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MINERAL OIL ADDITIVE

Jeffrey H. Bartlett, Westfield, and Thomas Cross, Jr., Union, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

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This invention relates to mineral oil compositions and particularly to lubricating oils with which an additive has been incorporated to improve the properties of the same.

Modern developments in the design of internal combustion engines, with increasing engine speeds and compression ratios, have imposed a severe strain on the lubricants employed. In particular, the crankcase oil is raised to a high temperature and in the course of its circulation through the engine is rapidly exposed to air under conditions highly conducive to destructive oxidation. Oxidative breakdown of the oil results in the formation of acidic products which corrode bearing surfaces and do considerable harm to the engine generally. Furthermore, the metallic corrosion products have the effect of catalyzing further oxidative breakdown of the oil.

It is also known that in modern internal combustion engines, such as aviation gasoline engines operating at relatively high temperatures due to their high power output, or in high speed diesel engines due to incomplete combustion, piston rings have a tendency to become stuck in grooves. Lacquer and carbon formation appear to be the principal reasons for this occurrence. Moreover, scuffing of top lands due to the formation of hard carbon particularly when using high viscosity index oils may cause serious damage to the engine.

It has been found, in accordance with the present invention, that destructive oxidation of lubricating oils and deposition of carbon and lacquer may both be reduced to a considerable degree by the addition to the oil of a small amount of a new additive, which may be described as a product obtained by reacting a sulfide of phosphorus or other combinations of the elements sulfur and phosphorus with an ester of a polyhydric alcohol containing a neo-carbon atom, typified by pentaerythritol, such alcohol being fully esterified and the ester preferably containing at least one unsaturated organic acid radical. Metal salts of such products, when the metal is selected from the metals of group I or II of the periodic table, may also be employed to advantage, especially when the detergent effects of the additive are to be emphasized. These additives not only have the effect of reducing oxidation and the formation of carbon deposits or

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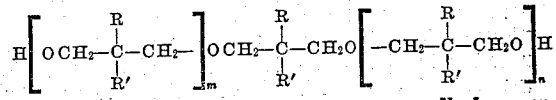
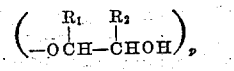
sludge in lubricating oils, but are also useful, when added to lubricants, for the purpose of protecting exposed metallic surfaces of such engines against rusting when the same are exposed to moisture or humid air. The additives are also useful generally as anti-oxidants in mineral oil products of all types.

Instead of pentaerythritol and alcohols of similar type, certain derivatives of these alcohols may likewise be employed in preparing the additives of the present invention. For example, dipentaerythritol and tripentaerythritol may be employed, as well as derivatives of all of such compounds obtained by reacting ethylene oxide or propylene oxide with the same, where there is introduced into the molecule one or more oxygen atoms in the form of ether linkages and additional short carbon chains, in accordance with the well-known methods of forming ether-alcohols.

The alcohols which may be employed in the formation of the new additives may be defined in their broadest scope by the formula



in which R is a methylol group or an alkyl group containing 1 to 3 carbon atoms, R′ is a methyl or methylol group, and m and n are numbers from 0 to 2, and in which one or more of the hydroxyl groups may be substituted by a radical of the formula



in which R_1 and R_2 each represent hydrogen or a methyl group, at least one being hydrogen, and in which p is a number from 1 to 10. It is obvious that in the last formula p represents the number of mols of ethylene oxide or propylene oxide which have been reacted with the hydroxyl group of the alcohol. Some of the more preferred alcohols coming within the above definition are pentaerythritol, dipentaerythritol, tripentaerythritol, 2 - methyl - 2 - methylol - 1,3 - propanediol (pentaglycerol), 2,2-dimethyl - 1,3 - propanediol (pentaglycol), tetra-(hydroxy ethyl ether) of pentaerythritol, 3 - methyl - 2,2 - dimethylol-1-butanol, and the like.

The acids which may be employed in esterifying the above described alcohols, in accordance with the present invention, are aliphatic monocarboxylic acids containing 8 to 30 carbon atoms per molecule. These acids may contain open or closed, straight or branched chain hydrocarbon groups, and may be saturated or unsaturated, but the acids most preferred are unsaturated open chain acids containing one double bond. It will be understood that the esters which may be employed in accordance with the present invention may be esters in which all of the acid radicals are alike or in which they are different, but it is highly desirable to employ esters in which at least one of the esterifying acid radicals contains a double bond. Examples of suitable acids include lauric, myristic, palmitic, stearic, arachidic, behenic, oleic, erucic, linoleic, undecylenic and homologous acids, also naturally occurring fatty acids and mixtures of fatty acids, such as those derived from coconut oil, palm oil, corn oil, soybean oil, fish oils, cottonseed oil, rapeseed oil, tallow and lard, also oxidized petroleum fractions and oxidized waxes, partially or completely hydrogenated acids of the above types, unsaturated acids produced by the hydrogenation and dehydrogenation of waxes, stearic acid, naphthenic acids, and other acids of similar types.

The esters derived from the alcohols and acids described above are reacted with a combination of the elements sulfur and phosphorus. It is preferable to employ a sulfide of phosphorus, such as P_2S_3, P_2S_5, P_4S_3, or P_4C_7, or mixtures thereof, but mixtures of elemental sulfur and elemental phosphorus may likewise be employed, in which case it is preferable to employ powdered sulfur and white phosphorus. Likewise, a mixture of one or more sulfides of phosphorus and elemental sulfur and/or elemental phosphorus may be employed. The amounts of sulfur and phosphorus which are advantageously employed depend upon the number of double bonds present in the ester in double-bonded hydrocarbon groups, and it is preferred to react from 0.1 to 1 atom of phosphorus and 0.1 to 3 atoms of sulfur for each such double-bond on the ester molecule. In general, the higher proportions of phosphorus and sulfur or sulfide of phosphorus may be employed when the ester molecule contains saturated oil-solubilizing hydrocarbon groups. In general, the tempearture at which the reaction of the sulfide of phosphorus or mixture of sulfur and phosphorus with the ester is carried out is from 200 to 500° F., and the time required to substantially complete the reaction is generally from 1 to 10 hours. It is generally desirable to employ a solvent for the ester, in which case the solvent should be relatively inert to phosphorus and sulfur. Such solvents include, for example, benzene, o-dichlorbenzene, mineral oils, and the like. In preparing an additive for a mineral oil, it is usually convenient to employ such a mineral oil as the medium for the reaction, and thus prepare a concentrate for convenient use in blending with the oil.

As stated above, the reaction products prepared as described may be employed as such or in the form of their metal salts. The metals employed are preferably group II metals and the calcium salts are particularly desirable and convenient to prepare. Such metal salts may be conveniently prepared by reacting the phosphorus and sulfur reaction product with metallic oxides or hydroxides. Such metallic compounds may be added to the reaction mixture in which the phosphorus and sulfur reaction products are formed, and the mixture heated to a temperature of the range of 50–400° F.

The additives of the present invention are preferably added to mineral oils in proportions ranging from 0.01% to 15%, the proportion being preferably about 1.0 to 5.0% when employed as corrosion inhibitors and detergents in mineral lubricating oils. The proportions giving the best results will vary somewhat according to the nature of the additive and the specific quality characteristics of the oil to be improved by the use of the additive. For commercial purposes, when the additives are to be employed in mineral lubricating oils, it is convenient to prepare concentrated oil solutions in which the amount of additive in the compositions ranges from 25 to 50% by weight, and to transport and store them in such form. In preparing lubricating oil compositions for use as crankcase lubricants, the additive concentrate is merely blended with the base oil in the required amount.

Below are given detailed descriptions of preparations of several examples of mineral oil additives of the type described above as well as various laboratory tests which were applied to determine their effectiveness when employed in lubricating oil compositions. It is to be understood that these examples are given to illustrate the present invention and are not to be construed as limiting the scope thereof in any way.

Example 1

(*a*) 565 gms. (2 mols) of oleic acid and 569 gms. (2 mols) of stearic acid were placed in a 3-liter round bottom flask equipped with a mechanical stirrer. A stream of nitrogen was passed through the flask to insure an inert atmosphere. The mechanical stirrer was then started at a vigorous rate and the contents were heated to 302° F. 136 gms. (1 mol) of pentaerythritol was added slowly over a period of 10 minutes. The mixture was then heated at 446° F. for 3½ hours. The product was found to have a neutralization number of 12.11.

(*b*) 400 gms. (0.33 mol) of the mixed oleate-stearate ester of pentaerythritol, prepared as described above, was placed in a 1-liter round bottom flask equipped with a mechanical stirrer. A slow stream of nitrogen was bubbled through the product and the temperature of the contents of the flask was raised to 250° F. 37.3 gms. (0.17 mol) of phosphorus pentasulfide was added slowly over a period of 1 hour, after which the mixture was heated at 300° F. for 3 hours and filtered through a filter aid. The product was blended in an extracted Mid-Continent mineral oil of S. A. E.–20 viscosity grade to form a 40% by weight concentration. This concentrate showed the following analysis:

Phosphorus	percent	0.66
Sulfur	do	2.27
Neutralization No.		16.78

Example 2

(*a*) 568 gms. (2 mols) of stearic acid was placed in a 3-necked flask equipped with a stirrer. Nitrogen was bubbled in slowly and the contents heated to 302° F., after which 68 gms. (0.5 mol) of pentaerythritol was added slowly and the contents then heated to 446° F. for 3½ hours. The product had a neutralization number of 29.07.

(*b*) 200 gms. (0.17 mol) of the above ester was placed in a small 3-necked flask equipped with

a stirrer. Nitrogen was bubbled in slowly and the contents heated to 248° F., after which 18.6 gms. (0.084 mol) of P_2S_5 was added over a period of 1 hour. The temperature was then raised to 302° F. and held at this point for 3 hours. A filter aid was added and the product filtered hot.

Analysis:

Phosphorus ----------percent--	0.25
Sulfur ----------do----	6.37
Neutralization No. ----------	5.14

Example 3

(*a*) 2225 gms. (7.88 mols) of oleic acid was placed in a 5-liter 3-necked flask and heated to 302° F. while bubbling nitrogen through the mixture. 238 gms. (1.75 mols) of pentaerythritol was then added over a period of 10 minutes, after which the temperature was raised gradually over a period of 1 hour to a temperature of 446° F. and held at this point for 4½ hours additional. The product was dissolved in 3 l. of toluene and the solution given three washings with 5% aqueous sodium carbonate solution and three washings with water, and finally evaporated on a steam bath in the presence of nitrogen and filtered through celite. The product consisted of pentaerythritol tetraoleate.

Analysis:

Neutralization No. ----------	1.13
Saponification No. ----------	181.9
Bromine No. ----------	50

(*b*) 200 gms. (0.168 mol) of the pentaerythritol tetraoleate prepared as described above and 328 gms. of a solvent extracted Mid-Continent neutral distillate oil of 44.1 seconds viscosity (Saybolt) at 210° F. was charged into a 2-liter 3-necked flask equipped with a stirrer, a nitrogen inlet tube, thermometer, and gas exit tube. After heating the mixture to 250° F. 18.6 gms. (0.084 mol) of P_2S_5 was added and heating continued to 300° F., at which point it was maintained for 5 hours. The product was filtered while hot through celite, leaving about 2 gms. of unreacted P_2S_5. The product was considered as containing 40% active ingredient.

Analysis:	Percent
Phosphorus ----------	0.94
Sulfur ----------	2.18

Example 4

A 2-liter 3-necked flask equipped as in Example 3(*b*) was charged with 200 gms. (0.168 mol) pentaerythritol tetraoleate (prepared as described in Example 3(*a*)) and 344 gms. of solvent extracted Mid-Continent distillate oil of 44.1 seconds viscosity (Saybolt) at 210° F. and heated to 300° F. 10.7 gms. (0.34 mol) powdered sulfur was then added and the temperature raised to 325° F. where it was maintained for 3 hours and then allowed to drop to 250° F., when 18.6 gms. (0.084 mol) of P_2S_5 was added and the temperature raised again to 300° F. and maintained at this point for three hours. The product was filtered through celite leaving about 2 gms. of unreacted sulfur and P_2S_5. The product contained about 40% active ingredient.

Analysis:	Percent
Phorsphorus ----------	0.84
Sulfur ----------	3.75

Example 5

A preparation was made according to the method of Example 3, except that 0.75 mol of P_2S_5 was used for each mol of pentaerythritol tetraoleate.

Analysis:	Percent
Phosphorus ----------	1.37
Sulfur ----------	3.32

Example 6

(*a*) 229 gms. (0.9 mol) dipentaerythritol, 1654 gms. (5.9 mols) oleic acid, 10 cc. xylene, and 1 gm. calcium hydroxide were charged into a 3-liter 3-necked flask equipped with stirrer, water trap, reflux condenser, thermometer, and nitrogen inlet tube, and the mixture refluxed at 356–446° F. for 9½ hours, during which time 89 cc. of water was collected. The product was then diluted with 1500 cc. toluene and the solution given three washings with 5% aqueous sodium hydroxide and three washings with water and evaporated on the steam bath in the presence of nitrogen. The product consisted of dipentaerythritol hexaoleate.

Analysis:

Neutralization No----------	0.35
Saponificatoin No----------	126.8
Acetyl No----------	2.0

(*b*) The product obtained in (*a*) was reacted with P_2S_5, using 200 gms. (0.109 mol) of dipentaerythritol hexaoleate, 17.9 gms. (0.081 mol) of P_2S_5 and 328 gms. of mineral oil solvent. The preparation was carried out in the manner described in Example 3(*b*), the solvent being the same. The resulting product contained about 40% active ingredient.

Analysis:	Percent
Phosphorus ----------	0.92
Sulfur ----------	2.29

Example 7

Dipentaerythritol hexaoleate (prepared as described in Example 6(*a*)) was reacted with sulfur and P_2S_5 in the proportions of 3 mols of sulfur and 0.75 mol of P_2S_5 for each mol of the ester, the conditions of the preparations being the same as in Example 4, in which 200 gms. dipentaerythritol hexaoleate, 342 gms. of oil solvent, 10.3 gms. sulfur, and 17.9 gms. P_2S_5 were used. The product contained about 40% active ingredient.

Analysis:	Percent
Phosphorus ----------	0.85
Sulfur ----------	3.85

Example 8

100 gms. (0.084 mol) of pentaerythritol tetralinoleate (a commercial product), 9.4 gms. (0.042 mol) P_2S_5 and 164 gms. of the mineral oil solvent employed in Example 3(*b*) were reacted under conditions described in Example 3(*b*). The product contained about 40% active ingredient.

Analysis:	Percent
Phosphorus ----------	0.89
Sulfur ----------	2.12

Example 9

100 gms. (0.073 mol) of the tetraoleate of pentaerythritol hydroxy ethyl ether (commercial product), 8.1 gms. (0.037 mol) of P_2S_5, and 162 gms. of the solvent employed in Example 3(*b*) were reacted under the conditions of Example 3(*b*), the product containing about 40% active ingredient.

Analysis:	Percent
Phosphorus ----------	0.81
Sulfur ----------	2.17

Example 10

200 gms. of the 40% oil concentrate product of Example 1(*b*) were charged into a 1-liter, 3-necked flask equipped with stirrer, thermometer, and gas inlet and exit tubes. To this was added 5.3 gms. of calcium hydroxide and the mixture heated at 200–250° F. for 4 hours and filtered through Hy-flo, a filter aid.

Analysis:	Percent
Ash	1.70
Calcium	0.31

Example 11

The calcium salt of the product of Example 3(*b*) was prepared in the manner described in Example 10, using 200 gms. of the reaction product and 5 gms. of calcium hydroxide.

Analysis:	Percent
Ash	0.63
Calcium	0.098

Example 12

The calcium salt of the product of Example 4 was prepared in the manner described in Example 10, using the same weight proportions of reaction product and calcium hydroxide.

Analysis:	Percent
Ash	0.42
Calcium	0.059

Example 13

The calcium salt of the product of Example 5 was similarly prepared.

Analysis:	Percent
Ash	0.41
Calcium	0.034

Example 14

The calcium salt of the product of Example 6(*b*) was similarly prepared.

Analysis:	Percent
Ash	0.10
Calcium	0.012

Example 15

The calcium salt of the product of Example 7 was similarly prepared.

Analysis:	Percent
Ash	0.07
Calcium	0.007

Example 16

The potassium salt of the product of Example 1(*b*) was similarly prepared, using 162 gms. of the said product, 162 gms. of the same diluent, and 5.5 gms. of finely ground potassium sulfide. The mixture was heated at 350° F. for two hours and filtered through Hy-flo.

Analysis:	Percent
Ash	1.26
Potassium	0.50

Example 17.—Carbon black dispersion test

In this test, which is used to measure the dispersive power of the lubricating oils, 500 cc. of a 1% blend of the active ingredient in a solvent extracted Mid-Continent paraffinic oil of 52 seconds viscosity (Saybolt) at 210° F. is agitated with 6% by weight of carbon black and allowed to settle for 24 hours at 200° F. For comparison a similar amount of unblended base oil is similarly treated. The test was applied to the products of Example 1(*b*) and Example 16. Since these products are 40% oil concentrates, 2.5% by weight of each was employed in preparing the blends for the test. The results are shown in Table I.

TABLE I

Oil	Observation After 24 Hours	
	Ccs. of Clear Oil	Ccs. of Dispersion
Base Oil	160	340
Base Oil+1% Pentaerythritol oleate-stearate-P_2S_5 reaction product	0	500
Base Oil+1% Potassium salt of pentaerythritol oleate-stearate-P_2S_5 reaction product	0	500

Example 18.—Indiana oxidation test

In this test a glass plate is inserted in the test oil and the weight of the varnish film deposited on the plate during 48 hours is measured. The oil during the test is held at 341° F., and air is passed through the oil at the rate of 10 liters per hour. This test was applied to a base oil consisting of a solvent extracted Mid-Continent oil of S. A. E.–20 grade and to a blend of this oil and 2.5% of the 40% concentrate product of Example 10. The results are as follows.

TABLE II

Oil	Varnish on Glass Plate (mg.)
Base Oil	3.0
Base Oil+2.5% product of Example 10	1.5

Example 19.—Laboratory bearing corrosion test

Blends were made of the products (40% concentrates in oil) of Examples 1 to 15, inclusive, in a lubricating oil base consisting of a well refined, solvent extracted paraffinic mineral lubricating oil of S. A. E.–20 viscosity grade in such proportions that in each case a blend was prepared containing 0.25% of the active ingredient. These blends and a sample of the unblended base oil were submitted to a corrosion test designed to test the effectiveness of the additive in inhibiting corrosion of a typical copper-lead bearing.

In this test 500 cc. of the oil was placed in a glass oxidation tube (13 inches long and 2⅝ inches in diameter) fitted at the bottom with a ¼ inch air inlet tube perforated to facilitate air distribution. The oxidation tube was then immersed in a heating bath so that the oil temperature was maintained at 325° F. during the test. Two quarter secions of automotive bearings of copper-lead alloy of known weight having a total area of 25 sq. cm. were attached to opposite sides of a stainless steel rod which was then immersed in the test oil and rotated at 600 R. P. M., thus providing sufficient agitation of the sample during the test. Air was then blown through the oil at the rate of 2 cu. ft. per hour. At the end of each 4-hour period the bearings were removed, washed with naphtha and weighed to determine the amount of loss by corrosion. The bearings were then repolished (to increase the severity of the test), reweighed, and then subjected to the test for additional 4-hour periods in like manner. The results are given in Table III below as "corrosion life," which indi-

cates the number of hours required for the bearings to lose 100 mg. in weight, determined by interpolation of the data obtained in the various periods.

Example 20.—Copper strip test

Each of the products of Examples 3 to 15 was blended in a lubricating oil base consisting of a solvent extracted Mid-Continent neutral distillate of 44.1 seconds viscosity (Saybolt) at 210° F., in an amount sufficient to form a blend containing 0.75% of active ingredient. These blends and a sample of the unblended base oil were submitted to a copper strip corrosion test which was a modification of C. R. C. method L–16–445. This method comprises immersing a polished metallic copper strip in the oil blend to be tested for periods of ½ and 3 hours at 212° F. and noting the extent of staining. Numerical ratings from 1 to 10 denote discoloration ranging from no staining to a black surface film, respectively.

The results of the tests described in Examples 19 and 20 are given in Table III, which follows.

TABLE III

Additive Prep.	Ester Treated	Mol Ratio, Ester/P_2S_5	Mol Ratio, Ester/S	Bearing Corrosion Life (Hrs.)	Copper Strip Corrosion Test	
					½ Hr.	3 Hr.
None	None			9	2	2
Example 1 (b)	Pentaerythritol Oleate-Stearate	1:0.5		21		
Example 2 (b)	Pentaerythritol Stearate	1:0.5		13		
Example 3 (b)	Pentaerythritol Tetraoleate	1:0.5		14	2	2
Example 4	do	1:0.5	1:2	18	2	2
Example 5	do	1:0.75		18	3	3
Example 6 (b)	Dipentaerythritol Hexaoleate	1:0.75		14	4	7
Example 7	do	1:0.75	1:3	20	2	2
Example 8	Pentaerythritol Tetralinoleate	1:0.5		14	3	7
Example 9	Tetraoleate of Pentaerythritol Hydroxy Ethyl Ether.	1:0.5		13	3	3
Example 10 [1]	Pentaerythritol Oleate-Stearate	1:0.5		22		
Example 11 [1]	Pentaerythritol Tetraoleate	1:0.5		17	3	3
Example 12 [1]	do	1:0.5	1:2	14	2	2
Example 13 [1]	do	1:0.75		32	3	4
Example 14 [1]	Dipentaerythritol Hexaoleate	1:0.75		13	4	7
Example 15 [1]	do	1:0.75	1:3	18	2	3
Example 16 [2]	Pentaerythritol Oleate-Stearate	1:0.5		34		

[1] Calcium salt.
[2] Potassium salt.

The products of the present invention may be employed not only in ordinary hydrocarbon lubricating oils but also in the "heavy duty" type of lubricating oils which have been compounded with such detergent type additives as metal soaps, metal petroleum sulfonates, metal phenates, metal alcoholates, metal alkyl phenol sulfides, metal organo phosphates, phosphites, thiophosphates and thiophosphites, guanidine salts, metal xanthates and thioxanthates, metal thiocarbamates, and the like. Other types of additives, such as phenols and phenol sulfides, may also be present.

The lubricating oil base stocks used in the compositions of this invention may be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced by solvent extraction with solvents such as phenol, sulfur dioxide, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed in admixtures with mineral oils.

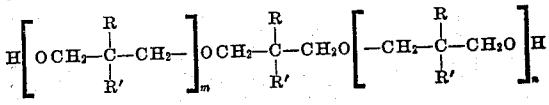
For the best results of base stock chosen should normally be an oil which with the new additive present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils, no strict rule can be laid down for the choice of the base stock. The additives are normally sufficiently soluble in the base stock, but in some cases auxiliary solvent agents may be used. The lubricating oils will usually range from about 40 to 150 seconds (Saybolt) viscosity at 210° F. The viscosity index may range from 0 to 100 or even higher.

Other agents than those which have been mentioned may be present in the oil composition, such as dyes, pour point depressants, heat thickened fatty oils, sulfurized fatty oils, sludge dispersers, anti-oxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, and the like.

Assisting agents which are particularly desirable as plasticizers and defoamers are the higher alcohols having preferably 8–20 carbon atoms, e. g., octyl alcohol, lauryl alcohol, stearyl alcohol, and the like.

What is claimed is:

1. A mineral oil containing dissolved therein 0.01 to 15% of a member of the class consisting of: (A) the products obtained by reacting a combination of the elements sulfur and phosphorus with an ester of an alcohol selected from the group consisting of alcohols of the formula

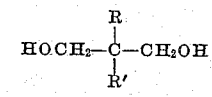


in which R is a member of the group consisting of methylol radicals and alkyl radicals containing 1 to 3 carbon atoms, R′ is a member of the group consisting of methyl and methylol radicals, and m and n are numbers from 0 to 2, said ester being derived from said alcohol by substituting all of the free hydroxyl groups thereof with radicals of monobasic carboxylic acids containin 8 to 30 carbon atoms per molecule; and (B) salts of said products and a metal selected from groups I and II of the periodic table; the re-

actants being employed in such proportions that from 0.2 to 0.4 atom of phosphorus and 0.5 to 1 atom of sulfur are present for each acid radical present in the ester, and the reaction being conducted at a temperature in the range of about 200° to about 300° F.

2. A composition according to claim 1 in which the mineral oil is a lubricating oil fraction.

3. A mineral oil containing dissolved therein 0.01 to 15% of the product obtained by reacting a combination of the elements sulfur and phosphorus with an ester of an alcohol of the formula



in which R is a member of the group consisting of methylol groups and alkyl groups containing 1 to 3 carbon atoms, and R′ is a member of the group consisting of methyl and methylol groups, said ester being derived from said alcohol by substituting all of the free hydroxyl groups with radicals of monobasic carboxylic acids containing 8 to 30 carbon atoms per molecule, at least one such radical containing a double bonded hydrocarbon chain, the reactants being employed in such proportions that from 0.1 to 1 atom of phosphorus and 0.1 to 3 atoms of sulfur are present for each double bonded hydrocarbon chain in the ester molecule, and the reaction being conducted at a temperature in the range of about 200° to about 300° F.

4. A composition according to claim 3 in which the mineral oil is a lubricating oil fraction.

5. A composition according to claim 3 in which the alcohol from which the ester is derived is pentaerythritol.

6. A composition according to claim 5 in which all of the acid radicals of the ester are unsaturated radicals.

7. A composition according to claim 5 in which the ester is pentaerythritol tetraoleate.

8. A mineral lubricating oil containing dissolved therein 0.01 to 15% of a product obtained by reacting about one molecular proportion of pentaerythritol tetraoleate with about 0.5 to 0.75 molecular proportion of phosphorus pentasulfide at a temperature in the range of about 200° to about 300° F.

9. A mineral lubricating oil containing dissolved therein 0.01 to 15% of a product obtained by reacting one molecular proportion of pentaerythritol tetraoleate with 0.5 molecular proportion of phosphorus pentasulfide at a temperature of 250 to 300° F.

10. A mineral lubricating oil containing dissolved therein 0.01 to 15% of a product obtained by reacting one molecular proportion of dipentaerythritol hexaoleate with 0.75 molecular proportion of phosphorus pentasulfide at a temperature of about 250 to 300° F.

11. A composition according to claim 3 in which the additive is a group II metal salt of the reaction product defined in said claim.

12. A composition according to claim 11 in which the metal is calcium.

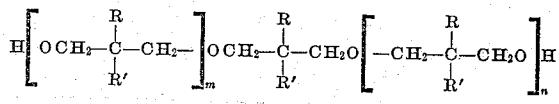
13. A mineral lubricating oil containing dissolved therein 0.1 to 15% of the calcium salt of a product obtained by reacting about one molecular proportion of pentaerythritol tetraoleate with about 0.5 to 0.75 molecular proportion of phosphorus pentasulfide at a temperature in the range of about 200° to about 300° F.

14. A mineral lubricating oil containing dissolved therein 0.01 to 15% of the calcium salt of the product obtained by reacting one molecular proportion of pentaerythritol tetraoleate with 0.75 molecular proportion of phosphorus pentasulfide at a temperature of about 250 to 300° F.

15. A composition consisting essentially of a mineral lubricating oil and an additive as defined in claim 1, the amount of said additive in the composition being 25 to 50% by weight.

16. A composition consisting essentially of a mineral lubricating oil and an additive as defined in claim 14, the amount of said additive in the composition being 25 to 50% by weight.

17. As a new composition of matter a member of the class consisting of: (A) the products obtained by reacting a combination of the elements sulfur and phosphorus with an ester of an alcohol selected from the group consisting of alcohols of the formula



in which R is a member of the group consisting of methylol radicals and alkyl radicals containing 1 to 3 carbon atoms, R′ is a member of the group consisting of methyl and methylol radicals, and m and n are numbers from 0 to 2, said ester being derived from said alcohol by substituting all of the free hydroxyl groups thereof with radicals of monobasic carboxylic acids containing 8 to 30 carbon atoms per molecule; and (B) salts of said products and a metal selected from groups I and II of the periodic table; the reactants being employed in such proportions that from 0.2 to 0.4 atom of phosphorus and from 0.5 to 1 atom of sulfur are present for each acid radical in the ester molecule, and the reaction being conducted at a temperature in the range of about 200° to about 300° F.

18. As a new composition of matter a product obtained by reacting a sulfide of phosphorus with pentaerythritol tetraoleate, the proportions of the reactants being such that about 0.2 to about 0.4 atom of phosphorus and 0.5 to 1 atom of sulfur are present for each acid radical in the ester molecule, the reaction being conducted at a temperature in the range of about 200° to about 300° F.

19. As a new composition of matter the calcium salt of the reaction product as defined in claim 18.

JEFFREY H. BARTLETT.
THOMAS CROSS, JR.

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