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MINERAL OIL COMPOSITION

Henry G. Berger, Glen Rock, and Everett W. Fuller, Woodbury, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

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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 copper-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 oleyl alcohol and phosphorus pentasulfide. More specifically, it has been found that an extremely stable oil having outstanding detergent, oxidation and corrosion characteristics is obtained 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 characteristized are obtained by incorporating a small amount of the

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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, chlorsulfonic 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 sodium, 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 phosphorus pentasulfide and oleyl alcohol 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. Several of the foregoing are described more completely in the examples presented hereinbelow.

The oil-soluble, phosphorus- and sulfur-containing reaction products contemplated herein are

those obtained by reacting substantially one mol of P_2S_5 and four mols of oleyl alcohol at a temperature between about 125° C. and about 150° C., and preferably at about 150° C.

As contemplated herein, both technically pure and commercial grades of oleyl alcohol may be reacted with P_2S_5 under the above-mentioned reaction conditions in order to obtain the desired products. Inasmuch as commercial oleyl alcohol or "ocenol" is available in large quantities and is relatively inexpensive it is preferred herein.

It is well known that aliphatic alcohols will react with P_2S_5 under moderate temperature conditions to give products that consist principally of the corresponding dialkyl dithiophosphoric acids. In the case of oleyl alcohol this reaction may be expressed by the following equation:

$$4C_{18}H_{35}OH + P_2S_5 \rightarrow 2(C_{18}H_{35}O)_2PSSH + H_2S$$

The sulfur and phosphorus analysis and the acidity (as represented by the neutralization number, or N. N. value) of the products thus formed at 50–60° C. check fairly well with the above formula. The dialkyl dithiophosphates have been proposed as addition agents for petroleum oils. However, the products prepared by reacting oleyl alcohol and P_2S_5 in this way are not entirely satisfactory for this purpose because of their high acidity, their tendency to evolve H_2S, their corrosive action with copper, and their general instability when used in petroleum oils.

Also when oleyl alcohol and P_2S_5 are reacted at somewhat higher temperatures, that is at about 100° C., products of a somewhat lower acidity are obtained although this value is still higher than is desirable for materials that are to be added to petroleum oils. The stability of these products prepared at about 100° C. is also unsatisfactory.

It has been found, however, that when the above reaction is carried out at temperatures from about 125° C. to about 150° C. the products are much less acidic in character and are substantially more stable than those described above. Although the acidity is much lower, these products have approximately the same phosphorus and sulfur contents as the dioleyl dithiophosphoric acids prepared at lower temperatures. Using an oleyl alcohol with a bromine number of 43 a reaction product was obtained at 95° C. with a bromine number of 39.6, which checks fairly well with a calculated value of 38 for a dioleyl dithiophosphoric acid prepared from this oleyl alcohol. When this same oleyl alcohol was reacted with P_2S_5 at 150° C., the resulting product had a bromine number of only 19.4. The above properties together with an increase in viscosity for the material made at 125° C. to 150° C. indicate a difference in chemical structure for these new reaction products.

It has also been found that when oleyl alcohol and P_2S_5 are reacted at temperatures much above 150° C., further less desirable changes take place. At higher temperatures the product becomes cloudy and an insoluble sludge separates which may contain a considerable proportion of the phosphorus present. The solubility of the reaction products in petroleum oils becomes less and in general these materials are not as satisfactory as those prepared at 125° C. to 150° C.

Two other factors influence the quality of the reaction products prepared at 125° C. to 150° C. In the first place, the time of reaction is important. This should be long enough to permit complete reaction to take place between the oleyl alcohol and the P_2S_5 and to give a product with a maximum acidity (N. N. value) of about 25. However, too long heating will result in a cloudy product or even in the deposition of an insoluble sludge containing a part of the phosphorus. The reactants should not be heated beyond the time of incipient clouding to obtain the most satisfactory products. It has been found that 6 hours heating at 125° C. or 2 hours heating at 150° C., with the quantities used in the examples provided hereinbelow, gives satisfactory results. In general, then, the reaction time may be described as a "relatively short time." Another factor that should be controlled is the molar ratio of the oleyl alcohol and the P_2S_5. It has been found that the phosphorus- and sulfur-containing reaction products prepared from substantially one mol of P_2S_5 and four mols of oleyl alcohol, or ocenol, are best suited for use in mineral oils. However, this ratio may be varied somewhat without detracting from the value of the final products. In general, a molar excess of P_2S_5 not greater than about 25 per cent of the 1 to 4 ratio may be used. When too large an excess of P_2S_5 is used, the reaction products are undesirable. For example, when P_2S_5 and oleyl alcohol were reacted in a molar ratio of 1 to 2 at 125° C. to 150° C. semi-solid mixtures having little oil solubility were obtained.

Experimental data is presented in Table I to illustrate some of the statements made above. The various products shown therein were prepared by reacting substantially one mol of P_2S_5 and four mols of ocenol with stirring at the indicated temperatures. The reaction mixtures thus obtained were then filtered through clay. As defined in Table I, a stable product is one which, when used as a 1 per cent solution in oil, does not evolve H_2S, corrode copper, or form a cloud in the oil when heated for 24 hours at 100° C.

Table I

Reaction		Composition of Product			Appearance	Stability
Temp.	Time	Per Cent P	Per Cent S	N. N.		
° C.						
50–60	6	4.81	10.2	78	Clear	Unstable.
95	2½	4.68	9.9	53	do	Do.
125	6	4.64	9.8	21	do	Stable.
150	2	4.54	9.8	15	do	Do.
150	5	3.72	9.9	6	Cloudy	Fairly Stable.
175	2	3.22	10.1	4	Precipitate	Do.

The reaction products of oleyl alcohol and P_2S_5 prepared at 125° C. to 150° C. are superior not only to related products prepared at lower and at higher temperatures from these same reactants but they are also superior to corresponding products prepared from the long chain saturated alco-

hols and P_2S_5 at temperatures within the range of 125–150° C. Thus the reaction products of one mol of P_2S_5 with four mols of such alcohols as stearyl alcohol and lauryl alcohol at 150° C. are highly acidic in nature when heated for the time specified for preparing our oleyl alcohol-P_2S_5 products, and if heated for a prolonged period of time decomposition sets in accompanied by the formation of insoluble sludge and an appreciable loss of phosphorus and sulfur. This is illustrated by the results shown in Table II. The products were prepared by reacting one mol of P_2S_5 with four mols of the alcohol at 150° C. for the time indicated and then filtering the reaction mixtures through clay.

Table II

Alcohol	Time	Per Cent P	Per Cent S	N. N.	Remarks
Oleyl	2	4.54	9.8	15	Clear Product.
Stearyl	2	5.55	9.7	67	Do.
Do	6			49	Slightly Cloudy.
Do	9	2.76	9.4	10	Resinous Deposit.
Lauryl	3	6.69	12.95	91	Clear Product.
Do	7	4.54	10.4	10	Resinous Deposit.

To summarize the above statements, it has been found that by reacting approximately one mol of P_2S_5 with four mols of oleyl alcohol for a few hours at temperatures from about 125° C. to about 150° C. products are formed which are exceptionably suitable as mineral oil additives. These products are superior to those obtained by reacting the same ingredients at lower or at higher temperatures and in different mol ratios, and are also superior to the reaction products of other long chain alkyl alcohols with P_2S_5 under the same conditions of temperature, time and molar ratio.

Further details regarding the character of the aforesaid reaction products may be obtained by referring to copending application Serial No. 524,490, filed February 29, 1944, of Everett W. Fuller, Henry G. Berger and Robert H. Williams, now Patent No. 2,411,153, issued November 19, 1946.

The oil compositions contemplated herein may also contain, in addition to an oil detergent and an oleyl alcohol-P_2S_5 reaction product, a small amount of one or more other oil-soluble, phosphorus- and sulfur-containing reaction products. One such reaction product is that obtained by reaction of phosphorus pentasulfide and a cycle stock characterized by an olefin and an aromatic content of from about 3 per cent to about 7 per cent and from about 40 per cent to about 60 per cent, respectively, under the following reaction conditions: (1) between about 1 per cent and about 8 per cent by weight of P_2S_5 based upon the weight of said cycle stock, (2) a temperature between about 125° C. and about 200° C., and (3) a relatively short contact time.

The aforesaid reaction products of P_2S_5 and cycle stocks defined above are described in more detail in copending application Serial No. 515,418, filed December 23, 1943, of Henry G. Berger et al.

Other oil-soluble, phosphorus- and sulfur-containing reaction products which may be incorporated in an oil composition containing small amounts of an oil detergent and of an oleyl alcohol-P_2S_5 reaction product, are those obtained by reacting a dicyclic terpene and a phosporus sulfide at a temperature above about 100° C.

Further details regarding the character of the said 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.

In the following examples, typical and preferred metal sulfonates and other oil-soluble metal detergents and oleyl alcohol-P_2S_5 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 $AlCl_3$ at about 60° C. for about 2 hours. The excess benzene was then distilled off by warming to 115° C. with a stream of N_2 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 $AlCl_3$ 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% SO_3, while maintaining the temperature at 35°–50° 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 overnight at about 75° C. The lower layer, consisting mostly of dilute sulfuric acid, was withdrawn leaving diwax benzene sulfonic acid in the upper layer. This upper layer was treated with 3170 parts by weight of barium hydroxide octahydrate ($Ba(OH)_2.8H_2O$) 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 benzene sulfonate in the petroleum motor oil, which is identified herein as product C. It contained 10% barium and 2.0% sulfur.

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

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% barium.

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% barium and 0.9% sulfur.

Example 7

Cobalt salt of triwax phenol carboxylate

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

Example 8

Vanadyl oleyl phthalate

A mol of aleyl 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

Oleyl alcohol-P_2S_5 reaction product

Approximately 4 mols of ocenol, a commercial material consisting essentially of oleyl alcohol, and 1 mol of P_2S_5 were reacted at about 150° C. for 2 hours and the reaction mixture thus obtained was filtered through clay. The filtrate—product X—contained 5.0% phosphorus and 9.8% sulfur and had a neutralization number (N. N.) of 12.

Example 10

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 Y—containing 12.5% sulfur and 5.1% phosphorus.

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 oil-soluble, phosphorus- and sulfur-containing oleyl alcohol-P_2S_5 reaction products which may also have in combination small amounts of other oil-soluble, phosphorus- and sulfur-containing reaction products such as those described above.

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 arrangement 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% FeO_3) 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 bearings and the percentage of 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 III below.

Table III

Detergent	Per Cent Wt.	Stabilizer	Per Cent Wt.	N. N.	Per Cent Vis. Increase	Bearing Loss, Grams
Nil		Nil		7.39	95	1.269
Product A	2	do		10.57	183	0.770
Do	2	Product X	1.5	1.30	6	0.098
Do	2	do	0.5	2.51	22	0.040
		Product Y	0.1			
Do	2	Product X	0.5	1.03	7	0.002
		Product Y	0.25			
Product B	2	Nil		5.97	46	1.195
Do	2	Product X	1.5	1.13	3	0.003
Product F	5	Nil		5.31	50	0.719
Do	5	Product X	1.0	0.72	0	0.000
Do	5	do	0.5	3.32	13	0.413

It will be apparent from inspection of the results presented in Table III that the blank oil is unsatisfactory in view of its corrosivity as shown by the high neutralization number and bearing weight loss. The viscosity increase is high also. When a detergent alone is added to the oil there is little or no improvement in any of these factors, and in some instances the oil is impaired. However, when a small amount of an oleyl alcohol-P_2S_5 reaction product, such as product X, is added to the oil containing any one of the detergents, the neutralization number and bearing weight loss are greatly decreased. Also, there is substantially less increase in viscosity. A corresponding improvement is obtained when small amounts of a pinene-P_2S_5 reaction product and of an aleyl alcohol-P_2S_5 reaction product are added to an oil containing one of the detergents.

Example 12

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 with 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 dividing the specific neutralization number of the oil alone which is run in the engine preceding the oil blend, by the neutralization number of the oil blend. Ratings of greater than 1 indicate that the oil blend is less acidic than the oil alone and, therefore, superior thereto; and ratings of less than 1 indicate that the oil blend is more acidic than the oil alone and, therefore, inferior thereto. Average results for the oil alone (unblended oil) are presented inasmuch as the neutralization number and kinematic viscosity of the oil alone vary slightly when samples of the same are run in the same engine; this variation is attributed to the condition of the engine parts and other factors involved in the test. The results of these tests are set forth in Table IV below.

Table IV

Detergent	Per Cent Wt.	Stabilizer	Per Cent Wt.	36 Hour Results		
				N. N.	Kv. @ 210° F.	N. N. Rating
Oil Alone	average results			10.0	10.5	
Product A	2	Nil		9.9	11.19	0.77
Do	2	Product X	0.5	1.0	6.41	7.9
		Product Y	0.25			
Product E	1.5	Nil		14.2	14.58	0.46
Do	1.5	Product X	1.5	1.4	6.68	5.6
Product F	1.5	Nil		8.7	10.26	1.2
Do	1.5	Product X	1.5	1.1	6.49	6.5
Product G	0.03	Nil		20.9	32.47	0.62
Do	0.05	Product X	1.0	7.1	10.70	2.1

The above results show that when the detergents alone were used in the oil, the neutralization number ratings were low and the final viscosities were high; whereas, when an oleyl alcohol-P_2S_5 reaction product was added, greatly improved results were obtained. A corresponding improvement was obtained when small amounts of an oleyl alcohol-P_2S_5 reaction product and of a pinene-P_2S_5 reaction product were incorporated in an oil containing a detergent.

Example 13

The effectiveness of the oil composition of this invention in actual engine tests is further demonstrated by the following results which were obtained in a Chevrolet engine. This test consisted of operating a Chevrolet engine for 36 hours at 30 brake horsepower with an oil temperature of 280° F. and a jacket temperature of 200° F. A solvent-refined oil having an S. U. V. of 65 seconds at 210° F. was used. At the end of the test, the neutralization number (N. N.) of the oil and the average weight loss of a half bear-

ing were determined. Copper-lead bearings were used. The results are presented in Table V below.

Table V

Detergent	Per Cent Wt.	Stabilizer	Per Cent Wt.	N. N. Value	Bearing Loss, (Grams)
Oil Alone				6.5	1.210
Product E	1.5	Product X	1.5	2.5	0.392
Product F	1.5	do	1.5	1.9	0.328

Example 14

A single cylinder caterpillar Diesel engine was run for 96 hours at 19.8 B. H. P. and 1000 R. P. M. The oil temperature and the water temperature were both maintained at 195° F. The piston was then removed and noted for cleanliness. A solvent refined S. A. E. 30 grade Mid-Continent oil was used in the tests, the results of which are shown in Table VI below.

Table VI

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

Oil+1.5% product F+1.5% product X—ran the full 96 hours—piston still in good condition.

Test V

Further tests were made in a Lycoming aero engine under the conditions noted below.

A. *High temperature test.*—A single cylinder Lycoming engine was operated at a speed of 2000 R. P. M. with an oil temperature of 250° F. for 30 hours. The cylinder was covered to prevent heat loss so that an average cylinder temperature of 375° F. was maintained. A solvent-refined S. A. E. 50 grade oil was used. The results are tabulated below in Table VII.

Table VII

Oil alone gave stuck rings within 13 hours.

Oil+4% product G ran the full 30 hours with 0.147-inch ring wear.

Oil+4% product G+1% product X ran the full 30 hours with only 0.073-inch ring wear.

Oil+3% product F+1.5% product X ran the full 30 hours with only 0.063-inch ring wear.

The above results show that when a detergent alone is incorporated in an oil, the oil runs the full 30 hours of test without ring sticking, but ring wear is relatively high. The combination of detergent and stabilizer in the oil, however, prevents ring sticking and lowers ring wear.

B. *Low temperature test.*—The above Lycoming engine was operated at the same speed and oil temperature but with the cylinder uncovered. The average cylinder temperature in this case was 325° F. The results of these tests are shown below in Table VIII.

Table VIII

Oil alone gave stuck rings within 40 hours.

Oil+1.5% product F+1.5% product X went 99 hours before ring sticking.

Oil+0.2% product H+1.5% product X went 55 hours before ring sticking.

The foregoing results show the improvement obtained by using the proposed combinations in an oil tested under these conditions.

As indicated hereinabove, preference is given herein to those oil detergents defined as metal sulfonates of wax-substituted aromatic hydrocarbons. The metal sulfonates of wax-substituted aromatic hydrocarbons are very effective in oils when used in combination with the oleyl alcohol-P_2S_5 reaction product. In addition they have an appreciable effect in lowering the pour point of an oil which differentiates them from metal sulfonates derived from petroleum oil. This difference is indicated by the results shown in Table IX below. The oil used in the pour tests was a solvent refined oil having an S. U. V. of 65 seconds at 210° F., and A. S. T. M. pour tests are reported in degrees Fahrenheit (°F.).

Table IX

Detergent	Conc. Per Cent (Wt.)	A. S. T. M. Pour Test, ° F.
Oil alone		+20
Basic barium diwax benzene sulfonate in oil (Product A)	1.0	−20
Barium salt of petroleum sulfonate (Product D)	1.0	+20

The results set forth in Tables III through VIII demonstrate the outstanding qualities of the mineral oil compositions contemplated herein. As shown in these tables, our oil compositions possess a high degree of resistance to oxidation and particularly deirable detergent properties. The results presented in Table IX 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 per cent to about 10 per cent of an oil detergent are used in an oil, but a concentration of about 4 per cent has been found to be satisfactory for most purposes. The concentration of oil-soluble, phosphorus- and sulfur-containing reaction products of oleyl alcohol and P_2S_5, as defined above may be varied from about 0.5 per cent to about 5.0 per cent; in general, however, about 1.0 per cent 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 cycle stocks and P_2S_5, and dicyclic terpenes and phosphorus sulfides, as defined above. Oils of excellent quality are obtained with from about 0.25 per cent to about 1.0 per cent of such reaction products, incorporated with the aforesaid quantities of an oil detergent and of an oleyl alcohol 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 an oleyl alcohol-P_2S_5 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 a dicyclic terpene or a cycle stock, in amounts substantially in excess of those described above.

In preparing the mineral oil compositions and concentrates contemplated herein, an oil deter-

gent and an oleyl alcohol-P_2S_5 reaction product, as defined above, may be incorporated in a mineral oil in any one of several ways. For example, the oleyl alcohol reaction product may be added to an oil fraction containing an oil detergent; also, an oil detergent may be added to the reactants (oleyl alcohol and P_2S_5) 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 oleyl alcohol and P_2S_5 to form a complex reaction product under the reaction conditions enumerated above; the product obtained in that 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 an oleyl alcohol-P_2S_5 reaction product, as defined above, 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 an oleyl alcohol-P_2S_5 reaction product of the type defined above in the concentrations previously described, and is inclusive of oil compositions obtained or prepared by any of the several procedures, hereinabove described. 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 considered as limiting the scope of this invention thereto. For example, 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 herein.

I claim:

1. An improved mineral oil composition comprising a viscous mineral oil fraction having in admixture therewith: a minor proportion, from about 0.5% to about 10%, of an oil-soluble metal salt, selected from the group consisting of metal sulfonates and metal carboxylates; and a minor proportion, from about 0.5% to about 5.0% of an oil-soluble phosphorus- and sulfur-containing reaction product obtained by reaction of substantially one mol of phosphorus pentasulfide and 4 mols of oleyl alcohol at a temperature from about 125° C. to about 150° C., the reaction time-reaction temperature relationship being so maintained that the acidity (N. N.) of said reaction product is not greater than about 25.

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 sulfonate; and a minor proportion, from about 0.5 per cent to about 5.0 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., the reaction time-reaction temperature relationship being so maintained that the acidity (N. N.) of said reaction product is not greater than about 25.

3. 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 salt of a wax-substituted aromatic sulfonic acid; and a minor proportion, from about 0.5 per cent to about 5.0 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., the reaction time-reaction temperature relationship being so maintained that the acidity (N. N.) of said reaction product is not greater than about 25.

4. 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 salt of a wax-substituted benzene sulfonic acid; and a minor proportion, from about 0.5 per cent to about 5.0 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., the reaction time-reaction temperature relationship being so maintained that the acidity (N. N.) of said reaction product is not greater than about 25.

5. 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 barium salt of a diwax-substituted benzene sulfonic acid; and a minor proportion, from about 0.5 per cent to about 5.0 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., the reaction time-reaction temperature relationship being so maintained that the acidity (N. N.) of said reaction product is not greater than about 25.

6. 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 barium salt of a diwax-substituted benzene sulfonic acid; and a minor proportion, from about 0.5 per cent to about 5.0 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 ocenol at about 150° C. for about two hours.

7. 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 sulfurized barium triwax phenol carboxylate; and a minor proportion, from about 0.5 per cent to about 5.0 per cent, of an oil-soluble, phosphorus- and sulfur-containing re-

action 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., the reaction time-reaction temperature relationship being so maintained that the acidity (N. N.) of said reaction product is not greater than about 25.

8. 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 cobalt salt of triwax phenol carboxylate; and a minor proportion, from about 0.5 per cent to about 5.0 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., the reaction time-reaction temperature relationship being so maintained that the acidity (N. N.) of said reaction product is not greater than about 25.

9. A mineral oil concentrate comprising a viscous mineral oil fraction having in admixture therewith: an oil-soluble metal salt selected from the group consisting of metal sulfonates and metal carboxylates and 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 of from about 125° C. to about 150° C., the reaction time-reaction temperature relationship being so maintained that the acidity (N. N. of said reaction product is not greater than about 25, the quantity of said metal salt in said concentrate being greater than about 10 per cent and the quantity of said reaction product therein being greater than about 5 per cent, the relative proportions of said metal salt and of said reaction product therein being such that when said concentrate is diluted with mineral oil, the mineral oil composition so formed will contain from about 0.5 per cent to about 10 per cent of said metal salt and from about 0.5 per cent to about 5.0 per cent of said reaction product.

HENRY G. BERGER.
EVERETT W. FULLER.

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