

UNITED STATES PATENT OFFICE

2,383,498

MINERAL OIL COMPOSITION

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No Drawing. Application July 10, 1943,
Serial No. 494,262

17 Claims. (Cl. 252-34)

This invention has to do with the stabilization of petroleum products against the deleterious effects of oxidation and deterioration with use. More specifically, it has to do with the improvement or stabilization of mineral oil fractions, particularly viscous mineral oils, by the use of novel reaction products, or a novel class of reaction products, which when admixed with a mineral oil fraction in minor proportions will prevent or delay undesirable changes taking place in the oil.

It is well known to those familiar with the art that substantially all of the various fractions obtained from mineral oils and refined for their numerous uses are susceptible to oxidation. This susceptibility of an oil fraction to oxidation and the manner in which oxidation manifests itself within the oil varies with the type and degree of refinement to which the oil has been subjected and the conditions under which the oil is used or tested. In other words, the deleterious products formed in an oil fraction as a result of oxidation and the degree to which they are formed depends upon the extent to which the various unstable constituents, which may act as oxidation catalysts, have been removed by refining operations, and also upon the conditions of use.

A large number of compounds and compositions have been proposed for use as improving or stabilizing agents for petroleum products. For example, various compounds or reaction products containing metalloids or metals, or combinations of one or more of such elements, have been credited with improving petroleum products in certain respects.

This invention relates to metal salts of phosphorus- and sulfur-containing reaction products possessed of the capacity of effecting a high degree of improvement in mineral oil fractions. More particularly, the present invention is predicated upon the discovery of a new and novel class of oil soluble ammonium and metal salts of acidic, phosphorus- and sulfur-containing reaction products obtained by reacting substantially 1 mol of phosphorus pentasulfide (P_2S_5) with 4 mols of an unsaturated ketone at a temperature between about $135^\circ C.$ and about $200^\circ C.$ Particularly preferred of such salts are those in which the aforesaid acidic reaction products were prepared at a reaction temperature from about 135° to about $150^\circ C.$

Also contemplated by the present invention are the ammonium and metal salts of acidic, phosphorus- and sulfur-containing reaction products

obtained by reacting substantially 1 mol of P_2S_5 with 4 mols of a sulfurized ketone (unsaturated), or of a related reaction product obtained by sulfurizing an acidic reaction product of the type initially described with elementary sulfur. Sulfurized ketones (unsaturated) and sulfurized acidic, phosphorus- and sulfur-containing reaction products of P_2S_5 and unsaturated ketones are described in detail in a copending application Serial No. 491,946, filed June 23, 1943, of the present applicants with E. A. Oberright.

While all unsaturated ketones are contemplated for use herein, particularly preferred is dioleyl ketone, which is also referred to as di-heptadecenyl ketone; and contemplated for use also is the technical grade of dioleyl ketone commonly referred to as "oleone."

While the exact chemical structure of the reaction products obtained in the aforesaid reaction of an unsaturated ketone and P_2S_5 , and of a sulfurized ketone (unsaturated) and P_2S_5 , is not known at this time, it has been found that such reaction products are acidic in character as evidenced by their neutralization number (N. N.) and by their ability to form metal salts, and contain appreciable amounts of both phosphorus and sulfur. These reaction products are believed to be new inasmuch as previous disclosures have shown that compounds containing sulfur, not phosphorus and sulfur, are formed in the reaction of P_2S_5 with certain ketones. More specifically, Spring, in the Bull. Soc. Chim. (France) 2, 40, 67, has disclosed that a dimer thioketone, $C_8H_{12}S_2$, is obtained when acetone is warmed with P_2S_5 ; and Gatterman in the Ber. 28, 2877, has disclosed that thiobenzophenone is obtained when benzophenone in benzene solution is heated with P_2S_5 for several hours at $130^\circ C.$ in a bomb. It would appear that the reaction products from which the ammonium and metal salts of this invention are prepared are new; and consequently, it would appear that said ammonium and metal salts are new.

The ammonium and metal salts of this invention are prepared by reacting the aforesaid acidic, phosphorus- and sulfur-containing reaction products with ammonia or with a suitable metal compound, such for example as a hydroxide, oxide, alcoholate, etc. It will be understood that acidic, neutral and basic polyvalent metal salts of said reaction products will be prepared by using a

suitable metal compound. While all metals are contemplated as constituents of these metal salts, the metals of group II of the periodic table are preferred, and of these barium is particularly preferred.

Although the salts of this invention are generally prepared as described above, several modifications may be made in the foregoing methods in order that particularly desirable ammonium and metal salts may be obtained. For example, we have found that the use of a non-oxidizing or inert gas, for providing a non-oxidizing atmosphere above the reaction mixture of P_2S_5 and said ketone, is beneficial in that the intermediate reaction products obtained therefrom are characterized by increased stability and lighter color; and the ammonium and metal salts thereof are similarly characterized. Illustrative of inert gases which may be used for this purpose are nitrogen, carbon dioxide, etc. A second modification which may be resorted to involves the use of a substantially inert diluent in the preparation of the aforesaid acidic reaction product and in the preparation of the corresponding ammonium and metal salts. Representative of such diluents are acid treated kerosene and tetra chlor ethane. Diluents of this type may be removed after the formation of acidic reaction product or may be removed after the formation of said salts by any suitable means, such as by distillation. In this connection, a substantially inert mineral oil may be used as the diluent and in such case the acidic reaction product will be obtained in a mineral oil blend or concentrate. Correspondingly, when such a mineral oil diluent is used in the preparation of the corresponding salts, mineral oil blends or concentrates of the desired salts will be obtained. A further modification in the preparation of a salt from one of the aforesaid reaction products involves the use of a carrier which combines with the water of the reaction; carriers such as butyl alcohol, ethyl alcohol, etc., are satisfactory for this purpose.

The following examples, in which a particularly preferred ketone—oleone—is used, are shown below in order to illustrate typical metal salts and typical procedures for their preparation.

EXAMPLE ONE

NEUTRAL BARIUM SALT OF P_2S_5 -OLEONE REACTION PRODUCT

(a) Preparation of P_2S_5 -Oleone Reaction Product

	Grams
Oleone.....	100
P_2S_5	12
Nitrogen gas.	

One hundred grams of oleone, 12 grams of P_2S_5 (a 4:1 ratio of oleone to P_2S_5) and 200 grams of a mineral oil diluent (Saybolt Universal viscosity—S. U. V.—of 45 seconds at 210° F.) were charged to a reaction vessel equipped with a mechanically driven stirrer, an upright Liebig condenser, a thermometer, and an inlet tube which extended to within a few inches above the reaction mixture. The atmosphere above the mixture was constantly swept with nitrogen, which was introduced through the inlet tube, so as to maintain the mixture in a non-oxidizing atmosphere. The reaction mixture was stirred and heated at 135° C. for 3 hours. It was then filtered through "Hi-Flo," a chemically calcined natural, diatomaceous silica filter aid of the finest pore size, on a steam heated Buchner funnel to remove any

deleterious by-products and unreacted P_2S_5 . The reaction was considered complete when a polished copper strip immersed in a 3 per cent blend of the reaction product—that is, a 1 per cent blend of the concentrate—in mineral oil for 3 hours at 150° C. showed only a slight tarnish or discoloration. The reaction product in the mineral oil diluent is a light green-brown oil and contains 0.96 per cent phosphorus and 2.2 per cent sulfur, and has a neutralization number (N. N.) of 20.0.

(b) Preparation of neutral barium salt of (a)

Two hundred and seventy-six grams of the reaction product obtained in (a) were mixed with 20 grams of $Ba(OH)_2 \cdot 8H_2O$, sufficient to neutralize the acid constituent or constituents of the acidic reaction product and 100 mls. of butyl alcohol in a reaction vessel equipped with a mechanically-driven stirrer, a Liebig condenser in an inclined position, a thermometer and an inlet tube (for nitrogen) extending to within a few inches of the reaction mixture. The mixture was stirred and heated at about 155° C. for 1 hour. During this time water and alcohol which are present are distilled off through the inclined condenser. The remaining reaction mixture is diluted with an equal volume of benzol and filtered through "Hi-Flo" to remove any deleterious materials that may have formed. Benzol is then distilled from the filtrate at a maximum temperature of 155° C. under diminished pressure. The reaction product so obtained is a light green viscous oil containing 2.2 per cent barium, 2.1 per cent sulfur, and 0.9 per cent phosphorus, and has no neutralization number (N. N.=0). The reaction product is then the neutral barium salt of the P_2S_5 -oleone reaction product in mineral oil. This reaction product is identified hereinafter as Product one.

EXAMPLE TWO

THE BASIC BARIUM SALT OF P_2S_5 -OLEONE REACTION PRODUCT

Two hundred and twenty grams of the reaction product prepared as described in Example one (a) were mixed with 18 grams of $Ba(OH)_2 \cdot 8H_2O$ and 100 mls. of butyl alcohol and worked up as described in Example one (a). The reaction product, the basic barium salt of the aforesaid P_2S_5 -oleone reaction product in mineral oil is a light green oil containing 2.32 per cent barium, 2.44 per cent sulfur and 0.84 per cent phosphorus, and is slightly alkaline. This product is designated "Product two."

EXAMPLE THREE

BARIUM SALT OF P_2S_5 -SULFURIZED OLEONE REACTION PRODUCT

(a) Preparation of P_2S_5 -sulfurized oleone reaction product

Seventy-five grams of oleone, 8.5 grams of elementary sulfur and 150 grams of mineral oil diluent are charged to a reaction vessel equipped with a mechanically-driven stirrer, an upright Liebig condenser, a thermometer and an inlet tube extending to within a few inches above the mixture. The atmosphere above the mixture is constantly swept with nitrogen gas (introduced through the aforesaid inlet tube) in order to maintain a non-oxidizing atmosphere above the mixture. The mixture is stirred and heated at

170° C. for 3 hours and the reaction product so obtained is a sulfurized oleone.

The reaction product obtained in (a) is allowed to cool to 140° C. and 9.0 grams of P_2S_5 are then added. The reaction mixture is stirred and heated at 140° C. for 2 hours and is then filtered through "Hi-Flo" on a steam heated Buchner funnel in order to remove any deleterious by-products and any unreacted P_2S_5 . The reaction product is a brown viscous oil containing 5.1 per cent sulfur and 0.67 per cent phosphorus and having a neutralization number (N. N.) of 14.5.

(b) Preparation of barium salt of (a)

Two hundred and eighty-three grams of the mineral oil blend obtained in (a) were treated with 22 grams of barium hydroxide and 100 mls. of butyl alcohol and the reaction mixture worked up as described in Example one. The reaction product is a brown viscous oil containing 0.96 per cent barium, 4.7 per cent sulfur and 0.62 per cent phosphorus, and has a neutralization number of 1.1. This corresponds to the barium salt of (a) in mineral oil; this is referred to hereinafter as Product three.

EXAMPLE FOUR

AMMONIUM SALT OF P_2S_5 -OLEONE REACTION PRODUCT

(a) Preparation of P_2S_5 -oleone reaction product

This reaction product is obtained as described in Example one (a) hereinabove.

(b) Preparation of ammonium salt of (a)

The mineral oil concentrate containing the P_2S_5 -oleone reaction product as prepared in (a) was treated with ammonia by bubbling ammonia gas therethrough at 100° C. for 2½ hours. Following treatment with ammonia, nitrogen is passed through the reaction mixture for half an hour to remove any excess ammonia. The reaction product is a 1:2 blend of ammonium salt of the P_2S_5 -oleone reaction product in mineral oil. This blend contains 0.66 per cent nitrogen, 3.0 per cent sulfur and 0.9 per cent phosphorus, and has a neutralization number of 12.5; this is Product four (b).

(c) Preparation of P_2S_5 -oleone reaction product

	Grams
Oleone	75
P_2S_5	10.5
Mineral oil	75
Nitrogen gas.	

The apparatus described in Example one was used in this preparation and the procedure of Example one was followed with the exception that the reaction mixture was slowly heated and held constant at that temperature for 3 hours. The reaction mixture in mineral oil is an amber colored oil and contains 1.17 per cent phosphorus and 4.1 per cent sulfur. This product is referred to hereinafter as Product four (c).

(d) Ammonium salt of (c)

The mineral oil blend obtained in (a) was treated with ammonia by bubbling ammonia gas therethrough for 1 hour and thereafter blown with nitrogen for half an hour to remove any excess ammonia. The reaction product is a 1:1 blend of the ammonium salt of P_2S_5 -oleone reaction product in mineral oil. This blend contains 0.4 per cent nitrogen, 4.0 per cent sulfur, and 1.2 per cent phosphorus; this is Product four (d).

Copper strip tests were made on the reaction products obtained in Example four (a), (b), (c) and (d) by immersing a polished copper strip in a 3 per cent mineral oil blend in such products and heating the same for 3 hours at 150° C. While the reaction products of Example four (a) and (c) did not tarnish the polished copper strip, the mineral oil blends became slightly cloudy, darker in color, and a small quantity of material precipitated out in each case. In contrast to these tests, the reaction products of Example four (b) and (d) did not become cloudy, nor dark, and there was no precipitation in either case; and such reaction products did not tarnish the polished copper strip immersed therein.

CORROSION TEST

Motor oils especially those refined by certain solvent-extraction methods tend to oxidize when submitted to high temperatures and to form products corrosive to metal bearings. This corrosive action may be quite severe with certain bearings such as those having the corrosion susceptibility of cadmium-silver alloys; and may cause their failure within a comparatively short time. The following test was used to determine the corrosive action of motor oil on an automotive connecting rod bearing.

The oil used was a Pennsylvania solvent refined oil having an S. U. V. of 53 seconds at 210° F. The oil was tested by adding a section of a bearing containing a cadmium-silver alloy surface weighing about 6 grams and heating it to 175° C. for 22 hours while a stream of air was bubbled against the surface of the bearing. The loss in weight of the bearing during this treatment is a measure of the amount of corrosion that has taken place. A sample of the oil containing a stabilizing agent was run at the same time as a sample of the straight oil and the loss in weight of the bearing section in the inhibited oil can thus be compared directly with the loss of the section in the uninhibited oil. The results obtained in this test are set forth in Table one below.

TABLE ONE

Improving agent	Per cent conc.	Bearing loss, milligrams	
		Inhibited oil	Uninhibited oil
Product one.....	0.75	0	53
	0.375	0	53
	0.75	0	34
Product three.....	0.375	0	34
	0.1875	1	34
Product four (b).....	0.75	0	53
	0.375	1	53

ACCELERATED UNDERWOOD OXIDATION TEST

This test is used to determine the corrosive nature of lubricating oils under simulated operating conditions. The apparatus used consists of a circulating arrangement whereby an oil at 325° F., under a pressure of 10 pounds per square inch, is sprayed against a standard cadmium-nickel bearing for a period of 5 hours. The amount of oil under constant circulation in the system is 1500 cc. In passing through the system the oil under test comes in contact with cast iron, steel, stainless steel, copper and the aforesaid cadmium-nickel bearing, and is also exposed to aeration. The oil used in this test contains a small amount of an accelerator, namely, iron

naphthenate (commercially referred to as Nuodex, 6 per cent Fe_2O_3) which greatly increases the rate of oxidation of the oil. The deterioration suffered by the oil is shown by the development of acidity therein as measured by the neutralization number (N. N.) and the loss in weight in grams of the cadmium-nickel bearing, and the percentage of viscosity increase.

The specific base oil used in this test was a solvent refined oil having a S. U. V. of 65 seconds at 210° F. and containing 0.17 per cent Nuodex; and the oil blend under test contained a small amount of Product one in this base oil. The results of these tests are shown in Table two below:

TABLE TWO

Addition agent	Per cent conc.	Initial N. N.	N. N.	Per cent vis. inc.	Bearing loss, grams
After 5 hours					
Untreated oil.....		0.25	8.8	126	0.446
Product one.....	3.0	0.25	0.55	4.8	0.003
Product four (b).....	3.0	0.37	0.40	2.7	0.001
After 10 hours					
Untreated oil.....		0.25			
Product one.....	3.0	0.25	0.77	9.0	0.003
Product four (b).....	3.0	0.37	0.50	5.9	0.001
After 15 hours					
Untreated oil.....		0.25			
Product one.....	3.0	0.25	1.23	14.0	0.003
Product four (b).....	3.0	0.37	0.72	13.0	0.001

C. F. R. BEARING CORROSION TEST

In this test, a C. F. R. fuel test engine, from which all equipment applying only to fuel test work has been removed, is used. Oil at a controlled temperature is delivered by a metering pump from an external heating sump to the test connecting rod bearing, through the drilled crankshaft. All other engine parts are lubricated with oil drawn from the same external sump by a double capacity C. F. R. oil pump. A copper-lead alloy test bearing is placed in the large end of the connecting rod. The jacket temperature is maintained at about 212° F., and the oil temperature at about 285° F. During the test, the compression ratio and engine speed are maintained at 5.5 and 1200 R. P. M., respectively. The engine is operated for a standard time which has been taken as the time (in hours) required for a loss of 0.200 gram of the copper-lead alloy test bearing when a blank oil is used. The effectiveness of an oil addition agent is measured by the time required for a similar loss when a blend of the same oil and an addition agent is used; and is rated in terms of a ratio, defined as the ratio of the hours for the oil blend for standard 0.200 gram corrosion to the hours for the blank oil for the same corrosion.

A solvent refined oil having an S. U. V. of 55 seconds at 210° F.—the blank oil—and a blend of the same oil and a small amount of Product three were tested in the engine described above. The neutralization numbers (N. W.) of the blank oil and of the oil blend were determined after several time intervals, as were the bearing losses of the test bearings. The results are shown below in Table three wherein it is evident that the oil blend is greatly superior to the blank oil.

TABLE THREE

Improving agent	Per cent conc.	Neutralization number				
		20 hrs.	40 hrs.	41 hrs.	63 hrs.	83 hrs.
None.....		1.7		3.6		
Product three.....	2.0	0.6	1.3		2.1	2.9

Improving agent	Per cent conc.	Bearing loss in grams				
		18 hrs.	20 hrs.	38 hrs.	75 hrs.	83 hrs.
None.....		0.033		0.200		
Product three.....	2.0		0.008		0.200	0.277

Ratio=75:38=2:1 (approx.).

OPERATION TESTS

We have also carried out tests of an oil and oils blends containing representative ammonium and metal salts of the type contemplated herein to determine the comparative behavior of the unblended oil and the improved oil compositions under actual operating conditions.

(a) Lauson engine test

In this test, a single-cylinder Lauson engine was operated with an oil temperature of 290° F. and a jacket temperature of 212° F. The oil used was an S. A. E. 10 motor oil, solvent refined, and the oil blends used were blends of said oil and typical metal and ammonium salts, Product two and Product four (d), respectively. The neutralization number (N. N.) and viscosity in centistokes at 210° F., of the blank oil and the oil blends, were determined after 36 hours. The results are as shown below in Table-four.

TABLE FOUR

Improving agents	Per cent conc.	N. N.	Kinematic vis. @ 210° F.
None.....		6.8	54.6
Product two.....	3.0	1.7	47.7
None.....		10.3	66.0
Product four (d).....	2.0	2.0	47.6

(b) Ring-sticking test

This test was carried out in a single-cylinder C. F. R. engine cooled with a diethylene glycol-water mixture held at a temperature of about 390° F. The oil temperature was held at about 150° F. during the test. The engine was operated continuously over a time interval of 28 hours at a speed of about 1200 R. P. M., which is equivalent to a road speed of about 25 miles per hour.

The conditions observed at the end of the test were (a) the extent to which the piston rings were stuck, (b) the extent to which the slots in the oil rings were filled with deposits, (c) the amount of carbonaceous deposits on the piston and (d) the neutralization number (acidity) of the oil, at the end of the test. The oil used was a lubricating oil having an S. U. V. of 120 seconds at 210° F. and the results, which are recorded in Table five below, show a marked improvement in mineral oil compositions of the type contemplated herein over the oil above.

In running these tests a comparative run was made with a sample of the blank oil and a sample of the oil containing the improving agent. In Table five, Product one is the barium salt of an acidic, phosphorus- and sulfur-containing reaction product of P_2S_5 and oleone prepared above.

TABLE FIVE

Improving agent	Conc., per cent	Ring condition									Grams carbon deposits	N. N.
		Degrees stuck					Per cent slots filled					
		1	2	3	4	5	3	4	5			
None.....	0	360	360	300	360	300	30	40	20	12.4	1.4	
Product one	3	60	0	0	0	0	0	tr	0	7.0	1.0	

(tr=trace).

The foregoing test results show that these new ammonium and metal salts prevent the corrosion of inert metal bearings and inhibit the development of acids, the increase in viscosity and the formation of gummy deposits in engines during use. The great effectiveness of these salts is indicated by the small amounts necessary to stabilize petroleum oils. They may be used in varying concentrations of from about 0.05 per cent to 5 per cent or more depending upon the type of oil, the conditions under which the blend is to be used, etc. In general, however, concentrations of from about 0.5 per cent to about 3.0 per cent of said salts will be sufficient to effect substantial improvement of the oil in which they are incorporated. They may be used either in straight petroleum oils or in oils containing other improving agents that have been added for other purposes, such, for example, as pour point depressants, viscosity index improvers, etc., in which case they serve to stabilize the resulting blends without detracting from the advantages of one or more of the addition agents.

It is, of course, to be understood that while we have described certain typical procedures in making the oil addition agents contemplated herein and have referred to certain specific ammonium and metal salts and to specific mineral oils, the invention is not to be interpreted as being limited to these specific features of the foregoing descriptive material. Therefore, this invention is to be interpreted as inclusive of procedures which will be apparent to those skilled in the art and correspondingly inclusive of other typical ammonium and metal salts and other petroleum products coming within the scope of the appended claims.

We claim:

1. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a salt of an acidic, phosphorus- and sulfur-containing reaction product, said reaction product being selected from the group consisting of a reaction product obtained by reaction, at a temperature between about 135° C. and about 200° C., of substantially one mol of P_2S_5 and four mols of an unsaturated ketone; a reaction product obtained by reaction, at a temperature between about 135° C. and about 200° C., of substantially one mol of P_2S_5 and four mols of a sulfurized ketone, said sulfurized ketone being obtained by sulfurizing an unsaturated ketone with elementary sulfur at a temperature above about 150° C.; and a reaction product obtained by sulfurizing, with elementary sulfur at a temperature above about 150° C., an intermediate acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of an unsaturated ketone at a temperature between about 135° C. and about 200° C.; said salt being

selected from the group consisting of ammonium and metal salts.

2. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion from about 0.5 per cent to about 3.0 per cent of a salt of an acidic, phosphorus- and sulfur-containing reaction product, said reaction product being selected from the group consisting of a reaction product obtained by reaction, at a temperature between about 135° C. and about 200° C., of substantially one mol of P_2S_5 and four mols of an unsaturated ketone; a reaction product obtained by reaction, at a temperature between about 135° C. and about 200° C., of substantially one mol of P_2S_5 and four mols of a sulfurized ketone, said sulfurized ketone being obtained by sulfurizing an unsaturated ketone with elementary sulfur at a temperature above about 150° C.; and a reaction product obtained by sulfurizing, with elementary sulfur at a temperature above about 150° C., an intermediate acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of an unsaturated ketone at a temperature between about 135° C. and about 200° C.; said salt being selected from the group consisting of ammonium and metal salts.

3. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of an unsaturated ketone at a temperature between about 135° C. and about 200° C., said salt being selected from the group consisting of ammonium and metal salts.

4. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of an unsaturated ketone at a temperature between about 135° C. and about 200° C. in the presence of a non-oxidizing gas, said salt being selected from the group consisting of ammonium and metal salts.

5. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of an unsaturated ketone at a temperature between about 135° C. and about 200° C., in the presence of nitrogen, said salt being selected from the group consisting of ammonium and metal salts.

6. An improved mineral oil composition comprising a viscous mineral oil fraction and in ad-

mixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of an unsaturated ketone at a temperature between about 135°C . and about 200°C ., in the presence of a substantially inert diluent, said salt being selected from the group consisting of ammonium and metal salts.

7. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of diolel ketone at a temperature between about 135°C . and about 200°C ., said salt being selected from the group consisting of ammonium and metal salts.

8. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of diolel ketone at a temperature between about 135°C . and about 200°C ., said salt being selected from the group consisting of ammonium and metal salts.

9. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of diolel ketone at a temperature of about 135°C . in the presence of nitrogen and in the presence of a substantially inert diluent, said salt being selected from the group consisting of ammonium and metal salts.

10. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction, at a temperature between about 135°C . and about 200°C ., of substantially one mol of P_2S_5 and four mols of a sulfurized ketone, said sulfurized ketone being obtained by sulfurizing an unsaturated ketone with elementary sulfur at a temperature above about 150°C ., and said salt being selected from the group consisting of ammonium and metal salts.

11. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction, at a temperature between about 135°C . and about 200°C ., of substantially one mol of P_2S_5 and four mols of a sulfurized ketone, said sulfurized ketone being obtained by sulfurizing an unsaturated ketone with from about 5 per cent to about 15 per cent by weight of elementary sulfur at a temperature above about 150°C ., and said salt being selected from the group consisting of ammonium and metal salts.

12. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction, at about 135°C .,

of substantially one mol of P_2S_5 and four mols of sulfurized diolel ketone being obtained by sulfurizing diolel ketone with about 10 per cent by weight of elementary sulfur at a temperature of about 170°C ., and said salt being selected from the group consisting of ammonium and metal salts.

13. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by sulfurizing, with elementary sulfur at a temperature above about 150°C ., an intermediate acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of an unsaturated ketone at a temperature between about 135°C . and about 200°C .; said salt being selected from the group consisting of ammonium and metal salts.

14. A mineral oil concentrate containing a minor proportion of a salt of an acidic, phosphorus- and sulfur-containing reaction product, said concentrate being selected from the group consisting of: a concentrate obtained by reacting substantially one mol of P_2S_5 and four mols of an unsaturated ketone at a temperature between about 135°C . and about 200°C . in the presence of a substantially inert mineral oil and substituting the P_2S_5 reaction mixture so obtained with a salt group; a concentrate obtained by reacting, at a temperature between about 135°C . and about 200°C ., in the presence of a substantially inert mineral oil, substantially one mol of P_2S_5 and four mols of a sulfurized ketone, and substituting the P_2S_5 reaction mixture so obtained with a salt group, said sulfurized ketone being obtained by sulfurizing an unsaturated ketone with elementary sulfur at a temperature above about 150°C .; and a concentrate obtained by sulfurizing, with elementary sulfur at a temperature above about 150°C . and in the presence of a substantially inert mineral oil, an intermediate acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of an unsaturated ketone at a temperature between about 135°C . and about 200°C . in the presence of said mineral oil, and substituting the sulfurized reaction product so obtained with a salt group; said salt being selected from the group consisting of ammonium and metal salts, and said salt group being selected from the group consisting of ammonium and metal.

15. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a barium salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of diolel ketone at about 135°C . in the presence of a substantially inert mineral oil.

16. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of an ammonium salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of P_2S_5 and four mols of diolel ketone at about 135°C . in the presence of a substantially inert mineral oil.

17. An improved mineral oil composition com-

prising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to stabilize said oil fraction, of a barium salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction at about 140° 5 C. of substantially one mol of P_2S_5 and four mols of a sulfurized dioleyl ketone in the presence of

a substantially inert mineral oil, said sulfurized dioleyl ketone being obtained by sulfurizing dioleyl ketone with elementary sulfur at about 170° C. in the presence of said mineral oil.

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