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MINERAL OIL COMPOSITION

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23 Claims. (Cl. 252—32.7)

This invention has to do in a general way with mineral oil compositions and is more particularly related to compositions comprised of mineral oil and a minor proportion of an added ingredient 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 the various uses are in and of themselves usually deficient in one or more respects, so 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 ingredient which will have the effect of inhibiting oxidation, such an ingredient being known to the trade as an oxidation inhibitor or a sludge inhibitor, a gum inhibitor, etc.

It is also the practice to add other ingredients 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 ingredients 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 in the oils, which, without the added ingredient, would 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 lubricating oil fractions to form carbonaceous deposits which cause the piston rings to become stuck in their slots and which fill the slots in the oil ring or rings, thus materially reducing the efficiency of the engine. Ingredients have been developed, which, when added to the oil, will reduce this natural tendency of the oil to form deposits which interfere with the function of the piston rings.

It has also been discovered that certain types of recently developed 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 on such alloys has led to the development of corrosion inhibitors which may be used in solvent-refining oils to protect such bearing metals against this corrosive action.

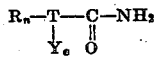
In the lighter mineral oil fractions, such as those used for fuel purposes, particularly in internal combustion engines, it has been found that the combustion characteristics of the fuel may be controlled and improved by adding minor proportions of various improving agents thereto.

The various ingredients which have been developed for use in mineral oil fractions to improve such fractions in the several characteristics enumerated above are largely specific to their particular applications. Therefore, it has generally been the practice to add a separate ingredient for each of the improvements which is 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 phosphorus- and sulfur-containing and are formed by the reaction of a phosphorus sulfide and an amide of an alkyl-substituted aromatic carboxylic acid. Contemplated also as

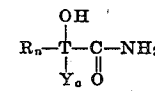
coming within the class of phosphorus- and sulfur-containing reaction products are the metal, ammonium and organic amine derivatives of said reaction products.

The amides of alkyl-substituted aromatic carboxylic acids from which the reaction products or compounds of this invention are obtained may be represented by general Formula I:

I 

wherein 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 particularly preferred of such a group 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 and Y is selected from the group consisting of hydroxyl, mercapto, mercaptal, mercaptol, ester (organic and inorganic), thioester, keto, thioketo, alkoxy, aroxy, thioether, polysulfide, oxime, amido, thioamido, carbamido, aralkyl, alkyl, alkaryl, aryl, hydrogen, nitro, nitroso, nitrosamino, amino, amidine, imino, N-thio, diazo, hydrazino, cyano, cyanate, thiocyanate, azo, hydrazo and azoxy radicals; and *a* is an integer, preferably from 0 to 3, and represents the number of Y substituents occupying the unsatisfied positions on the nucleus T. Included among the inorganic ester substituents represented by Y are inorganic acyl groups of acidic metalloid elements which are considered to be components or constituents of the acid of the known metallic or acid metalloid elements: phosphorus, silicon and boron. They are derivatives from an inorganic halide selected from the group consisting of PCl_3, PCl_5, BCl_3, $SiCl_4$, $POCl_3$, $PSCl_3$, and $PNCl_2$, in the reaction of said halide with a hydroxyaromatic carboxylic acid, followed by subsequent water washing of the reaction mixture. Such substituents are discussed at length in application Serial No. 463,966, filed October 30, 1942 (now Patent No. 2,357,287, issued September 5, 1944), in which one of the present inventors, O. M. Reiff, is a co-inventor.

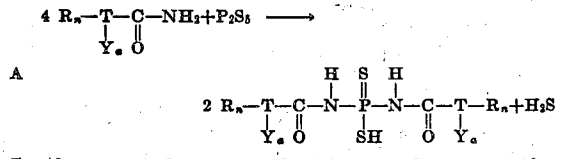
Those amides in which the nucleus T contains a hydroxyl group, as represented by general Formula II, are particularly desirable compounds:

II 

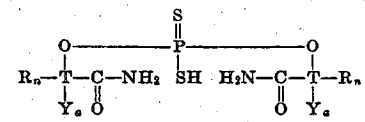
wherein the symbols R, Y, *n* and *a* are defined above.

The amides 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 amides prepared by reaction of an alkyl-substituted hydroxyaromatic carboxylic acid or metal salt thereof with an acyl chloride such as $SOCl_2$, SO_2Cl_2, PCl_3, $POCl_3$, BCl_3, $SiCl_4$ and $PNCl_2$, followed by reaction with ammonia. Particularly preferred of the acyl chlorides for use in the aforesaid reaction is PCl_3. The alkyl-substituted hydroxyaromatic carboxylic acids and metal salts thereof are well known to the art and preparation thereof need not be described here; typical of such acids and salts and methods for their preparation are shown in Patent 2,253,811 issued to O. M. Reiff.

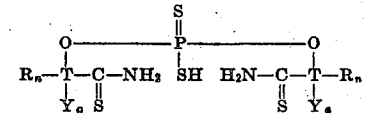
The reaction products or compounds contemplated herein are all characterized by the presence of substantial amounts of phosphorus and sulfur therein. For example, when 4 mols of an amide of the type represented by general Formula I are reacted with substantially 1 mol of P_2S_5 as described hereinafter, it is most probable that the reaction product is predominantly comprised of a phosphorus- and sulfur-containing product shown in Equation A below:



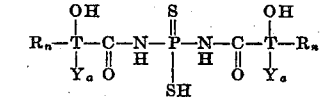
In the event, however, that the nucleus T of the amide reactant is substituted with a hydroxyl group (Y), as typified by general Formula II, it is most probable that the reaction product contains appreciable quantities of the following products:



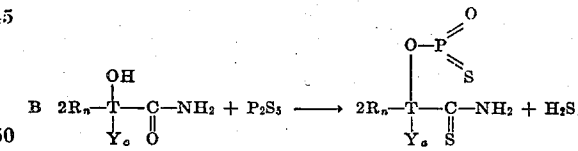
and



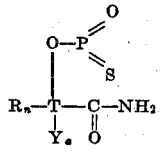
in addition to the product:



Correspondingly, when 2 mols of an amide of the type identified by general Formula II are reacted with substantially 1 mol of P_2S_5, the reaction most probably predominates in the manner indicated by Equation B:



While the phosphorus- and sulfur-containing product shown in Equation B most probably predominates, a lesser quantity of the following product may also be contained therein:



It will be understood that when inorganic acyl radicals, such as those referred to hereinabove, are present in the alkyl-substituted amide before reaction with P_2S_5, that the P_2S_5 reaction product will contain compounds such as those shown above in description of Equations A and B in which an inorganic acyl group is represented by symbol Y, and it will further be understood that these inorganic acyl groups may in some instances also undergo chemical change in the P_2S_5 reaction. For example, if the hydrogen of the hydroxy substituents of two alkyl-substituted hydroxyaromatic carboxylic acid molecules is replaced by a chlorinated phosphoryl group

(=P—Cl), ammonia will react with this group to form a =P—NH_2 group. This group would be reactive with P_2S_5.

With regard to the metal salts of the aforesaid reaction products or compounds, it will be apparent that the aforesaid hydrogen attached to the sulfur atom in the —SH group will be replaced by a metal group represented hereinafter by the symbol M.

The metals contemplated herein may be broadly classified as the metals of groups 1 to 8 inclusive of the 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, colombium, 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. Other rare earth metals suitable for the metal type of compounds contemplated herein are those commercially available as 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 are the metals calcium, barium and zinc.

As described above T represents an aromatic nucleus which may be mono- or polycyclic. Typical nuclei contemplated herein are benzene, naphthalene, anthracene, phenanthrene, diphenyl, etc.

As aforesaid, compounds represented by the phosphorus- and sulfur-containing reaction products shown in Equations A and B, contain at least one oil solubilizing substituent such as an alkyl group. Oil solubility is imparted to the compounds or reaction products of this invention with alkyl substituents, such substituent or substituents containing at least ten carbon atoms in alkyl groups, such as, 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 nucleus having these 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 multifunctional reaction products of the addition agents 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, etc., may be utilized. In compounds 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 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 are capable of remaining uniformly dispersed in mineral oil either as a true solution or 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 polycyclic and whether such nucleus carries other substituents such as represented above by Y.

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 present on 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 hydrogens on the 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.

It will be understood that the oil improving agents of this invention may be pure compounds of the type represented by the reaction products shown in Equations A and B. In preparing the oil improving products defined hereinabove, however, those containing at least one wax (R) group obtained by procedures in which wax substitution of an aromatic hydrocarbon is effected with a chlorinated wax by the Friedel-Crafts reaction, the final oil improving product is usually a mixture of different compounds and for this reason the products contemplated herein are contemplated as reaction products as well as compounds.

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 content of the chlorinated wax." Thus wax-phenol carboxylic acid (3–16) indicates that the wax phenol used in obtaining the acid is the product 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 will be resorted to hereinafter to describe the wax-substituted hydroxyaromatic carboxylic acids (and the corresponding metal salts) used in the preparation of the preferred compounds or reaction products contemplated herein and will also be resorted to to describe said final compounds or reaction products.

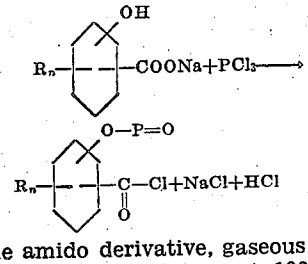
In order to more fully demonstrate the reaction products contemplated herein as mineral oil improving agents the following illustrative examples of preferred reaction products are described below.

EXAMPLE 1

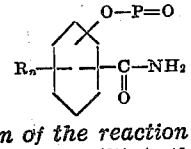
REACTION PRODUCT OF P_2S_5 AND ALKYL-SUBSTITUTED AND PHOSPHORYL-SUBSTITUTED BENZAMIDE

(a) *Preparation of alkyl-substituted phosphoryl benzamide.*—Eight hundred grams of 1:3 mineral oil blend of the mono-sodium salt of wax phenolic acid (3–14), prepared as described in Reiff Patent 2,197,832, are heated to 50° C. and 33.4 grams of PCl_3 (1 mol) are added slowly thereto with stirring. The temperature is raised to 100° C. to insure complete reaction. The combined phosphite ester and acid chloride being formed as indicated in Equation C:

C



To form the amido derivative, gaseous ammonia is introduced into the mixture at 100° C. until an excess of ammonia is present as determined by the use of wet litmus paper. The reaction product at this stage may be represented by the following formula:



b. Preparation of the reaction product of P_2S_5 and (a).—In order to facilitate the reaction of the product obtained (*a*) and P_2S_5, and to form a product having a light color, it has been found desirable to first remove the sodium chloride and ammonium chloride by-products at this stage. This is accomplished by adding 100 cc. of butanol and 10 cc. of water and stirring the resultant mixture for about one hour, followed by the removal of butanol and water by raising the temperature to about 180° C. During this treatment, the chemically combined salts are completely precipitated and are then removed by filtering the mixture through "Hi Flo." The amide is then reacted with 27 grams of P_2S_5 (½ mol) for four hours at about 175° C. to obtain the final product. The amount of P_2S_5 used in this example corresponds to Equation B shown above. The product, in mineral oil, is characterized by the following: phosphorus, 1.6%; sulfur, 1.6%; nitrogen, 0.4%; and neutralization number 20.0 (titration in 50% ethyl alcohol-water mixture with phenolphthalein indicator). This product is referred to hereinafter as reaction product I.

EXAMPLE 2

BARIUM SALT OF REACTION PRODUCT I

The barium salt of the phosphorus- and sulfur-containing reaction product obtained in Example 1 can be readily prepared by reaction of said reaction product with barium hydroxide. This is accomplished by adding 60 cc. of butanol and 77 grams of $Ba(OH)_2.8H_2O$ to 800 grams of the said reaction product and, with rapid stirring, heating the resultant mixture to 150° C. The barium salt thus formed is 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 1:3 blend in mineral oil, analyzes as follows: barium, 3.0%; sulfur, 1.6%; phosphorus, 1.6%; and nitrogen 0.4%. This product is referred to hereafter as reaction product II.

While the use of 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 P_2S_5 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 3

CALCIUM SALT OF REACTION PRODUCT I

A quantity (800 grams) of the reaction product I, obtained as described in Example 1, 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 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 2 above. The reaction mixture is then filtered with the aid of "Hi Flo" in order to obtain the finished product in approximately a 1:3 mineral oil blend. The product analyzes as follows: calcium, 1.1%; sulfur, 1.7%; phosphorus, 1.7%; and nitrogen, 0.4%. This product is referred to hereafter as reaction product III.

EXAMPLE 4

ZINC SALT OF REACTION PRODUCT I

The zinc salt of reaction product I is readily formed by double decomposition of zinc chloride in solution in butanol with the sodium salt of reaction product I, or by reaction of zinc butylate with reaction product I. The zinc salt is generally formed by adding a butanol solution of zinc chloride to reaction product I, followed by the addition of an equivalent amount of sodium butylate. A quantity (800 grams) of the reaction product I obtained as described in Example 1 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 3 above. The zinc salt thus obtained is approximately a 1:3 mineral oil blend, and analyzes as follows: zinc, 2%; sulfur, 1.7%; phosphorus, 1.6%; and nitrogen, 0.4%. This product is referred to hereafter as reaction product IV.

EXAMPLE 5

REACTION PRODUCT OF P_2S_5 AND DIAMYL-SUBSTITUTED PHOSPHORYL-SUBSTITUTED BENZAMIDE

This product was obtained by reaction of 827 grams of the 1:3 mineral oil blend of the mono-sodium salt of diamyl phenol carboxylic acid (prepared as indicated in Patent 2,197,832), 116 grams of PCl_3, 29 grams of ammonia and 95 grams of P_2S_5, as described in Example 1 (*a*) and (*b*). When this product is referred to hereafter, it will be referred to as reaction product V.

EXAMPLE 6

BARIUM SALT OF REACTION PRODUCT V

Prior to reaction with barium hydroxide, reaction product V was desalted with butanol and

water as described in Example 1 (*a*) and (*b*), and steamed as described in Example 2. The reaction product V so treated is then reacted with barium hydroxide at 150° C. The finished product, in approximately a 1:3 mineral oil blend, is obtained by filtering the reaction product with the aid of "Hi Flo." Analysis of the 1:3 mineral oil blend showed: barium, 1.9%; surfur, 2.6%; phosphorus, 2.6%; and nitrogen, 0.45%. This product is identified hereafter as reaction product VI.

It will be apparent to those familiar with 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 that such compounds or reaction products are contemplated herein.

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.

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 I.

Table I

Improving agent	Conc. by weight (percent) of 1:3 oil blend	A. S. T. M. pour point, degrees F.
None	0	+20
Reaction product I	½	−25
Reaction product II	½	−20
Reaction product III	½	−15
Reaction product IV	½	−20

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 II below:

Table II

Improving agent	Conc. by weight (percent) of 1:3 oil blend	Kinematic viscosity		V. I.
		100° F.	210° F.	
None	0	30.55	4.82	78.5
Reaction product I	4	31.79	4.99	85.1
Reaction product II	4	32.48	5.07	87.0
Reaction product III	4	32.72	5.12	89.5
Reaction product IV	4	32.56	5.10	89.0

Corrosion Inhibition

The protective action of the phosphorus- and sulfur-containing reaction products contemplated herein upon copper-lead bearings was tested in a C. F. R. engine. In this test the engine is run at a speed of 200 R. P. M. with the jacket temperature held at 212° F. to give an oil temperature to the bearing of 275° F. The engine is stopped at 20 hour intervals in order to determine the bearing loss (in milligrams) and the acidity of the oil, the latter being measured by the neutralization number (N. N.). The oil used in this test was a motor oil having a Saybolt viscosity of 67 seconds at 210° F. The results are tabulated below in Table III.

Table III

Improving agent	Conc. by weight (percent) of 1:3 oil blend	N. N.	Bearing loss (gram)	Hours run
None	0	3.3	0.270	40
Reaction product II	4	1.9	0.153	115
Reaction product III	4	3.0	0.205	105
Reaction product IV	4	3.1	0.210	96
Reaction product VI	4	2.2	0.158	150

A motor oil and blends of the same motor oil 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 of 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., and the oil blends used were blends of the said oil and said preferred improving agents. After 36 hours the acidity (as measured by the N. N.) and the kinematic viscosity of the oil and of the oil blends were measured. The results are shown in Table IV below:

Table IV

Improving agent	Conc. by weight (percent) of 1:3 oil blend	N. N.	Kin. vis. at 210° F.
None	0	10.0	12.71
Reaction product I	4	2.9	6.93
Reaction product II	4	1.4	6.37
Reaction product III	4	1.6	6.31
Reaction product IV	4	2.3	7.26
Reaction product V	4	1.3	6.00
Reaction product VI	4	1.2	6.05

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 improved 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 carbonaceous 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 V below:

Table V

Improving agent	Conc. by weight (percent) of 1:3 oil blend	Ring condition								Carbon deposits	N. N.
		Degrees stuck					Slots filled				
		1	2	3	4	5	3	4	5		
None	0	360	360	360	360	360	60	70	70	14.0	2.4
Reaction product I	4	0	0	0	0	0	5	0	0	4.7	1.6
Reaction product II	4	150	0	0	0	0	0	0	0	4.8	1.7
Reaction product III	4	270	0	0	0	0	0	0	0	5.4	1.6
Reaction product IV	4	120	0	0	0	0	5	0	0	5.7	1.6
Reaction product V	4	0	0	0	0	0	5	0	0	6.4	1.6
Reaction product VI	4	180	0	0	0	0	0	0	0	7.4	0.9

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 may be used in amounts ranging from about ½ per cent to about 8 per cent.

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 considered 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 mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reacting a phosphorus sulfide and an amide of an alkyl-substituted aromatic carboxylic acid.

2. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, from about ½ per cent to about 8 per cent, of an oil-soluble, phosphorus- and sulfur- containing reaction product obtained by reacting a phosphorus sulfide and an amide of an alkyl-substituted aromatic carboxylic acid.

3. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reacting a phosphorus sulfide and an amide of an alkyl-substituted aromatic carboxylic acid, said alkyl substituent containing at least about twenty carbon atoms.

4. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reacting a phosphorus sulfide and an amide of a wax-substituted aromatic carboxylic acid.

5. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, metal-, phosphorus- and sulfur- containing reaction product obtained by reacting a phosphorus sulfide and an amide of an alkyl-substituted aromatic carboxylic acid, followed by substituting the phosphorus- and sulfur- containing phosphorus sulfide-amide reaction product thus obtained with metal.

6. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reacting phosphorus pentasulfide and an amide of an alkyl-substituted aromatic carboxylic acid.

7. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reacting phosphorus pentasulfide and an amide of an alkyl-substituted hydroxy-aromatic carboxylic acid.

8. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, metal-, phosphorus- and sulfur- containing reaction product obtained by first reacting phosphorus pentasulfide and an amide of an alkyl-substituted hydroxy-aromatic carboxylic acid, followed by substituting the phosphorus- and sulfur- containing phosphorus pentasulfide-amide reaction product obtained in the first reaction 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 mineral oil fraction, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reacting substantially one mol of phosphorus pentasulfide and two mols of an amide of an alkyl-substituted hydroxyaromatic carboxylic acid.

10. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reacting substantially one mol of phosphorus pentasulfide and four mols of an amide of an alkyl-substituted hydroxyaromatic carboxylic acid.

11. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reacting substantially one mol of phosphorus penta-

sulfide and four mols of an alkyl- and phosphoryl-substituted benzamide.

12. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, barium-, phosphorus- and sulfur- containing reaction product obtained by first reacting substantially one mol of phosphorus pentasulfide and four mols of an alkyl- and phosphoryl-substituted benzamide, followed by substituting the phosphorus- and sulfur- containing reaction product obtained in the first reaction with barium.

13. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, zinc-, phosphorus- and sulfur- containing reaction product obtained by first reacting substantially one mol of phosphorus pentasulfide and four mols of an alkyl- and phosphoryl-substituted benzamide, followed by substituting the phosphorus- and sulfur- containing reaction product obtained in the first reaction with zinc.

14. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an intimate mixture of oil-soluble phosphorus- and sulfur- containing reaction products obtained by reacting a phosphorus sulfide and an amide of an alkyl-substituted aromatic carboxylic acid, 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.

15. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an intimate mixture of oil-soluble, metal-, phosphorus- and sulfur- containing reaction products obtained by reacting a phosphorus sulfide and an amide of an alkyl-substituted aromatic carboxylic acid, followed by substituting the phosphorus- and sulfur- containing phosphorus sulfide-amide reaction product obtained in the first reaction with metal, 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.

16. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an intimate mixture of oil-soluble, phosphorus- and sulfur- containing reaction products obtained by reacting substantially one mol of phosphorus pentasulfide and two mols of an amide of an alkyl-substituted hydroxyaromatic carboxylic acid, 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.

17. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an intimate mixture of oil-soluble, phosphorus- and sulfur- containing reaction products obtained by reacting substantially one mol of phosphorus pentasulfide and four mols of an amide of an alkyl-substituted hydroxyaromatic carboxylic acid, 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.

18. As a new composition of matter, a phosphorus- and sulfur- containing reaction product obtained by reacting a phosphorus sulfide and an amide of an alkyl-substituted aromatic carboxylic acid.

19. As a new composition of matter, a metal-, phosphorus- and sulfur- containing reaction product obtained by first reacting a phosphorus sulfide and an amide of an alkyl-substituted aromatic carboxylic acid, followed by substituting the phosphorus- and sulfur- containing phosphorus sulfide- amide reaction product obtained in the first reaction with metal.

20. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, phosphorus- and sulfur- containing reaction product obtained by reacting phosphorus pentasulfide and an amide of an alkyl- and phosphoryl- substituted aromatic carboxylic acid.

21. An improved mineral oil composition comprising a mineral oil fraction having in admixture therewith a minor proportion, sufficient to impart improvement to said mineral oil fraction, of an oil-soluble, metal-, phosphorus- and sulfur-containing reaction product obtained by first reacting phosphorus pentasulfide and an amide of an alkyl- and phosphoryl- substituted aromatic carboxylic acid, followed by substituting the phosphorus- and sulfur- containing phosphorus pentasulfide-amide reaction product obtained in the first reaction with metal.

22. As a new composition of matter, a phosphorus- and sulfur- containing reaction product obtained by reacting phosphorus pentasulfide and an amide of an alkyl- and phosphoryl- substituted aromatic carboxylic acid.

23. As a new composition of matter, a metal-, phosphorus- and sulfur- containing reaction product obtained by first reacting phosphorus pentasulfide and an amide of an alkyl- and phosphoryl- substituted aromatic carboxylic acid, followed by substituting the phosphorus- and sulfur- containing phosphorus pentasulfide-amide reaction product obtained in the first reaction with metal.

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