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COMPOUNDED LUBRICATING OIL

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15 Claims. (Cl. 252-42.7)

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.

1

It is known that the addition of certain types 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 15used for such purposes include the metal derivatives of such organic compounds as fatty acids, naphthenic acids, alcohols, phenols and ketones. However, these various metal compounds generally have the disadvantage of tending to corrode 20 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 in-95 vention 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, 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 certain metal phenates and thiophenates, more specifi-40 cally, the calcium, barium, strontium, magnesium, and zinc phenates and thiophenates containing as a substituent in the aromatic nucleus an alkyl group having at least 5 carbon atoms. It has been found that such products are unusually satisfactory in inhibiting bearing corrosion, in being stable in the presence of water, and in being adaptable to use with a wide variety of lubricating oil base stocks. The elements sulfur and phosphorus may be introduced into the phenate molecule by 50 those obtained by reaction of a sulfide of phos-

2

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 of metal organic compounds to lubricating oils 10 compositions herein described 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, and in many cases it is not necessary to have alkyl groups present to impart sufficient solubility. The invention includes the reaction products of phosphorus sulfides with compounds analogous to the phenates and thiophenates, 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 a copending application we have described the preparation of reaction products of elemental sulfur with metal phenates and the use of such products in lubricating oil compositions. It was there shown that the sulfur atoms were linked directly to the metal atoms in the molecules of the 30 reaction product. It is believed that the same type of reaction occurs when metal phenates are treated with phosphorus sulfides or with phosphorus and sulfur, giving compounds in which the phosphorus and sulfur atoms are linked to-35 gether in the molecule to form a group which is attached directly to the metal atom, probably through secondary valences.

> One basis for this belief is that when these products are treated with hydrochloric acid they lose a large proportion of their phosphorus content, an appreciable amount of sulfur and practically all of the metal. On the other hand, when a metal organo thiophosphate is similarly 45 treated, only a small amount of sulfur and substantially no phosphorus is lost from the compound.

Some of the more preferred products to be used in accordance with the present invention are

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phorus or of the elements sulfur and phosphorus with the following compounds: Barium tertiary octyl phenate Calcium tertiary octyl phenate Barium diamyl phenate Barium cetyl phenate Zinc isohexadecyl phenate

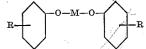
Calcium salt of petroleum phenols

Barium salt of wax-alkylated phenol

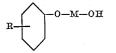
Magnesium salt of octadecyl cresol

Barium salt of phenol alkylated with refinery olefin polymers

The invention includes the reaction products of phosphorus and sulfur or sulfides of phosphor- 15 us with not only the normal phenates and thiophenates and the like, but the basic metal phenates and thiophenates as well. In a normal phenate of a divalent metal the ratio of metal to phenol is 1 to 2 as in the following formula:



25 In a basic metal phenate the ratio of metal to phenol may be 2 to 2 or even 3 to 2. In the case of a 2 to 2 ratio the formula may be



These basic phenates are formed, for example, by reacting phenols with more than the amount of metallic oxide or hydroxide necessary to form the normal phenates. Reaction products of phosphorus sulfides with basic metal alkyl phenates are particularly useful in extreme pressure lubricants and are advantageous in motor oils prepared from naphthenic base stocks.

It is also intended to include within the scope of this invention products obtained by the reaction of phosphorus sulfides with metal salts of alkylated phenol sulfides and with metal salts of alkylated hydroxy carboxylic acids, for example, barium tert.-octyl phenol sulfide or the barium phenate-zinc carboxylate of lauryl salicylic acid.

It is likewise often practical to apply this reaction with phosphorus sulfides to other organic compounds containing the -OM or -SM group, such as the metal alcoholates, mercaptides or ketonates; for example, calcium octadecylate, barium salts of wax alcohols, etc., and to use the products formed as additives for mineral oil 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 the elements sulfur and phosphorus with a compound having the formula

ArXMT

In this formula 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, 65 tene polymer oil. Alkylation of phenol with about or it may be a condensed nucleus, exemplified by naphthalene, anthracene and the like. X in the formula is a non-metal of group VI of the periodic table. M is a divalent metal of group II of the periodic table, the most important being cal- 70 cium, barium, strontium, magnesium and zinc, although for some purposes corresponding compounds containing tin, lead, cobalt or nickel will also be found to be desirable. T in the formula represents either a hydroxyl group or the group 75 as much as two molecular equivalents of diiso-

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(OM) nXAr

where M, X, and Ar have the meanings given above and n is 0, 1 or 2. 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

(RArX)₂M

10 where R represents at least one alkyl radical attached to the nucleus, the total number of carbon atoms in all of such alkyl radicals being at least 5 when the compound is to be dissolved in hydrocarbon oils, other symbols having the meanings given above. 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, aryl, carboxyl, hydroxyl, alkoxy, 20 sulfhydryl, nitro, ester, keto, amino, aldehydo, chlormethyl, aminomethyl, alkyl thiomethyl, alkyl xantho methyl, metal substituted carboxyl, metal substituted hydroxyl or sulfhydryl groups, halogen atoms, etc. Alkyl radicals attached to the nucleus may have a total of 5 to 12 carbon atoms in all of such groups, but in some cases as many as 16 to 20 or more carbon atoms in a single group or a plurality of groups may be preferred. If more than one alkyl group is present in a single molecule, whether or not attached to 30 the same aryl nucleus, such groups may be alike or different. Also included within the class of metal derivatives defined above are the metal salts of phenol sulfides and alkylated phenol sul-35 fides.

Suitable alkylated phenols for use in the present invention may be prepared by alkylating phenol, cresol, naphthol or other phenolic compounds with such alkylating agents as alcohols, alkyl halides, alkyl phosphates, olefins, and the like, with 40 the aid of catalysts such as metal halides, hydrochloric acid, hydrofluoric acid, sulfuric acid, phosphoric acid, activated clay, etc. Conveniently, olefinic material such as petroleum refinery gases, containing mixtures of olefins, may be 45used, or preferably individual olefins may be employed, such as butene, amylene or an olefin polymer, such as diisobutylene or triisobutylene. High molecular weight alkylated phenols may also be used, for example, those prepared by con-50 densing 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 55 cashew nut shell liquid or from other vegetable sources may likewise be used. Halogenated or nitrated phenols will also find application in this invention, particularly if the final additive is to 60 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 buan equal molar proportion of diisobutylene gives para-tert.-octyl phenol, also known as diisobutyl phenol or tetramethyl butyl phenol. This phenolic material is especially desirable because of its ease of preparation and because products made from it are highly satisfactory for the present invention. In many instances, however, a higher degree of alkylation may be advantageous and for this reason the phenol may be alkylated with



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butylene to give, under proper conditions, essentially di-tert.-octyl phenol; or it may be alkylated with other olefin polymers such as triisobutylene, other isobutylene polymers, or a normal butene polymer. 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 converting the phenolic materials to metal 10 phenates any convenient and effective means may be employed. For example, sodium or potassium salts may first be formed by reaction with NaOH or KOH and those salts then converted to the desired divalent metal salts by 15 double decomposition. Another method which may be used is the reaction of an alcoholate of the desired metal with the alkylated phenol. When possible, of course, the most convenient method is to react the alkylated phenol directly 20 with the oxide or hydroxide of the desired metal. Thus, the barium salts can be prepared directly by adding barium hydroxide to a mineral oil solution of the alkyl phenol at elevated temperature.

In accordance with the present invention, the 25 metallic phenate or other analogous metallic derivative of an aromatic hydroxy or mercapto compound is caused to react with the elements sulfur and phosphorus. This may be accomplished by adding a mixture of the substances 30 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 P_2S_5 , P4S3, P4S7, etc., or the like, or by treating with both sulfur and/or phosphorus and a sulfide of 35phosphorus, 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 40 be used in any of its allotropic forms.

However, it is ordinarily more convenient to use a sulfidfie of phosphorus. In carrying out the reactions described above the proportions of phosphorus sulfide and metal phenate are so 45 chosen that from 0.5 to 2 atoms of phosphorus are reacted with one atom of polyvalent metal, the preferred ratio being within the limits of about 0.8 to 1.2 atoms of phosphorus per atom of metal. Depending upon which sulfide of phos-50 phorus is selected, the atomic ratio of sulfur to metal will then lie within the limits of about 1.5 to 1 to 4 to 1, preferably from about 2 to 1 to 3 to 1. These preferred ratios give the products the optimum content of phosphorus and sulfur 55 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 60 by fusing the metal phenate 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 65 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 70 and then readily blended with a lubricating oil base stock in the desired concentration to form a finished lubricating oil blend.

The additives may generally be prepared by taining the desired percentage of additive. Thus, dissolving an alkylated phenol in a mineral oil 75 when using a 40% concentrate, 2.5% of this ma-

or other suitable solvent and treating the same with a metal hydroxide, e. g., $Ba(OH)_{2.8H_2O}$, at 90° to 230° C., preferably at 150° to 190° C. After a further 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 generally be from about 10 minutes to an hour, although in some cases longer periods may be required. When the material will no longer stain a strip of copper immersed in it, the reaction is considered complete. The product is then filtered, giving a concentrate of the desired additive.

If a calcium salt is to be prepared, a less direct action is preferred, since the reaction of alkylated phenols with calcium oxide or hydroxide does not proceed as readily as in the case of barium compounds. Calcium alkyl phenates are preferably prepared by reacting alkyl phenols with calcium methylate or other calcium alcoholate.

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, 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 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 it is known that sulfides of phosphorus will react with alcohols, such reaction is relatively slow under the preferred conditions of the present invention, whereas the reaction with the metal phenates is extremely rapid, so that by the time the latter reaction has been completed there will have been relatively little or no reaction between the higher alcohol and the sulfide of phosphorus. Hence substantially all of the alcohol is present as such in the final product.

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 a tetraisobutylene, cracked gas 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 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 25% of this ma-

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terial 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. 10

EXAMPLE 1

A mixture of 618 parts by weight of tert.-octyl phenol (prepared by reacting diisobutylene with phenol in the presence of SnCl4 and HCl catalysts 15 at 20° to 85° C.), 240 parts of commercial stearyl alcohol and 1200 parts of mineral oil (a solvent extracted Mid-Continent parafiinic oil of 52 seconds Saybolt viscosity at 210° F.) was heated to 120° C. Then over a two hour period 632 parts of barium hydroxide (Ba(OH)2.8H2O) were added. During the reaction a stream of nitrogen gas was passed through the mixture to minimize oxidation. After an additional one-half hour of heating at the same temperature, 266 parts of phosphorus pentasulfide (P2S5) were added in two approximately equal portions over a ten minute period. The temperature rose immediately to 130° C. and was held at 120° to 130° C. for one hour. The reaction product was then filtered, using Hyflo filter aid. The filtered concentrate was 30 found to have the following analysis:

Per	cent	
Barium	6.99	
Sulfur	4.97	
Phosphorus	1.69	1

The metal content of the product obtained in the above example was lower than that theoretically expected for the proportion of reactants used. This was found to be the result of using an old sample of barium hydroxide octahydrate which had absorbed large quantities of carbon dioxide, forming barium carbonate, which is not suitable for this type of reaction. In subsequent 45 preparations it was found that when using the same proportions of reactants as in Example 1 but employing fresh Ba(OH) 2.8H2O, the product obtained had a higher metal content than that of Example 1, or conversely, a product having the same metal content as that of Example 1 could be prepared by using less of the fresh barium hydroxide octahydrate.

EXAMPLE 2

To a mixture of 700 parts of di-tert.-amylphenol, 250 parts of stearyl alcohol and 1260 parts of the mineral oil used in Example 1, heated to 150° C., were added 472 parts of barium hydroxide, $Ba(OH)_{2.8H_2O}$. The temperature was then raised to 170° C. and 45 minutes later cooled to 150° C. 60 There were then added 150 parts of phosphorus tetritaheptasulfide (P4S7), commercially known as phosphorus trisulfide. Heating was continued at 150° C. for $1\frac{1}{2}$ hours, and the product was 65 filtered. Analysis of the resulting additive concentrate was as follows:

Per	cent	
Barium	6.40	
Sulfur	2.85	7
Phosphorus	2.06	

EXAMPLE 3

The procedure of Example 2 was repeated using the same proportions of reactants and the same 75 at 130° C. for another hour and the reaction prod-

temperatures, except that 200 parts of P_2S_5 were used instead of the 150 parts of P4S7, and a slightly lower temperature of 130° C. was employed during the P2S5 addition and the subsequent heating. After filtration the additive concentrate was found to have the following analysis:

		1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -	Per	cent
	Barium			6.95
^	Sulfur Phosphorus			4.83
U	Phosphorus			2.10

EXAMPLE 4

The distinguishing feature of this preparation is that a basic barium phenate was used in the reaction.

A mixture of 412 parts of water-washed p-tert.octyl phenol (prepared as in Example 1), 203 parts of commercial stearyl alcohol and 1015 parts of the mineral oil used in Example 1 was 20 heated to 150° C. 625 parts of Ba(OH) 2.8H2O were added over $1\frac{1}{2}$ hours and the temperature raised to 190° C. for 1 hour and then cooled to 130° C. 266 parts of P2S5 were added and the temperature raised to 150° C. for one hour and 25 the product filtered, yielding an additive concentrate which contained: Per cont

	ICI	COILO
	Barium	9.69
	Sulfur	5.57
0	Sulfur Phosphorus	3.38

EXAMPLE 5

To reduce the tendency of the product of Ex-35 ample 1 to stain copper a portion was heated for one hour in a stream of air at 150° to 160° C., the treatment causing it to darken in color and to become more viscous although clearer in appearance. The resulting product contained 4.35% sulfur and 2.14% phosphorus. 40

EXAMPLE 6

A mixture of 618 parts of water-washed p-tert.octyl phenol (prepared as in Example 1), 240 parts of commercial stearyl alcohol, and 1200 parts of the mineral oil used in Example 1 was heated to 150° C. Then over a 11/2 hour period 465 parts of Ba(OH) 2.8H2O were added. The temperature was then raised to 180° C. for one 50 hour, then cooled to 130° C. for 15 minutes while 266 parts of P_2S_5 were added. The temperature was again raised to 180° to 190° C. for an additional hour and the reaction product filtered. The resulting additive concentrate had the fol-55 lowing analysis:

L C1	CETT
Barium	6.80
Sulfur	
Phosphorus	

EXAMPLE 7

A mixture of 618 parts of p-tert.-octyl phenol (prepared as in Example 1), 225 parts of stearyl alcohol, and 1123 parts of the mineral oil used in Example 1 was heated to 150° C. Then 450 parts of barium hydroxide (Ba(OH)2.8H2O) were added over a 90 minute period. The temperature 70 was then raised to 170° C. for one hour. 70 parts of lump sulfur were incorporated and the temperature was raised to 190° C. for an additional hour and then cooled to 130° C. After addition of 200 parts of P2S5 the temperature was held

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(prepared as in Example 8) and 1080 parts of a refined mineral lubricating oil of 52 seconds Saybolt viscosity (210° F.) was heated to 180° C. and 260 parts of Ba(OH)_{2.8H2}O added thereto. The reaction product was cooled to 150° C. and filtered, yielding a 40% concentrate of the barium alkyl phenate in oil. It contained 6.05% barium.

EXAMPLE 12

A mixture of 4944 parts of p-tert.-octyl phenol. 1072 parts of commercial stearyl alcohol and 8984 parts of SAE-20 refined mineral oil was heated to 180° C. Then 3720 parts of Ba(OH)_{2.8H2}O were added gradually over a 3 hour period, the temperature being maintained at 180° C. during this time and for an additional hour after all of the barium hydroxide had been added. 1064 parts of phosphorus pentasulfide, P2S5, were then added over a period of 5 to 10 minutes, this step causing the temperature to rise to 196° C. The temperature was then lowered to 190° C. and heating was continued until a sample withdrawn from the reaction vessel was found to be relatively non-staining to a copper test strip. The reaction mixture was then filtered to give the finished additive concentrate. Analysis: Barium 9.86%; sulfur 4.43%; phosphorus 2.06%.

EXAMPLE 13

A mixture of 300 parts of p-tert.-octyl phenol thenic oil of 50 seconds Saybolt viscosity at 210° F. was heated to 95° C. Then 150 parts of Ba(OH)_{2.8H2}O were slowly added and the temperature gradually raised to about 150° C. and heated until substantially all of the water of reaction had been removed. The product obtained was quite viscous when hot and practically solid when cool.

200 parts of this material were heated with 10 removal of a small amount of insoluble matter, the resulting additive was found to contain 3.71% sulfur and 1.55% phosphorus.

EXAMPLE 14

The purpose of the following test was to determine the corrosion inhibiting effect of adding a small quantity of various products prepared as in preceding examples to a lubricating oil base. The same base oil was used in all cases, this be-50 ing a well refined solvent extracted paraffinic type mineral lubricating oil of S. A. E. 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 were placed in a glass oxidation tube (13" long and $2\frac{5}{8}$ " diameter) fitted at the bottom with a 1/4" bore air inlet tube perforated $\mathbf{0}$ 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 70 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 be-A mixture of 578 parts of C12-20 alkylated phenol 75 fore continuing for another four hour period.

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uct filtered. analysis:	The	product	had	the	following	
Barium		1997 - 1997 -		-	Per cent 9.07	
Sulfur				_ <u></u>	8.18	5
Phosphorus .				·	2.38	

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EXAMPLE 8

In the production of secondary butyl alcohol from refinery butenes the latter are contacted 10 with 75% to 90% sulfuric acid at 20° to 30° C. to form butyl sulfuric esters which are subsequently hydrolyzed to form the alcohol. During contact with the sulfuric acid some of the butenes polymerize and form what is known as a polymer oil. 15 Since the refinery butene feed stock may contain 40-50% of olefinic material in which, in addition to n-butene, 1 to 2% of butadiene, 1 to 3%of isobutene and 1 to 2% of the dimer and/or trimer of isobutene may be present, the exact 20 nature of the polymer oil obtained is not certain. However, it can reasonably be assumed that it comprises a mixture of polymers and copolymers of these various olefins. For the alkylation of phenol to form products useful for preparing ma- 25terials of the present invention the buttene polymer is steam distilled up to 400° F. and the bottoms, boiling essentially from 400° to 650° F., used as the alkylating material. A mixture of 100 parts of phenol and about 240 parts of the 30 and 200 parts of a conventionally refined naphpolymer oil fraction is saturated with hydrogen chloride at 80° and 130° F. and 10 parts of aluminum chloride are added over a half hour period with stirring. Stirring is continued for an additional $1\frac{1}{2}$ hours at 120° F. and the product is 35° water washed and then stripped of unreacted material by distilling to 270° F. with nitrogen and then up to 400° F. with steam. The desired phenol remains as the bottoms from this distillation. The product contains alkyl groups having 40 parts of P2S5 for three hours at 170-200° C. After an average of 16 to 20 carbon atoms per molecule.

EXAMPLE 9

In this preparation the alkylated phenol employed was one having a side chain of 16 to 20 carbon atoms prepared as in Example 8. 578 45 parts of the alkylated phenol were added to 1080 parts of the mineral oil used in Example 1 and the mixture heated to 150° C. To this were then added 250 parts of barium hydroxide

(Ba(OH) 2.8H2O)

over a one hour period after which the temperature was raised to 170° C. for an additional hour. After cooling the mixture to 120° C., 150 55 parts of P_2S_5 were added and the temperature maintained at 120° to 130° C. for one hour and the product filtered. The additive concentrate had the following analysis:

	cent	
Barium	 5.49	60
Sulfur	 3.95	
Phosphorus	 1.76	

EXAMPLE 10

To reduce the copper staining tendency of the 65 product of Example 9 a portion was heated for one hour at 210° C. in a stream of nitrogen. The product had the analysis:

	Per		
Barium		5.49	7
T HODDIGI GD		1.00	

EXAMPLE, 11

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.

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was borne out by the results of the tests in actual engine operation.

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 improve-

Table I

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		Cu	nulativ	ze bear	ing we	ight lo	ss mg./	25 sq. o	m.		
Oil blend	4 hrs.	8 hrs.	12 hrs.	16 hrs.	20 hrs.	24 hrs.	28 hrs.	32 hrs.	36 hrs.	40 hrs.	Corrosion life, hrs.
Base oil	5 0 0 0 0 0 0 0 0 0 37	$ \begin{array}{c} 181 \\ 0 \\ 2 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 88 \end{array} $	$ \begin{array}{c} 0\\ 8\\ 5\\ 2\\ 5\\ 0\\ 0\\ 1\\ 0\\ 155\\ \end{array} $	9 18 16 6 11 12 12 3 1	$21 \\ 29 \\ 27 \\ 13 \\ 19 \\ 24 \\ 36 \\ 3 \\ 5 \\$	$38 \\ 42 \\ 48 \\ 20 \\ 29 \\ 46 \\ 58 \\ 6 \\ 7 \\$	51 56 66 32 46 	123 77 88 40 57 116 17 14	97 106 52 71 	64 86 26 25	6. 30. 35. 50. 44. 36-37 ¹ . 30. Not determined. ² 9.

By extrapolation.
 Difficult to extrapolate accurately as weight loss was only 25-26 mg. after 40 hours of test.

taining phosphorus and sulfur were very effective in reducing the corrosiveness of the base oil toward the alloy bearings. By contrast, a metal phenate which had not been treated with a phosphorus sulfide was substantially ineffective in re- 30 ducing the corrosiveness.

EXAMPLE 15

In the following tests, lubricating oil blends containing additives of the present invention 35 were tested in a single cylinder Caterpillar Diesel engine run under high temperature, high load conditions, namely, 18.7 B. H. P. output, 850 R. P. M., 195° F. oil temperature and 140° F. atmospheric temperature for 60 hour periods. 40 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 45 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 52 seconds viscosity Saybolt at 210° F. Results of these tests are shown in the following table.

Table II

		Engin	e demerits	5	Cu-Pb con-	5
Oil blend	Over- all	Ring zone	Piston skirt varnish	Rings stuck	necting rod bear- ing wt. loss, mg.	
Base oil	1.46	1, 55	1.00	1	82	C
Base oil+2.5% prod- uct of Example 1	0.69	0.59	0	0	1 None	
Base oil+2.5% prod- uct of Example 2	0.86	1.10	0.25	0	25	
Base oil+2.5% prod- uct of Example 3	0.79	0.67	· 0	0	1 None	(
Base oil+2.5% prod- uct of Example 5	0.67	0.65	0	0	14	

1 Bearings gained slightly in weight.

It will be readily seen that the performance of 70 the base oil in the engine was materially improved by incorporation of the agents of the present invention. It should likewise be noted that the capacity of these additives to inhibit corrosiveness, as indicated by laboratory tests, 75 ing:

It will be observed that all of the products con- 25 ment 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

- Calcium mahogany sulfonates Tin salt of wax alkylated phenol sulfide Strontium mahogany sulfonates Magnesium cetyl phenate Nickel oleate
- Calcium dichlorostearate
- Aluminum-calcium mixed soap of fatty acids from oxidation of petroleum fractions Calcium isohexadecyl phenol sulfonate Barium octadecylate
- 50 Calcium phenyl stearate
- Nickel dibutyl dithiocarbamate
- Nickel amyl xanthate Barium dioctyl dithiophosphate Zinc methyl cyclohexyl dithiophosphate
- Calcium dihexadecyl monothiophosphite Calcium cetyl phosphate
- 55 Barium mahogany sulfonates Zinc diisopropyl salicylate Tin naphthenate

Aluminum naphthenate 60

- Magnesium mahogany sulfonates
- Calcium double salt of octadecyl phenol sulfonic acid
- Barium phenate-zinc sulfonate of isohexadecyl phenol sulfonic acid 65

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. Examples of such compositions include the follow-

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Per cent 1. Additive concentrate of the present invention _____ 15 Calcium mahogany sulfonates_____ 0.6Mineral lubricating oil_____ 97.9 Б 2. Additive concentrate of the present inven-2.5tion _____ 1.5Barium mahogany sulfonates_____ __ 96 Mineral lubricating oil 3. Zinc mahogany sulfonates_____ 3.0 10 Additive concentrate of the present inven-3.0 tion ______ Mineral lubricating oil_____ 94

13

The lubricating oil base stocks used in the com-15 positions 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, propane, 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 additive 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, anti-oxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like, may also be employed.

Assisting agents which are particularly desirable are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon The alcohols may be saturated straight atoms. and branched chain aliphatic alcohols such as octyl alcohol (C₈H₁₇OH), lauryl alcohol (C12H25OH), cetyl alcohol (C16H33OH), stearyl alcohol, sometimes referred to as octadecyl alcohol, (C18H37OH), heptadecyl alcohol (C17H35OH), 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 vari-25ous 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 30 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 35 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

40 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 lu-45 bricants 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

⁵⁰ 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 anti-oxid-

55 ants for the fuel but also as stabilizers for the anti-knock agent itself. Since these additives exhibit anti-oxidant properties and are believed also to possess ability to modify surface activity, they may be employed in asphalts, road oils,

- 60 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-ox-idants, 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

70 which are given by way of illustration only, but it is to be limited solely by the terms of the appended claims.

We claim:

may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, **75** ing a small quantity, sufficient to stabilize said material of a reaction product of a sulfide of phosphorus with a compound of the formula

(RArX)₂M

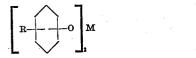
where Ar is an aromatic nucleus, R is an alkyl 5 radical having at least 5 carbon atoms, X is a member of the group consisting of oxygen and sulfur, and M is a divalent metal of group II of the periodic table and selected from the group consisting of calcium, barium, strontium, mag- 10 nesium and zinc.

2. A mineral lubricating oil containing a small quantity, sufficient to stabilize said oil, of a reaction product of a sulfide of phosphorus with a compound of the formula

(RArX)2M

where Ar is an aromatic nucleus, R is an alkyl radical having at least 5 carbon atoms, X is a member of the group consisting of oxygen and sulfur, and M is a divalent metal of group II of the periodic table and selected from the group consisting of calcium, barium, strontium, magnesium and zinc.

3. A mineral lubricating oil containing a small quantity, sufficient to stabilize said oil, of a reaction product of a sulfide of phosphorus with a compound of the formula



where R is an alkyl radical having at least 5 carbon atoms, M is a divalent metal of group II of 35 the periodic table and selected from the class consisting of calcium, barium, strontium, magnesium and zinc.

4. A lubricating oil according to claim 3 in which R of the formula is a tertiary octyl radical. 40

5. A mineral lubricating oil containing a small quantity, sufficient to stabilize said oil, of a reaction product of a sulfide of phosphorus with a product obtained by reacting barium hydroxide with a tertiary octyl phenol.

6. A mineral lubricating oil containing a small quantity, sufficient to stabilize said oil, of a reaction product of elemental sulfur and elemental

phosphorus with a product obtained by reacting barium hydroxide with a tertiary octyl phenol.

7. A mineral lubricating oil containing a small quantity, sufficient to stabilize said oil, of a product obtained by reacting about one molecular proportion of phosphorus pentasulfide in a mineral oil with about two molecular proportions of the barium salt of an alkylated phenol at 100° to 150° C., the alkyl group of the phenol having at least 5 carbon atoms.

8. A mineral lubricating oil according to claim 7 in which the additive is obtained by reacting the sulfide of phosphorus with the metal salt in the presence of a minor proportion of a higher fatty 15 alcohol.

9. A mineral lubricating oil according to claim 7 in which the barium salt is the barium salt of p-tert.-octyl phenol.

10. A mineral lubricating oil containing a product prepared according to claim 7 which product has been heated at a temperature of 150° to 160° C. until its copper staining tendency has been substantially reduced.

11. A mineral lubricating oil containing a small quantity, sufficient to stabilize said oil, of a reaction product of phosphorus tetritaheptasulfide (P_4S_7) , with a barium diamyl phenate.

12. A mineral lubricating oil containing a small quantity, sufficient to stabilize said oil, of a reaction product of elemental sulfur and a sulfide of phosphorus with a metallic salt of an alkylated phenol, the metal of said salt being a divalent metal of group II of the periodic table and selected from the class consisting of calcium, magnesium, strontium, and zinc.

13. A mineral lubricating oil containing a small quantity, sufficient to stabilize said oil, of a product formed by reacting barium p-tert.-octyl phenate first with elemental sulfur and then with phosphorus pentasulfide.

14. A mineral lubricating oil according to claim 2 in which the sulfide of phosphorus is phosphorus pentasulfide.

15. A mineral lubricating oil according to claim 45 3 in which the sulfide of phosphorus is phosphorus pentasulfide.

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