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MINERAL OIL COMPOSITION

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13 Claims. (Cl. 252—32.7)

1

This invention has to do with mineral oil compositions and is more particularly related to compositions comprised of mineral oil and a characterizing agent which will improve the oil in one or more respects.

It is well known to those familiar with the art that mineral oil fractions refined for various uses are in and of themselves usually deficient in one or more respects, such that their practical utility is limited even in the particular field for which they have been refined. For example, mineral oil fractions refined for use as lubricants have a tendency to oxidize under conditions of use with the formation of sludge or acidic oxidation products; also the lighter fractions such as gasoline and kerosene tend to oxidize with the formation of color bodies, gum, etc. In order to prevent the formation of these products and thereby extend the useful life of the oil fraction, it is common practice to blend with such oil fractions an additive material which has the effect of inhibiting oxidation, such a material being known in the trade as an oxidation inhibitor, a sludge inhibitor, a gum inhibitor, etc.

It is also the practice to add other materials to mineral oil fractions for the purpose of improving "oiliness" characteristics and the wear-reducing action of such mineral oils when they are used as lubricants, particularly when the oils are used for the purpose of lubricating metal surfaces which are engaged under extremely high pressures and at high rubbing speeds.

Various other materials have been developed for the purpose of depressing the pour point of mineral oil fractions which have been refined for use as lubricants. Most refining treatments provide oils containing a small amount of wax which, without the added material, tend to crystallize at temperatures which render the oil impracticable for use under low temperature conditions. Additive agents have also been developed for improving the viscosity index of lubricating oil fractions. In the case of internal combustion engines, particularly those operating with high cylinder pressures, there is a decided tendency for the ordinary oil fractions to form carbonaceous deposits which cause the piston rings to stick in their slots and which fill the slots in the oil ring or rings, thus materially reducing the efficiency of the engine. Materials have been developed which, when added to the oil, will reduce this normal tendency of the oil to form deposits.

It has also been discovered that certain types of hard metal alloy bearings, such as cadmium-silver alloy bearings, are attacked by ingredients in certain types of oils, particularly oils of high viscosity index obtained by various methods of solvent-refining. This corrosive action has led to the development of corrosion inhibitors which may be used in solvent-refined oils to protect such bearing metals.

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In the lighter mineral oil fractions, such as those used for fuel purposes, particularly in internal combustion engines, it has been found that the combustion characteristics of the fuel may be controlled and improved by adding minor proportions of various improving agents thereto.

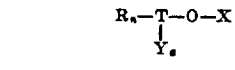
The various characterizing materials which have been developed for use in mineral oil fractions to improve the same in the several respects enumerated above are largely specific to their particular applications. Therefore, it has generally been the practice to add a separate material for each of the improvements to be effected.

The present invention is predicated upon the discovery of a class or group of oil-soluble reaction products or compounds which, when added to mineral oil fractions in minor proportions, will improve the oil fractions in several respects. These multi-functional reaction products or compounds are acidic, contain phosphorus, sulfur and nitrogen, and are formed by the reaction of a phosphorus sulfide and a phosphorus amine of an alkyl-substituted hydroxyaromatic compound. Contemplated also as coming within the class of phosphorus-, sulfur- and nitrogen-containing reaction products are the metal, ammonium and organic amine derivatives thereof.

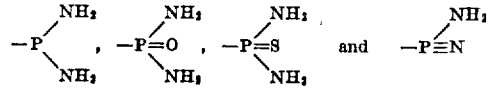
While any of the well known phosphorus sulfides, such as P_2S_3, P_2S_5, P_4S_3, P_4S_7, etc., may be used in the preparation of the compounds or reaction products contemplated herein P_2S_5 is preferred.

The phosphorus amines of alkyl-substituted hydroxyaromatic compounds from which the reaction products or compounds of this invention are obtained may be represented by general Formulae I and II:

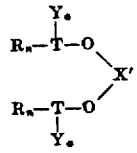
I



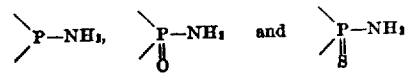
wherein X is a phosphorus amino group selected from the group consisting of:



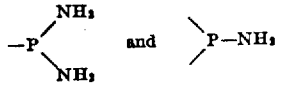
II



wherein X' is a phosphorus amine group selected from the group consisting of:



of these groups of general Formulae I and II, groups



are preferred; T is an aromatic nucleus, either mono- or poly-cyclic; R is an oil-solubilizing aliphatic or alkyl hydrocarbon group or groups, which preferably contains a total of ten or more carbon atoms, and especially preferred of such groups is one having at least twenty carbon atoms, such as an aliphatic "wax" group, and is attached by one valence only to at least one aromatic nucleus T; n is a small whole number from 1 to 4; Y is selected from the group consisting of hydroxyl, mercapto, mercaptal, mercaptol, keto, thioketo, alkoxy, aroxy, thioether, polysulfide, aralkyl, alkyl, alkaryl, aryl, hydrogen, nitro, nitroso, N-thio, cyano, cyanate and thiocyanate radicals; a is an integer, preferably from 0 to 3, and represents the number of Y substituents occupying the unsatisfied positions on the nucleus T.

It will be understood that when substituents like —OH, —SH and keto groups are present in a phosphorus amine of an alkyl-substituted hydroxyaromatic compound before reaction with a phosphorus sulfide, that they may in some instances also react with the phosphorus sulfide. In all cases, however, the predominant reaction is that which takes place between the phosphorus sulfide and a phosphorus amino group, (X or X'), as defined above.

As indicated hereinabove, the metal, ammonium and organic amine salts of the compounds or reaction products of phosphorus sulfides and phosphorus amines of alkyl-substituted hydroxyaromatic compounds are also contemplated herein. The ammonium salts, as will be clear, are obtained by reacting ammonia gas with the aforesaid reaction products. Organic salts such as amine salts are obtained by reacting an amine such as diamylamine and the reaction product together at suitable temperatures, such as 200° F. The metals which may be incorporated into our compounds or reaction products may be broadly classified as the metals of groups 1 to 8 inclusive of Mendeléeff's Periodic System. These metals comprise the following: alkali metals, lithium, sodium, potassium, rubidium and caesium; the alkaline earth group, beryllium, magnesium, calcium, strontium and barium; the metals zinc, cadmium, mercury, scandium; the metals aluminum, gallium, indium, thallium, titanium, zirconium, cerium, thorium, germanium, tin and lead; vanadium, columbium and tantalum; arsenic, antimony and bismuth; chromium, molybdenum, tungsten and uranium; rhenium, manganese, iron, cobalt and nickel; ruthenium, rhodium and palladium; osmium, iridium and platinum.

Some of the rare earth metals are given in the foregoing list of metal substituents. Other rare earth metals suitable for the metal type materials are those of the cerium and yttrium groups, namely a mixture of praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thallium and lutecium.

Particularly preferred of such metals, however, are the metals barium, calcium and zinc.

As described above in connection with general Formula I, the symbol T represents an aromatic nucleus which may be mono- or poly-cyclic. Typical nuclei contemplated herein are those of the compounds benzene, naphthalene, anthracene, phenanthrene, diphenyl, etc.

The compounds or reaction products of this invention contain, as aforesaid, at least one oil-solubilizing substituent such as an alkyl group. Oil solubility is imparted to our compounds or reaction products with an alkyl substituent, such substituent or substituents containing at least ten carbon atoms in alkyl groups such, for example, as one decyl group or two amyl groups. Within this general group of alkyl substituents preference is given to long-chain high molecular weight aliphatic hydrocarbon groups, because reaction products or compounds characterized by an aryl group having the latter alkyl substituents are not only oil soluble but possess the added properties of improving the pour point and viscosity index of the oil to which they are added. Petroleum wax is a preferred source of the high molecular weight alkyl substituent and, for this reason, the preferred multi-functional reaction products are referred to as "wax" substituted. It is to be understood, however, that other equivalent long-chain aliphatic compounds such as ester waxes, high molecular weight alcohols, aliphatic polymers, etc., may be utilized. In compounds or reaction products of the preferred sub-class, that is, those containing a wax substituent, the wax group cooperates with the aryl nucleus to which it is attached and cooperates with the other substituents on the aryl nucleus to impart pour depressing and viscosity index improving properties to these agents. These preferred alkyl-substituted compounds or reaction products are capable of remaining uniformly dispersed in mineral oil either as a true solution or as a colloidal suspension under normal conditions of handling and use. There appears to be, however, a critical zone or region in the degree of alkyl- or wax-substitution below which these compounds or reaction products are not readily soluble in viscous mineral oil fractions. This degree of alkyl—or wax—substitution for our oil-soluble or oil-miscible reaction products or compounds, which may or may not contain a metal substituent, may vary over relatively wide limits, depending upon whether the aryl nucleus is mono- or poly-cyclic and whether such nucleus carries other substituents such as represented above by Y.

In the event chlorinated paraffin wax (or a chlorinated hydrocarbon of the type which characterizes chlorinated paraffin wax) is used as the alkylating agent for introducing an alkyl group into a hydroxy-substituted aryl nucleus (T—OH), the product obtained is referred to as wax substituted. To further identify these wax-substituted products, we have adopted the convenient designation (A—B), indicating with (A) the number of atomic proportions of chlorine in the chlorinated wax reacted with one mol of phenol,

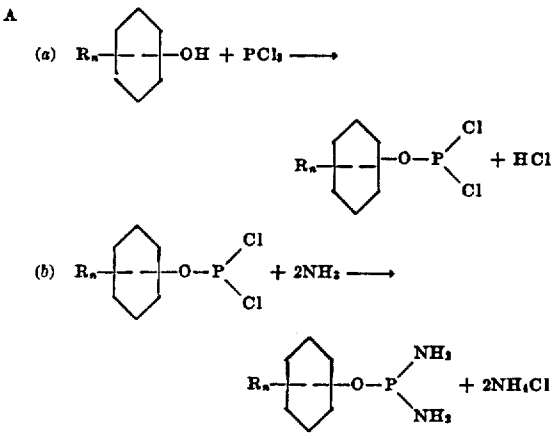
and indicating with (B) the percentage of chlorine in the chlorinated wax. Thus, wax-phenol (3–16) indicates that the wax-phenol is obtained by reacting one mol of phenol with a quantity of chlorinated wax of 16% chlorine content containing three atomic proportions of chlorine. This designation is resorted to herein in describing the phosphorus amines of wax-substituted hydroxyaromatic compounds used in the preparation of the preferred compounds or reaction products contemplated herein and is also resorted to in describing the phosphorus sulfide reaction products thereof (together with their salts).

It should also be understood that the wax group in the preferred sub-class may be polyvalent in nature, in which event each of the polyvalent wax radicals or groups will be attached to a plurality of the aryl nuclei.

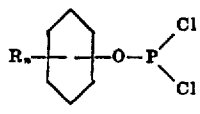
With regard to the number of other groups which may be attached to the aryl nuclei, this will vary with the extent to which it is desired to effect substitution of the nucleus with the alkyl or wax derivatives for obtaining the desired properties in the product. It is, of course, limited to the number of replaceable hydrogen atoms of an aromatic nucleus which are available for substitution. As will be apparent to those skilled in the art, the maximum number of R groups which can be attached to a single aromatic nucleus will vary as the nucleus is mono- or poly-cyclic and also as the nucleus is otherwise substituted.

The phosphorus amines represented above by general Formulae I and II may be prepared by any one of several methods well known to those familiar with the art. Preferred, however, are those phosphorus amines prepared by reaction of an alkyl-substituted hydroxyaromatic compound or alkali metal salt thereof with a phosphorus halide such as PCl_3, PCl_5, $POCl_3$; $PSCl_3$ and $PNCl_2$, followed by reaction with ammonia. By way of illustration, the preparation of a phosphorus amine derived from the preferred phosphorus halide, PCl_3, is represented in Equation A following:

A



In forming the product

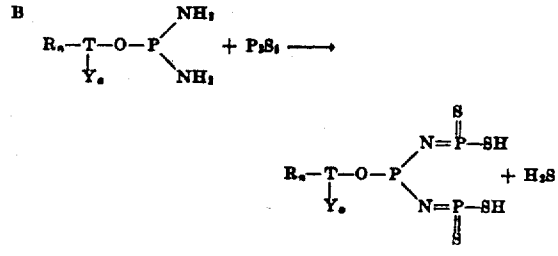


PCl_3 may be used in excess of a molar concentration; the excess of PCl_3 is then removed by distillation before introducing ammonia.

As aforesaid, the compounds or reaction products contemplated herein are all characterized

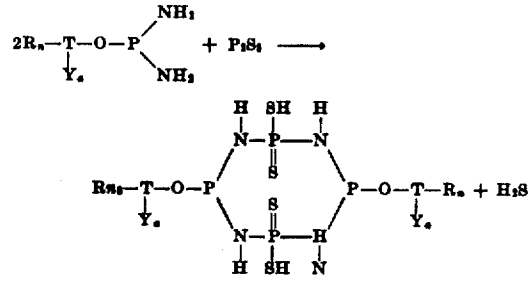
by the presence of substantial amounts of phosphorus, sulfur and nitrogen therein. For example, when 1 mol of a phosphorus amine (Equation A) of an alkyl-substituted hydroxyaromatic compound is reacted with substantially 1 mol of P_2S_5 as described hereinafter, it is most probable that the reaction product is predominantly comprised of a phosphorus-, sulfur- and nitrogen-containing product shown in Equation B below:

B



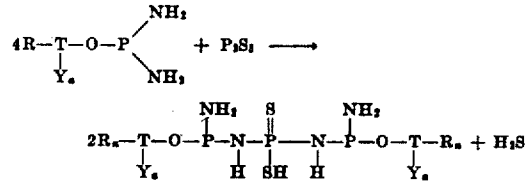
With a ratio of 2:1 (phosphorus amine: P_2S_5), the predominant reaction most probably is that represented in Equation C below:

C



In the event, however, that the molar ratio is about 4:1, the predominant reaction product most probably is that shown in Equation D following:

D



It will be clear from the foregoing that the molar ratio of reactants can be varied in order to control, to an appreciable degree, the amount of phosphorus, sulfur and nitrogen in our compounds or reaction products. Products obtained, however, with a molar ratio of from 1:1 to 4:1 (phosphorus amine: P_2S_5) are preferred. It will also be clear that when the phosphorus amine reactant is other than the preferred reactant shown in Equations A through C above, the reaction products will correspondingly differ in character. It will further be understood that, as indicated hereinabove, certain Y substituents are also capable of reacting with phosphorus sulfides, thereby influencing the character of the final products.

The reaction temperatures and reaction times used in preparing the products of this invention may be varied considerably. The most desirable conditions are those shown in the illustrative examples provided hereinbelow.

In order to more fully demonstrate the reaction products contemplated herein as mineral oil improving agents the following illustrative examples of preferred reaction products are described below.

EXAMPLE I

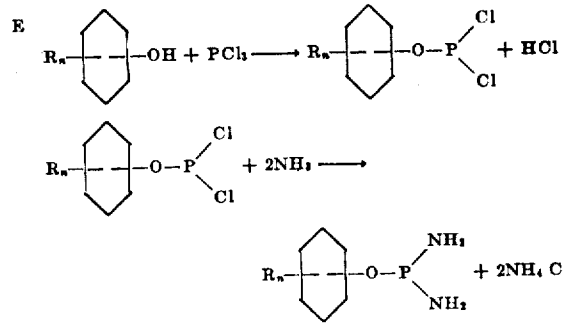
Reaction Product of P_2S_5 and Phospho-Amino Derivative of Alkyl-Substituted Phenol

(a) Preparation of phospho-amino derivative of alkyl-substituted phenol

Six hundred grams of 1:2 mineral oil blend of wax-phenol (3–14), prepared as described in Reiff Patent 2,191,498, is heated to 50° C. and 35 grams of PCl_3 are added slowly thereto with stirring. The temperature is raised to 100° C. and maintained for one hour to insure reaction, whereby the phosphorus dichloride derivative is formed. The phospho-amino derivative is then formed by introducing gaseous ammonia into the reaction mixture obtained above, ammonia being run into the reaction mixture until a slight excess is indicated by test with wet litmus paper.

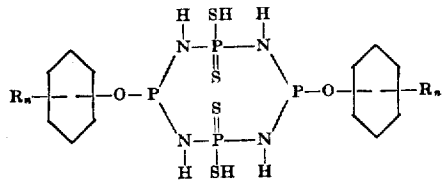
In order to facilitate the reaction with P_2S_5 and to form a light-colored product, it is desirable to remove ammonium chloride formed in the preceding operation. This is accomplished by adding to the reaction mixture 100 cc. of butanol and 10 cc. of water, and stirring the resultant mixture for about one hour. Butanol and water are then removed by heating the latter mixture to about 180° C. During this treatment, ammonium chloride is precipitated and is removed by filtering the mixture through "Hi Flo," a diatomaceous earth which is substantially 100% silica.

The reactions involved in the formation of the alkyl-substituted, phospho-amino phenol are the following:



(b) Preparation of reaction product of P_2S_5 and (a)

The product obtained in (a) is reacted with 28.4 grams of P_2S_5 (½ mol) for 4 hours at about 175° C., then mixed with "Hi Flo," a diatomaceous earth which is substantially 100% silica, and filtered to form the final product. The amount of P_2S_5 used here corresponds to Equation B shown above. The product, in mineral oil, is characterized by the following: phosphorus, 2.0%; sulfur, 2.5%; nitrogen, 0.4%; and neutralization number 20.0 (titration in 50% ethyl alcohol-water mixture with phenol-phthalein indicator). The predominant compound in the product is believed to be:



The product is referred to hereinafter as product I.

EXAMPLE II

Barium Salt of Product I

The barium salt of product I can be readily prepared by reaction of said product with barium hydroxide. This is accomplished by adding 60 cc. of butanol and 77 grams of $Ba(OH)_2.8H_2O$ to 630 grams of product I and, with rapid stirring, heating the resultant mixture to 150° C. The barium salt thus formed is then mixed with "Hi Flo," a diatomaceous earth which is substantially 100% silica, and filtered, and then steamed at 150° C. until an amount, equivalent to the volume of the reaction product, of water is collected from the steaming operation. By this means, odoriferous by-products and all traces of butanol are removed. The final product, which is approximately a 1:2 blend in mineral oil, analyzes as follows: barium, 4.0%; phosphorus, 2.0%; sulfur, 2.3%; and nitrogen, 0.4%. This product is referred to hereinafter as product II.

While the use of an hydroxide is the preferred method of forming the barium salt, the salts of other metals, and the barium salts as well, can be formed by using an alcoholate of the desired metal or can be formed by double decomposition of the sodium salt of the phosphorus sulfide reaction products—which are formed by reaction with sodium butylate—with a chloride of the desired metal. These reactions are preferably carried out with butanol as the solvent in order to obtain suitable mixing of the reactants.

EXAMPLE III

Calcium Salt of Product I

A quantity (630 grams) of product I, obtained as described in Example I, is reacted with 28.4 grams of $CaCl_2$ and a sodium butylate containing 12 grams of sodium. The calcium salt is formed by heating the reaction mixture thus obtained to 150° C., whereupon substantially all of the butanol, released in the reaction, is removed, followed by steaming the butanol-free mixture at 150° C. as described in Example II above. The reaction mixture is then filtered with the aid of "Hi Flo," a diatomaceous earth which is substantially 100% silica, in order to obtain the finished product in approximately a 1:2 mineral oil blend. The product—product III—analyzes as follows: calcium, 1.2%; sulfur, 2.2%; phosphorus, 2.0%; and nitrogen, 0.4%.

EXAMPLE IV

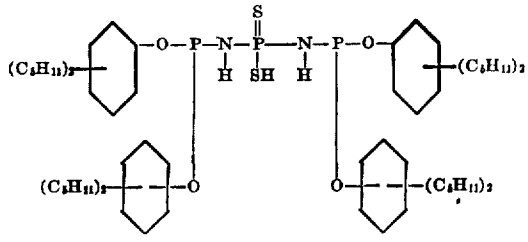
Zinc Salt of Product I

The zinc salt of product I is readily formed by double decomposition of zinc chloride in solution in butanol with the sodium salt of product I, or by reaction of zinc butylate with product I. The zinc salt is generally formed by adding a butanol solution of zinc chloride to product I, followed by addition of an equivalent amount of sodium butylate. A quantity (630 grams) of product I, obtained as described in Example I, is reacted with 34.8 grams of zinc chloride and 12 grams of sodium in the form of sodium butylate. The reaction is carried out as described in Example III above. The zinc salt thus obtained is approximately a 1:2 mineral oil blend and is characterized as follows: zinc, 2.1%; sulfur, 2.2%; phosphorus, 2.0%; and nitrogen, 0.4%. This product is identified as product IV.

EXAMPLE V

REACTION PRODUCT OF P_2S_5 AND PHOSPHO-AMINO DERIVATIVE OF DIAMYLPHENOL

This product was obtained by reaction of 900 grams of a 1:2 mineral oil blend of mixed diamylphenols (1.28 mol), 90 grams (0.64 mol) of PCl_3, ammonia gas and 71 grams (0.25 mol) of P_2S_5, as described in Example I (*a*) and (*b*). The product—product V—so obtained is believed to be predominantly comprised of the following compound:



EXAMPLE VI

BARIUM SALT OF PRODUCT V

Prior to reaction with barium hydroxide, product V, was desalted with butanol and water, as described in Example I (*a*) and (*b*), and steamed, as described in Example II. A quantity (960 grams) of product V so treated is then reacted with 70 grams of $Ba(OH)_2.8H_2O$ at 150° C. The finished product, in approximately a 1:2 mineral oil blend, is obtained by filtering the reaction product in the presence of "Hi Flo," a diatomaceous earth which is substantially 100% silica. Analysis of the 1:2 mineral oil blend showed: barium, 3.0%; sulfur, 5.0%; phosphorus, 4.0%; and nitrogen 0.4%.

It will be apparent to those skilled in the art that the compounds or reaction products contemplated herein, and illustrated hereinabove by products I through VI, can be obtained in the free state rather than in mineral oil blends as above. All that is necessary in this regard is the substitution of a diluent such as kerosene, Stoddard's solvent, etc., for the mineral oil diluent used in the foregoing examples, followed by removal of said diluent after the reactions have been completed. It is to be understood, therefore, that such compounds or reaction products are contemplated herein as new compositions of matter.

To demonstrate the effectiveness of the compounds or reaction products of the type described above and illustrated by the foregoing examples, in the mineral oil compositions contemplated by this invention, we have conducted several comparative tests, the results of which are listed below, with representative mineral oils alone and with the same oils blended with the preferred reaction products prepared in the foregoing examples. The concentration of additive in the oil is based on the weight per cent of the pure compound contained in the concentrated oil blends.

Pour point depression

This series of tests was conducted with a mineral lubricating oil fraction having a Saybolt viscosity of 67 seconds at 210° F. and an A. S. T. M. pour point of 20° F. The results of these tests are listed below in Table 1.

TABLE 1

Improving Agent	Conc. by Wt. (Per cent)	A. S. T. M. Pour Point (° F.)
None	0	+20
Product I	0.125	−25
Product II	0.125	−25
Product III	0.125	−25
Product IV	0.125	−25

Viscosity index improvement

The improvement obtained by the mineral oil addition agents contemplated herein in the viscosity index of a mineral oil to which they are added is clearly shown by the illustrative data in Table 2 below.

TABLE 2

Improving Agent	Conc. by Wt. (Per cent)	Kinematic Viscosity		V. I.
		100° F.	210° F.	
None	0	30.55	4.82	78.5
Product I	1	32.11	5.01	84.4
Product II	1	31.87	5.02	87.2
Product III	1	32.71	5.12	89.7
Product IV	1	32.12	5.06	89.0

Corrosion inhibition

A motor oil and blends of the same containing preferred improving agents of the type contemplated herein were also tested in a single-cylinder Lauson engine which was operated for 36 hours at an oil temperature at 290° F. and a jacket temperature of 212° F. The motor oil used was a solvent-refined oil having a Saybolt viscosity of 45 seconds at 210° F. (a kinematic viscosity of 5.8 centistokes at 210° F.). The oil blends used were blends of the said oil and said prepared improving agents. After 36 hours the acidity (as measured by the neutralization number, N. N.) and the kinematic viscosity of the oil and of the oil blends were measured. The results are shown in Table 3 below:

TABLE 3

Improving Agent	Conc. by Wt. (Per cent)	N. N.	Kin. Vis. at 210° F.
None	0	10.0	12.71
Product I	1	2.9	6.93
Product II	1	0.75	6.57
Product IV	1	4.7	8.22

Operation test

In addition to the foregoing tests, comparative tests have also been made between an oil and oil blends of the same oil containing representative improving agents of the type contemplated herein to determine the comparative behavior of the unblended oil and of the blended oils under actual operating conditions. The test was carried out in a single cylinder C. F. R. engine operated continuously over a time interval of 28 hours with a cooling medium held at a temperature of about 390° F. and the oil temperature held at about 150° F. The engine was operated at a speed of 1200 R. P. M.

The oil used in these tests was a motor oil of 120 seconds Saybolt viscosity at 210° F., and the conditions observed therein were: (*a*) the extent to which the piston rings were stuck; (*b*) the extent to which the slots in the oil rings were filled with deposit; (*c*) the amount of carbona-

ceous deposits in the oil; and (*d*) the acidity or neutralization number (N. N.) of the oil. The results obtained in this test are set forth in Table 4 below:

TABLE 4

Improving Agent	Conc. by Wt. (Per cent)	Ring Condition								Carbon Deposits	N. N.
		Degrees Struck					Slots Filled				
		1	2	3	4	5	3	4	5		
None	0	360	360	360	360	360	60	70	70	14.0	2.4
Product I	1	0	0	0	0	0	5	trace	trace	4.7	1.6
Product II	1	60	0	0	0	0	trace	0	0	5.6	1.6
Product III	1	0	0	0	0	0	5	5	trace	6.0	1.5
Product IV	1	------	------	------	------	------	------	------	------	------	------

The amount of improving agent used may be varied depending upon the character of the oil with which it is blended and the proportions desired in the final oil composition. The improving agents of the type contemplated herein are generally used in amounts ranging from about $\frac{1}{8}$ per cent to about 5 per cent, although preferred are amounts of the order of 1 per cent. It will be understood, however, that larger amounts of the improving agents may be present in oil concentrates, which are also contemplated herein.

It is to be understood that while the preferred procedures which may be followed for the preparation of the reaction products contemplated herein are described hereinabove and various representative constituents in these improving agents have been referred to, such procedures and constituents have been used for illustrative purposes only. The invention, therefore, is not to be construed as limited by the specific examples given but includes within its scope such changes and modifications as fairly come within the spirit of the appended claims.

We claim:

1. An improved mineral oil composition comprising a viscous mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said oil fraction, of an oil-soluble, acidic, phosphorus-, sulfur- and nitrogen-containing reaction product obtained by reacting a phosphorus sulfide and a phosphorus amine of an alkyl-substituted hydroxyaromatic compound.

2. An improved mineral oil composition comprising a viscous mineral oil fraction having in admixture therewith a minor proportion, from about $\frac{1}{8}$ per cent to about 5 per cent, of an oil-soluble, acidic, phosphorus-, sulfur- and nitrogen-containing reaction product obtained by reacting a phosphorus sulfide and a phosphorus amine of an alkyl-substituted hydroxy-aromatic compound.

3. An improved mineral oil composition comprising a viscous mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said oil fraction, of an oil-soluble, acidic, phosphorus-, sulfur- and nitrogen-containing reaction product obtained by reacting a phosphorus sulfide and a phosphorus amine of an alkyl-substituted hydroxyaromatic compound, said alkyl substituent containing at least about ten carbon atoms.

4. An improved mineral oil composition comprising a viscous mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said oil fraction, of an oil-soluble, acidic, phosphorus-, sulfur- and nitrogen-containing reaction product obtained by reacting a phosphorus sulfide and a phosphorus amine of a paraffin wax-substituted hydroxyaromatic compound.

5. An improved mineral oil composition comprising a viscous mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said oil fraction, of an oil-soluble, acidic, phosphorus-, sulfur- and nitrogen-containing reaction product obtained by reacting phosphorus pentasulfide and a phosphorus amine of an alkyl-substituted hydroxyaromatic compound.

6. An improved mineral oil composition comprising a viscous mineral oil having in admixture therewith a minor proportion, sufficient to impart improvement to said oil fraction, of an oil-soluble, acidic, phosphorus-, sulfur- and nitrogen-containing reaction product obtained by reacting substantially one mol of phosphorus pentasulfide and two mols of a phospho-amino-, paraffin wax-substituted phenol.

7. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said fraction, of an oil-soluble, metal-, phosphorus-, sulfur- and nitrogen-containing reaction product obtained by reacting a phosphorus sulfide and a phosphorus amine of an alkyl-substituted hydroxyaromatic compound, followed by substituting the acidic, phosphorus-, sulfur- and nitrogen-containing phosphorus sulfide-phosphorus amine reaction product thus obtained with metal, said alkyl substituent containing at least about ten carbon atoms.

8. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said fraction, of an oil-soluble, metal-, phosphorus-, sulfur- and nitrogen-containing reaction product obtained by reacting a phosphorus sulfide and a phosphorus amine of a paraffin wax-substituted hydroxyaromatic compound, followed by substituting the acidic, phosphorus-, sulfur- and nitrogen-containing reaction product thus obtained with metal.

9. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said fraction, of an oil-soluble, metal-, phosphorus-, sulfur- and nitrogen-containing reaction product obtained by reacting phosphorus pentasulfide and a phosphorus amine of an akyl-substituted hydroxyaromatic compound, followed by substituting the acidic, phosphorus-, sulfur- and nitrogen-containing phosphorus pentasulfide-phosphorus amine reaction product thus obtained with metal, said alkyl substituent containing at least about ten carbon atoms.

10. An improved mineral oil composition com-

prising a viscous mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said oil fraction, of an oil-soluble, barium salt of an acidic, phosphorus-, sulfur- and nitrogen-containing reaction product obtained by reacting phosphorus pentasulfide and a phosphorus amine of a paraffin wax-substituted phenol.

11. An improved mineral oil composition comprising a viscous mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said oil fraction, of an oil-soluble, barium salt of an acidic, phosphorus-, sulfur- and nitrogen-containing reaction product obtained by reacting phosphorus pentasulfide and a phosphorus amine of diamyl phenol.

12. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said oil fraction, of an intimate mixture of oil-soluble, acidic, phosphorus-, sulfur- and nitrogen-containing reaction products obtained by reacting a phosphorus sulfide and a phosphorus amine of an alkyl-substituted hydroxyaromatic compound, said reaction products differing from each other with respect to the nature of said alkyl substituents which are comprised essentially of aliphatic hydrocarbon groups corresponding substantially to the different aliphatic hydrocarbons contained in paraffin wax.

13. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said oil fraction, of an intimate mixture of oil-soluble, metal-, phosphorus-, sulfur- and nitrogen-containing reaction products obtained by reacting a phosphorus sulfide and a phosphorus amine of an alkyl-substituted hydroxyaromatic compound, followed by substituting the acidic, phosphorus-, sulfur- and nitrogen-containing phosphorus sulfide - phosphorus amine reaction product thus obtained with metal, said metal reaction products differing from each other with respect to the nature of said alkyl substituents which are comprised essentially of aliphatic hydrocarbon groups corresponding substantially to the different aliphatic hydrocarbons contained in paraffin wax.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,361,957	Musselman	Nov. 7, 1944
2,363,133	Loane et al.	Nov. 21, 1944
2,382,309	Hamilton	Aug. 14, 1945
2,393,934	Reiff et al.	Jan. 29, 1946
2,403,474	Bartleson	July 9, 1946
2,403,894	Bartleson	July 9, 1946

Certificate of Correction

Patent No. 2,441,331. May 11, 1948.

ORLAND M. REIFF ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 6, line 33, for that portion of the formula reading "R_{N_3}" read R_N; column 7, line 47, for "$2NH_4C$" read $2NH_4Cl$; column 10, line 65, for "interival" read *interval*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 9th day of November, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

prising a viscous mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said oil fraction, of an oil-soluble, barium salt of an acidic, phosphorus-, sulfur- and nitrogen-containing reaction product obtained by reacting phosphorus pentasulfide and a phosphorus amine of a paraffin wax-substituted phenol.

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