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[54] SULFUR AND PHOSPHORUS BEARING LUBRICANT

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Related U.S. Application Data

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** .... **252/18**; 252/25; 252/32.7 E; 252/46.6; 252/48.6; 252/49.8; 252/397; 252/400 A

[51] **Int. Cl.**[2] **C10M 3/18**; C10M 5/14; C10M 7/20; C10M 7/24

[58] **Field of Search** .... 252/32.7 E, 18, 25, 46.6, 252/48.6, 49.8, 397, 400 A

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[57] **ABSTRACT**

The performance of lubricants having a mineral oil or synthetic oil base can be improved greatly by dithiophosphates of zinc, lead, tin, tungsten, molybdenum, niobium, lanthanum, antimony, bismuth, chromium, vanadium, or cadmium esterified with alkyl, aryl, or alkyl-aryl groups in synergistic cooperation with additives free from heavy metals, but containing sulfur and phosphorus, such as sulfides of phosphorus and known addition agents.

11 Claims, No Drawings

SULFUR AND PHOSPHORUS BEARING LUBRICANT

This application is a division of the copending application Ser. No. 227,234, filed Feb. 17, 1972, now U.S. Pat. No. 3,840,463.

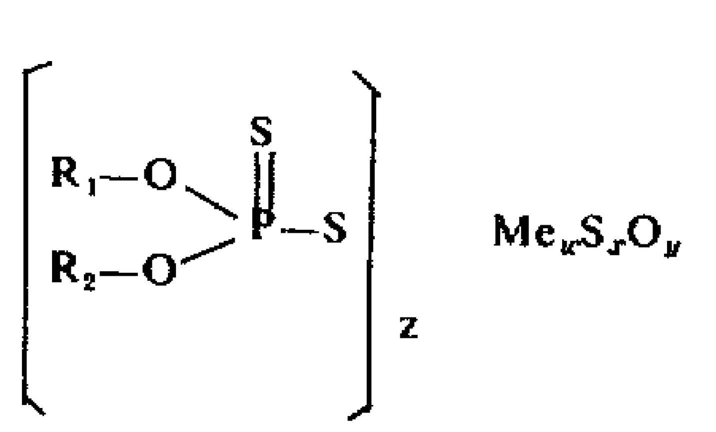
This invention relates to heavy-duty lubricants, and particularly to addition agents for such lubricants and to the lubricants containing the same.

It is known to mix lubricant base oils, which may be petroleum fractions or synthetic liquids, with compounds containing sulfur and phosphorus to improve the lubrication performance.

It has now been found that such base oils can be improved to an extent not available heretofore by the addition of a synergistic mixture of metalorganic compounds and compounds free from heavy metal and containing sulfur and phosphorus. The mixtures of the invention are added to natural or synthetic base oils in amounts of 0.1% to 20% of the weight of the base, the lower limit being useful for lubricants intended for relatively light duty, and the higher limit typically being reached in concentrates intended to be diluted with more base oil. For heavy duty service in automotive engines and transmissions, the lubricant ready for use should contain between 1 and 12% of a mixture of the invention.

The metalorganic component in the mixtures of the invention contains zinc, lead, tin, tungsten, molybdenum, niobium, lanthanum, antimony, bismuth, chromium, vanadium, or cadmium. The organic moiety of the compound should include alkyl radicals, also sulfur and phosphorus. The metalorganic compounds best suited for the mixtures of the invention are alkyl, aryl, and alkyl-aryl dithiophosphates of the heavy metals enumerated.

The metalorganic compounds of the invention thus have the formula



In these formulas, R_1, R_2 are members of the group consisting of straight-chained, branched, and cyclic alkyl having 2 to 10 carbon atoms, phenyl, o-alkylphenyl, or p-alkylphenyl, the alkyl groups of the alkylphenyls having 1 - 6 carbon atoms.

Me is one of the heavy metals referred to above, y is 0 or an integer up to 4, x is zero or an integer up to 6, z is 2 or 3, and w is 1 or 2.

The dithiophosphates of heavy metals according to the above formula are known, and many are staple articles of commerce sold, for example, by R. T. Vanderbilt Co. Inc. of New York, N.Y. The following compounds are representative of the metalorganic compounds in the mixtures of the invention:

antimony 0,0-diethyldithiophosphate,
antimony 0,0-dipropyldithiophosphate,
antimony 0,0-dibutyldithiophosphate,
antimony 0,0-dipentyldithiophosphate,
antimony 0,0-dicyclopentyldithiophosphate,
antimony 0,0-dihexyldithiophosphate,
antimony 0,0-dicyclohexyldithiophosphate,
antimony 0,0-diheptyldithiophosphate,
antimony 0,0-dioctyldithiophosphate,

antimony 0,0-dinonyldithiophosphate,
antimony 0,0-didecyldithiophosphate,
antimony 0,0-diphenyldithiophosphate
antimony 0,0-di-o-methylphenyldithiophosphate,
antimony 0,0-di-p-methylphenyldithiophosphate
antimony 0,0-di-o-ethylphenyldithiophosphate,
antimony 0,0-di-o-propylphenyldithiophosphate,
antimony 0,0-di-o-butylphenyldithiophosphate,
antimony 0,0-di-o-pentylphenyldithiophosphate,
antimony 0,0-di-o-hexylphenyldithiophosphate,
antimony 0,0-di-p-hexylphenyldithiophosphate,

the corresponding bismuth and lanthanum N-dialkyldithiophosphates in which z is 3, w is one, and x and y are 0; the corresponding 0,0-disubstituted dithiophosphates of lead, zinc, tin, and cadmium wherein z is 2, w is 1, and x and y are 0; the corresponding 0,0-substituted dithiophosphates of molybdenum, tungsten, chromium, vanadium, and niobium wherein z is 2, w is 2, x is 2, and y is 2.

The metalorganic compounds are preferably present in lubricants of the invention which are ready for use in amounts of 0.5 to 4%, and may be present in concentrates in amounts of up to 15%, all percentage figures being by weight unless otherwise stated specifically.

Suitable sulfur-phosphorus compounds free from heavy metal include the phosphorus sulfides, such as P_4S_7, P_2S_5 (P_5S_{10}), and P_4S_3, and corresponding polysulfides containing additional sulfur, also thiophosphates in which phosphorus is directly bound to sulfur, and the like. Sulfur may be replaced in these compounds partly or entirely by selenium or tellurium. Preferred compounds of this type are obtained by sulfurization and/or phosphorization of organic substances containing one or more olefinic double bonds, e.g., sperm oil butadienes or terpenes. Sulfurzied sperm oil esterified with dithiophoshpate, sulfurized terpene esterified with dithiophosphate, and sulfurized sperm oil phosphated by reaction with phosphorus pentoxide are among the more complex compounds free from heavy metals which constitute the second component of the synergistic mixtures of this invention.

The last-mentioned compounds also are known and constitute ingredients of complex commercial mixtures, not capable of precise structural analysis, such as Anglamol 99 (Lubrizol Corp., Cleveland, Ohio), which has a nominal sulfur content of 31.5% and a phosphorus content of 1.75%.

The sulfur and phosphorus bearing components of the mixtures of the invention which are free of heavy metal may be present in the improved lubricants in the same amounts as the metalorganic compounds, and the same ranges of concentration are preferred. The individual values, however, are preferably chosen in such a manner that the sulfur-phosphorus compounds are present in amounts of two to six times the weight of the metalorganic compound.

The mixtures are combined with base oils conventional in the manufacture of lubricants. Good results are obtained with mineral oils having viscosities between 1.8°E (Engler) at 20°C and 35°E at 50°C. Synthetic oils, such as diisodecyl phthalate, trimethyl adipate, or the dioctyl ester of sebacic acid, are most favorably affected at viscosities between 1.8°E at 20°C to about 6.5°E at 50°C.

As compared to known lubricants, the lubricant compositions of the invention substantially reduce wear of the lubricated surfaces, improve the adhesion of the interfacial lubricant film, enhance the oxidation resistance and thus the useful life of the lubricant, and reduce the coefficient of friction and thus the operating temperature.

It is a particular advantage of this invention that the listed improvements are available over very wide ranges of viscosities as mentioned above. Thus, oils of low viscosity may be employed where lubricants of high viscosity were required heretofore, as in automotive transmissions and differential gearing. The same lubricant composition of the invention may be employed in an automotive vehicle in the transmission and differential gearing as well as in the engine. When the components are suitably matched, the lubricant compositions of the invention may be adapted to a wide variety of operating conditions and unusual applications, and only few preliminary tests are needed for arriving at the most suitable composition.

The following Examples further illustrate the invention. In these Examples, lubricant compositions of the invention and controls were tested in an apparatus commercially available under the name "Lubrimeter" from Sommer & Runge in Berlin, Germany. The specific testing device employed was of the improved Lohmaier design. Its basic elements are a piston pin and two small, rotating rollers frictionally engaging the pin. The wear of the pin and of the rollers under a constant load is determined. The apparatus also permits the measurement of the coefficient of friction, temperature, and contact pressure at the end of a test run. The condition of the engaged surfaces, particularly changes in the surface of the rollers, can be measured and/or observed.

In all tests, the velocity of relative sliding movement was 0.6 m/sec. The relative travel amounted to 51,840 m in 24 hours. 0.4 Liter oil was circulated to make the rate of oil application 45 liters per hour.

EXAMPLE 1

Comparison tests were performed on the afore-described testing device between a lubricant composition of the invention and two controls. The base in each case was a petroleum lubricant having a viscosity of 90 SAE. The composition (I) of the invention contained 1.5% molybdenum dioctyl-dithiophosphate and 6.5% Anglamol 99. The controls contained 8% of the molybdenum compound (III) and 8% Anglamol 99 (II) respectively.

The following results were achieved:

Composition	I	II	III
Wear loss,mg	0.074	1.49	0.66
Terminal contact pressure, kp/mm²	91	27	36
Coefficient of friction, μ			
after 5 min.	0.066	0.078	0.054
after 12 hrs.	0.058	0.094	0.052
after 24 hrs.	0.054	0.090	0.053
Condition of contact area	Very smooth	Smooth	Rough
Sludge formation	Slight	Heavy	Very heavy

As is evident from the above data, replacing 15% Anglamol in a base oil containing 8% Anglamol by the molybdenum compound of the invention reduces the weight loss by wear to approximately one twentieth although the metalorganic compound, even when used alone in an amount of 8%, only moderately reduces wear. The contact pressure figures, as determined at the end of the test runs, indicate the enlargement of the contact area by wear and confirm the wear values de-

termined by weight loss. The condition of the frictionally engaged surfaces is far superior with the combination of the invention than with either component alone, resulting in a corresponding reduction in sludge. The coefficient of friction produced by the metalorganic compound alone is somewhat lower initially, but there is no significant difference after 24 hours.

EXAMPLE 2

In the lubricants I and III described in Example 1, the molybdenum compound was replaced by equal weights of zinc dioctyl-dithiophosphate to form a Composition IV of the invention and a control V. The lubricants were tested under the same conditions as in Example 1 so that the results listed below are directly comparable with those reported above for Compositions I to III.

Composition	IV	V
Wear loss, mg	0.115	0.148
Terminal contact pressure, kp/mm²	76	67
Coefficient of friction, μ		
after 5 min.	0.076	0.095
after 12 hrs.	0.059	0.070
after 24 hrs.	0.059	0.067
Condition of contact areas	Very smooth	Fine grooves
Sludge formation	Very slight	Slight

EXAMPLE 3

Antimony dioctyl-dithiophosphate was substituted for the zinc compound of Compositions IV and V in the Compositions VI and VII respectively with the following results:

Composition	VI	VII
Wear loss, mg	0.074	0.60
Terminal contact pressure kp/mm²	85	102
Coefficient of friction, μ		
after 5 min.	0.070	0.064
after 12 hrs.	0.060	0.062
after 24 hrs.	0.058	0.058
Condition of contact areas	Very smooth	Fine grooves
Sludge formation	Slight	Very heavy

EXAMPLE 4

The following data were obtained by testing a composition VIII differing from Composition VI by containing 15% lead diamyl-dithiocarbamate instead of the antimony compound, all other conditions being unchanged.

Wear loss, mg	0.065
Terminal contact pressure, kp/mm²	89
Coefficient of friction, μ	
after 5 min.	0.065
after 12 hrs.	0.059
after 24 hrs.	0.058
Condition of contact areas	Very smooth

-continued

Sludge formation	Slight

EXAMPLE 5

When 15% cadmium di-(2-ethylhexyl)-dithiophosphate was substituted for the lead compound in Composition VIII, the test results obtained with the resulting Compound IX under otherwise identical conditions were as follows:

Wear loss, mg	0.173
Terminal contact pressure, kp/mm²	65
Coefficient of friction, μ	
after 5 min.	0.078
after 12 hrs.	0.061
after 24 hrs.	0.062
Condition of contact areas	Very smooth
Sludge formation	moderate

EXAMPLE 6

In the procedure of Example 5, 1% molybdenum di-(2-ethylhexyl)-dithiophosphate and 05% zinc di-(2-ethylhexyl)-dithiophosphate were substituted for the corresponding cadmium compound, and the Composition X so obtained yielded the following test results under the standard conditions reported above:

Wear loss, mg	0.065
Terminal contact pressure, kp/mm²	100
Coefficient of friction, μ	
after 5 minutes	0.060
after 12 hours	0.051
after 24 hours	0.050
Condition of the contact areas	Very smooth
Sludge formation	Very slight

The tests described in the several Examples employed the same base oil and the same sulfur and phosphorus bearing component free from heavy metal and the same weight ratio of the metalorganic compounds to the other components to permit direct comparison of the results obtained. Substantially the same relationship of the test results was found when the mineral oil base of SAE 90 was replaced by a fraction of lower viscosity or by a synthetic lubricating oil. A combination of 1.5% metalorganic compound and 6.5% Anglamol 99 was found to produce particularly good lubricants with the mineral oil base used, but the ratio had to be varied within the limits indicated above to produce the best possible lubricant characteristics for other base oils, mineral or synthetic, and was readily determined for each particular set of conditions by a few elementary trial runs. No specific rules can be based on physical or chemical characteristics of the base oil or of the additives.

Anglamol 99 is merely representative of the phosphorus and sulfur bearing additive compositions, usually of undefinable chemical composition, which are now on the market, and tests performed with other proprietary products and with the welldefined sulfides of phosphorus show the synergistic cooperation with the metalorganic compounds described above.

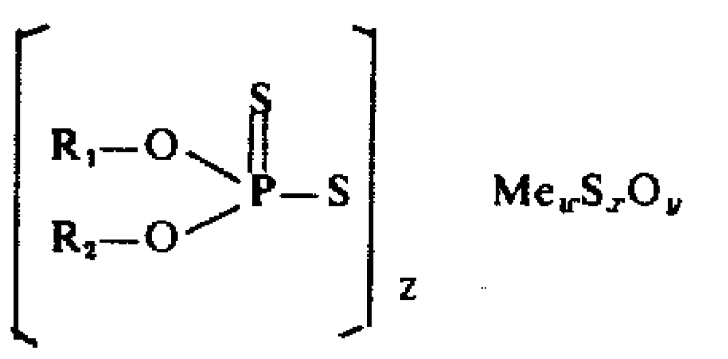
While the invention has been described with particular reference to specific embodiments, it is to be understood, therefore, that it is not limited thereto, but is to be construed broadly and restricted solely by the scope of the appended claims.

What is claimed is:

1. In a lubricant composition including a base oil of mineral or synthetic origin and a lubrication-improving additive containing chemically bound phosphorus and sulfur while free from chemically bound heavy metal, the improvement which comprises:

a. a metalorganic dithiophosphate in an amount sufficient to enhance the lubrication-improving effect of said additive,

b. said dithiophosphate having the formula



wherein R_1 and R_2 are members of the group consisting of straight-chained alkyl, branched alkyl, and cycloalkyl having 2 to 10 carbon atoms, phenyl, o-alkylphenyl, or p-alkylphenyl, the alkyl of said alkylphenyl having 1 to 6 carbon atoms;

Me is a metal of the group consisting of zinc, lead, tin, tungsten, molybdenum, niobium, lanthanum, antimony, bismuth, chromium, vanadium, or cadmium;

w is 1 or 2;

x is zero or an integer not greater than 6;

y is zero or an integer not greater than 4;

z is 2 or 3.

2. In a composition as set forth in claim **1**, the amount of said lubrication-improving additive being between one and six times the weight of said dithiophosphate.

3. In a composition as set forth in claim **2**, said phosphorus being directly bound to said sulfur in said lubricationimproving additive.

4. In a composition as set forth in claim **2**, said lubrication-improving additive being a phosphorus sulfide.

5. In a composition as set forth in claim **2**, the combined amount of said lubrication-improving additive and of said dithiophosphate being between 0.1 and 20% of the weight of said base oil.

6. In a composition as set forth in claim **2**, said lubrication-improving additive being a substance obtained by sulfurization and/or phosphorization of an organic substance containing one or more olefinic double bonds.

7. In a composition as set forth in claim **1**, w being 1, x and y being zero, and z being 3 when Me is lead, bismuth, or lanthanum; w being 1, x and y being zero, and z being 2 when Me is lead, zinc, tin, or cadmium; and each of w, x, y, and z being 2 when Me is molybdenum, tungsten, chromium, vanadium, or niobium.

8. In a composition as set forth in claim **7**, said additive being a member of the group consisting of sulfides and polysulfides of phosphorus, thiophosphates, and products of the sulfurization and phosphorization of organic compounds containing at least one olefinic double bond.

9. In a composition as set forth in claim **8**, the combined amount of said lubrication-improving additive and of said dithiophosphate being between 0.1 and 20% of the weight of said base oil.

10. In a composition as set forth in claim **9**, said metal being antimony, cadmium, lead, molybdenum, or zinc.

11. In a composition as set forth in claim **10**, R_1 and R_2 being each amyl, octyl, 2-ethylhexyl.

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