

UNITED STATES PATENT OFFICE

2,451,346

COMPOUNDED LUBRICATING OIL

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14 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 applications Serial Number 493,734, filed July 7, 1943, now Patent Number 2,409,686, issued October 22, 1946, and Serial Number 560,192, filed October 24, 1944.

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 temperature. 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 engine cleanliness, improving oil film strength, 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 the oils to which they are added.

It was disclosed in the aforementioned co-pending application Serial Number 493,734 (Patent Number 2,409,686) that the products obtained by the reaction of the elements sulfur and phosphorus, e. g., as a phosphorus sulfide, with certain metal phenates and thiophenates are very satisfactory additives for mineral lubricating oils, since they are valuable detergents and at the same time do not exhibit the corrosiveness characteristic of many detergent additives known to the art. Similarly, in co-pending application Serial Number 560,192 it was disclosed that the reaction products of the elements sulfur and phosphorus with metal salts of hydroxy and mercapto substituted aromatic sulfides were very valuable lubricating oil additives. It was also disclosed in the aforementioned co-pending applications that valuable products could be formed on reacting the sulfur and phosphorus not only

with the normal metal salts of phenols, phenol sulfides and the like, but that in place of the normal salts basic salts, containing a greater proportion of metal in the compound than is present in a compound in which all of the primary valences of the metal are satisfied by the organic groups, may likewise be used. The use of these basic metal salts to form new products by reaction with elemental sulfur and phosphorus or with a phosphorus sulfide and the use of such products as additives for lubricating oils and as antioxidant materials generally for organic materials form the subject matter of the present invention. In accordance with this invention, not only the metal phenates and metal salts of phenol sulfides and the like, but any basic metal salt of an acidic organic compound may be reacted in a similar manner to form valuable additives, which meet the requirements for a satisfactory additive for mineral lubricating oils which are discussed above. By the term "acidic organic compound" is meant any organic compound which contains an OH or SH group in which the H may be replaced by metal. The best known examples of such acidic organic compounds are alcohols, mercaptans, phenols, thiophenols, carboxylic acids, xanthic acids, sulfonic acids, and the like. It is believed that the basic salts have at least one hydroxyl group attached to the metal atom which has replaced the hydrogen of a hydroxyl or sulfhydryl group. Therefore, only polyvalent metals can be present in such salts.

The new products of the present invention are adaptable to use with a wide variety of petroleum lubricating oil base stocks. They are also useful as antioxidants and for other purposes when incorporated in organic materials other than lubricating oils, as will be more fully explained hereinafter. The materials are also useful as agents for imparting extreme pressure properties to lubricants, wherein the film strength of the lubricant is greatly increased by the presence of the additives. Furthermore, certain of the additives, particularly those containing wax-alkylated aromatic groups, will be found useful as pour depressors.

The new products of the present invention may be more accurately defined as the products obtained by reacting the elements sulfur and phosphorus with a compound having the characterizing structure



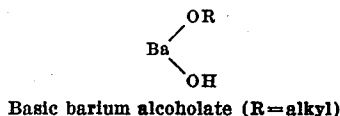
in which R is an organic group, X is oxygen, sulfur, selenium or tellurium, M is a polyvalent metal, and m and n are small integers whose sum is equal to the valence of M. It is to be understood that where more than one RX group is present these may be alike or different, and that M may be attached to more than one X atom,

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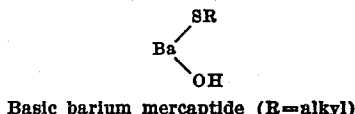
two or more of which may be attached to the same organic group. M of the formula may be any polyvalent metal, such, for example, as calcium, barium, strontium, zinc, aluminum, tin, cobalt, nickel or magnesium, but the divalent metals of group II of the periodic table are especially preferred. It is believed that in the reaction products the sulfur and phosphorus atoms are closely associated with the metal atom, probably through secondary valences.

Several of the more important classes of basic metal salts of acidic compounds which may be reacted with sulfides of phosphorus or other combinations of sulfur and phosphorus in accordance with the present invention are illustrated by the compounds whose formulas are shown below.

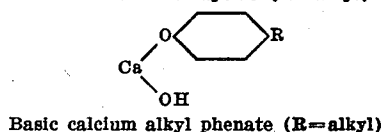
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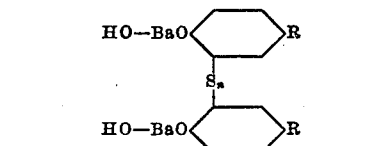
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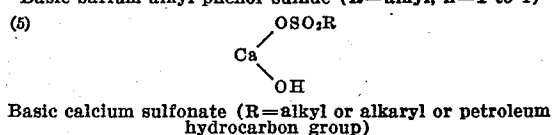
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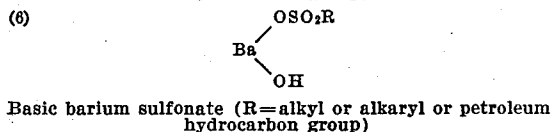
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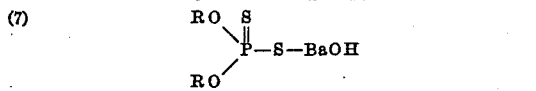
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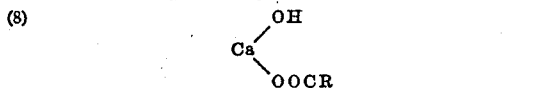
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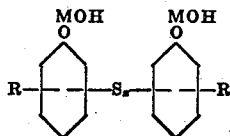
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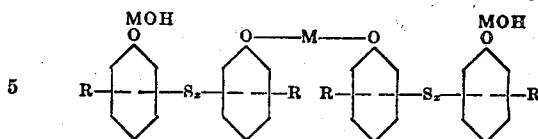


In the case of compounds having more than one OH or SH group in the molecule, for example alkyl phenol sulfides or dihydric phenols, it is possible to prepare basic metal salts having various ratios of metal to organic groups. As an illustration, a basic metal salt of an alkyl phenol sulfide may have a ratio of metal to phenol sulfide of 1.5 to 1, 2 to 1, or even 3 to 1. In the case of a 2:1 ratio of the formula may, for example, be

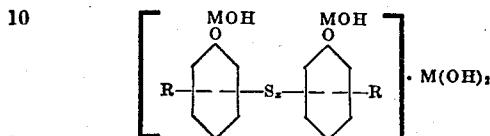


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In the case of a 1.5:1 ratio the formula may be

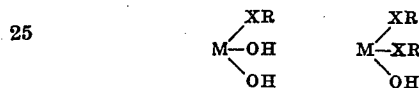


In the case of a 3:1 ratio the formula may be



Intermediate ratios of metal to phenol sulfide, such as 1.8:1 or 2.3:1, may occur in which mixtures of the above types of basic compounds are obtained.

In addition to the basic salts prepared from divalent metals, basic metal salts formed from trivalent metals may be used, such salts being illustrated by the following general formulas:



in which M is a trivalent metal, X is oxygen or sulfur, and R is an organic group.

The following types of compounds are the more important acidic compounds which may be used to form basic metal salts which in turn are reacted with sulfur and phosphorus, or with a phosphorus sulfide, to form the new additives of the present invention: alcohols, mercaptans, carboxylic acids (e. g., fatty acids, naphthenic acids, alkylated benzoic and salicylic acids), sulfurized unsaturated acids, alkylated phenols, alkylated naphthols, alkyl phenol sulfides and polysulfides, alkyl naphthol sulfides and polysulfides, sulfonic acids (e. g., petroleum sulfonic acids, alkyl aromatic sulfonic acids and alkyl phenol sulfonic acids), xanthic acids, dithiocarbamic acids, organo substituted acids of phosphorus (e. g., phosphorous, phosphoric, phosphonic, and phosphinic acids and the corresponding thio acids), etc.

It is to be understood that in any of the above types of compounds the organic radicals may contain various substituted atoms or groups such as alkyl, cycloalkyl, aralkyl, aryl, carboxyl, hydroxyl, alkoxy, aroxy, sulphydryl, nitro, ester (organic and/or inorganic), keto, amino, aldehyde, chloromethyl, aminomethyl, alkyl, thiomethyl, alkyl xanthomethyl, metal substituted carboxyl, metal substituted sulfo, metal substituted hydroxyl or sulphydryl groups, halogen atoms, etc.

One method for converting the acidic compounds to basic metal salts consists merely in adding a metallic oxide or hydroxide to a solution of the acidic compound in a quantity greater than that required to form the normal salt, the reaction generally being conducted at an elevated temperature.

It may be found that in some cases not all of the metallic base which has been added for the purpose of forming a pure basic metal salt will react with the organic compound. However, substantial quantities of the metal base, above that required to form a normal salt, will usually react, and the product may therefore consist of a mixture of the normal salt and the basic salt. It is to be understood that the invention includes the use of such mixtures as well as pure basic salts

in the subsequent reaction with sulfur and phosphorus.

Specific examples of compounds which may be treated with sulfur and phosphorus in accordance with the present invention include, among others, the following: basic barium salt of tert.-octyl phenol sulfide, basic calcium salt of cetyl phenol, basic barium salt of wax-alkylated phenol or salicylic acid, basic zinc salt of methylcyclohexyl thiophosphoric acid, basic calcium petroleum sulfonates, basic barium salt of 2,4-diamylphenol sulfide, basic magnesium salt of octadecyl alcohol, basic aluminum salt of phenylstearic acid, and basic barium salt of C₁₆-C₂₄ branched chain alkyl phenol sulfides.

In accordance with the present invention, the basic metallic salt of the acidic organic compound is caused to react with the elements sulfur and phosphorus. This may be accomplished by adding a mixture of the substances in elementary form, or first one element and then the other, to the heated metallic compound, or by adding a sulfide of phosphorus, such as P₂S₅, P₄S₃, P₄S₇, or the like, or by treating with both sulfur and/or phosphorus and a sulfide of phosphorus, or by treating with any other substance or substances containing essentially only the elements sulfur and phosphorus. The phosphorus may be used either in the white (yellow) or red allotropic form, and sulfur may likewise be used in any of its allotropic forms. However, it is ordinarily more convenient to use a sulfide of phosphorus. In many instances valuable products may also be prepared by reaction of the basic metal salts with oxides of phosphorus in place of or in addition to the sulfides of phosphorus.

In carrying out the reactions described above, the proportions of phosphorus sulfide and basic metallic salt are so chosen that from 0.05 to 2 atoms of phosphorus are reacted with one atom of metal, the preferred ratio being within the limits of about 0.1 to 0.8 atom of phosphorus per atom of metal, depending on which sulfide of phosphorus is selected. These preferred ratios give the products the optimum content of phosphorus and sulfur to impart to them the maximum amount of inhibiting power. In general, these same ratios will be employed also when the reaction is conducted with elemental sulfur and elemental phosphorus.

Although the reaction can be brought about by heating the metal salt directly 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 product 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 a lubricating oil base stock in the desired concentration to form a finished lubricating oil blend.

When preparing a reaction product of sulfur and phosphorus with a basic metal salt of an alkylated phenol, the phenol may be dissolved in a mineral oil or other suitable solvent and treated with an excess of a metal hydroxide, e. g., Ba(OH)₂·8H₂O, at 90° to 230° C., preferably at 150° to 190° C. After a period of heating, free sulfur and free phosphorus, or a sulfide of phosphorus, or other mixture of the elements, is added, heating being continued preferably at 100° to 150° C. to complete the reaction. The

period of heating will be at least 10 minutes and generally about 1 hour, although in some cases longer heating may be required. The product is then filtered giving a concentrate of the desired additive.

It has been found that good results are obtained when preparing these additives in mineral oils if a minor proportion of an alcohol, such as stearyl, lauryl, cetyl, 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 an auxiliary solvent for the final product. Best results are obtained by adding a sufficient quantity of alcohol to give a concentration of about 3% to about 15% in 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 octadecylamine, stearonitrile or lauronitrile. The products obtained by treating the reaction products of sulfur halides and diisobutylene with phenol 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 sulfur and phosphorus in the presence of a small proportion of an olefinic material, such as 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% and preferably from 0.1% to 2%, 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 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 be employed. As has been pointed out elsewhere in the specification, it is oftentimes convenient to prepare concentrates of the additive in oil, containing, say, 25% to 75% of the effective addition agent, the concentrate later being added to a suitable lubricating oil base stock to give a finished product 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

NORMAL BARIUM PHENATE- P_2S_5 REACTION PRODUCT

A mixture of 618 parts of water-washed p-tert.-octyl phenol (prepared by alkylation of phenol with diisobutylene in the presence of $SnCl_4$ -HCl catalyst at 20–85° C.), 240 parts of commercial stearyl alcohol, and 1200 parts of refined mineral lubricating oil of SAE 20 grade was heated to 150° C. Then, over a period of 1½ hours, 465 parts of $Ba(OH)_2 \cdot 8H_2O$ was added. The temperature was raised to 180° C. for one hour, and then lowered to 130° C. for 15 minutes while 266 parts of P_2S_5 was added. The temperature was again raised to 180–190° C. for an additional hour and the reaction product was filtered, giving an additive concentrate containing approximately 40% of additive ingredient. Analysis of the concentrate: Ba—6.80%; S—5.70%; P—3.07%.

EXAMPLE 2

BASIC BARIUM PHENATE- P_2S_5 REACTION PRODUCT

A mixture of 412 parts of water-washed p-tert.-octyl phenol, 203 parts of commercial stearyl alcohol, and 1015 parts of SAE 20 grade refined mineral lubricating oil was heated to 150° C. 625 parts of $Ba(OH)_2 \cdot 8H_2O$ was added over 1½ hours and the temperature raised to 190° C. for 1 hour and then cooled to 130° C. 266 parts of P_2S_5 was added and the temperature raised to 150° C. for one hour and the product filtered, yielding an additive concentrate which contained: Ba—9.69%; S—5.57%; P—3.38%.

EXAMPLE 3

BASIC BARIUM SALT OF TERT.-OCTYL PHENOL SULFIDE

Tertiary octyl phenol, prepared by alkylation of phenol with diisobutylene using BF_3 catalyst, was converted to the sulfide, employing a ratio of 1.6 mols of $SnCl_4$ 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 SAE 20 grade refined paraffinic mineral lubricating oil. 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 $Ba(OH)_2 \cdot 8H_2O$ 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.

EXAMPLE 4

BASIC BARIUM TERT.-OCTYL PHENOL SULFIDE- P_2S_5 REACTION PRODUCT

(Mol ratio P_2S_5 to metal salt=0.4/1)

2000 grams of the concentrate of Example 3 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 5

NORMAL BARIUM TERT.-OCTYL PHENOL SULFIDE

The preparation of a normal metal salt of an alkyl phenol sulfide is shown in this example.

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 $SnCl_4$ 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 SAE 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 $Ba(OH)_2 \cdot 8H_2O$ 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 normal barium tert.-octyl phenol sulfide, 6% stearyl alcohol, and 54% mineral lubricating oil. Analysis of concentrate: Ba—8.92%; S—3.40%.

EXAMPLE 6

NORMAL BARIUM TERT.-OCTYL PHENOL SULFIDE- P_2S_5 REACTION PRODUCT

(Mol ratio P_2S_5 to metal salt=0.2/1)

2470 grams of an oil concentrate of 40% normal barium tert.-octyl phenol sulfide, 6% stearyl alcohol, and 54% mineral oil, prepared as in Example 5, were heated to 180° C. Then over a 1 hour period 77 grams 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 a commercial 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 7

NORMAL BARIUM TERT.-OCTYL PHENOL SULFIDE- P_2S_5 REACTION PRODUCT

(Mol ratio P_2S_5 to metal salt=0.2/1)

2000 grams of the concentrate of basic barium tert.-octyl phenol sulfide of Example 3 was heated to 180° C. and to it was added 60 grams of P_2S_5 over a period of one hour. Heating was continued for an additional 3-hour period after which the product was filtered and then blown with nitrogen at 95° C. for 6 hours. The final additive concentrate contained 12.29% barium, 0.92% phosphorus and 4.9% sulfur.

EXAMPLE 8

BEARING CORROSION TESTS

The purpose of the following test was to determine the corrosion inhibiting effect of adding a small quantity of products prepared as in preceding examples to a lubricating oil base. The same base oil was used in all cases, this being a well refined solvent extracted paraffinic type mineral lubricating oil of SAE 20 grade. Each oil blend contained 0.625% of additive concentrate

of 40% strength, so that the amount of additive actually present in the final blend was 0.25%. The tests were conducted as follows: 500 cc. of oil to be tested was placed in a glass oxidation tube (13" long and 2 3/8" diameter) fitted at the bottom with a 1/4" 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 "corrosion life" indicates the number of hours required for the bearings to lose 100 mgs. in weight, determined by interpolation or extrapolation of the data obtained. The results are shown in Table I.

TABLE I

Oil Blend	Cumulative Bearing Weight Loss (Mg./25 sq. cm.)										Corrosion Life, Hrs.
	4 Hrs.	8 Hrs.	12 Hrs.	16 Hrs.	20 Hrs.	24 Hrs.	28 Hrs.	32 Hrs.	36 Hrs.	40 Hrs.	
Base Oil.....	5	181	-----	-----	-----	-----	-----	-----	-----	-----	6
Base Oil+Product of Example 1.....	0	0	0	12	24	46	-----	-----	-----	-----	136
Base Oil+Product of Example 2.....	0	0	2	6	13	20	32	40	52	64	150

¹By extrapolation.

It will be seen that the product of Example 2, prepared from a basic metal alkyl phenate, was more effective as a bearing corrosion inhibitor than was the product of Example 1, prepared from a normal metal alkyl phenate.

EXAMPLE 9

126 HOUR CATERPILLAR DIESEL ENGINE TESTS

Engine tests on various lubricating oil blends were conducted 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 comprised an SAE 30 grade solvent extracted Mid-Continent oil, the same oil compounded with the additive of Example 5, and the same oil compounded with the additive of Example 4. After each engine test was completed the engine parts were examined and given demerit ratings based on their condition, particular attention being paid to the ring zone condition. The individual ratings were weighted according to their relative importance and an overall demerit 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 performance of the oil. The results obtained are presented in the table below. It will be seen that an additive of the present invention (blend 2) improved the performance of the base oil to a greater extent than did an untreated metal alkyl phenol sulfide (blend 1).

TABLE II

126 hour Caterpillar Diesel Engine tests

Oil Blend	Engine Demerit Ratings	
	Overall	Ring Zone
Base Oil.....	2.24	2.32
Blend 1—Base Oil+2.5% of Additive Concentrate of Example 5.....	1.53	1.47
Blend 2—Base Oil+2.5% of Additive Concentrate of Example 4.....	1.21	1.00

EXAMPLE 10

36 HOUR CHEVROLET ENGINE TESTS

Blends of the additives of Examples 6 and 7 were prepared in a lightly treated SAE 30 viscosity Mid-Continent base stock of 81 viscosity index and then tested in a Chevrolet engine run for 36 hour periods under the following conditions: 14.2/1 air/fuel ratio, 30 brake horsepower, 3150 R. P. M., 280° F. oil temperature, 200° F. water jacket temperature. In the same manner as described in Example 9 the various engine parts were examined and given demerit ratings after each test. It will be seen from the results of these tests, given in the table below, that the

additive of the present invention (blend 2), prepared from a basic metal phenol sulfide, was much more effective than a similar additive (blend 1) prepared from a normal metal phenol sulfide. Particularly to be noted is that the former additive was especially effective in reducing the sludge and varnish forming tendencies of the lightly refined base oil.

TABLE III

36 hour Chevrolet engine tests

Oil Blend	Engine Demerits			
	Overall	Ring Zone	Piston Skirt Varnish	Sludge
Blend 1—Base Oil+2.5% of additive concentrate of Example 6 (Prepared from Normal Barium Octyl Phenol Sulfide).....	1.20	0.70	5.17	1.16
Blend 2—Base Oil+2.5% of Additive Concentrate of Example 7 (Prepared from Basic Barium Octyl Phenol Sulfide).....	0.66	0.63	1.25	0.44

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 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 thio-xanthates, and the like.

The additives of the present invention may be used in conjunction with any of the additional additives mentioned in application Serial Number 493,734 (now Patent No. 2,409,686, patented October 26, 1946).

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 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, sludge dispersers, antioxidants, thickeners, viscosity index improvers, and any of the agents commonly used as additives, a number of which are disclosed in application Serial Number 493,734. Of special importance are the higher alcohols having eight or more carbon atoms per molecule. The latter 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 composition.

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 antioxidants, 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 in 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 petroleum hydrocarbon material containing a stabilizing amount of a product obtained by reacting a sulfide of phosphorus with a basic polyvalent metal salt of an acidic organic compound at a temperature of about 100° C.-180° C. for a period of at least 10 minutes, in the ratios of 0.05-2 atomic proportions of phosphorus for each metal atomic proportion of metal in the salt and 0.75-2.5 atomic proportions of sulfur for each atomic proportion of phosphorus.

2. A composition according to claim 1 in which the hydrocarbon material is a lubricating oil fraction.

3. A compounded lubricant consisting essentially of a mineral lubricating oil base and a stabilizing amount of a product obtained by reacting a sulfide of phosphorus with a basic polyvalent metal salt of an acidic organic compound at a temperature of at about 100° C.-180° C. for a period of at least 10 minutes in the ratio of 0.05-2 atomic proportions of phosphorus for each atomic proportion of metal in the salt.

4. A composition according to claim 3 in which the metal salt is a salt of a phenol.

5. A composition according to claim 4 in which the metal salt is the salt of an alkylated phenol.

6. A composition according to claim 5 in which the alkylated phenol is a tertiary octyl phenol.

7. A composition according to claim 3 in which the sulfide of phosphorus is phosphorus pentasulfide and in which the metal salt is a basic barium salt of a tertiary octyl phenol.

8. A composition according to claim 3 in which the metal salt is a basic metal salt of a phenol sulfide.

9. A composition according to claim 8 in which the metal salt is a basic metal salt of a tertiary octyl phenol sulfide.

10. A compounded lubricant consisting essentially of a mineral lubricating oil base and a stabilizing amount of a product obtained by reacting phosphorus pentasulfide with a basic barium

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salt of a tertiary octyl phenol sulfide at a temperature of about 100° C.-150° C. for a period of at least 10 minutes, in the ratio of 0.05-2 atomic proportions of phosphorus for each atomic proportion of barium.

11. A compounded lubricant consisting essentially of a mineral lubricating oil base and a stabilizing amount of a product obtained by reacting a sulfide of phosphorus with a basic metal salt of a sulfonic acid at a temperature of about 100° C.-180° C. for a period of at least 10 minutes in the ratios of 0.05-2 atomic proportions of phosphorus for each atomic proportion of metal.

12. A composition according to claim 11 in which the sulfonic acid is a petroleum sulfonic acid.

13. A composition according to claim 11 in which the sulfide of phosphorus is phosphorus pentasulfide and in which the metal salt is the basic barium salt of petroleum sulfonic acid.

14. A compounded lubricant consisting essentially of a mineral lubricating oil base and a stabilizing proportion of a product obtained by reacting phosphorus pentasulfide with a basic barium salt of tertiary octyl phenol sulfide at a temperature of about 180° C., for a period of

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about four hours, the molecular ratio of phosphorus pentasulfide to the metal salt being from 0.2:1 to 0.4:1.

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