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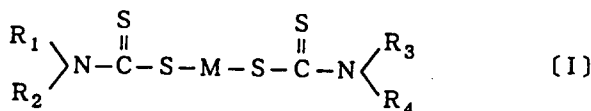
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(54) **LUBRICATING OIL COMPOSITION.**

(57) A lubricating oil composition prepared by compounding a base oil with a metal dithiocarbamate represented by general formula (I) and an oil-soluble amino compound, wherein M represents zinc, copper, nickel, iron, cadmium, silver, lead, antimony, tin or bismuth; and R₁, R₂, R₃ and R₄ represent each independently a C₁ to C₁₃ oleophilic group provided that each group has on average more than one up to four carbon atoms. The composition contains scarcely any or no phosphorus and is excellent in wear resistance, extreme-pressure properties, frictional characteristics, oxidation stability and coking resistance, thus being suitably usable as a lubricating oil for internal combustion engines of automobiles.



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TECHNICAL FIELD

The present invention relates to lubricating oil compositions, and more specifically to lubricating oil compositions, which contain very little or no phosphorus and are excellent in anti-wear properties, extreme-pressure characteristics, friction characteristics, oxidation stability, coking resistance and the like. The lubricating oil compositions according to the present invention are suitably used, in particular, as lubricating oils for internal combustion engines of automobiles.

BACKGROUND ART

Zinc dithiophosphate (hereinafter abbreviated as "Zn-DTP") such as zinc dialkyldithiophosphate or zinc diaryldithiophosphate is one of lubricating oil additives which are worldwide used. Zn-DTP serves as both antioxidant and corrosion inhibitor and additionally has excellent anti-wear properties, and is hence used widely not only in lubricating oils for internal combustion engines of automobiles (hereinafter abbreviated as the "engine oil"), but also in hydraulic fluids.

As described above, Zn-DTP is commonly used in a field of lubricating oils including engine oils from the viewpoint of both excellent multifunctionality and effect. However, in the case where Zn-DTP is used as an engine oil, it involves a problem that the capability of an exhaust emission control system is remarkably reduced because phosphorus (P) contained therein poisons catalysts for exhaust emission control devices and oxygen sensors in automobiles. In order to lower the content of phosphorus in engine oils, therefore, it has heretofore been attempted to reduce the amount of Zn-DTP to be added.

However, when the amount of Zn-DTP to be added is reduced, the anti-wear properties of an engine oil added with Zn-DTP is deteriorated, resulting in problems, for example, of reduction in durability of engine, and the like. Accordingly, while the amount of Zn-DTP to be added has been decreased, it has been combined with other additives (for example, ashless detergent-dispersant, metal detergent) to impart performance necessary for an engine oil.

By the way, various metal salts of dithiocarbamic acid (hereinafter abbreviated as "M-DTCs") are organometallic anti-wear agents as with Zn-DTP. However, these salts involve no potential problem of poisoning catalysts for exhaust emission control devices because they contain no phosphorus atom in their molecules. However, these metal dithiocarbamates do not impart sufficient anti-wear properties. Therefore, various proposals for their combination systems with Zn-DTP have been made (Japanese Patent Application Laid-Open Nos. 111805/1976, 113604/1979).

Zinc dithiocarbamate (hereinafter abbreviated as "Zn-DTC") which is one of the metal dithiocarbamates is soluble in oils if its lipophilic groups have at least 5 carbon atoms on the average. Therefore, it is used as an additive for lubricating oils. However, this compound is insufficient in anti-wear effect compared with Zn-DTP and can not hence be substituted for Zn-DTP. On the other hand, Zn-DTC whose lipophilic groups have at most 4 carbon atoms on the average is commonly used as a vulcanization accelerator for rubbers, but is hardly employed as a lubricating oil additive due to its low solubility in lubricating oils. Zn-DTC whose lipophilic groups each have 4 carbon atoms is only used as an antioxidant, metal deactivator and bearing-corrosion inhibitor for lubricating oils in a low concentration.

In order to clarifying automobile emissions, there has been an increasing tendency to limit the content of phosphorus in recent years. There has thus been a greater demand than before for developing a lubricating oil composition containing very little or no phosphorus. However, any additive substitutable for Zn-DTP has not been yet found under the circumstances.

DISCLOSURE OF THE INVENTION

It is an object of the present invention to provide a lubricating oil composition, which contains very little or no phosphorus and is excellent in anti-wear properties, extreme-pressure characteristics, friction characteristics, oxidation stability, coking resistance and the like.

The present inventors have carried out an extensive investigation with a view toward overcoming the problems involved in the prior art. As a result, it has been found that when an M-DTC whose lipophilic groups have at most 4 carbon atoms on the average (hereinafter abbreviated as the "short-chain M-DTC"), said compound heretofore having attracted no attention as a lubricating oil additive due to its extremely low solubility in lubricating oils, is combined with an oil-soluble amine compound such as a succinimide or alkylamine, both compounds form a complex with each other, so that the short-chain M-DTC turns oil-soluble.

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Features of the present invention will hereinafter be described in detail.

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Metal Dithiocarbamate (M-DTC):

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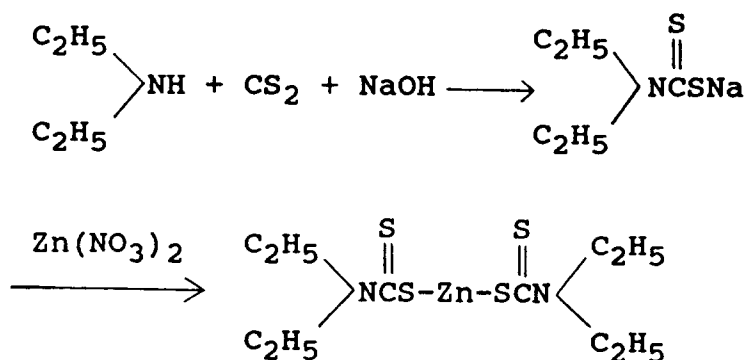
As examples of the metal atom (M), may be mentioned zinc, copper, nickel, iron, cadmium, silver, lead, antimony, tin and bismuth.

If the average number of carbon atoms of the four lipophilic groups in this short-chain M-DTC is 1 (if all the lipophilic groups are methyl groups), a uniform lubricating oil composition can not be obtained even when such a compound is combined with the oil-soluble amine compound because its solubility in the lubricating oil is poor. The M-DTC exhibits its function when it is adsorbed on the surface of a metal. Therefore, if it is dissolved excessively, it can not be expected that the salt shows a sufficient effect. However, the salt is no good unless dissolved. The lower limit of the average number of carbon atoms of the lipophilic groups is preferably at least 2 from the viewpoint of both solubility and function such as anti-wear properties.

If the average number of carbon atoms of the four lipophilic groups in the M-DTC exceeds 4, it has good solubility in lubricating oils, but the anti-wear properties of the resulting lubricating oil composition is deteriorated. Such a salt can not be used as an additive substitutable for Zn-DTP. The upper limit of the average number of carbon atoms of the lipophilic groups is preferably at most 3 from the viewpoint of function such as anti-wear properties.

In general, in view of easy synthesis and function such as anti-wear properties, the short-chain M-DTC is preferably such that all the four lipophilic groups have the same number of carbon atoms, with an M-DTC whose four lipophilic groups are all alkyl groups having 2 or 3 carbon atoms being particularly preferred. The metal atom (M) is preferably zinc from the viewpoint of easy availability and function such as anti-wear properties.

The short-chain M-DTC can be synthesized in accordance with the conventionally-known methods. For example, zinc diethyldithiocarbamate can be synthesized by reacting diethylamine, carbon disulfide and sodium hydroxide with each other to prepare sodium diethylthiocarbamate and then reacting zinc nitrate with this product.



Oil-Soluble Amine Compound:

As examples of the oil-soluble amine compound useful in the practice of this invention, may be mentioned ashless detergent-dispersants based on a polyalkenylsuccinimide, alkylbenzylamine or the like, alkylamines, alkyldiamines, and alkylpolyamines.

Examples of the polyalkenylsuccinimide-based, ashless detergent-dispersants include those obtained by reacting polybutenylsuccinic anhydride with a polyamine such as a polyethylene polyamine.

Lubricating Oil Composition:

The above-described short-chain M-DTC is very low in solubility in lubricating oils. Therefore, it can not be used as a lubricating oil additive by itself. However, when it is combined with the oil-soluble amine compound, its solubility in lubricating oils is improved. In addition, the combination system exhibits excellent anti-wear function identical with Zn-DTP, and also reduces the coefficient of friction of the resulting lubricating oil composition. Further, the combination system contains no phosphorus and hence does not poisons catalysts for exhaust emission control devices and oxygen sensors in automobiles.

The improvement in the solubility of the short-chain M-DTC is considered to be owing to the formation of a complex of the short-chain M-DTC and the oil-soluble amine compound. Namely, it is considered that the metal atom (M) in the short-chain M-DTC forms a coordinate bond with the nitrogen atom (N) in the oil-soluble amine compound to form the complex, so that the short-chain M-DTC turns oil-soluble by action of a long lipophilic group in the oil-soluble amine compound.

The mixing proportion of the short-chain M-DTC in the lubricating oil composition is generally 0.05-1.5 wt.%, preferably 0.2-0.8 wt.%. If the mixing proportion of the short-chain M-DTC is too low, its anti-wear effect becomes insufficient. If the proportion is too high, its dissolution becomes insufficient. The mixing proportion of the oil-soluble amine compound is generally 0.1-10 wt.%, preferably 0.2-5 wt.%. If the mixing proportion of the oil-soluble amine compound is too low, the solubility of the short-chain M-DTC becomes insufficient. If the proportion is too high, the anti-wear properties of the resultant lubricating oil composition may be reduced on the contrary.

Although the short-chain M-DTC and the oil-soluble amine compound may be mixed separately into a lubricating oil to form their complex in the lubricating oil, it is preferable that the complex of both compounds should be preformed before they are added to the lubricating oil because the short-chain M-DTC can be dissolved in the lubricating oil with ease to obtain a uniform lubricating oil composition.

The preformation of the complex of the short-chain M-DTC with the oil-soluble amine compound is preferably conducted by a method in which both compounds are added to a lubricating base oil in proportions to give high concentrations, and the resulting mixture is then heated. For example, when a mineral oil containing 2-7 wt.% of the short-chain M-DTC and 5-25 wt.% of the ashless detergent-dispersant is stirred for preferably 1-60 minutes, more preferably 1-30 minutes at preferably 40-200 °C, more preferably 60-180 °C, both compounds form a complex with each other to dissolve uniformly in the mineral oil. As the heating temperature becomes higher, the complex is formed in a shorter period of time into a uniform solution. The thus-obtained solution of the complex in a high concentration is diluted with the lubricating base oil, thereby permitting the easy provision of a uniform lubricating oil composition with both compounds contained in desired proportions therein.

The lubricating oil compositions according to the present invention are used as lubricating oils led by engine oils for automobiles and including gear oils, trans-axle oils, hydraulic fluids, spindle oils, machine oils and the like, said lubricating oils all requiring anti-wear properties, good friction characteristics or oxidation resistance.

Other anti-wear agents, friction modifier, ashless detergent-dispersants, anti-oxidants, metal detergents, viscosity index improver, pour point depressants, rust preventives, defoaming agents, corrosion inhibitors, etc. can suitably be added to the lubricating oil compositions according to this invention, as needed.

As examples of the anti-wear agents, may be mentioned metal salts (Zn, Pb, Sb, Mo, etc.) of dithiophosphoric acid, oil-soluble metal salts (Zn, Pb, Sb, Mo, etc.) of dithiocarbamic acid, sulfur compounds, phosphate esters, phosphite esters, phosphate ester amine salts and phosphite ester amine salts. These additives are generally used in a proportion of 0.05-5.0 wt.%.

Examples of the friction modifier include amine-, phosphate ester-, molybdenum- and alcohol-based agents. These agents are generally used in a proportion of 0.05-5.0 wt.%.

Examples of the ashless detergent-dispersants include succinimide-, succinamide-, benzylamine- and ester-based, ashless dispersants. These dispersants are generally used in a proportion of 0.5-7.0 wt.%.

As examples of the antioxidants, may be mentioned amine-based antioxidants such as alkylated diphenylamines, phenyl- α -naphthylamines and alkylated- α -naphthylamines, and phenol-based antioxidants such as 2,6-di-tert-butylphenol and 4,4'-methylenebis(2,6-di-tert-butylphenol). These antioxidants are generally used in a proportion of 0.05-2.0 wt.%.

Examples of the metal detergents include Ca sulfonate, Mg sulfonate, Ba sulfonate, Ca phenate and Ba phenate. These detergents are generally used in a proportion of 0.1-5.0 wt.%.

As examples of the viscosity index improver, may be mentioned polymethacrylate-, polyisobutylene-, ethylene-propylene copolymer- and hydrogenated styrene-butadiene copolymer-based viscosity index improvers. These viscosity index improvers are generally used in a proportion of 5-35 wt.%.

As examples of the rust preventives, may be mentioned alkenylsuccinic acids and their partial esters.

As examples of the defoaming agents, may be mentioned dimethyl polysiloxane and polyacrylates.

The lubricating oil compositions according to the present invention can be provided as phosphorus-free products without adding any phosphorus-containing compound such as Zn-DTP. As with the lubricating oil composition making use of Zn-DTP, they can exhibit excellent anti-wear properties, and moreover reduce the coefficient of friction. The combined use of the combination system according to this invention with the conventional Zn-DTP can reduce the proportion of the Zn-DTP to be used to a significant extent and can hence provide lubricating oil compositions containing far less phosphorus than the conventionally-known compositions. As needed, an oil-soluble M-DTC whose lipophilic groups have at least 5 carbon atoms on the average may be further added to the lubricating oil compositions according to this invention.

The lubricating oil compositions according to the present invention have as good anti-wear properties, extreme-pressure characteristics, oxidation stability, coking resistance and the like as those principally containing Zn-DTP and are lower in coefficient of friction than such compositions. As reasons why the

lubricating oil compositions according to this invention show excellent anti-wear properties, not entirely understood up to the present, may be mentioned, for example, the following reasons: (1) since the size of the lipophilic groups of the short-chain M-DTC is small compared with that of the conventional long-chain M-DTC whose lipophilic groups have at least 5 carbon atoms on the average, an occupied area per molecule is narrow, and it is hence easy to be adsorbed in a high density on the surface of a metal; (2) since the number of moles per weight is great, its adsorbing rate on the metal surface is high; and (3) since its lipophilic groups are short and its thermal decomposition temperature is hence low, it is easy to decompose under frictional heat to form a reaction film on the metal surface.

EXAMPLES

The present invention will hereinafter be described in more detail on the basis of the following examples and comparative examples. It is however to be noted that the present invention is not limited to the following examples only.

Example 1:

In a reactor equipped with a stirrer, were mixed respective Zn-DTCs whose lipophilic groups each have 2, 3 and 4 carbon atoms, respectively, shown in Table 1, an oil-soluble amine compound (succinimide) and a lubricating base oil in a proportion of 1:6:35 (weight ratio). The resulting mixtures were separately heated and stirred for 5 minutes at 120 °C. It was confirmed that the crystals of the Zn-DTCs completely dissolved in the base oil to form respective complexes. Portions of each of these mixtures were diluted with the same base oil as that first used in such a manner that the content of the Zn-DTC was 0.5 wt.% (content of the commercially-available succinimide-based dispersant: 3.0 wt.%) or 1.0 wt.% (content of the commercially-available succinimide-based dispersant: 6.0 wt.%), thereby obtaining respective lubricating oil compositions.

In the same manner as described above, lubricating oil compositions were also prepared by separately using, as oil-soluble amine compounds, benzylamine, an alkylamine and an alkyldiamine.

The proportions of the Zn-DTCs to the amine compounds and the amounts of the Zn-DTCs added into the base oils are shown in Table 1.

For the sake of comparison, lubricating oil compositions prepared in the same manner as described above except that the complex-forming treatment with the oil-soluble amine compound was not conducted in advance (Run Nos. 1, 6, 9 and 13). For the sake of comparison, lubricating oil compositions were also prepared in the same manner as described above except that both short-chain Zn-DTC and oil-soluble amine compound were used, but the complex-forming treatment was not conducted (Run Nos. 11-12).

The base oils and additives used are as follows:

(1) Base oil:

Mineral oil: 100-SN Mineral oil (100 neutral mineral oil).

Synthetic oil: Mixed oil composed of 80 wt.% of a poly- α -olefin and 20 wt.% of diisodecyl adipate.

(2) Zn-DTC:

C₂: Zinc diethyldithiocarbamate.

n-C₃: Zinc di-n-propyldithiocarbamate.

n-C₄: Zinc di-n-butyldithiocarbamate.

(3) Oil-soluble amine compound:

Succinimide: Commercially-available polybutenyl-succinimide-based dispersant.

Benzylamine: Commercially-available polybutenyl-benzylamine-based dispersant.

Alkylamine: Oleylamine.

Alkyldiamine: N-Beef tallow-alkyl trimethylenediamine.

(Solubility of Zn-DTC)

Each of the lubricating oil compositions prepared by diluting with the respective base oils was visually observed right after the preparation (right after the mixing) and upon elapsed time of 4 weeks after the

preparation. The solubility of each Zn-DTC was evaluated in accordance with the following standard of 3 ranks:

- : Uniformly dissolved,
 △: Clouding occurred,
 x: Precipitate was recognized.

The results are given collectively in Table 1.

Table 1

Run No.	Base oil	Number of Carbons of lipophilic groups in Zn-DTC	Oil-soluble amine compound (SOA)	Weight ratio Zn-DTC/SOA
1	M*1 oil	C ₂	-	1/0
2			Succinimide	1/6
3			Benzylamine	1/6
4			Alkylamine	1/1.1
5			Alkyldiamine	1/1.17
6		n-C ₃	-	1/0
7			Succinimide	1/6
8			Succinimide	1/6
9		n-C ₄	-	1/0
10			Succinimide	1/6
11		C ₂	Succinimide	1/6
12		n-C ₄	Succinimide	1/6
13	S*2 oil	C ₂	-	1/0
14			Succinimide	1/6

*1: Mineral oil, *2: Synthetic oil.

Table 1 (Cont'd)

Run No.	Added amount of Zn-DTC wt.%	Solubility		Complex-forming treatment
		Right after mixing	After 4 weeks	
1	0.05	x	x	Not conducted
2	0.5	○	○	Conducted
3	0.5	○	○	Conducted
4	0.5	○	○	Conducted
5	0.5	○	○	Conducted
6	0.1	x	x	Not conducted
7	0.5	○	○	Conducted
8	1.0	○	○	Conducted
9	0.5	○	Δ	Not conducted
10	1.0	○	○	Conducted
11	0.2	x	x	Not conducted
12	1.0	○	○	Not conducted
13	0.05	x	x	Not conducted
14	0.5	○	○	Conducted

As apparent from Table 1, the Zn-DTCs whose lipophilic groups each have at most 4 carbon atoms are hardly soluble in the base oil, but are improved in solubility by forming respective complexes with the oil-soluble amine compounds. Their storage stability also becomes good.

Zinc di-n-butylditiocarbamate whose lipophilic groups each have 4 carbon atoms is soluble in the base oil even by itself if it is dissolved in a small amount. However, its solution clouds upon elapsed time of 4 weeks after its preparation, and its uniformity is impaired (Run No. 9). However, its combined use with the oil-soluble amine compound permits the improvement in solubility without conducting the complex-forming treatment (heating treatment in a high concentration) in advance, and it hence dissolves uniformly even in a high concentration (Run No. 12).

Example 2:

With respect to lubricating oil compositions according to the present invention, a Shell four-ball test for anti-wear properties was conducted to evaluate their anti-wear properties. The results are shown in Table 2. The lubricating oil compositions to be tested were each prepared by adding Zn-DTP or Zn-DTC to a mineral oil or synthetic oil and then blending further 4.0 wt.% of a commercially-available viscosity index improver (polyalkylmethacrylate).

For the sake of comparison, the results obtained by separately using commercially-available Zn-DTP (Run Nos. 15-16, 25) and commercially-available Zn-DTC (Run Nos. 17-18, 26) whose alkyl groups each have 5 carbon atoms are also shown in Table 2.

The mineral oil and synthetic oil were the same as those used in Example 1. The respective Zn-DTCs whose lipophilic groups each have 2, 3 and 4 carbon atoms, respectively, were subjected to the complex-

forming treatment with succinimide in a high concentration (heating treatment in a high concentration) in advance and then used (Run Nos. 19-23, 27, 28). In Table 2, the term "Added amount of active ingredient" means the proportion of Zn-DTP or Zn-DTC as a anti-wear agent in the mineral oil composition. The contents of the ashless detergent-dispersant (succinimide) in the mineral oil compositions were each controlled to give a concentration of 3.0 wt.% in the form of a commercially-available additive. In Run No. 24, the Zn-DTC whose lipophilic groups each have 2 carbon atoms was subjected to the complex-forming treatment with the alkyldiamine like Run No. 5 and then used. The alkyldiamine was prepared to be 0.66 wt.%.

10 <Shell four-ball test for anti-wear properties>

Conditions of the Shell four-ball test for anti-wear properties are as follows:

Conditions 1: load 40 kg, oil temperature 90 °C, number of revolutions 1800 rpm, test time 30 minutes.

15 Conditions 2: load 40 kg, oil temperature 90 °C, number of revolutions 3600 rpm, test time 30 minutes.

The results are shown in Table 2.

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Table 2

Run No.	Base oil	anti-wear agent	Added amount of AI*3 wt. %	Conditions 1		Conditions 2	
				Wear diam. mm	Coef. of friction	Wear diam. mm	Coef. of friction
15	M*4 oil	Commercial Zn-DTP (i-C ₃ /s-C ₆)	0.2	0.64	0.120		
16			0.5	0.49	0.113	0.67	0.104
17		Commercial Zn-DTC (n-C ₅)	0.2	1.11	0.099		
18			0.5	0.41	0.075	2.19	0.099
19		n-C ₄ Zn-DTC (*1)	0.2	0.76	0.112		
20			0.5	0.43	0.090	2.09	0.097
21		n-C ₃ Zn-DTC (*1)	0.5	0.45	0.096	2.02	0.088
22		C ₂ Zn-DTC (*1)	0.2	0.81	0.113		
23			0.5	0.40	0.063	0.81	0.096
24		C ₂ Zn-DTC (*2)	0.5	0.43	0.061	0.67	0.083
25	S*5 oil	Commercial Zn-DTP (i-C ₃ /s-C ₆)	0.5	0.51	0.105		
26		Commercial Zn-DTC (n-C ₅)	0.5	0.62	0.091		
27		n-C ₄ Zn-DTC (*1)	0.5	0.48	0.089		
28		C ₂ Zn-DTC (*1)	0.5	0.49	0.101		

***1: Those obtained by subjecting to the complex-forming treatment with succinimide.**

***2: That obtained by subjecting to the complex-forming treatment with the alkyldiamine.**

***3: Active ingredient.**

***4: Mineral oil.**

***5: Synthetic oil.**

As apparent from Table 2, the lubricating oil compositions (Run Nos. 19-24, 27-28) according to the present invention have excellent anti-wear properties substantially equal to that of the lubricating oil compositions containing the commonly used Zn-DTP and show better coefficients of friction than those thereof. They are also far excellent in anti-wear properties compared with the lubricating oil compositions containing the commercially-available Zn-DTC.

Example 3:

With respect to lubricating oil compositions according to the present invention, a critical load upon seizing was measured by a Shell four-ball test for extreme-pressure characteristics to evaluate their extreme-pressure characteristics. The results are shown in Table 3. The lubricating oil compositions to be tested were each prepared by adding Zn-DTP or Zn-DTC to a mineral oil and then blending further 4.0 wt.% of a commercially-available viscosity index improver (polyalkylmethacrylate).

For the sake of comparison, the results obtained by separately using commercially-available Zn-DTP (Run Nos. 29-30) and commercially-available Zn-DTC (Run No. 31) whose alkyl groups each have 5 carbon atoms are also shown in Table 3.

The mineral oil as described above was used as a lubricating base oil. The Zn-DTCs whose lipophilic groups each have 2 and 4 carbon atoms, respectively, were subjected to the complex-forming treatment with succinimide in a high concentration (heating treatment in a high concentration) in advance and then used. In Table 3, the term "Added amount of active ingredient" means the proportion of Zn-DTP or Zn-DTC as a anti-wear agent in the mineral oil composition. The contents of the ashless detergent-dispersant (succinimide) in the mineral oil compositions were each controlled to give a concentration of 3.0 wt.%.

The results are shown in Table 3.

Table 3

Run No.	Base oil	anti-wear agent	Added amount of AI*1 wt.%	Initial seizure load Kg	welding load Kg	Complex-forming treatment
29	M*2 oil	Commercial Zn-DTP (i-C ₃ /s-C ₆)	0.5	63	200	Not conducted
30			1.0	80	250	Not conducted
31		Commercial Zn-DTC (n-C ₅)	0.5	63	200	Not conducted
32		C ₂ Zn-DTC	0.5	80	250	Conducted
33		n-C ₄ Zn-DTC	0.5	63	250	Conducted

*1: Active ingredient.

*2: Mineral oil.

As apparent from Table 3, it is understood that the lubricating oil compositions (Run Nos. 32-33) according to the present invention have extreme-pressure characteristics identical with or better than the

lubricating oil composition containing the commonly used Zn-DTP.

Example 4:

5 With respect to lubricating oil compositions according to the present invention, coking resistance and oxidation stability were evaluated. The lubricating oil compositions to be tested were each prepared by adding Zn-DTP or Zn-DTC and a phenol-based antioxidant (only Run Nos. 38, 39) to a mineral oil and then blending further 4.0 wt.% of a commercially-available viscosity index improver (polyalkylmethacrylate).

10 The mineral oil as described above was used as a lubricating base oil. The Zn-DTCs whose lipophilic groups each have 2 and 4 carbon atoms, respectively, were subjected to the complex-forming treatment with succinimide in a high concentration in advance and then used.

In a test for coking resistance, the contents of the ashless detergent-dispersant (succinimide) in the mineral oil compositions were each controlled to give a concentration of 3.0 wt.%. Further, a metal detergent (overbased calcium sulfonate) was added in a proportion of 3.0 wt.%.

15 In a test for oxidation stability, the contents of the ashless detergent-dispersant (succinimide) in the mineral oil compositions were each controlled to give a concentration of 3.0 wt.%. In Run Nos. 38-39, a phenol-based antioxidant [4,4'-methylenebis-(2,6-di-tert-butylphenol)] was further added.

〈Test for coking resistance〉

20 After a glass capillary (tube) is kept at 290 °C, an oil to be tested and air are passed through the glass capillary for 16 hours. The deposit adhered to the tube after testing is weighed to score the degree of coking on the tube so as to evaluate the oil by a merit rating (10 points = clean).

25 〈Test for oxidation stability〉

Testing Method for Oxidation Stability of Lubricating Oil for Internal Combustion Engine prescribed in JIS K-2514 is followed. Metal pieces of iron and copper and an oil to be tested are placed into a beaker, and the contents are kept for 72 hours at 165.5 °C with stirring. With respect to the test oil after oxidation, 30 the increase in acid number, increase in viscosity, amount of insolubles and degree of corrosion of the metal pieces are evaluated.

〈Corrosion of metal〉

35 The corrosion of the metals is evaluated by visually observing the surface of each metal after testing and rating as "medium" where corrosion is recognized to a considerable extent, "slight" where corrosion is recognized to a slight extent and "none" where no corrosion is recognized.

The results are shown in Table 4. In Table 4, "Added amount" means the proportion of Zn-DTP or Zn-DTC contained as an active ingredient in additives.

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Table 4

Run No.	Base oil	Additive		Coking resistance (290°C)			Oxidation stability (165.5°C x 72 hr)		
		Kind	Added amount of AI*1 wt. %	Deposit mg	Rating	Increase of acid number KOH mg/g	Increase of viscosity %	Insolubles %	Corrosion of metal
34	M*2 oil	Commercial Zn-DTP (i-C ₃ /s-C ₆)	0.5	0.6	9	5.0	46	2.6	Medium
35		n-C ₅ Zn-DTC	0.5	0.5	9	9.1	46	3.7	Slight
36		n-C ₄ Zn-DTC	0.5	0.5	9	9.9	48	3.6	None
37		C ₂ Zn-DTC	0.5	0.5	9	11.1	110	8.9	None
38		n-C ₄ Zn-DTC Phenol-based antioxidant	0.5 0.2	-	-	7.0	44	2.3	None
39		C ₂ Zn-DTC Phenol-based antioxidant	0.5 0.2	-	-	7.0	22	0.7	None

*1: Active ingredient. *2: Mineral oil.

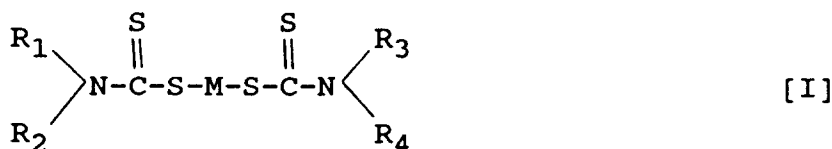
As apparent from Table 4, it is understood that the lubricating oil compositions according to the present invention have excellent functions as to coking resistance and oxidation stability.

INDUSTRIAL APPLICABILITY

According to the present invention, there are provided lubricating oil compositions, which contain very little or no phosphorus and are excellent in anti-wear properties, extreme-pressure characteristics, friction characteristics, oxidation stability, coking resistance, and the like. The lubricating oil compositions according to the present invention permit the solution of the problem of poisoning catalysts for exhaust emission control devices of automobiles, which is caused by phosphorus in Zn-DTP contained in the conventional engine oils, because they exhibit functions such as excellent anti-wear properties even when no Zn-DTP is used, or the amount of Zn-DTP to be used is highly reduced. Therefore, the lubricating oil compositions according to the present invention are suitably used, in particular, as lubricating oils for internal combustion engines of automobiles.

Claims

1. A lubricating oil composition comprising a lubricating base oil, an oil-soluble amine compound and a metal dithiocarbamate represented by the following general formula [I]:



- wherein M means zinc, copper, nickel, iron, cadmium, silver, lead, antimony, tin or bismuth, and R₁, R₂, R₃ and R₄ are, independently of each other, selected from lipophilic groups having 1-13 carbon atoms, the average number of carbon atoms of said four lipophilic groups exceeding 1, but being at most 4.
2. A lubricating oil composition as claimed in claim 1, wherein the four lipophilic groups of the metal dithiocarbamate are alkyl groups each having 2 or 3 carbon atoms.
 3. A lubricating oil composition as claimed in claim 1 or 2, wherein the metal dithiocarbamate is zinc dithiocarbamate.
 4. A lubricating oil composition as claimed in any one of claims 1 through 3, wherein the oil-soluble amine compound is selected from the group consisting of polyalkenyl-succinimide-based ashless detergent-dispersants, alkylbenzylamine-based ashless detergent-dispersants, alkylamines, alkyldiamines and alkylpolyamines.
 5. A lubricating oil composition as claimed in any one of claims 1 through 4, wherein the metal dithiocarbamate represented by the general formula [I] and the oil-soluble amine compound are blended in the lubricating oil composition in proportions of 0.05-1.5 wt.% and 0.1-10 wt.%, respectively.
 6. A lubricating oil composition as claimed in any one of claims 1 through 5, wherein the metal dithiocarbamate represented by the general formula [I] and the oil-soluble amine compound are contained in the form of a complex of both compounds in the lubricating oil composition.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP92/00999

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int. C1 ⁵ C10M141/12/(C10M141/12, C10M133:06, C10M133:44, C10M139:00), C10N10:02, C10N10:04, C10N10:08, C10N10:10, C10N10:16, C10N30:06, C10N30:10		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC	C10M141/00-141/12, 133/00-133/58, 139/00, C10N10:00-10:16, 30:06, 30:10	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	JP, A, 51-111805 (Showa Oil Co., Ltd.), October 2, 1976 (02. 10. 76), Claim (Family: none)	1-6
A	JP, A, 54-113604 (Asahi Denka Kogyo K.K.), September 5, 1979 (05. 09. 79), Claim (Family: none)	1-6
¹⁰ 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 document 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 "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		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
October 16, 1992 (16. 10. 92)	November 10, 1992 (10. 11. 92)	
International Searching Authority	Signature of Authorized Officer	
Japanese Patent Office		