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COMPOUNDED LUBRICATING OIL

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24 Claims. (Cl. 252—32.7)

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This invention relates to lubricants and other organic materials subject to deterioration in the presence of 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.

This is a continuation-in-part of our co-pending application Serial Number 493,734, filed July 7, 1943, which issued October 22, 1946, as Patent Number 2,409,686.

It is known that the addition of certain types of metal 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 compounds 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 and which exhibit the desirable properties of promoting general engine cleanliness, improving film strength properties, reducing ring sticking, piston skirt varnish formation and the like, and which not only do not exhibit the corrosion promoting tendencies characteristic of the above metal compounds, but also inhibit the corrosiveness of oils to which they are added.

The new class of products which have now been found to be highly satisfactory as addition agents are the products obtained by the reaction of the elements sulfur and phosphorus with metal salts of hydroxy and mercapto substituted aromatic sulfides. When these compounds are to be used as additives for mineral oils, they should contain as a substituent in each aromatic nucleus at least one alkyl group, the total number of carbon atoms

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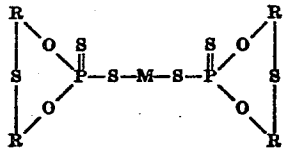
in such groups being at least five. It has been found that such products are usually satisfactory in inhibiting bearing corrosion, and in being adaptable to use with a wide variety of petroleum lubricating oil base stocks. The elements sulfur and phosphorus may be introduced into the metallic salt molecule by reacting the latter with both elemental sulfur and elemental phosphorus, or by reacting the same with a sulfide of phosphorus. The reaction may generally be brought about in a solution of lubricating oil or other petroleum oil, whereby concentrates may be prepared which may be conveniently stored or shipped and added to lubricating oils when required.

The new sulfur and phosphorus containing compositions herein described are also useful as antioxidants for other purposes when incorporated in organic materials other than lubricating oils, as will be more fully explained hereinafter, and in some cases it may not be necessary to have alkyl groups present to impart sufficient solubility. The invention also includes the reaction products of phosphorus sulfides or phosphorus and sulfur with compounds analogous to the salts of phenol sulfides and thiophenol sulfides, but containing selenium and tellurium in place of oxygen or sulfur, and with compounds in which aromatic nuclei other than benzene nuclei are present.

In our co-pending application Serial Number 493,734 we have described the preparation of reaction products of phosphorus and sulfur or phosphorus sulfides with metal phenates and the use of such products in lubricating oil compositions. It was there shown that the sulfur and phosphorus atoms were probably linked directly to the metal atoms in the molecules of the reaction product. It is believed that the same type of reaction occurs when metal salts of phenol sulfides and the like are treated with phosphorus sulfides or with phosphorus and sulfur, giving compounds in which the phosphorus and sulfur atoms are linked together in the molecule to form a group which is attached directly to the metal atom.

Although the exact structures of the compounds formed by the processes of the present invention have not been established, there is evidence to show that they are not metal salts of alkyl phenol sulfide esters of thio-acids of phosphorus. It is possible to prepare metal salts

of this type by reaction of an alkyl phenol sulfide with a sulfide of phosphorus followed by conversion of the reaction product to a metal salt. Such products have the representative structure:



in which R represents an alkylated aromatic group.

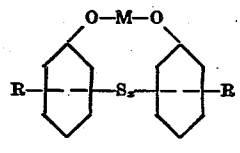
However, it is believed metal salts of this type do not result when the alkyl phenol sulfide is first converted to a metal salt and then treated with a sulfide of phosphorus or with any other combination of sulfur and phosphorus. One basis for this belief is that in the reaction no inorganic metal sulfide is formed, which would be the case if a thiophosphate salt was produced in the reaction.

In addition, there is no appreciable loss of metal content in the organic material during the reaction with the sulfide of phosphorus, the metal content of the filtered product being in the same order of magnitude as that of the original metal phenol sulfide. If the mechanism of the reaction were the conversion of the metal phenol sulfide to a metal organo thiophosphate of the type shown above, approximately 50% of the metal content would be lost, but this has been found not to be the case. Furthermore, there is an evolution of H_2S during the treatment of the metal phenol sulfides with phosphorus sulfides, and it is not expected that such H_2S evolution would occur if the reaction were the conversion of the metal phenol sulfide to a metal salt of an alkyl phenol sulfide ester of a thio-acid of phosphorus.

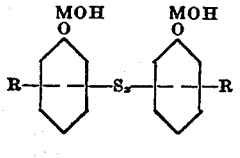
Some of the more preferred products to be used in accordance with the present invention are those obtained by reaction of a sulfide of phosphorus or a combination of the elements sulfur and phosphorus with the following compounds:

Barium tert.-octyl phenol sulfide
Barium di-tert.-amyl phenol sulfide
Calcium isohexadecyl phenol sulfide
Tin wax alkylated salicylic acid sulfide
Magnesium tert.-amyl phenol sulfide

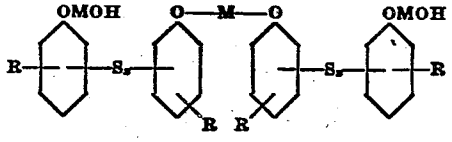
The invention includes the reaction of phosphorus and sulfur or sulfides of phosphorus with not only the normal metal salts of phenol sulfides, thiophenol sulfides and the like, but the basic metal salts as well. In a normal phenol sulfide salt of a divalent metal the mol ratio of metal to phenol sulfide is 1:1, as in the following formula:



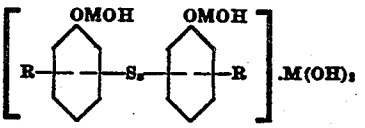
In a basic salt the ratio of metal to phenol sulfide may be 2:1, or even 3:1. In the case of a 2:1 ratio the formula may, for example, be



In the case of a 1.5:1 ratio the formula may be



In the case of a 3:1 ratio the formula may be



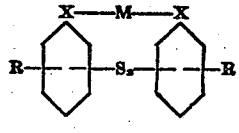
Intermediate ratios of metal to phenol uslfide, such as 1.8:1 or 2.3:1 may occur, in which mixtures of the above types of compounds are found. These basic salts are formed, for example, by reacting phenol sulfides with more than the amount of metallic oxide or hydroxide necessary to form the normal salts. Reaction products of phosphorus sulfides with basic metal salts of alkyl phenol sulfides are particularly useful in extreme pressure lubricants, and are especially advantageous for imparting color stability to lubricants.

The new class of addition agents employed in accordance with the present invention may be defined in its broadest scope as the reaction products of any combination of the elements sulfur and phosphorus with a metal salt of a compound having the formula

$$RAr(XH)—Y_x—R'$$

in which Ar is an aromatic nucleus and may, for illustration, be a benzene nucleus, or it may consist of a plurality of rings, as in biphenyl, or it may be a condensed nucleus, exemplified by naphthalene, anthracene and the like. R in the formula is hydrogen or at least one organic group and is preferably an alkyl group. X in the formula is a non-metal of group VI of the periodic table; Y is a member of the sulfur family; x is an integer from 1 to 4; and R' is an organic group which may be either aryl, alkyl, aralkyl, or alkylaryl, and which may contain substituent atoms or groups, such as halogen, nitro, amino, hydroxy, alkoxy, aroxy, mercapto, carboxy, and the like. The metals which may be substituted for the hydrogen in the —XH group of the above formula in forming salts of such compounds may be any metals, the most important for the purposes of the present invention being calcium, barium, strontium, magnesium, and zinc, although for some purposes corresponding compounds containing tin, lead, aluminum, cobalt or nickel will also be found to be especially desirable.

Compounds particularly suited for the purposes of the present invention are formed by reacting sulfur and phosphorus or a phosphorus sulfide with a compound of the formula

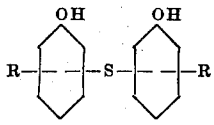


where R represents at least one alkyl radical attached to the nucleus, the total number of carbon atoms in all of such radicals attached to each benzene nucleus being at least five when the compound is to be dissolved in hydrocarbon oils, X is oxygen or sulfur, M is a divalent metal of group II of the periodic table, and x is an integer from 1 to 4.

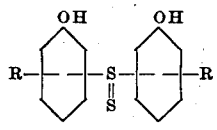
It should be understood that the above general formulas include compounds in which various substituent atoms or groups may be attached to the aromatic nucleus, such as alkyl, cycloalkyl, aralkyl, aryl, carboxyl, hydroxyl, alkoxy, aroxy, sulfhydryl, nitro, ester (organic and/or inorganic), keto, amino, aldehydo, chlormethyl, aminomethyl, alkyl thiomethyl, alkyl xanthomethyl, metal substituted carboxyl, metal substituted sulfo, metal substituted hydroxyl or sulfhydryl groups, halogen atoms, etc. Different types of atoms or groups may be attached to the same aromatic nucleus. Alkyl radicals attached to the nucleus may have a total of five to twenty-five carbon atoms in all of such groups, and in some cases as many as sixteen to twenty or more carbon atoms in a single group, as in a wax chain group, or in a plurality of groups, may be preferred. If more than one alkyl group is present in a single molecule, whether or not attached to the same aryl nucleus, such groups may be alike or different. Such alkyl or other hydrocarbon groups may contain substituent groups, such as those named above as substituents in the aromatic nucleus. The various groups or atoms attached to the aromatic nucleus may be in any positions relative to one another.

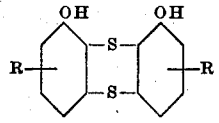
Alkyl phenol sulfides, whose metal salts may be used to prepare the reaction products of the present invention, may be illustrated by the following general classes of compounds:

1. Alkyl phenol thioethers

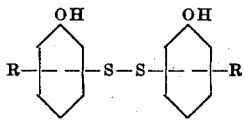


2. Alkyl phenol disulfides

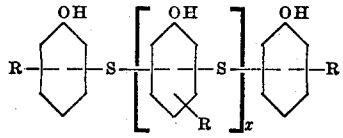




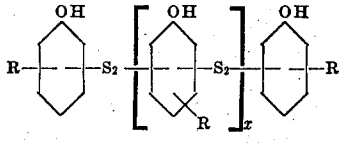
and



3. Polmers of alkyl phenol sulfides



and



In all of the above formulas under the headings 1 to 3, R represents an alkyl group containing preferably at least four carbon atoms, and x is a small whole number not greater than about six.

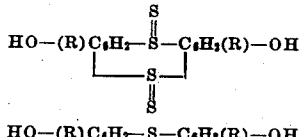
When the products are to be employed as additives for lubricating oils, exceptionally good results can be obtained by employing metal salts of alkyl phenol sulfides having C_{16}–C_{20} branched chain alkyl groups. These can be conveniently prepared from phenols which have been alkylated with suitable branched chain polymers obtained by polymerizing low boiling olefins such as propylene, butylenes, or amylenes, or mixtures of these olefins.

It should be understood that generally throughout the specification the term alkyl phenol sulfide is meant to include not only the monosulfides but also the di- and polysulfides and polymers of alkyl phenol sulfides as well. Thus, although the reaction of two mols of an alkylated phenol with one mol of sulfur dichloride (SCl_2) will give essentially an alkyl phenol monosulfide, small amounts of polysulfides and of polymeric materials will also be formed.

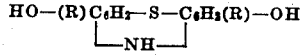
This is even more usually the result when more than the theoretically required proportion of sulfur halide is used in preparing the alkyl phenol sulfide, as for example when 2 mols of alkyl phenol are treated with 1.5 mols of sulfur dichloride. Similarly, the alkyl phenols may be treated with more than theoretical quantities of sulful monochloride (S_2Cl_2) or with mixtures of sulfur mono- and dichloride or with first one halide and then the other.

Other compounds whose metal salts may be used in accordance with this invention are illustrated by the following:

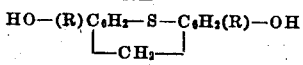
HO—(R)C_6H_3—Se—C_6H_3(R)—OH



HO—(R)C_6H_3—S—C_6H_3(R)—OH



HO—(R)C_6H_3—S—C_6H_3(R)—OH



HO—(R)$C_{10}H_5$—S—$C_{10}H_5$(R)—OH

HO—(RO)C_6H_3—S—C_6H_3(OR)—OH

HO—(RO)C_6H_3—S—C_6H_2(R')(OR)—OH

HO—(R)C_6H_3—S—C_6H_4—ORH

HO—(R)C_6H_3—S—C_6H_3(R)—OOCR'

HO—(R)C_6H_3—S—C_6H_4—OR'

HO—(R)C_6H_3—S—C_6H_4—COOR'

HO—(R)C_6H_3—S—CH_2—C_6H_5

HO—(R)C_6H_3—S—C_6H_3(R)N(R')(R")

HO—(R)C_6H_3—S—C_nH_{2n+1} (straight or branched chain)

HO—(R)C_6H_3—S—R'

HO—(R)C_6H_3—S—C_6H_3(R)NH_2

HO—(R)(NH_2)C_6H_2—S—C_6H_2(NH_2)(R)—OH

HO—(R)(OH)C_6H_2—S—C_6H_2(OH)(R)—OH

HS—(R)C_6H_3—S—C_6H_3(R)—SH

HO—(R)(COR)C_6H_2—S—C_6H_3(R)(COR)—OH

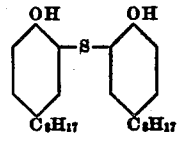
In these formulas R, R', etc., represent organic radicals.

In all of the above described type formulas, both general and specific, where R is used to represent an alkyl radical, such radicals may be illustrated by the following species, which are radicals particularly preferred in the compounds, it being understood that the list is merely illustrative and does not restrict the scope of the groups of the formulas. These include n-butyl, isobutyl, tert.-butyl, n-amyl, isoamyl, cyclohexyl, n-octyl, iso-

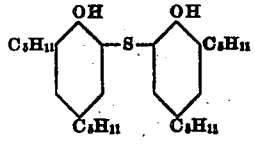
octyl, tert.-octyl, dodecyl, octadecyl, wax chain and C_{16}–C_{24} branched chain radicals.

Structures of the several typical compounds whose salts may be reacted with combinations of phosphorus and sulfur in accordance with the present invention may be given to show what is believed to be the relative positions of the various groups in the aromatic nuclei, but it is to be understood again that these formulas are given as illustrations only. These typical examples are the following:

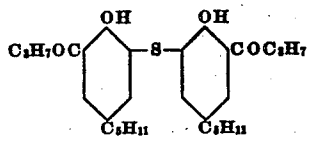
(a)



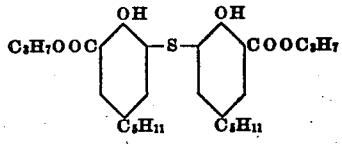
(b)



(c)



(d)



Specific examples of compounds which may be treated with a phosphorus sulfide in accordance with the present invention include the following, which are not to be construed as limiting the invention in any manner:

Calcium tert.-octyl phenol sulfide
Barium 2,4-di-tert.-amyl phenol sulfide
Cobalt tert.-amyl phenol sulfide
Barium salt of 2-hydroxy-3,5-di-tert.-amyl-4'-diethylamino diphenyl sulfide
Zinc salt of salicylic acid sulfide octyl ester
Barium 2-stearoyl-4-amyl phenol sulfide
Mixed calcium-barium tert.-octyl phenol sulfide
Tin salt of C_{16}–C_{20} branched chain alkyl phenol sulfide
Barium salt of bis (2,4-diamyl phenol)-4 amyl-phenol dithioether (prepared from 2 moles of 2,4-di-tert.-amyl phenol and one mole of p-tert.-amyl phenol, sulfurized with sulfur chloride and neutralized with barium hydroxide)

When the salts employed are those of polyvalent metals, it is not essential that all of the valences be satisfied by hydroxyaryl sulfide groups; some of them may be satisfied by other acidic organic groups such as carboxy, aroxy, alkoxy, organo-substituted inorganic acid groups such as phosphoric, phosphorous, thiophosphoric, thiophosphorous, phosphonic, phosphinic, sulfonic, sulfinic, and the like.

Thus, for example, the present invention also includes reaction products of phosphorus sulfides with such compounds as:

Calcium mixed salt of tert.-amyl phenol sulfide and iso-octyl salicylate
Aluminum mixed salt of tert.-octyl phenol sulfide and stearic acid
Tin mixed salt of di-tert.-amyl phenol sulfide and naphthenic acids

Barium mixed salt of tert.-octyl phenol sulfide and petroleum mahogany sulfonic acids
Nickel mixed salt of tert.-amyl phenol sulfide and amyl xanthic acid
Zinc mixed salt of isododecyl phenol sulfide and methyl cyclohexyl thiophosphoric acid
Nickel mixed salt of tert.-amyl phenol sulfide and oleic acid
Magnesium mixed salt of tert.-octyl phenol sulfide and cetyl phenol

As has been mentioned previously in this specification, the term phenol sulfide is meant to include not only the monosulfide but also disulfides, polysulfides, or polymers, or mixtures of any of these in any proportion.

For the objects stated, the metal salts of alkylated phenol sulfides have been preferably prepared from phenolic compounds readily obtained by synthetic alkylation of the simple phenols, followed by treatment with a sulfur chloride, and then neutralization with a metallic base.

Suitable synthetic alkyl phenols for preparing the desired phenol sulfide salts are preferably those containing secondary or tertiary alkyl radicals, because alkylation of a simple phenol occurs more readily with branched chain aliphatic reactants. Commonly, the alkylation reaction involves a condensation of olefins with the simple phenols, the reaction being catalyzed by anhydrous metal halides, boron fluoride, hydrofluoric acid, stannic chloride with hydrogen chloride, sulfuric acid, phosphoric acid, or certain activated clays. As olefinic reactants, refinery gases containing propylene, butylenes, amylenes, etc., are economically useful, although individual olefins or olefin-containing mixtures derived from other sources may be used. Preferred individual olefins are the butenes, amylenes and olefin polymers, such as diisobutylene or triisobutylene or normal olefin polymers or copolymers of normal and secondary or tertiary olefins or copolymers of olefins and diolefins. The reaction temperature is usually controlled to avoid side reactions. In employing sulfuric acid, a liquid phase reaction at relatively low temperature is preferred, while with phosphoric acid the reaction may be carried out in the vapor phase.

Suitable alkylated phenols for conversion to phenol sulfides may be thus prepared by alkylating phenol, cresol, naphthol or other phenolic compounds. High molecular weight alkylated phenols may also be used, for example, those prepared by condensing phenols with chlorinated petrolatum or chlorinated paraffin wax 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 those obtained from other vegetable oil sources may likewise be used. Halogenated or nitrated phenols will also find application in this invention, particularly if the final additive is to be employed in extreme pressure lubricants.

One class of alkyl phenols which are particularly preferred 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 equal molar proportion of diisobutylene gives p-tert.-octyl phenol, also known as diisobutyl phenol or tetramethyl butyl phenol. This phenolic material is especially desirable because of the ease of its preparation and because products made from it are highly satisfactory for the present invention. In many instances, how-

ever, 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 triisobutylene or other isobutylene polymers. For many purposes it is preferable to employ alkylated phenols having branched alkyl groups of from 16 to 30 carbon atoms. Suitable products may be prepared by alkylating phenol with certain of the polymeric materials obtained as by-products in the manufacture of butyl alcohol from petroleum refinery butenes. These consist essentially of polymers of n-butene with small percentages of isobutene and other olefins and give alkylated phenols having branched chain alkyl groups of 16–20 or 20–24 carbon atoms depending on the polymeric material used in the alkylation. 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 it is intended to use such mixtures in practicing this invention.

For conversion of phenols to phenol sulfides, the phenol is reacted with sulfur dichloride to produce essentially a phenol monosulfide having a thioether linkage, while sulfur monochloride may be used to produce essentially the phenol disulfide. About one-half to one mol of sulfur halide is used with each mol of phenol, and the reaction is preferably carried out in a solvent such as dichlorethane, chloroform, petroleum naphtha, benzol, xylol, toluol, and the like.

For converting the phenol sulfides to metal salts it is usually sufficient merely to add a metal or a metallic oxide, hydroxide, sulfide, alkoxide, hydride or carbide to a mineral oil solution or other solution of the phenol sulfide at an elevated temperature. Thus, barium salts of alkylated phenol sulfides are prepared by reacting the sulfide with barium hydroxide, preferably in the form of the hydrate, $Ba(OH)_2.8H_2O$. In some instances it may be preferable to prepare heavy metal salts from the alkali metla salt by double decomposition. The calcium salts are conveniently prepared by reacting alkyl phenol sulfides with calcium methylate or other calcium alcoholate.

In many cases the metal alkyl phenol sulfide prepared by neutralizing with a metal hydroxide may occur as a hydrated salt. Use of hydrated salts prepared in this manner or by any other method is also contemplated in the processes of the present invention.

In accordance with the present invention, the metallic salt of a phenol sulfide or other metallic derivative of a hydroxy or mercapto aromatic sulfide is caused to react with the elements sulfur and phosphorus. This may be accomplished by adding a mixture of the substances in elemental form, or first one element and then the other, to the heated metallic compound, or by adding a sulfide of phosphorus, such as P_2S_5, P_4S_3, P_4S_7, or the like, or by treatment with sulfur and/or phosphorus and a sulfide of phosphorus, or by treatment with any other substance or substances containing essentially only the elements phosphorus and sulfur. The phosphorus may be used either in the white (yellow) or red allotropic form, and the sulfur may likewise be used in any of its allotropic forms.

However, it is ordinarily more convenient to use a sulfide of phosphorus. In carrying out the reactions described above the proportions of phosphorus sulfide and metal salt of phenol sulfide are so chosen that from 0.03 to 2 atomic proportions of phosphorus are reacted with 1 atomic proportion of polyvalent metal, the preferred ratio being within the limits of about 0.06 to 0.75 molecular proportions of the phosphorus sulfide for each atomic proportion of metal, when the phosphorus sulfide contains 2 atoms of phosphorus per molecule. This preferred ratio gives the products the optimum content of phosphorus and sulfur to impart to them the maximum amount of inhibiting power and detergent action. In general, these same ratios will be employed when the reaction is conducted with elemental sulfur and elemental phosphorus.

Although the reaction can be brought about by fusing the metal salt with phosphorus and sulfur, or with a phosphorus sulfide, it is more convenient to carry out the reaction with the aid of solvents, particularly high boiling hydrocarbon solvents, such as xylol or a petroleum fraction. A particularly preferred reaction medium is a lubricating oil fraction, since the final reaction products can thus be obtained as a mineral oil concentrate of the desired additive, which may be conveniently shipped or stored as such and then readily blended with the lubricating oil base stock in the desired concentration to form a finished lubricating oil blend.

The additives may generally be prepared by first dissolving an alkylated phenol sulfide in a mineral oil or other suitable solvent and treating the same with a metal hydroxide, e. g., $Ba(OH)_2.8H_2O$, at about 80–200° C., preferably 110–150° C. After a further period of heating, free sulfur and free phosphorus, or a sulfide of phosphorus, or other mixture or combination of the elements, is added, heating being continued at 100–200° C., preferably at 150–180° C., to complete the reaction. The period of heating will be at least 10 minutes and generally at least 1 hour, although in some cases a longer period may be required. The product is then filtered, giving a concentrate of the desired additive. If the products are found to have a slight odor of hydrogen sulfide, this can be substantially eliminated by blowing the products with a suitable gas such as dry or moist air or nitrogen or superheated steam at temperatures of 80–150° C., or by treating with a neutralizing agent such as barium or calcium hydroxide or calcium oxide. A combination of these treating steps may also be employed. For example, satisfactory results have been obtained by treating the products with 2–5% of barium hydroxide at 150° C. before the filtering step, followed by nitrogen blowing at 100–120° C. after filtration. If the blowing step is found to be necessary in commercial operation, one convenient method is to treat the material with the gas in countercurrent flow in a suitable tower.

If desired, the metal phenol sulfide salt may be subjected to a heat-treating step, e. g., for 8–10 hours at 150–180° C., or it may be blown with dry or moist carbon dioxide, before adding the sulfide of phosphorus, in order to render the final product non-sensitive to the presence of water when blended in lubricating oil. In general, however, this step will not be necessary, inasmuch as the products of the present invention are substantially non-water-sensitive, as will be demonstrated hereinafter.

It has been found that good results are obtained when preparing these additives in mineral oil if a minor proportion of a higher alcohol, such as

stearyl, lauryl or cetyl alcohol, or wool fat alcohol or the like, is added to the reaction mixture in which the compounds of the present invention are prepared. This alcohol reduces foaming during the process and acts as an auxiliary solvent for the final product. The best results are obtained by adding a sufficient quantity of alcohol to give a concentration of about 3% to about 15% of the final additive concentrate.

Although some of the alcohol present will be found to react with the phosphorus sulfide, this will in no way impair the efficiency of the additive and may in some cases enhance its desirable qualities. Should it be desired to have the higher alcohol present in substantially unchanged form, it can be added to the reaction mixture just prior to the filtration step. Other materials which may be used instead of the higher alcohols to serve as plasticizers, foam reducing agents, etc. include the high molecular weight amines and nitriles, such as stearonitrile or lauronitrile. The products obtained by condensing phenol with the reaction products of sulfur halides and diisobutylene have also been found to be efficient agents for this purpose.

It has also been found that products of better oil solubility can often be obtained when carrying out the reaction with phosphorus sulfides in the presence of a small proportion of an olefinic material, such as a tetraisobutylene, cracked wax or an unsaturated alcohol.

Generally, the additives of the present invention are most advantageously blended with lubricating oil base stocks in concentrations between the approximate limits of 0.02% and 5.0% and preferably from 0.1% to 2.0%, although larger amounts may be used for some purposes. The exact amount of addition agent required for maximum improvement depends to a certain extent on the particular products used, the nature of the lubricating oil base stock and the general operating conditions of the engine in which the lubricant is to be employed. This same general range of concentration will also be effective when the additives are to be used in greases and in extreme pressure lubricants, although in the latter instance greater amounts, up to 20%, may also be employed.

As has been pointed out elsewhere in this specification, it is often convenient to prepare concentrates of the additives in oil, containing, say, 25 to 75% of effective addition agent, the concentrate later being added to a suitable lubricating oil base stock to give a finished blend containing the desired percentage of additive. Thus, when using a 40% concentrate, 2.5% of this material may be blended with a suitable base stock to give a finished oil containing 1% of effective addition agent.

In the following examples are described various preparations of products in accordance with this invention and the results obtained on testing the same in various lubricating oil blends. It is to be understood that these examples, given for illustrative purposes only, are not to be construed as limiting the scope of the invention in any way.

EXAMPLE 1

Tertiary octyl phenol was prepared by alkylating phenol with diisobutylene in the presence of $SnCl_4$-HCl catalyst substantially as described in the Buc patent, U. S. 2,332,555. A 40% solution of tertiary octyl phenol was prepared in a petroleum hydrocarbon solvent of approximately 200–300° F. boiling point. Over a 3-hour period sulfur dichloride was added to this solution in the ratio 1.6 mols of SCl_2 to each 2 mols of tert.-octyl phenol, the temperature being maintained at 25–35° C. After maintaining the same temperature for an additional half hour the reaction mixture was heated to 100° C. and the solvent stripped off under vacuum, leaving the tert.-octyl phenol sulfide as a residue.

2617 pounds of tert.-octyl phenol sulfide prepared in the above manner was dissolved in 4580 pounds of S. A. E. 20 grade mineral lubricating oil together with 512 pounds of commercial stearyl alcohol and the solution heated to 120° C. Over a 3 hour period 1952 pounds of

$Ba(OH)_2.8H_2O$

was added gradually, the mixture being well stirred and the temperature being maintained at 120° C. The temperature was raised to 140° C., 1% by weight of a filter aid added, and the mixture filtered, giving about 1000 gallons of an additive concentrate containing approximately 40% of barium tert.-octyl phenol sulfide, 6% stearyl alcohol, and 54% mineral lubricating oil. Analysis of concentrate: 8.92% Ba; 3.40% S.

EXAMPLE 2

As starting material for the preparation of a reaction product of a barium salt, there was used a concentrate containing 40% by weight of barium tert.-octyl phenol sulfide, 6% of stearyl alcohol, and 54% of a refined mineral oil of 52 seconds viscosity Saybolt at 210° F., prepared as described in Example 1. 30.3 kg. of this concentrate was treated with 2.31 kg. of P_2S_5 by heating the concentrate to 170° C. and adding the phosphorus sulfide gradually with agitation over a period of 1 hour, during which the temperature rose to 180–190° C. The temperature was then held at 160–180° C. for an additional 2 hour period and the final product filtered. The resulting additive concentrate contained 8.10% barium, 2.12% phosphorus, and 7.93% sulfur.

EXAMPLE 3

To demonstrate the reproducibility of the preparation of the present invention, Example 2 was repeated, using 29.95 kg. of the concentrate of Example 1 and 2.3 kg. of P_2S_5, and the same reaction times and temperatures. The filtered concentrate analyzed 8.14% barium, 2.06% phosphorus, and 7.96% sulfur.

EXAMPLE 4

This example demonstrates the preparation of an additive concentrate of the present invention on a plant scale. In essentially the same manner as described in Example 1, an oil solution of tert.-octyl phenol sulfide and stearyl alcohol was treated with $Ba(OH)_2.8H_2O$, but the reaction product was not filtered. (A portion of the reaction product which was filtered to prepare a finished additive concentrate contained 8.97% barium and 3.51% sulfur.) 1231 pounds of the unfiltered reaction product was placed in a reactor and heated to 180° C. Then, over a five hour period 72.5 pounds of P_2S_5 was gradually added, the mixture being agitated and kept at the 180° C. temperature. (Mol ratio P_2S_5 to barium tert.-octyl phenol sulfide=0.4/1.) Heating and agitation were then continued at the same temperature for an additional four hour period, after which time the temperature was lowered to 140° C. and the reaction mixture blown with inert gas for five hours to remove H_2S. 20 lbs. of Hyflo filter aid was added and the mixture then filtered to give

the final desired additive concentrate. Analysis of this concentrate showed it to contain 8.37% barium, 1.70% phosphorus, and 6.98% sulfur.

EXAMPLE 5

In this example a mol ratio of phosphorus sulfide to metal phenol sulfide of 0.2 to 1 was employed. 2470 g. of an oil concentrate of 40% barium tert.-octyl phenol sulfide, 6% stearyl alcohol, and 54% mineral oil, prepared as in Example 1, was heated to 180° C. Then over a 1 hour period 77 g. of P_2S_5 was added in small portions. Heating was continued for an additional 3 hour period at 180° C. and the product was then filtered, using Hyflo filter aid. The filtered product was blown with nitrogen for 8 hours at 95° C. to remove residual H_2S. The final additive concentrate contained 8.86% barium, 0.81% phosphorus, and 5.12% sulfur.

EXAMPLE 6

This example demonstrates the preparation of an additive similar to that of Example 2, but employing P_4S_7 instead of P_2S_5. The starting material was an additive concentrate prepared in the same manner as that described in Example 1, containing 40% barium tert.-octyl phenol sulfide, 6% stearyl alcohol and 54% mineral oil. Analysis of the concentrate showed it to contain 8.97% barium and 3.51% sulfur.

1200 grams of this concentrate was heated to 180° C. Then over a one hour period 73 grams of P_4S_7 was added in small portions. (Mol ratio of P_4S_7 to metal phenol sulfide=0.4/1.) The mixture was heated for an additional 3 hour period at 180° C. and was then filtered, using Hyflo filter aid. The filtered product was blown with nitrogen for 10 hours at 100° C. to remove residual H_2S. The finished additive concentrate contained 8.54% barium, 6.78% sulfur, and 2.19% phosphorus.

EXAMPLE 7

The preparation of a product of the present invention employing a basic metal salt of an alkyl phenol sulfide is shown in this example. Tertiary octyl phenol, prepared by alkylation of phenol with diisobutylene using BF_3 catalyst, was converted to the sulfide by essentially the same procedure as described in Example 1, employing a ratio of 1.6 mols of SCl_2 to 2 mols of tert.-octyl phenol. 7740 grams of this tert.-octyl phenol sulfide and 1500 grams of stearyl alcohol were dissolved in 13,500 grams of refined paraffinic mineral lubricating oil (52 seconds Saybolt viscosity at 210° F.). The mixture was heated with stirring to 120–125° C. under an atmosphere of nitrogen, and then over a 6 hour period 11,990 grams of $Ba(OH)_2.8H_2O$ was added. The temperature was then raised to 135–140° C. and heating and stirring were continued for an additional 2 hours. 1% by weight of filter aid was added and the mixture filtered, giving a concentrate containing approximately 42% of basic barium tert.-octyl phenol sulfide, slightly less than 6% stearyl alcohol and slightly more than 52% mineral lubricating oil. Analysis of the concentrate showed it to contain 12.97% barium and 2.99% sulfur.

2000 grams of this concentrate was heated to 180° C. and to it was added 129 g. of P_2S_5 over a period of 1 hour. Heating was continued for an additional 3 hour period and the product filtered and blown with nitrogen for 6 hours at 100° C. The final additive concentrate contained 11.70% barium, 1.8% phosphorus, and 6.56% sulfur.

EXAMPLE 8

A reaction product of the present invention employing a mixed calcium-barium alkyl phenol sulfide was prepared as follows: A mixture of 1110 grams of tert.-octyl phenol sulfide, 1620 grams of S. A. E. 20 grade mineral lubricating oil, 180 grams of commercial stearyl alcohol, and 205 grams of calcium hydroxide was placed in a 12-liter reaction flask equipped with a stirrer and water trap reflux condenser and heated at 120–125° C. for 10 hours, at the end of which time 83% of the theoretical amount of water from the reaction had been removed through the water trap. The mixture was then heated to 150° C. and filtered, employing Hyflo filter aid. The oil concentrate of calcium tert.-octyl phenol sulfide contained 2.82% calcium and and 4.13% sulfur.

1500 grams of the concentrate obtained in the above manner was heated to 120° C. and over a 1½ hour period 476 grams of barium hydroxide octahydrate was added with constant stirring. Heating was continued for two additional hours at 140° C., a stream of nitrogen being blown through the mixture during the entire reaction period. The product was then filtered, giving an oil concentrate containing approximately 40% calcium-barium tert.-octyl phenol sulfide, 6% stearyl alcohol, and 54% mineral lubricating oil. Analysis: 2.26% calcium; 7.53% barium; 3.66% sulfur.

1000 grams of the calcium-barium tert.-octyl phenol sulfide concentrate was placed in an iron kettle and heated to 180° C. with stirring and nitrogen blowing. Then over a period of 30 minutes 60 grams of P_2S_5 was added, the temperature rising to 195° C. during the first 15 minutes and then returning to 180° C. Heating was continued for an additional 30 minutes, the mixture then being cooled to 150° C. and filtered. The filtered product was blown with nitrogen for 4 hours at 180° C. to ensure the removal of any residual H_2S that may have been present. The final additive concentrate contained 7.11% barium, 2.21% calcium, 1.76% phosphorus, and 6.94% sulfur, and for blending purposes was considered to contain 40% by weight of effective additive.

EXAMPLE 9

The preparation of a reaction product from barium diamyl phenol sulfide is described.

(*a*) 1404 grams (6 mols) of 2,4-diamyl phenol was dissolved in 4212 grams of a petroleum solvent naphtha (200–235° F. boiling range; 65–70% aromatics) and placed in a reaction vessel equipped with a stirrer and reflux condenser. Over a period of 2 hours 464 grams (4.5 mols) of sulfur dichloride was added to the stirred solution, the temperature being maintained at 20–25° C. The mixture was stirred for an additional hour and was then heated at reflux temperature for 2 hours, after which time the solvent was stripped off at a maximum temperature of 300° F. in a stream of nitrogen. The resulting diamyl phenol sulfide contained 10.05% sulfur.

(*b*) In the same manner as described in part (*a*) diamyl phenol disulfide was prepared from 1404 grams of 2,4-diamyl phenol and 608 grams of sulfur monochloride, this being 1.5 mols of S_2Cl_2 per 2 mols of alkyl phenol. The product contained 16.55% sulfur.

(*c*) 170 grams of diamyl phenol sulfide (from part (*a*)) and 180 grams of diamyl phenol disulfide (from part (*b*)) were dissolved in 550

grams of refined mineral lubricating oil of S. A. E. 20 grade. 110 grams of commercial stearyl alcohol was added and the temperature raised to 110° C. Over a period of 1½ hours 273 grams of barium hydroxide octahydrate was added, the mixture being stirred and blown with nitrogen and the temperature being maintained at 110–120° C. After an additional 15 minute period of stirring and nitrogen blowing the mixture was heated to 130° C. and filtered, giving a concentrate containing 40% barium diamyl phenol sulfide-disulfide, 10% stearyl alcohol, and 50% mineral lubricating oil. Analysis: 5.96% barium; 3.44% sulfur.

327 grams of the oil concentrate of barium diamyl phenol sulfide-disulfide was heated with stirring to 110° C. Over a five minute period 32.7 grams of P_2S_5 was added, causing the temperature to rise to 150° C. The temperature was then lowered to 130° C. and held there for one hour, after which the reaction product was filtered. The filtered concentrate containing approximately 40% of actual additive, analyzed 5.53% barium, 2.39% phosphorus and 7.78% sulfur.

EXAMPLE 10

This example demonstrates the preparation of an additive of the present invention in so-called "pure" form, that is, not as an additive concentrate in mineral oil solution.

(*a*) 2060 grams (10 mols) of tert.-octyl phenol was dissolved in approximately 5 liters of chloroform in a 12-liter reaction flask equipped with a stirrer and reflux condenser. Over a period of 3½ hours 850 grams (7.5 mols plus 10% excess) sulfur dichloride was added, the reaction mixture being maintained at 25–35° C. Following this step the mixture was heated at 55° C. for 5 hours to complete the reaction. The final product was 6420 ml. of chloroform solution which contained 2305 grams of tert.-octyl phenol sulfide. Analysis of a portion of solvent-free product showed it to contain 11.33% sulfur, which would correspond to a product having on the average about 1.6 atoms of sulfur for each pair of aromatic nuclei.

(*b*) 2496 ml. of the chloroform solution obtained in part (*a*), containing 922 grams of the tert.-octyl phenol sulfide, was placed in a 5 liter flask fitted with a water trap condenser and about 75% of the chloroform removed under vacuum. Then 2 liters of pure xylene was added and the temperature raised to 140° C., causing the remaining chloroform to distill over into the water trap from which it was removed. Over a period of 14 hours 651 grams of $Ba(OH)_2.8H_2O$ was added with stirring, the temperature being maintained at 140° C., and water of reaction being removed through the water trap. After an additional 3-hour heating period no additional water collected in the trap. The mixture was then filtered and most of the xylene removed by heating the filtrate on the steam bath. The remaining solvent was removed by heating under vacuum at 140° C. The product was a resinous solid, containing 20.65% Ba and 8.46% S.

(*c*) 350 grams of the solid barium tert.-octyl phenol sulfide obtained in part (*b*) was dissolved in 1500 cc. of xylene in a 5-liter flask, fitted with a stirrer and a reflux condenser, and heated to 140° C. Over a period of 4 hours 52.2 grams of P_2S_5 was gradually added with stirring, and heating at 140° C. was continued for an additional 3 hour period. A stream of nitrogen was passed through the mixture during the entire 7 hour period to facilitate H_2S removal. The xylene solution containing the final product was filtered and the filtrate freed of solvent by heating on the steam bath and finally under vacuum at 100° C. The final product was a light yellow solid material soluble in mineral oil. It contained 18.40% barium, 16.04% sulfur, and 3.96% phosphorus.

EXAMPLE 11

The purpose of the following test was to determine the corrosion inhibiting effect of adding a small quantity of various products prepared as in the preceding examples to a lubricating oil base, this being a well refined solvent extracted paraffinic type mineral lubricating oil of S. A. E. 20 grade. With the exception of one blend, each oil contained 0.625% of additive concentrate prepared in accordance with the said examples, which is equivalent to about 0.25% of the actual additive. In the case of the product of Example 10, only 0.25% of material was blended in the oil, inasmuch as this product was not an additive concentrate but was "pure" additive. A comparative test was made with a sample of unblended oil base.

The tests were conducted as follows: 500 cc. of oil to be tested was placed in a glass oxidation tube (13" long and 2⅝" 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 of known weight having a total area of 25 sq. cm. 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 the rate of 2 cu. ft. per hour. To increase the severity of the test, the bearings were washed and weighed at the end of each four hour period and then polished and reweighed before continuing for another four hour period. The results show the cumulative weight loss at the end of each four hour period. The results are shown in Table I.

TABLE I

Oil Blend	Cumulative Bearing Weight Loss (Mg./25 sq. cm.)									
	4 Hrs.	8 Hrs.	12 Hrs.	16 Hrs.	20 Hrs.	24 Hrs.	28 Hrs.	32 Hrs.	36 Hrs.	40 Hrs.
Base Oil	0	173								
Base Oil+0.625% Product of Ex. 2	0	0	0	0	0	6	12	13	19	24
Base Oil+0.625% Product of Ex. 3	0	0	0	1	7	17	25	31	38	48
Base Oil+0.625% Product of Ex. 5	0	2	19	35	58	84	136			
Base Oil+0.625% Product of Ex. 6	0	0	1	5	13	21	25	32	44	52
Base Oil+0.25% Product of Ex. 10	0	0	2	3	13	23	28	35	42	49

EXAMPLE 12

In the following tests, a lubricating oil blend containing an additive of the present invention

and an unblended oil were tested in a single cylinder C. F. R. engine run under the following conditions: 1800 R. P. M., 265° F. oil temperature, and 200° F. water jacket temperature for 55 hour periods. After each test was completed the engine parts were examined and given demerit ratings based on their condition. The individual ratings were weighted according to their relative importance and an overall rating calculated from them. It should be pointed out that the lower the demerit rating the better the engine condition and hence the better the oil performed in the engine. In these tests the base oil was a solvent extracted Mid-Continent paraffinic oil of 46 seconds viscosity Saybolt at 210 F., to which had been added a small amount of polybutene to give a lubricating oil of 52 seconds viscosity at 210° F. Results of these tests are shown in the following table.

TABLE II

Oil Blend	Engine Demerits				
	Overall	Ring Zone	Piston Skirt Varnish	Ring Sticking	Sludge
Base Oil	2.78	3.3	4.0	2.75	1.7
Base Oil+2.5% Product of Ex. 2	0.68	1.4	0.5	0.0	0.1

It may be readily seen that the performance of the base oil in the engine was materially improved by the incorporation of the agent of the present invention.

EXAMPLE 13

Lubricating oil blends of various of the additives whose preparations have been described in the foregoing examples were prepared with the same base oil as described in Example 12. The base oil and each of the various blends were tested in a Chevrolet engine run for 36 hours under the following conditions: 30 brake horsepower, 3150 R. P. M., 280° F. oil temperature, and 200° F. water jacket temperature.

In order to measure the corrosiveness of each oil blend, two of the connecting rods of the engine were equipped with copper-lead bearings. At the end of each test the various parts of the engine were examined and given demerit ratings based on their appearance. The various demerit ratings were then employed to calculate an overall demerit rating for the engine, this serving as a measure of the performance of the lubricating oil in the test As before, the lower the demerit rating the more satisfactory the performance of the oil. The results of these tests are presented in Table III. It will be observed that a reaction product of the present invention, prepared by reaction of a metal alkyl phenol sulfide with a phosphorus sulfide (blend 2) was more satisfactory in this test than the metal alkyl phenol sulfide itself (blend 1). It should also be noted that even better results were obtained with an oil blend containing both a metal sulfonate and an additive of the present invention (blend 3). It should likewise be noted that the capacity of the additive to inhibit corrosiveness, as indicated by laboratory tests, was borne out by the results of the tests in actual engine operations.

TABLE III

Chevrolet engine tests

[36 hours—30 B. H. P.—3150 R. P. M.—oil 280° F.—water jacket 200° F.]

Oil Blend	Engine Demerit Ratings				
	Overall	Ring Zone	Piston Skirt Varnish	Sludge	Cu-Pb-Bearing Wt. Loss; Grams per Bearing
Base oil	1.93	3.47	2.33	1.47	4.09
Blend 1—Base Oil +2.5 Wt. percent of Concentrate of Example 1 [1]	0.44	0.61	0.38	0.16	0.07
Blend 2—Base Oil+2.5 Wt. percent of Concentrate of Example 5 [1]	0.31	0.26	0.25	0.09	0.04
Blend 3—Base Oil+1.5 percent of Basic Calcium Sulfonate [2] +2.13 percent of concentrate of Example 4 [3]	0.28	0.19	0.08	0.03	0.07

[1] Equals 1 percent of effective additive.
[2] Contained 33 percent excess calcium over theoretical.
[3] Equals 0.85 percent of effective additive in addition to the metal sulfonate.

EXAMPLE 14

A further series of engine tests were made in a single cylinder Caterpillar Diesel engine, each test being run for 126 hours under the following conditions: 19.8 brake horsepower, 1000 R. P. M., 160° F. oil temperature, 180° F. water jacket temperature. The oil blends tested contained additives of the present invention in an S. A. E. 30 grade solvent extracted Mid-Continent lubricating oil.

In the same manner as described in Example 13, the engine condition was rated on a demerit basis with the results shown in Table IV. It will be seen that here again, where a different lubricating oil base stock was used and a different engine test employed, an additive of the present invention (blend 2) gave greater improvement than an untreated metal alkyl phenol sulfide (blend 1) and that superior results were obtained with a combination of a metal petroleum sulfonate and an additive of the present invention (blend 3).

TABLE IV

Caterpillar Diesel engine tests

[126 hours—19.8 B. H. P.—1,000 R. P. M.—160° F. oil temp.—180° F. jacket temp.]

Oil Blend	Engine Demerit Ratings	
	Overall	Ring Zone
Base Oil	2.24	2.32
Blend 1—Base Oil+2.5 Wt. Per Cent of Additive Concentrate of Example 1	1.53	1.47
Blend 2—Base Oil+2.5 Wt. Per Cent of Additive Concentrate of Example 7	1.21	1.00
Blend 3—Base Oil+2.25% of Additive Concentrate of Example 3+1.58% of Basic Calcium Sulfonate [1]	0.63	0.02

[1] Contained about 40% excess calcium over theoretical.

EXAMPLE 15

Lubricating oil blends were prepared by adding to separate portions of an S. A. E. 20 grade extracted Mid-Continent oil 2.5% by weight of the additive concentrates prepared as described in Example 1 and as described in Example 5. Each oil was tested for water sensitivity, i. e., the tendency of the additive to separate from the oil in the presence of water. This test was conducted as follows: 600 cc. of the oil blend is emulsified with 1% water by means of a motor-driven eggbeater-type mixer operated at maximum speed for 15 minutes. After stirring, 500 cc. of the emulsion is poured into a 500 cc. graduated cylinder and allowed to stand for 24 hours. At the end of this period the amount of emulsion layer separated from the oil is noted. The smaller the amount of separation the better the water resistant qualities of the additive.

The results obtained in this test are shown in Table V.

TABLE V

Additive in Oil Blend	Water Sensitivity, cc./500 cc. of blend
Barium tert.-Octyl Phenol Sulfide (Example 1)	60
Reaction Product of Barium tert.-Octyl Phenol Sulfide and P_2S_5 (Example 5)	1

It will readily be seen that the phosphorus sulfide treated metal alkyl phenol sulfide was substantially non-water-sensitive, whereas the untreated metal alkyl phenol sulfide was appreciably sensitive to the presence of water.

Although in most instances the additives of the present invention will of themselves impart sufficient improvement to lubricating oils to give very satisfactory results, still greater improvement may often be obtained by employing these addition agents in conjunction with other additives of the detergent type, such as metal soaps, metal phenates, metal alcoholates, metal phenol sulfides, metal organo phosphates, thiophosphates, phosphites and thiophosphites, metal sulfonates, metal thiocarbamates, metal xanthates and thioxanthates, and the like.

Thus, the addition agents of our invention may be used in mineral lubricating oils in conjunction with one or more of the following representative materials:

Barium tert.-octyl phenol sulfide
Cobalt tert.-amyl phenol sulfide
Tin salt of wax alkylated phenol sulfide
Calcium mahogany sulfonates
Barium mahogany sulfonates
Strontium mahogany sulfonates
Magnesium mahogany sulfonates
Zinc mahogany sulfonates
Magnesium cetyl phenate
Calcium ortho stearoyl phenate
Calcium salt of condensation product of amyl phenol and formaldehyde
Nickel oleate
Calcium dichlorostearate
Aluminum-calcium mixed soap of fatty acids from oxidation of petroleum fractions
Calcium isohexadecyl phenol sulfonate
Barium octadecylate
Calcium phenyl stearate
Nickel dibutyl dithiocarbamate
Nickel amyl xanthate
Barium dioctyl dithiophosphate

Zinc methyl cyclohexyl dithiophosphate
Calcium dihexadecyl monothiophosphite
Zinc tert.-octyl phenol sulfide thiophosphate
Calcium cetyl phosphate
Magnesium lauryl salicylate
Zinc diisopropyl salicylate
Tin naphthenate
Aluminum naphthenate
Calcium double salt of octadecyl phenol sulfonic acid
Barium phenate-zinc sulfonate of isohexadecyl phenol sulfonic acid
Barium di-tert.-amyl phenol sulfide
Calcium phenate-barium carboxylate of octadecyl salicylic acid.

Particularly advantageous are lubricant compositions in which the additives of the present invention are employed in conjunction with metal salts of petroleum mahogany sulfonic acids.

The advantageous properties of lubricating oil blends containing both metal mahogany sulfonates and additives of the present invention have already been shown in some of the foregoing examples. In addition to being highly desirable crankcase lubricating oils these additive blends also possess rust preventive properties. For example, an S. A. E. 10 grade lubricating oil containing 1.5% calcium sulfonates and 0.85% of the reaction product of barium tert.-octyl phenol sulfide and P_2S_5 (0.4:1 mol ratio P_2S_5 to phenol sulfide salt) was found to be a satisfactory rust preventive as defined by Government specification AXS-934. Sand blasted steel panels were dipped in this oil composition, the excess oil allowed to drain off, and the oil coated panels subjected to the humidity cabinet test and to the salt water immersion test. Panels coated with the above composition remained in the humidity cabinet (100% humidity at 100° F.) for 200 hours without rusting. Other panels similarly coated remained immersed in synthetic sea water (aqueous solution containing NaCl, $MgCl_2$, $CaCl_2$, and Na_2SO_4) for 20 hours without rusting.

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 coil 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 voltolized 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 lubrication 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, voltolized fatty oils or fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Specific examples of such other agents include phenyl alpha naphthylamine, voltolized sperm oil, 2,6-di-tert.-butyl-4-methyl phenol, sulfurized sperm oil, p-tert.-amyl phenol sulfide, dibenzyl disulfide, polyisobutylene, sulfurized wax olefins, tricresyl phosphate, diamyl trisulfide, and the condensation product of phenol with a sulfur chloride-diisobutylene reaction product. 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

($C_{12}H_{25}OH$)

cetyl alcohol ($C_{16}H_{33}OH$), stearyl alcohol, sometimes referred to as octadecyl alcohol ($C_{18}H_{37}OH$), 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 alcohols 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 additives 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 oils 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 hydrocarbon material subject to deterioration by atmospheric oxygen containing a stabilizing amount of a product obtained by reacting a sulfide of phosphorus with a divalent group II metal salt of a compound having the characterizing structure

$$R—Ar(XH)—Y_x—R'$$

in which the groups R, XH and $Y_x—R'$ are all connected to the aromatic nucleus Ar, and in which R represents at least one alkyl group of 4 to 24 carbon atoms and R' represents an aryl group, X is an element of the group consisting of oxygen and sulfur, Y is a member of the sulfur family of elements, and x is an integer from 1 to 4, at a temperature of 100–200° C. for a period of at least 10 minutes, the proportions of reactants being such that from 0.03–2 atomic proportions of phosphorus are present for each atomic proportion of metal.

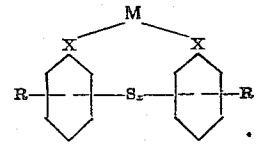
2. A hydrocarbon product subject to deterioration by atmospheric oxygen containing a stabilizing amount of a product obtained by reacting a sulfide of phosphorus with a divalent group II metal salt of a compound having the characterizing structure

$$R—Ar(XH)—Y_x—Ar(XH)—R$$

where Ar is an aromatic nucleus, R is an alkyl radical of 4–24 carbon atoms, X is an element of the group consisting of oxygen and sulfur, Y is a member of the sulfur family of elements, and x is an integer from 1 to 4, at a temperature of 100–200° C. for a period of at least 10 minutes, the proportions of reactants being such that 0.03–2 atomic proportions of phosphorus are present for each atomic proportion of metal.

3. A hydrocarbon material subject to deterioration by atmospheric oxygen containing a stabilizing amount of a product obtained by react-

ing a sulfide of phosphorus with a compound of the formula



where R is an alkyl radical of 4–24 carbon atoms, X is an element of the group consisting of oxygen and sulfur, M is a divalent metal of group II of the periodic table, and x is an integer from 1 to 4, at a temperature of 100–200° C. for a period of at least 10 minutes, the proportions of reactants being such that 0.03–2 atomic proportions of phosphorus are present for each atomic proportion of metal.

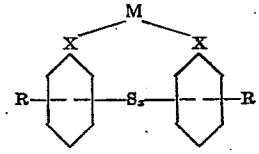
4. A mineral lubricating oil containing a stabilizing quantity of a product obtained by reacting a sulfide of phosphorus with a divalent group II metal salt, of a compound having the characterizing structure

$$R—Ar(XH)—Y_x—R'$$

in which the groups R, XH and Y_x—R are all connected to the aromatic nucleus Ar and in which R represents at least one alkyl group of 4 to 24 carbon atoms and R' represents an aryl group, X is an element of the group consisting of oxygen and sulfur, Y is a member of the sulfur family of elements, and x is an integer from 1 to 4, at a temperature of 100–200° C. for a period of at least ten minutes, the proportions of reactants being such that 0.03–2 atomic proportions of phosphorus are present for each atomic proportion of metal.

5. A mineral lubricating oil according to claim 4 in which Ar of the formula represents a benzene nucleus and X represents oxygen.

6. A mineral lubricating oil containing a stabilizing amount of a product obtained by reacting a sulfide of phosphorus with a compound of the formula



where R is an alkyl radical of 4–24 carbon atoms, X is a member of the group consisting of oxygen and sulfur, M is a divalent metal of group II of the periodic table, and x is an integer from 1 to 4, at a temperature of 100–200° C. for a period of at least 10 minutes, the proportions of reactants being such that 0.03–2 atomic proportions of phosphorus are present for each atomic proportion of metal.

7. A mineral lubricating oil containing a stabilizing quantity of a product obtained by reacting a sulfide of phosphorus with a metal salt of an alkylated phenol sulfide in which the alkyl groups attached to each benzene nucleus contain a total of at least 5 carbon atoms, and in which the metal of the salt is a divalent metal of group II of the periodic table, at a temperature of 100–200° C. for a period of at least 10 minutes, the proportions of reactants being such that 0.03–2 atomic proportions of phosphorus are present for each atomic proportion of metal.

8. A mineral lubricating oil according to claim 7 in which each benzene nucleus of the metal salt contains a substituent tert.-octyl radical.

9. A mineral lubricating oil containing a stabilizing quantity of a product obtained by reacting a sulfide of phosphorus with a barium salt of a tert.-octyl phenol sulfide, at a temperature of 150–180° C. for a period of at least 1 hour, the proportions of reactants being such that 0.06–0.75 atomic proportion of phosphorus is present for each atomic proportion of barium.

10. A mineral lubricating oil containing a stabilizing quantity of a product obtained by reacting about 0.06 to about 0.75 molecular proportion of phosphorus pentasulfide with one molecular proportion of the barium salt of a tert.-octyl phenol sulfide, at a temperature of 150–180° C. for a period of at least 1 hour.

11. A mineral lubricating oil according to claim 10 in which the additive was obtained by reacting the sulfide of phosphorus with the metal salt in the presence of a mineral oil as a reaction medium and a small proportion of a higher fatty alcohol.

12. A mineral lubricating oil containing a stabilizing quantity of a product obtained by heating a concentrated mineral lubricating oil solution containing about 40% of barium tert.-octyl phenol sulfide, about 6% of stearyl alcohol, and about 54% of a refined mineral lubricating oil to about 150–180° C., gradually adding about 0.4 molecular proportion of phosphorus pentasulfide for each molecular proportion of the barium salt while maintaining the temperature not higher than about 190° C., further maintaining the temperature at about 160° to about 180° C. for at least 2 hours, and filtering the final product.

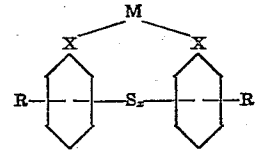
13. A mineral lubricating oil containing a stabilizing quantity of a product obtained by heating a concentrated mineral lubricating oil solution containing about 40% of barium tert.-octyl phenol sulfide, about 6% of stearyl alcohol, and about 54% of a refined mineral lubricating oil to about 150–180° C., gradually adding about 0.2 molecular proportion of phosphorus pentasulfide for each molecular proportion of the barium salt while maintaining the temperature not higher than about 190° C., further maintaining the temperature at about 160° to about 180° C. for at least 2 hours, and filtering the final product.

14. As a new composition of matter a sulfur and phosphorus containing product obtained by reacting a sulfide of phosphorus with a divalent group II metal salt of a compound having the characterizing structure

$$R—Ar(XH)—Y_x—Ar(XH)—R$$

where Ar is an aromatic nucleus, R is an alkyl radical of 4–24 carbon atoms, X is an element of the group consisting of oxygen and sulfur, Y is a member of the sulfur family of elements, and x is an integer from 1 to 4, at a temperature of 100–200° C. for a period of at least 10 minutes, the proportions of reactants being such that 0.03–2 atomic proportions of phosphorus are present for each atomic proportion of metal.

15. As a new composition of matter an oil-soluble sulfur and phosphorus containing product obtained by reacting a sulfide of phosphorus with a compound of the formula



where R is an alkyl radical of 4–24 carbon atoms, X is an element of the group consisting of oxygen and sulfur, M is a divalent metal of group II of

the periodic table, and x is an integer from 1 to 4, at a temperature of 100–200° C. for a period of at least 10 minutes, the proportions of reactants being such that 0.03–2 atomic proportions of phosphorus are present for each atomic proportion of metal.

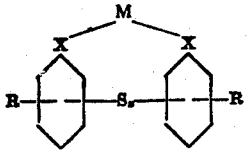
16. As a new composition of matter an oil-soluble sulfur and phosphorus containing product obtained by reacting a sulfide of phosphorus with a metal salt of an alkylated phenol sulfide in which the alkyl groups contain 4–24 carbon atoms and in which the metal is a divalent metal of group II of the periodic table, at a temperature of 100–200° C. for a period of at least 10 minutes, the proportions of reactants being such that 0.03–2 atomic proportions of phosphorus are present for each atomic proportion of metal.

17. A new composition of matter according to claim 16 in which the metal of the metal salt is barium.

18. As a new composition of matter an oil-soluble product obtained by reacting phosphorus pentasulfide with the barium salt of a p-tert.-octyl phenol sulfide at a temperature of 150–180° C. for a period of at least 1 hour, the proportions of reactants being such that 0.06–0.75 atomic proportion of prosphorus is present for each atomic proportion of barium.

19. A concentrate consisting essentially of a mineral lubricating oil containing 25–75% of the product obtained by reacting a divalent group II metal salt of an alkyl phenol sulfide with a sulfide of phosphorus at a temperature of 100–200° C. for a period of at least ten minutes, the proportion of reactants being such that 0.03–2 atomic proportions of phosphorus are present for each atomic proportion of metal.

20. The method of preparing an oil-soluble sulfur and phosphorus containing product having antioxidant properties in the presence of organic materials which comprises reacting a sulfide of phosphorus with a compound of the formula



where R is an alkyl radical of 4–24 atoms, X is an element of the group consisting of oxygen and sulfur, M is a divalent metal of the group II of the periodic table and x is an integer from 1 to 4, at a temperature of 100–200° C. for a period of at least 10 minutes, the proportions of reactants being such that 0.03–2 atomic proportions of phosphorus are present for each atomic proportion of metal.

21. The method of preparing an oil-soluble sulfur and phosphorus containing product having antioxidant properties in the presence of organic material which comprises reacting a sulfide of phosphorus with a metal salt of an alkylated phenol sulfide in which the alkyl groups attached to each benzene nucleus contain a total of 4–24 carbon atoms and in which the metal is a divalent metal of group II of the periodic table, at a temperature of 100–200° C. for a period of at least 10 minutes, the proportions of reactants being such that 0.05–2 atomic proportionst of phosphorus are present for each atomic proportion of metal.

22. The method of preparing an oil-soluble sulfur and phosphorus containing product having antioxidant properties in the presence of organic material which comprises reacting phosphorus pentasulfide with the barium salt of a tert.-octyl phenol sulfide, at a temperature of 150–180° C. of a period of at least 1 hour, the proportions of reactants being such that 0.06–0.75 atomic proportion of phosphorus is present for each atomic proportion of barium.

23. The method of preparing an oil-soluble sulfur and phosphorus containing product which imparts detergent and anti-corrosion properties to mineral lubricating oils which comprises reacting about 0.06 to about 0.75 molecular proportion of phosphorus pentasulfide with 1 molecular proportion of the barium salt of p-tert.-octyl phenol sulfide in the presence of a mineral lubricating oil solvent and a small quantity of stearyl alcohol at a temperature of about 140° to about 190° C. for a period of at least one hour.

24. A mineral lubricating oil additive concentrate containing about 54% of mineral lubricating oil, about 6% of stearyl alcohol, and about 40% of the product obtained by reacting barium tert.-octyl phenol sulfide with phosphorus pentasulfide at a temperature of 150–180° C. for a period of at least 1 hour, the proportions of reactants being such that 0.06–0.75 atomic proportion of phosphorus is present for each atomic proportion of barium.

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