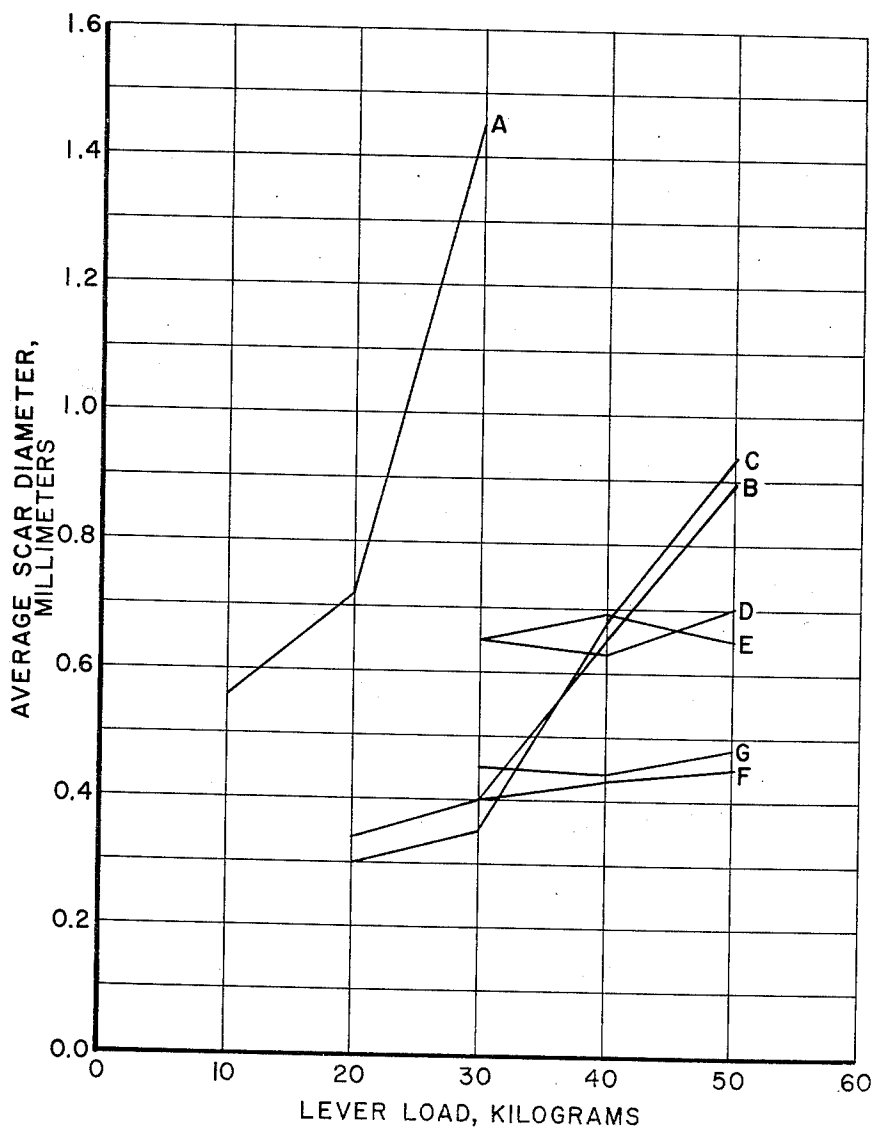


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MOLYBDENUM AND TUNGSTEN HALIDES AND SULFIDES OF
ORGANIC SUBSTITUTED DITHIOPHOSPHORIC ACIDS
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1

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MOLYBDENUM AND TUNGSTEN HALIDES AND SULFIDES OF ORGANIC SUBSTITUTED DITHIOPHOSPHORIC ACIDS

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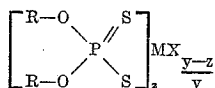
4 Claims. (Cl. 260-429)

This invention relates to new chemical compounds having particular utility as additives in lubricating oils.

As is well known to those skilled in the art, uncompounded lubricating oils frequently fail to provide satisfactory lubrication to surfaces engaging under extreme pressure. The failure of lubricants to provide proper lubrication under high operating pressures results in the rubbing surfaces of machinery suffering considerable wear even to such an extent where they must be replaced.

This invention is based upon the discovery of novel addition agents which when blended in minor proportions with lubricating oils impart to the resulting composition significantly improved extreme pressure characteristics.

The novel compounds of the invention which have been found particularly useful as addition agents for lubricating oils and the like are molybdenum and tungsten salts of organic substituted dithiophosphoric acids having the general formula:

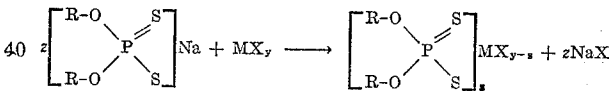


in which R is an oil-solubilizing organic radical such as aryl, alkyl, alkoxyalkyl, aralkyl, cycloalkyl, aryloxyalkyl, acylaryl and alkoxyaryl radicals; M is molybdenum or tungsten and X is a halogen or sulfur, y is the valency of the metal M, z is an integer of at least one but less than the valency of the metal M and represents the number of dithiophosphate ester groups in the product, and v is the valency of X. More specifically, compounds of this class include a molybdenum or tungsten salt of dialkyl dithiophosphates and dicycloalkyl dithiophosphates such as dibutyl dithiophosphate, butyl hexyl dithiophosphate, amyl octyl dithiophosphate, dihexyl dithiophosphate, di-n-octyl dithiophosphate, diisooctyl dithiophosphate, didecyl dithiophosphate, dilauryl dithiophosphate, dihexadecyl dithiophosphate, dioctadecyl dithiophosphate, dicyclopentyl dithiophosphate, dicyclohexyl dithiophosphate, and so forth. Those dialkyl dithiophosphates in which the alkyl group has at least 4 carbon atoms and preferably more than 6 carbon atoms as for example from 6 to 30 are preferred since the longer alkyl chains tend to increase the solubility of the dithiophosphates in lubricating oils. The molybdenum and tungsten diaryl dithiophosphates and the diaryl dithiophosphates in which the aryl group bears an alkyl or cycloaliphatic group are also useful, such as for example diphenyl dithiophosphate, di-2,4-diamylphenyl dithiophosphate, di-2,4-dihexylphenyl dithiophosphate, and the various di-wax substituted diaryl dithiophosphates. The diaryloxyalkyl dithiophosphates such as di-2,4-dibutylphenoxyethyl dithiophosphate, di-2,4-diamylphenoxypropyl dithiophosphate; the diacylaryl dithiophosphates such as dicaproylphenyl dithiophosphate, and the dialkoxyaryl dithiophosphates such as diethoxyphenyl

2

dithiophosphate, dibutyloxyphenyl dithiophosphate and the like are likewise useful. The organic substituents of the new compounds are not critical and can be selected from a variety of organic radicals on the basis of their ability to impart oil-solubility to the compounds. From the examples herein it is clear that R in the above formula may be selected from the group consisting of phenyl, caproylphenyl, alkyl, cycloalkyl, alkylphenyl, alkylphenoxyalkyl, and alkoxyphenyl radicals and wherein said alkyl radical contains 4 to 18 carbon atoms, said cycloalkyl radical contains 5 to 6 carbon atoms, the alkyl portion of said alkylphenyl radical contains 1 to 8 carbon atoms, the alkyl portions of said alkylphenoxyalkyl radical contains 2 to 5 carbon atoms and the alkyl portion of said alkoxyphenyl radical contains 2 to 4 carbon atoms.

The halogen containing molybdenum and tungsten salts embraced by this invention are prepared by reacting the desired metal halide with an alkali metal salt of a partial ester of dithiophosphoric acid. Methods of preparing the partial esters of dithiophosphoric acids and the alkali metal salts thereof are known to the art. For example, an alkali metal salt of an ester of dithiophosphoric acid can be prepared by first reacting an appropriate alcohol or hydroxyaromatic compound with phosphorus pentasulfide and then reacting the partially esterified acid thus formed with sodium or potassium hydroxide. With regard to the proportions of reactants employed in the preparation of the compounds of this invention, the amounts of the alkali metal salt of the dithiophosphate ester and of the molybdenum or tungsten halide can be varied considerably; however, in all cases the mols of dithiophosphate compound employed will be less than the number required for reaction with all of the halogen atoms. The principal reaction involved in preparing the novel compounds of the invention can probably be expressed by the following illustrative equation, although it is understood that it is not desired to be bound by any theory of reaction:



In the above equation, R, M, y and z have the meaning indicated previously and X is a halogen.

Sulfur can be made to replace part or all of the halogen in the above reaction product simply by causing hydrogen sulfide to react therewith in the presence of a tertiary amine or other acid scavenger.

The synthesis of the oil-soluble molybdenum and tungsten salts of the invention will be better understood from the following illustrative examples.

EXAMPLE I

To a solution of 376 grams (1 mol) of sodium diisooctyl dithiophosphate in 500 milliliters of carbon tetrachloride is added 84 grams (0.31 mol of molybdenum pentachloride in small portions over a two hour period. The temperature is maintained at approximately 55° to 60° C. during the addition. The reaction mixture is permitted to stand for a time as for example overnight, and the sodium chloride which is formed in the reaction is filtered off. The carbon tetrachloride is distilled off to leave approximately 390 grams of molybdenum tris-(diisooctyl dithiophosphate) dichloride. The product is a viscous brown liquid which turns blue on exposure to air

3

for several hours. It is soluble in the common organic solvents.

Analysis.—Calculated for Mo: 7.82 percent. Found for Mo: 7.78 percent.

EXAMPLE II

To a solution of 316 grams (1.0 mol) of sodium dicyclohexyl dithiophosphate in 1000 milliliters of carbon tetrachloride is added 84 grams (0.31 mol) of molybdenum pentachloride in small portions over a two hour period. The temperature is maintained at approximately 55° to 60° C. during the addition. The reaction mixture is permitted to stand for a time and the sodium chloride which is formed in the reaction is filtered off. The carbon tetrachloride is distilled off to leave molybdenum tris-(dicyclohexyl dithiophosphate) dichloride.

EXAMPLE III

50 grams (0.04 mol) of the molybdenum tris-(diisooctyl dithiophosphate) dichloride as prepared in Example I is dissolved in 100 milliliters of benzene containing approximately 0.08 mol of pyridine. Hydrogen sulfide is then bubbled slowly through the solution for about 1 hour. After standing for approximately one hour, the mixture is filtered and the solvent is removed from the filtrate under reduced pressure. Upon analysis of the final product the sulfur content was found to have increased from 13.06 percent to 16.57 percent while the chlorine content decreased from 9.70 percent to 3.58 percent. The product is a brown liquid, soluble in common organic solvents.

EXAMPLE IV

To a solution of 330 grams (1.0 mol) of sodium dicresyl dithiophosphate in 1000 milliliters of carbon tetrachloride is added 84 grams (0.31 mol) of molybdenum pentachloride in small portions over a two hour period. The temperature is maintained at approximately 55° to 60° C. during the addition. The reaction mixture is permitted to stand for a time, as for example overnight, and the sodium chloride which is formed in the reaction is filtered off. The carbon tetrachloride is distilled off to leave molybdenum tris-(dicresyl dithiophosphate) dichloride.

EXAMPLE V

To a solution of 432 grams (1.0 mol) of sodium didecyl dithiophosphate in 1000 milliliters of carbon tetrachloride is added 110 grams (0.31 mol) of tungsten pentachloride in small portions over a two hour period. The temperature is maintained at approximately 55° to 60° C. during the addition. The reaction mixture is permitted to stand for a time, as for example overnight, and the sodium chloride which is formed in the reaction is filtered off. The carbon tetrachloride is distilled off to leave tungsten tris-(didecyl dithiophosphate) dichloride.

EXAMPLE VI

To a solution of 528 grams (1.0 mol) of sodium dioctylphenyl dithiophosphate in 1000 milliliters of carbon tetrachloride is added 110 grams (0.31 mol) of tungsten pentachloride in small portions over a two hour period. The temperature is maintained at approximately 55° to 60° C. during the addition. The reaction mixture is permitted to stand for a time and the sodium chloride which is formed in the reaction is filtered off. The carbon tetrachloride is distilled off to leave tungsten tris-(dioctylphenyl dithiophosphate) dichloride.

EXAMPLE VII

To a solution of 488 grams (1.0 mol) of sodium dodecyl dithiophosphate in 1000 milliliters of carbon tetrachloride is added 202 grams (1.0 mol) of molybdenum trichloride in small portions over a two hour period. The temperature is maintained at approximately 55° to

4

60° C. during the addition. The reaction mixture is permitted to stand for a time and the sodium chloride which is formed in the reaction is filtered off. The carbon tetrachloride is distilled off to leave molybdenum dodecyl dithiophosphate dichloride.

EXAMPLE VIII

47 grams (0.04 mol) of molybdenum tris(dicresyl dithiophosphate) dichloride as prepared in Example IV is dissolved in 100 milliliters of benzene containing approximately 0.08 mol of pyridine. Hydrogen sulfide is bubbled through the solution until precipitation of pyridine hydrochloride is complete. After standing for approximately one hour, the mixture is filtered and the solvent is removed from the filtrate under reduced pressure to leave molybdenum tris-(dicresyl dithiophosphate) sulfide.

The novel molybdenum and tungsten organic substituted dithiophosphates embraced by the invention are particularly useful as additives to lubricating oils to improve the extreme pressure characteristics thereof. When employed for this purpose the additives of the invention are employed in lubricating oil compositions preferably in amounts ranging from about 0.05 to about 5 percent or more by weight. The exact amount of the additives to be employed will depend to a great extent upon the purpose for which the oil is intended. For example, an oil intended for use at high temperatures and high pressures should contain more of the additive as compared to the amounts required for an oil intended for less severe usage.

The lubricating oil to which the additives of the invention are added to form a lubricating composition having improved extreme pressure characteristics can be any mineral oil of lubricating viscosity such as naphthenic base, paraffinic base and mixed base lubricating oils. Synthetic lubricating oils such as polymerized olefins, organic esters such as di-2-ethyl hexyl sebacate and di-2-ethylhexyl azelate and the like, can also be used as the base oil to form a lubricating composition in accordance with the invention. If desired, blends of oils of suitable viscosity may be employed instead of a single oil.

To prepare an improved lubricating composition the additives disclosed herein can be added to the lubricating oil base directly or in the form of a mineral oil concentrate in an amount to give the desired concentration in the final lubricating composition. Slight heating of the mixture may be advantageously employed to facilitate blending of the additives in the composition.

To demonstrate the effectiveness of the molybdenum and tungsten salts of the type described above in mineral oil compositions, several comparative tests were conducted with a mineral oil alone and with the same oil blended with a commercially available extreme pressure additive. The mineral oil employed had the following inspection:

Gravity: ° API	29.7
Viscosity SUV: Sec.—	
100° F.	326
210° F.	55.5
Flash OC: ° F.	460
Fire OC: ° F.	510

A four ball wear test was conducted as follows:

Three steel balls are securely fastened so that rotation is impossible. A fourth steel ball in a rotating spindle is placed so that it is entirely supported by the other three balls forming a pyramid. The three immobile steel balls and the rotating single steel ball are forced into contact with each other in response to a vertically applied load. Sufficient test lubricant is poured into a test cup to cover the three lower balls at a predetermined depth. The spindle is revolved at 1800 r.p.m. while electrical heating units heat the oil to a temperature of 248° F. At the conclusion of the test, wear is measured by examina-

5

tion of the scars on the clean surfaces of the three stationary balls; the two maximum right angle diameters of each wear scar being measured to the closest 0.01 millimeter and averaged. The antiwear properties are rated by the difference in the scar diameters.

The results of the test are given below in Table I.

Table I

Compound Added	Percent Concentration	Lever Load (kilograms)	Average Scar Diameter
None (Oil Alone)-----	0	10	0.56
		20	0.72
		30	1.45
Zinc diisooctyl dithiophosphate....	0.5	20	0.74
		30	0.40
		40	0.65
		50	0.89
		20	0.30
		30	0.35
		40	0.68
Molybdenum tris-(diisooctyldithiophosphate) dichloride.....	1.0	50	0.93
		30	0.65
		40	0.63
		50	0.70
		30	0.65
Compound prepared in Example III-----	1.0	40	0.69
		50	0.65
		30	0.40
		40	0.43
		50	0.45
		30	0.45
	1.0	40	0.44
	1.0	50	0.48

The results recorded in Table I are shown graphically in FIGURE 1 of the drawings. Thus, curve A shows the results obtained with the oil alone. Curves B and C represent the results obtained with zinc diisooctyl dithiophosphate, a commercially available extreme pressure additive at concentrations of 0.5 and 1.0 percent respectively. Curves D and E represent the results obtained with a lubricating oil composition containing molybdenum tris-(diisooctyl dithiophosphate) dichloride at concentrations of 0.5 and 1.0 percent by weight respectively. Curves F and G represent the results obtained with a lubricating oil composition containing the reaction product of Example III at concentrations of 0.5 and 1.0 percent by weight respectively.

The curves shown in FIGURE 1 clearly show the superiority of the lubricating compositions containing the additives of this invention particularly in the upper pressure range. It will be seen also from the test results that only small amounts of the additives need be employed to obtain significant improvement in the extreme pressure characteristics of the lubricating composition.

6

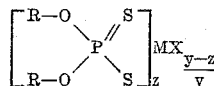
In addition to the additives disclosed herein, there may be present in the lubricating composition other conventional additives such as pour point depressants, anti-rust agents, antioxidants, viscosity index improvers and the like.

It is apparent from the foregoing description that the invention provides a new class of chemical compounds which exhibit particular utility as additives to lubricating oils.

Those modifications and equivalents which fall within the spirit of the invention and the scope of the appended claims are to be considered part of the invention.

I claim:

1. Compounds of the generic formula:



wherein R is selected from the group consisting of phenyl, caproylphenyl, alkyl, cycloalkyl, alkylphenyl, alkylphenoxyalkyl, and alkoxyphenyl radicals and wherein said alkyl radical contains 4 to 18 carbon atoms, said cycloalkyl radical contains 5 to 6 carbon atoms, the alkyl portion of said alkylphenyl radical contains 1 to 8 carbon atoms, the alkyl portions of said alkylphenoxyalkyl radical contains 2 to 5 carbon atoms and the alkyl portion of said alkoxyphenyl radical contains 2 to 4 carbon atoms; M is a metal selected from the group consisting of molybdenum and tungsten; X is an element selected from the group consisting of the chlorine and sulfur; y is the valency of the metal M; z is an integer of at least one but less than the valency of the metal M; and v is the valency of X.

2. The compound molybdenum tris-(diisooctyl dithiophosphate) dichloride.

3. The compound molybdenum tris-(diisooctyl dithiophosphate) sulfide.

4. The compound molybdenum didodecyl dithiophosphate dichloride.

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