

UNITED STATES PATENT OFFICE

2,420,893

COMPOUNDED LUBRICATING OIL

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6 Claims. (Cl. 252—32.7)

1

This invention relates to lubricants and other organic materials subject to deterioration in the presence of air or oxygen, and it relates more particularly to mineral lubricating oil compositions for use as crankcase lubricants for internal combustion engines and to addition agents suitable for retarding the deterioration of such oils and for improving other properties of the same.

It is known that the addition of certain types of metal-containing organic compounds to lubricating oils improves various properties thereof, such as their oiliness characteristics and their detergent action in engines, particularly manifested in the maintenance of a clean engine condition during operation. Various metal compounds which have been used for such purposes include the metal derivatives of such organic materials as fatty acids, naphthenic acids, sulfonic acids, alcohols, phenols, and ketones. However, these various metal compounds generally have the disadvantage of tending to corrode alloy bearings, such as those of cadmium-silver and copper-lead, now so widely used in automotive engines; and this is especially true in engines which operate at relatively high speeds and high temperatures. It is an object of the present invention to provide a new class of addition agents for oils which are to be used as crankcase lubricants for internal combustion engines, the new additives having the primary function of preventing normal deterioration of the oil and of inhibiting any corrosive tendencies of the oil. A further object is to provide addition agents which may be added to lubricating oils containing detergent additives of the types described above, the new compounds being capable of inhibiting any corrosiveness imparted to the oils by such detergent additives. Furthermore, these new materials have of themselves the property of imparting detergent properties to oils to which they are added.

The new class of additives which have now been found to be highly satisfactory for the purpose described are the metal salts of thiophosphorous and thiophosphoric acids which contain at least one alkylated aromatic sulfide substituent.

2

These compounds may also be thought of as alkyl phenol sulfides which have been esterified by acid metal salts of thiophosphorous or thiophosphoric acids. Such compounds may be formed by reacting together an alkyl phenol sulfide, a metallic oxide or hydroxide and a sulfide of phosphorus such as phosphorus pentasulfide. By using an alkyl phenol sulfide containing alkyl side chains of sufficient length to render the compound oil-soluble, the reaction may be conducted readily in mineral oil solution. When the final product is to be used as an ingredient in compounded mineral lubricating oils, the aromatic sulfide group should contain alkyl groups having on the average a total of at least four carbon atoms for each aromatic nucleus.

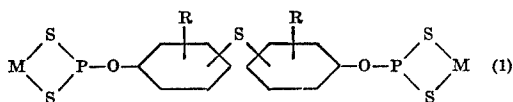
The salts of the class described which are most generally preferred for use in accordance with the present invention are the salts of divalent metal of group II of the periodic table, preferably salt of calcium, barium, strontium, magnesium or zinc although salts of other metals such as tin, nickel, aluminum, etc., are likewise useful. The element selenium and tellurium may also be present as substitutes for sulfur wherever sulfur occurs in the compound. Aromatic sulfide groups containing aromatic nuclei other than benzene nuclei may be present. Furthermore, it is intended to include as members of the new class of additive compounds in which only one of the hydroxyl or sulfhydryl groups of the phenol or thiophenyl sulfide is esterified with the radical of the acid of phosphorus, remaining hydroxyl or sulfhydryl groups being either unsubstituted or substituted with a metal or with an ester, ether, aryl, or similar group. Such compounds containing metal substituted hydroxyl or sulfhydryl groups may be formed, for example, by reacting a metal mono salt of an alkylated phenol sulfide with a sulfid of phosphorus and an appropriate metal oxide.

It is to be understood that the new class of additives includes salts in which one or more of the hydrogen atoms of the acid of phosphorus are substituted by an aromatic sulfide group or the like. Various types of salts illustrative of the

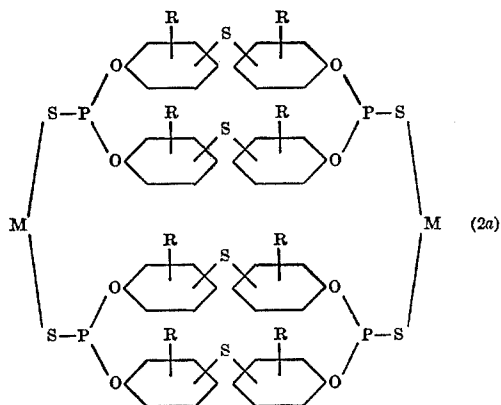
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present invention are shown in the following structural formulas, in which M represents a typical divalent metal and R represents an alkyl group:

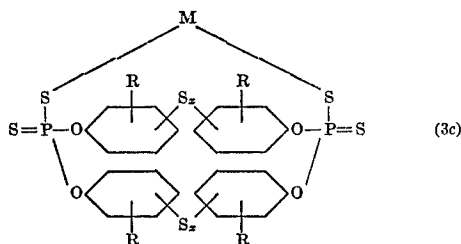
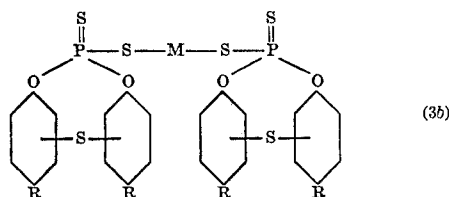
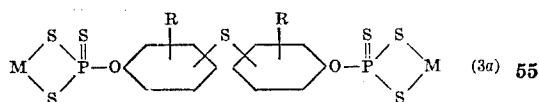
metal derivatives of mono-substituted dithiophosphorous acid:



metal derivatives of di-substituted monothiophosphorous acid:

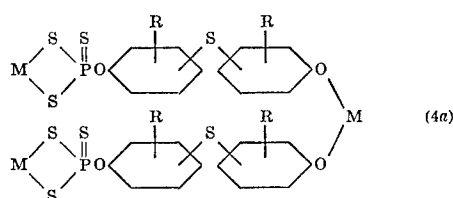


Similar derivatives of mono- and dithiophosphoric acid may be formed, of which the following are examples:



4

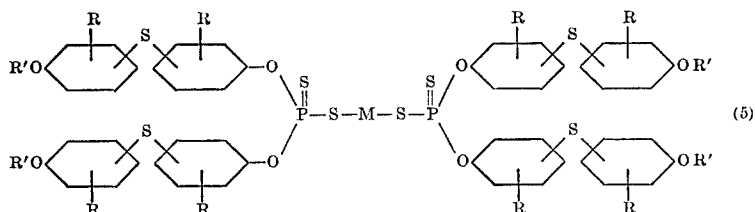
Compounds in which only one of the hydroxyl groups of an alkylated phenol sulfide is esterified by an acid of phosphorus, the other being reacted to form a metal salt or an ester, ether or the like, are illustrated by the following:



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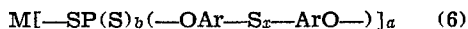


In the above formulas R represents at least one alkyl group, M represents a metal atom, and R' represents an organic group.

It is to be understood that the above formulas are illustrative only and do not limit the scope of the present invention. For example, one or more of the sulfur atoms attached to the phosphorus atom may be replaced by oxygen, with the provision that at least one sulfur atom remains so attached. Also, the oxygen of the phenol sulfide group may be replaced by sulfur, as in derivatives of thiophenol sulfides. There may also be more than one sulfur atom connecting the two aryl groups, as in polysulfides containing up to four sulfur atoms in the interconnecting group. Also, metals other than divalent metals may be present in the salts. The positions of the various groups in the ring are not to be considered as limited to those shown in the foregoing examples. It should be understood that the additives of the present invention, illustrated by the above formulas, include compounds in which various substituent atoms or groups may be attached to the aromatic nucleus, such as alkyl, aryl, carboxyl, hydroxyl, alkoxy, sulfhydryl, nitro, ester, keto, amino, aldehyde, chloromethyl, amino methyl, alkyl thiomethyl, alkyl xanthomethyl, methyl substituted carboxyl, methyl substituted hydroxyl or sulfhydryl groups, halogen atoms, etc. Alkyl radicals attached to an aromatic nucleus may have a total of four to twenty-four carbon atoms in all of such groups, and in many cases sixteen to twenty-four or more carbon atoms in a single group or a plurality of groups are preferred.

The most preferred compounds of the present

invention, that is, the metal salts of the thio-phosphorous and thiophosphoric acid diesters of alkylated phenol sulfides may be defined by the following general formula:



in which M is a metal, Ar is an alkylated aromatic group, a is the valence of M, b is 0 or 1, and x is 1 to 4. Substituent atoms or groups may be present as mentioned previously.

A convenient and satisfactory method of preparing the preferred compounds of the present invention consists in reacting together an alkyl phenol sulfide, a sulfide of phosphorus and a metallic oxide or hydroxide. The sulfides of phosphorus which may be employed include P_2S_5 , P_2S_3 , P_4S_3 and P_4S_7 , as well as mixtures of those with sulfur and/or phosphorus. As stated above, when the phenol sulfide contains solubilizing alkyl groups, the reaction may take place in solution in a mineral oil. A light naphtha solvent may be used, and the solvent removed by evaporation after the reaction has been completed; but if the product is to be used as an additive for lubricating oils, it is convenient to cause the reaction to take place in a lubricating oil medium and to prepare a concentrate of the salt in such medium without separation from the solvent. Such concentrates, containing, say, 25% to 75% of additive, are often useful in saving shipping weight and storage space and in facilitating blending operations when preparing the final lubricating oil blend for commercial use. When preparing a concentrate of the type described, it has been found advantageous to add a higher alcohol, such as stearyl alcohol, to the reaction mixture after completion of the reaction in order to facilitate filtration of the final product. In many instances the presence of the higher alcohol is beneficial in the final lubricating oil composition, since it often enhances the detergent and sludge dispersive qualities of the lubricant and aids the solubility of the metal-containing additives and at the same time imparts some oiliness properties to the lubricant.

Among the alkyl phenol sulfides which may be employed as starting materials for the preparation of additives in accordance with the present invention are included tert.-amyl phenol sulfide, tert.-octyl phenol sulfide, diamyl phenol sulfide, cetyl phenol sulfide, octadecyl phenol sulfide, wax alkylated phenol sulfide, octyl cresol sulfide, or the corresponding disulfides or polysulfides or polymers. Also mixtures of mono and polysulfides and/or polymers may be employed. These various phenol sulfides are prepared by reaction of the corresponding alkylated phenol with various proportions of sulfur mono-chloride or dichloride substantially as described in U. S. Patents 2,139,321, 2,139,766, 2,174,248 and 2,198,828.

For preparing the alkylated phenol sulfides suitable alkylated phenols may be obtained by alkylating phenol, cresol, naphthol or other phenolic compounds with such alkylating agents as alcohols, alkyl halides, alkyl phosphates, olefins, terpenes and the like, with the aid of catalysts such as aluminum chloride, boron fluoride, stannic chloride and other metal halides, hydrochloric acid, hydrofluoric acid, sulfuric acid, phosphoric acid, activated clay, etc. Conveniently, olefinic material, such as petroleum refinery gases containing mixtures of olefins, may be used,

or preferably individual olefins may be employed such as butene, pentene or an olefin polymer such as di-isobutylene or tri-isobutylene. Low molecular weight polymers of ethylene, propene, pentene, or isopentene or mixtures of these may also be utilized in alkylating the phenols. High molecular weight alkylated phenols may also be employed, for example, those prepared by condensing phenols with chlorinated paraffin wax, chlorinated petrolatum, or with a chlorinated kerosene or gas oil. Naturally occurring phenols, such as those obtained by alkaline extraction of certain petroleum stocks or those obtained from cashew nut shell liquid or from other vegetable sources may likewise be used.

One class of alkyl phenols which are particularly useful are those which have been prepared by alkylation of phenol with an olefin polymer such as diisobutylene or a refinery butene polymer oil. Alkylation of phenol with about an equimolecular proportion of diisobutylene give para-tert.-octyl phenol, also known as diisobutyl phenol or tetramethyl butyl phenol. This phenolic material is especially desirable because of its ease of synthesis and because products made from it are highly satisfactory for the present invention. In many instances, however, a higher degree of alkylation may be advantageous and for this reason the phenol may be alkylated with as much as two molecular equivalents of diisobutylene to give, under proper conditions, essentially di-tert.-octyl phenol, or it may be alkylated with other olefin polymers such as tri-isobutylene, other isobutylene polymers, or a normal butene polymer. The latter type of polymer is obtained as a by-product in the manufacture of butyl alcohol from petroleum refinery butenes. When used as an alkylating agent it gives alkyl phenol having highly branched alkyl groups of about sixteen to twenty carbon atoms. It should be understood that in many cases the alkylation products may be mixtures of various compounds rather than entirely one specific alkyl phenol and that such mixtures may be used in practicing the invention.

The methods of preparing the new products of the present invention and the use of the same in lubricating oils are illustrated in the following examples in which such preparations and uses are described in detail. These examples are given for illustrative purposes only and are not to be considered as limiting the scope of the invention in any way.

EXAMPLE 1

221 parts by weight of tert.-octyl phenol sulfide was dissolved in 365 parts of a solvent extract of Mid-Continent paraffinic oil of 52 seconds viscosity Saybolt at 210° F. and heated to 100° C with stirring. (The tert.-octyl phenol sulfide was prepared by alkylation of phenol with diisobutylene, followed by reaction with sulfur dichloride. The material contained 10.2% sulfur.) Over a period of 10 minutes 20.5 parts of ZnO was added and during the following 15 minutes the temperature was raised gradually to 140° C. Over a period of 30 minutes 55.5 parts of P_2S_5 (fine than 40 mesh) was added and the temperature raised to 160° C. There was an evolution of H_2S during this step and the mixture assumed a dark brown color. The temperature was raised to 180° C. and stirring was continued for 1½ hours to complete the reaction as shown by the

7

disappearance of the ZnO. Then 73 parts of commercial stearyl alcohol was added to facilitate filtration and the product was filtered immediately, giving a mineral oil concentrate containing approximately 40% of the zinc salt of the thiophosphate ester of tert.-octyl phenol sulfide and 10% of stearyl alcohol. Analysis showed the concentrate to contain the following:

	Per cent
zinc -----	1.17
sulfur -----	6.60
phosphorus -----	2.12

EXAMPLE 2

This preparation was similar to that of Example 1 except that a larger quantity of ZnO was employed. 221 parts of tert.-octyl phenol sulfide prepared as described in Example 1) was dissolved in 365 parts of the paraffinic oil described in Example 1. The solution was heated to 120° C. and 41 parts of ZnO was added over a 10 minute period. The temperature was raised to 40° C. 55.5 parts of P₂S₅ was then added over a 30 minute period; the temperature was then raised to 180° C. and held at this point for 2 hours. 13 parts of stearyl alcohol was added and the product filtered through Hyflo filter aid (a diatomaceous earth) giving a mineral oil concentrate of 40% zinc salt of the thiophosphate salt of tert.-octyl phenol sulfide and 10% stearyl alcohol. Analysis showed the concentrate to contain the following:

	Per cent
zinc -----	1.03
sulfur -----	5.85
phosphorus -----	2.22

EXAMPLE 3

A solution of 889 parts (2 molecular proportions) of tert.-octyl phenol sulfide (prepared as in Example 1) in 1,465 parts of the paraffinic oil of Example 1 was heated to 120°-140° C. Then over a 30 minute period 81 parts (1 molecular proportion) of ZnO was added, followed by 222 parts (1 molecular proportion) of P₂S₅ during the following 30 minutes. The temperature was then raised to 180° C. and the heating continued for ½ hours. 252 parts of commercial stearyl alcohol was added and the product filtered immediately to give a solution of 40% zinc thiophosphate ester of tert.-octyl phenol sulfide and 10% stearyl alcohol. Analysis showed that the mineral oil concentrate contained the following:

	Per cent
zinc -----	1.35
sulfur -----	6.21
phosphorus -----	2.36

EXAMPLE 4

88 grams (2 molecular proportions) of tert.-octyl phenol sulfide was dissolved in 770 cc. of an aromatic petroleum naphtha (200°-280° F. boiling range; 65%-70% aromatic content). The solution was heated to 110° C. under reflux and 2 grams (1 molecular proportion) of P₂S₅ was added over a 20 minute period. The temperature was held at 110° C. for 4 hours with stirring, when the P₂S₅ was completely absorbed, and the product was then filtered giving a clear brown

8

filtrate comprising a solution of the thiophosphoric acid ester of tert.-octyl phenol sulfide.

EXAMPLE 5

One-half of the solution prepared in Example 4 was mixed with 200 cc. of aromatic petroleum naphtha and heated to 110° C. in a 3-necked flask equipped with a stirrer and reflux condenser, the latter being fitted with a trap for the removal of condensed water. Over a 1 hour period 16 grams of Ba(OH)₂·8H₂O was added, after which heating and stirring were continued for 4 hours at 110° C., when the barium hydrate had become completely absorbed. The product was then filtered giving a clear light brown solution. Removal of the solvent by vacuum stripping gave an oil-soluble transparent solid. The material was redissolved in petroleum ether and dried to give a fine brown solid product, which was the barium salt of the thiophosphoric acid ester of tert.-octyl phenol sulfide.

EXAMPLE 6

The remaining half of the solution from Example 4 was treated in the same manner as in Example 5, except that 5 grams of ZnO was used in place of 16 grams of Ba(OH)₂·8H₂O. However, after 3 hours of heating at 110° C. there appeared to be no reaction between the zinc oxide and the ester. To facilitate the reaction 200 cc. of water was added and heating was continued at 110° C. for 16 hours. 500 cc. of benzene was added and the mixture heated under reflux in order to remove water through the reflux trap. The remaining solution was then filtered, using Hyflo filter aid, and the filtrate dried under vacuum at 180° C. The dried product was redissolved in ether, filtered and dried, yielding a zinc salt of the thiophosphoric acid ester of tert.-octyl phenol sulfide as an oil-soluble brown resinous material.

EXAMPLE 7

The corrosion inhibiting properties of the materials prepared as described in the previous examples were determined by adding small quantities of the products to a lubricating oil base consisting of a solvent extracted Mid-Continent paraffinic oil of 52 seconds Saybolt viscosity at 210° F. and testing the blends so prepared by means of the test method described below. Each blend was so prepared as to contain 1% of the additive salt.

The test for each blend and for a sample of the unblended base oil was conducted as follows: 500 cc. of the oil to be tested was placed in a glass oxidation tube (13" long and 25" diameter) fitted at the bottom with a ¼" bore air inlet tube perforated to facilitate air distribution. The oxidation tube was then immersed in a heated bath so that the oil temperature was maintained at 325° F. during the test. Two quarter sections of automotive bearings of copper-lead alloy and two of cadmium-silver alloy of known weight having a total area of 25 sq. cm. for each alloy were attached to opposite sides of a stainless steel rod which was then immersed in the oil and rotated at 600 R. P. M., thus providing sufficient agitation of the sample during the test. Air was then blown through the oil at 2 cu. ft. per hour. The bearings were washed with naphtha and weighed at the end of a 16 hour period. The weight losses of the bearings are shown in Table I.

9
Table I

Oil	Bearing Weight Loss (mg./25 sq. cm.)	
	Cu-Pb	Cd-Ag
Base Oil.....	11	0
Base Oil+1% barium salt of Example 5.....	10	10
Base Oil+1% zinc salt of Example 6.....	10	10
Base Oil+2.5% zinc salt concentrate of Example 1.....	10	0
Base Oil+2.5% zinc salt concentrate of Example 3.....	0	0

¹ Bearings gained slightly in weight.

EXAMPLE 8

A further series of bearing corrosion tests were conducted according to the method described in Example 7, except that only the two copper-lead bearing quarters were present, and instead of continuing the tests for one 16 hour period the bearings were cleaned, weighed, and repolished every 4 hours. The base oil used was a well refined solvent extracted paraffinic type mineral lubricating oil of S. A. E. 20 viscosity grade. Table II shows the cumulative bearing weight losses that had accumulated at the end of each 4 hour period up to a total of 16 hours.

Table II

Oil	Cumulative Bearing Weight Loss (mg./25 sq. cm.)			
	4 hrs.	8 hrs.	12 hrs.	16 hrs.
Base Oil.....	0	187	-----	-----
Base Oil+1% barium salt of Example 5.....	2	6	21	40
Base Oil+1% zinc salt of Example 6.....	4	9	25	63
Base Oil+2.5% zinc salt concentrate of Example 1.....	0	0	11	54
Base Oil+2.5% zinc salt concentrate of Example 3.....	1	5	21	30

EXAMPLE 9

The Underwood oxidation test was applied to a base oil consisting of a solvent extracted paraffinic oil of 47.5 seconds viscosity at 210° F. and a viscosity index of 113 and to a blend consisting of the same base oil to which had been added 2.5% of an additive concentrate consisting of 50% each of the concentrates of Example 1 and Example 2. The test was conducted as follows:

The polished bearings of the Underwood machine were thoroughly abraded with emery cloth to expose a fresh surface so that corrosion would proceed uniformly, and then accurately weighed. The apparatus was filled with 1,500 cc. of the lubricant under test and the pump and heater started. The oil pressure was regulated to 10 lbs./sq. in. by means of by-pass valves and maintained at this pressure throughout the test. As soon as the oil had attained the test temperature of 325° F. the heater and pump were turned off just long enough to put the already prepared and weighed bearings in place. Two copper-lead bearing halves were used simultaneously in the test, the bearings being mounted on a polished copper baffle (2" x 10") which served to catalyze oxidation of the oil. At the end of the test period of 5 hours the bearings were removed, cleaned with naphtha, dried and weighed. A new copper-lead bearing was then placed in the machine and the test conducted for an additional 5 hour period. To accelerate corrosion iron naphthenate in an equivalent of 0.01% Fe₂O₃ was added to

10

each oil sample. Table III shows the cumulative bearing weight loss for the complete 10 hour run as well as the neutralization number of the oil and the naphtha insoluble sludge determined at the end of the test.

Table III

Oil	Cumulative Bearing Weight Loss (mg.)	Used Oil Inspections	
		Neut. No.	Naphtha Insoluble Sludge, per cent
Base Oil.....	570	7.6	0.1 ¹
Base Oil+2.5% additive concentrate of zinc salt.....	6	2.0	0.1 ¹

It will readily be seen from the results of the tests of Examples 7, 8 and 9 that the additives of the present invention are very effective inhibitors of bearing corrosion when added to lubricating oil compositions. The used oil inspection data of Example 9 show that the additives also served to inhibit deterioration of the lubricating oil.

EXAMPLE 10

In the following tests samples of an unblended base oil consisting of a solvent extracted Coastal naphthenic oil of 60 seconds viscosity (Saybolt) at 210° F. and of the base oil containing 2.5% of zinc salt concentrate consisting of 50% each of the concentrates of Examples 1 and 2 were tested in a 6-cylinder Chevrolet engine run under high speed and high temperature conditions, namely, 3150 R. P. M., 280° F. oil temperature, 200° F. cooling jacket temperature, and an air/fuel ratio of 14.2/1, for periods of 36 hours. After each test was completed the engine parts were examined and given demerit ratings based on their condition. The individual demerits were weighted and an overall rating calculated from them. The lower demerit rating indicated a better engine condition and hence a better performance of the oil in the engine. The results are shown in Table IV.

Table IV

Oil	Engine Demerits			
	Overall	Ring Zone	Sludge	Cu-Pb Bearing Wt. Loss ¹
Base Oil.....	3.37	2.61	4.63	0.40
Base Oil+2.5% zinc salt concentrate.....	0.67	0.42	0.19	0.10 ¹

¹ Gms./bearing of about 50 sq. cm. area.

Although the metal salts of the present invention may be used as the sole additive in lubricating oil compositions, in many instances it will be found of great advantage to employ them in conjunction with other addition agents, particularly with detergent type additives, such as metal soaps, metal petroleum sulfonates, metal phenates, metal alcoholates, metal alkyl phenol sulfides, metal organophosphates, thiophosphates phosphites and thiophosphites, metal salicylates metal xanthates and thioxanthates, metal phenol sulfonates, metal thiocarbamates, reaction products of metal alkyl phenates and sulfur, reaction products of metal alkyl phenates and phosphorus sulfides, and the like.

Thus the metal alkyl phenol sulfide thiophosphates and thiophosphites may be used in lu-

11

lubricating oils containing such addition agents as barium, tert.-octyl phenol sulfide, calcium tert.-amyl phenol sulfide, nickel oleate, barium octadecylate, calcium phenyl stearate, zinc diisopropyl salicylate, aluminum naphthenate, calcium cetyl phosphate, barium di-tert.-amyl phenol sulfide, calcium petroleum sulfonate, zinc nethyl cyclohexyl thiophosphate, calcium dichlo-octearate, tin naphthenate, aluminum-calcium mixed soap of fatty acids from the oxidation of petroleum fractions, barium mahogany sulfonates, etc.

Particularly advantageous are lubricant compositions in which the additives of the present invention are used in conjunction with metal salts of petroleum mahogany sulfonic acids, with mixtures of the metal sulfonates and metal alkyl phenol sulfides, or with mixtures of the metal sulfonates and reaction products of metal phenates and sulfur.

Examples of such compositions include the following:

- 1) S. A. E. 30 grade refined lubricating oil containing:
 - 1% barium salt of tert.-octyl phenol sulfide thiophosphite,
 - 1% calcium petroleum sulfonate
- 2) S. A. E. 20 grade solvent extracted lubricating oil containing:
 - 0.8% zinc salt of tert.-octyl phenol sulfide thiophosphate,
 - 0.6% barium di(tert.-amyl) phenol sulfide,
 - 1.7% mixed calcium-sodium petroleum sulfonates.
- (3) Paraffinic lubricating oil containing:
 - 2.3% barium mahogany sulfonates,
 - 1.2% calcium lauryl phenol sulfide thiophosphate.
- (4) Mid-Continent lubricating oil containing:
 - 1.5% calcium isohexadecyl phenol sulfide,
 - 0.9% magnesium diamyl phenol sulfide thiophosphite.
- (5) Pennsylvania lubricating oil (S. A. E. 30) containing:
 - 1.5% calcium mahogany sulfonate,
 - 0.5% barium salt of C₁₆-C₂₀ alkylated phenol sulfide,
 - 0.5% barium salt of C₁₆-C₂₀ alkylated phenol disulfide,
 - 1.0% zinc tertiary octyl phenol sulfide thiophosphate.
- 6) Phenol extracted lubricating oil (S. A. E. 10) containing:
 - 1.0% calcium mahogany sulfonate,
 - 1.0% magnesium isohexadecyl phenate,
 - 1.0% zinc tertiary octyl phenol disulfide thiophosphate.
- 7) Paraffinic lubricating oil (S. A. E. 30) containing:
 - 1.5% basic calcium mahogany sulfonate,
 - 1.0% calcium octadecylate,
 - 1.0% zinc isohexadecyl phenol sulfide thiophosphate.
- 8) Solvent extracted Coastal oil containing:
 - 1.5% calcium sulfonate,
 - 0.75% barium tert.-octyl phenol sulfide thiophosphate,
 - 1.0% additive concentrate prepared by reaction of barium tert.-octyl phenate with sulfur.¹

¹ Method of preparation described in the copending application of Dilworth T. Rogers and John G. McNab, Serial No. 486,428, filed May 10, 1943.

12

The following examples demonstrate the use of such additive combinations in internal combustion engine lubrication:

EXAMPLE 11

- A lubricating oil blend was prepared by adding to a portion of the base oil used in Example 10 a 3-component additive comprising 2.5% of the additive concentrate of Example 3, 1.5% of mixed sodium-calcium petroleum sulfonates (ratio of 1 part by weight of sodium sulfonate to 7.4 parts calcium sulfonate) and 1.16% of an additive concentrate prepared by reaction of barium tert.-octyl phenate with sulfur at 170° C. (The concentrate contained 40% additive, 10% stearyl alcohol and 50% mineral lubricating oil.) This additive blend was tested in a Chevrolet engine for 36 hours in the same manner as described in Example 10. The following results were obtained:

Table V

Oil	Engine Demerits			Cu Pb Bearing Wt. Loss (Mg.)
	Overall	Ring Zone	Sludge	
Base Oil.....	3.37	2.61	4.63	0.404
Base Oil+3-Component Additive.....	0.26	0.14	0.12	0.387

By comparing the results of the above test with those of Example 10 it will be noted that the 3-component additive blend was even more effective than the alkyl phenol sulfide thiophosphate salt alone in maintaining engine cleanliness. Also although the presence of the metal sulfonates caused some sacrifice of bearing corrosion inhibition the blended oil was still less corrosive than the base oil.

EXAMPLE 12

A 3-component additive blend containing the same types of additives in the same proportions and in the same base stock as in Example 11 was subjected to a 126 hour engine test in a single cylinder Caterpillar Diesel engine run under the following conditions: 165° F. oil temperature, 180° cooling jacket temperature, 1000 R. P. M., 19.8 B. H. P. load. Examination of the various engine parts after the test showed that the oil performed much more satisfactorily than a widely marketed commercial heavy duty oil run in the same engine under the same conditions. The results are tabulated below:

Table VI

Oil Tested	Engine Demerits		
	Overall	Ring Zone	Sludge
3-Component Blend.....	0.46	0.0	0.25
Commercial Heavy Duty Oil.....	1.01	0.84	0.50

Particularly to be noted is that with the 3-component blend the ring zone demerit was zero, that is, there were absolutely no deposits of any kind in the ring grooves or slits or on the ring lands or sides.

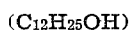
The lubricating oil base stocks used in the compositions of this invention may be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly

those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichloro ethyl ether, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coal tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or volatilized products may be employed, either alone or in admixture with mineral oils.

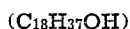
For the best results the base stock chosen should normally be that oil which without the new additives present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubricating of certain low and medium speed Diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of Diesel service, particularly with high speed Diesel engines, and in aviation engine and other gasoline engine service, oils of higher viscosity index are often preferred, for example, up to 75 to 100, or even higher, viscosity index.

In addition to the materials to be added according to the present invention, other agents may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, volatilized fats, volatilized mineral oils, and/or volatilized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like may also be employed.

Assisting agents which are particularly desirable are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol ($C_8H_{17}OH$), lauryl alcohol



cetyl alcohol ($C_{16}H_{33}OH$), stearyl alcohol, sometimes referred to as octadecyl alcohol,



heptadecyl alcohol ($C_{17}H_{35}OH$), and the like; the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols, such as naphthenic alcohols and aryl substituted alkyl alcohols, for instance phenyl octyl alcohol, or octadecyl benzyl alcohol or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes, the wool fat, sperm oil or other natural products rich in alcohols may be used *per se*. Products prepared synthetically by chemical processes may also be used, such as alcohol prepared by the oxidation of petroleum hydrocarbons, e. g., paraffin wax, petrolatum, etc.

These assisting agents serve to enhance the detergent and sludge dispersive qualities and aid the solubility of the metal-containing additive and at the same time impart some oiliness properties to the lubricating oil compositions.

In addition to being employed in crankcase lubricants the additives of the present invention may also be used in extreme pressure lubricants, engine flushing oils, industrial oils, general machinery oils, process oils, rust preventive compositions, and greases. Also their use in motor fuels, Diesel fuels and kerosene is contemplated. A particular application in this regard is their use in motor fuels containing tetraethyl lead or other anti-knock agents, the additives of the present invention serving not only as antioxidants for the fuel but also as stabilizers for the anti-knock agent itself. Since these additives exhibit antioxidant properties and are believed also to possess ability to modify surface activity, they may be employed in asphalts, road oils, waxes, fatty oil of animal or vegetable origin, soaps, and plastics. Similarly, they may be used in natural and synthetic rubber compounding both as vulcanization assistants and as anti-oxidants, and generally they may be used in any organic materials subject to deterioration by atmospheric oxygen.

The present invention is not to be considered as limited by any of the examples described herein which are given by way of illustration only but it is to be limited solely by the terms of the appended claims.

We claim:

1. A mineral lubricating oil containing a stabilizing quantity of a metal salt of a thiophosphoric acid ester of an octyl phenol sulfide.

2. A mineral lubricating oil containing a stabilizing quantity of a zinc salt of a dithiophosphoric acid ester of a tert.-octyl phenol sulfide.

3. A mineral lubricating oil containing a stabilizing quantity of a barium salt of a dithiophosphoric acid ester of a tert.-octyl phenol sulfide.

4. A method of preparing a lubricating oil concentrate containing a zinc salt of a dithiophosphoric acid ester of a tert.-octyl phenol sulfide which comprises dissolving the tert.-octyl phenol sulfide in a mineral lubricating oil and heating the solution thus formed in the presence of zinc oxide and phosphorus pentasulfide at a temperature of 100° to 180° C.

5. The method of preparing a lubricating oil concentrate containing about 40% of the zinc salt of a dithiophosphoric acid ester of a tert.-octyl phenol sulfide which comprises dissolving about two molecular proportions of tert.-octyl

15

phenol sulfide in a suitable quantity of a mineral lubricating oil, heating the solution thus formed to about 120° to 140° C., adding about one molecular proportion of zinc oxide and about one molecular proportion of phosphorus pentasulfide and heating at about 180° C. until the solid reactants are substantially completely absorbed in the solution, adding about 10% by weight of lauryl alcohol, based on the total weight of the mixture, and filtering the solution, the amount of lubricating oil solvent used being sufficient to form a concentrated solution which, after filtering, contains about 40% by weight of the zinc salt formed in the reaction.

6. The method of preparing a barium salt of dithiophosphoric acid ester of a tert.-octyl phenol sulfide which comprises dissolving about two molecular proportions of a tert.-octyl phenol sulfide in a petroleum naphtha, heating the solution under reflux while gradually adding about one molecular proportion of phosphorus pentasulfide, continuing the refluxing of the solution until the phosphorus pentasulfide is substantially completely absorbed, filtering the resulting solution, heating the solution further under

16

reflux in equipment provided with means for the removal of condensed water while adding gradually about one-half molecular proportion of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, continuing the refluxing until the barium compound is substantially completely absorbed, filtering the resulting solution and removing the solvent by evaporation.

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