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MINERAL OIL COMPOSITION

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This invention has to do with a new and novel mineral oil composition and, more particularly, has to do with a mineral oil composition containing minor proportions of an oil-soluble detergent and of an oil-soluble, phosphorus- and sulfur-containing reaction product.

It is well known to those familiar with the art that mineral oils are generally characterized by one or more undesirable characteristics which limit their use. One such characteristic is their instability under operating conditions normally encountered in present day engines, such that after a relatively short time, metal engine parts become contaminated with sludge, lacquer and resinous materials. In many instances, the said materials form in and about piston rings causing them to stick, the phenomenon being referred to as "ring-sticking." As a consequence of the instability of the oil, engine operating efficiency is seriously reduced. Another undesirable characteristic of mineral oils is their tendency to oxidize, whereupon acidic materials are formed. These acidic materials corrode metal engine parts, particularly alloy bearings such as those of the cadmium-silver, copper-lead, etc., type.

It is also well known in the art that numerous materials have been proposed as improving or fortifying agents for use in mineral oils to counteract or retard the aforesaid undesirable characteristics. Of the improving agents previously proposed, oil-soluble metal sulfonates have been found to be satisfactory in imparting detergent properties to mineral oils. Unfortunately, however, such sulfonates fail to improve, and in some cases even impair, other characteristics of mineral oils. In some instances, for example, metal sulfonates have increased the formation of acidic materials in mineral oils during use, thus inducing corrosion of metal parts with which the oils come in contact.

It has now been found that the corrosion and oxidation characteristics of an oil containing a small amount of an oil-soluble metal sulfonate can be greatly improved by incorporating therewith a small amount of an oil-soluble, phosphorus- and sulfur-containing reaction product of a dicyclic terpene and a phosphorus sulfide. More specifically, it has been found that an extremely stable oil having outstanding detergent, oxidation and corrosion characteristics is ob-

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tained by incorporating in an oil containing a metal sulfonate, a small amount of a reaction product of the aforesaid type. It has also been found that oils similarly characterized are obtained by incorporating a small amount of the said reaction product into oils containing small amounts of oil-soluble salts of organic acids, which possess detergent properties.

All oil-soluble metal sulfonates are contemplated herein, typical of which are those obtained from aromatic hydrocarbons or substituted aromatic hydrocarbons, and a sulfonating agent such as strong sulfuric acid, oleum, chlorosulfonic acid and the like. Other typical sulfonates are those obtained by treatment of paraffins, naphthenes and various petroleum fractions—paraffinic, naphthenic or aromatic—with the same reagents. Preferred, however, are the metal salts of sulfonic acids of wax-substituted benzene and naphthalene, wherein the wax substituent is a long-chain aliphatic hydrocarbon group containing at least about 18 carbon atoms and is obtained from paraffin wax.

All metals are contemplated herein as constituents of the said metal sulfonates. Especially suitable, however, are calcium, barium and zinc. It is to be understood that when the metal substituent is polyvalent, basic as well as neutral metal sulfonates are obtained and serve the purposes of this invention. Typical and preferred sulfonates are the sodium, basic calcium, basic barium, neutral barium, zinc and dibasic aluminum salts of diwax-benzene sulfonate. Several such materials are described in further detail hereinafter in the examples.

As indicated hereinabove, oils containing other detergents—oil-soluble salts of organic acids possessing cleansing or detergent action in oil—are also substantially improved in character when a small amount of the aforesaid oil-soluble, phosphorus- and sulfur-containing reaction product of a phosphorus sulfide and a dicyclic terpene is incorporated therein. Typical oil detergents contemplated herein are: metal salts of carboxylic acids, as a calcium salt of an alkylated carboxylic acid; metal salts of hydroxyaromatic carboxylic acids, as a barium phenate-carboxylate of an alkyl-substituted phenol carboxylic acid; sulfides of metal salts of hydroxyaromatic carboxylic acids, as a barium

phenate-carboxylate of an alkyl-substituted phenol carboxylic acid disulfide; metal salts of acid esters, as vanadyl oleyl phthalate; etc. Oil-soluble salts of organic acids such as the foregoing typical salts are well known in the art and may be prepared by any suitable method.

The oil-soluble, phosphorus- and sulfur-containing reaction products contemplated herein are those obtained by reacting a dicyclic terpene and a phosphorus sulfide at a temperature above about 100° C. Although any one of the several phosphorus sulfides such as P₂S₄ (or P₂S₂), P₄S₆ (or P₂S₃), P₄S₈, P₂S₅ (or P₄S₁₀), P₄S₇, etc., may be used in the preparation of the said reaction products, particularly preferred are those reaction products obtained from P₂S₄.

"Dicyclic terpenes" are defined herein as those terpenes which are characterized by the presence of one double bond in the molecule and which are comprised of two ring systems. Typical of such terpenes are pinene, camphene and fenchene. Contemplated as coming within this particular designation are those materials which are predominantly comprised of one or more dicyclic terpenes; representative of such materials are the essential or volatile oils which are predominantly comprised of such a terpene, or terpenes, and are typified by turpentine oil, the predominant constituent of which is pinene. Preferred of the dicyclic terpene reactants are pinene and turpentine oil. Accordingly, the preferred reaction products are those obtained from P₂S₄ and pinene, and P₂S₅ and turpentine oil.

Although a complete understanding of the chemical composition of the reaction products contemplated here is not known at this time, a partial understanding of their composition may be realized by noting the characteristics involved in the reaction. The reaction between phosphorus pentasulfide and pinene, for example, commences at about 100° C. and is exothermic in nature. During the reaction, the reaction mixture increases appreciably in viscosity and little, if any, hydrogen sulfide is evolved therefrom. The reaction product obtained in this reaction contains phosphorus and sulfur in substantially the same amounts as was added in the phosphorus sulfide used. It would appear, then, that the reaction is one of addition; that is, addition of the phosphorus sulfide to the one unsaturated bond present in pinene.

While the reaction temperature for the reaction described above should be one of at least about 100° C., the preferred temperatures fall within the range of about 100° C. to about 160° C.

The proportions of reactants used herein may be varied in order to prepare reaction products having different degrees of oil solubility and different degrees of oil improving power. It is preferred, however, to use about 1 mol of a phosphorus sulfide with 4 mols of a dicyclic terpene for the preparation of a reaction product readily soluble in petroleum oils. For example, when more than 1 mol of P₂S₄ is used with 4 mols of pinene, a viscous gel-like reaction product is obtained and this product is difficultly soluble in petroleum oils. Also when less than 1 mol of P₂S₄ is used with 4 mols of pinene, a viscous oil somewhat insoluble in mineral oils is obtained after the unreacted pinene has been recovered by distillation. Accordingly, it is to be understood that while effective mineral oil improving agents of the type contemplated herein can be obtained by using different ratios of reactants, particularly preferred improving agents are those obtained

by using approximately 1 mol of a phosphorus sulfide for every 4 mols of a dicyclic terpene.

There is, however, still another desirable procedure for preparing the reaction products contemplated here. In order to obtain a relatively non-viscous reaction product, a blend of a dicyclic terpene, such as pinene, and a comparatively inert solvent such as a petroleum oil, may be treated as described above to provide an oil blend of the reaction product. The preferred procedure of this type involves the use of a 1:1 blend of dicyclic terpene and petroleum oil with a phosphorus sulfide, the molar ratio of said terpene to said sulfide being 4:1.

Further details regarding the character of the aforesaid dicyclic terpene-phosphorus sulfide reaction products may be obtained by referring to copending application Serial No. 482,482, filed April 9, 1943, of Everett W. Fuller et al.

The oil compositions contemplated herein may also contain, in addition to an oil detergent and a dicyclic terpene-phosphorus sulfide reaction product, a small amount of one or more other oil-soluble, phosphorus- and sulfur-containing reaction products. One such reaction product is that which is obtained by reaction of approximately 1 mol of phosphorus pentasulfide with 4 mols of oleyl alcohol, or ocolol, at a temperature between about 125° C. and about 150° C. for a relatively short time. These reaction products are described in further detail in copending application Serial No. 524,490, filed February 29, 1944, of Everett W. Fuller et al., now U. S. Patent No. 2,411,153, issued November 19, 1946.

In the following examples, typical and preferred metal sulfonates and other oil-soluble metal detergents and dicyclic terpene-phosphorus sulfide reaction products are described in order to further explain the oil addition agents contemplated herein.

EXAMPLE 1

Basic barium diwax benzene sulfonate

A paraffin wax having an average of 24 carbon atoms to the molecule and a melting point of 126° F. was chlorinated at about 95° C. with chlorine gas until the weight of the wax had increased about 10%. The chlorowax (10% Cl) thus obtained was then blown with nitrogen to remove any occluded chlorine and hydrogen chloride.

One thousand and twenty (1020) parts of the above chlorowax was then reacted with 458 parts by weight of benzene in the presence of 62 parts of AlCl₃ at about 60° C. for about 2 hours. The excess benzene was then distilled off by warming to 115° C. with a stream of N₂ gas bubbling through the mixture. The monowax benzene thus formed was treated with an additional 1020 parts of chlorowax and the mixture heated to 85° C. until reaction stopped. It was allowed to stand overnight at about 60° C. and then decanted from the settled AlCl₃ sludge and filtered. The product consisted essentially of diwax benzene.

Five thousand two hundred (5200) parts of the diwax benzene, prepared as described above, were treated with successive 250 parts of oleum, containing 15% SO₃, while maintaining the temperature at 35°-55° C. After 2600 parts of oleum had been added and the reaction had ceased, 3000 parts of water were added while the mixture was thoroughly stirred. An S. A. E. 30 grade motor oil (5400 parts) was then added and the mixture was allowed to settle over night at about 75° C. The lower layer, consisting mostly of dilute sulfuric acid, was withdrawn leaving

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diwax benzene sulfonic acid in the upper layer. This upper layer was treated with 3170 parts by weight of barium hydroxide octahydrate



which represents an excess of barium hydroxide over that required to neutralize the diwax benzene sulfonic acid and any free sulfuric acid occluded therein. The reaction mixture thus formed was heated to about 140° C. for about 6 hours with nitrogen gas bubbling through it to remove water and it was then filtered through a layer of clay. The product—product A—consisted of an approximately 50% oil blend of basic barium diwax benzene sulfonate (analysis: 5.17% barium and 1.5% sulfur).

EXAMPLE 2

Zinc diwax benzene sulfonate

A diwax benzene sulfonic acid was prepared as described in Example 1 above and this was then treated with zinc acetate. After distilling off the acetic acid, the product was filtered through clay leaving a material—product B—that contained 3.36% zinc and 1.6% sulfur.

EXAMPLE 3

Basic barium diwax naphthalene sulfonate

Five hundred (500) parts of chlorowax, containing 12% chlorine, were added to 500 parts of Stoddard solvent and 108 parts of naphthalene. The mixture was warmed to 50–60° C. and 30 grams of AlCl_3 were added gradually. When the reaction stopped the mixture was heated to 90° C. and blown with N_2 gas to remove HCl . It was then allowed to stand overnight at room temperature. The lower sludge layer was removed and the oil layer was filtered through clay. This consisted essentially of diwax naphthalene.

The diwax naphthalene was treated with 250 parts of oleum (15% SO_3) by adding the latter slowly so as to keep the temperature at 40–50° C. One thousand (1000) parts of water were then added with stirring and this was followed by 500 parts of an S. A. E. 30 grade motor oil. The mixture was allowed to stand at 60–70° C. overnight and the oil layer was then withdrawn. This consisted essentially of 50% diwax naphthalene sulfonic acid in motor oil. This acid was treated with an excess of barium hydroxide and the mixture was heated to a maximum temperature of 150° C. in the presence of a stream of nitrogen to remove the water. After filtering, the Stoddard solvent was removed by heating to 170° C. at a vacuum of 5 mm. This left an approximately 50% solution of the basic barium diwax naphthalene sulfonate in the petroleum motor oil, which is identified herein as product C. It contained 10% Ba and 2.0% S.

EXAMPLE 4

Barium salt of petroleum oil sulfonate

A Mid-Continent distillate of 95 seconds Saybolt viscosity at 100° F. was treated with oleum, the sludge was settled and removed, and the oil layer was neutralized with caustic soda solution. The sodium sulfonates thus formed were recovered by adding ethyl alcohol, separating the alcohol layer, and then evaporating off the alcohol. This left a mixture of oil and sodium sulfonates. This was contacted with a water solution of barium chloride and, after separation

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of the oil layer and drying, the latter—product D—was found to contain 6.9% Ba and 2.5% S.

EXAMPLE 5

Barium triwax phenol carboxylate

A barium salt of a triwax phenol carboxylate—product E—was prepared by the method described in U. S. Patent 2,197,835. It was formed in an oil blend and contained 4.0% Ba.

EXAMPLE 6

Sulfurized barium triwax phenol carboxylate

A sulfurized barium triwax phenol carboxylate—product F—was prepared by the method described in U. S. Patent 2,256,441. It was prepared in an oil blend and analyzed to give 4% Ba and 0.9% S.

EXAMPLE 7

Cobalt salt of triwax phenol carboxylate

A cobalt salt—product G—was prepared corresponding to the barium salt above (product E). This cobalt salt contained 1.83% Co.

EXAMPLE 8

Vanadyl oleyl phthalate

A mol of oleyl alcohol was reacted with a mol of phthalic anhydride to give the half ester of oleyl phthalate. This was neutralized with sodium hydroxide and the sodium salt thus formed was treated with vanadyl chloride to give the vanadyl salt of oleyl phthalate (3.94% vanadium), which is identified herein as product H.

EXAMPLE 9

Pinene- P_2S_5 reaction product

Eight hundred (800) parts by weight of pinene and an equal weight of a motor oil (Saybolt Universal viscosity of 45 seconds at 210° F.) were heated to 105° C. with stirring. Three hundred and twenty-six (326) parts of P_2S_5 (a ratio of 4 mols of pinene to 1 mol of P_2S_5) were added slowly the temperature rising to 115° C. because of the exothermic reaction. The mixture was then heated to 150° C. for 1 hour, 20 parts of clay were added and the resultant mixture filtered. The filtrate, consisting of 1842 parts by weight, was then vacuum topped at 5 mm. pressure to a pot temperature of 150° C. The residue consisting of 1693 parts by weight was a clear, viscous oil—product X—containing 12.5% sulfur and 5.1% phosphorus.

EXAMPLE 10

Oleyl alcohol- P_2S_5 reaction product

Approximately 4 mols of oenol, a commercial material consisting essentially of oleyl alcohol, and 1 mol of P_2S_5 were reacted at about 150° C. for 2 hours. The resulting product—product Y—contained 5.0% phosphorus and 9.8% sulfur.

The following test results are provided to demonstrate the properties of mineral oils containing small amounts of oil detergents and the outstandingly superior properties of mineral oils containing small amounts of the said detergents and of the aforesaid dicyclic terpene-phosphorus sulfide reaction products, which may also have in combination small amounts of other oil-soluble, phosphorus- and sulfur-containing reaction products such as the oleyl alcohol- P_2S_5 product.

EXAMPLE 11

An accelerated oxidation test has been used in order to determine the corrosive nature of lubricating oils under simulated operating conditions. The apparatus used consists of a circulating system whereby 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 comes into 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 designated as Nuodex, 6% Fe₂O₃) which greatly increases the rate of oxidation of the oil. The degree of oxidation suffered by the oil is shown by the development of acidity therein as measured by the neutralization number (N. N.), the loss in weight of the cadmium-nickel bearing and the percentage viscosity increase.

The oil used was a solvent refined oil having a Saybolt Universal viscosity of 65 seconds at 210° F. and containing 0.17% of Nuodex. The results of these tests are shown in Table I below.

Table I

Detergent	Percent Wt.	Stabilizer	Percent Wt.	N. N.	Percent Visc. Increase	Brg. Loss, Grams
Nil		Nil		7.39	95	1.299
Product A	2	do		10.57	183	.770
Do	2	Product X	.25	2.05	16	.165
Do	2	do	.35	1.60	8	.062
Do	2	do	.50	.75	5	.000
Do	2	Product X	.10	2.51	22	.040
		Product Y	.50			
Do	2	Product X	.25			
Do	2	Product Y	.50	1.03	7	.002
Product B	2	Nil		5.97	46	1.195
Do	2	Product X	.50	2.40	17	.158
Product G	5	Nil		5.31	50	.719
Do	1.5	Product X	.25	0.72	7	.013

It will be apparent from inspection of the results presented in Table I that the blank oil is unsatisfactory in view of its corrosivity as shown by the neutralization number value and the bearing weight loss. The viscosity increase is also high. When a detergent alone is added to the oil there is little or no improvement in any of these factors. However, when a small amount of the pinene-P₂S₅ reaction product, product X, is added to the oil containing any one of the detergents, both the neutralization number formation and the bearing weight loss are greatly decreased. There also is less increase in viscosity. A corresponding improvement is obtained when small amounts of a pinene-P₂S₅ reaction product and of an oleyl alcohol-P₂S₅ reaction product are added to an oil containing one of the detergents.

EXAMPLE 12

The corrosivity of an oil and of an oil containing an oil detergent toward alloy bearings is demonstrated by the following test. Also demonstrated is the non-corrosive nature of the oil compositions contemplated herein, which contain small amounts of a phosphorus- and sulfur-containing reaction product of the aforesaid type, and an oil detergent.

This test involves operating a single-cylinder C. F. R. engine containing copper-lead bearings, at an oil temperature of 285° F. and a jacket temperature of 212° F. The engine is stopped at

various time intervals and the top bearing is weighed to determine the corrosion loss thereof. The corrosion loss is plotted against the test time interval and each run is continued until a loss of 0.200 gram is obtained. The oil is rated by dividing the time (in hours) required for a 0.200 gram loss for an oil blend, by the time (in hours) required for the same loss for a blank oil that was run in the engine immediately preceding it. A rating of less than 1 indicates an oil inferior to the blank oil, and a rating greater than 1 indicates an oil superior thereto. The oil used in the test is a solvent-refined oil having an S. U. V. of 318 seconds at 100° F. The results are presented in Table II below.

Table II

Detergent	Per Cent Wt.	Stabilizer	Per Cent Wt.	Rating
Product A	4	Nil		0.54
Do	4	Product X	.50	1.8
Product C	2	do	.50	2.9
Product F	3	Nil		0.6
Do	2	Product X	.50	2.3
Do	1.5	Product X	.25	2.9
		Product Y	.50	

The results presented above in Table II demonstrate that an oil containing a small amount of

an oil detergent is more corrosive than the oil alone. When a small amount of a reaction product of the type defined above is added to such an oil, the corrosive nature of the oil is greatly counteracted.

EXAMPLE 13

Tests of an oil, of oil blends containing only an oil detergent, and of oil blends containing an oil detergent and an oil-soluble, phosphorus- and sulfur-containing reaction product as defined above, were carried out to determine further the comparative behavior of the unblended oil, the oil containing only the detergent and the oil containing a detergent and said reaction product, under actual operating conditions.

In this test a single-cylinder Lauson engine was operated for 36 hours at an oil temperature of 290° F. and a jacket temperature of 212° F. The oil used was a solvent-refined oil having a Saybolt Universal viscosity of 45 seconds at 210° F. (kinematic viscosity 5.75 at 210° F.). After 36 hours, the acidity, as measured by the neutralization number (N. N.) and the kinematic viscosity of the oil were determined. The neutralization number (N. N.) rating is obtained by comparing the neutralization number of the oil blend with the neutralization number of the blank oil, which is run in the engine preceding the run with the oil blend. Ratings of greater than 1 indicate that the oil blend is less acidic than the blank oil and, therefore, superior

thereto, and ratings of less than 1 indicate that the oil blend is more acidic than the blank oil and, therefore, inferior thereto. The results of these tests are set forth in Table III below.

Table III

Detergent	Per Cent Wt.	Stabilizer	Per Cent Wt.	36 Hours		Rating N. N.
				N. N.	K. V. 210	
Oil Alone.....	Average	Results.....		10.0	10.5	
Product A.....	2	Nil.....		9.9	11.19	0.77
Do.....	2	Product X.....	.25	1.0	6.41	7.9
Do.....	4	Product Y.....	.50			
Do.....	4	Product X.....	.50	3.3	7.20	3.7
Do.....	4	Product X.....	.25	1.3	6.52	7.6
Do.....	4	Product Y.....	.50			
Product B.....	2	Product X.....	.50	3.2	7.72	3.8
Product C.....	2	Product X.....	.50	1.4	6.26	11.2
Product D.....	1	Product X.....	.50	1.2	6.12	5.5
Product F.....	2	Product X.....	.50	1.2	6.28	8.5
Product G.....	4	Product X.....	.50	1.3	6.29	3.4
Product H.....	.03	Nil.....		20.9	32.47	0.62
Do.....	.05	Product X.....	.50	3.0	7.11	3.7

EXAMPLE 14

A single cylinder Caterpillar Diesel engine was run for 96 hours at 19.8 brake horsepower and 1000 R. P. M. The oil temperature and the water temperature were both maintained at 195° F. The piston was then removed and rated for cleanliness. The results of several engine tests are presented in Table IV below.

Table IV

A solvent refined S. A. E. 30 grade Mid-Continent oil was used in the following tests.

Oil alone—test stopped due to ring sticking at 48 hours.

Oil+4% product A+0.5% product X—piston in excellent condition.

Oil+2% product A+0.25% product X+0.5% product Y—piston in good condition.

Oil+2% product C+0.5% product X—piston in excellent condition.

An acid refined S. A. E. 30 grade oil from a Coastal crude was used in the following tests.

Oil alone—heavy lacquer and deposits on piston.

Oil+4.5% product F+0.6% product X—piston in good condition.

Oil+4.5% product E+0.6% product X—piston in good condition.

The test results in Table IV demonstrate that oils containing small amounts of a detergent and of a pinene-P₂S₅ reaction product are particularly suitable for use in Diesel engines of the Caterpillar type.

EXAMPLE 15

A three cylinder General Motors 3-71 Diesel engine was run at 2000 R. P. M. with an oil temperature of 230° F. and a jacket temperature of 180° F. When the air box pressure increased more than 3 inches of mercury over the original pressure, the ports were considered sufficiently closed to stop the test. In Table V below the time in hours to reach this condition is noted. A solvent refined S. A. E. 30 grade Mid-Continent oil was used in these tests.

Table V

	Hours to port closure
Oil alone.....	122
Oil+4% product A+0.5% product X.....	285
Oil+2% product A+0.25% product X+0.5% product Y.....	196
Oil+1.5% product E+0.75% product X.....	240
Oil +2% product F+0.25% product X.....	272

The above results show that our oil compositions are highly effective in improving the quality of an oil used in the General Motors type of Diesel engine.

As indicated hereinabove, preference is given herein to those oil detergents defined as metal sulfonates of wax-substituted aromatic hydrocarbons. This preference is influenced by their outstanding pour depressing properties as illustrated below in Table VI which gives results for products A and C, barium salts of diwax benzene sulfonic acid and diwax naphthalene sulfonic acid respectively, and for product D, a barium salt of a sulfonic acid derived from petroleum oil. The two former materials are effective in lowering the pour point while the latter is ineffective. These tests were made on a solvent refined S. A. E. 30 grade of 45 seconds Saybolt Universal viscosity at 210° F.

Table VI

Detergent	Percent	A. S. T. M. Pour Point °F.
Oil alone.....		+20
Product A.....	1.0	-20
Product C.....	1.0	-15
Product D.....	1.0	+20

The results set forth in Tables I through V above demonstrate the outstanding qualities of the mineral oil compositions contemplated herein. As shown in the said tables, they possess a high degree of resistance to oxidation and particularly desirable detergent properties. The results presented in Table VI above further demonstrate the superior quality of the preferred oil detergents, metal salts of wax-substituted aromatic hydrocarbon sulfonic acids, as evidenced by their pour depressant properties.

As contemplated by the present invention, concentrations of from about 0.5% to about 10% of an oil detergent are used in an oil fraction, but concentrations of the order of about 4% have been found to be satisfactory for most purposes. The concentration of an oil soluble, phosphorus- and sulfur-containing reaction product of a dicyclic terpene and a phosphorus sulfide may be varied from about 0.1% to about 3.0%; in general, however, about 0.5% will be satisfactory.

As indicated hereinabove, the mineral oil compositions of this invention may also contain one or more other oil-soluble, phosphorus- and sulfur-containing reaction products, such as those obtained from oleyl alcohol and P₂S₅, as defined above. Oils of excellent quality are obtained with from about 0.25% to about 2.0% of such a reac-

tion product, incorporated with the aforesaid quantities of an oil detergent and of a dicyclic terpene reaction product of the type defined above.

Mineral oil concentrates are also contemplated herein, such concentrates containing substantially larger concentrations of an oil detergent and of a dicyclic terpene-phosphorus sulfide reaction product, than those enumerated above. That is, relatively large amounts of the said materials may be incorporated in an oil fraction in which they are readily soluble, and the oil concentrate so obtained may thereafter be diluted with a suitable quantity of the said oil fraction prior to use. It is to be understood that these mineral oil concentrates may also contain one or more of the aforesaid other oil-soluble, phosphorus- and sulfur-containing reaction products, such as those obtained from oleyl alcohol in amounts substantially in excess of those described above.

In preparing the mineral oil compositions and concentrates contemplated herein, an oil detergent and a dicyclic terpene-phosphorus sulfide reaction product, as defined hereinabove, may be incorporated in a mineral oil in any one of several ways. For example, the dicyclic terpene reaction product may be added to an oil fraction containing an oil detergent; also, an oil detergent may be added to the reactants (dicyclic terpene and phosphorus sulfide) used in the preparation of the said reaction product and, in such case, will be present during the reaction. It is possible that the oil detergent may react with the dicyclic terpene and phosphorus sulfide to form a complex reaction product under the reaction conditions enumerated above; the product obtained in this manner may then be added to an oil fraction. Accordingly, it will be apparent that the mineral oil compositions and concentrates of this invention are complex in nature, for it is possible that an oil detergent and a dicyclic terpene-phosphorus sulfide reaction product may be present individually in an oil fraction, or may also be present therein as a physical combination or, further, may be present therein in the form of a single chemical composition. In the same connection, it will also be apparent that an oil detergent and a reaction product of the aforesaid type may enter into chemical reaction when the oil composition is used as a lubricant under certain conditions, such for example, as a lubricant in an engine operating at relatively high temperatures.

In view of the foregoing, the term "mineral oil composition," as used herein, and as recited in all of the appended claims, is inclusive of all mineral oil fractions containing an oil detergent and a dicyclic terpene-phosphorus sulfide reaction product of the type defined above, in the concentrations previously enumerated, and is inclusive of all compositions obtained or prepared by any of the aforesaid several procedures. Correspondingly, the term "mineral oil concentrate" is inclusive of all mineral oil fractions containing relatively large amounts of the said oil detergent and said reaction product.

It is to be understood that the examples, procedures and oil compositions described hereinabove are illustrative only and are not to be construed as limiting the scope of this invention thereto. For example, all dicyclic terpenes as

broadly recited above may be used in place of pinene shown in the examples: however, pinene is preferred. Similarly, any phosphorus sulfide may be used in place of phosphorus pentasulfide shown in the examples, but the latter sulfide is preferred. Also, while the sulfonates and other illustrative oil detergents are preferred of their class, all compounds coming within the aforesaid definition of an oil detergent may be used. Furthermore, the mineral oil fractions disclosed above are but typical of the fractions which may be used.

This application is a division of our copending application Serial No. 539,597, filed June 9, 1944, now U. S. Patent No. 2,416,281, issued February 25, 1947.

We claim:

1. An improved mineral oil composition comprising a viscous mineral oil fraction having in admixture therewith: a minor proportion, from about 0.5 per cent to about 10 per cent, of an oil-soluble metal sulfonate; a minor proportion, from about 0.1 per cent to about 3.0 per cent, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reaction of a phosphorus sulfide and a material selected from the group consisting of a dicyclic terpene and an essential oil predominantly comprised of a dicyclic terpene, at a temperature greater than about 100° C.; and a minor proportion, from about 0.25 per cent to about 2.0 per cent, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of phosphorus pentasulfide and four mols of oleyl alcohol at a temperature from about 125° C. to about 150° C. for a relatively short time.

2. An improved mineral oil composition comprising a viscous mineral oil fraction having in admixture therewith: a minor proportion, from about 0.5 per cent to about 10 per cent, of an oil-soluble, metal petroleum sulfonate; a minor proportion, from about 0.1 per cent to about 3.0 per cent, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reaction of a phosphorus sulfide and a material selected from the group consisting of a dicyclic terpene and an essential oil predominantly comprised of a dicyclic terpene, at a temperature greater than about 100° C.; and a minor proportion, from about 0.25 per cent to about 2.0 per cent, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of phosphorus pentasulfide and four mols of oleyl alcohol at a temperature from about 125° C. to about 150° C. for a relatively short time.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,375,222	Griffin et al.	May 8, 1945
2,379,453	Noland	July 3, 1945
2,411,153	Fuller et al.	Nov. 19, 1946
2,416,281	Berger	Feb. 25, 1947