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(54) Title: MOLYBDENUM COMPLEXES CONTAINING LUBRICANT COMPOSITIONS

(57) Abstract

The invention relates to lubricating oil compositions comprising a major amount of an oil of lubricating viscosity and a minor amount of at least one compound containing a heterometallic tetranuclear core, preferably cubane, more preferably thiocubane, having 1, 2 or 3 molybdenum atoms, the other metal atoms being Co, Cr, Cu, Ni, W, Mn, Zn or Fe, preferably Cu, and bonded thereto ligands capable of rending the compound oil–soluble or oil–dispersible. The formulated lubricating oil has enhanced friction reducing and anti–wear properties.

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MOLYBDENUM COMPLEXES CONTAINING LUBRICANT COMPOSITIONS

The present invention relates to lubricant compositions and a method of making them.

BACKGROUND OF THE INVENTION

Molybdenum disulfide is a known lubricant additive. Unfortunately, it has certain known disadvantages some of which are caused by its insolubility in lubricating oils. Therefore, certain oil-soluble molybdenum sulfur-containing compounds have been proposed and investigated as lubricant additives. U.S.-A-2,951,040, -3,419,589; -3,840,463; -4,966,719; -4,995,966; and -4,978,464 are illustrative of descriptions of oil-soluble molybdenum compounds and their preparation.

U.S.-A-4,705,641 describes the mixture of certain copper salts and molybdenum salts in a basestock as antioxidants and antiwear agents and Shibahara, Coord. Chem. Rev. 123, 730148 (1993) discloses certain molybdenum and heteronuclear compounds. U.S.-A- 4,730,064 describes mixed copper-molybdenum complexes. However, none of the above describes the uses or benefits of copper/molybdenum/sulfur complexes in lubrication.

There is a continuing need for additives that demonstrate enhanced lubricating properties, particularly friction reduction and/or anti-wear, and antioxidancy and that are compatible with existing additive packages. The present invention addresses this need.

SUMMARY OF THE INVENTION

In a first aspect, the invention is a lubricating oil composition comprising, or made by mixing, a major amount of an oil of lubricating viscosity and, as an additive, a minor amount of at least one compound containing a heterometallic tetranuclear core having 1,2 or 3 molybdenum atoms, the other metal atoms being Co, Cr, Cu, Ni, Mn, W, Zn or Fe, and bonded thereto ligands capable of rendering the compound oil-soluble or oil-dispersible. Preferably, the core is a cubane core, optionally including S atoms in a thiocubane core.

Additionally, oxygen and selenium can substitute for sulfur in the core of many of these compounds.

The tetranuclear compounds are useful in formulating lubricating oil compositions having enhanced lubricating (i.e., friction reducing and anti-wear) properties.

In a second aspect, the invention is a method for preparing a compound as defined in the first aspect of the invention and which has a thiocubane core, which method comprises reacting a mono-, di- or tri- molybdenum source, a source of said other metal atoms, and a source of said ligands, e.g. in a liquid medium, to form said compound.

The present invention also provides in a third aspect, a method of lubricating mechanical engine components particularly an internal combustion engine by adding an oil of lubricating viscosity containing at least one compound as defined in the first aspect of the invention and operating the engine.

Also included, in a fourth aspect, is an additive concentrate for blending with lubricating oils, comprising an oleagenous carrier with one or more additives including an additive as defined in the first aspect of the invention, whereby the concentrate contains from 1 to 90 weight percent, such as 1 to 50 based on the weight of the concentrate of the additive.

Further included, in a fifth aspect, is use of an additive as defined in the first aspect of the invention for enhancing one or more lubricating properties of a lubricating oil composition.

Preferred compounds have a thiocubane core, and are of the formula $M_{4-y}Mo_yS_4L_nQ_z$, and mixtures thereof, wherein M represents Co, Cr, Cu, Ni, Mn, W, Zn or Fe, L represents independently selected ligands, Q represents neutral electron donating compounds, y is in the range from 1 to 3 preferably 2 to 3, and n is in the range from 2 to 6 and z is in the range from 0 to 4. Preferred thiocubane cores contain Cu and Mo and the more preferred cores have the formula Cu Mo_3S_4 and $CuMo_2S_4$. The compounds are oil-soluble or dispersible.

The lubricant compositions of this invention demonstrate enhanced lubricating properties, particularly antiwear and friction-reducing properties, and are compatible with other additives used in formulating commercial lubricating compositions.

DETAILED DESCRIPTION OF THE INVENTION

• OIL OF LUBRICATING VISCOSITY

The lubricant compositions of the present invention include a major amount of oil of lubricating viscosity. This oil may be selected from vegetable, animal, mineral or synthetic oils. The oils may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gas engine oil, mineral lubricating oil, motor vehicle oil, and heavy duty diesel oil. The oils may be unrefined, refined and re-refined. In general, the viscosity of the oil will range from 2 centistokes to 30 centistokes and especially in the range of 5 centistokes to 20 centistokes at 100°C.

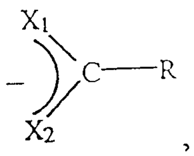
• COMPOUND

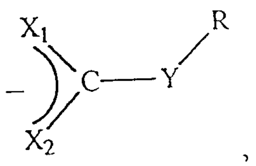
The minor amount of the compound should be an effective amount to produce the enhanced lubricating performance, particularly friction reducing and/or antiwear properties in the oil. The lubricant compositions may include a mixture of the compounds containing the heterometallic tetranuclear cores of the types disclosed herein, the lubricating oil and/or any other additives per se, and/or of any intermediates and reaction products occurring as a result of the mixture.

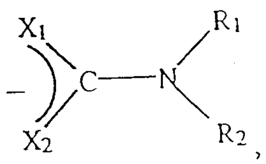
In the compounds of the formula $M_{4-y}Mo_yS_4L_nQ_z$, and mixtures thereof, defined above, M is preferably Cu; L preferably represent independently selected, preferably monoanionic, ligands having organo, preferably hydrocarbyl, groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil; and Q preferably represents water, amines, alcohols, phosphines, and ethers. For example, when the compound is a dicopper-dimolybdenum sulfur complex, M is Cu, y is 2, n is 4 and z is 2 and, when the compound is a monocopper trimolybdenum sulfur compound, M is Cu, y is 3, n is 5 and z ranges from 0 to 1.

The ligands, or ligands L, may be independently selected from the group of:

—X—R,







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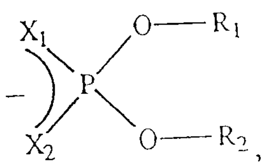
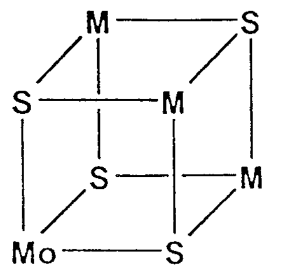


and mixtures thereof, wherein X, X_1, X_2, and Y are independently selected from the group of oxygen and sulfur, and wherein R_1, R_2, and R are independently selected from the group consisting of hydrogen and organo, groups that may be the same or different. Preferably the organo groups are hydrocarbyl groups such as alkyl, (e.g., in which the carbon atom attached to the remainder of the ligand is primary, secondary, tertiary) aryl, substituted aryl and ether groups. More preferably, all ligands are the same. Importantly, the organo groups of the ligands have a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil. The compound's oil solubility or dispersibility may be influenced by the number of carbon atoms in the ligands. In the compounds in the present invention, the total number of carbon atoms present among all of the organo groups of the compounds' ligands typically will be at least 21, such as at least 25, at least 30, or at least 35. Preferably the ligand source chosen has a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil. For example, the number of carbon atoms in each alkyl group will generally range between about l to 100, preferably l to 40 and more preferably between 3 to 20. Preferred ligands include dialkyldithiophosphate ("ddp"), xanthates, thioxanthates, and dialkyldithiocarbamate ("dtc"), and of these dialkyldithiocarbamate is more preferred.

Organic ligands containing at least two of the above functionalities are also capable of binding to at least one of the cores and serving as ligands. The ligands may be multidentate. Without wishing to be bound by any theory, it is believed that one or more cores may be bound or interconnected by means of at least one multidentate ligand. This includes the case of a multidentate ligand having multiple connections to one core. Such structures fall within the scope of this invention. Those skilled in the art will recognize that formation of the compounds requires selection of ligands having the appropriate charges to balance the core's charge.

The term "hydrocarbyl" denotes a substituent having carbon atoms directly attached to the remainder of the ligand and is predominantly hydrocarbyl in character within the context of this invention. Such substituents include the following: (1) hydrocarbon substituents, that is, aliphatic (for example alkyl or alkenyl), alicyclic (for example cycloalkyl or cycloalkenyl) substituents, aromatic-, aliphatic and alicyclicsubstituted aromatic nuclei and the like, as well as cyclic substituents wherein the ring is completed through another portion of the ligand (that is, any two indicated substituents may together form an alicyclic group); (2) substituted hydrocarbon substituents, that is, those containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbyl character of the substituent. Those skilled in the art will be aware of suitable groups (e.g., halo, especially chloro and fluoro, amino, alkoxyl, mercapto, aikylmercapto, nitro, nitroso, sulfoxy, etc.); (3) hetero substituents, that is, substituents which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms,

Compounds having the formula $M_{4-y}Mo_yS_4L_nQ_z$ useful as additives in the present invention are believed to have at least one cubane, preferably thiocubane core of the formula $M_{4-y}Mo_yS_4$ surrounded by ligand, wherein M, y and k, L_n, and Q_z, are as previously defined. The cubane cores are illustrated by the structures:



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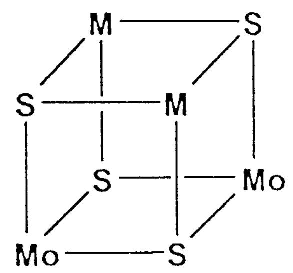

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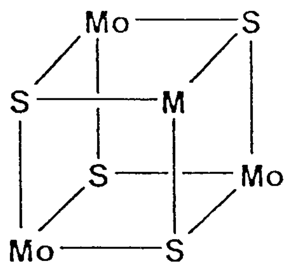
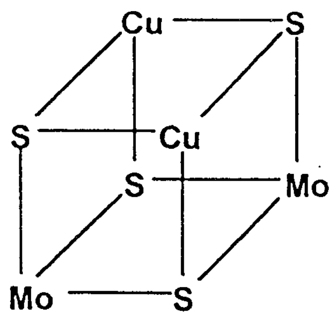
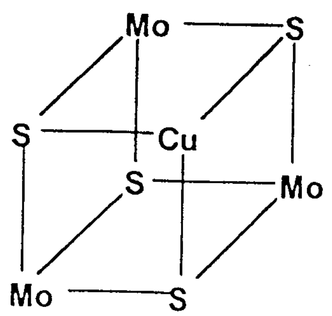


wherein M is selected from the metals described previously.

When M is Cu the preferred cores are illustrated by the following structures:



for the $Cu_2Mo_2S_4$ core; and



for the Cu Mo_3S_4 core.

The compounds useful as additives in the present invention can be prepared generally as follows:

Oil-soluble or dispersible tetranuclear thiocubane compounds can be prepared by reacting a molybdenum source with a source of a non-molybdenum metal ("M' as defined above) component(s), for example, in suitable liquid(s)/solvent(s); if desired, additional ligands can be included in the reaction or added once an initial complex is formed. For example, tetranuclear thiocubane compounds with three molybdenum atoms may be synthesized by reacting a trinuclear molybdenum source such as Mo_3S_4 $(dtc)_4$ with a nonmolybdenum metal ("M" wherein M is as described above) source such as CuCl followed by ligand substitution with a ligand such as a thiolate. Similarly, a tetranuclear thiocubane compounds with two molybdenum atoms may be synthesized by reacting a dinuclear molybdenum source such as $Mo_2S_4(dtc)_2$ with a non-molybdenum metal ("M" as described above) source such as CuCl followed by ligand substitution with a ligand such as a carboxylate. Tetranuclear thiocubane compounds with one molybdenum atom may be synthesized by reacting a molybdenum source such as $Mo(C0)_6$ with a nonmolybdenum metal ("M" as described above) source such as $M_3S_4(dtc)_4$ and a ligand source such as thiuram disulfide. Suitable liquid(s)/solvent(s) may be, e.g., aqueous or organic.

In general, the compounds can be purified by well known techniques such as chromatography; however, it may not be necessary to purify the compounds.

The lubricating compositions contain minor effective amounts, preferably ranging from I ppm to 2000 ppm molybdenum from the compounds containing the heterometallic tetranuclear core (of the types described previously), such as 5 to 1000, preferably 20 to 1000, more preferably 5 to 750 ppm, most preferably 10 to 300 ppm, all based on the weight of the lubricating composition. For example, with the copper molybdenum sulfur-containing compounds, the enhancement in lubricating performance can be seen at concentrations of Cu from the heterometallic tetranuclear core-containing compounds (of the types described previously) of at least I ppm to 1000 ppm, preferably I to 200 ppm. Within the above ranges one skilled in the art can select the particular combination of amounts desired to produce the enhancement in antioxidancy and lubricating properties (friction reduction and/or anti-wear), desired for the particular application. The selection within these ranges may be accomplished to optimize for enhanced antioxidancy, friction reducing or anti-wear performance or all three.

These benefits can be achieved in basestock as well as fully formulated lube oils. Essentially or substantially phosphorous free and/or sulfur free oils also may be treated. A lubricating composition that is essentially or substantially free of phosphorus and/or sulfur is one in which the amount of phosphorus and/or sulfur is not more than is inherently present in base oils of lubricating viscosity.

The lubricating oil compositions of the present invention may be prepared by combining a major amount of an oil of lubricating viscosity and an effective minor amount of compounds containing the heterometallic tetranuclear cores which are described more specifically above. This preparation may be accomplished by admixing the complex directly with the oil or by first combining the complex in a suitable carrier fluid to achieve oil solubility or dispersibility, then adding the mixture to the lubricating oil.

Concentrates of the compounds in a suitable oleagenous, preferably hydrocarbon, carrier provide a convenient means of handling the compounds before their use. Oils of lubricating viscosity, such as those described above, as well as aliphatic, naphthenic, and aromatic hydrocarbons are examples of suitable carrier fluids for the concentrates. These concentrates may contain I to 90 weight percent of the compound based on the weight of concentrate, such as 1 to 50; preferred is I to 70 weight percent, more preferably, 20 to 70 weight percent.

The lubricating oil compositions made by combining an oil of lubricating viscosity herein and at least one compound containing a heterometallic tetranuclear, preferably cubane, core of the types and in the amounts described herein may be used to lubricate mechanical engine components, particularly an internal combustion engine by adding the lubricating oil composition thereto.

The terms "oil-soluble" or "dispersible" used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or capable of being suspended in the oil in all proportions. These do mean, however, that they are, for instance, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

Advantageously, the use of a compound containing the heterometallic tetranuclear cores as described in the present invention, may decrease the need for the use of separate metal, e.g., copper and molybdenum additives, thus providing an opportunity to decrease attendant blending and related costs.

Known lubricant additives may also be used for blending in the lubricant compositions of this invention. These include, for example, those containing phosphorous, dispersants, detergents, e.g., single or mixed metal, pour point depressants, viscosity improvers, antioxidants, surfactants, other friction modifiers, and antiwear agents. These can be combined in proportions known in the art.

It will be understood that the various components of the composition, the essential components as well as the optional and customary components, may react under the conditions of formulation, storage, or use, and that the invention also provides the product obtainable or obtained as a result of any such reaction .

EXAMPLES

The invention will be more fully understood by reference to the following examples illustrating various modifications of the invention which should not be construed as limiting the scope thereof.

As used herein "coco" is an alkyl chain or mixtures of chains of varying even numbers of carbon atoms, typically of from C8 to C18.

The procedures and equipment used for the Falex Block-On-Ring tests herein were similar to those used in ASTM G77-83 (Ranking Resistance of Materials to Sliding Wear Using Block-On-Ring Wear Test).

Example 1: Synthesis of $Cu_2Mo_2S_4(coco_2dtc)_2(dodecylthiolate)_2$

Copper (I) chloride (0.2 g, 2 mmol) and $Mo_2S_4(coco_2dtc)_2$ (1.2 g, I mmol) were mixed together in a 1: 1 solution of dichloromethane and methanol (total volume, 50 mL) and stirred at room temperature for eight hours. A methanol solution (25 mL) of potassium dodecylthiolate (0.51 g, 2 mmol) was then added to the copper-molybdenum containing solution. Additional dichloromethane (50 mL) was added to the flask and the solution was stirred for 24 hours. The dichloromethane was distilled and the methanol decanted. The tarry material at the bottom of the flask was dissolved in pentane, filtered, and dried under vacuum to yield $Cu_2Mo_2S_4(coco_2dtc)_2$ $(dodecylthiolate)_2$.

Example 2: Synthesis Of $Cu_2Mo_2S_4(coco_2dtc)_2$(oleate)2

Copper (I) chloride (0.2 g, 2 mmol) and $Mo_2S_4(coco_2dtc)_2$ (1.2 g, I mmol) were mixed together in a 1:1 solution of dichloromethane and methanol (total volume, 50 mL) and stirred at room temperature for eight hours. A methanol solution (25 mL) of potassium oleate (0.67 g, 2 mmol) was then added to the copper- molybdenum containing solution. Additional dichloromethane (50 mL) was added to the flask and the solution was stirred for 24 hours. The dichloromethane was distilled and the methanol decanted. The tarry material at the bottom of the flask was dissolved in pentane, filtered, and dried under vacuum to yield $Cu_2Mo_2S_4(coco_2dtc)_2(oleate)_2$.

Example 3: Synthesis of $CuMo_3S_4(octyl_2dtc)_4(thiolate)$

Copper (I) chloride (0. I g, I mmol) and $Mo_3S_4(octyl_2dtc)_4$ (1.68 g, I mmol) were added to tetrahydrofuran ("THF") (50 mL), stirred at room temperature for 24 hours, and the reaction was filtered. A methanol solution (10 mL) of potassium dodecylthiolate (0.25 g, I mmol) was then added to the copper-molybdenum filtrate. The combined solution was stirred for eight hours, after which the THF was distilled, the tar redissolved in pentane, the solution filtered, and the pentane distilled to yield $CuMo_3S_4(octyl_2dtc)_4(thiolate)$.

Example 4: Synthesis $CuMo_3S_4(octyl_2ddp)_4(thiolate)$

Copper (I) chloride (0. I g, I mmol) and $Mo_3S_4(octyl_2ddp)_4$ (1.83 g, I mmol) were added to THF (50 mL), stirred at room temperature for 24 hours, and the reaction was filtered. A methanol solution (10 mL) of potassium dodecylthiolate (0.25 g, I mmol) was then added to the copper-molybdenum filtrate. The combined solution was stirred for eight hours, after which the THF was distilled, the tar redissolved in pentane, the solution filtered, and the pentane distilled to yield $CuMo_3S_4(octyl_2ddp)_4(thiolate)$.

In Examples 5 to 8 the compounds in the invention were evaluated for friction and wear performance in a Falex Block-On-Ring test procedure. The data were acquired at a speed of 420 rpm (44 radians/sec), 220 lb. (100 kg), and a temperature of 100°C for 2h. In Examples 5 -9 the samples tested consisted of temperature of 100°C for 2h. In Examples 5 -9 the samples tested consisted of Solvent 150 Neutral (S15ON) lubricating oil, l% zinc dialkyldithiophosphate ("ZDDP"), and the additive compounds containing 500 ppm molybdenum based on the total weight of the lubricating oil. Friction coefficients are reported as both the end of run value and the average value over the entire 2 hours. Data reported included the block wear scar volume, measured by profilometry, the end of test friction coefficient ("Last Coef"), and the average friction coefficient ("Avg. Coef") obtained over the 2 hour test. The end of test friction coefficient is that friction coefficient determined at the end of the test period and the average friction coefficient provides information on the activity of the added material, i.e., samples that attain the same low friction coefficients faster are considered to contain more active, friction-reducing compounds.

Example 9 (Comparative)

For comparative purposes, the Falex Block-On-Ring was conducted using only Solvent 150 Neutral (S15ON) and 1% ZDDP. The results are shown in Table 1.

TABLE I

SI5ON + 1% ZDDP + Additive (at 500 ppm Mo)

Test Run	Additive	Wear Vol. ($10^{-}2mm^3$)	Last Coef	Avg. Coef
Ex. 5	$Cu_2Mo_2S_4(coco_2dtc)_2(dodecylthiol)_2$	0.85	0.042	0.051
Ex. 6	$Cu_2Mo_2S_4(coco_2dtc)_2(oleate)2$	0.84	0.035	0.046
Ex. 7	$CuMo_3S_4(octyl_2dtc)_4(dodecylthiol)$	1.65	0.044	0.055
Ex 8.	$CuMo_3S_4(octyl_2ddp)_4(dodecylthiol)$	2.37	0.053	0.074
Ex. 9	None	1.06	0.111	0.112

In Examples l0 to 12 the compounds were evaluated for friction and wear performance in a Falex Block-On-Ring test procedure. The data were obtained at a speed of 420 rpm (44 radians/sec), 220 lb. (100 kg), and a temperature of 100°C for 2h. In Examples 5-9 the samples tested consisted of 10W30 fully formulated motor oil, combined with the additive compounds containing 500 ppm molybdenum based on the total weight of the lubricating oil.

Example 13 (Comparative)

For comparative purposes, the Falex Block-On-Ring test was conducted using a 10W30 fully formulated motor oil. The results are shown in Table II.

TABLE II

10W30 + Additives (at 500 ppm Mo)

Test Run	Additive	Wear Vol. ($10^{-2}mm^3$)	Last Coef	Avg. Coef
Ex. 10	$Cu_2Mo_2S_4(coco_2dtc)_2(dodecylthiol)_2$	0.91	0.034	0.042
Ex. 11	$Cu_2Mo_2S_4(coco_2dtc)_2$(oleate)2	0.76	0.035	0.041
Ex. 12	$CuMo_3S_4(octyl_2dtc)_4$(dodecylthiol)	1.76	0.029	0.038
Ex. 13	None	2.86	0.132	0.130

CLAIMS

1. A lubricating oil composition comprising, or made by mixing, a major amount of an oil of lubricating viscosity and, as an additive, a minor amount of at least one compound containing a heterometallic tetranuclear core having 1,2 or 3 molybdenum atoms, the other metal atoms being Co, Cr, Cu, Ni, Mn, W, Zn or Fe, and bonded thereto ligands capable of rendering the compound oil-soluble or oil-dispersible.

2. The composition of claim 1 wherein the core is a cubane core, optionally including S atoms in a thiocubane core.

3. The composition of any of the preceding claims wherein the compounds have the formula $M_{4-y}Mo_yS_4L_nQ_z$ thereof, wherein M represents Co, Cr, Cu, Ni, Mn, W, Zn or Fe;

L represents independently selected ligands;

Q represents neutral electron-donating compounds;

y is in the range from 1 to 3;

n is in the range from 2 to 6; and

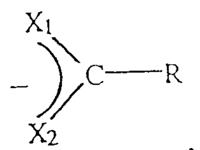
z is in the range from 0 to 4.

4. The composition of claim 3 wherein the formula is Cu $Mo_3S_4L_z$ or $Cu_2Mo_2S_4L_4Q_z$

wherein L, Q and z are defined as in claim 3.

5. The composition of claim 3 or claim 4 wherein the ligands, or ligands L, are represented by at least one structure having the formula:

—X—R,



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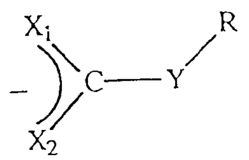

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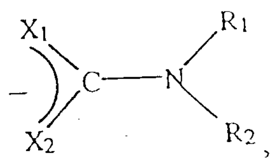

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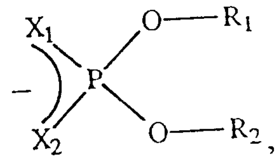


wherein X, X_1, X_2 and Y are oxygen or sulfur and wherein R^1, R^2, and R independently represent hydrogen atoms or organo groups, such as hydrocarbyl groups.

6. The composition of claim 5 wherein the organo groups independently represent alkyl, aryl, substituted aryl, or ether groups.

7. The composition of claim 6 wherein the organo groups are alkyl groups each having from 1 to 100, for example 1 to 40, such as 3 to 20, carbon atoms.

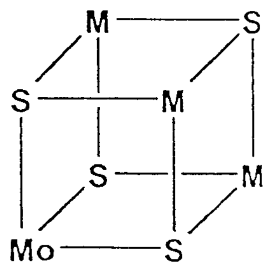
8. The composition of any of claims 5 to 7 wherein the total number of carbon atoms in all ligands' organo groups is at least 21, such as 21 to 800.

9. The composition of any of the preceding claims wherein the ligands are or L independently represents dialkyldithiophosphate, thioxanthate, dialkylphosphate, dialkyldithiocarbamate, dialkylthiophosphate, or zanthate ligands.

10. The composition of any preceding claim wherein the weight of Mo from the compound(s) is at least 1 ppm, for example, 1 to 2000 ppm Mo such as 5 to 1000 preferably 20 to 1000, based on the weight of the lubricating oil composition.

11. The composition of claim 10 wherein the Mo is present in an amount of 5 to 750 ppm Mo based on the weight of the lubricating oil composition.

12. The composition of any of claims 2 to 11 wherein the thiocubane core is represented by the structure:



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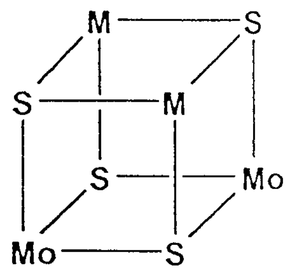
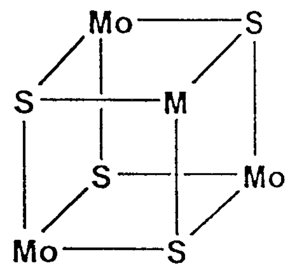


or



wherein M is defined as in claim 3.

13. The composition of any preceding claim further comprising one or more dispersants, detergents, pour point depressants, viscosity modifiers surfactants, antiwear agents and antioxidants.

14. An additive concentrate for blending with an oil of lubricating viscosity, comprising or made by mixing, an oleaginous carrier and from 1 to 200,000 ppm by weight, for example 50 to 150,000 such as 50 to 100,000, of the

molybdenum of an additive as defined in any of claims 1 to 12, based on the weight of the concentrate.

15. An additive concentrate for blending with an oil of lubricating viscosity comprising or made by mixing, an oleaginous carrier with one or more additives including an additive as defined in any of claims 1 to 12, whereby the concentrate contains from 1 to 90 weight percent, such as 1 to 50, of additives based on the weight of the concentrate.

16. A method for lubricating an internal combustion engine comprising operating the engine and lubricating the engine with a lubricating oil composition as claimed in any of claims 1 to 13.

17. The use of an additive or additives as defined in any of claims 1 to 12 for enhancing one or more lubricating properties of a lubricating oil composition.

18. A method for preparing a compound as defined in claim 1, and which has a thiocubane core, which method comprises reacting a mono-, di- or tri-molybdenum source, a source of said other metal atoms, and a source of said ligands to form said compound.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/07135

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10M159/18 C07F11/00 C10M135/18 C10M137/10 //C10N10:02, 10:04,10:12,10:14,10:16,30:06,40:25

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)
IPC 6 C10M C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, 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.
A	EP 0 417 972 A (EXXON RESEARCH ENGINEERING CO) 20 March 1991 cited in the application see abstract see page 2, line 30 - page 3, line 19 see claims 1-12	1-18
X	US 4 730 064 A (HALBERT THOMAS R ET AL) 8 March 1988 cited in the application	18
A	see abstract see figure 2 see column 2, line 18 - line 36 see column 2, line 51 see column 2, line 54 - column 3, line 5 see column 3, line 15 - line 21 see examples 5,6	1-17

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"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

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"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
9 April 1998	24.04.98
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Perakis, N

INTERNATIONAL SEARCH REPORT

...formation on patent family members

Intern   ial Application No
PCT/EP 97/07135

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0417972 A	20-03-91	US 4978464 A	18-12-90
		CA 2023201 A	08-03-91
		JP 3100098 A	25-04-91
US 4730064 A	08-03-88	EP 0319624 A	14-06-89
		JP 1143879 A	06-06-89