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**ORGANIC MOLYBDENUM COMPOUNDS  
CONTAINING SULFUR AND METHOD  
OF PREPARATION**

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No Drawing. Filed Oct. 1, 1965, Ser. No. 492,289  
20 Claims. (Cl. 260-429)

**ABSTRACT OF THE DISCLOSURE**

A process for the preparation of molybdenum (VI) dialkyldithiocarbamate complexes and sulfurized derivatives thereof in substantially high yields by the dilute nitric acid acidification of alkali dialkyldithiocarbamates and alkali molybdates and the subsequent treatment thereof with hydrogen sulfide to form the sulfurized derivatives of the reaction product. These compounds have utility as additives for lubricants.

The invention relates generally to novel lubricant additives and methods of preparing the same. More particularly, the invention is concerned with organic, sulfur containing molybdenum compounds and their preparation.

The beneficial properties of molybdenum disulfide ( $\text{MoS}_2$ ) as a lubricant or additive are well known in the art. However, molybdenum disulfide has certain disadvantages, for example, it is generally insoluble in lubricating oils and in certain instances difficult even to suspend in the oils. The present invention avoids these disadvantages by way of the discovery of certain organic molybdenum compounds and methods by which these compounds can be prepared in good yields. These organic molybdenum compounds contain sulfur and are readily suspendable or soluble in most lubricants. The method of using the compounds enables their operation in such a fashion as to still take advantage of the lubricating properties of molybdenum disulfide in that the compounds react with other constituents in the lubricants or within themselves to form a molybdenum sulfide film. This formation of molybdenum sulfide takes place at high temperatures and/or pressures resulting generally in the presence of molybdenum sulfide only at the place of contact between the mating surfaces of the parts to be lubricated. That is, the contact between the mating surfaces causes high temperatures and/or pressures resulting in formation of molybdenum sulfide at the place of contact where it is most needed. This in return allows a more practical use of the lubricant additive.

It is therefore an object of this invention to provide new molybdenum (VI) dioxide dialkyldithiocarbamates which are useful as lubricant additives.

Another object is to provide certain new materials useful as lubricant additives, which materials are obtained by the treatment of molybdenum (VI) dialkyldithiocarbamates with hydrogen sulfide.

A further object is to provide novel methods for the preparation and isolation of the molybdenum (VI) dioxide dialkyldithiocarbamates, and the hydrogen sulfide treated molybdenum (VI) dialkyldithiocarbamates, thereby enabling their preparation in substantially high yields of commercial practicability.

Still another object of this invention is to provide lubricant compositions utilizing the new lubricant additives such that their lubricating properties can be taken advantage of in an effective manner.

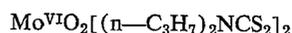
Other objects of the present invention will become apparent to those skilled in the art upon a reading of the fol-

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lowing description taken in conjunction with the specific examples provided for illustrative purposes.

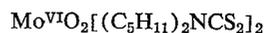
The hexavalent (VI) molybdenum compounds or complexes of the present invention are termed molybdenum (VI) dioxide dialkyldithiocarbamates and certain materials believed to be thiomolybdates formed by hydrogen sulfide treatment of these molybdenum (VI) dioxide dialkyldithiocarbamates.

One of the complexes is molybdenum (VI) dioxide di-n-propyldithiocarbamate, the formula for which is:



The material is prepared by dilute nitric acid acidification of sodium dipropyldithiocarbamate and sodium molybdate. The dipropyldithiocarbamate can be conveniently prepared by adding a slight excess of carbon disulfide to an equimolar, aqueous suspension of di-n-propylamine and sodium hydroxide. After stirring for a period sufficient to permit reaction, such as for example, one hour, the mixture is filtered giving a clear, light yellow solution of sodium di-n-propyldithiocarbamate. The sodium di-n-propyldithiocarbamate is reacted with sodium molybdate in the proportion of about 1.5 moles to about 2 moles of the sodium di-n-propyldithiocarbamate per mole of sodium molybdate. The reaction is carried out in an aqueous liquid phase by dissolving the constituents, and thereafter acidifying with dilute nitric acid in an amount of about 2 moles to about 4 moles of diluted  $\text{HNO}_3$  per mole of sodium molybdate. The unusual discovery was made that this acidification step was critical in preparing the molybdenum (VI) dioxide dialkyldithiocarbamates, and that other acids produced molybdenum (V) complexes and/or poor yields, whereas when dilute nitric acid was used to carry out the acidification step at a temperature range of from about  $0^\circ\text{C}$ . to about  $25^\circ\text{C}$ ., high yields were obtained. The nitric acid is preferably introduced as a dilute solution of a more concentrated form ranging from about 1% to about 10% by weight. The nitric acid solution is slowly added to an agitated mixture of the sodium molybdate and sodium di-n-propyldithiocarbamate. The crude product from the acidification reaction can be readily recovered from the aqueous reaction medium, for example, by extracting with an organic solvent, such as chloroform, benzene or the like, and thereafter precipitating the extracted product to yield a relatively pure orange crystalline product of  $\text{Mo}^{\text{VI}}\text{O}_2[(n-\text{C}_3\text{H}_7)_2\text{NCS}_2]_2$ . The crystalline solids product is air-stable and melts at  $110.0-110.5^\circ\text{C}$ . It is readily soluble in aromatic and most polar organic solvents, but insoluble in water and aliphatic hydrocarbons. It can be suspended as a lubrication additive in SAE-90 base gear oil by heating a mixture of the  $\text{Mo}^{\text{VI}}[(n-\text{C}_3\text{H}_7)_2\text{NCS}_2]_2$  and the oil to  $130^\circ\text{C}$ ., resulting in a suspension wherein negligible settling occurs after two weeks.

Another embodiment of the invention, the molybdenum (VI) dioxide diamyldithiocarbamate, has the formula:



This material is prepared by the nitric acid acidification of sodium diamyldithiocarbamate and sodium molybdate. The diamyldithiocarbamate can be conveniently prepared in the following manner: A commercial grade diamylamine in solution with NaOH is reacted with carbon disulfide to make the sodium salt, sodium diamyldithiocarbamate, which is put in aqueous solution with sodium molybdate and then acidified with dilute nitric acid, thereby producing a crude product including pentavalent molybdenum compounds in the form of a purple tar precipitate. The crude product is extracted with an organic solvent such as toluene, and the resultant solution is subjected to further oxidation to convert the pentavalent molybdenum

compound to the hexavalent state. For this purpose, oxidizing agents of the type, including t-butyl hydroperoxide, t-butyl peroxide, or cumene hydroperoxide can be employed. The oxidizing agent is used in an amount of from about 0.2 to about 0.5 mole per mole of total molybdenum present. For example, a toluene solution of the purple tar is then carefully oxidized with t-butyl hydroperoxide to give a solution of the hexavalent complex which is orange in color. Isolation of the product is then achieved by extraction with aromatic hydrocarbons and precipitation in cold petroleum ether. The product is a dark orange tar. Infrared spectrum shows it to be a molybdenum (VI) complex.

A further embodiment of the invention is molybdenum (VI) dioxide di-2-ethylhexyldithiocarbamate having the formula:



This material is again prepared by nitric acid acidification of sodium di-2-ethylhexyldithiocarbamate and sodium molybdate. The sodium di-2-ethylhexyldithiocarbamate can be conveniently prepared by adding carbon disulfide to an aqueous suspension of di-2-ethylhexylamine and sodium hydroxide. This mixture is filtered to obtain a solution, milky white in color. An aqueous solution of sodium molybdate is added to this filtrate. After cooling, the mixture is acidified with a cold solution of dilute nitric acid (temperature range, about 0° C. to about 10° C.) to give a purple suspension and purple tar product. The complex is then extracted with a solvent such as benzene and oxidized with an oxidizing agent of the type such as t-butyl hydroperoxide, t-butyl peroxide or cumene hydroperoxide. The product  $\text{Mo}^{\text{VI}}\text{O}_2[(\text{C}_8\text{H}_{17})_2\text{NCS}_2]_2$  is then precipitated from petroleum ether, and further recovery is effected by vacuum evaporation. The product is soluble in aromatic solvents, 10 percent soluble in ligroine at room temperature, and stable to storage. The product gives stable suspensions when added to gear oil as a ligroine solution.

With respect to the variables involved in the process of preparing the molybdenum (VI) dioxide dialkyldithiocarbamates, the following ranges or proportions have been found suitable for the purpose of performing the invention. The nitric acid acidification can be carried out within the temperature range of about minus 5° C. to about 50° C. However, best results were obtained when the acidification was carried out within a preferred temperature range of about 0° C. to about 25° C. The molar ratio of nitric acid to sodium molybdate in the acidification can vary from about 1:1 to about 6:1, with the preferred molar ratio being about 2:1 to about 4:1 within which the most suitable results are obtained. The nitric acid is introduced as a dilute solution prepared from a more concentrated nitric acid, said solution having an  $\text{HNO}_3$  content of about 1% to about 10% by weight.

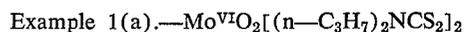
The molar ratio of the sodium dialkyldithiocarbamate to sodium molybdate may vary within the range of about 1:1 to about 5:1. Best results were obtained at a preferred molar ratio of about 1.5:1 to about 2.0:1.

With respect to the strong oxidizing agent used in the preparation of molybdenum (VI) dioxide dialkyldithiocarbamates wherein the alkyl group contains four or more carbon atoms, oxidizing agents of the type t-butyl peroxide, t-butyl hydroperoxide or cumene hydroperoxide have been found suitable. In carrying out the oxidation, the ratio of the moles of oxidizing agent present to the total moles of molybdenum present may vary from a molar ratio of about 0.1:1 to about 1:1. However, best results have been obtained when a preferred molar ratio is used of about 0.2:1 to about 0.5:1.

It is also contemplated within the scope of the present invention that the molybdenum (VI) dioxide dialkyldithiocarbamate complexes can be subjected to further treatment with hydrogen sulfide to effect conversion thereof to what is believed to be a corresponding thiomolybdate complex. This is carried out by contacting a solution of the

molybdenum dialkyldithiocarbamate with  $\text{H}_2\text{S}$  for a period of time sufficient to effect a replacement of an oxygen atom with a sulfur atom. An embodiment of the invention in this regard is the material formed by hydrogen sulfide treatment of molybdenum (VI) dioxide di-2-ethylhexyldithiocarbamate. This complex in a solution of benzene is reacted with  $\text{H}_2\text{S}$  by bubbling  $\text{H}_2\text{S}$  through the solution. The product in good yield is recovered by vacuum evaporation resulting in a purple-black, fluid tar. This product, believed to be a thiomolybdate, is soluble in most organic solvents and is 50 percent soluble in ligroine at room temperature. It is readily suspendable in SAE-90 gear oil, which suspension is stable. The formula of this product is believed to be  $\text{MoOS}[(\text{C}_8\text{H}_{17})_2\text{NCS}_2]$ .

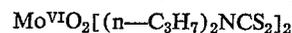
Satisfactory methods of preparing the compounds of the invention will now be described by way of examples. It should be understood that these examples are provided by way of further illustration, and they should not be construed as limiting the scope of the present invention as set forth in the subjoined claims.



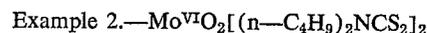
The molybdenum (VI) dioxide di-n-propyldithiocarbamate was prepared as follows: A solution of sodium di-n-propyldithiocarbamate was made by adding a slight excess of carbon disulfide to an equimolar, aqueous suspension of di-n-propylamine (0.060 g. mole) and sodium hydroxide. This solution was stirred for one hour, then filtered to obtain a clear, light yellow solution of sodium di-n-propyldithiocarbamate (0.060 g. mole) which was used immediately by placing it in solution with sodium molybdate dihydrate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , 0.041 g. mole) and 250 ml. of water. This solution was then acidified by the careful addition of dilute nitric acid, at a temperature range of 0° C. to 5° C., with 209 ml. of an acid solution containing 0.13 g. mole  $\text{HNO}_3$  being added. The product of the acidification was a crude brownish tar which was purified by precipitation from benzene-petroleum ether (B.P. 30–60° C.) to give a relatively pure orange crystalline product. The complex was further purified by careful crystallization from toluene-ligroine (B.P. 66–75° C.). Using the above preparation, there resulted 9.80 grams of the product  $\text{Mo}^{\text{VI}}\text{O}_2[(n\text{—C}_3\text{H}_7)_2\text{NCS}_2]_2$ , which represented a yield of 70 percent. The product was an air-stable, yellow-orange crystalline solid which melted at approximately 110° C.



A solution of sodium di-n-propyldithiocarbamate was made by adding a slight excess of carbon disulfide to an equimolar, aqueous suspension of dipropylamine (0.60 g. mole) and sodium hydroxide. This solution was stirred for one hour, then filtered to obtain a clear, light yellow solution of sodium di-n-propyldithiocarbamate (0.60 g. mole) which was used immediately by placing it in solution with sodium molybdate dihydrate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , 0.36 g. mole) and 1700 ml. of water. This solution was then acidified by the careful addition of dilute nitric acid, at a temperature range of about 0° C. to about 6° C., with 935 ml. of an acid solution containing 1.20 g. moles  $\text{HNO}_3$  being added. The product of the acidification was a crude brownish tar which was purified by precipitation from benzene-petroleum ether (B.P. 30–60° C.) to give a relatively pure orange crystalline product. The complex was further purified by careful crystallization from toluene-ligroine (B.P. 66–75° C.). Using the above preparation, there resulted 127.0 grams of the product



which represented a yield of 88 percent. The product was an air-stable, yellow-orange crystalline solid which melted at approximately 110° C.



The molybdenum (VI) dioxide di-n-butyldithiocarbamate was prepared as follows: A solution of sodium di-

n-butylthiocarbamate was made by adding a slight excess of carbon disulfide to an equimolar aqueous suspension of di-n-butylamine (0.40 g. mole) and sodium hydroxide. This solution was stirred for one hour, then filtered to obtain a clear, light yellow solution of sodium dibutylthiocarbamate (0.40 g. mole) which was used immediately by placing it in solution with sodium molybdate dihydrate (0.29 g. mole) and 2000 ml. of water. This solution was then acidified by careful addition of dilute nitric acid at a temperature range of from 0° C. to 6° C., with 890 ml. of an acid solution containing 0.87 g. mole HNO<sub>3</sub> being added. The product of the acidification was a purple tar, and this was dissolved in toluene. To this toluene solution, t-butyl hydroperoxide was then slowly added to prevent excess oxidation, in an amount equalling 0.065 g. mole. This resulted in a pure crystalline product of 77 grams representing a yield of 72 percent. The product was an orange crystalline solid which was precipitated out of solution by the addition of petroleum ether and cooling. The product, molybdenum (VI) dioxide di-n-butylthiocarbamate, consisted of yellow-orange crystals with a melting point of approximately 70° C. This product was soluble in aromatic solvents and halogenated solvents. At 25° C., 0.11 gram of the product dissolved in 100 ml. of ligroine (B.P. 66–75° C.), while 0.36 gram dissolved in the same amount of solvent at 45° C. The complex could be dispersed in gear oil as a benzene solution to form a stable suspension.

Example 3.—Mo<sup>VI</sup>O<sub>2</sub>[(C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>NCS<sub>2</sub>]<sub>2</sub>

A commercial grade diamylamine (0.04 g. mole, 6.29 grams) was placed in equimolar aqueous suspension with NaOH. A slight molar excess of carbon disulfide was added to the aqueous suspension and the mixture was stirred for one hour, then filtered to obtain a solution of sodium diamylthiocarbamate (0.04 g. mole). This solution was used fresh by placing it in solution with sodium molybdate dihydrate (0.03 g. mole, 7.26 grams); total water in the solution was approximately 150 ml. To this was carefully added a solution of 8 ml. of 15 N nitric acid in 200 ml. of water. This resulted in formation of a purple tar. A toluene solution of this tar was then oxidized carefully with t-butyl hydroperoxide (0.01 g. mole) to give an orange solution. The product



was isolated by precipitation with cold petroleum ether to give 5.5 grams of a dark orange tar representing a yield of 47 percent. This tar gave orange solutions with aromatic solvents.

Example 4.—Mo<sup>VI</sup>O<sub>2</sub>[(C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>NCS<sub>2</sub>]<sub>2</sub>

A commercial grade di-2-ethylhexylamine (48.4 grams, 0.20 mole) and NaOH (9.50 grams, 0.222 mole) were placed in aqueous suspension with 1200 ml. of water. To this was added carbon disulfide (17.6 grams, 0.231 mole) and the mixture was stirred for two hours. The mixture was then filtered to obtain a milky white solution, and a solution of sodium molybdate dihydrate (26.00 grams, 0.17 mole) in 500 ml. of water was added to the filtrate. After cooling to 3° C., the mixture was acidified with a cold solution of 30 ml. of 15 N nitric acid in 400 ml. of water to obtain a purple suspension and purple tar.

The complex was extracted with benzene, and after oxidizing the solution with t-butyl hydroperoxide (0.068 g. mole), it was allowed to stand overnight. A large amount of petroleum ether was then added and cooling caused 8.1 grams of a dark brown, thick tar to settle out. The decanted liquid was then vacuum evaporated on a water bath to obtain 41.4 grams of a dark, thick liquid. The yield of molybdenum (VI) di-2-ethylhexylthiocarbamate complex was 63 percent. This product was soluble in aromatic solvents, ten percent soluble in ligroine (B.P. 66–75° C.), but was insoluble in petroleum ether (B.P. 30–60° C.). This complex when added to gear oil as ligroine solution, gave a stable suspension. After two months storage, this material gave a clear orange solution with benzene and acetone, and a hazy orange solution with ligroine. The complex was stable to storage.

Example 5.—H<sub>2</sub>S treated Mo<sup>VI</sup>O<sub>2</sub>[(C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>NCS<sub>2</sub>]<sub>2</sub>

A benzene solution of the Mo<sup>VI</sup>O<sub>2</sub>[(C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>NCS<sub>2</sub>]<sub>2</sub> complex (prepared in the manner of Example 4) was reacted with hydrogen sulfide by bubbling H<sub>2</sub>S through the solution for approximately three hours. This resulted in a product, which was recovered by vacuum evaporation, of a purple-black, fluid tar. A weight recovery of 95 percent was realized from the vacuum evaporation. It is believed that the H<sub>2</sub>S reacted with the complex to form the corresponding thiomolybdate by replacement of oxygen with sulfur. The product of reacting H<sub>2</sub>S with the above complex was obtained in good yields and is believed to have the formula:



The product was soluble in most organic solvents and was at least 50 percent soluble in ligroine (B.P. 66–75° C.) at room temperature. The product was readily suspended in SAE-90 gear oil, and this suspension was found to be stable for a least twenty days.

Example 6.—H<sub>2</sub>S treated Mo<sup>VI</sup>O<sub>2</sub>[(n-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>NCS<sub>2</sub>]<sub>2</sub>

A benzene solution of the molybdenum (VI) dioxide di-n-butylthiocarbamate complex (prepared in the manner set out in Example 2) was reacted with hydrogen sulfide by bubbling H<sub>2</sub>S through the solution for approximately three hours. After standing a few hours, a very fine solid settled out. This was a bright orange crystalline solid, and it was isolated in 40 percent yield based on a starting molybdenum content. After crystallization from benzene-petroleum ether, it had a melting point of about 243° C. The elemental analysis of this solid corresponded to a formula for the product which is believed to be MoOS[(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>NCS<sub>2</sub>]. The product was soluble in aromatic solvents and most other organic solvents. The product was readily suspendable in gear oil.

In the way of further identifying the molybdenum (VI) dioxide dialkylthiocarbamate compounds comprising the invention, samples were subjected to infrared spectrographic analysis and the data obtained are set forth in Table 1, which shows the characteristic absorption peaks for the C=N, C-S and Mo-O bonds. These data were obtained on the di-n-propyl, diamyl and di-2-ethylhexyl compounds, prepared in accordance with the methods as described in the preceding examples.

TABLE 1

Compound	Infrared Spectra-Absorption in cm. <sup>-1</sup>		
	C=N	C-S	Mo-O
Mo <sup>VI</sup> O <sub>2</sub> [(n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>2</sub> .....	1,522	600-602; 971	844 <sup>v</sup> , 873 <sup>v</sup> , 909 <sup>w</sup> , 930 <sup>w</sup>
Mo <sup>VI</sup> O <sub>2</sub> [(C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>2</sub> .....	1,504	952	877 <sup>v</sup> , 909 <sup>v</sup> , 926 <sup>m</sup>
Mo <sup>VI</sup> O <sub>2</sub> [(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>2</sub> .....	1,493; 1,453	965-970	877-885 <sup>m</sup> , 913 <sup>m</sup> , 934-940 <sup>m</sup>

NOTE.—<sup>s</sup>=strong; <sup>m</sup>=medium; <sup>w</sup>=weak; <sup>v</sup>=very.

These data are believed to substantiate the compounds as hexavalent molybdate complexes of dialkyldithiocarbamate in accordance with the structural formulae representing the di-n-propyl, diamyl and di-2-ethylhexyl derivatives investigated.

The products prepared in accordance with the invention were found to have highly beneficial properties as lubricant additives among other uses, such as for example, antioxidants, rubber accelerators and fungicides.

The evaluation test data for lubricating properties of the compounds of the present invention are set out in the following Tables 2 and 3. The compounds were tested as additives to a commercially available lithium grease in Table 2, and as additives to a commercially available gear oil in Table 3.

Two types of tests were used. One of these was the well known 4-Ball E.P. test using the 4-Ball machine to measure the extreme pressure properties or load-carrying capacity of the lubricants. The specific test procedure is identified as Federal Test Method Standard No. 791—Lubricants, Liquid Fuels and Related Products; Methods of Testing—Method No. 6503 (Dec. 12, 1955). Briefly, this test consists of four metal balls stacked in a pyramid with the bottom three balls held stationary. The fourth ball is then positioned on top of the three and rotated to leave a wearing scar on each of the three lower balls. The average diameter of the wear scar on each of these stationary balls is then measured to indicate how effective the lubricant is in preventing wear. This 4-Ball test is also used to determine how much load the rotating ball can withstand before it is simply welded to the lower three balls, i.e., how effective the lubricant is in preventing the weld.

The other tests used were oscillation tests run on an oscillation friction testing machine. These tests consist of applying lubricant between two 1.0 inch diameter flat washers and thereafter oscillating the washers relative to each other under preselected loads and then counting the number of oscillations until seizure occurs.

TABLE 2.—EVALUATIONS IN AMOCO LITHIUM GREASE WITH 3% BY WEIGHT OF ADDITIVE ADDED

[A. Oscillation Tests]			
Type Additive	Oscillations to Seizure		
	219	182	544
MoVIO <sub>2</sub> [(n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>2</sub> .....	219	182	544
MoVIO <sub>2</sub> [(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>2</sub> .....	849	48	1,484
MoOS[(n-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>2</sub> .....	3,331	918	931
(H <sub>2</sub> S treated dibutyl)			
Base Grease (additive free).....	95	67	110

[B. Shell 4-Ball E.P. Tests]			
Type Additive	Wear Scar (mm.)		Weld Load (kg.)
	70 kg.	110 kg.	
	MoVIO <sub>2</sub> [(n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>2</sub> .....	0.36	
MoVIO <sub>2</sub> [(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>2</sub> .....	1.62	1.88	180
MoOS[(n-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>2</sub> .....	0.73	1.77	280
(H <sub>2</sub> S treated dibutyl)			
Base Grease (additive free).....	2.30	2.32	180

TABLE 3.—EVALUATIONS IN SHELL DENTAX SAE-90 GEAR OIL, WITH 3% BY WEIGHT OF THE ADDITIVE ADDED

[Shell 4-Ball E.P. Tests]			
Type Additive	Wear Scar (mm.) 200 kg.		Weld Load (kg.)
	2.22	300	
MoVIO <sub>2</sub> [(n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>2</sub> .....	2.22	300	
MoVIO <sub>2</sub> [(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> NCS <sub>2</sub> ] <sub>2</sub> .....	2.32	260	
Base Gear Oil (no additive).....	( <sup>1</sup> )	140	

<sup>1</sup> The base gear oil welded at 200 kg.

The compounds of the invention when used as lubricant additives, such as in a hydrocarbon vehicle, can be employed at varying concentrations from about ½% to about 80% by weight to give a lubricant composition. Generally, when used as additives in greases concentrations of up to 15% are beneficial, with ½% to 10% by weight normally preferred; when used as additives to oils, such as gear oils, extreme pressure (E.P.) oils and

motor oils, concentrations of about 1% to about 5% by weight are normally used; when used as additives to paste-type lubricants, such as the MoS<sub>2</sub> type, pastes formed from oil-additive mixtures, and pastes for E.P. situations, concentrations up to about 80% by weight may be employed.

The compounds of the invention generally are not oil soluble, and therefore when used as additives to lubricants or hydrocarbon vehicles, they are normally added as dispersions or suspensions through the use of organic carrier solvents, or the additive in solid product form is dispersed or suspended in the lubricant as finely divided particles. The average particle size can vary up to about twenty microns. Generally, however, it is less than ten microns, with the preferred range being an average particle size of about one micron or less.

While it will be apparent that the embodiments of the invention herein disclosed are well calculated to fulfill the objects of the invention, it will be appreciated that the invention is susceptible to modification, variation and change without departing from the proper scope or fair meaning of the subjoined claims.

What is claimed is:

- The method of making molybdenum (VI) dioxide dialkyldithiocarbamate comprising the steps of:
  - adding sodium molybdate to a solution of sodium dialkyldithiocarbamate in an amount equal to a molar ratio of sodium molybdate to sodium dialkyldithiocarbamate between about 1:1 and about 1:5,
  - acidifying said solution at a temperature of about minus 5° C. to about 50° C. with dilute nitric acid in an amount equal to a molar ratio of nitric acid to sodium molybdate between about 1:1 and about 6:1, and
  - recovering molybdenum (VI) dioxide dialkyldithiocarbamate.
- The method of making molybdenum (VI) dioxide dialkyldithiocarbamate comprising the steps of:
  - adding sodium molybdate to a solution of sodium dialkyldithiocarbamate in an amount equal to a molar ratio of sodium molybdate to sodium dialkyldithiocarbamate between about 1:1.5 and about 1:2,
  - acidifying said solution at a temperature of about 0° C. to about 25° C. with dilute nitric acid in an amount equal to a molar ratio of nitric acid to sodium molybdate between about 2:1 and about 4:1, and
  - recovering molybdenum (VI) dioxide dialkyldithiocarbamate.
- The method of making molybdenum (VI) dioxide dialkyldithiocarbamate wherein the alkyl contains from four to eight carbon atoms, comprising the steps of:
  - adding sodium molybdate to a solution of sodium dialkyldithiocarbamate wherein the alkyl contains from four to eight carbon atoms in an amount equal to a molar ratio of sodium molybdate to sodium dialkyldithiocarbamate between about 1:1 and about 1:5,
  - acidifying said solution at a temperature of about minus 5° C. to about 50° C. with dilute nitric acid in an amount equal to a molar ratio of nitric acid to sodium molybdate between about 1:1 and about 6:1, to thereby form a first product,
  - oxidizing the first product with a strong oxidizing agent selected from the group consisting of organic peroxides and organic hydroperoxides, and
  - recovering the molybdenum (VI) dioxide dialkyldithiocarbamate.
- The method of making molybdenum (VI) dioxide dialkyldithiocarbamate wherein the alkyl contains from four to eight carbon atoms, comprising the steps of:
  - adding sodium molybdate to a solution of sodium dialkyldithiocarbamate wherein the alkyl contains from four to eight carbon atoms in an amount equal to a molar ratio of sodium molybdate to sodium di-

- alkyldithiocarbamate between about 1:1.5 and 1:2,  
 (b) acidifying said solution at a temperature of about 0° C. to about 25° C. with dilute nitric acid in an amount equal to a molar ratio of nitric acid to sodium molybdate between about 2:1 and about 4:1, to thereby form a first product,  
 (c) oxidizing the first product with a strong oxidizing agent selected from the group consisting of organic peroxides and organic hydroperoxides, and  
 (d) recovering the molybdenum (VI) dioxide dialkyldithiocarbamate.
5. The method of claim 1 comprising the additional steps of contacting said molybdenum (VI) dioxide dialkyldithiocarbamate with hydrogen sulfide for a period of time sufficient to effect a replacement of an oxygen atom with a sulfur atom, and recovering the product therefrom.
6. The method of claim 2, comprising the additional steps of contacting said molybdenum (VI) dioxide dialkyldithiocarbamate with hydrogen sulfide for a period of time sufficient to effect a replacement of an oxygen atom with a sulfur atom, and recovering the product therefrom.
7. The method of claim 3, comprising the additional steps of contacting said molybdenum (VI) dioxide dialkyldithiocarbamate with hydrogen sulfide for a period of time sufficient to effect a replacement of an oxygen atom with a sulfur atom, and then recovering the product.
8. The method of claim 4, comprising the additional steps of contacting said molybdenum (VI) dioxide dialkyldithiocarbamate with hydrogen sulfide for a period of time sufficient to effect a replacement of an oxygen atom with a sulfur atom, and recovering the product therefrom.
9. The method of making molybdenum (VI) dioxide di-n-propyldithiocarbamate comprising the steps of:  
 (a) adding sodium molybdate to a solution of sodium di-n-propyldithiocarbamate in an amount equal to a molar ratio of sodium molybdate to sodium di-n-propyldithiocarbamate between about 1:1 and about 1:5,  
 (b) acidifying said solution at a temperature of about minus 5° C. to about 50° C. with dilute nitric acid in an amount equal to a molar ratio of nitric acid to sodium molybdate between about 1:1 and about 6:1, and  
 (c) recovering molybdenum (VI) dioxide di-n-propyldithiocarbamate.
10. The method of making molybdenum (VI) dioxide di-n-propyldithiocarbamate comprising the steps of:  
 (a) adding sodium molybdate to a solution of sodium di-n-propyldithiocarbamate in an amount equal to a molar ratio of sodium molybdate to sodium di-n-propyldithiocarbamate between about 1:1.5 and about 1:2,  
 (b) acidifying said solution at a temperature of about 0° C. to about 25° C. with dilute nitric acid in an amount equal to a molar ratio of nitric acid to sodium molybdate between about 2:1 and about 4:1, and  
 (c) recovering molybdenum (VI) dioxide di-n-propyldithiocarbamate.
11. The method of making molybdenum (VI) dioxide di-n-butyldithiocarbamate comprising the steps of:  
 (a) adding sodium molybdate to a solution of sodium di-n-butyldithiocarbamate in an amount equal to a molar ratio of sodium molybdate to sodium di-n-butyldithiocarbamate between about 1:1 and about 1:5,  
 (b) acidifying said solution at a temperature of about minus 5° C. to about 50° C. with dilute nitric acid in an amount equal to a molar ratio of nitric acid to sodium molybdate between about 1:1 and about 6:1 to thereby form a first product,  
 (c) oxidizing said first product with a strong oxidizing

- agent selected from the group consisting of organic peroxides and organic hydroperoxides, and  
 (d) recovering molybdenum (VI) dioxide di-n-butyldithiocarbamate.
12. The method of making molybdenum (VI) dioxide di-n-butyldithiocarbamate comprising the steps of:  
 (a) adding sodium molybdate to a solution of sodium di-n-butyldithiocarbamate in an amount equal to a molar ratio of sodium molybdate to sodium di-n-butyldithiocarbamate between about 1:1.5 and about 1:2,  
 (b) acidifying said solution at a temperature of about 0° C. to about 25° C. with dilute nitric acid in an amount equal to a molar ratio of nitric acid to sodium molybdate between about 2:1 and about 4:1 to thereby form a first product,  
 (c) oxidizing said first product with a strong oxidizing agent selected from the group consisting of t-butyl peroxide, t-butyl hydroperoxide and cumene hydroperoxide, and  
 (d) recovering molybdenum (VI) dioxide di-n-butyldithiocarbamate.
13. The method of making molybdenum (VI) dioxide diamyldithiocarbamate comprising the steps of:  
 (a) adding sodium molybdate to a solution of sodium diamyldithiocarbamate in an amount equal to a molar ratio of sodium molybdate to sodium diamyldithiocarbamate between about 1:1 and 1:5,  
 (b) acidifying said solution at a temperature of about minus 5° C. to about 50° C. with dilute nitric acid in an amount equal to a molar ratio of nitric acid to sodium molybdate between about 1:1 and about 6:1 to thereby form a first product,  
 (c) oxidizing said first product with a strong oxidizing agent selected from the group consisting of organic peroxides and organic hydroperoxides, and  
 (d) recovering molybdenum (VI) dioxide diamyldithiocarbamate.
14. The method of making molybdenum (VI) dioxide diamyldithiocarbamate comprising the steps of:  
 (a) adding sodium molybdate to a solution of sodium diamyldithiocarbamate in an amount equal to a molar ratio of sodium molybdate to sodium diamyldithiocarbamate between about 1:1.5 and about 1:2,  
 (b) acidifying said solution at a temperature of about 0° C. to about 25° C. with dilute nitric acid in an amount equal to a molar ratio of nitric acid to sodium molybdate between about 2:1 and about 4:1 to thereby form a first product,  
 (c) oxidizing said first product with a strong oxidizing agent selected from the group consisting of t-butyl peroxide, t-butyl hydroperoxide and cumene hydroperoxide, and  
 (d) recovering molybdenum (VI) dioxide diamyldithiocarbamate.
15. The method of making molybdenum (VI) dioxide di-2-ethylhexyldithiocarbamate comprising the steps of:  
 (a) adding sodium molybdate to a solution of sodium di-2-ethylhexyldithiocarbamate in an amount equal to a molar ratio of sodium molybdate to sodium di-2-ethylhexyldithiocarbamate between about 1:1 and 1:5,  
 (b) acidifying said solution at a temperature of about minus 5° C. to about 50° C. with dilute nitric acid in an amount equal to a molar ratio of nitric acid to sodium molybdate between about 1:1 and about 6:1 to thereby form a first product,  
 (c) oxidizing said first product with a strong oxidizing agent selected from the group consisting of organic peroxides and organic hydroperoxides, and  
 (d) recovering molybdenum (VI) dioxide di-2-ethylhexyldithiocarbamate.
16. The method of making molybdenum (VI) di-2-ethylhexyldithiocarbamate comprising the steps of:  
 (a) adding sodium molybdate to a solution of sodium

## 11

di-2-ethylhexyldithiocarbamate in an amount equal to a molar ratio of sodium molybdate to sodium di-2-ethylhexyldithiocarbamate between about 1:1.5 and about 1:2,

- (b) acidifying said solution at a temperature of about 0° C. to about 25° C. with dilute nitric acid in an amount equal to a molar ratio of nitric acid to sodium molybdate between about 2:1 and about 4:1 to thereby form a first product, 5
- (c) oxidizing said first product with a strong oxidizing agent selected from the group consisting of t-butyl peroxide, t-butyl hydroperoxide and cumene hydroperoxide, and 10
- (d) recovering molybdate (VI) di-2-ethylhexyldithiocarbamate. 15

17. The method of claim 11, comprising the additional steps of contacting said molybdenum (VI) dioxide di-n-butyl-dithiocarbamate with hydrogen sulfide for a period of time sufficient to effect a replacement of an oxygen atom with a sulfur atom, and then recovering the product. 20

18. The method of claim 12, comprising the additional steps of contacting said molybdenum (VI) di-n-butyl-dithiocarbamate with hydrogen sulfide for a period of time sufficient to effect a replacement of an oxygen atom with a sulfur atom, and then recovering the product. 25

19. The method of claim 15, comprising the additional

## 12

steps of contacting said molybdenum (VI) dioxide di-2-ethylhexyldithiocarbamate with hydrogen sulfide for a period of time sufficient to effect a replacement of an oxygen atom with a sulfur atom, and then recovering the product.

20. The method of claim 16, comprising the additional steps of contacting said molybdenum (VI) dioxide di-2-ethylhexyldithiocarbamate with hydrogen sulfide for a period of time sufficient to effect a replacement of an oxygen atom with a sulfur atom, and then recovering the product.

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