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MINERAL OIL COMPOSITION

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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 fractions an additive ingredient which will have the effect of inhibiting oxidation, such ingredients being known to the trade as oxidation inhibitors or 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 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 tend-

ency 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-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.

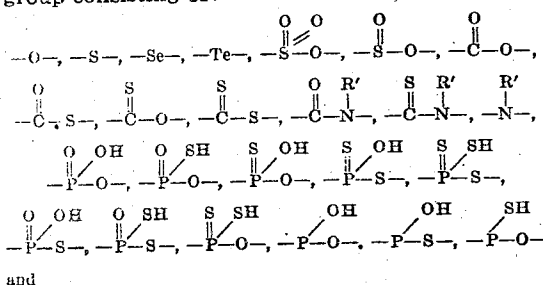
The present invention is predicated upon the discovery of a group or class of oil-soluble metal-organic reaction products or compounds which, when added to mineral oil fractions in minor proportions, will improve the oil fractions in several respects. These multi-functional reaction products or compounds are formed by the reaction of basic polyvalent-metal salts of alkyl-substituted aromatic hydrocarbon compounds and hydrogen sulfide, and may be broadly designated as the metal hydrosulfides of basic polyvalent-metal salts of alkyl-substituted aromatic hydrocarbons. All of the reaction products or compounds contemplated herein contain as characterizing groups: at least one polyvalent metal hydrosulfide group ($-M-SH$) and an aryl nucleus (T) substituted with at least one oil-solubilizing alkyl group and substituted with an atom or group represented by the symbol X .

The most probable formula for the reaction products or compounds contemplated herein is:

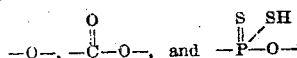


wherein T is an aromatic nucleus, either mono- or poly-cyclic; R is an oil-solubilizing aliphatic or alkyl hydrocarbon group, preferably one having at least twenty carbon atoms, such as an aliphatic "wax" group, and is attached by one valence only to at least one aromatic nucleus T ;

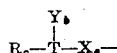
a is equal to the number of R substituents attached to a single nucleus T and is equal to a whole number from 1 to 4; Y is selected from the group consisting of hydroxyl, metaloxy, mercapto, mercaptal, mercaptol, carboxyl, metal carboxylate, ester, thioester, keto, thioketo, alkoxy, aryloxy, thioether, polysulfide, aldehyde, thioaldehyde, oxime, amido, thioamido, carbamido, aralkyl, alkyl, alkaryl, aryl, halogen, nitro, nitroso, nitrosamino, amino, amidine, imino, N-thio, diazo, hydrazino, cyano, cyanate, thiocyanate, azoxy, azo and hydrazo radicals; b is equal to the number of Y substituents attached to a single aryl nucleus T and is equal to a numeral from 0 to 4; c is equal to the number of (X-M-SH) groups and is a whole number from 1 to 2; M is a polyvalent metal; and X is a radical selected from the group consisting of:



wherein R' in such X groups is selected from the group consisting of hydrogen and alkyl, alkaryl, aryl and aralkyl radicals. Although as contemplated herein X may be any of the several groups enumerated above, particularly preferred of such groups are:



In general, the substituted aryl nucleus may be represented by



and may be any organic radical characterized by an alkyl-substituted aromatic group to which the polyvalent metal may be attached at the aryl nucleus either directly or through an intervening inorganic element or organic radical.

Some of the reaction products or compounds contemplated herein may have two or more alkyl- and -XMSH- substituted aromatic nuclei such as those in which the aromatic nucleus (T) are connected by an ether, thioether, polysulfide, or keto group represented by the symbol Y defined above. A particularly preferred reaction product or compound of this type is one in which two or more benzene nuclei are connected through one or more disulfide groups.

It will be understood that, although M is shown in Formula I above, and in the group (-X-M-SH) as having only two bonds or valences, the symbol M broadly defines a polyvalent metal having two or more bonds or valences. This will be further understood from the following typical polyvalent metals contemplated as constituents in the reaction products of this invention. Thus, M is a polyvalent metal and may be 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, colum-

bium, gallium, gold, indium, iridium, molybdenum, osmium, rubidium, selenium, tantalum, tellurium, thorium, titanium, tungsten, uranium, and zirconium. Preferred of such metals, however, are the divalent metals, and of the latter, calcium, barium and cobalt are particularly preferred.

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

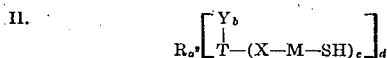
As aforesaid, compounds described by general Formula I contain at least one oil-solubilizing substituent such as an alkyl group. Oil solubility is imparted to the compounds or reaction products contemplated herein with alkyl substituents, such substituent or substituents should contain at least 10 carbon atoms in alkyl groupings, such as, two amyl groups. Within this general class 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 or addition agents are referred to as "wax" substituted. It is to be understood, however, that other equivalent long-chain aliphatic hydrocarbon 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 in imparting pour depressing and viscosity index improving properties to these agents. These preferred metal-organic 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 compositions are not readily soluble in viscous mineral oil fractions. This degree of alkyl- or wax-substitution for our oil-soluble or oil-miscible metal-organic compound 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 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 aryl nuclei, each of which aryl nuclei has at least one -X-M-SH substituent, and each of which may have attached to it one or more monovalent wax substituents and may, in addition, have other substituents such as represented above by Y.

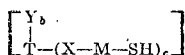
Formula I above is, as aforesaid, the most probable formula by which the reaction products or compounds contemplated herein may be represented; the formula, however, is not completely self-explanatory, for the scope of the formula is much more comprehensive in view of the various ways by which an alkyl group and particularly a "wax" group, or "wax" groups, may be attached to two or more aromatic nuclei (T).

It should be borne in mind that (wax)_a, as repre-

sented by R_a in Formula I, may be one or more monovalent or polyvalent aliphatic hydrocarbon groups of at least twenty carbon atoms or a mixture of such groups. Therefore, to illustrate more completely and more accurately the field of invention, taking into consideration the polyvalent "wax" type of compound or composition, and also taking into consideration the possibility of other substituents (R and Y) in the aryl nucleus, the following probable formula has been devised:



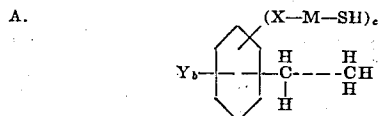
in which the symbols T, Y, X, M, a, b and c have the same significance described above under Formula I; R represents an oil-solubilizing alkyl or "wax" group as defined above in connection with general Formula I; v represents the valence of the alkyl or wax radical R, which we have found for best results in obtaining oil-miscible products should be one to four; and d represents a whole number preferably from one to four, and indicates the total number of groups



present in the molecule represented by Formula II and which are attached to the aliphatic group or groups represented by R.

In the foregoing probable Formula II, which represents the reaction products or compounds contemplated herein, it will be observed that the reaction products or compounds represented thereby include those materials in which all of the "wax" substituent (R) is monovalent ($v=1$ and $d=1$), or in which all of the "wax" substituent is polyvalent (v and d preferably being equal to 2, 3 or 4). Since R is defined as always being "at least one" and may therefore include several such groups, it will also be observed that this general Formula II is inclusive of reaction products or compounds having aliphatic groups or radicals of different valences (preferably from 1 to 4) in the same molecule. Also, it will be observed that in our reaction products or compounds when d is any whole number from one to four, the number of aromatic nuclei in the molecule may likewise vary from one to four. Therefore, it will be seen that the relationship between d and v in Formula II in its broadest construction is such that when d is equal to one, v is equal to one, and when d is greater than one, the valence v of at least one of the R's is equal to d in order to tie the several nuclei or T's together, the valence of any remaining R's being any whole number equal to or less than d .

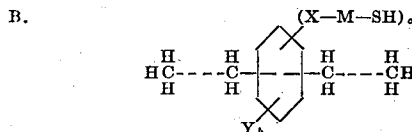
The more simple types of reaction products or compounds coming under general Formula II in which v and d are both equal to one and in which there is only one "wax" substituent, R, may be illustrated by the following formula showing T for purposes of illustration as a mono-cyclic nucleus:



In the above Formula A, the chain corresponds to the symbol "R" above and represents an oil-solubilizing aliphatic hydrocarbon group, which, for the preferred multi-functional oil-improving agents has at least twenty carbon atoms.

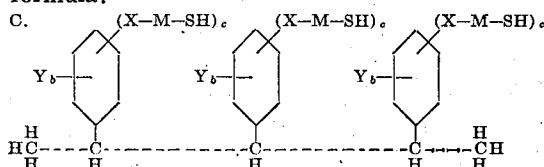
Since R has been defined as "at least one," it

will be apparent that there may be more than one heavy alkyl ("wax") substituent attached to the nucleus T. Such a reaction product or compound, wherein v and d are both equal to one and in which there are two such monovalent R groups, may be represented by the following formula:

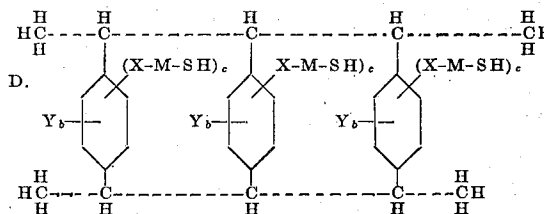


in which the chains and substituent characters have the same significance defined above.

Reaction products or compounds of the type satisfying general Formula II, in which R is polyvalent and v and d are both more than one and in which there is only one such polyvalent R group, may be illustrated by the following formula:

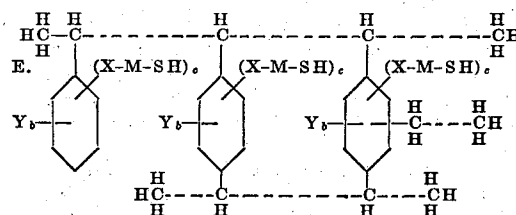


In this same type of reaction product or compound indicated by Formula C, there also may be more than one R ("wax") group (represented by the chain), such reaction product or compound in which there are, for example, two polyvalent R groups being illustrated by the following formula:



The possible molecular structure of reaction products or compounds in which the aryl nucleus T is poly-cyclic will be obvious from the foregoing illustrative formulae A to D inclusive and the possible molecular structure of compounds in which v and d are both equal to two and four will be readily understood from the illustrative Formulae C and D.

Other possible molecular structures of reaction products or compounds coming under general Formula II are those having a plurality of R ("wax") groups of different valences. Such a reaction product or compound may be typified by the following Formula E in which the symbols have the same significance as in the formulae above:

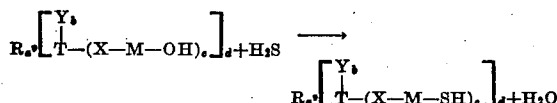


With regard to the number of R groups going to make up a single molecule, this will vary with the extent to which it is desired to effect substitution of the nucleus with the alkyl or "wax" derivatives for obtaining the desired properties

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 also be apparent that replaceable hydrogens on the nuclei may all be substituted with polyvalent "wax" substituents.

It will be understood that the oil-improving agents contemplated by this invention may be pure compounds satisfying the probable Formulae I and II above with a mono- or poly-cyclic nucleus as T substituted with at least one XMSH group and at least one oil-solubilizing alkyl group, such as a "wax" group, and with or without one or more of the various Y substituents. However, in preparing the oil-improving products defined hereinabove, 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 corresponding to different values of *d* and *v* and to different numbers of "wax" (R) groups, and for this reason the products contemplated herein are described as reaction products as well as compounds.

The reaction products or compounds contemplated herein are broadly defined as the metal hydrosulfides of basic polyvalent-metal salts of alkyl-substituted aromatic hydrocarbon compounds, and are obtained herein by reacting hydrogen sulfide with basic metal salts of such organic compounds such that water is eliminated and the desired reaction products or compounds are formed. Such procedure may, for illustrative purposes, be represented by the following reaction:



wherein all symbols are as hereinabove defined.

A general procedure which may be followed for the preparation of the reaction products or compounds defined hereinabove is illustrated by the following in which a typical aromatic hydrocarbon, a hydroxyaromatic compound, is used. The hydroxyaromatic compound is first substituted, or alkylated, with one or more oil-solubilizing groups to the desired extent as by reacting said hydrocarbon with a chlorinated paraffin wax in the presence of a Friedel-Crafts catalyst. The wax-substituted compound so obtained is then converted to the corresponding alkali metal salt, or alkali metal aryl oxide, by reaction with an alkali metal. The alkali metal salt so formed is then reacted with two equivalents of a polyvalent metal hydroxide whereupon the basic metal salt of the wax-substituted hydroxyaromatic compound is formed. The basic metal salt so obtained is then reacted with H₂S to form the desired reaction product of the class contemplated herein.

Where other Y substituents, such as a sulfide or disulfide group, are desired, they are usually introduced into the aromatic compound after the alkali metal salt, as above, is formed and before the corresponding basic metal salt is formed. It will be obvious to those familiar with the art that

various modifying substituents as defined above by the symbol Y may be introduced by modifying the foregoing general procedure by the use of any of the well-known chemical methods. Such modifications will be made apparent by Examples I, II and III provided hereinafter.

Typical basic polyvalent-metal salts of organic compounds which may be reacted with H₂S to form the polyvalent-metal hydrosulfides contemplated herein are disclosed in Patent 2,197,835 issued to O. M. Reiff. The basic metal salts are described therein as metal compounds wherein one valence of a polyvalent metal (as, for example, a divalent metal) is satisfied by a hydroxyl group. A preferred method of preparation of these basic metal salts consists in the use of one extra equivalent of alkali hydroxide in the neutralization of the corresponding free aromatic acid or corresponding free hydroxyaromatic compound, etc., which is substituted with at least one R substituent, at least one X group, and which may or may not be substituted with Y substituents, followed by treatment with an amount of polyvalent-metal salt (preferably a halide) equivalent to the alkali hydroxide used. While this is the preferred method of forming these basic metal salts, basic metal salts are formed to a certain extent even when exactly equivalent amounts of reactants are used. Another method of formation consists in reacting the organic compound, which is substituted with at least one R substituent, at least one X group, and which may or may not be substituted with Y substituents, with a metal hydroxide. It is to be understood, however, that while we have pointed out a preferred procedure for forming the aforesaid basic metal salts, and have mentioned other such procedures, the present invention is not to be confined to such procedures; for, as aforesaid, these basic metal salts may be prepared in any way known to the art.

To more fully describe the metal-organic compounds or compositions contemplated herein, the following typical procedures for the preparation of representative compounds or compositions are provided.

EXAMPLE I

REACTION PRODUCT OF BASIC COBALTOUS PHENATE-COALTOUS CARBOXYLATE OF WAX PHENOL CARBOXYLIC ACID (3-14) AND H₂S

(a) Preparation of sodium phenate-sodium carboxylate of wax-phenol carboxylic acid (3-14)

A wax-substituted phenol prepared according to the procedure provided in U. S. Patent 2,197,834, issued to O. M. Reiff, in which a quantity of chlorwax containing 3 atomic proportions of chlorine (14 per cent chlorine in the chlorwax) is reacted with one mol of phenol, may, for brevity herein, be designated "wax-phenol (3-14)." Parenthetical expressions of this type (A-B) will be used hereinafter in connection with the alkylated hydroxyaromatic compounds to designate (A) the number of atomic proportions of chlorine in chlor-aliphatic material reacted with one mol of hydroxyaromatic compound in the Friedel-Crafts reaction, and (B) the chlorine content of the chlor-aliphatic material. In the wax-substituted phenol referred to above, A=3 and B=14. This same designation will also apply to the metal-organic compounds or compositions contemplated herein.

The sodium phenate-sodium carboxylate of

wax-phenol carboxylic acid (3-14) was prepared according to the procedure furnished in U. S. Patent 2,197,834, referred to above.

(b) *Preparation of basic cobaltous phenate-cobaltous carboxylate of wax-phenol carboxylic acid (3-14)*

A solution of 21 grams of potassium hydroxide dissolved in 100 cc. of butanol was added to 400 grams of a mineral oil blend of the sodium phenate-sodium carboxylate of wax-phenol carboxylic acid (3-14) prepared in I (a), said blend comprising 1 part of said disodium salt and 10 parts of mineral oil. A butanol solution containing 47.2 grams of cobaltous chloride was then added gradually and the mixture was heated at the reflux temperature for about 30 minutes. Then, butanol was distilled off and the reaction product filtered through Hi-Flo whereupon the finished product, basic cobaltous phenate-cobaltous carboxylate of wax-phenol carboxylic acid (3-14) was obtained.

(c) *Preparation of reaction product of I (b) and H₂S*

A mixture of 200 grams of the mineral oil blend of the dicobaltous salt obtained according to I (b) was heated to about 212° F., and with rapid agitation of the mixture, a current of H₂S was introduced into said mixture. Water was formed in the reaction. The mixture was stirred for about three hours with H₂S flowing therethrough, after which time, water was no longer liberated. A current of nitrogen was then introduced to displace any unreacted H₂S. The finished product was thus obtained.

EXAMPLE II

REACTION PRODUCT OF BASIC BARIUM PHENATE OF WAX PHENOL (3-14) DISULFIDE AND H₂S

(a) *Preparation of wax-phenol (3-14) disulfide*

Five-hundred grams of a mineral oil blend of wax-sodium phenate (3-14) prepared according to the procedure furnished in U. S. Patent 2,197,833, was diluted with 100 cc. of benzol. To this mixture was slowly added at room temperature 12.7 grams of sulfur monochloride, the rate of addition being slow enough to avoid appreciable temperature rise. After the sulfur monochloride was added, the mixture was stirred for one hour at room temperature, after which time, 4 cc. of water and 50 cc. of methanol were added. The resulting mixture was then heated to about 80° C. whereupon sodium chloride formed in the reaction was precipitated. The reaction mixture was filtered to remove the sodium chloride.

(b) *Preparation of basic barium phenate of wax-phenol (3-14) disulfide*

A solution of 32.6 grams of BaO in methanol was slowly added to the reaction product obtained in II (a)—wax-phenol (3-14) disulfide. The resulting mixture was then heated to about 125° C. so as to facilitate the reaction and to remove methanol. The mixture was then filtered through Hi-Flo to obtain the basic barium phenate of wax-phenol (3-14) disulfide in approximately a one-third blend in mineral oil.

(c) *Preparation of reaction product of II (b) and H₂S*

Two-hundred grams of the mineral oil blend obtained according to the procedure in II (b) was heated to about 212° F. and a current of H₂S introduced therein. The mixture was rapidly

agitated so as to accelerate the absorption of the gas. Water was formed in the reaction and after three hours of introducing H₂S and stirring the mixture, water no longer was liberated. A current of nitrogen was then introduced to displace any unreacted H₂S and thus obtain the finished product.

EXAMPLE III

REACTION PRODUCT OF BASIC BARIUM SALT OF WAX-SUBSTITUTED DIPHENYL, DITHIOPHOSPHORIC ACID AND H₂S

(a) *Preparation of dithiophosphoric acid derivative of wax phenol (3-14)*

Petroleum wax of ASTM melting point of 126° F. was chlorinated by introducing chlorine at about 150° F. until 14% by weight of chlorine was absorbed. One hundred grams of this chlorwax were mixed with 12.3 grams of phenol and 3 grams of AlCl₃ were added at about 150° F. at a rate slow enough to avoid excessive foaming caused by the evolution of hydrogen chloride. The reaction temperature was then raised to 350° F. and the mixture was stirred for about one hour at this temperature to complete the reaction. A quantity of 207 grams of solvent-refined mineral oil of Saybolt viscosity of 45 seconds at 210° F. was then added, followed by 7.4 grams of P₂S₅, and the resulting mixture was heated for 4 hours at 350° F. During the first hour of heating the mixture, H₂S was steadily evolved and at the end of the remaining time no H₂S was evolved. The reaction mixture was cooled to about 100° C. and water was gradually added in order to decompose the aluminum chloride complex. Emulsions formed in the water-washing operation were broken by adding butanol. The product was then filtered through "Hi-Flo" and the butanol distilled under vacuum to obtain the product in a 1/3 mineral oil blend.

(b) *Preparation of basic barium salt of wax-substituted diphenyl, dithiophosphoric acid (3-14)*

One-hundred grams of the mineral oil blend obtained in III (a) were reacted with 8 grams of Ba(OH)₂·8H₂O by heating the mixture at 150° C. for one hour in order to remove all the water of reaction. The mixture was then filtered through Hi-Flo to obtain the finished product in a one-third mineral oil blend.

(c) *Reaction product of III (b) and H₂S*

One-hundred grams of the mineral oil blend obtained in III (b) above were heated to about 212° F. and at this temperature a current of H₂S was introduced. The mixture was stirred rapidly during the addition of H₂S in order to accelerate the absorption of the gas. The mixture was stirred for about 3 hours whereupon water was no longer liberated in the reaction. A current of nitrogen was then introduced into the reaction mixture so as to displace any unreacted H₂S and thereby obtain the finished product.

Although the foregoing procedures represent preferred embodiments for the preparation of the compounds or compositions of this invention, other procedures which will be apparent to those familiar with the art may be used. It is to be understood that all such procedures are contemplated herein.

To demonstrate the effectiveness of the compounds or compositions of the type described above by the general Formulae I and II in the mineral oil compositions contemplated herein, 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 typical and preferred improving agents contemplated by this invention, reaction products of basic divalent-metal salts of organic compounds and H₂S.

POUR POINT DEPRESSION

The reaction products of basic divalent-metal salts of organic compounds and H₂S contemplated herein are effective pour point depressants. The following results were obtained from blends of mineral lubricating oil having a Saybolt Universal viscosity of 67 seconds at 210° F. and containing the aforesaid metal hydrosulfides prepared according to the procedures outlined above. The pour point of the oil alone was 20° F., and as clearly indicated by Table I below, the metal hydrosulfide reaction products contemplated herein are effective in very small amounts to reduce the pour point by as much as 40° F.

Table I

Reaction product added	ASTM pour tests (° F.) on oil blends		
	0%	1/8%	1/4%
None.....	+20	-----	-----
Reaction product of basic barium phenate-barium carboxylate of wax-phenol carboxylic acid (3-14) and H ₂ S.....	-----	-5	-15
Reaction product of basic barium phenate of wax-phenol (3-14) disulfide and H ₂ S.....	-----	-10	-20
Reaction product of basic cobaltous phenate-cobaltous carboxylate of wax-phenol carboxylic acid (3-14) and H ₂ S.....	-----	-5	-20
Reaction product of basic barium salt of wax-diphenyl (3-14) dithiophosphoric acid and H ₂ S.....	-----	-5	-15

VISCOSITY INDEX

Table II below shows the effectiveness of the metal hydrosulfide reaction products contemplated herein as viscosity index improving agents. The oil used in these tests was a motor lubricating oil fraction having a kinematic viscosity of 30.17 at 100° F.

Table II

Reaction product added	Per cent	Kinematic visc.		V. I.
		100° F.	210° F.	
None.....	0	30.17	4.80	79.8
Reaction product of basic barium phenate-barium carboxylate of wax-phenol carboxylic acid (3-14) and H ₂ S.....	2	34.01	5.25	91.0
Reaction product of basic barium phenate of wax-phenol (3-14) disulfide and H ₂ S.....	2	33.09	5.14	89.1
Reaction product of basic cobaltous phenate-cobaltous carboxylate of wax-phenol carboxylic acid (3-14) and H ₂ S.....	2	33.66	5.23	91.8
Reaction product of basic barium salt of wax-diphenyl (3-14) dithiophosphoric acid and H ₂ S.....	2	35.2	5.38	92.9

OPERATION TEST

In addition to the foregoing tests, comparative test runs have been made on a solvent refined mineral oil of Saybolt Universal viscosity of 45 seconds at 210° F. and on the same oil containing a small amount of a typical improving agent of the type contemplated herein. The test runs were made in a single-cylinder Lauson engine which was cooled with water held at 212° F. so as to maintain an oil temperature of about 290° F. The oil and oil blend were tested for acidity, represented by the neutralization number (N. N.), and for change in viscosity at certain time intervals as a measure of the degree of oxidation.

Table III

Reaction product added	Per cent	N. N.	Saybolt vis. @ 210° F.	Hours run
None.....	0	5.1	50.21	24
Reaction product of basic barium phenate of wax-phenol (3-14) disulfide and H ₂ S.....	2	0.5	45.53	24
None.....	0	6.9	52	36
Reaction product of basic barium salt of wax diphenyl (3-14) dithiophosphoric acid and H ₂ S.....	1	2.0	47	36

From the foregoing results it will be apparent that the reaction products of basic divalent-metal salts of organic compounds and H₂S contemplated by this invention are effective multi-functional oil-improving agents. The improved properties obtained and the degree of improvement in a particular property may be varied with the metal substituents, the metal hydrosulfide substituents represented by the group —X—M—SH, the aryl substituents, and the degree of substitution of the aryl nucleus with R, —X—M—SH and Y groups. As aforesaid, it is to be understood that the symbol M is not limited in scope to divalent metals which it typifies in the foregoing formulae and groups, but is broad to polyvalent metals.

The amount of improving agent used may be varied, depending upon the mineral oil or the mineral oil fraction with which it is blended and the properties desired in the final oil composition. The metal hydrosulfide reaction products of the type contemplated herein may be used in amounts ranging from 0.1 per cent to 5 per cent, and, in general, compositions of the desired improved properties may be obtained with these improving agents in amounts of from 1/8 per cent to 2 per cent.

It is to be understood that while we have described certain preferred procedures which may be followed in the preparation of the reaction products of H₂S and basic polyvalent-metal salts of organic compounds used as improving agents in the mineral oil compositions contemplated by this invention and have referred to various typical constituents in these improving agents, such procedures and examples 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:

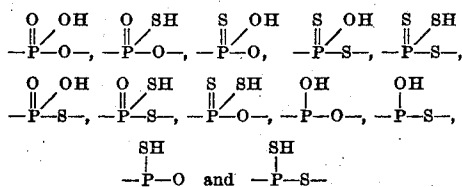
1. An improved mineral oil composition comprising a viscous mineral oil and in admixture therewith a minor proportion, from about 0.1 per cent to about 5 per cent, of an oil-soluble metal hydrosulfide of a basic polyvalent-metal salt of an alkyl-substituted aromatic hydrocarbon compound, said alkyl substituent being an oil-solubilizing alkyl group.

2. An improved mineral oil composition comprising a viscous mineral oil having in admixture therewith a minor proportion of an oil soluble metalorganic compound having the general formula:



wherein T is an aromatic nucleus; R is an oil-

nucleus T; v represents the valence of the alkyl group and is equal to a numeral from 1 to 4; a is the number of R substituents attached to a single nucleus T and is a numeral from 1 to 2; M is a polyvalent metal; X is a radical selected from the group consisting of:



and d represents the number of



groups and is a numeral from 1 to 4; said metal-organic compound being present in a minor proportion sufficient to improve said mineral oil in at least one of the following respects: pour point, viscosity index, and resistance to oxidation.

8. An improved mineral oil composition comprising a viscous mineral oil having in admixture therewith a minor proportion of an oil-soluble, cobaltous hydrosulfide of a basic cobaltous phenate-cobaltous carboxylate of a wax-phenol carboxylic acid, said cobaltous hydrosulfide being present in a minor proportion sufficient to improve said mineral oil in at least one of the following respects: pour point, viscosity index, and resistance to oxidation.

9. An improved mineral oil composition comprising a viscous mineral oil having in admixture therewith a minor proportion of an oil-soluble, barium hydrosulfide of a basic barium phenate of a wax-phenol disulfide, said barium hydrosulfide being present in a minor proportion

sufficient to improve said mineral oil in at least one of the following respects: pour point, viscosity index, and resistance to oxidation.

10. An improved mineral oil composition comprising a viscous mineral oil having in admixture therewith a minor proportion of an oil-soluble, barium hydrosulfide of a basic barium salt of a wax-substituted diphenyl dithiophosphoric acid, said barium hydrosulfide being present in a minor proportion sufficient to improve said mineral oil in at least one of the following respects: pour point, viscosity index, and resistance to oxidation.

11. An improved mineral oil composition comprising a viscous mineral oil and in admixture therewith a minor proportion of an oil-soluble metal hydrosulfide of a basic polyvalent-metal salt of an alkyl-substituted aromatic hydrocarbon compound, said alkyl substituent being an oil-solubilizing alkyl group, and said metal hydrosulfide being present in a minor proportion sufficient to improve said mineral oil in at least one of the following respects: pour point, viscosity index, and resistance to oxidation.

12. An improved mineral oil composition comprising a viscous mineral oil and in admixture therewith a minor proportion of an oil-soluble metal hydrosulfide of a basic divalent-metal salt of an alkyl-substituted aromatic hydrocarbon compound, said alkyl substituent being an oil-solubilizing alkyl group, and said metal hydrosulfide being present in a minor proportion sufficient to improve said mineral oil in at least one of the following respects: pour point, viscosity index, and resistance to oxidation.

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