Patented Jan. 11, 1949

2,459,113

UNITED STATES PATENT OFFICE

2,459,113

MINERAL OIL COMPOSITION

Edward A. Oberright, Woodbury, N. J., assignor to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

No Drawing. Application July 6, 1945, Serial No. 603,590

13 Claims. (Cl. 252—32.7)

1

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 important respects.

It is well known to those familiar with the art that mineral oil fractions refined for their 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 fraction an additive ingredient which will inhibit oxidation, such ingredients being known to the trade as oxidation inhibitors, antioxidants, sludge inhibitors, gum inhibitors, 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 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.

2

It has also been discovered that certain types of recently-developed hard metal alloys, 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-refined 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 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 group or class 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.

The novel addition agents contemplated by this invention as multifunctional improvers for mineral oils are oil-soluble phosphorus-containing and phosphorus- and sulfur-containing reaction products obtained by reacting an aldehyde, a hydroxyaromatic compound and a polyamine in which each amino group is characterized by the presence of at least one hydrogen atom to form a condensation product and thereafter reacting the latter with either: a phosphorus halide to form a phosphorus-containing reaction product; a phosphorus sulfide or thiohalide to form a phosphorus- and sulfur-containing reaction product; or a phosphorus halide, phosphorus thiohalide or a phosphorus sulfide and a sulfurizing material such as elementary sulfur, a sulfur halide or a mixture thereof to form a phosphorus- and sulfur-containing reaction product. Preferred phosphorus-containing reaction products are those obtained by condensing about one molar equivalent of an aldehyde with at least one-half molar equivalent of a polyamine of the aforesaid character and with a quantity of an alkyl-substituted hydroxyaromatic compound sufficient that the content of the hydroxyaromatic substituent is about one molar equivalent, followed by reaction with at least one molar equivalent of a phosphorus

halide. Similarly, preferred phosphorus- and sulfur-containing reaction products are those obtained by reacting a condensation product of the aforesaid preferred type with either a phosphorus sulfide, or a phosphorus halide and a sulfur halide. Metal salts of these phosphorus-containing and phosphorus- and sulfur-containing reaction products are also contemplated herein.

Aldehydes contemplated by the present invention are the aliphatic aldehydes, typified by formaldehyde (such as trioxymethylene), acetaldehyde, and aldol (β-hydroxy butyraldehyde); aromatic aldehydes, representative of which is benzaldehyde; heterocyclic aldehydes, such as furfural; etc. The aldehyde may contain a substituent group such as hydroxyl, halogen, nitro and the like; in short, any substituent which does not take a major part in the reaction. Preference, however, is given to the aliphatic aldehydes, formaldehyde being particularly preferred.

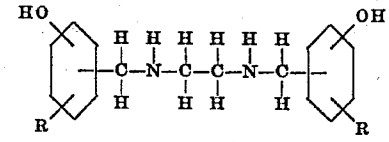
The polyamines contemplated herein are those in which each amino group is characterized by the presence of at least one hydrogen atom. Such polyamines may contain only primary amino groups, only secondary amino groups, or both primary and secondary groups. Typical polyamines are the aliphatic homologs, ethylene diamine, propylene diamine, polyalkene polyamines (e. g., diethylene triamine, triethylene tetramine); the aromatic homologs, o-, m- and p-phenylene diamine, diamino naphthalenes, etc. Of this class of amines, preference is given to the diamines in which two primary amino groups are attached to adjacent carbon atoms, and particular preference is accorded ethylene diamine.

Representative hydroxyaromatic compounds contemplated by the present invention are phenol, resorcinol, hydroquinone, catechol, cresol, xylenol, hydroxydiphenyl, benzylphenol, phenylethylphenol, phenol resins, methylhydroxydiphenyl, guiacol, alpha and beta naphthol, alpha and beta methylnaphthol, tolylynaphthol, xylylnaphthol, benzylnaphthol, anthranol, phenyl-methylnaphthol, phenanthrol, monomethyl ether of catechol, phenoxyphenol, chlorphenol, and the like. Preference in general is to the monohydroxy phenols otherwise unsubstituted, particular preference being given to phenol and alpha and beta naphthol.

The hydroxyaromatic compounds may also contain one or more substituent groups such as carboxyl, halogen, nitro and the like; here again, any substituent may be present which does not take a predominant part in the condensation with the aldehyde and the polyamine. Preferred of such substituents is a carboxyl group.

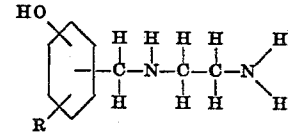
As indicated hereinabove, the hydroxyaromatic compound may contain one or more alkyl substituents such as short-chain groups, typified by methyl, ethyl, amyl, etc.; or long-chain, relatively-high-molecular-weight hydrocarbon groups having at least twenty carbon atoms, typified by alkyl groups derived from petroleum wax, which is a predominantly straight-chain aliphatic hydrocarbon of at least twenty carbon atoms. It will be obvious to those skilled in the art that the maximum number of alkyl groups is limited by the number of valences on the aromatic nucleus available for substitution. Naturally, the maximum number of such groups which can be attached to a single aromatic nucleus will vary as the nucleus is mono- or poly-cyclic and as the nucleus is otherwise substituted, with such groups as carboxy, nitro, amino, halogen and the like.

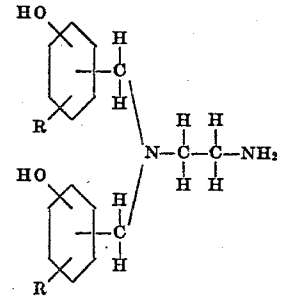
The present application has been purposely directed to condensation products of the aforesaid reactants for, as yet, the theory of reaction is not fully understood. Some evidence is available—for example, quantitative analysis of the reaction product—to point to the presence of a major quantity of one compound. For instance, when typical reactants, such as an alkyl-substituted phenol, formaldehyde and ethylene diamine, are reacted as hereinafter described, analysis indicates that the predominant product is:



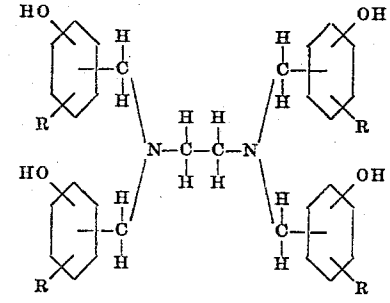
wherein R is an alkyl group.

Probably also present in the condensation product are compounds of the following type:





and



It will be apparent, therefore, that when the condensation product is reacted with a phosphorus compound of the foregoing type, or with such a compound and a sulfurizing material, the reaction product obtained thereby is of greater chemical complexity. For this reason, it will be clear that the foregoing is for illustrative purposes only and is not to be construed as limiting the present invention to a theory of reaction because the present invention is directed primarily to condensation products obtained by inter-reaction of the reactants described herein as multi-functional improving agents for lubricating oils and the like.

In preparing the intermediate or condensation products contemplated herein, the reactants may be added to each other in any order. A typical procedure involves adding the aldehyde to an alcohol solution of the hydroxyaromatic compound and the amine. The reaction may also be carried out in the presence of other diluents or solvents such, for example, as tetrachlorethane, chlorbenzene, mineral oil, etc. In the event that

mineral oil is used as a diluent, the mineral oil may be retained, rather than separated from the reaction product, thereby providing a mineral oil concentrate.

The reaction temperature may be varied considerably, depending upon the time of reaction, the specific reactants used, etc. For example, the reaction can be carried out at room temperature over a relatively long period of time or at the reflux temperature of the solvent over a comparatively short period. By way of illustration, the reactants, in quantities such as shown in the following examples, may be thoroughly mixed at room temperature for several hours and the reaction completed at the reflux temperature of the solvent for an additional period of several hours.

The reaction product may be water washed to assure complete removal of any unreacted amine and this is recommended when the amine is high boiling. When an alcohol is used as a diluent in the reaction, it is distilled from the reaction mixture, thereby also removing any unreacted amine and water of reaction or water added with the reactants (Formalin, for example, is generally used in a 37% aqueous solution.)

As stated above, the general procedure for preparing the contemplated condensation products involves the inter-reaction of a hydroxy-aromatic compound, an aliphatic aldehyde, and a polyamine wherein the amino groups have at least one free hydrogen.

A typical, and also preferred, alkyl-substituted hydroxyaromatic compound which may be used is a wax-substituted phenol, "wax-phenol." The term "wax" as used herein designates petroleum wax or aliphatic hydrocarbons or hydrocarbon groups of the type which characterize petroleum wax. These so-called "wax" substituents may be obtained by alkylation of the phenol or hydroxyaromatic hydrocarbon with a relatively-high-molecular weight aliphatic hydrocarbon or mixture of such hydrocarbons (such as petroleum wax) by any suitable alkylation procedure such, for example, as by a Friedel-Crafts condensation of chlorinated petroleum wax with phenol.

As indicated hereinabove, the reaction products contemplated herein may be prepared by reacting a condensation product of the type described above with a phosphorus halide, a phosphorus sulfide or thiohalide, or at least one such phosphorus compound and a sulfurizing material. This reaction is preferably carried out in the presence of an inert diluent such as tetrachlorethane, benzene, chlorbenzene, mineral oil, etc. These diluents—except heavy mineral oils—are removed after the reaction by distillation of the reaction mixture which contains the desired reaction product. When a mineral oil is used as the diluent, however, it may be retained, thereby providing a mineral oil concentrate containing the reaction product.

The reaction temperature may be varied considerably, depending upon the reaction time and the specific phosphorus, and/or sulfur, reactant used. Temperatures of the order of about 20° C. to about 200° C. are generally maintained with a phosphorus halide. The preferred procedure, however, involves adding a phosphorus halide to a condensation product at room temperature (20–25° C.) and thereafter heating the reaction mixture so formed at the reflux temperature of the diluent for several hours. Related phosphorus- and sulfur-containing reaction products, in general, are also prepared under the foregoing conditions by reacting a condensation product with a phosphorus compound and with or without a sulfurizing material.

The phosphorus halides and sulfides which may be used herein are represented by the following: PCl_3, $POCl_3$, $PSCl_3$, PCl_5, P_2S_3, P_3S_4, P_2S_5, P_4S_7, etc. Preferred of these materials are PCl_3 and P_2S_5. While only the phosphorus chlorides are recited above, the corresponding bromides, iodides and fluorides may also be used, but the chlorides are more desirable in view of their lower cost and availability.

As indicated above, the sulfurizing materials are elementary sulfur, sulfur halides and mixtures thereof. Of these materials, sulfur halides are preferred, with sulfur monochloride particularly preferred.

Metal salts of the aforesaid phosphorus-, and phosphorus- and sulfur-, containing reaction products, as indicated above, also fall within the scope of the present invention. Any metal may be used the oxide or hydroxide of which (in alcohol solution, if necessary) can be reacted with the intermediate condensation product, or a salt of which can be reacted in alcohol solution with the sodium salt of the intermediate product. Among the metals contemplated for this purpose are: copper, beryllium, magnesium, calcium, strontium, barium, radium, zinc, cadmium, mercury, germanium, tin, lead, vanadium, chromium, manganese, iron, cobalt, nickel, ruthenium, palladium, platinum, aluminum, antimony, arsenic, bismuth, cerium, columbium, gallium, gold, indium, iridium, molybdenum, osmium, rubidium, selenium, tantalum, tellurium, thorium, titanium, tungsten, uranium, and zirconium. Preference is given to metals of the alkaline earth group, particularly to barium. As noted above, the metal is preferably introduced by reaction of its oxide or hydroxide with the intermediate condensation product. Where necessary, an alcohol solution of the oxide or hydroxide is used. The metal salts can also be prepared by reacting the sodium salt of the intermediate product with an alcohol solution of a salt of the desired metal, such as stannous chloride, lead acetate, thorium nitrate, titanium tetrachloride, etc.

Details of a preferred procedure for making the condensation products of this invention where the aforesaid wax-phenol is employed as the alkyl-substituted hydroxyaromatic compound may be obtained from the following examples:

EXAMPLE I

A. *Alkylation of phenol*

A paraffin wax melting at approximately 120° F. and predominantly comprised of compounds having at least twenty carbon atoms in their molecules is melted and heated to about 200° F., after which chlorine is bubbled therethrough until the wax has absorbed about 16 percent of chlorine, such product having an average composition between a monochlor wax and a di-chlor wax. Preferably, the chlorination is continued until about one-sixth the weight of the "chlor-wax" formed is chlorine. A quantity of chlor-wax thus obtained, containing two atomic proportions of chlorine, is heated to a temperature varying from just above its melting point to not over 150° F., and one mol of phenol (C_6H_5OH) is admixed therewith. The mixture is heated to about 150° F., and a quantity of anhydrous aluminum chloride corresponding to about 3 percent of the weight of chlor-wax in the mixture is slowly added with active stirring. The rate of

addition of the aluminum chloride should be sufficiently slow to avoid violent foaming, and during such addition the temperature should be held at about 150° F. After the aluminum chloride has been added, the temperature of the mixture may be increased slowly over a period of from 15 to 25 minutes to a temperature of about 250° F. and then should be more slowly increased to about 350° F. To control the evolution of HCl gas the temperature of the mixture is preferably raised from 250° F. to 350° F., at a rate of approximately one degree per minute, the whole heating operation occupying approximately two hours from the time of adding the aluminum chloride. If the emission of HCl gas has not ceased when the final temperature is reached, the mixture may be held at 350° F. for a short time to allow completion of the reaction. However, to avoid possible cracking of the wax, the mixture should not be heated appreciably above 350° F., nor should it be held at that temperature for any extended length of time.

It is important that all unreacted or non-alkylated hydroxy-aromatic material (phenol) remaining after the alkylation reaction be removed. Such removal can be effected generally by water-washing, but it is preferable to treat the water-washed product with superheated steam, thereby insuring complete removal of the unreacted material and accomplishing the drying of the product in the same operation.

A wax-substituted phenol prepared according to the above procedure in which a quantity of chlorwax containing two atomic proportions of chlorine and having a chlorine content of 16 percent is reacted with 1 mol of phenol will be hereinafter designated as "wax-phenol (2–16)."

B. *Formation of condensation product*

One hundred and fifty grams of wax-phenol (3–16), prepared according to the foregoing procedure, and 19.2 grams of a 69 per cent solution of ethylene diamine in water were dissolved in butyl alcohol. To the resulting alcohol solution, 17.8 grams of a 37 percent aqueous solution of formaldehyde in water—Formalin—were added dropwise at room temperature (about 25° C.). A small amount of benzene was then added to provide a uniform reaction mixture, which was stirred at room temperature for 3 hours. The reaction mixture was then stirred for 8 hours at reflux (about 110° C.) and, thereafter, water washed until the washings were neutral. The solvents, butyl alcohol and benzene, were removed from the reaction product by distillation of the latter to a maximum temperature of 175° C. at 10 mms. pressure, thereby obtaining the condensation product.

C. *Phosphorus-containing condensation product*

Seventy-five grams of the condensation product obtained in B, above, were dissolved in 150 grams of mineral oil having a S. U. V. of 65 seconds at 210° F., and benzol (400 cc.) was then added thereto. Phosphorus trichloride (5.05 grams) was added dropwise to the mineral oil-benzol solution at about 25° C., and the reaction mixture so obtained was stirred for one hour at this temperature. The reaction mixture was then stirred at reflux (80° C.) for two hours, and was washed with sodium acetate solution to remove any hydrochloric acid complexes that might have formed in the reaction, by the action of evolved HCl on the reaction product. Benzol was removed by distillation to a maximum temperature of 175° C. at 10 mms. pressure, entrained water also being removed. The nitrogen- and phosphorus-containing reaction product (Product One) is a 1:2 blend in mineral oil.

EXAMPLE II

Stannous Salt of Phosphorus-Containing Condensation Product

A. *Condensation product*

A condensation product was prepared from the following materials in the manner described in Example One (B), above:

	Grams
Wax-phenol (2–14)	150
Formaldehyde (37% aqueous solution)	19.5
Ethylene diamine (69% aqueous solution)	20.8
Butyl alcohol solvent.	

B. *Phosphorus-containing condensation product*

Twenty-five grams of the condensation product obtained in A, above, was blended with 75 grams of mineral oil (S. U. V. of 65 seconds at 210° F.) and tetrachlorethane was added thereto. PCl_3 (1.72 grams) was added thereto, while stirring at 75° C., and the resulting reaction mixture was stirred and heated at 100° C. for two hours. A quantity of sodium butylate containing 1.72 grams of sodium was then added, followed by 8.28 grams of stannous chloride. The reaction mixture thus obtained was refluxed at 120° C. for two hours and then filtered through "Hi-Flo" clay. Solvents—tetrachloroethane and butylalcohol—were distilled from the reaction mixture by distilling the latter to a maximum temperature of 175° C. at 10 mms. pressure. The mineral oil blend (1:3) thus obtained contains the tin- and phosphorus-containing reaction product (Product Two).

EXAMPLE III

A. *Condensation product*

Ethylene diamine, 43 grams of a 70 percent solution of the same in water, was added to 86 grams of Formalin (35% solution) while agitating and cooling the same during one hour. Diamylphenol, 234 grams, was added thereto. The reaction temperature gradually increased to about 100° C. whereupon water was distilled from the reaction mixture. The reaction mixture was blown with nitrogen gas and then heated at 160° C. for two hours. Benzol, 200 ccs., were added to the reaction mixture and the resulting reaction mixture was washed with water until the washings were neutral. Benzol and water were removed from the water-washed reaction mixture by distilling the same to a maximum temperature of 195° C. at 5 mms. pressure. The condensation product thus obtained was diluted with mineral oil (S. U. V. of 65 seconds at 210° F.) to form a 1:1 oil blend; the nitrogen content of the oil blend was 2.78 percent.

B. *Phosphorus- and sulfur-containing reaction product*

Two hundred and seventy-six grams of condensation product (A) was mixed with 100 cc. of benzol. PCl_3 (12 grams) in 50 cc. of benzol was added dropwise at 25° C. during a period of one hour. S_2Cl_2 (17 grams) in 50 cc. of benzol was then added thereto under the same conditions. The reaction mixture so obtained was then stirred at 25° C. for 3 hours and heated at reflux, 85° C., for a similar period of time. The reaction mixture was washed with Na_2CO_3 and thereafter was washed with water until the wash-

ings were neutral. The water-washed reaction mixture was distilled to a maximum temperature of 150° C. at 5 mms. thereby removing benzol. The benzol-free reaction mixture was then filtered through Hi-Flo in a steam heated funnel. The product (Product Three) is a 1:1 oil blend containing: 3.9 percent sulfur, 0.96 percent phosphorus and 1.79 percent nitrogen.

EXAMPLE IV

Phosphorus- and Sulfur-Containing Reaction Product

One hundred and thirty-eight grams of condensation product Three (A), in a 1:1 mineral oil blend, and 7 grams of P_2S_5 were heated for two hours at 150–160° C. The reaction mixture was filtered through Hi-Flo in a steam-heated funnel under 10 mms. pressure. The filtrate (Product Four) is a 1:1 oil blend containing 2.9 percent sulfur and 1.32 percent phosphorus.

As stated hereinbefore, the reaction products contemplated by this invention and illustrated by the above examples, when added to lubricating oils in minor proportions, have been found to improve these oils in several important respects. This phenomenon is demonstrated by the following tables, which give the results of the various tests conducted to determine the effectiveness of these reaction products as addition agents for lubricating oils. The percent of material added to the oil in the following tables is the percent of concentrated material and does not include the oil in which the product was made.

Pour Point Depression

Tests were conducted in the conventional manner to determine the A. S. T. M. pour points of blends of these reaction products with a Mid-Continent solvent-refined oil of Saybolt Universal viscosity of 67 seconds at 210° F. as compared with the pour point of the blank oil. The results given in Table I below demonstrate the effectiveness of the reaction products contemplated herein as pour point depressants.

Table I

Addition Agent	Percent Added	A. S. T. M. Pour Point Values
		° F.
None		+25
Product One	1/8	−25
Do	1/16	0
Product Two	1/4	−25
Do	1/8	−15

Viscosity Index Improvement

A mineral oil of 41.8 seconds Saybolt Universal viscosity at 210° F. was tested in the conventional manner to determine the improvement in viscosity index values effected by various of the reaction products contemplated by this invention. This improvement is clearly demonstrated by the results set forth in Table II below.

Table II

Addition Agent	Percent Added	Viscosity Index Values	
		Inhibited Oil	Uninhibited Oil
Product One	1	83.7	77.7
Product Two	1	85.8	77.7

Corrosion Test

In this test the reaction product was blended with a Pennsylvania solvent-refined oil of Saybolt Universal viscosity of 53 seconds at 210° F., and a section of a bearing containing a cadmium-silver alloy surface and weighing about 6 grams was added to this blend. The oil was heated to 175° C. for 22 hours while a stream of air was bubbled against the surface of the bearing. The loss in weight of the bearing during this treatment measured the amount of corrosion that had taken place. A sample of the straight oil was subjected to the same test at the same time, and the difference between the losses in weight of the two bearing sections demonstrated conclusively the effectiveness of the reaction products contemplated herein as corrosion-inhibitors.

Table III

Addition Agent	Percent Added	Bearing Loss, mgms.	
		Inhibited Oil	Uninhibited Oil
Product Three	1/4	1	23
Product Four	1/4	0	20

Socony-Vacuum Turbine Test

Twenty-five cc. samples of a furfural-refined Rodessa crude of Saybolt Universal viscosity of 150 seconds at 100° F. and of blends of this same oil and typical reaction products were subjected to the following test to determine the effectiveness of the reaction products contemplated by this invention as inhibitors for turbine oils: To each sample were added 1 gram of iron granules and 24 inches of 18 gauge copper wire. The samples were then heated to a temperature of 200° F. with 5 liters of air per hour bubbling therethrough. Two cc. of distilled water were added each day. The results of the tests which were made for color and acidity or neutralization number and amount of sludge formed after certain time intervals are set forth in Table IV below.

Table IV

Addition Agent	Per cent Added	Hours	Lovibond Color	N. N.	Sludge, mgms.
None		162	245	17.8	389
Product One	1/10	166	7	0.9	102

Operation Test

To demonstrate the effectiveness of the reaction products under actual operating conditions of an automotive engine, unblended oils and improved oils, containing the reaction products, were subjected to the Lauson engine test. The tests were carried out in a single-cylinder Lauson engine operated continuously over a time interval of 16 hours with the cooling medium held at a temperature of about 212° F., and the oil temperature held at about 280° F. The engine was operated at a speed of about 1830 R. P. M. At the end of each test the oil was tested for acidity (N. N.) and viscosity. The base oil used here is a solvent refined oil having an S. U. V. of 44 seconds at 210° F.

Table V

Addition Agent	Percent Added	S. U. V. @ 210° F.	N. N.
None		51.53	3.9
Product One	½	45.18	0.6
None		66.07	11.2
Product Two	½	48.91	2.7
None		57.43	12.2
Product Three	1	46.33	1.3

It will be apparent from the foregoing test data that the reaction products of this invention are effective not only to inhibit corrosion and the various effects of oxidation upon mineral oils, such as formation of rust, sludge, color bodies and other undesirable products, but also to depress the pour point.

The improved properties obtained and the degree of improvement effected may be varied with the aldehyde, polyamine, hydroxyaromatic compound, phosphorus halide or sulfide, and metal, if the latter is present.

The amount of improving agent used varies with the mineral oil or lubricating oil fraction with which it is blended and with the properties desired in the final oil composition. These reaction products may be added to mineral oil in amounts of from about 0.01 to about 10 percent, but amounts of from about 0.1 to about 5 percent generally provide satisfactory improvement.

It is to be understood that although I have described certain preferred procedures which may be followed in the preparation of the novel reaction products contemplated herein as multifunctional addition agents for mineral oils and have indicated representative reactants for use in their preparation, such procedures and reactants are merely illustrative and the invention is not to be considered as limited thereto or thereby but includes within its scope such changes and modifications as fairly come within the spirit of the appended claims.

I claim:

1. An improved mineral oil containing a minor proportion, sufficient to inhibit said oil against the deleterious effects of oxidation, of an oil-soluble, phosphorus-containing reaction product obtained by reacting one molar equivalent of an aldehyde with about one molar equivalent of a hydroxyaromatic compound and at least about one-half molar equivalent of a polyamine in which each amino group has at least one hydrogen atom, in the presence of an inert diluent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product, and reacting said product with about one molar equivalent of a phosphorus compound selected from the group consisting of a phosphorus halide, a phosphorus thiohalide and a phosphorus sulfide, in the presence of an inert solvent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the inert solvent and for a time sufficient to effect phosphorization of said condensation product.

2. An improved mineral oil containing a minor proportion, from about 0.01 per cent to about 10 per cent, of an oil-soluble, phosphorus-containing reaction product obtained by reacting one molar equivalent of an aldehyde with about one molar equivalent of a hydroxyaromatic compound and at least about one-half molar equivalent of a polyamine in which each amino group has at least one hydrogen atom, in the presence of an inert diluent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product, and reacting said product with about one molar equivalent of a phosphorus compound selected from the group consisting of a phosphorus halide, a phosphorus thiohalide and a phosphorus sulfide, in the presence of an inert solvent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the inert solvent and for a time sufficient to effect phosphorization of said condensation product.

3. An improved mineral oil containing a minor proportion, sufficient to inhibit said oil against the deleterious effects of oxidation of an oil-soluble, phosphorus-containing reaction product obtained by reacting one molar equivalent of an aldehyde with about one molar equivalent of a hydroxyaromatic compound and at least about one-half molar equivalent of a polyamine in which each amino group has at least one hydrogen atom, in the presence of an inert diluent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product, and reacting said product with about one molar equivalent of a phosphorus halide, in the presence of an inert solvent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the inert solvent and for a time sufficient to effect phosphorization of said condensation product.

4. An improved mineral oil containing a minor proportion, sufficient to inhibit said oil against the deleterious effects of oxidation of an oil-soluble, phosphorus-containing reaction product obtained by reacting one molar equivalent of an aldehyde with about one molar equivalent of a hydroxyaromatic compound and at least about one-half molar equivalent of a polyamine in which each amino group has at least one hydrogen atom, in the presence of an inert diluent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product and reacting said product with about one molar equivalent of phosphorus trichloride, in the presence of an inert solvent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the inert solvent and for a time sufficient to effect phosphorization of said condensation product.

5. An improved mineral oil containing a minor proportion, sufficient to inhibit said oil against the deleterious effects of oxidation of an oil-soluble, phosphorus-containing reaction product obtained by reacting one molar equivalent of formaldehyde with a wax-phenol in sufficient amount to provide about one molar equivalent of the phenol substituent thereof and at least about one-half molar equivalent of a polyamine in which each amino group has at least one hydrogen atom, in the presence of an inert diluent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product and reacting said product with about one molar equivalent of phosphorus trichloride, in the presence of an inert solvent at a tempera-

ture falling within the range varying between about 20° C. and the reflux temperature of the inert solvent and for a time sufficient to effect phosphorization of said condensation product.

6. An improved mineral oil containing a minor proportion, sufficient to inhibit said oil against the deleterious effects of oxidation of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reacting one molar equivalent of an aldehyde, with about one molar equivalent of a hydroxyaromatic compound and at least about one-half molar equivalent of a polyamine in which each amino group has at least one hydrogen atom, in the presence of an inert diluent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product and reacting said product with about one molar equivalent of a phosphorus sulfide, in the presence of an inert solvent at a temperature falling within the range varying between about 20° C. and the reflux temperature of the inert solvent and for a time sufficient to effect phosphorization and sulfurization of said condensation product.

7. An improved mineral oil containing a minor proportion, sufficient to inhibit said oil against the deleterious effects of oxidation of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reacting one molar equivalent of an aldehyde, with about one molar equivalent of a hydroxyaromatic compound and at least about one-half molar equivalent of a polyamine in which each amino group has at least one hydrogen atom, in the presence of an inert diluent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product and reacting said product with about one molar equivalent of phosphorus pentasulfide, in the presence of an inert solvent at a temperature falling within the range varying between about 20° C. and the reflux temperature of said inert solvent and for a time sufficient to effect phosphorization and sulfurization of said condensation product.

8. An improved mineral oil containing a minor proportion, sufficient to inhibit said oil against the deleterious effects of oxidation of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reacting one molar equivalent of formaldehyde, with about one molar equivalent of diamyl phenol and at least about one-half molar equivalent of ethylene diamine, in the presence of an inert diluent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product and reacting said product with about one molar equivalent of phosphorus pentasulfide, in the presence of an inert solvent at a temperature falling within the range varying between about 20° C. and the reflux temperature of the inert solvent and for a time sufficient to effect phosphorization and sulfurization of said condensation product.

9. An improved mineral oil containing a minor proportion, sufficient to inhibit said oil against the deleterious effects of oxidation of an oil-soluble, metal- and phosphorus-containing reaction product obtained by reacting one molar equivalent of an aldehyde, with about one molar equivalent of a hydroxyaromatic compound and at least about one-half molar equivalent of a polyamine in which each amino group has at least one hydrogen atom, in the presence of an inert diluent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product, reacting said product with about one molar equivalent of a phosphorus compound selected from the group consisting of a phosphorus halide, a phosphorus thiohalide and a phosphorus sulfide, in the presence of an inert solvent at a temperature falling within the range varying between about 20° C. and the reflux temperature of the inert solvent and for a time sufficient to effect phosphorization of said condensation product and introducing a metal into the phosphorized reaction product so obtained.

10. An improved mineral oil containing a minor proportion, from about 0.01 per cent to about 10 per cent, of an oil-soluble, metal- and phosphorus-containing reaction product obtained by reacting one molar equivalent of an aldehyde, with about one molar equivalent of a hydroxyaromatic compound and at least about one-half molar equivalent of a polyamine in which each amino group has at least one hydrogen atom, in the presence of an inert diluent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product, reacting said product with about one molar equivalent of a phosphorus compound selected from the group consisting of a phosphorus halide, a phosphorus thiohalide and a phosphorus sulfide, in the presence of an inert solvent at a temperature falling within the range varying between about 20° C. and the reflux temperature of the inert solvent and for a time sufficient to effect phosphorization of said condensation product and introducing a metal into the phosphorized reaction product so obtained.

11. An improved mineral oil containing a minor proportion, sufficient to inhibit said oil against the deleterious effects of oxidation, of an oil-soluble, tin- and phosphorous-containing reaction product obtained by reacting one molar equivalent of formaldehyde, with a wax-phenol in an amount sufficient to provide about one molar equivalent of the phenol substituent thereof and about one-half molar equivalent of ethylene diamine, in the presence of an inert diluent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product, reacting said product with phosphorus trichloride, in the presence of an inert solvent at a temperature falling within the range varying between about 20° C. and the reflux temperature of the inert solvent and for a time sufficient to effect phosphorization of said condensation product, and introducing a metal into the phosphorized reaction product so obtained.

12. An improved mineral oil containing a minor proportion, sufficient to inhibit said oil against the deleterious effects of oxidation, of an oil-soluble, phosphorus- and sulfur-containing reaction product obtained by reacting one molar equivalent of an aldehyde with about one molar equivalent of a hydroxyaromatic compound and at least about one-half molar equivalent of a polyamine in which each amino group has at least one hydrogen atom, at a temperature falling within the range varying between about 20° C.

and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product, reacting said product with a phosphorus compound selected from the group consisting of a phosphorus halide, a phosphorus thiohalide and a phosphorus sulfide, in the presence of an inert solvent at a temperature falling within the range varying between about 20° C. and the reflux temperature of the inert solvent and for a time sufficient to effect phosphorization of said condensation product, then reacting the phosphorized condensation product with a sulfurizing material selected from the group consisting of elementary sulfur, a sulfur halide and a mixture thereof, under the same reaction conditions employed in the phosphorization reaction to effect sulfurization of the phosphorized condensation product.

13. An improved mineral oil containing a minor proportion, sufficient to inhibit said oil against the deleterious effects of oxidation, of an oil-soluble, metal-, phosphorus- and sulfur-containing reaction product obtained by reacting one molar equivalent of an aldehyde with about one molar equivalent of a hydroxyaromatic compound and at least about one-half molar equivalent of a polyamine in which each amino group has at least one hydrogen atom, in the presence of an inert diluent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the diluent and for a time sufficient to effect condensation, to produce a condensation product, reacting said product with about one molar equivalent of a phosphorus compound selected from the group consisting of a phosphorus halide, a phosphorus thiohalide and a phosphorus sulfide, in the presence of an inert solvent, at a temperature falling within the range varying between about 20° C. and the reflux temperature of the inert solvent and for a time sufficient to effect phosphorization of said condensation product, then reacting the phosphorized condensation product with a sulfurizing material selected from the group consisting of elementary sulfur, a sulfur halide and a mixture thereof, under the same reaction conditions employed in the phosphorization reaction to effect sulfurization of the phosphorized condensation product, and introducing a metal into the phosphorized and sulfurized reaction product so obtained.

EDWARD A. OBERRIGHT.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,146,584	Lipkin	Feb. 7, 1939
2,263,445	Reiff	Nov. 18, 1941
2,279,218	Badertscher et al.	Apr. 7, 1942
2,282,710	Dietrich	May 12, 1942
2,322,379	McCleary	June 22, 1943
2,334,594	Zimmer	Nov. 16, 1943
2,336,006	Fuller	Dec. 7, 1943
2,339,710	Lincoln	Jan. 18, 1944
2,340,036	Zimmer	Jan. 25, 1944
2,353,192	Sargent et al.	July 11, 1944
2,361,957	Musselman	Nov. 7, 1944
2,363,134	McCleary	Nov. 21, 1944