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(54) **Lubricating oil composition**

(57) Disclosed herein is a lubricating oil composition containing a major portion of a lubricating base oil and a minor portion of additives comprising a zinc di (primary alkyl) dithiophosphate and a zinc di (secondary alkyl) dithiophosphate in proportions to give a weight ratio in phosphorus content of from 20:80 to 80:20, a sulfur compound in a proportion to give a sulfur content of from 300 to 1,200 ppm (weight basis), and an oxymolybdenum sulfide dithiocarbamate or an oxymolybdenum sulfide dithiophosphate in a proportion to give a molybdenum content of from 200 to 2,000 ppm (weight basis).

The lubricating oil composition according to the present invention has excellent antiwear properties and even at elevated temperatures and in the presence of nitrogen oxides, exhibits high oxidation resistance and retains good friction-reducing properties, so that it can be suitably used as a lubricating oil for internal combustion engines.

EP 0 768 366 A1

Description

Field of the Invention

The present invention relates to a novel lubricating oil composition. More specifically, the present invention is concerned with a lubricating oil composition, which has excellent friction-reducing properties and high antiwear properties, is free from deterioration even in an air atmosphere containing NOx gas, retains friction-reducing properties over an extended period of time and accordingly, which is usable as a lubricating oil for internal combustion engines, automatic transmissions, dampers or power steering systems and makes it possible to achieve high gas mileage especially as a lubricating oil for internal combustion engines.

Lubricating oils are used in internal combustion engines and in driving units and gears such as automatic transmissions, dampers and power steering systems to ensure smooth operation thereof. In particular, a lubricating oil for an internal combustion engine serves to cool the inside of the engine, to clean and disperse combustion products and to protect the engine from rusting and corrosion in addition to lubrication of various sliding portions such as piston rings and their associated cylinder liner, bearings for a crankshaft and a connecting rod, and a valve-operating mechanism including cams and valve lifters.

As can be appreciated from the foregoing, a lubricating oil for internal combustion engines is required to meet diverse property requirements. Moreover, keeping step with the trend toward internal combustion engines of higher performance such as those achieving higher gas mileage and higher power output and permitting more severe operating conditions in recent years, there is an increasing demand for lubricating oils of still higher performance. As a basic function of a lubricating oil for internal combustion engines, it is especially important to assure smooth operation of the engines while protecting them from wearing and seizure under all condition. Lubricated portions of an engine mostly remain under fluid lubrication conditions but around the top and bottom dead centers of its valve-operating system or a piston, they tend to come under boundary lubrication conditions.

In an internal combustion engine, combustion gas partly leaks between a cylinder and its piston and penetrates as blowby gas into a crank case. NOx gas is contained at a considerably high level in combustion gas. In addition to oxygen contained in the blowby gas, this NOx gas also deteriorates the lubricating oil for the internal combustion engine. Due to the move toward internal combustion engines of higher performance in recent years, the concentration of NOx gas in a crank case tends to increase. To meet the above-described property or performance requirements and also to remain free from deterioration even in an NOx-containing air atmosphere, a variety of additives are incorporated in a lubricating oil for internal combustion engines, including, for example, an antiwear agent, a metallic detergent, a friction modifier, a nonash dispersant and an antioxidant.

In an internal combustion engine, a great deal of energy is lost at frictional parts to which a lubricating oil is applied. A friction modifier is therefore added to a lubricating oil as a measure for reducing the friction loss and increasing the gas mileage. Usable examples of the friction modifier generally include organic molybdenum compounds, fatty esters and alkylamines. These friction modifiers show their effects in an early stage after the initiation of their use but when subjected to oxidative deterioration by oxygen in the air, their effects are lost. A marked reduction in their effects is observed especially in the presence of NOx gas.

As a measure for making an improvement in the gas mileage of internal combustion engines, it is practiced, besides the addition of a friction modifier, to reduce the viscosity of a lubricating oil or to add a zinc dialkyl dithiophosphate containing primary alkyl groups as its alkyl groups. However, a reduction in the viscosity of a lubricating oil or the addition of a zinc dialkyl dithiophosphate containing primary alkyl groups as its alkyl groups develops a new problem, that is, a reduction in antiwear properties.

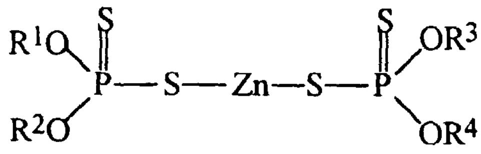
An object of the present invention is therefore to provide a lubricating oil composition which can retain friction-reducing effects for engines over an extended period of time without being adversely affected by NOx gas and possesses and exhibits both excellent friction-reducing properties and high antiwear properties.

The present inventors have discovered a lubricating oil composition with a zinc di (primary alkyl) dithiophosphate and a zinc di (secondary alkyl) dithiophosphate, a specific sulfur compound, and an oxymolybdenum sulfide dithiocarbamate or an oxymolybdenum sulfide dithiophosphate added in specific proportions to a lubricating base oil which has been found to attain the above object, leading to the completion of the present invention.

The Present Invention

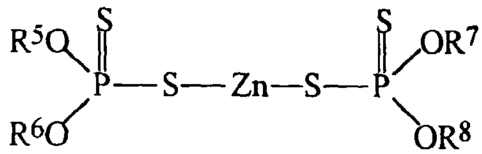
The present invention therefore provides a lubricating oil composition comprising a major portion of lubricating base oil and a minor portion of the following components:

(A) a zinc di (primary alkyl) dithiophosphate represented by the following formula [1]:



[1]

wherein R^1, R^2, R^3 and R^4 individually represent primary alkyl groups having 1 to 20 carbon atoms, and a zinc di (secondary alkyl) dithiophosphate represented by the following formula [2]:

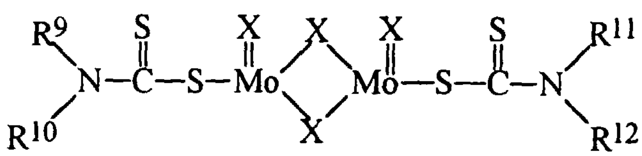


[2]

wherein R^5, R^6, R^7 and R^8 individually represent secondary alkyl groups having 3 to 7 carbon atoms,

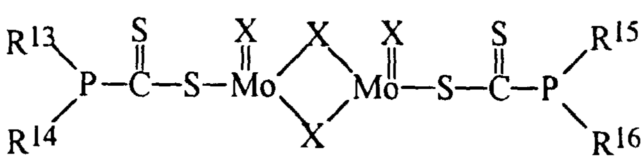
(B) one or more sulfur compounds selected from the group consisting of zinc dialkyl dithiocarbamates, copper dialkyl dithiocarbamates or nickel dialkyl dithiocarbamates in which each alkyl group has 2 to 18 carbon atoms, tetraalkylthiuram disulfides in which each alkyl group has 2 to 18 carbon atoms, disulfides containing one or more alkyl groups having 2 to 18 carbon atoms, disulfides containing one or more aryl groups having 6 to 18 carbon atoms or one or more alkylaryl or arylalkyl groups having 7 to 18 carbon atoms, thiadiazole compounds having one or more sulfur-containing substituent groups and 3 to 24 carbon atoms, olefin sulfides, sulfurized fish oil and sulfurized whale oil, and

(C) an oxymolybdenum sulfide dithiocarbamate represented by the following formula [3]:



[3]

wherein R^9, R^{10}, R^{11} and R^{12} individually represent alkyl groups having 1 to 30 carbon atoms, cycloalkyl groups having 5 to 30 carbon atoms, aryl groups having 6 to 30 carbon atoms, or alkylaryl or arylalkyl groups having 7 to 30 carbon atoms, and Xs represent oxygen or sulfur atoms, or an oxymolybdenum sulfide dithiophosphate represented by the following formula [4]:



[4]

wherein R^{13}, R^{14}, R^{15} and R^{16} individually represent alkyl groups having 1 to 30 carbon atoms, cycloalkyl groups having 5 to 30 carbon atoms, aryl groups having 6 to 30 carbon atoms, or alkylaryl or arylalkyl groups having 7 to 30 carbon atoms, and Xs represent oxygen or sulfur atoms; wherein

(A) the weight ratio of the phosphorus content of said zinc di (primary alkyl) dithiophosphate to that of said zinc di (secondary alkyl) dithiophosphate ranges from 20:80 to 80:20, and the amount of phosphorus derived from said zinc di (primary alkyl) dithiophosphate and zinc di (secondary alkyl) dithiophosphate ranges from 0.07 to 0.15 wt% based on the total weight of said lubricating oil composition;

(B) the amount of sulfur derived from said sulfur compounds other than said zinc di (primary alkyl) dithiophosphate, zinc di (secondary alkyl) dithiophosphate and oxymolybdenum sulfide dithiophosphate ranges from 300 to 1,200 ppm (weight basis) based on the total weight of said lubricating oil composition; and

(C) the amount of molybdenum derived from said oxymolybdenum sulfide dithiocarbamate or oxymolybdenum sulfide dithiophosphate ranges from 200 to 2,000 ppm (weight basis) based on the total weight of said lubricating oil composition.

In a preferred embodiment of the present invention, the weight ratio of the phosphorus content of said zinc di (primary alkyl) dithiophosphate to that of said zinc di (secondary alkyl) dithiophosphate in the above-described lubricating oil composition can range from 25:75 to 80:20.

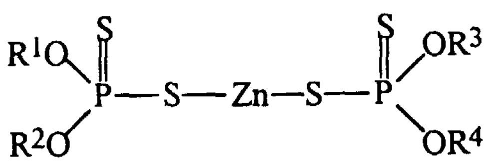
In each of the above-described lubricating oil compositions according to the present invention, R^1, R^2, R^3 and R^4 in the formula [1] can individually represent primary alkyl groups having 8 to 13 carbon atoms and R^5, R^6, R^7 and R^8 in the formula [2] can individually represent secondary alkyl groups having 4 to 6 carbon atoms, as another preferred embodiment of the present invention.

No particular limitation is imposed on the lubricating base oil employed in the lubricating oil composition according to the present invention. Those commonly employed as base oils in conventional lubricating oils, for example, mineral oils and synthetic oils, can be used. Examples of the mineral oils include raffinates obtained by solvent-refining of raw materials for lubricating oils by using an aromatic extraction solvent such as phenol or furfural; hydrogenated oils obtained by hydrogenation of raw materials for lubricating oils by using a hydrogenation catalyst such as cobalt, molybdenum or the like supported on silica-alumina as a carrier; mineral oils such as lubricating oil fractions obtained by isomerization of wax, for example, 60 neutral oil, 100 neutral oil, 150 neutral oil, 300 neutral oil, 500 neutral oil, and bright stocks.

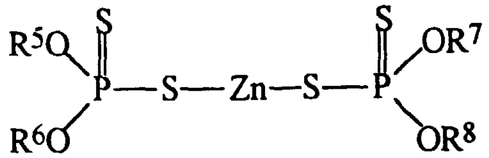
On the other hand, examples of the synthetic oils include poly-α-olefin oligomers, polybutene, alkylbenzene, polyol esters, polyglycol esters, dibasic acid esters, phosphate esters and silicone oils. These base oils can be used either singly or in combination. It is also possible to use one or more mineral oils in combination with one or more synthetic oils.

Preferred as base oils for use in the lubricating oil composition according to the present invention are those having viscosities at 100°C in a range of from 3 to 20 mm^2/s. Of these, particularly preferred are hydrogenated oil and isomerized wax oils, which contain 3 wt% or less of aromatic components, 50 ppm or less (weight basis) of sulfur and 50 ppm or less (weight basis) of nitrogen.

The lubricating oil composition according to the present invention contains the zinc di (primary alkyl) dithiophosphate represented by the formula [1] and the zinc di (secondary alkyl) dithiophosphate represented by the formula [2].



[1]



[2]

In the formula [1], R^1, R^2, R^3 and R^4 individually represent primary alkyl groups having 1 to 20 carbon atoms, which may be the same or different. Referring to the formula [1], a primary alkyl group means an alkyl group in which two hydrogen atoms and one carbon atom are bonded to the carbon atom directly bonded to an oxygen atom or an alkyl group in which three hydrogen atoms are bonded to the carbon atom directly bonded to an oxygen atom. Each primary alkyl group in the formula [1] can be either linear or branched. Illustrative of such primary alkyl groups are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, and 2-ethyl hexyl. In the lubricating oil composition according to the present invention, a zinc di (primary alkyl) dithiophosphate with primary alkyl groups having 3-12 carbon atoms as its primary alkyl groups can be used particularly preferably.

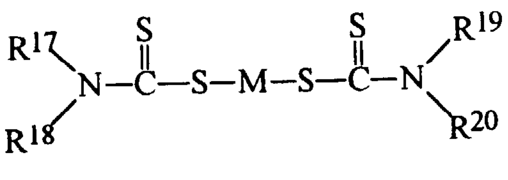
In the formula [2], R^5, R^6, R^7 and R^8 individually represent secondary alkyl group having 3 to 7 carbon atoms, which may be the same or different. Referring to the formula [2], a secondary alkyl group means an alkyl group in which one hydrogen atom and two carbon atoms are bonded to the carbon atom directly bonded to an oxygen atom. Illustrative of such secondary alkyl groups are isopropyl, secondary butyl, 1-methylbutyl, 1-methylpentyl, 1-methylhexyl, 1-ethylpropyl, 1-ethylbutyl, 1-ethylpentyl, 1-n-propylbutyl, 1,2-dimethylpropyl, 1,3-dimethylbutyl, 1,3-dimethylbutyl, 1,2-dimethylpentyl, 1,3-dimethylbutyl, 1,3-dimethylbutyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1-ethyl-2-methylpropyl, 1-ethyl-2-methylbutyl, 1-ethyl-3-methylbutyl, 1-isopropylbutyl, and 1-isopropyl-2-methylpropyl.

In the lubricating oil composition according to the present invention, the zinc di (primary alkyl) dithiophosphate represented by the formula [1] and the zinc di (secondary alkyl) dithiophosphate represented by the formula [2] are added to the lubricating base oil in such amounts that the weight ratio of the phosphorus content of the former dithiophosphate to that of the latter dithiophosphate ranges from 20:80 to 80:20, preferably from 25:75 to 80:20, more preferably from 30:70 to 70:30. The addition of the zinc di (primary alkyl) dithiophosphate and the zinc di (secondary alkyl) dithiophosphate at a weight ratio in phosphorous content of from 20:80 to 80:20 makes it possible to improve the friction-reducing properties without reducing the antiwear properties. If the weight ratio of the phosphorus content of the zinc di (primary alkyl) dithiophosphate to that of the zinc di (secondary alkyl) dithiophosphate is smaller than 20: 80, that is, the proportion of the zinc di (primary alkyl) dithiophosphate is unduly small relative to that of the zinc di (secondary alkyl) dithiophosphate, there is the potential problem that the resulting lubricating oil composition may not be provided with sufficient friction-reducing properties. If the weight ratio of the phosphorus content of the zinc di (primary alkyl) dithiophosphate to that of the zinc di (secondary alkyl) dithiophosphate exceeds 80:20, that is, the proportion of the zinc di (secondary alkyl) dithiophosphate is unduly small relative to that of the zinc di (primary alkyl) dithiophosphate, there is the potential problem that the resulting lubricating oil composition may be provided with lowered antiwear properties.

In the lubricating oil composition according to the present invention, the zinc di (primary alkyl) dithiophosphate and the zinc di (secondary alkyl) dithiophosphate are incorporated in amounts so that the amount of phosphorus derived therefrom is in the range 0.07 to 0.15 wt%, preferably 0.08 to 0.10 wt% based on the total weight of the lubricating oil composition. An amount of phosphorus derived from the zinc di (primary alkyl) dithiophosphate and the zinc di (secondary alkyl) dithiophosphate smaller than 0.07 wt% of the total weight of the lubricating oil composition may disadvantageously lead to insufficient antiwear properties. On the other hand, an amount of phosphorus derived from the zinc di (primary alkyl) dithiophosphate and the zinc di(secondary alkyl) dithiophosphate greater than 0.15 wt% of the total weight of the lubricating oil composition is not expected to bring about an additional improvement in effects in proportion to the increase in the amount of phosphorus.

The lubricating oil composition according to the present invention further contains one or more sulfur compounds selected from the group consisting of zinc dialkyl dithiocarbamates, copper dialkyl dithiocarbamates or nickel dialkyl dithiocarbamates in which each alkyl group has 2 to 18 carbon atoms, tetraalkylthiuram disulfides in which each alkyl group has 2 to 18 carbon atoms, disulfides containing one or more alkyl groups having 2 to 18 carbon atoms, disulfides containing one or more aryl groups having 6 to 18 carbon atoms or one or more alkylaryl or arylalkyl groups having 7 to 18 carbon atoms, thiadiazole compounds having one or more sulfur-containing substituent groups and 3 to 24 carbon atoms, olefin sulfides, sulfurized fish oil and sulfurized whale oil.

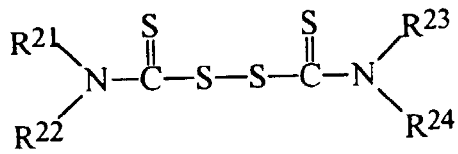
Illustrative examples of dialkyl dithiocarbamates usable for addition to the lubricating oil composition according to the present invention include compounds represented by the following formula [5]:



[5]

In the formula [5], M represents a zinc atom, a copper atom or a nickel atom, R^{17}, R^{18}, R^{19} and R^{20} individually represent alkyl groups having 2 to 18 carbon atoms, which may be the same or different. In the formula [5], the alkyl groups which are represented by R^{17}, R^{18}, R^{19} and R^{20} and have 2 to 18 carbon atoms can either be linear or branched. Their examples include ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl.

Illustrative examples of tetraalkylthiuram disulfides usable for addition to the lubricating oil composition according to the present invention include compounds represented by the following formula [6]:



[6]

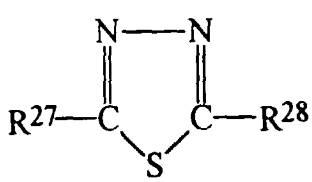
In the formula [6], R^{21}, R^{22}, R^{23} and R^{24} individually represent alkyl groups having 2 to 18 carbon atoms, which may be the same or different. In the formula [6], the alkyl groups which are represented by R^{21}, R^{22}, R^{23} and R^{24} and have 2 to 18 carbon atoms can be either linear or branched. Their examples include ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl.

Illustrative examples of disulfides usable for addition to the lubricating oil composition according to the present invention include compounds represented by the following formula [7]:

$$R^{25}\text{-S-S-}R^{26} \qquad [7]$$

In the formula [7], R^{25} and R^{26} individually represent alkyl groups having 2 to 18 carbon atoms, aryl groups having 6 to 18 carbon atoms, or alkylaryl or arylalkyl groups having 7 to 18 carbon atoms, preferably alkyl groups having 6 to 12 carbon atoms, aryl groups having 6 to 12 carbon atoms, or alkylaryl or arylalkyl groups having 7 to 12 carbon atoms, which may be either the same or different. In the formula [7], the alkyl groups which are represented by R^{25} and R^{26} and have 2 to 18 carbon atoms can be either linear or branched. Their examples include ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl. Further, examples of the aryl groups having 6 to 18 carbon atoms and the alkylaryl and arylalkyl groups having 7 to 18 carbon atoms, which are represented by R^{25} and R^{26}, include phenyl, naphthyl, benzyl, phenethyl, methylbenzyl, and diphenylmethyl. In the lubricating oil composition according to the present invention, dibenzyl disulfide can be used as a particularly preferred disulfide.

Illustrative examples of thiadiazole compounds which contain one or more sulfur-containing substituent groups and are usable for addition to the lubricating oil composition according to the present invention include compounds represented by the following formula [8]:



[8]

wherein R^{27} and R^{28} individually represent monovalent groups having 3 to 24 carbon atoms and containing one or more sulfur atoms, which may be the same or different.

Illustrative examples of the monovalent groups which are represented by R^{27} and R^{28} in the formula [8] and contain one or more sulfur atoms, include 5-thianonyl, 2,5-dithiahexyl, 3,4-dithiahexyl, 4,5-dithiahexyl, 3,4,5-trithiaheptyl, 3,4,5,6-tetrathiaoctyl, 5-thia-2-heptenyl, 4-thiacyclohexyl, 1,4-dithianaphthyl, 5-(methylthio) octyl, 4-(ethylthio)-2-pentenyl, 4-(methylthio) cyclohexyl, 4-mercaptophenyl, 4-(methylthio) phenyl, and 4-(hexylthio) benzyl. Of these, particularly preferred are groups containing 2 to 4 sulfur atoms successively bonded together in their chains, such as a 3,4-dithiahexyl group represented by the following formula [9], a 4,5-dithiahexyl group represented by the following formula [10], a 3,4,5-trithiaheptyl group represented by the following formula [11] and a 3,4,5,6-tetrathiaoctyl group represented by the following formula [12]:

$$CH_3CH_2\text{-S-S-}CH_2CH_2\text{-} \qquad [9]$$

CH_3-S-S-$CH_2CH_2CH_2$- [10]

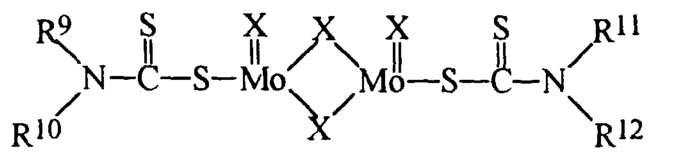
CH_3CH_2-S-S-S-CH_2CH_2- [11]

CH_3CH_2-S-S-S-S-CH_2CH_2- [12]

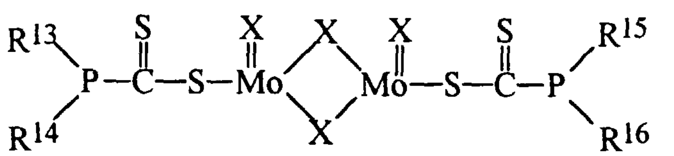
Illustrative examples of olefin sulfides which can be added to the lubricating oil composition according to the present invention include olefin sulfides (polysulfides) obtained by subjecting polymers of isobutylene and the like to sulfurization treatment and having sulfur contents of from 25 to 40 wt%. As the sulfurized fish oil and sulfurized whale oil, those obtained by similarly subjecting fish oil and whale oil to sulfurization treatment can be exemplified.

In the lubricating oil composition according to the present invention, the dialkyl dithiocarbamates represented by the formula [5], the tetraalkylthiuram disulfides represented by the formula [6], the disulfides represented by the formula [7], the thiadiazole compounds represented by the formula [8] and the olefin sulfides, the sulfurized fish oil and the sulfurized whale oil can be used either singly or in combination. One or more of these sulfur compounds are added in such amount(s) that the amount of sulfur derived from the sulfur compound(s) ranges from 300 to 1,200 ppm (weight basis) of the total weight of the lubricating oil composition. If the sulfur compound(s) are added in such an amount that the amount of sulfur derived from the sulfur compound(s) is smaller than 300 ppm (weight basis) or greater than 1,200 ppm (weight basis), there is the potential problem that the effect of retaining friction-reducing properties over an extended period of time may not be exhibited sufficiently.

In the lubricating oil composition according to the present invention, the oxymolybdenum sulfide dithiocarbamate represented by the following formula [3] or the oxymolybdenum sulfide dithiophosphate represented by the following formula [4] is incorporated:



[3]



[4]

In the formula [3], R^9, R^{10}, R^{11} and R^{12} individually represent hydrocarbon groups having 1 to 30 carbon atoms, and Xs represent oxygen or sulfur atoms. In the formula [3], the hydrocarbon groups represented by R^9, R^{10}, R^{11} and R^{12} may all be the same or different. Further, in the formula [3], all Xs can be sulfur atoms or oxygen atoms, or some X(s) can be sulfur atom(s) and the remaining X(s) can be oxygen atom(s). Examples of the hydrocarbon groups represented by R^9, R^{10}, R^{11} and R^{12} include alkyl groups having 1 to 30 carbon atoms, alkenyl groups having 2 to 30 carbon atoms, cycloalkyl groups having 5 to 30 carbon atoms, aryl groups having 6 to 30 carbon atoms, and alkylaryl and arylalkyl groups having 7 to 30 carbon atoms. Specific examples of the hydrocarbon groups having 1 to 30 carbon atoms include methyl, ethyl, propyl, butyl, pentyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, cyclohexyl, dimethylcyclohexyl, ethylcyclohexyl, butylcyclohexyl, heptylcyclohexyl, phenyl, benzyl, dimethylphenyl, methylbenzyl, phenethyl, naphthyl, and dimethylnaphthyl. In the lubricating oil composition according to the present invention, particularly preferred as R^9, R^{10}, R^{11} and R^{12} in the formula [3] are alkyl groups having 8 to 13 carbon atoms.

In the formula [4], R^{13}, R^{14}, R^{15} and R^{16} individually represent hydrocarbon groups having 1 to 30 carbon atoms, and Xs represent oxygen or sulfur atoms. In the formula [4], the hydrocarbon groups represented by R^{13}, R^{14}, R^{15} and R^{16} may all be the same or different. Further, in the formula [3], all Xs can be sulfur atoms or oxygen atoms, or some

X(s) can be sulfur atom(s) and the remaining X(s) can be oxygen atom(s). Examples of the hydrocarbon groups represented by R^9, R^{10}, R^{11} and R^{12} include alkyl groups having 1 to 30 carbon atoms, alkenyl groups having 2 to 30 carbon atoms, cycloalkyl groups having 5 to 30 carbon atoms, aryl groups having 6 to 30 carbon atoms, and alkylaryl and arylalkyl groups having 7 to 30 carbon atoms. Specific examples of the hydrocarbon groups having having 1 to 30 carbon atoms include methyl, ethyl, propyl, butyl, pentyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, cyclohexyl, dimethylcyclohexyl, ethylcyclohexyl, methylcyclo-hexylmethyl, cyclohexylethyl, propylcyclohexyl, butylcyclohexyl, heptylcyclohexyl, phenyl, benzyl, dimethylphenyl, methylbenzyl, phenethyl, naphthyl, and dimethylnaphthyl. In the lubricating oil composition according to the present invention, particularly preferred as R^{13}, R^{14}, R^{15} and R^{16} in the formula [4] are alkyl groups having 8 to 13 carbon atoms.

In the lubricating oil composition according to the present invention, such oxymolybdenum sulfide dithiocarbamates or oxymolybdenum sulfide dithiophosphates can be used either singly or in combination. Further, the oxymolybdenum sulfide dithiocarbamate or oxymolybdenum sulfide dithiophosphate is added in an amount such that the amount of molybdenum derived from the oxmolybdenum sulfide dithiocarbamate or oxymolybdenum sulfide dithiophosphate ranges from 200 to 2,000 ppm (weight basis), preferably from 300 to 800 ppm (weight basis). If the amount of the oxymolybdenum sulfide dithiocarbamate or oxymolybdenum sulfide dithiophosphate is so small that the amount of molybdenum derived from the oxymolybdenum sulfide dithiocarbamate or oxymolybdenum sulfide dithiophosphate is lower than 200 ppm (weight basis) of the total weight of the lubricating oil composition, there is the potential problem that the improving effect of friction-reducing properties may not be fully exhibited. Even if the amount of the oxymolybdenum sulfide dithiocarbamate or oxymolybdenum sulfide dithiophosphate is so much that the amount of molybdenum derived from the oxymolybdenum sulfide dithiocarbamate or oxymolybdenum sulfide dithiophosphate is in excess of 2,000 ppm (weight basis) of the total weight of the lubricating oil composition, its effect cannot be expected to be improved in proportion to the increase in its amount, and the use of the dithiocarbamate or dithiophosphate in such an excess amount may cause a sludge or the like.

In the lubricating oil composition according to the present invention, it is possible to incorporate various additives, which have heretofore been commonly employed in lubricating oils, to extents not impairing the object of the present invention. Examples of such additives include other antiwear agents, metallic detergents, other friction modifiers, nonash dispersants, antioxidants, viscosity index improvers, pour-point depressants, anti-foaming agents, rust preventives, and corrosion inhibitors.

Examples of the other friction modifiers include partial esters of polyhydric alcohols, amines, amides, and sulfate esters.

Examples of the metallic detergents include calcium salicylate, magnesium salicylate, calcium sulfonate, magnesium sulfonate, barium sulfonate, calcium phosphonate, and barium phenate. These metallic detergents can be added generally in a proportion of from 0.1 to 5.0 wt%.

Examples of the other antiwear agents include metal thiophosphates, sulfur compounds, phosphate esters, and phosphite esters. These antiwear agents can be added generally in a proportion of from 0.05 to 5.0 wt%.

Examples of the nonash dispersants include those of the succinimide, succinamide, benzylamine and ester types. These nonash dispersants can be added generally in a proportion of from 0.5 to 7.0 wt%.

Examples of the antioxidants include phenolic antioxidants such as 2,6-di-t-butyl-4-methylphenol and 4,4'-methylenebis (2,6-di-t-butylphenol). These antioxidants can be added generally in a proportion of from 0.05 to 4.0 wt%.

Examples of the viscosity index improvers include those of the polymethacrylate, polyisobutylene, ethylene-propylene copolymer and hydrogenated styrene-butadiene copolymer types. These viscosity index improvers can be added generally in a proportion of from 0.5 to 35 wt%.

Examples of the pour-point depressants include poly (alkyl methacrylate), chlorinated paraffin-naphthalene condensates, and alkylated polystyrenes.

Examples of the anti-foaming agents include dimethyl polysiloxane and polyacrylic acid.

Examples of the rust preventives include fatty acids, partial esters of alkenylsuccinic acids, fatty acid soaps, alkylsufonate salts, polyhydric alcohol esters of fatty acids, fatty acid amines, paraffin oxides, and alkyl polyoxyethylene ethers.

Examples of the corrosion inhibitors include benzotriazole and benzoimidazole.

Examples

The present invention will hereinafter be described in further detail by the following Examples. It should however be borne in mind that the present invention is not limited by the following Examples.

Incidentally, each average cam wear was measured in accordance with ASTM RR:D-2:1266.

The coefficient of friction of each lubricating oil composition was measured using a reciprocating sliding friction tester ("SRV Friction Tester") under the following conditions: frequency: 50 Hz, amplitude: 3 mm, load: 25 N, temperature: 80°C, and testing time: 25 minutes.

Each oxidation test by NOx-containing air was conducted on 150 mℓ of the corresponding test oil under the following conditions: temperature: 130°C, nitrogen oxides (NOx) concentration: 1 vol%, flow rate: 2 ℓ/hour, and testing time: 8 hours.

Example 1

A lubricating oil composition was prepared by adding, to a paraffinic mineral oil having a viscosity of 4.0 mm^2/s at 100°C, calcium sulfonate as a metallic detergent in a proportion of 2.0 wt%, succinimide as a nonash dispersant in a proportion of 5.0 wt%, hindered phenol as an antioxidant in a proportion of 1.0 wt%, poly (alkyl methacrylate) as a viscosity index improver in a proportion of 5.0 wt%, zinc di-2-ethylhexyl dithiophosphate and zinc di-1-methylbutyl dithiophosphate in proportions to give a weight ratio in phosphorus content of 80:20 and a phosphorus content of 0.10 wt%, dibenzyl disulfide in a proportion to give a sulfur content of 500 ppm (weight basis), and oxymolybdenum-N, N-dioctyl sulfide dithiocarbamate to give a molybdenum content of 500 pm (weight basis).

An average cam wear when this lubricating oil composition was used was 6.8 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation and was still 0.11 after the oxidation test.

Example 2

A lubricating oil composition was prepared with the same formula as that of Example 1 except that zinc di-2-ethylhexyl dithiophosphate and zinc di-1-methylbutyl dithiophosphate were added to give a weight ratio in phosphorus content of 75:25 and a phosphorus content of 0.10 wt%. An average cam wear when this lubricating oil composition was used was 5.5 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation and was still 0.11 after the oxidation test.

Example 3

A lubricating oil composition was prepared with the same formula as that of Example 1 except that zinc di-2-ethylhexyl dithiophosphate and zinc di-1-methylbutyl dithiophosphate were added to give a weight ratio in phosphorus content of 70:30 and a phosphorous content of 0.10 wt%. An average cam wear when this lubricating oil composition was used was 4.6 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation and was still 0.11 after the oxidation test.

Example 4

A lubricating oil composition was prepared with the same formula as that of Example 1 except that zinc di-2-ethylhexyl dithiophosphate and zinc di-1-methylbutyl dithiophosphate were added to give a weight ratio in phosphorus content of 50:50 and a phosphorus content of 0.10 wt%. An average cam wear when this lubricating oil composition was used was 3.6 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation but was 0.12 after the oxidation test.

Example 5

A lubricating oil composition was prepared with the same formula as that of Example 1 except that zinc di-2-ethylhexyl dithiophosphate and zinc di-1-methylbutyl dithiophosphate were added to give a weight ratio in phosphorus content of 30:70 and a phosphorus content of 0.10 wt%. An average cam wear when this lubricating oil composition was used was 2.5 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation but was 0.13 after the oxidation test.

Example 6

A lubricating oil composition was prepared with the same formula as that of Example 1 except that zinc di-2-ethylhexyl dithiophosphate and zinc di-1-methylbutyl diothiophosphate were added to give a weight ratio in phosphorus content of 25:75 and a phosphorus content of 0.10 wt%. An average cam wear when this lubricating oil composition was used was 2.2 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation but was 0.13 after the oxidation test.

Example 7

A lubricating oil composition was prepared with the same formula as that of Example 1 except that zinc di-2-ethylhexyl dithiophosphate and zinc di-1-methylbutyl dithiophosphate were added to give a weight ratio in phosphorus content of 20:80 and a phosphorus content of 0.10 wt%. An average cam wear when this lubricating oil composition was used was 2.0 mil. Further, the coefficient of friction of the lubricating oil composition was 0.12 immediately after its preparation but was 0.14 after the oxidation test.

Example 8

A lubricating oil composition was prepared with the same formula as that of Example 4 except that a poly-α-olefin having a viscosity of 4.0 mm^2/s at 100°C was used as a lubricating base oil.

An average cam wear when this lubricating oil composition was used was 3.5 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation but was 0.12 after the oxidation test.

Example 9

A lubricating oil composition was prepared with the same formula as that of Example 1 except that zinc di-2-ethylhexyl dithiophosphate and zinc di-1-methylbutyl dithiophosphate were added to give a weight ratio in phosphorus content of 50:50 and a phosphorus content of 0.08 wt%. An average cam wear when this lubricating oil composition was used was 4.5 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation but was 0.13 after the oxidation test.

Example 10

A lubricating oil composition was prepared with the same formula as that of Example 1 except that zinc di-2-ethylhexyl dithiophosphate and zinc di-1-methylbutyl dithiophosphate were added to give a weight ratio in phosphorus content of 50:50 and a phosphorus content of 0.10 wt% and that dibenzyl disulfide was added to give a sulfur content of 300 ppm (weight basis). An average cam wear when this lubricating oil composition was used was 4.2 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation but was 0.13 after the oxidation test.

Example 11

A lubricating oil composition was prepared with the same formula as that of Example 1 except that zinc di-2-ethylhexyl dithiophosphate and zinc di-1-methylbutyl dithiophosphate were added to give a weight ratio in phosphorus content of 50:50 and a phosphorus content of 0.10 wt% and that dibenzyl disulfide was added to give a sulfur content of 1,200 ppm (weight basis). An average cam wear when this lubricating oil composition was used was 3.5 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation but was 0.14 after the oxidation test.

Example 12

A lubricating oil composition was prepared with the same formula as that of Example 1 except that zinc di-2-ethylhexyl dithiophosphate and zinc di-1-methylbutyl dithiophosphate were added to give a weight ratio in phosphorus content of 30:70 and a phosphorus content of 0.10 wt% and that in lieu of dibenzyl disulfide, 2,5-di(4,5-dithianoyl)-1,3,4-thiadiazole was added to give a sulfur content of 500 ppm (weight basis). An average cam wear when this lubricating oil composition was used was 2.8 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation but was 0.13 after the oxidation test.

The results of Examples 1 to 12 are summarized in Table 1.

TABLE 1-1

	Examples					
	1	2	3	4	5	6
Base Oil	Mineral oil	Mineral Oil	Mineral Oil	Mineral Oil	Mineral Oil	Mineral Oil
Metallic detergent (wt%) Calcium sulfonate	2.0	2.0	2.0	2.0	2.0	2.0
Ashless dispersant (wt%) Succinimide	5.0	5.0	5.0	5.0	5.0	5.0
Antioxidant (wt%) Hindered phenol	1.0	1.0	1.0	1.0	1.0	1.0
Viscosity Index Improver (wt%) Polyalkylmethacrylate	5.0	5.0	5.0	5.0	5.0	5.0
ZnDTP Primary/Secondary (phosphorus content in weight ratio)	80:20	75:25	70:30	50:50	30:70	25:75
ZnDTP content as phosphorus (wt%)	0.10	0.10	0.10	0.10	0.10	0.10
Dibenzyl disulfide as sulfur (ppm)	500	500	500	500	500	500
2,5-di(4,5-dithianonyl)-1,3,4 -thiaziazole content as sulfur (ppm)	-	-	-	-	-	-
MoDTC content as Mo (ppm)	500	500	500	500	500	500
Average cam wear (mils)	6.8	5.5	4.6	3.6	2.5	2.2
Friction coefficient - Immediately after the production - Immediately after oxidation test	 0.11 0.11	 0.11 0.11	 0.11 0.11	 0.11 0.12	 0.11 0.13	 0.11 0.13

ZnDTP (primary): zinc di-2-ethylhexyldithiophosphate
ZnDTP (secondary): zinc di-1-methylbutyl dithiophosphate
MoDTC: Sulfurized oxymolybdenum-N, N-dioctyldithiocarbamate

TABLE 1-2

	Examples					
	7	8	9	10	11	12
Base Oil	Mineral oil	Synthetic Oil	Mineral Oil	Mineral Oil	Mineral Oil	Mineral Oil
Metallic detergent (wt%) Calcium sulfonate	2.0	2.0	2.0	2.0	2.0	2.0
Ashless dispersant (wt%) Succinimide	5.0	5.0	5.0	5.0	5.0	5.0
Antioxidant (wt%) Hindered phenol	1.0	1.0	1.0	1.0	1.0	1.0
Viscosity Index Improver (wt%) Polyalkylmethacrylate	5.0	5.0	5.0	5.0	5.0	5.0
ZnDTP Primary/Secondary (phosphorus content in weight ratio)	20:80	50:50	50:50	50:50	50:50	30:70
ZnDTP content as phosphorus (wt%)	0.10	0.10	0.08	0.10	0.10	0.10
Dibenzyl disulfide as sulfur (ppm)	500	500	500	300	1200	-
2,5-di(4,5-dithianonyl)-1,3,4 -thiaziazole content as sulfur (ppm)	-	-	-	-	-	500
MoDTC content as Mo (ppm)	500	500	500	500	500	500
Average cam wear (mils)	2.0	3.5	4.5	4.2	3.5	2.8
Friction coefficient - Immediately after the production - Immediately after oxidation test	 0.12 0.14	 0.11 0.12	 0.11 0.13	 0.11 0.13	 0.11 0.14	 0.11 0.13

ZnDTP (primary): zinc di-2-ethylhexyldithiophosphate
ZnDTP (secondary): zinc di-1-methylbutyl dithiophosphate
MoDTC: Sulfurized oxymolybdenum-N, N-dioctyldithiocarbamate

The average cam wears when the lubricating oil compositions of the present invention in Examples 1 to 12 were used were all small, thereby demonstrating that these lubricating oil compositions all had excellent antiwear properties. Further, the lubricating oil compositions of the present invention in Examples 1 to 12 were low in the coefficient of friction immediately after their preparation and indicated good friction characteristics. Even when they were subjected to oxidation under heating at 130°C for 8 hours in the presence of an NOx gas, their coefficients of friction remained substantially unchanged. It is therefore appreciated that those lubricating oil compositions had good oxidation resistance. From a comparison among the results of Examples 1 to 7, it is also appreciated that the oxidation resistance becomes better with the amount of the zinc (primary alkyl) dithiophosphate while the antiwear properties become better with the amount of the zinc (secondary alkyl) dithiophosphate.

Comparative Example 1

A lubricating oil composition was prepared by adding, to a paraffinic mineral oil having a viscosity of 4.0 mm^2/s at 100°C, calcium sulfonate as a metallic detergent in a proportion of 2.0 wt%, succinimide as a nonash dispersant in a proportion of 5.0 wt%, hindered phenol as an antioxidant in a proportion of 1.0 wt%, poly(alkyl methacrylate) as a viscosity index improver in a proportion of 5.0 wt%, zinc di-2-ethylhexyl dithiophosphate in a proportion to give a phosphorus content of 0.10 wt%, dibenzyl disulfide in a proportion to give a sulfur content of 500 ppm (weight basis), and oxymolybdenum-N, N-dioctyl sulfide dithiocarbamate to give a molybdenum content of 500 ppm (weight basis).

An average cam wear when this lubricating oil composition was used was 14.0 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation and was still 0.11 after the oxidation test.

Comparative Example 2

A lubricating oil composition was prepared with the same formula as that of Comparative Example 1 except that instead of zinc di-2-ethylhexyl dithiophosphate, zinc di-2-ethylhexyl dithiophosphate and zinc di-1-methylbutyl dithiophosphate were added to give a weight ratio in phosphorus content of 90:10 and a phosphorus content of 0.10 wt%. An average cam wear when this lubricating oil composition was used was 10.5 mil. Further, the coefficient of friction of the lubricating oil composition was 0.11 immediately after its preparation and was still 0.11 after the oxidation test.

Comparative Examples 3 to 8

Lubricating oil compositions of the formulas shown in Table 2 were prepared, and their average cam abrasion losses, their coefficients of friction immediately after the preparation and their coefficients of friction after their oxidation tests were measured.

The formulas and results of Comparative Examples 1 to 8 are summarized in Table 2.

TABLE 2

	Examples							
	1	2	3	4	5	6	7	8
Base Oil	Mineral oil	Mineral Oil	Mineral Oil	Mineral Oil	Mineral Oil	Mineral Oil	Mineral Oil	Mineral Oil
Metallic detergent (wt%) Calcium sulfonate	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Ashless dispersant (wt%) Succinimide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Antioxidant (wt%) Hindered phenol	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Viscosity Index Improver (wt%) Polyalkylmethacrylate	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
ZnDTP Primary/Secondary (phosphorus content in weight ratio)	100:0	90:10	10:90	0:100	50:50	50:50	50:50	50:50
ZnDTP content as phosphorus (wt%)	0.10	0.10	0.10	0.10	0.06	0.10	0.10	0.10
Dibenzyl disulfide as sulfur (ppm)	500	500	500	500	500	-	1500	500
MoDTC content as Mo (ppm)	500	500	500	500	500	500	500	-
Average cam wear (mils)	14.0	10.5	1.5	1.2	9.0	3.8	3.8	4.0
Friction Coefficient Immediately after the production Immediately after oxidation test	 0.11 0.11	 0.11 0.11	 0.11 0.16	 0.11 0.17	 0.11 0.17	 0.11 0.19	 0.11 0.16	 0.20 0.20

ZnDTP (primary): zinc di-2-ethylhexyldithiophosphate
ZnDTP (secondary): zinc di-1-methylbutyl dithiophosphate
MoDTC: Sulfurized oxymolybdenum-N, N-dioctyldithiocarbamate

The lubricating oil composition of Comparative Example 1, which was added with the zinc di (primary alkyl) dithiophosphonate but was not added with any zinc di (secondary alkyl) dithiophosphate, was greater in average cam abrasion loss and hence inferior in antiwear properties compared with the lubricating oil composition of Example 1 although both the lubricating oil compositions contained the same amount of phosphorus derived from the zinc dialkyl dithiophosphate(s). The lubricating oil composition of Comparative Example 2, which contained the zinc di (primary alkyl) dithiophosphate in the larger proportion and the zinc di (secondary alkyl) dithiophosphate in the smaller proportion, was also poor in antiwear properties.

The lubricating oil composition of Comparative Example 3, which contained the zinc di (primary alkyl) dithiophosphate in the smaller proportion and the zinc di (secondary alkyl) dithiophosphate in the larger proportion, was smaller in average cam abrasion loss and hence had good antiwear properties, but was larger in the coefficient of friction after the oxidation test and was hence inferior in oxidation resistance. The lubricating oil composition of Comparative Example 4, which was not added with any zinc di (primary alkyl) dithiophosphate but was added with the zinc di (secondary alkyl) dithiophosphate alone, was still better in antiwear properties, but had the high coefficient of friction even immediately after its preparation and was hence low in friction-reducing properties.

The lubricating oil composition of Comparative Example 5, in which the zinc di (primary alkyl) dithiophosphate and the zinc di (secondary alkyl) dithiophosphate were used to give the weight ratio in phosphorus content of 50:50 but they were added in small amounts and the amount of phosphorus derived from the zinc di (alkyl) dithiophosphates was 0.06 ppm (weight basis), was inferior in antiwear properties and also poor in oxidation resistance.

The lubricating oil composition of Comparative Example 6, in which no sulfur compound was added at all, and the lubricating oil composition of Comparative Example 7, in which dibenzyl disulfide was added to give the sulfur content of 1,500 ppm (weight basis), were both high in the coefficient of friction after their oxidation tests. It is therefore understood that addition of such a sulfur compound in an adequate amount is needed to impart good oxidation resistance.

The lubricating oil composition of Comparative Example 8, in which no oxymolybdenum sulfide thiocarbamate was added at all, had a high coefficient of friction even immediately after its preparation and was hence inferior in friction-reducing properties.

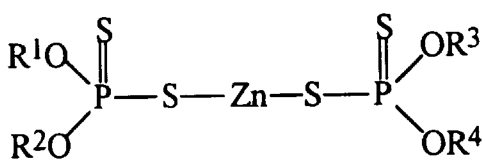
Advantageous Effects of the Invention

The lubricating oil composition according to the present invention has excellent antiwear properties and even at elevated temperatures and in the presence of nitrogen oxides, exhibits high oxidation resistance and retains good friction-reducing properties, so that it can be suitably used as a lubricating oil for internal combustion engines.

Claims

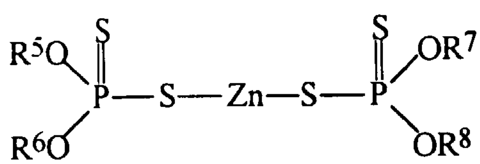
1. A lubricating oil composition comprising a major portion of a lubricating base oil and a minor portion of additives comprising:

(A) a zinc di (primary alkyl) dithiophosphate represented by the following formula [1]:



[1]

wherein R^1, R^2, R^3 and R^4 individually represent primary alkyl groups having 1 to 20 carbon atoms, and a zinc di (secondary alkyl) dithiophosphate represented by the following formula [2]:

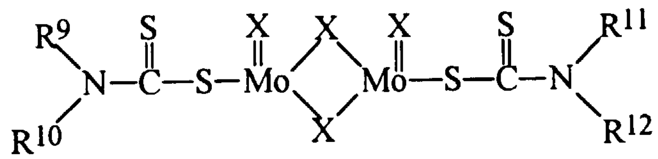


[2]

wherein R^5, R^6, R^7 and R^8 individually represent secondary alkyl groups having 3 to 7 carbon atoms,

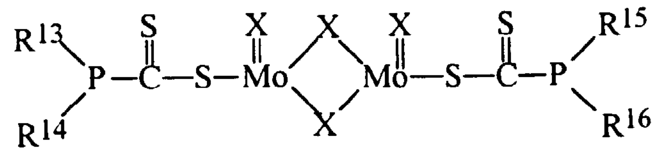
(B) one or more sulfur compounds selected from the group consisting of zinc dialkyl dithiocarbamates, copper dialkyl dithiocarbamates or nickel dialkyl dithiocarbamates in which each alkyl group has 2 to 18 carbon atoms, tetraalkylthiuram disulfides in which each alkyl group has 2 to 18 carbon atoms, disulfides containing one or more aryl groups having 6 to 18 carbon atoms or one or more alkylaryl or arylalkyl groups having 7 to 18 carbon atoms, thiadiazole compounds having one or more sulfur-containing substituent groups and 3 to 24 carbon atoms, olefin sulfides, sulfurized fish oil and sulfurized whale oil, and

(C) one or more oxymolybdenum sulfide compound selected from oxymolybdenum sulfide dithiocarbamate represented by the following formula [3]:



[3]

wherein R^9, R^{10}, R^{11} and R^{12} individually represent alkyl groups having 1 to 30 carbon atoms, cycloalkyl groups having 5 to 30 carbon atoms, aryl groups having 6 to 30 carbon atoms, or alkylaryl or arylalkyl groups having 7 to 30 carbon atoms, and Xs represent oxygen or sulfur atoms; or oxymolybdenum sulfide dithiophosphate represented by the following formula [4]:



[4]

wherein R^{13}, R^{14}, R^{15} and R^{16} individually represent alkyl groups having 1 to 30 carbon atoms, cycloalkyl groups having 5 to 30 carbon atoms, aryl groups having 6 to 30 carbon atoms, or alkylaryl or arylalkyl groups having 7 to 30 carbon atoms, and Xs represent oxygen or sulfur atoms; wherein

(A) the weight ratio of the phosphorus content of said zinc di (primary alkyl) dithiophosphate to that of said zinc di (secondary alkyl) dithiophosphate ranges from 20:80 to 80:20, and the amount of phosphorus derived from said zinc di (primary alkyl) dithiophosphate and zinc di (secondary alkyl) dithiophosphate ranges from 0.07 to 0.15 wt% based on the total weight of said lubricating oil composition;

(B) the amount of sulfur derived from said sulfur compounds other than said zinc di (primary alkyl) dithiophosphate, zinc di (secondary alkyl) dithiophosphate and oxymolybdenum sulfide dithiophosphate ranges from 300 to 1,200 ppm (weight basis) based on the total weight of said lubricating oil composition; and

(C) the amount of molybdenum derived from said oxymolybdenum sulfide dithiocarbamate, oxymolybdenum sulfide dithiophosphate and mixtures thereof ranges from 200 to 2,000 ppm (weight basis) based on the total weight of said lubricating oil composition.

2. The lubricating oil composition of claim 1 wherein the weight ratio of the phosphorus content of the zinc di (primary alkyl) dithiophosphate to that of the zinc di (secondary alkyl) dithiophosphate is in the range 25:75 to 80:20.

3. The lubricating oil composition of claim 1 wherein the weight ratio of the phosphorus content of the zinc di (primary alkyl) dithiophosphate to that of the zinc di (secondary alkyl) dithiophosphate is in the range 30:70 to 70:30.

4. The lubricating oil composition of any preceding claim wherein the amount of phosphorus derived from said zinc di (primary alkyl) dithiophosphate and zinc di (secondary alkyl) dithiophosphate ranges from 0.08 to 0.10 wt%

based on the total weight of said lubricating oil composition.

5. The lubricating oil composition of any preceding claim wherein the amount of molybdenum derived from the oxymolybdenum sulfide dithiocarbamate, oxymolybdenum sulfide dithiophosphate and mixtures thereof range from 300 to 800 ppm (weight basis) based on the total weight of said lubricating oil composition.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 7382

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US-A-5 356 547 (KATSUYA RARAI) * column 2, line 30 - line 54; examples 6,10 *	1,5	C10M141/10 //(C10M141/10, 135:04,135:06, 135:18,135:18, 135:22,135:28, 137:10, 137:10), C10N10:02, C10N10:04, C10N10:12, C10N10:16, C10N30:06, C10N40:25
A	EP-A-0 113 045 (HONDA MOTOR CO. LTD) * examples 14,15,19-21 *	1-5	
A	US-A-4 395 343 (L.DE VRIES) * column 10, line 65 - column 11, line 8; claims 1,2 *	1	
A	EP-A-0 304 011 (KYODO OIL TECHNICAL) * claim 1 *	1-5	
P,A	EP-A-0 699 739 (JAPAN ENERGY CORP.) * page 1, line 1 - line 8 * * page 3, line 29 - page 5, line 10 *	1-5	
P,A	WO-A-96 06904 (TONEN CORP.) * the whole document *	1-5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 January 1997	Rotsaert, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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EPO FORM 1503 03.82 (P04C01)