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METHOD OF LUBRICATION EMPLOYING A MIXED METAL SULFIDE LUBRICANT AND BEARING SURFACE WITH SAME APPLIED THERETO

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This invention relates to a novel solid lubricant and to a method for preparing same. More specifically, it relates to mixed metal sulfide lubricants and to the preparation thereof.

The use of molybdenum and tungsten disulfides as dry or solid lubricants is known. Their ability to perform a lubricating function between bearing surfaces is believed to be due to the fact that they have a crystalline, layer-lattice structure that permits sulfide layers to move with relative ease over intermediate molybdenum or tungsten layers. Other heavy metal sulfides, whether naturally occurring or synthesized, have not been found to exhibit desirable lubricating properties as such.

It has now been found that it is possible to synthesize a solid or dry lubricant of excellent properties by thermally decomposing a mixed metal tetrathio compound, in which one of the metals is molybdenum or tungsten, to the corresponding mixed metal sulfide. This is believed to be accomplished in accordance with the following reaction:



wherein M is molybdenum or tungsten, Me is another heavy metal of group Ib, IIb, IVa, Va, Vlb, VIb, VIIb and VIII of the periodic table, x and y are integers and twice y/x corresponds to the valence of Me.

The reaction is carried out under non-oxidizing conditions, e.g., in an inert atmosphere such as nitrogen, or under subatmospheric pressure and at a temperature at least equal to the vaporization temperature of sulfur at the prevailing pressure. Thus, for example, if the reaction is carried out under nitrogen at atmospheric pressure, the temperature should be at least about 450° C. and preferably between 450 and about 600° C. If the reaction is carried out at subatmospheric pressure, e.g., about 146 mm. Hg, the temperature should be at least 350° C. and preferably between about 350 and 400° C. The heating time should be sufficient to thermally decompose substantially all of the tetrathio compound to the mixed metal sulfide. This ordinarily requires at least about one hour, the preferred heating time being about one to four hours.

The initial mixed metal tetrathio compound may be obtained in known manner such as by double decomposition of solutions of alkali- or ammonium tetrathiomolybdate or tungstate with solutions of appropriate metal salts such as the sulfates, halogenides, nitrates and acetates of the heavy metals. The salts that deserve particular mention as being appropriate for this purpose are the salts of mono- and divalent copper, divalent zinc, mono- and divalent mercury, monovalent silver, divalent manganese, nickel, cobalt, cadmium and lead, trivalent chromium and bismuth, di- and trivalent iron and di- and tetravalent tin.

The mixed metal tetrathiomolybdates or tungstates thus prepared can, after careful drying at low temperatures of the order of 110° C., be heated for thermal decomposi-

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tion under non-oxidizing conditions. Under these conditions the heating of the tetrathio compound results in the separation of excess sulfur as indicated in the formula and in the transformation of the molybdenum or tungsten from the hexavalent to the tetravalent form. An opportunity to recover the liberated sulfur is provided.

It has been found that under the conditions described the thermal decomposition not only results in a formation of a layer-lattice structure for the molybdenum or tungsten disulfide that is formed, which is similar to that of natural molybdate, but also that the sulfide of the other metal appears to be incorporated into the lattice structure. The mixed sulfides that are formed possess desirable lubricant qualities that are quite unexpected. One important advantage of the method of the invention is that high yields of lubricant products can be obtained and that the method does not produce gaseous by-products that create any recovery problems.

These and other advantages, as well as the utility of the invention, will readily become apparent from the following examples included to illustrate the best modes now contemplated of carrying out the invention.

Example 1

One mol of lead nitrate $\text{Pb}(\text{NO}_3)_2$ and one mol of ammonium tetrathiomolybdate $(\text{NH}_4)_2\text{MoS}_4$ were separately dissolved in hot water and the two solutions were rapidly poured together under vigorous stirring. After allowing the combined solution to stand, a precipitate of lead tetrathiomolybdate was separated, filtered, washed with water to remove soluble impurities and dried at 110° C. The loose powder was placed and kept for one hour in a tube heater heated to 500° C., a stream of nitrogen being passed through the heater and passed through a cooled trap for separation of sulfur. A grey powder having a dull finish after grinding in a mortar was obtained.

In a similar manner, cupric sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, mercuric nitrate $\text{Hg}(\text{NO}_3)_2$, manganous sulfate $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$, cadmium chloride CdCl_2 and ferroammonium sulfate $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ were reacted with ammonium tetrathiomolybdate or sodium tetrathiomolybdate and the resulting tetrathiomolybdates of copper, mercury, manganese, cadmium and iron were thermally decomposed, after drying, to the corresponding mixed metal sulfides.

Several of these mixed metal sulfides were applied to bearing surfaces and tested in an Almen Wieland machine. The results of these tests and of comparative tests with natural and synthetic molybdenum disulfides are tabulated immediately below:

Mixed Sulfides	Frictional Force at a Load of—		
	500 kgs.	1,000 kgs.	1,500 kgs.
Ferric sulfide-Molybdenum sulfide.....	38	40	50
Cadmium sulfide-Molybdenum sulfide.....	29	43	56
Lead sulfide-Molybdenum sulfide.....	30	46	48
Natural Molybdenum disulfide.....	36	49	61
Synthetic Molybdenum disulfide.....	30	38	45

It is apparent from the data in the table that the mixed sulfides are at least equal in effectiveness as lubricants to natural and synthetic molybdenum disulfide in so far as friction at various load levels is concerned. Inspection of the bearings after the tests showed that the mixed metal sulfides are also fully equivalent in that the test bearings were free of grooves, had highly polished mirror surfaces and showed no measurable abrasion.

Example 2

Tetrathiotungstates of tin, chromium, nickel and zinc were heated in separate porcelain containers hermetically

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sealed from the air and provided with an exhaust valve in a muffle furnace to a temperature of 470° C. for one-half hour and thereafter for two additional hours at 525° C.

After cooling, it was found that the resulting mixed sulfides of tin sulfide-tungsten sulfide, chromium sulfide-tungsten sulfide, nickel sulfide-tungsten sulfide and zinc sulfide-tungsten sulfide could easily be pulverized in a mortar and that their appearance resembled that of pulverized tungsten disulfide. Several of these mixed sulfides were applied to bearing surfaces and tested on an Almen Weiland machine in dry operation and compared with commercially available tungsten disulfide. The test results are as follows:

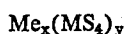
Mixed Sulfides	Frictional Force at a Load of—		
	500 kgs.	1,000 kgs.	1,500 kgs.
Tin sulfide-Tungsten sulfide.....	32	50	71
Nickel sulfide-Tungsten sulfide.....	40	53	59
Tungsten disulfide.....	26	43	56

It appears from the data in the table that the mixed sulfides prepared in accordance with the method of Example 2 are likewise equivalent to tungsten sulfide as solid lubricants. Here again inspection of the test bearings revealed that they were mirror-smooth and that there was no measurable abrasion.

It is to be expected that numerous modifications will readily become apparent to those skilled in the art upon reading this description. All such modifications are to be included within the scope of the invention as defined in the appended claims.

We claim:

1. A method of lubricating a bearing surface which comprises applying thereto, as a lubricant, a mixed metal sulfide having a crystalline, layer-lattice structure and prepared by thermal decomposition of a mixed metal tetrathio compound having the general formula

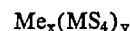


wherein M is a metal selected from the group consisting of molybdenum and tungsten, Me is another heavy

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metal of groups Ib, IIb, IVa, Va, VIb, VIIb and VIII of the periodic system, x and y are integers, and twice x/y corresponds to the valence of Me.

2. A bearing surface having applied thereto a mixed metal sulfide having a crystalline, layer-lattice structure and prepared by thermal decomposition of a mixed metal tetrathio compound having the general formula



wherein M is a metal selected from the group consisting of molybdenum and tungsten, Me is another heavy metal of groups Ib, IIb, IVa, Va, VIb, VIIb and VIII of the periodic system, x and y are integers, and twice x/y corresponds to the valence of Me.

3. A bearing surface as defined in claim 2 wherein M is molybdenum and Me is lead.

4. A bearing surface as defined in claim 2 wherein M is molybdenum and Me is copper.

5. A bearing surface as defined in claim 2 wherein M is molybdenum and Me is mercury.

6. A bearing surface as defined in claim 2 wherein M is molybdenum and Me is manganese.

7. A bearing surface as defined in claim 2 wherein M is molybdenum and Me is cadmium.

8. A bearing surface as defined in claim 2 wherein M is molybdenum and Me is iron.

9. A bearing surface as defined in claim 2 wherein M is tungsten and Me is tin.

10. A bearing surface as defined in claim 2 wherein M is tungsten and Me is chromium.

11. A bearing surface as defined in claim 2 wherein M is tungsten and Me is nickel.

12. A bearing surface as defined in claim 2 wherein M is tungsten and Me is zinc.

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