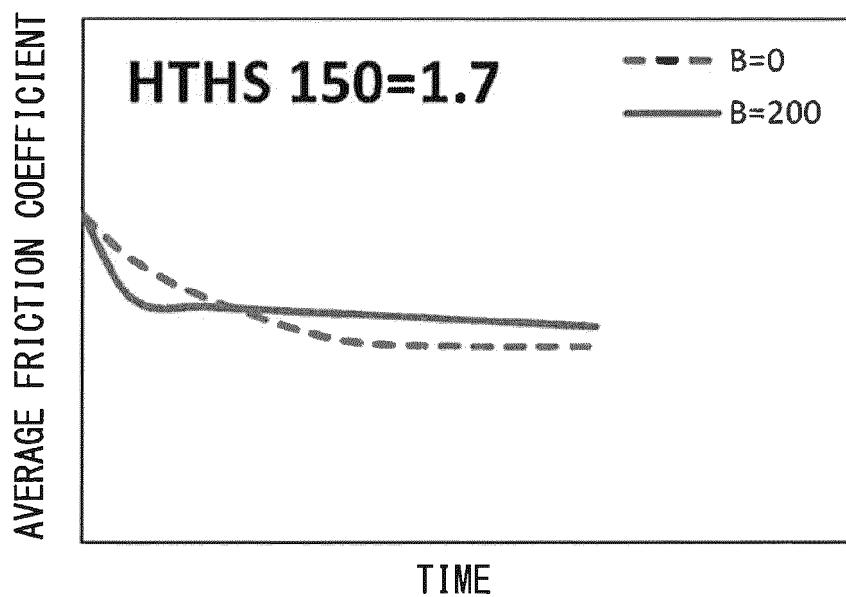
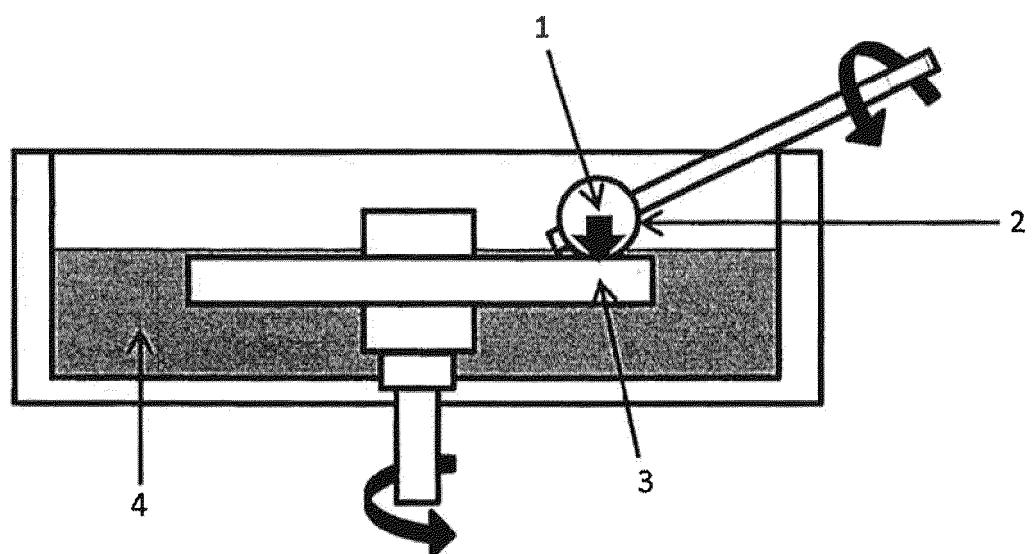


FIG. 3



## INTERNATIONAL SEARCH REPORT

International application No
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5	A. CLASSIFICATION OF SUBJECT MATTER INV. C10M157/10 ADD.										
	According to International Patent Classification (IPC) or to both national classification and IPC										
10	B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C10M C10N										
	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched										
15	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data										
20	C. DOCUMENTS CONSIDERED TO BE RELEVANT										
	<table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>WO 2017/099140 A1 (EXXONMOBIL RES &amp; ENG CO [US]; TOYOTA MOTOR CO LTD [JP]) 15 June 2017 (2017-06-15) paragraphs [0064] - [0082], [0084], [0085]; table 1 &amp; EP 3 388 500 A1 (EXXONMOBIL RES &amp; ENG CO [US]; TOYOTA MOTOR CO LTD [JP]) 17 October 2018 (2018-10-17) examples 1,2,6 and comparative examples 3, 4; paragraphs [0065] - [0087]; table 1 paragraphs [0005], [0007], [0009], [0018], [0020], [0029], [0037] paragraphs [0039] - [0041], [0048], [0051], [0053] ----- -----</td> <td>1-10</td> </tr> <tr> <td>X,P</td> <td></td> <td>1-10</td> </tr> </tbody> </table>		Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	WO 2017/099140 A1 (EXXONMOBIL RES & ENG CO [US]; TOYOTA MOTOR CO LTD [JP]) 15 June 2017 (2017-06-15) paragraphs [0064] - [0082], [0084], [0085]; table 1 & EP 3 388 500 A1 (EXXONMOBIL RES & ENG CO [US]; TOYOTA MOTOR CO LTD [JP]) 17 October 2018 (2018-10-17) examples 1,2,6 and comparative examples 3, 4; paragraphs [0065] - [0087]; table 1 paragraphs [0005], [0007], [0009], [0018], [0020], [0029], [0037] paragraphs [0039] - [0041], [0048], [0051], [0053] ----- -----	1-10	X,P		1-10
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.									
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40	<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.										
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50	Date of the actual completion of the international search  5 April 2019	Date of mailing of the international search report  16/04/2019									
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