(19) Europäisches
Patentamt
European
Patent Office
Office européen
des brevets

(11) **EP 1 783 196 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
09.05.2007 Bulletin 2007/19

(21) Application number: **05780924.6**

(22) Date of filing: **25.08.2005**

(51) Int Cl.:
C10M 137/10 $^{(2006.01)}$ ***C10M 141/10*** $^{(2006.01)}$
C10M 159/12 $^{(2006.01)}$ ***C10M 177/00*** $^{(2006.01)}$

(86) International application number:
PCT/JP2005/015400

(87) International publication number:
WO 2006/025246 (09.03.2006 Gazette 2006/10)

(84) Designated Contracting States:
DE FR GB

(30) Priority: **30.08.2004 JP 2004249807**

(71) Applicant: **IDEMITSU KOSAN CO., LTD.**
Tokyo 100-8321 (JP)

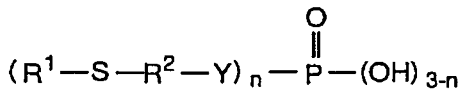
(72) Inventors:
- **KOSHIMA, Hiroaki**
  Chiba 299-0293 (JP)
- **IIZUKA, Shinya**
  Chiba 299-0293 (JP)
- **ISHIKAWA, Motoharu**
  Chiba 299-0107 (JP)

(74) Representative: **HOFFMANN EITLE**
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)

(54) ADDITIVE FOR LUBRICANT

(57) An additive for lubricants exhibiting high oxidation stability, high thermal stability, and high No_x resistance, and having excellent functions as an extreme-pressure additive or wear-resistant agent and a lubricant composition containing the addtive are provided.

The present invention provides an additive for lubricants comprising a phosphate ester derivative represented by the general formula [I]:



$$(R^1—S—R^2—Y)_n—\overset{\overset{\large O}{\|}}{P}—(OH)_{3-n} \quad \cdots [I]$$

wherein Y represents sulfur (S) or oxygen (O); R^1 represents a monovalent organic group having 4 to 24 carbon atoms; R^2 represents a divalent organic group having 1 to 6 carbon atoms; and n represents an integer of 1 to 3. The present invention also provides a lubricant composition containing the derivative.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

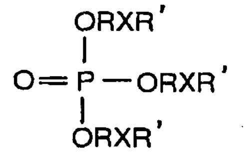
[0001] The present invention relates to additives for lubricants. In particular present invention relates to an additive for lubricants comprising a novel phosphate ester derivative, a reaction product of the phosphate ester derivative with a zinc compound, or a mixture of the phosphate ester derivative with an organic zinc compound and to a lubricant composition containing the additive. This additive exhibits high oxidation stability, high thermal stability, and high No_x resistance, and has excellent functions as an extreme-pressure additive or wear-resistant agent.

Background Art

[0002] During the operation of machinery, lubricant oils must have abilities of preventing or controlling galling of metal surfaces of machine parts caused by sliding or rolling contact therebetween. Additives, therefore, serve a significantly important role in improved wear resistance of lubricant oils and a prolonged service life of machinery.

[0003] Base oils cannot, by themselves, satisfy a variety of particular properties required for a wide range of lubricant compositions such as lubricant oils for internal-combustion engines and drive systems- Thus, additives for lubricant oils must be used in order to improve characteristics essential for lubricant compositions. Lubricant oils having one or more of these characteristics suitable for use in such lubricant compositions have been studied.

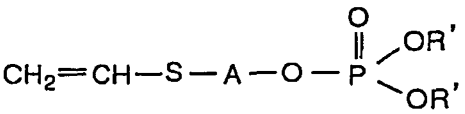
[0004] For example, Patent Document 1, as lubricant oil, discloses phosphorus- and sulfur-containing phosphate ester compounds represented by the general formula:



$$\mathrm{O{=}P(ORXR')(ORXR')(ORXR')}$$

wherein R represents a saturated aliphatic hydrocarbon group having 2 or 3 carbon atoms, each X independently represents oxygen or sulfur, and each R' represents an alkyl group having 1 to 18 carbon atoms. This document, however, does not disclose actual applications of this compound.

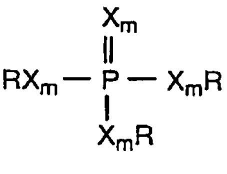
[0005] Patent Document 2 discloses a phosphoric ester derivative represented by the general formula:



$$\mathrm{CH_2{=}CH{-}S{-}A{-}O{-}P({=}O)(OR')(OR')}$$

wherein A represents an alkylene group having 2 to 6 carbon atoms, and each R' represents an alkyl group having 2 to 4 carbon atoms. This compound is copolymerized with an acrylic ester for an application as a flame proofing agent.

[0006] Patent Document 3 discloses an ester-based lubricant composition containing an aromatic amine and an organic thiophosphate or thiophosphite represented by the general formula:



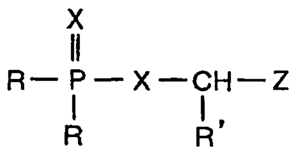
$$RX_m{-}P({=}X_m)(X_mR){-}X_mR$$

wherein X is O or S (at least one being S), m = 0 or 1 (at least three m's being 1), and each R represents an alkyl or aromatic group. This composition is used as antioxidant.

[0007] Patent Document 4 discloses a phosphorus- and sulfur-containing compound represented by the general formula:

Ya-S-Yb

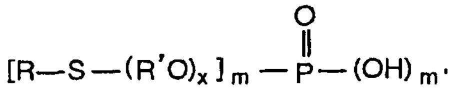
wherein Ya corresponds to:



$$R-\overset{\overset{X}{\|}}{\underset{\underset{R}{|}}{P}}-X-\underset{\underset{R'}{|}}{CH}-Z,$$

wherein Z represents a hydrocarbyl group, each R represents, for example, a hydrocarbyl or hydrocarbyloxy group, and R' represents a hydrogen atom or a divalent hydrocarbyl group; X represents sulfur or oxygen, and Yb represents, for example, a hydrocarbyl group. This compound is used as antioxidant and an anti-wear additive.

[0008] Patent Document 5 discloses an alkylthiophosphate ester represented by the general formula:



$$[R-S-(R'O)_x]_m-\overset{\overset{O}{\|}}{P}-(OH)_{m'}$$

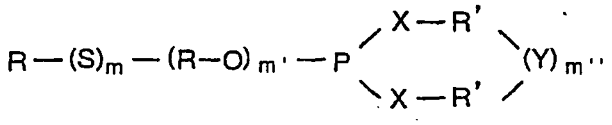
wherein R represents, for example, an alkyl or cycloalkyl group, R' represents an alkyl group, x represents 1 to 4, m represent 1 or 2, and m+m' = 3. This ester is used as a corrosion inhibitor for ferrous metals.

[0009] Patent Document 6 discloses an alkoxypolyethyleneoxy acid phosphite ester represented by the general formula:

$$RO\text{-}(CH_2CH_2O)_xP(R')\text{-}OH$$

wherein R represents an alkyl or alkenyl group, R' represents, for example, an alkoxy group, x represents 2 to 4. This ester is used as an additive that improves water permissible range of oil.

[0010] Patent Document 7 discloses a cyclic phosphate represented by the general formula:



wherein R represents, for example, an alkyl group, R' represents an alkylene group, X represents O, NH, or S, m represents 1 to 3, m' represents 1 to 12, and m" represents 0 or 1. This phosphate is used as an anti-wear additive, antioxidant, and friction modifier for lubricant compositions such as automotive transmission fluids.

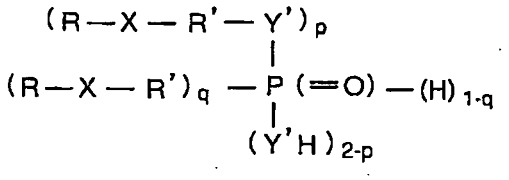
[0011] Patent Document 8 discloses a phosphorus and nitrogen containing derivative of a sulfur-containing compound prepared by reacting at least one sulfur composition with a di- or tri-hydrocarbyl phosphite and/or an amine compound. This derivative is an additive useful for fuel, lubricant, and functional fluid compositions.

[0012] Patent Documents 9 and 10 disclose a reaction product of (1) a β-hydroxythioether reactant, (2) dihydrocarbyl hydrogen phosphite, trihydrocarbyl phosphite, or a mixture thereof, and (3) a compound containing a specific nucleophilic group. These products are used as anti-wear agents and antioxidants.

[0013] Patent Document 11 discloses phosphorus- and sulfur-containing phosphite compounds represented by the general formula:

$$(R\text{-}X'\text{-}R'\text{-}Y')_m\text{-}P\text{-}(OH)_{3-m}$$

wherein X' represents S (sulfur), Y' represents S (sulfur) or O (oxygen), R represents an organic group having 6 to 20 carbon atoms, R' represents an organic group having 1 to 6 carbon atoms, and m represents an integer of 1 to 3; and the general formula:



$$\begin{array}{rcl} & (R-X-R'-Y')_p & \\ & | & \\ (R-X-R')_q & -P(=O) & -(H)_{1-q} \\ & | & \\ & (Y'H)_{2-p} & \end{array}$$

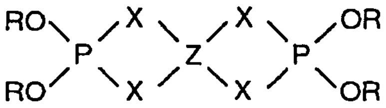
wherein X', Y', R, and R' are defined as above, p represents an integer of 0 to 2, and q represents an integer of 0 or 1, p and q being not 0 at the same time.

[0014] Patent Document 12 discloses a composition prepared by heating an imide dispersion containing boron and a phosphate and/or phosphite represented by the general formula:

$$A\text{-}(RO)\text{-}(R'O)\text{-}P\text{-}(O)_m$$

wherein A represents H or OH, m represents 0 or 1, A is OH when m is 0 or H or OH when m is 1, and R and R' each represent H or hydrocarbon containing at least one S or O atom.

[0015] Patent Document 13 discloses a phosphate compound represented by the general formula:



wherein R's each represent a hydrogen atom or a hydrocarbon group having 1 to 30 carbon atoms, X's each represent oxygen or sulfur, and Z represents a metal atom. This compound is used as an anti-wear additive with base value retention property.

[0016] Lubricant oils containing these conventional additives, however, do not exhibit satisfactory extreme-pressure properties, wear resistance, or friction characteristics under severe conditions of heavy load.

Patent Document 1: US Patent No. 2,750,342
Patent Document 2: US Patent No. 2,960,523
Patent Document 3: US Patent No. 3,446,738
Patent Document 4: US Patent No. 4,081,387
Patent Document 5: US Patent No. 4,511,480
Patent Document 6: US Patent No. 4,579,672
Patent Document 7: US Patent No. 4,776,969
Patent Document 8: WO88/03554
Patent Document 9: WO89/12666
Patent Document 10: JP-T-Hei3-500061
Patent Document 11: JP-A-Hei11-171892
Patent Document 12: US Patent No. 6,352,962
Patent Document 13: JP-A-2002-294271

Disclosure of Invention

Problems to be solved by the Invention

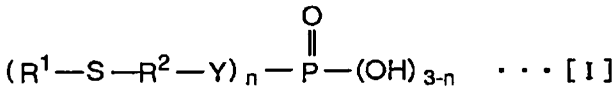
[0017] An object of the present invention that has been made under such circumstances is to provide a novel sulfur-containing organic phosphorus compound and an additive for lubricant oils containing the compound, and to provide a lubricant composition exhibiting excellent extreme-pressure properties, wear resistance, and friction characteristics under severe operation conditions of heavy load in internal-combustion engines and drive system machines.

Means for Solving the Problems

[0018] The inventors intensively studied to achieve the object described above; discovered that a specific phosphate ester derivative exhibited excellent thermal stability, oxidation stability, No_x resistance, and base value retention property and was useful as an extreme-pressure agent, an anti-wear agent, and a friction modifier; and completed the present invention.

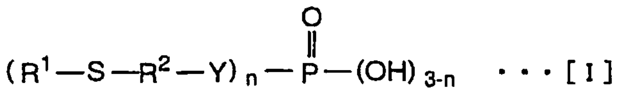
[0019] Accordingly, the present invention provides the following additives for lubricants and the like:

1. An additive for lubricants comprising a phosphate ester derivative (A) represented by the general formula [I]:



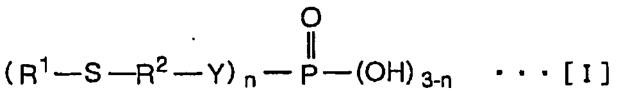
$$(R^1{-}S{-}R^2{-}Y)_n{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}(OH)_{3-n} \quad \cdots [I]$$

wherein Y represents sulfur (S) or oxygen (O); R^1 represents a monovalent organic group having 4 to 24 carbon atoms; R^2 represents a divalent organic group having 1 to 6 carbon atoms; and n represents an integer of 1 to 3.
2. An additive for lubricants comprising a reaction product of a zinc compound (B) with a phosphate ester derivative (A) represented by the general formula [I]:



$$(R^1{-}S{-}R^2{-}Y)_n{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}(OH)_{3-n} \quad \cdots [I]$$

wherein Y represents sulfur (S) or oxygen (O); R^1 represents a monovalent organic group having 4 to 24 carbon atoms; R^2 represents a divalent organic group having 1 to 6 carbon atoms; and n represents an integer of 1 to 3.
3. An additive for lubricants comprising a mixture of an organic zinc compound (C) and a phosphate ester derivative (A) represented by the general formula [I]:



$$(R^1{-}S{-}R^2{-}Y)_n{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}(OH)_{3-n} \quad \cdots [I]$$

wherein Y represents sulfur (S) or oxygen (O); R^1 represents a monovalent organic group having 4 to 24 carbon atoms; R^2 represents a divalent organic group having 1 to 6 carbon atoms; and n represents an integer of 1 to 3.
4. The additive for lubricants described in one of Aspects 1 to 3, wherein Y in the phosphate ester derivative represented by the general formula (I) is oxygen (O).
5. The additive for lubricants described in Aspect 2, wherein the zinc compound (B) is at least one compound selected from the group consisting of zinc metal, zinc oxide, organic zinc compounds, zinc salts of oxyacids, zinc halides, and zinc complexes.
6. The additive for lubricants described in Aspect 2, wherein the zinc compound (B) is at least one compound selected from the group consisting of zinc, zinc oxide, zinc hydroxide, zinc carbonate, dimethylzinc, diphenylzinc, and zinc complexes.
7. The additive for lubricants described in Aspect 3, wherein the organic zinc compound (C) is at least one compound selected from the group consisting of zinc alkylcarboxylates, zinc alkenylcarboxylates, zinc alkylphenylcarboxylates, and zinc alkenylphenylcarboxylates.
8. The additive for lubricants described in Aspect 3, wherein the organic zinc compound (C) is at least one compound selected from the group consisting of zinc oleate, zinc isostearate, zinc stearate, zinc alkylphenylcarboxylates, and zinc alkylsalicylates.
9. An additive composition for lubricants comprising the additive for lubricants described in any one of Aspects 1 to 8.
10. A lubricant composition comprising a lubricant base oil and the additive for lubricants described in any one of Aspects 1 to 8 in an amount of 0.001 to 0.5% by mass in terms of elemental phosphorus.
11. A lubricant composition for internal-combustion engines comprising a lubricant base oil and the additive for lubricants described in any one of Aspects 1 to 8 in an amount of 0.001 to 0.5% by mass in terms of elemental phosphorus.
12. A method of producing an additive for lubricants comprising reacting the phosphate ester derivative (A) with a zinc compound (B) described in Aspect 2 or 4.

Advantages of the Invention

[0020] The lubricant composition of the present invention exhibits superior base value retention in a No_x atmosphere, namely, superior long drain capability, as well as excellent wear resistance and high-temperature detergency.

[0021] Accordingly, the composition is effectively used as lubricant oils for internal-combustion engines with a high No_x gas concentration and a relatively high-temperature atmosphere, for example, crankcase oils of internal-combustion engines such as petrol engines, diesel engines, and gas engines using natural gas, liquid petroleum gas (LPG), cracked gas, and coal cracked gas. The lubricant composition of the present invention is applicable to lubricant oils, such as transmission oils, gear oils, bearing oils, shock absorber oils, and industrial lubricant oils, which require base value retention property, wear resistance, and high-temperature detergency.

Best Mode for Carrying out the Invention

[0022] A first aspect of the present invention is an additive for lubricants comprising a phosphate ester derivative (A) represented by the general formula [I] described above.

[0023] In the general formula [I], R^1 is preferably a hydrocarbon group having 4 to 24 carbon atoms and more preferably an alkyl group having 8 to 16 carbon atoms. If the number of the carbon atoms in R^1 is less than 4, the additive exhibits poor characteristics in solubility in oil, extreme pressure properties, wear resistance, friction property, and lubricity, and has strong corrosive action. Examples of R^1 include alkyl groups, such as a butyl group, a pentyl group, hexyl groups, heptyl groups, octyl groups, nonyl groups, decyl groups, undecyl groups, dodecyl groups, tridecyl groups, tetradecyl groups, pentadecyl groups, hexadecyl groups, heptadecyl groups, octadecyl groups, nonadecyl groups, and eicodecyl groups; cycloalkyl groups, such as a cyclohexyl group, methylcyclohexyl groups, ethylcyclohexyl groups, propylcycloalkyl groups, and dimethylcycloalkyl groups; aryl groups, such as a phenyl group, methylphenyl groups, ethylphenyl groups, propylphenyl groups, trimethylphenyl groups, butylphenyl groups, and naphthyl groups; arylalkyl groups, such as benzyl group, phenylethyl groups, methylbenzyl groups, phenylpropyl groups, and phenylbutyl groups.

[0024] In the general formula [I], R^2 is preferably a hydrocarbon group having 1 to 6 carbon atoms and more preferably an alkylene group having 1 to 4 carbon atoms. Examples of R^2 include divalent aliphatic groups, such as a methylene group, an ethylene group, a 1,2-propylene group, a 1,3-propylene group, butylene groups, pentylene groups, and hexylene groups; alicyclic groups having two bonding sites derived from alicyclic hydrocarbons, such as cyclohexane and methylcyclopentane; and phenylene groups.

[0025] Y represents sulfur (S) or oxygen (O), at least one S atom being contained in the general formula [I], and n represents an integer of 1 to 3, preferably 1 or 2, and more preferably 2.

[0026] Examples of the phosphate ester derivative represented by the general formula [I] includes tri(hexylthioethoxy) phosphate, tri(octylthioethoxy) phosphate, tri(dodecylthioethoxy) phosphate, tri(hexadecylthioethoxy) phosphate, di(hexylthioethoxy) phosphate, di(octylthioethoxy) phosphate, di(dodecylthioethoxy) phosphate, di(hexadecylthioethoxy) phosphate, mono(hexylthioethoxy) phosphate, mono(octylthioethoxy) phosphate, mono(dodecylthioethoxy) phosphate, and mono(hexadecylthioethoxy) phosphate.

[0027] Methods of producing the phosphate ester derivative represented by the general formula [I] are not particularly limited. For example, the phosphate ester derivative can be prepared by the reaction of hydrocarbylthioalkylalcohol represented by the general formula [II]:

$$R^1\text{-S-}R^2\text{-YH} \qquad [II]$$

wherein Y represents sulfur (S) or oxygen (O), and R^1 and R^2 are defined as above; or hydrocarbylthioalkoxide represented by the general formula [III]:

$$R^1\text{-X-}R^2\text{-YNa} \qquad [III]$$

wherein X, Y, R^1, and R^2 are defined as above; with phosphorus oxychloride ($POCl_3$) in the absence of catalyst or presence of a base.

[0028] The proportion of the hydrocarbylthioalkylalcohol or hydrocarbylthioalkoxide used in the reaction is generally 0.1 to 5.0 mol, preferably 1 to 3 mol, and more preferably 1.5 to 2.5 mol for 1 mol of phosphorus oxychloride.

[0029] The reaction temperature is selected within the range of generally -60°C to 100°C and preferably -30°C to 50°C. The reaction may be carried out in the absence of catalyst or presence of a base. Examples of the base include triethylamine and pyridine. For the reaction, a solvent such as xylene, toluene, tetrahydrofuran (THF), or diethyl ether may be used.

[0030] In another example of the methods, the ester can be prepared by the reaction of alkylthioalkylalcohol represented by the general formula [II]:

$$R^1\text{-S-}R^2\text{-YH} \qquad [II]$$

wherein Y represents sulfur (S) or oxygen (O), and R^1 and R^2 are defined as above, with diphosphorus pentoxide (P_2O_5).

[0031] The proportion of the alkylthioalkylalcohol used in the reaction is generally 1 to 12 mol, preferably 2 to 6 mol, and more preferably 3 to 4 mol for 1 mol of diphosphorus pentoxide.

[0032] The reaction temperature is selected within the range of generally 0°C to 140°C, preferably 30°C to 110°C, and more preferably 50°C to 90°C. For the reaction, a solvent such as xylene, toluene, THF, diethyl ether, or chloroform may be used.

[0033] A second aspect of the present invention is an additive for lubricants comprising a reaction product of the phosphate ester derivative (A) described above with a zinc compound (B).

[0034] The zinc compound (B) is preferably selected from zinc metal, zinc oxide, organic zinc compounds, zinc salts of oxyacids, zinc halides, and zinc complexes. Examples of the zinc compound include zinc, zinc oxide, zinc hydroxide, zinc carbonate, zinc dimethyl, zinc diphenyl, and zinc complexes.

[0035] The reaction of the phosphate ester derivative (A) with the zinc compound (B) can be carried out in the absence or presence of a catalyst. The proportion of the phosphate ester derivative used in the reaction is generally 0.1 to 5.0 mol, preferably 1 to 3 mol, and more preferably 1.5 to 2.5 mol for 1 mol of zinc compound.

[0036] The reaction temperature is selected within the range of generally room temperature to 200°C and preferably 40°C to 150°C. For the reaction, a solvent such as xylene, toluene, or hexane may be used.

[0037] A third aspect of the present invention is an additive for lubricants comprising a mixture of the phosphate ester derivative (A) described above and an organic zinc compound (C).

[0038] The organic zinc salt (C) is preferably selected from zinc alkylcarboxylates, zinc alkenylcarboxylates, zinc alkylphenylcarboxylates, and zinc alkenylphenylcarboxylates. Examples of the organic salt include zinc oleate, zinc isostearate, zinc stearate, zinc alkylphenylcarboxylates, and zinc alkylsalicylates.

[0039] As described above, the phosphate ester derivative (A) can be used alone as the additive for lubricants, and is preferably used in the form of a reaction product of the component (A) with the zinc compound (B) or a mixture of the component (A) and the organic zinc compound (C). These reaction product and mixture may be used alone or in combination of two or more different types.

[0040] The effective amount of these additives depends on applications. In general, these additives may be used in an amount of generally 0.001 to 1.0%, preferably 0.005 to 0.5% by mass, in terms of elemental phosphorus, of a base oil.

[0041] Examples of usable base oil include a variety of mineral oils and synthetic oils, which may be appropriately selected depending on applications. Examples of the mineral oils include paraffinic mineral oils, naphthenic mineral oils, and intermediate mineral oils, and more specifically include solvent-refined or hydro-refined light neutral oils, medium neutral oils, heavy neutral oils, and bright stocks.

[0042] Examples of synthetic oil include poly-α-olefins, α-olefin copolymers, polybutene, alkylbenzenes, polyol esters, dibasic acid esters, polyvalent alcohol esters, polyoxyalkylene glycols, polyoxyalkylene glycol esters, polyoxyalkylene glycol ethers, and cycloalkane compounds.

[0043] These base oils for lubricants may be used alone or in combination of two or more. Any combination of mineral oils and synthetic oils may also be available.

[0044] The additive composition for lubricants in accordance with the present invention may contain various components conventionally used in lubricant compositions, such as detergents and dispersants, antioxidants, rust inhibitors, antiforming agents, viscosity index improvers, pour-point depressants, demulsifying agents, other extreme-pressure agents, and anti-wear agents, within the scope of the object of the present invention.

EXAMPLES

[0045] The following examples illustrate the present invention, but do not serve to limit the scope of the invention in any way.

Example 1

[0046] Under a nitrogen stream, 13.2 g (0.55 mol) of sodium hydroxide and 100 mL of xylene were placed into a 500 mL flask, and 95.2 g (0.5 mol) of octylthioethanol in 100 mL xylene solution was added dropwise with stirring. The mixture was refluxed for five hours to promote the reaction.

[0047] Aside from this, 38.3 g (0.25 mol) of oxophosphorus chloride and 100 mL of THF were placed into an ice-cooled 1000 mL flask under a nitrogen stream, and the reaction mixture was added dropwise by spending two hours and was allowed to react for one hour at room temperature.

[0048] After 10 g (0.55 mol) of water was added dropwise to the resultant solution, the solution was stirred for one hour at room temperature and 100 mL of water was added followed by stirring for one hour at room temperature. The solution was allowed to stand and the organic layer was separated from the aqueous layer. Into the organic layer, 100 mL of water was added followed by stirring. This cycle was repeated twice. Xylene and THF were distilled out from the organic layer, and the unconverted octylthioethanol and octylthioethyl chloride byproduct were removed by vacuum distillation. The yield of the resultant octylthioethyl phosphate was 75 g.

Example 2

[0049] After 45 g of actylthioethyl phosphate prepared in Example 1, 50 mL of toluene, and 1 g of water were placed into a 300 mL flask, the mixture was heated to 70°C. Next, 4.1 g (0.05 mol) of zinc oxide was added to the flask, and the mixture was allowed to react at 70°C for three hours. Toluene and water were removed by vacuum distillation, and the residue was diluted with 15 g of mineral oil (150N equivalent), and the product was filtered. The yield of the reaction product was 60 g.

Example 3

[0050] The reaction was carried out as in Example 1 except that 123.3 g (0.5 mol) of dodecylthioethanol was used instead of octylthioethanol. The yield of the reaction product (dodecylthioethyl phosphate) was 92 g.

Example 4

[0051] The reaction was carried out as in Example 2 except that 55 g of dodecylthioethyl phosphate (the reaction product in Example 3) was used instead of the reaction product in Example 1. The yield of the reaction product was 70 g.

Example 5

[0052] The reaction was carried out as in Example 1 except that 81.1 g (0.5 mol) of hexylthioethanol was used instead of octylthioethanol. The yield of the reaction product (hexylthioethyl phosphate) was 61 g.

Example 6

[0053] The reaction was carried out as in Example 2 except that 33 g of hexylthioethyl phosphate (the reaction product in Example 5) was used instead of the reaction product in Example 1. The yield of the reaction product was 50 g.

Example 7

[0054] The reaction was carried out as in Example 1 except that 42.2 g (0.275 mol) of phosphorus oxychloride was used instead of 38.3 g (0.25 mol) of phosphorus oxychloride. The yield of the reaction product (octylthioethyl phosphate) was 62 g.

Example 8

[0055] The reaction was carried out as in Example 2 except that the reaction product in Example 7 was used instead of the reaction product in Example 1. The yield of the reaction product was 60 g.

Example 9

[0056] The reaction was carried out as in Example 1 except that 34.5 g (0.225 mol) of phosphorus oxychloride was used instead of 38.3 g (0.25 mol) of phosphorus oxychloride. The yield of the reaction product was 78 g.

Example 10

[0057] The reaction was carried out as in Example 2 except that the reaction product in Example 9 (octylthioethyl phosphate) was used instead of the reaction product in EXAMPLE 1. The yield of the reaction product was 61 g.

Example 11

[0058] 142.8 g (0.75 mol) of octylehioethanol and 500 mL of toluene were placed into a 1000 mL flask, and 35.0 g (0.25 mol) of diphosphorus pentoxide was added gradually. Then the system was stirred at 80°C for six hours, and toluene was removed by vacuum distillation. The yield of the reaction product was 178 g.

Example 12

[0059] After 112.8 g (0.4 mol) of oleic acid, 16.2 g (0.2 mol) of zinc oxide, 50 mL of toluene, and 2 g of water were placed into a 500 mL flask, and the mixture was allowed to react at 70°C for 3 hours. After toluene and water were removed by vacuum distillation, the residue was diluted with 30 g of mineral oil (150N equivalent) and the product was filtered. The yield of the reaction product was 145 g.

Example 13

[0060] The reaction was carried out as in Example 12 except that 113.6 g (0.4 mol) of stearic acid was used instead of oleic acid. The yield of the reaction product was 148 g.

Example 14

[0061] The reaction was carried out as in Example 12 except that 122.4 g (0.4 mol) of dodecylsalicylic acid was used instead of oleic acid. The yield of the reaction product was 156 g.

Examples 15 to 23 and Comparative Examples 1 and 2

[0062] According to the formulations shown in Table 1, the phosphate ester derivatives obtained in the above examples, a commercially available anti-wear agent or dibutyl phosphate, and various additives were added to 100N mineral base oil or 500N mineral base oil to prepare lubricant oil compositions of the present invention (Examples 15 to 23) and lubricant oil compositions for comparison (Comparative Examples 1 and 2).

Table 1

Composition of lubricant (parts by mass)	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20	Example 21	Example 22	Example 23	Comparative Example 1	Comparative Example 2
100N mineral Oil*1	62.70	62.60	62.70	62.70	62.70	62.07	62.10	61.52	62.07	63.30	62.72
500N mineral oil*2	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Compound of Example 1	-	-	-	-	-	1.20	1.20	1.20	-	-	-
Compound of Example 2	1.60	-	-	-	-	-	-	-	-	-	-
Compound of Example 4	-	1.70	-	-	-	-	-	-	-	-	-
Compound of Example 6	-	-	1.60	-	-	-	-	-	-	-	-
Compound of Example 8	-	-	-	1.60	-	-	-	-	-	-	-
Compound of Example 10	-	-	-	-	1.60	-	-	-	-	-	-
Compound of Example 11	-	-	-	-	-	-	-	-	1.20	-	-
Compound of Example 12	-	-	-	-	-	1.03	-	-	1.03	-	-
Compound of Example 13	-	-	-	-	-	-	1.00	-	-	-	1.00
Compound of Example 14	-	-	-	-	-	-	-	1.58	-	-	-
Anti-wear agent*3	-	-	-	-	-	-	-	-	-	1.00	-

(continued)

Table 1

Composition of lubricant (parts by mass)	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20	Example 21	Example 22	Example 23	Comparative Example 1	Comparative Example 2
Dibutyl phosphate ester	-	-	-	-	-	-	-	-	-	-	0.58
Viscosity index improver	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Pour point depressant	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Metal-based detergen*4	3.20	3.20	3.20	3.20	3.20	3.20	3.20	3.20	3.20	3.20	3.20
Ashless dispersant A*5	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50
Ashless dispersant B*6	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Antioxidant*7	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Other additives*8	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50

(continued)

Table 1

Composition of lubricant (parts by mass)	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20	Example 21	Example 22	Example 23	Comparative Example 1	Comparative Example 2
Phosphorus content in composition (mass %)	0.084	0.082	0.082	0.084	0.084	0.082	0.082	0.082	0.082	0.082	0.085

(Note)
*1: Refined hydrotreated mineral oil. Kinematic viscosity at 100°C: 4.5 mm^2/s. Sulfur content; less than 0.0% by mass.
*2: Refined hydrotreated mineral oil. Kinematic viscosity at 100°C: 10.9 mm^2/s. Sulfur content; less than 0.01 mass%.
*3: Zinc secondary-dialkyldithiophosphate. Phosphorus content: 8.2% by mass. Zinc content: 9.0% by mass. Sulfur content: 17.1% by mass.
*4: Calcium salicylate. Ca content: 7.94% by mass.
*5: Polybutenyl succinic imide. Nitrogen content: 1.56% by mass.
*6: Polybutenyl succinic imide,borate. Nitrogen content: 1.76% by mass. Boron content: 2.0% by mass.
*7: Mixture of dialkyldiphenylamine and hindered phenol antioxidant.
*8: Metal deactivator, antiforming agent, demulsifying agent etc.

[0063] The prepared compositions were each subjected to No_x resistance test, cam lifter wear test, and Falex test.

(1) No_x resistance test
Nitrogen monoxide (NO) gas (concentration: 8000 ppm) at 6 L/hr and air at 6 L/hr were injected into 250 mL of sample oil in the presence of iron-copper catalyst (test piece for oxidation test JIS K-2514). The sample was maintained at a temperature of 140°C and the base value (hydrochloric acid method) after accelerated deterioration was measured. A smaller reduction in the base value refers to higher base value retention in a nitrogen oxide gas atmosphere, which is used in internal-combustion engines. Lubricant oils with higher base value retention can be used for longer time periods.
(2) Cam lifter wear test
A JASO M328-95 cam lifter wear test was carried out to measure rocker arm pad scuffing area, rocker arm wear, and cum wear after 100 hour testing. For each testing, a lubricant composition having a value of 10 or less exhibits superior wear resistance.
(3) Falex test

[0064] After running-in for 5 minutes under the conditions of pin material: AISI-3153, block material: AISI-1137, oil volume: 300 mL, number of rotations: 290 rpm, oil temperature: 100°C, and load: 1112 N, the load was continuously increased at a oil temperature of 100°C to measure seizure load according to ASTM D3233. Lubricant oil having higher seizure load exhibits superior load-carrying capacity.

Table 2-1

Nox resistance test		Example 15	Example 16	Example 17	Example 18	Example 19
Base value after Nox resistance test	After 96 hours	2.12	2.05	2.15	2.15	2.02
(Hydrochloric acid method) mgKOH/g	After 144 hours	1.1	0.85	1.15	1.12	0.93

Table 2-2

Nox resistance test		Example 20	Example 21	Example 22	Example 23	Comparative Example 1	Comparative Example 2
Base value after Nox resistance test	After 96 hours	2.05	1.98	2.21	2.02	1.21	2.05
(Hydrochloric acid method) mgKOH/g	After 144 hours	0.82	0.85	0.95	0.91	0.25	0.91

Table 3

JASO M 328-95 cam lifter wear test	Example 15	Example 20	Comparative Example 1	Comparative Example 2
Scuffing area of rocker arm pad (%)	8.5	5.4	9.3	10
Cum nose wear (μm)	6.7	6.9	26.8	6.7

Table 4

Falex test	Example 15	Example 20	Comparative Example 1	Comparative Example 2
Seizure load N	3620	3800	3900	2400

[0065] The results of the Nox resistance test shown in Table 2 show that the lubricant compositions (Examples 15 to 23) of the present invention exhibit superior base value retention under the nitrogen oxide gas atmosphere. In contrast, Comparative Example 1 containing zinc dithiophosphate instead of the anti-wear agent of the present invention exhibits significantly poor base value retention.

[0066] The results of the cam lifter wear test shown in Table 3 show that the lubricant compositions (Examples 15 and 20) of the present invention exhibit superior wear resistance whereas Comparative Example 1 exhibits significantly poor wear resistance.

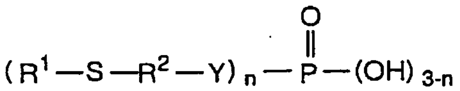
[0067] Comparative Example 2 exhibits satisfactory base value retention under the nitrogen atmosphere (Table 2) and satisfactory wear resistance (Table 3), but the load-carrying capacity is significantly inferior to that of the lubricant oil compositions (Examples 15 and 20) of the present invention(Table 4).

Industrial Applicability

[0068] The lubricant oil composition of the present invention can be used as, for example, lubricant oils for internal-combustion engines, transmission lubricant oils, gear oils, bearing oils, shock absorber oils, and industrial lubricant oils.

Claims

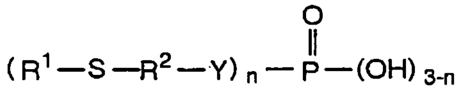
1. An additive for lubricants comprising a phosphate ester derivative (A) represented by the general formula [I]:



$$(R^1-S-R^2-Y)_n-\overset{\displaystyle O}{\overset{\|}{P}}-(OH)_{3-n} \quad \cdots [I]$$

wherein Y represents sulfur (S) or oxygen (O); R^1 represents a monovalent organic group having 4 to 24 carbon atoms; R^2 represents a divalent organic group having 1 to 6 carbon atoms; and n represents an integer of 1 to 3.

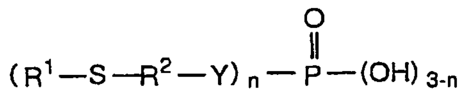
2. An additive for lubricants comprising a reaction product of a zinc compound (B) with a phosphate ester derivative (A) represented by the general formula [I]:



$$(R^1-S-R^2-Y)_n-\overset{\displaystyle O}{\overset{\|}{P}}-(OH)_{3-n} \quad \cdots [I]$$

wherein Y represents sulfur (S) or oxygen (O); R^1 represents a monovalent organic group having 4 to 24 carbon atoms; R^2 represents a divalent organic group having 1 to 6 carbon atoms; and n represents an integer of 1 to 3.

3. An additive for lubricants comprising a mixture of an organic zinc compound (C) and a phosphate ester derivative (A) represented by the general formula [I]:



$$(R^1-S-R^2-Y)_n-\overset{\displaystyle O}{\overset{\|}{P}}-(OH)_{3-n} \quad \cdots [I]$$

wherein Y represents sulfur (S) or oxygen (O); R^1 represents a monovalent organic group having 4 to 24 carbon atoms; R^2 represents a divalent organic group having 1 to 6 carbon atoms; and n represents an integer of 1 to 3.

4. The additive for lubricants in accordance with any one of Claims 1 to 3, wherein Y in the general formula (I) is oxygen (O).

5. The additive for lubricants in accordance with Claim 2, wherein the zinc compound (B) is at least one compound selected from the group consisting of zinc metal, zinc oxide, organic zinc compounds, zinc salts of oxyacids, zinc halides, and zinc complexes.

6. The additive for lubricants in accordance with Claim 5, wherein the zinc compound (B) is at least one compound selected from the group consisting of zinc, zinc oxide, zinc hydroxide, zinc carbonate, dimethylzinc, diphenylzinc, and zinc complexes.

7. The additive for lubricants in accordance with Claim 3, wherein the organic zinc compound (C) is at least one compound selected from the group consisting of zinc alkylcarboxylates, zinc alkenylcarboxylates, zinc alkylphenylcarboxylates, and zinc alkenylphenylcarboxylates.

8. The additive for lubricants in accordance with Claim 7, wherein the organic zinc compound (C) is at least one compound selected from the group consisting of zinc oleate, zinc isostearate, zinc stearate, zinc alkylphenylcarboxylates, and zinc alkylsalicylates.

9. An additive composition for lubricants comprising the additive for lubricants in accordance with any one of Claims 1 to 8.

10. A lubricant composition comprising a lubricant base oil and the additive for lubricants in accordance with any one of Claims 1 to 8 in an amount of 0.001 to 0.5% by mass in terms of elemental phosphorus.

11. A lubricant composition for internal-combustion engines comprising a lubricant base oil and the additive for lubricants in accordance with any one of Claims 1 to 8 in an amount of 0.001 to 0.5 % by mass in terms of elemental phosphorus.

12. A method of producing an additive for lubricants, comprising reacting the phosphate ester derivative (A) with the zinc compound (B) in accordance with Claim 2 or 4.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/015400

A. CLASSIFICATION OF SUBJECT MATTER

C10M137/10 (2006.01), ***C10M141/10*** (2006.01), ***C10M159/12*** (2006.01), ***C10M177/00*** (2006.01), *C10M125/04* (2006.01), *C10M125/10* (2006.01), *C10M125/18* (2006.01), *C10M129/28* (2006.01), *C10M129/48* (2006.01), *C10M129/54*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10M137/10 (2006.01), ***C10M141/10*** (2006.01), ***C10M159/12*** (2006.01), ***C10M177/00*** (2006.01), *C10M125/00* (2006.01)-*C10M125/30* (2006.01), *C10M129/26* (2006.01) -*C10M129/64* (2006.01), *C10M139/06* (2006.01), *C10M159/18* (2006.01),

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	1996-2005
Kokai Jitsuyo Shinan Koho	1971-2005	Toroku Jitsuyo Shinan Koho	1994-2005

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2750342 A (ESSO RESEARCH AND ENGINEERING CO.), 12 June, 1956 (12.06.56), (Family: none)	1,4,9-10 2-12
X Y	JP 4-230691 A (Institut Francais du Petrole), 19 August, 1992 (19.08.92), & CA 2049744 A1 & CN 1063493 A & DE 69120752 T2 & EP 477048 A1 & ES 2091891 T3 & FR 2666090 A1 & FR 2671084 A1 & US 5306436 A & US 5463132 A	1,4,9-10 2-12
Y	JP 2001-354987 A (Asahi Denka Kogyo Kabushiki Kaisha), 25 December, 2001 (25.12.01), (Family: none)	2-12

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

* Special categories of cited documents:
"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 filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" 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
"X" 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
"Y" 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 being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 08 November, 2005 (08.11.05)	Date of mailing of the international search report 22 November, 2005 (22.11.05)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/015400

Continuation of A. CLASSIFICATION OF SUBJECT MATTER
(International Patent Classification (IPC))

C10M139/06 (2006.01), *C10M159/18* (2006.01), *C10N10/04* (2006.01), *C10N30/06* (2006.01), *C10N30/08* (2006.01), *C10N30/10* (2006.01), *C10N40/25* (2006.01), *C10N70/00* (2006.01)

(According to International Patent Classification (IPC) or to both national classification and IPC)

Continuation of B. FIELDS SEARCHED
Minimum documentation searched (International Patent Classification (IPC))

C10N10/04 (2006.01), *C10N30/06* (2006.01)-*C10N30/10* (2006.01), *C10N40/25* (2006.01)-*C10N40/28* (2006.01), *C10N70/00* (2006.01)

Minimum documentation searched (classification system followed by classification symbols)

Form PCT/ISA/210 (extra sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 2750342 A **[0016]**
- US 2960523 A **[0016]**
- US 3446738 A **[0016]**
- US 4081387 A **[0016]**
- US 4511480 A **[0016]**
- US 4579672 A **[0016]**
- US 4776969 A **[0016]**
- WO 8803554 A **[0016]**
- WO 8912666 A **[0016]**
- JP 3500061 T **[0016]**
- JP 11171892 A **[0016]**
- US 6352962 B **[0016]**
- JP 2002294271 A **[0016]**