United States Patent Office 2,830,949 Patented Apr. 15, 1958

2,830,949

PHOSPHORUS- AND SULFUR-CONTAINING COMPLEX METAL SALTS OF OXIDIZED HYDROCARBONS AND OIL COMPOSITIONS THEREOF

Henry G. Berger, Glen Rock, Ferdinand P. Otto, Woodbury, and John W. Schick, Camden, N. J., assignors to Socony Mobil Oil Company, Inc., a corporation of New York

No Drawing. Application December 23, 1955 Serial No. 554,930

22 Claims. (Cl. 252—32.7)

The invention relates to a new class of phosphorus-, sulfur- and metal-containing oxidized hydrocarbon products and to a method for the preparation of these products. It also contemplates the use of these new products as addition agents for mineral lubricating oils, particularly oils designed for use in internal combustion engines.

It is well known that hydrocarbon lubricating oils tend to oxidize in use in an engine with attendant formation of oxidation products which are acidic in character and which exert a corrosive action on the engine parts, such as the hard metal alloy bearings. Furthermore, it is well known that the gradual deterioration of the oil in use due to oxidation, etc. is attended by formation of carbonaceous sludge and lacquer which adheres to the engine parts, particularly the piston ring grooves and skirts, thereby lowering the efficiency of the engine and frequently causing the rings to stick. To counteract these conditions, the art has developed chemical agents which when added in small amounts to engine lubricating oils have the ability to greatly retard the oxidation of the oil in use. Agents have also been developed which have the ability to prevent deposition of sludge materials on the engine parts, thereby keeping the engine clean and free from the clogging and sticking effects normally encountered. These two types of chemical agents are known in the art as antioxidants and detergents, respectively. The present invention provides a new class of chemical products which exhibit both antioxidant and detergent properties.

In a copending application, Serial No. 441,626, filed July 6, 1954, there is disclosed and claimed a method for oxidizing hydrocarbon oils in the presence of metal hydroxides to produce complex metal salts of the oxidized oils which are effective detergents for mineral lubricating oils.

It has now been found, in accordance with the present invention, that by reacting a hydrocarbon, such as a petroleum oil, which has been oxidized in the presence of a metal hydroxide, with a phosphorus sulfide, and then subjecting the resulting product to reaction with additional metal hydroxide in the presence of water, under the conditions hereinafter defined, a new class of reaction products are produced. These new products have high metal contents. They also contain substantial amounts of phosphorus and sulfur and they exhibit exceptional detergent properties, as well as being effective antioxidants for mineral lubricating oils.

Due to the complex nature of the products provided by the invention, no exact chemical formula can be ascribed to them at this time and they are, therefore, best described by the process of producing them. As far as is known, the products of the character provided by the invention have not been known heretofore. They are, therefore, believed to be new compositions of matter.

It is, therefore, the primary object of the invention to provide a new class of phosphorus-, sulfur- and metal-containing oxidized hydrocarbon products. It is also an object to provide mineral lubricating oils containing minor amounts of these new products, said oils having improved antioxidant and detergent properties. Other and further objects will be apparent from the following description.

It will be seen that broadly stated the present invention provides a method for the preparation of oil-soluble, phosphorus-, sulfur- and metal-containing reaction products which involves the steps of (1) forming a mixture of a hydrocarbon material, such as a petroleum oil, and a metal hydroxide, (2) contacting said mixture with an oxidizing gas at a temperature of from about 125° C. to about 325° C. to provide a metal-containing oxidized hydrocarbon product, (3) reacting the metal-containing oxidized hydrocarbon product with a phosphorus sulfide to provide a metal-, phosphorus- and sulfur-containing oxidized hydrocarbon product, (4) forming a mixture of the product produced in step 3 with water and a metal hydroxide at a temperature below the boiling point of water, (5) substantially completely dehydrating the mixture formed in step 4 and (6) filtering the dehydrated mixture from step 5 to remove insolubles therefrom.

As aforesaid, the exact nature of the products produced by the process of the invention is not known, however, analytical data indicate that these products are comprised principally of "complex salts," i. e., salts containing more equivalents of metal than so-called "normal salts." Thus, it has been found that products produced by the oxidation step of the process contain about two equivalents of metal per equivalent of acid-hydrogen formed in the course of the oxidation. For example, when such an oxidation product, prepared by oxidizing a petroleum oil and containing 1.50% calcium, was de-metallized by means of strong hydrochloric acid, the resulting acidic product had a neutralization number (N. N.) of 21 and a saponification number of 18. This neutralization number would account for only 50% of the calcium, assuming the formation of normal salts. This indicated that the remaining 50% of the calcium is present in the product as some type of complexed or coordination compound.

When the products produced in the oxidation step are reacted with phosphorus sulfide and the resulting products reacted with additional metal hydroxide in accordance with the subsequent steps of the invention, the metal contents thereof are substantially increased. The manner in which this further amount of metal is incorporated into the ultimate products is not fully understood. However, without intending to limit the invention in any way by theoretical considerations, it would appear that the phosphorus sulfide reacts with oxygenated groups contained in the oxidized hydrocarbon molecules, such as aldehyde, ketone or alcohol groups, to form cross-linked molecules. As shown in the examples presented hereinafter, the phosphorus sulfide reaction with the oxidized hydrocarbon intermediate is often attended by substantial gel formation, particularly where the hydrocarbon reactant has been subjected to relatively strong oxidation. This gel is broken by the water which is always added to the reaction at this point in the process. It appears, therefore, that in the presence of water, the cross-linked mol-

ecules are hydrolyzed to form new acids which react with additional metal hydroxide to produce the ultimate complex salt products of the invention. As in the case of the oxidized oil intermediate products, de-metallization of the final products indicates that their metal contents are greater on an equivalent basis than the metal contents of normal salts. Thus, such a product, containing 3.07% calcium, upon de-metallization with hydrochloric acid showed a neutralization number (N. N.) of 15. This acid number would account for only 0.54% calcium, assuming the formation of normal salts. This product, therefore, had a calcium content amounting to 500% excess or approximately 5 equivalents of calcium over that which would be expected in a normal salt product.

THE REACTANTS

The hydrocarbons utilizable as starting materials in the process of the invention may comprise any hydrocarbon or mixture of hydrocarbons capable of providing a product which is soluble in lubricating oil. In general, this solubility requirement is satisfied by hydrocarbons having molecular weights of from about 200 to about 1000, with those having molecular weights of from about 600 to about 1000 being particularly suitable. The hydrocarbons may be aliphatic hydrocarbons of either the straight-chained, branch-chained or cyclic type. Also, aromatic hydrocarbons which have aliphatic substituent groups of sufficiently high melocular weight to provide an oil-solubilizing character to the final products can be used. Thus, alkaryl type hydrocarbons containing at least one aliphatic substituent of at least about 8 carbon atoms, or several such substituents totaling at least about 8 carbon atoms per molecule are suitable. Examples of these would be octyl benzene, dodecyl benzene, wax benzene, etc.

Petroleum oils and petroleum oil fractions, such as petrolatums, waxes, etc., are a preferred class of hydrocarbon reactants, while refined oils, such as "Bright Stocks" are especially preferred. In terms of viscosity, oils having viscosities ranging from 2 to about 65 centistokes at 210° F. may be used, with those having viscosities of from about 20 to 45 centistokes at 210° F. being preferred. The characteristics of several different types of suitable oil stocks are shown in Table I.

Table I

Oil	Gravity, ° API	Pour point, ° F.	K. V. at 210 ° F., cs.	Avg. mol. wt.
Solvent-refined Mid-Continent distillate stock	30.0	20	6.2	350
Foots oil	36.3	90	3.6	360
Slack wax	29.8	85	25.8	700
Solvent-refined Mid-Continent bright stock	25.8	----------	25.9	720
Do	26.3	----------	32.9	840

The metal hydroxides utilizable as reagents in the invention are those of the metals of Groups I and II of Mendeleeff's Periodic Table of the Elements. Specifically, the hydroxides of calcium, sodium, barium, cobalt, strontium, zinc and magnesium are highly suitable, with calcium hydroxide being particularly preferred. Various grades of calcium oxide, calcium hydroxide and barium hydroxide may be used in the invention. However, grease-makers lime (96% CaOH) is preferred because of its high purity, small particle size and its property of being wetted by oil.

The phosphorus sulfide reactant used in the process may be either P_2S_5, P_4S_7 or P_4S_3, with phosphorus pentasulfide being preferred. Mixtures of the sulfides can also be used.

PROCESS CONDITIONS

In conducting the oxidation step of the process, the hydrocarbon reactant and the metal hydroxide reagent are charged to a reactor having means for the introduction of an oxidizing gas, such as air or oxygen. The amount of metal hydroxide charged to the hydrocarbon can range from about 0.5% up to about 25%, based on the weight of the hydrocarbon reactant. The reactants are mixed together and heated at a temperature of from about 125° C. to about 325° C., preferably 175° C. to 225° C., and maintained at this temperature while the oxidizing gas is passed through the mixture to effect oxidation of the hydrocarbon and reaction of the oxidized hydrocarbon with the metal hydroxide. The oxidation is continued until the hydrocarbon has attained a metal content of from about 0.05% to about 3%, by weight. It has been found that superior oil detergents are provided by the process of the invention when a relatively mild oxidation is used, i. e., an oxidation which provides an oxidation product which has a metal content of from about 0.05% to about 0.5%, and preferably about 0.1%. Furthermore, the products obtained using a mildly oxidized intermediate are better from the standpoint of antioxidant ability.

It should be noted that the amount of metal hydroxide charged to the hydrocarbon prior to the oxidation reaction should, in all instances, be in excess of that eventually utilized in the oxidation. Thus, we have found that at least about 15% of the metal hydroxide charged should remain unreacted at the end of the oxidation. It has been found that the metal hydroxide when present in such amounts serves to prevent undesirable side reactions, such as oxidative polymerization, which are detrimental to the provision of products of the nature and quality herein contemplated, particularly from the standpoint of color and solubility in lubricating oil. Also, with respect to the amount of metal hydroxide charged, although as much as 25% may be used, large excess amounts provide no particular advantage. Furthermore, the use of large excess amounts of the metal hydroxide reduces the fluidity of the reaction mass so that stirring of the reaction mixture and eventual filtration are made more difficult. In instances where these latter difficulties are encountered, however, they can be overcome by the addition of a diluent solvent, such as benzene, toluene or the like, which is subsequently distilled from the final product.

The oxidation time required to incorporate the desired amount of metal into the hydrocarbon reactant will, of course, vary depending upon the conditions employed, such as the equipment used, the rate of oxygen or air introduction, the temperature, the amount of metal hydroxide charged, the type of hydrocarbon being oxidized, etc. As will be seen from the examples which follow, the oxidation times used varied from about 3 hours up to about 85 hours. From a practical standpoint, it is, of course, desirable to use oxidation equipment and conditions which are conducive to effecting the oxidation to the desired extent in as short a time as possible. Accordingly, it is considered that modifications designed to increase the efficiency of the oxidation procedure, such as the use of oxidation catalysts and special reactors calculated to give a more efficient disbursal of the oxidizing gas in the hydrocarbon, etc., come within the broad purview of this invention.

Upon completion of the oxidation step the oxidized hydrocarbon product mixture may be filtered to remove the excess (unreacted) metal hydroxide and the phosphorus sulfide reagent added, or the phosphorus sulfide may be added directly to the oxidized hydrocarbon-metal hydroxide reaction mixture. In conducting the reaction, from about 5% to about 20%, by weight (based

on the weight of the hydrocarbon charge), of phosphorus sulfide is added to the oxidized hydrocarbon product and the two mixed together. The mixture is then heated to a temperature of from about 75° C. to about 150° C. for a sufficient time to complete the reaction. The reaction is usually complete in from about 10 minutes to about 10 hours. Although the temperature may be varied within the aforesaid range without significantly effecting the final product, the higher temperatures, i. e., from about 125° C. to about 150° C. give products which are usually dark in color and which, therefore, tend to darken the color of the oils in which they are used. The lower temperatures, however, i. e., from about 75° C. to about 110° C., give lighter colored products which provide better colored oil blends.

As will be seen from the examples, the metal contents of the ultimate complex salt products, on an undiluted basis, were increased from 1.94% for a 5% charge of P_2S_5 to 6.04% for a 15% charge on batches of the same oxidized oil product. However, the sharpest rise in metal content occurs with the first 7.5% of the P_2S_5 with only relatively slight increases above that amount. The use of about 10% of the phosphorus sulfide in the reaction is, therefore, considered to be the preferred amount to use.

The phosphorus contents of the finished products indicate that from about 70% to 100% of the phosphorus sulfide charged is reacted. However, the P/S ratio in the products ranges from 0.4 to 0.8 and for the most part averages about 0.6. This ratio is higher than 0.39 which is the P/S ratio in phosphorus pentasulfide, for example. It would appear then that some sulfur is lost in the reaction either as hydrogen sulfide or it is removed as an oil-insoluble salt during the filtration step.

As mentioned previously, gelation of the reaction mixture is apt to occur in the phosphorus sulfide reaction. This is paticularly so where the oxidized oil intermediate contains a relatively high percentage of metal, i. e., more than about 0.5%, and about 10%, or more of phosphorus sulfide is added. Gelation does not usually occur when the reaction is conducted on the more mildly oxidized hydrocarbons, i. e., those containing 0.5%, or less of metal. The gel formation, however, is in no way harmful, and as afore-indicated, the gel is quickly broken by the addition of water, which is added in all instances at this stage of the process.

In general with respect to the phosphorus sulfide reaction it can be said that the use of a 10% charge of the phosphorus sulfide and conduction of the reaction at a temperature of from about 75° C. to about 125° C. for about 1 hour using P_2S_5 as the phosphorus sulfide reactant are the preferred reaction conditions. It should be noted that somewhat longer reaction times, i. e., 5 to 6 hours, are required for best results where P_4S_7 is used as the sulfide reactant.

In this connection it has been found that both the phosphorus heptasulfide and the phosphorus trisulfide are not as reactive as the phosphorus pentasulfide under comparable conditions, the trisulfide giving salt products having the lowest metal contents. However, the use of a "triggering compound," such as sulfur, in conjunction with these reagents substantially increases their reactivity and also increases the metal content of the ultimate products. The produt obtained using the P_4S_7—S combination, for example, approaches that of the P_2S_5 products in metal content. Also, in the case of the P_4S_7 by extending the reaction time to 5 or 6 hours, products may be obtained which are comparable to the P_2S_5 products without the use of sulfur. The amount of sulfur used in conjunction with the P_4S_7 or P_4S_3 should be about 10% to 25% based on the phosphorus sulfide used.

In conducting the reaction of the phosphorus sulfide-oxidized hydrocarbon intermediate with the additional metal hydroxide in the presence of water, the metal hydroxide reagent can be either that which is already present in the reaction mixture (if the mixture was not filtered pior to the phosphorus sulfide reaction) or it can be a fresh charge of metal hydroxide. In any case, the amount of metal hydroxide present in the reaction mixture at this stage should be from about 2% to about 25% (based on the original hydrocarbon charge) the usual amount being about 10%. The amount of water necessary is small, generally from about 2% to about 10% being sufficient, although higher amounts may be used. The water is preferably added after cooling the reaction mixture to a temperature below the boiling point of water, preferably to about 90% C. Dehydration is then accomplished by heating the reaction mixture above the boiling point of water while passing a stream of nitrogen therethrough. The mixture is preferably heated to a temperature of from about 150° C. to about 200° C. and maintained at this temperature level until all of the water is driven off. The product is generally filtered at or near this latter temperature level in order to obtain relatively rapid filtration. Obviously, the dehydration may be accomplished in other ways, such as by adding a solvent, such as benzene, which may be subsequently distilled off as an azeotropic mixture.

The metal hydroxides used in the water-treating and dehydration steps of the invention are the same as those utilized in the oxidation step, i. e., the hydroxides of the metals of groups I and II of the periodic table of the elements. However, the mixed metal salt products, i. e., salt products containing more than one metal can be produced in the invention by the use of one metal hydroxide in the oxidation step and a different metal hydroxide in the water-treating and dehydration steps, as is illustrated in the examples which follow.

A full understanding of the nature of the products of the invention and the manner of their preparation may be had by reference to the following specific examples.

The oxidation step of the process is illustrated by Examples A to J.

EXAMPLE A

Twelve hundred grams of a percolated, solvent refined Mid-Continent type bright stock and 87 grams (7.2 weight percent) of calcium hydroxide were charged to a 3-liter, round-bottomed, 4-necked flask equipped with a stirrer, a thermometer and two medium-grained filter sticks for introduction and dispersion of air. The reaction mixture was heated and maintained at a temperature of about 190° C. while air was passed therethrough at a rate of 1.7 liters per hour per 100 grams of oil for 85 hours. The introduction of air was then stopped and the reaction mixture stirred with 48 grams (4%) of "Hyflo" (a diatomaceous earth filter aid), filtered and cooled. The filtered product contained 1.49% calcium.

EXAMPLE B

Two thousand grams of a percolated, solvent-refined, Mid-Continent type bright stock and 218 grams (11 weight percent) of calcium hydroxide were charged to an electrically heated column reactor, 60 inches long by 3 inches in diameter, having a fritted glass piece sealed in the bottom. Sixty liters of air per hour were passed up through the oil, maintained at 204° C., for 24 hours. A portion of the reaction mixture was contacted with 4 weight percent of "Hyflo" and filtered. Analysis showed the filtrate to contain 1.94% calcium. This example illustrates the use of a column type reactor which provides a much more efficient use of the oxidizing gas than the flask type reactor used in Example A. Consequently, the oxidation time in this example is considerably shorter.

Additional oxidations were conducted (Examples C to J) following the same general procedure employed in Example B, but varying the oxidation conditions. The pertinent data with respect to the several oxidation examples are summarized in Table II.

Table II

Example	Hydrocarbon Stock	Percent lime charged	Temperature, ° C.	Air rate, l./hr./100 g. oil	Oxidation time, hr.	Percent Ca in filtered product
A	Solvent-refined Mid-Continent type bright stock.	7.2	190	1.7	85	1.49
B	do	11	204	3.0	24	1.94
C	do	[1] 21	218	5.0	27	[2] 2.84
D	do	10	218	3.0	3	0.16
E	do	10	218	3.0	7	0.57
F	do	10	218	3.0	3	0.12
G	do	3.7	190	2.5	50	2.23
H	Foots oil	7.2	204	2.0	48	2.14
I	Slack wax	7.2	190	1.7	50	1.08
J	Conventional 100 sec. at 100° F. paraffin oil	10	204	3.0	3	0.1

[1] $Ba(OH)_2$ was charged instead of lime.
[2] Ba.

The following examples illustrate the reaction of oxidized hydrocarbon products, prepared in the manner illustrated by Examples A to K, with phosphorus sulfide and also the reaction of the products thus produced with additional metal hydroxide in the presence of water to produce the products of the invention. The amount of phosphorus sulfide charged to the oxidized hydrocarbon intermediate, or to the oxidized hydrocarbon-metal hydroxide mixture (unfiltered) is based on the metal hydroxide-free (filtered) oxidized product. The calculation of the phosphorus sulfide consumed is based upon the phosphorus content of the final product on the basis of an estimated 100% product yield.

EXAMPLE 1

Three hundred grams of filtered, oxidized solvent-refined, Mid-Continent type residual oil product containing 1.49% soluble calcium (Example A, Table II), diluted with 100 milliliters of xylene were charged into a 4-necked, round-bottomed flask equipped with a stirrer, thermometer and a gas inlet tube. This mixture was reacted with 30 grams of P_2S_5 (10%, by weight, of the oxidized oil product) at 130° F. to 145° C. for ¾ hour in an atmosphere of nitrogen. The mixture gelled. Two hundred milliliters of toluene were added to reduce the viscosity. Seventy-five milliliters of water and 100 grams of lime were added. The mixture was dehydrated to a temperature of 200° C. Five weight percent of "Hyflo" (filter aid) was added and the product filtered. The solvents were removed by distillation.

Analyses:		
Calcium	percent	6.03
Phosphorus	do	2.44
Sulfur	do	3.79
Calcium increase	do	305
P_2S_5 consumed	do	88
B–10 stability No.[1]		170

[1] The percentage of additive, multiplied by 100, that reduces the N. N. of the reference oil to a value of 2. Thus, the lower the stability number, the more effective the additive as an antioxidant.

EXAMPLE 2

One hundred and sixty-seven grams of a filtered, oxidized, solvent-refined, Mid-Continent type residual oil product containing 1.49% soluble calcium (Example A, Table II) were diluted with 100 milliliters of xylene. This was reacted directly with 17 grams of P_2S_5 (10%) and 50 grams of lime at 140° C. to 150° C. for 5 minutes. The mixture became gelatinous. Another 200 milliliters of xylene were added and the mixture stirred for about 6 hours. After cooling to about 80° C. to 90° C., 50 milliliters of water were carefully added. The gelatinous mixture became very fluid. The water was stripped up to 195° C. About 5%, by weight of "Hyflo" (filter aid) was added and the product filtered. The solvents were removed by distillation.

Analyses:	Percent
Calcium	6.5
Phosphorus	2.40
Sulfur	3.81
Calcium increase	329
P_2S_5 consumed	86

Comparing Examples 1 and 2, it is seen that the use of 6 hours reaction time and the addition of the lime along with the P_2S_5 in Example 2, as compared to the ¾-hour reaction time used in Example 1 did not significantly affect the product in any way.

EXAMPLE 3

Two hundred and twenty grams of an unfiltered, oxidized, solvent-refined, Mid-Continent, residual oil product-lime mixture containing 1.94% oil-soluble calcium (Example B, Table II) were diluted with 200 grams of conventional paraffin oil (100 seconds at 100° F.). This was reacted with 10 grams of P_2S_5 (5%) at 140° C. to 150° C. for 1 hour in an atmosphere of nitrogen. Twenty milliliters of water were carefully added to 80° C. to 90° C. followed by the addition of 60 grams of lime. The total mixture was dehydrated up to a temperature of 190° C. Four weight percent of "Hyflo" (filter aid) was added and the product filtered.

Analyses:	Percent
Calcium	[1] 2.25
Phosphorus	0.75
Sulfur	1.49
Calcium increase	132
P_2S_5 consumed	100

[1] 4.50% on undiluted basis.

EXAMPLE 4

This example is the same as Example 3 with the exception that 15 grams of P_2S_5 (7.5%, by weight, of the calcium oxidized residual oil product) were used.

Analyses:	Percent
Calcium	[1] 2.78
Phosphorus	1.02
Sulfur	1.90
Calcium increase	187
P_2S_5 consumed	98

[1] 5.56% on undiluted basis.

EXAMPLE 5

This example is the same as Example 3 with the exception the 20 grams of P_2S_5 (10%, by weight, of the calcium oxidized residual oil product) were used.

Analyses:	Percent
Calcium	[1] 2.85
Phosphorus	1.34
Sulfur	2.36
Calcium increase	194
P_2S_5 consumed	96

[1] 5.70% on undiluted basis.

EXAMPLE 6

This example is the same as described in Example 3 with the exception that 30 grams of P_2S_5 (15%, by weight, of calcium oxidized residual oil product) were used. A gel formed after 12 minutes reaction time. A small amount of water (about 2% by weight) broke the gel and restored the original fluidity.

Analyses:	Percent
Calcium	[1] 3.02
Phosphorus	1.84
Sulfur	3.04
Calcium increase	211
P_2S_5 consumed	88

[1] 6.04% on undiluted basis.

Examples 3 to 6 show the increase in metal content of the complex salt product attained by increasing the amount of P_2S_5 used from 5% to 7.5% to 10% and to 15%, respectively. The sharpest rise, however, occurs with the first 7.5% of P_2S_5, with more gradual increases being obtained with 10% and 15% of the P_2S_5.

EXAMPLE 7

Two hundred and seventy-seven grams of an unfiltered, oxidized, solvent-refined, Mid-Continent residual oil product-lime mixture containing 1.27% calcium (prepared after the fashion of Example B, Table II) and 125 grams of conventional paraffin oil (300 seconds of 100° F.) were reacted with 25 grams of P_2S_5 (about 10%, by weight, of the calcium oxidized residual oil product) at 100° C. to 110° C. for 3 hours in an atmosphere of nitrogen. Twenty-five milliliters of water (10%) were slowly added at 80° C. No additional lime was added over and above that which was present in the original mixture. The mixture was dehydrated up to a temperature of 190° C. Four weight percent of "Hyflo" (filter aid) was added and the product filtered.

Analyses:	Percent
Calcium	[1] 2.54
Phosphorus	1.62
Sulfur	3.22
Calcium increase	200
P_2S_5 consumed	87

[1] 3.81% on undiluted basis.

EXAMPLE 8

Two hundred grams of a filtered, oxidized, solvent-refined Mid-Continent type residual oil product containing 2.84% barium (Example C, Table II) were diluted with 200 grams of 100 seconds Mid-Continent oil. This was reacted with 20 grams of P_2S_5 (10%) at 140° C. to 150° C. for 1 hour in an atmosphere of nitrogen. Twenty milliliters of water were carefully added at 90° C. followed by the addition of 85 grams of barium hydroxide (dry). The total mixture was dehydrated up to a temperature of 190° C. Eight weight percent of "Hyflo" (filter aid) was added and the product filtered.

Analyses:	Percent
Barium	[1] 7.9
Phosphorus	1.30
Sulfur	2.14
Barium increase	460
P_2S_5 consumed	97

[1] 15.8% on undiluted basis.

This example illustrates the application of the process to a barium-oxidized oil using barium hydroxide as the water-complexing reagent.

EXAMPLE 9

Four hundred grams of an unfiltered, oxidized, Mid-Continent residual oil product (0.16% calcium)-lime mixture (Example D, Table II) and 40 grams of P_2S_5 were reacted in equipment described in Example 1 at 140° C. to 150° C. for 1 hour in an atmosphere of nitrogen. After cooling to 80° C. to 90° C., 40 milliliters of H_2O and 80 grams of lime were added. The mixture was slowly dehydrated to 190° C. Eight weight percent of "Hyflo" (filter aid) was added and the product filtered immediately.

Analyses:	Percent
Calcium	3.87
Phosphorus	2.14
Sulfur	3.38
P_2S_5 consumed	85
Calcium increase	2,300

This example shows the applicability of the process of the invention to a mildly oxidized oil (0.16% calcium).

EXAMPLE 10

Example 9 was duplicated with an unfiltered, oxidized, residual oil product containing 0.12% calcium (Example F, Table II).

Analyses:		
Calcium	percent	2.83
Phosphorus	do	1.97
Sulfur	do	3.00
B–10 stability No.		190

EXAMPLE 10*a*

Example 10 was duplicated except that the batch size was increased five-fold.

Analyses:		
Calcium	percent	2.78
Phosphorus	do	1.89
Sulfur	do	2.88
B–10 stability No.		185

EXAMPLE 10*b*

Example 10*a* was duplicated.

Analyses:	Percent
Calcium	2.79
Phosphorus	1.86
Sulfur	2.85

Examples 10, 10*a* and 10*b* show the reproduceability of the products of the process.

EXAMPLE 10*c*

Sixteen hundred and thirty-five grams of a filtered, oxidized, residual oil product containing 0.12% calcium (Example F, Table II) and 164 grams of P_2S_5 were reacted together at 140° C. to 150° C. for 2 hours. After cooling to 80° C. to 90° C., 400 milliliters of water were carefully added followed by 400 grams of barium hydroxide (dry). The mixture was dehydrated to a temperature of 190° C. About 5%, by weight, of "Hyflo" (filter aid) was added and the product immediately filtered.

Analyses:		
Calcium	percent	0.11
Barium	do	10.30
Phosphorus	do	2.09
Sulfur	do	2.24
B–10 stability No.		Ca 160
P_2S_5 consumed	percent	85

This example illustrates the production of a mixed metal salt of calcium and barium by the use of calcium

hydroxide in the oxidation step and barium hydroxide in the water-complexing step.

EXAMPLE 11

Four hundred grams of an unfiltered, oxidized, residual oil product containing 0.16% calcium (prepared in the manner of Example F, Table II) and 30 grams of P_2S_5 were reacted for 1 hour at 140° C. to 150° C. Twenty grams of lime were added in the absence of water. The temperature was raised to 190° C. Four weight percent of "Hyflo" (filter aid) was added and the product filtered immediately.

Analyses:	Percent
Calcium	0.06
Phosphorus	0.98
Sulfur	3.45

The poor metal content of this product shows the necessity for having water present in the reaction of the oxidized oil-P_2S_5 product with the additional metal hydroxide.

EXAMPLE 12

Four hundred grams of an unfiltered, calcium oxidized residual oil mixture containing 0.57% calcium (Example E, Table II) and 40 grams (10%) of P_2S_5 were reacted in equipment described in Example 1 at 140° C. to 150° C. for 1 hour in an atmosphere of nitrogen. After cooling to 80° C. to 90° C., 40 milliliters of water and 40 grams of lime were added. The mixture was slowly dehydrated to 190° C. Four weight percent of "Hyflo" (filter aid) was added and the product filtered.

Analyses:	Percent
Calcium	4.64
Phosphorus	2.47
Sulfur	4.29
P_2S_5 consumed	90

EXAMPLE 13

One hundred grams of a filtered, calcium-oxidized residual oil product containing 2.76% calcium (same as Example B, Table II, except oxidization time was 30 hours) were diluted with 150 grams of conventional paraffin oil (100 seconds at 100° F.). This was reacted with 10 grams (10%) of lime and 10 grams of P_2S_5 in equipment described in Example 1 at 140° C. to 155° C. for 1¼ hours in an atmosphere of nitrogen. A heavy gel formed when the mixture was cooled to 80° C. The gel broke when 20 milliliters of water and 20 grams of lime were added. The mixture was slowly dehydrated to 190° C. Eight weight percent of "Hyflo" (filter aid) was added and the product filtered.

Analyses:	Percent
Calcium	[1] 2.24
Phosphorus	1.15
Sulfur	1.98

[1] 5.6% on undiluted basis.

EXAMPLE 14

One hundred and thirty-eight grams of the product of Example 13, diluted with 62 grams of 100 seconds Mid-Continent type oil, was reacted with 6 grams of P_2S_5 (equivalent to 10% of the original calcium oxidized oil present in the mixture) at 140° C. to 150° C. for 1¼ hours. After cooling to 80° C., 20 milliliters of water and 20 grams of lime were added. The mixture was slowly dehydrated to 190° C. Five weight percent of "Hyflo" (filter aid) was added and the product filtered.

Analyses:	Percent
Calcium	[1] 2.72
Phosphorus	1.61
Sulfur	1.76

[1] 9.85% on undiluted basis.

EXAMPLE 15

Two hundred grams of a filtered, oxidized, solvent-refined, Mid-Continent type distillate oil product containing 2.23% soluble calcium (Example G, Table II) were diluted with 200 grams of conventional paraffin oil (100 seconds at 100° F.). This was charged to equipment described in Example 1 and reacted with 20 grams of P_2S_5 (10%, by weight, of the calcium oxidized distillate oil product) at 140° C. to 150° C. in an atmosphere of nitrogen. A gel formed after 5 minutes reaction time. Twenty milliliters of water were carefully added at 80° C. followed by the addition of 20 grams of lime. The mixture was dehydrated up to a temperature of 190° C. Four weight percent of "Hyflo" (filter aid) was added and the product filtered.

Analyses:	Percent
Calcium	[1] 2.43
Phosphorus	1.22
Sulfur	1.78
Calcium increase	118
P_2S_5 consumed	91

[1] 4.86% on undiluted basis.

EXAMPLE 16

Two hundred grams of a filtered, oxidized, foots oil product containing 2.14% soluble calcium (Example H, Table II) were diluted with 200 grams of conventional paraffin oil (100 seconds at 100° F.). This was charged to equipment described in Example 1 and reacted with 20 grams of P_2S_5 (10%, by weight, of the calcium-oxidized distillate wax product) at 140° C. to 150° C. for ½ hour in an atmosphere of nitrogen. Twenty milliliters of water were carefully added followed by the addition of 20 grams of lime. The mixture was dehydrated up to a temperature of 190° C. Four weight percent of "Hyflo" (filter aid) was added and the product filtered.

Analyses:	Percent
Calcium	[1] 2.68
Phosphorus	1.26
Sulfur	1.84
Calcium increase	150
P_2S_5 consumed	95

[1] 5.36% on undiluted basis.

EXAMPLE 17

Two hundred grams of a filtered, oxidized, slack wax product containing 1.08% soluble calcium (Example I, Table II) were diluted with 300 grams of conventional paraffin oil (100 seconds at 100° F.) This was charged to equipment described in Example 1 and reacted with 20 grams of P_2S_5 (10%, by weight, of the calcium oxidized residual wax product) at 140° C. to 150° C. for 1½ hours in an atmosphere of nitrogen. Twenty milliliters of water were carefully added followed by the addition of 40 grams of lime. The mixture was dehydrated up to a temperature of 190° C. Four weight percent of "Hyflo" (filter aid) was added and the product filtered.

Analyses:	Percent
Calcium	[1] 1.71
Phosphorus	1.06
Sulfur	1.36
Calcium increase	138
P_2S_5 consumed	98

[1] 2.57% on undiluted basis.

EXAMPLE 18

Twenty-one hundred and fifty grams of an unfiltered, calcium-oxidized wax benzene (2–12)[1] product containing 0.12% oil-soluble calcium metal (prepared under the conditions of Example F, Table II) were reacted with

[1] For preparation see U. S. Patent No. 2,476,972.

200 grams of phosphorus pentasulfide (10%, by weight, of the oil) under an atmosphere of nitrogent at 140° C. to 145° C. for 3 hours. The mixture was cooled to 80° C. to 90° C. Two hundred milliliters of water were carefully added. The mixture was dehydrated up to a temperature of 160° C. One hundred grams (5%) of "Hyflo" (filter aid) were added and the product filtered hot.

Analyses:

Calcium ----------percent--	2.53
Phosphorus ----------do----	1.37
Sulfur ----------do----	2.17
B–10 stability No----------	175

EXAMPLE 19

Four hundred and forty grams of an unfiltered mixture of calcium-oxidized dodecylbenzene residue [1] containing

[1] This is the high boiling residue from dodecylbenzene manufacture.

0.13% oil-soluble calcium metal (prepared after the fashion of Example K, Table II) were reacted with 40 grams of phosphorus pentasulfide (10%, by weight, of oil) under an atmosphere of nitrogen at 140° C. to 145° C. for 3 hours (equipment used is described in Example 1). The mixture was cooled to 80° C. to 90° C. Forty milliliters of water were carefully added. The mixture was dehydrated up to a temperature of 190° C. Twenty grams (5%, by weight) of "Hyflo" (filter aid) were added and the product filtered hot.

Analyses:	Percent
Calcium ----------	1.93
Phosphorus ----------	1.31
Sulfur ----------	2.11

EXAMPLE 20

Four hundred and forty grams of an unfiltered, calcium-oxidized white oil product (Nujol) containing 0.21% oil-soluble calcium metal and 1.46% oxygen (prepared under the conditions of Example F, Table II) were reacted with 40 grams of phosphorus pentasulfide (10%, by weight, of oil) for 3 hours at 150° C. in an atmosphere of nitrogen. The mixture was cooled to 80° C. to 90° C. Fourty milliliters of water were carefully added followed by 40 grams of lime. The mixture was dehydrated up to 150° C. Twenty grams (5%, by weight) of "Hyflo" (filter aid) were added and the mixture filtered hot.

Analyses:	Percent
Calcium ----------	3.51
Phosphorus ----------	2.13
Sulfur ----------	3.52

Examples 15 to 20 show the use of several different types of hydrocarbon reactants in the process of the invention.

EXAMPLE 21

Four hundred and forty grams of an unfiltered calcium-oxidized, Mid-Continent type residual oil product containing 0.24% oil-soluble calcium metal and 1.20% oxygen (prepared under the same conditions as Example F, Table II) were reacted with 40 grams of phosphorus heptasulfide (P_4S_7) at 150° C. for about 3 hours. The mixture was cooled to 80° C. to 90° C. Forty milliliters of water were carefully added followed by 40 grams of lime. The mixture was dehydrated up to 150° C. Twenty grams (5%, by weight) of "Hyflo" (filter aid) were added and the mixture filtered hot.

Analyses:

Calcium ----------percent--	1.99
Phosphorus ----------do----	1.98
Sulfur ----------do----	2.25
B–10 stability No----------	35
B–10A stability No. 24 hours----------	500

EXAMPLE 22

Example 21 was duplicated except that after the phosphorus heptasulfide was rapidly added, 5 grams of sulfur were slowly added over about 1 hour. The mixture was heated at 150° C. for an additional 2 hours. The final steps were the same as in Example 21.

Analyses:

Calcium ----------percent--	2.76
Phosphorus ----------do----	2.28
Sulfur ----------do----	2.75
B-10A stability No., 24 hours ----------	430

EXAMPLE 23

Example 21 was duplicated with the exception that 40 grams of phosphorus trisulfide (P_4S_3) were used.

Analyses:	Percent
Calcium ----------	0.70
Phosphorus ----------	0.62
Sulfur ----------	1.18

EXAMPLE 24

Example 22 was duplicated except that 40 grams of phosphorus trisulfide were substituted for phosphorus heptasulfide.

Analyses:

Calcium ----------percent--	1.21
Phosphorus ----------do----	1.04
Sulfur ----------do----	1.74
B–10 stability No----------	120

EXAMPLE 25

A mixture of 100 pounds of Mid-Continent type bright stock and 10 pounds of lime were air oxidized (1.5 cu. ft./min.) in a conical shaped steel container at 400° F. for 5 hours. The oxygen content of a filtered sample of oxidized oil was 2.08%.

The unfiltered oxidized oil-lime mixture was transferred to a 30-gallon glass-lined Pfaudler kettle and treated with 7.5 pounds of P_4S_7 (7.5%, by weight, of oxidized oil) at 220° F. for 6 hours in a nitrogen atmosphere. The mixture was cooled to 160° F. to 170° F. Ten pounds of water (10%) were added portionwise over 1 hour. After an additional 10 pounds of lime (10%) were added to complete the final neutralization, the water was removed over a 3-hour period up to a temperature of 150° C. Ten pounds of "Hyflo" (filter aid) were added to facilitate filtration through a conventional plate and frame filter press.

Analyses:	Percent
Calcium ----------	3.26
Phosphorus ----------	1.8
Sulfur ----------	2.44

Examples 21 to 26 illustrate the use of phosphorus heptasulfide and phosphorus trisulfide in the process of the invention. It will be seen that these sulfides provide products having metal contents somewhat lower than products prepared using phosphorus pentasulfide (compare Examples 21 and 23 with Example 9). However, the use of sulfur as a "triggering" agent in conjunction with with the P_4S_7 and P_4S_3 increased the metal contents of the ultimate products (compare Examples 22 and 24 with Examples 21 and 23, respectively). Example 25 shows that by extending the reaction time from 3 hours (Example 21) to six hours, the metal content of the P_4S_7 product was greatly increased.

EXAMPLE 26

Four hundred grams of a filtered, calcium-oxidized, Mid-Continent residual oil product containing 0.16% oil-soluble calcium metal (prepared under the conditions of Example D, Table II) were reacted with 40 grams of phosphorus pentasulfide for one hour at 140° C. to 150° C. in an atmosphere of nitrogen. The mixture was cooled

to 80° C. to 90° C. Forty milliliters of water were carefully added followed by 40 grams of zinc carbonate. The mixture was dehydrated up to 190° C. Sixteen grams (4%, by weight), of "Hyflo" (filter aid) were added and the mixture filtered hot.

Analyses:

Zinc	percent	2.26
Calcium	do	0.03
Phosphorus	do	2.15
Sulfur	do	2.52
B–10 stability No		190

EXAMPLE 27

Four hundred grams of a filtered, calcium-oxidized, Mid-Continent residual oil product containing 0.12% oil-soluble calcium metal (for oxidation conditions see Example F, Table II) were reacted with 30 grams of phosphorus pentasulfide (7.5%) for 3 hours at 170° C. in an atmosphere of nitrogen. One-half of the mixture was filtered.

Analyses:

Neutralization No	16 (1st break).
	24 (1st break).
Phosphorus	2.07 percent.
Sulfur	4.13 percent.
B–10 stability No	47.

Products of this type, i. e., those resulting from the reaction of the oxidized intermediate with the phosphorus sulfide and which have not been subjected to the water-complexing reaction with additional metal hydroxide, are outstanding as anti-oxidants for mineral lubricating oils.

The remaining half of the batch was cooled to 80° C. to 90° C. Twenty milliliters of water were carefully added followed by 20 grams of zinc oxide. The mixture was dehydrated up to 190° C. Ten grams (5%, by weight), of "Hyflo" (filter aid) were added and the mixture filtered hot.

Analyses:

Zinc	percent	1.20
Phosphorus	do	1.77
Sulfur	do	3.22
B–10 stability No		175

EXAMPLE 28

Four hundred grams of a filtered, Mid-Continent type, calcium-oxidized residual oil product containing 0.25% oil-soluble calcium metal and 1.20% oxygen (for oxidation conditions see Example F, Table II) were reacted with 40 grams of phosphorus pentasulfide (10%, by weight, of oil) for 3 hours at 150° C. in an atmosphere of nitrogen. The mixture was cooled to 80° C. to 90° C. Twenty milliliters of water were carefully added followed by a solution containing 16 grams of NaOH in 20 milliliters of water. The mixture was dehydrated up to 150° C. One hundred grams of this product were removed and filtered.

Analyses:

Calcium	percent	0.20
Sodium	do	2.30
Phosphorus	do	2.50
Sulfur	do	3.63
Base Number		8.9
B–10A stability No		200

EXAMPLE 29

To the remainder of the product from Example 28, a solution containing 27 grams of $ZnCl_2$ in 60 milliliters of water was added. The mixture was dehydrated up to 160° C. Fifteen grams (5%, by weight,) of "Hyflo" (filter aid) were added and the product filtered hot.

Analyses:

Zinc	percent	3.34
Calcium	do	0.20
Sodium	do	2.02
Phosphorus	do	2.24
Sulfur	do	2.99
Chlorine	do	3.84
B–10A stability No		600

Examples 26 to 28 illustrate the use of zinc carbonate, zinc oxide and sodium hydroxide, respectively, as metal salt reagents in the water-complexing step, while Example 29 shows the further complexing of the sodium hydroxide-complexed product with zinc chloride. It will be seen from the latter example that the reaction which occurs is a complexing of the zinc chloride with the sodium salt, rather than a metathetical exchange which would ordinarily occur by a reaction of a sodium salt with zinc chloride.

EXAMPLE 30

A mixture of two thousand grams of a Mid-Continent type residual oil and 100 grams of zinc oxide (5%, by weight,) were air oxidized at 420° F. for 3½ hours with an air rate equivalent to 3 l./100 grams of oil/hour.

Four hundred and twenty grams of this mixture containing 0.09% oil-soluble zinc metal and 0.70% oxygen were reacted with 40 grams of phosphorus pentasulfide at 150° C. for 3 hours in an atmosphere of nitrogen. The mixture was cooled to 80° C. to 90° C. and forty milliliters of water were carefully added. The mixture was dehydrated up to 150° C. Twenty grams of "Hyflo" (filter aid) were added and the mixture filtered hot.

Analyses:

Zinc	percent	2.20
Phosphorus	do	1.80
Sulfur	do	2.26
B–10A stability No.		420

EXAMPLE 31

(*a*) A sodium-oxidized residual oil intermediate was made by oxidizing a 3.5% caustic soda in oil mixture at 218° C. with an air rate equivalent to 5 l./hr./100 grams of oil. The oxygen and oil-soluble sodium contents of the oxidized product were 1.42% and 0.7%, respectively.

(*b*) Four hundred grams of the unfiltered sodium-oxidized residual oil-caustic soda mixture (*a*) were reacted with 30 grams of P_4S_7 (7.5 weight percent) for six hours at 105° C. in a nitrogen atmosphere. After cooling the mixture to 80° C., 40 milliliters of water were carefully added followed by 40 grams of lime. The mixture was dehydrated to a temperature of 150° C. Five percent of "Hyflo" (filter aid) was added and the mixture filtered.

Analyses:

Calcium	percent	1.71
Sodium	do	1.20
Phosphorus	do	1.94
Sulfur	do	1.79
B–10 stability No.		500

EXAMPLE 32

Example 31(*b*) was repeated on a filtered sample of the sodium-oxidized residual oil intermediate, Example 31(*a*), with the exception that 40 grams of P_2S_5 (10 weight percent) were substituted for the P_4S_7 and reacted for three hours.

Analyses:

Calcium	percent	2.62
Sodium	do	0.7
Phosphorus	do	2.30
Sulfur	do	2.68
B–10 stability No.		140

EXAMPLE 33

Four hundred grams of an unfiltered sodium-oxidized residual oil-caustic soda mixture containing 0.87% oxygen and 0.5% oil-soluble sodium were reacted with 40 grams of P_2S_5 (10 weight percent) for 4 hours at 105° C. in a nitrogen atmosphere. After cooling the mixture to 80° C., 20 milliliters of water were carefully added followed by a solution of 40 grams of caustic soda in 60 milliliters of water. The mixture was dehydrated to a temperature of 200° C. Five percent of Standard Super Cel (filter aid) was added and the mixture filtered.

Analyses:	Percent
Sodium	3.70
Phosphorus	1.82
Sulfur	2.20

Example 30 illustrates the use of zinc oxide in the oxidation and water-complexing steps of the invention. Examples 31 and 32, on the other hand, show the use of sodium hydroxide in the oxidation step with P_4S_7 as the phosphorus sulfide reactant in one case (Example 31) and P_2S_5 in another (Example 32), the water-complexing salt being calcium hydroxide. Example 33 shows the use of sodium hydroxide in both the oxidation and water-complexing steps.

EVALUATION OF PRODUCTS

The ability of the reaction products of the invention as detergents and antioxidants for engine lubricating oils has been demonstrated by subjecting oil blends of these products to engine tests. The detergent tests used were the Lauson D–4A, CFR diesel D–21, CFR diesel D–23 and L–1 caterpillar engine tests. The antioxidant tests were the Lauson D–4A and OS–2 tests. The several test procedures are described below. The results obtained in a representative number of tests are given in Tables III and IV. From these test results it is apparent that the products of the invention are outstanding detergents for engine lubricating oils when used either alone or in combination with known antioxidants. Also, it is seen that the products prepared from the mildly oxidized oils, i. e., those having less than 0.5% metal contents, are the best detergents (see Examples 9 and 10*a*, Table III). The data in Table III also show that the products of the invention are effective antioxidants, particularly those produced from the mildly oxidized oil intermediates.

Table IV

Product added	Conc., percent	Calcium in oil blend, percent	L–1 caterpillar test [a]			
			Test time, hr.	Piston rating	Lacquer demerits	Percent TGP
None			120	61.9	28.2	6
Do			120	57.4	[e] 31.0	7
X	4.0	0.11	120	98.8	[e] 0.7	0
			240	97.6	[e] 1.4	1
			480	94.9	[e] 3.4	2
X	4.0	0.11	120	99.9	0.0	0
			480	98.4	0.7	4
Y	2.8	0.11	120	99.8	[e-1] 0.0	0
			240	99.3	[e-1] 0.2	1
Y	2.2	0.088	240	98.8	[e-1] 0.5	1
			480	93.9	[e-1] 3.9	5
Z	2.9	0.088	120	99.3	[f] 0.0	4
			240	98.3	[f] 0.1	13
			480	97.1	[f] 0.8	20
Z	2.9	0.088	120	99.7	[g] 0.1	1
			240	99.0	[g] 0.4	6
			480	93.2	[g] 4.2	12

X—A product similar to that described in Ex. 10*a*; calcium=2.79%; phosphorus=1.86%; sulfur=2.85%.

Y—A product similar to that described in Ex. 12, except 15% P_2S_5 was used; calcium=4.02; phosphorus=2.56%; sulfur=2.62%.

Z—A pilot plant batch of a product similar to X. Calcium=3.07%; phosphorus=1.93%; sulfur=3.58%.

[a]—Base oil is an SAE 30 grade solvent-refined Mid-Continent oil, K. V. at 210° F.=11.08 cs., K. V. at 100° F.=101.4 cs.

[e]—Blend also contained 0.5% of a commercial antioxidant (a pinene-P_2S_5 reaction product).

[e-1]—Blend also contained 0.25% of a commercial antioxidant as in footnote [e].

[f]—Blend also contained 0.5% of a commercial antioxidant (a sulfurized terpene).

[g]—Blend also contained 0.5% of a commercial antioxidant (zinc dihexyldithiophosphate).

TGP—Top Grove Packing.

LAUSON ENGINE D–4A TEST

This test determines the effectiveness of the lubricating oil in preventing piston fouling as measured by the cleanliness of the rings, lands, grooves and piston skirts. Cleanliness ratings are assigned at the end of the test on a scale of from 100 to 0, a 100 rating signifying a perfectly clean condition and a zero rating representing the worst possible deposit condition. Bearing weight loss is also measured as supplemental data. A single cylinder, 4-cycle, liquid-cooled Lauson engine with splash lubrication and having a copper-lead bearing is employed in the test. The operating conditions are as follows:

Sample ——— gallon	1
Oil temperature ——— ° F	225
Jacket temperature ——— ° F	275
Speed ——— R. P. M	1825
Brake load ——— H. P	1.6
One-half throttle air-fuel ratio	13–1

Table III

Product added	Metal, percent	Percent phosphorus	Percent sulfur	Lauson D–4–A engine [a]			CFR D–21 diesel [b]		CFR D–23 diesel [b]		Lauson OS–2 engine [a]			Percent metal in oxidized oil intermediate
				Percent product	Rating	Avg. ½ brg. wt. loss, mg.	Percent product	Rating	Percent product	Rating	Percent product	Rating	Avg. ½ brg. wt. loss, mg.	
None					67	230		65		82		78	371	
None										[d] 82				
Ex. 2	Ca 6.5	2.40	3.81	1.38	76	78	1.38	86						1.49
Ex. 8	Ba 7.9	1.30	2.14						3.80	[c] 92				[f] 2.84
Ex. 9	Ca 3.87	2.14	3.38						2.27	[c] 94				0.16
Ex. 10*a*	Ca 2.78	1.89	2.88						3.16	[c] 95	3.16	84	68	0.12
Ex. 10*a*	Ca 2.78	1.89	2.88						[e] 3.96	[c] 97				0.12
Ex. 10*c*	{Ba 10.3 / Ca 0.11}	2.09	2.24								3.08	90	126	0.12
Ex. 12	Ca 4.64	2.47	4.29						1.90	[c] 89				0.57
Ex. 15	Ca 2.43	1.22	1.78						3.62	[c] 90				2.23
Ex. 16	Ca 2.68	1.26	1.84						3.28	[c] 86				2.14
Ex. 17	Ca 1.71	1.06	1.36						5.15	[c] 92				1.08

[a] The base oil was an SAE 20 grade solvent-refined, Pennsylvania oil (kin. vis. at 100° F.=63 cs.; kin. vis. at 210° F.=8.3 cs.). Metal content of oil blend equivalent to 0.3% Ba (0.088% Ca), except where noted.

[b] The base oil was an SAE 30 grade solvent-refined, Mid-Continent oil (kin. vis. at 100° F.=121 cs.; kin. vis. at 210° F.=12.2 cs.). Metal content of oil blend equivalent to 0.3% Ba (0.088% Ca).

[c] The oil blend also contained 0.5% of a commercial antioxidant (pinene-P_2S_5 product).

[d] The oil contained 1.0% of the commercial antioxidant as in (c).

[e] 25% more additive was used.

[f] Ba.

Oil was added every 20 hours. The duration of the test is 100 hours. The piston cleanliness rating and the bearing weight loss obtained with the test oil is compared to that obtained with the reference oil.

CFR DIESEL DETERGENCY TEST D–21

This test determines the effectiveness of the lubricating oil in preventing piston deposits and top ring wear. A single cylinder, CFR 4-cycle, supercharged diesel engine is used. The operating conditions are as follows:

Oil temperature	° F.	175
Jacket temperature	° F.	212
Speed	R. P. M.	1800
Brake load	H. P.	7.5

A one and one-half gallon sample of oil is used with addition of oil every 8 hours starting at 4 hours. The duration of the test is 60 hours. The diesel fuel used contained 1% sulfur. The results of the test are reported in terms of piston cleanliness ratings as in the D–4A test.

CFR DIESEL DETERGENCY TEST D–23

This test determines the effectiveness of an oil in preventing piston deposits and top ring wear. The operating conditions are as follows:

Oil temperature	° F.	175
Jacket temperature	° F.	212
Speed	R. P. M.	1800
Brake load	H. P.	4.5

A one and one-half gallon sample of oil is used at the start and oil is added every 8 hours starting at 4 hours. The duration of the test is 60 hours. The diesel fuel used contained 0.4% sulfur. The results are given in terms of piston cleanliness ratings using the same rating system as in the Lauson D–4A and diesel D–21 test.

CRC CATERPILLAR ENGINE TEST L–1

This is a specification engine test to determine the ability of an oil to prevent engine deposits including the piston and crankcase deposits. A single cylinder, 4-cycle caterpillar engine is used. The operating conditions are as follows:

Oil temperature	° F.	150
Jacket temperature	° F.	180
Speed	R. P. M.	1000
Brake load	H. P.	19.8

Twenty gallons of oil is used in the engine at the start of the test and the oil is changed at 120-hour intervals. The duration of the test is 480 hours. The diesel fuel used contained 0.4% sulfur. The condition of the engine at the end of the test is expressed by an engine cleanliness rating based on a scale from 0 to 100, 100 being a perfectly clean engine.

It will be appreciated that the products of this invention are actually oil solutions of the phosphorus-, sulfur- and metal-containing oxidized oil products, and although the products shown in the examples presented herein vary with respect to the concentration of the products in the oil, it will be understood that these differences can be eliminated by standardization of process procedure and also when required by distillation of a portion of the oil therefrom. The amount of product required to be added to a lubricating oil to provide the desired increase in the detergent ability thereof will, therefore, vary depending upon the process conditions utilized in preparing the particular products. In general, however, the amount of the product to be utilized will range from about 1% to about 10%, by weight, the usual amount being from about 2% to about 5%.

The products of the invention may also be added to oils containing other additives designed to improve the various characteristics thereof, such as pour point depressants, viscosity index improvers, defoamants, rust preventives, etc.

Although the invention has been described herein by means of certain specific embodiments and illustrative examples, it is not intended that it be limited in any way thereby, but only as indicated in the accompanying claims.

What is claimed is:

1. An oil-soluble, phosphorus-, sulfur- and metal-containing oxidized hydrocarbon reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a hydrocarbon having a molecular weight of from about 200 to 1000 and which is selected from the group consisting of aliphatic hydrocarbons and aromatic hydrocarbons having at least one nuclear hydrogen atom substituted by an aliphatic radical to provide a total of at least 8 aliphatic carbon atoms per molecule therein, and mixtures thereof, and (*b*) from about 0.5% to about 25%, based on the weight of said hydrocarbon, of a metal hydroxide, the metal constituent of which is selected from Groups I and II of Mendeleeff's Periodic Table of the Elements, (2) contacting said mixture with an oxidizing gas at a temperature of from about 125° C. to about 325° C. to effect oxidation of said hydrocarbon and reaction of said metal hydroxide with the oxidized hydrocarbon, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 3.0%, by weight, of metal into the oxidized hydrocarbon, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of hydrocarbon charged in step 1, of a phosphorus sulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and metal-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the hydrocarbon charged in step 1, of a metal hydroxide, the metal constituent of which is selected from Groups I and II of Mendeleeff's Periodic Table of the Elements, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

2. An oil-soluble, phosphorus-, sulfur- and metal-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 200 to about 1000 and (*b*) from about 0.5% to about 25%, based on the weight of said oil, of a metal hydroxide, the metal constituent of which is selected from Group II of Mendeleeff's Periodic Table of the Elements, (2) contacting said mixture with an oxidizing gas at a temperature of from about 125° C. to about 325° C. to effect oxidation of said oil and reaction of said metal hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 3.0%, by weight, of metal into the oxidized oil, (4) reacting the product of step 3 with from about 5% to about 20%, by weight, based on the oil charged in step 1, of a phosphorus sulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and metal-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the oil charged in step 1, of a hydroxide of a metal selected from Group II of Mendeleeff's Periodic Table of the Elements, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

3. An oil-soluble, phosphorus-, sulfur- and calcium-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular

weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25% of calcium hydroxide, (2) contacting said mixture with an oxidizing gas at a temperature of from about 125° C. to about 325° C. to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 3.0%, by weight, of calcium into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the hydrocarbon charged in step 1, of a phosphorus sulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the weight of the oil charged in step 1, of calcium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

4. An oil-soluble, phosphorus-, sulfur- and calcium-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25%, based on the weight of said oil, of calcium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 0.5%, by weight, of calcium into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of oil charged in step 1, of phosphorus pentasulfide, at a temperature of from about 75° C. to about 150° C. to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the weight of oil charged in step 1 of calcium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

5. An oil-soluble, phosphorus-, sulfur- and barium-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25%, based on the weight of said oil, of barium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said barium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 3.0%, by weight, of barium into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of the oil charged in step 1, of a phosphorus sulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and barium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the weight of the oil charged in step 1, of barium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

6. An oil-soluble, phosphorus-, sulfur- and barium-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25%, based on the weight of said oil, of barium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said barium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to 0.5%, by weight, of barium into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of the oil charged in step 1, of phosphorus pentasulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and barium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the weight of oil charged in step 1, of barium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

7. An oil-soluble, phosphorus-, sulfur-, calcium- and zinc-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25%, based on the weight of said oil, of calcium hydroxide, (2) contacting said mixture with an oxidizing gas at a temperature of from about 125° C. to about 325° C. to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 3.0%, by weight, of calcium into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of oil charged in step 1, of a phosphorus sulfide at a temperature of from about 100° C. to about 150° C. to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with zinc hydroxide and water at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

8. An oil-soluble, phosphorus-, sulfur-, calcium- and zinc-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25%, based on the weight of said oil, of calcium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to 0.5%, by weight, of metal into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of oil charged in step 1, of phosphorus pentasulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, based on the weight of the oil charged in step 1, of zinc hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

9. An oil-soluble, phosphorus-, sulfur- and calcium-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mix-

ture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25% of calcium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 0.5%, by weight, of calcium into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of oil charged in step 1, of phosphorus heptasulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the weight of oil charged in step 1, of calcium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

10. An oil-soluble, phosphorus-, sulfur- and calcium-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25% of calcium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 0.5%, by weight, of calcium into the oxidized oil, (4) reacting the product of step 3 with from about 5% to about 20%, by weight, based on the weight of the oil charged in step 1, of phosphorus trisulfide, at a temperature of from about 75° C. to about 125° C., to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, based on the weight of the oil charged in step 1, of calcium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

11. An oil-soluble, phosphorus-, sulfur, and calcium-containing reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25% of calcium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 0.5%, by weight, of calcium into the oxidized oil, (4) reacting the product of step 3 with from about 5% to about 20%, by weight, of phosphorus trisulfide and from about .05% to about 2% of sulfur, both percentages being based on the weight of oil charged in step 1, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, based on the weight of oil charged in step 1, of calcium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

12. A mineral lubricating oil containing a minor amount, sufficient to improve the detergent character thereof, of an oil-soluble, phosphorus-, sulfur- and metal-containing oxidized hydrocarbon reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a hydrocarbon having a molecular weight of from about 200 to about 1000 and which is selected from the group consisting of aliphatic hydrocarbons and aromatic hydrocarbons having at least one nuclear hydrogen atom substituted by an aliphatic radical to provide a total of at least 8 aliphatic carbon atoms per molecule therein, and mixtures thereof, and (*b*) from about 0.5% to about 25%, based on the weight of said hydrocarbon, of a metal hydroxide, the metal constituent of which is selected from Groups I and II of Mendeleeff's Periodic Table of the Elements, (2) contacting said mixture with an oxidizing gas at a temperature of from about 125° C. to about 325° C. to effect oxidation of said hydrocarbon and reaction of said metal hydroxide with the oxidized hydrocarbon, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 3.0%, by weight, of metal into the oxidized hydrocarbon, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of hydrocarbon charged in step 1, of a phosphorus sulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and metal-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the hydrocarbon charged in step 1, of a metal hydroxide, the metal constituent of which is selected from Groups I and II Mendeleeff's Periodic Table of the Elements, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

13. A mineral lubricating oil containing a minor amount, sufficient to improve the detergent character thereof, of an oil-soluble, phosphorus-, sulfur- and metal-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 200 to about 1000 and (*b*) from about 0.5% to about 25%, based on the weight of said oil, of a metal hydroxide, the metal constituent of which is selected from Group II of Mendeleeff's Periodic Table of the Elements, (2) contacting said mixture with an oxidizing gas at a temperature of from about 125° C. to about 325° C. to effect oxidation of said oil and reaction of said metal hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 3.0%, by weight, of metal into the oxidized oil, (4) reacting the product of step 3 with from about 5% to about 20%, by weight, based on the oil charged in step 1, of a phosphorus sulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and metal-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the oil charged in step 1, of a hydroxide of a metal selected from Group II of Mendeleeff's Periodic Table of the Elements, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

14. A mineral lubricating oil containing a minor amount, sufficient to improve the detergent character thereof, of an oil-soluble, phosphorus-, sulfur- and calcium-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25% of calcium hydroxide, (2) contacting said mixture with an oxidizing gas at a temperature of from about 125° C. to about 325° C. to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxi-

dation for a time sufficient to incorporate from about 0.05% to about 3.0%, by weight, of calcium into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the hydrocarbon charged in step 1, of a phosphorus sulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the weight of the oil charged in step 1, of calcium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

15. A mineral lubricating oil containing a minor amount, sufficient to improve the detergent character thereof, of an oil-soluble, phosphorus-, sulfur- and calcium-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25%, based on the weight of said oil, of calcium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 0.5%, by weight, of calcium into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of oil charged in step 1, of phosphorus pentasulfide, at a temperature of from about 75° C. to about 150° C. to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the weight of oil charged in step 1 of calcium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

16. A mineral lubricating oil containing a minor amount, sufficient to improve the detergent character thereof, of an oil-soluble, phosphorus-, sulfur- and barium-containing oxidized oil reaction product produced by the method which comprises the steps (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25%, based on the weight of said oil, of barium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said barium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 3.0%, by weight, of barium into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of the oil charged in step 1, of a phosphorus sulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and barium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the weight of the oil charged in step 1, of barium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

17. A mineral lubricating oil containing a minor amount, sufficient to improve the detergent character thereof, of an oil-soluble, phosphorus-, sulfur- and barium-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25%, based on the weight of said oil, of barium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said barium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to 0.5%, by weight, of barium into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of the oil charged in step 1, of phosphorus pentasulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and barium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the weight of oil charged in step 1, of barium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

18. A mineral lubricating oil containing a minor amount, sufficient to improve the detergent character thereof, of an oil-soluble, phosphorus-, sulfur-, calcium- and zinc-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25%, based on the weight of said oil, of calcium hydroxide, (2) contacting said mixture with an oxidizing gas at a temperature of from about 125° C. to about 325° C. to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 3.0%, by weight, of calcium into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of oil charged in step 1, of a phosphorus sulfide at a temperature of from about 100° C. to about 150° C. to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with zinc hydroxide and water at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

19. A mineral lubricating oil containing a minor amount, sufficient to improve the detergent character thereof, of an oil-soluble, phosphorus-, sulfur-, calcium- and zinc-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25%, based on the weight of said oil, of calcium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to 0.5%, by weight, of metal into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of oil charged in step 1, of phosphorus pentasulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, based on the weight of the oil charged in step 1, of zinc hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

20. A mineral lubricating oil containing a minor amount, sufficient to improve the detergent character thereof, of an oil-soluble, phosphorus-, sulfur- and calcium-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25% of calcium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 0.5%, by weight, of calcium into the oxidized oil, (4) reacting the product from step 3 with from about 5% to about 20%, by weight, based on the weight of oil charged in step 1, of phosphorus heptasulfide, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, by weight, based on the weight of oil charged in step 1, of calcium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

21. A mineral lubricating oil containing a minor amount, sufficient to improve the detergent character thereof, of an oil-soluble, phosphorus-, sulfur- and calcium-containing oxidized oil reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25% of calcium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 0.5%, by weight, of calcium into the oxidized oil, (4) reacting the product of step 3 with from about 5% to about 20%, by weight, based on the weight of the oil charged in step 1, of phosphorus trisulfide, at a temperature of from about 75° C. to about 125° C., to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, based on the weight of the oil charged in step 1, of calcium hydroxide and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

22. A mineral lubricating oil containing a minor amount, sufficient to improve the detergent character thereof, of an oil-soluble, phosphorus-, sulfur- and calcium-containing reaction product produced by the method which comprises the steps of (1) forming a mixture comprising (*a*) a petroleum oil having a molecular weight of from about 600 to about 1000 and (*b*) from about 0.5% to about 25% of calcium hydroxide, (2) contacting said mixture with an oxidizing gas, at a temperature of from about 125° C. to about 325° C., to effect oxidation of said oil and reaction of said calcium hydroxide with the oxidized oil, (3) continuing the oxidation for a time sufficient to incorporate from about 0.05% to about 0.5%, by weight, of calcium into the oxidized oil, (4) reacting the product of step 3 with from about 5% to about 20%, by weight, of phosphorus trisulfide and from about .05% to about 2% of sulfur, both percentages being based on the weight of oil charged in step 1, at a temperature of from about 75° C. to about 150° C., to form a phosphorus-, sulfur- and calcium-containing product, (5) providing a mixture of the reaction product from step 4 with from about 2% to about 25%, based on the weight of oil charged in step 1, of calcium hydroxide, and water, at a temperature below the boiling point of water, (6) substantially completely dehydrating the mixture formed in step 5 and (7) subjecting the dehydrated mixture to filtration to remove insolubles therefrom.

References Cited in the file of this patent

UNITED STATES PATENTS

2,419,325	Musselman	Apr. 22, 1947
2,420,274	Williams	May 6, 1947
2,427,272	Fuller	Sept. 9, 1947
2,451,346	McNab	Oct. 12, 1948