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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 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

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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 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.

If 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 application. 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 salts of certain reaction products 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 the oil-soluble, metal salts of acidic, phosphorus- and sulfur-containing reaction products obtained by reaction of a phosphorus sulfide and a primary or secondary aromatic amine.

The aforementioned acidic, phosphorus- and sulfur-containing reaction products may be prepared by reacting a phosphorus sulfide, such as P_2S_3, P_2S_5, P_4S_3, P_4S_7, etc., with an amine of the type contemplated herein. Of the phosphorus sulfides, phosphorus pentasulfide (P_2S_5) is particularly preferred.

The amines used in preparing the acidic, phosphorus- and sulfur-containing reaction products, from which the corresponding metal salts are derived, are primary and secondary alkyl-substituted aromatic amines characterized by at least about 10 carbon atoms in aliphatic groupings, that is, at least about 10 aliphatic carbon atoms. Included among such amines are alkyl-nuclear-

substituted primary and secondary aromatic amines and alkyl-N-substituted secondary aromatic amines wherein the aliphatic substituent contains at least about 10 carbon atoms. Illustrative of the amines contemplated herein are mono- and di-octadecenyl aniline, p-dodecyl aniline, paraffin wax-substituted aniline, mono- and di-octadecenyl diphenyl amine and paraffin wax-substituted naphthyl amine.

The aforesaid acidic, phosphorus- and sulfur-containing reaction products are preferably prepared by reacting substantially four mols of a primary or a secondary amine with one mol of a phosphorus sulfide, preferably P_2S_5, at temperatures from about 100° C. to about 1750 C. for several hours. During the reaction, hydrogen sulfide is readily evolved. That different reaction products may be obtained by reacting an amine of the aforesaid type with P_2S_5, is shown by varying the reaction time or reaction temperature, or both. If the reaction mixture of the amine and P_2S_5 is heated for a relatively short period of time, a product having a higher neutralization number is obtained, rather than a product of lower neutralization number when a relatively long reaction time is used. However, the intermediate products having a theoretical neutralization number based upon a substituted di-amide dithiophosphoric acid, which may be present in the reaction product, and those having neutralization numbers greater than, or less than, the theoretical value are not suitable as oil additives, inasmuch as they are corrosive to such metals as copper, are somewhat unstable with a gradual liberation of hydrogen sulfide and, therefore, have an objectionable odor.

In preparing the intermediate products, the reactants, amine and P_2S_5, may be added to each other in any order. A typical procedure involves adding the amine to P_2S_5. This reaction may also be carried out in the presence of diluents or solvents such, for example, as mineral oil, xylene, high-boiling naphthas and the like. In the event that mineral oil is used as a diluent, the mineral oil may be retained rather than separated from the intermediate product, thereby providing a mineral oil concentrate and the latter may thereafter be retained to obtain a metal salt of the acid present therein.

Metal salts of the acidic intermediate reaction products obtained as indicated above may be formed by reacting the said acidic product with a metal oxide or hydroxide. Wherever necessary, an alcoholic solution of the oxide or hydroxide may be used. Metal salts of the said acids may also be prepared by adding an alcoholic solution of a metal containing a reagent such as stannous chloride, lead acetate, thorium nitrate, titanium tetrachloride, etc. to a barium or sodium salt of the acid, followed by distilling off the alcohol and filtering out the precipitated sodium chloride or barium chloride. Among the metals contemplated herein are: sodium, potassium, copper, magnesium, calcium, barium, zinc, cadmium, mercury, tin, lead, chromium, manganese, iron, cobalt, nickel, aluminum, antimony, arsenic, bismuth, and titanium. Preference is given to metals of the alkaline earth group, particularly to barium.

In connection with the formation of the aforesaid metal salts, it has been found that the salts are preferably prepared by reacting the theoretical amount, or a small excess, of the metal-containing reagent with the intermediate product. When twice the theoretical amount of polyvalent metal-containing reagent is used, it appears that the basic metal salt of a polyvalent metal is formed.

The metal salts contemplated herein are illustrated by the following typical examples.

EXAMPLE I

A slurry of 16.8 grams of P_2S_5 in 150 grams of mineral oil (S. U. V. of 45 seconds at 210° F.) was stirred at 100° C. To this slurry was added a blend of 150 grams of di-octadecenyl aniline and 150 grams of the same mineral oil; this addition required 45 minutes. After the oil blend had been added to the slurry, the temperature of the resulting reaction mixture was raised to 125° C. and maintained for two hours in order to effect complete reaction of the P_2S_5. Hydrogen sulfide was evolved during the reaction. At the end of said two hour period, the reaction mixture was filtered through Hi-Flo clay on a steam heated funnel. The product had an odor of hydrogen sulfide and is approximately a 1/3 blend in mineral oil.

The aforesaid intermediate reaction product (375 grams) and 28.9 grams of barium hydroxide octahydrate with 150 ccs. of methanol were heated up to 70° C. to effect reaction of the barium hydroxide and to distill off the alcohol. When most of the alcohol and water of reaction were removed, the temperature was slowly raised to 150° C. The reaction mixture was heated at 150° C. for one hour, during which time hydrogen sulfide was evolved. The reaction mixture was then filtered through Hi-Flo clay on a steam-heated funnel. Two hundred grams of the filtrate from a total of 332 grams was further reacted with 9.3 grams of barium hydroxide octahydrate using the same procedure. The product finally obtained is a barium salt and is designated herein as product I. Product I has the following analysis: neutralization number, 0.2; phosphorus, 2.55 per cent; sulfur, 1.95 per cent; nitrogen, 2.40 per cent; barium, 14.58 per cent.

The di-octadecenyl aniline used in this example was prepared by the procedure described in U. S. Patent No. 2,118,493, issued to Coffey and Haddock, by reacting the following materials: 510 grams of ocenol (technical oleyl alcohol), 93 grams of aniline, 43 grams of aniline hydrochloride, 71 grams of zinc chloride. The di-octadecenyl aniline so obtained contained 2.84 per cent nitrogen and had a molecular weight of 531.

EXAMPLE II

Para-dodecyl aniline (36 grams) 7.6 grams of P_2S_5 and 42 grams of mineral oil (S. U. V. at 45 seconds at 210° F.) were heated together at 150° C. for 3½ hours during which time hydrogen sulfide was evolved. The reaction mixture was then filtered at 100° C. through Hi-Flo clay on a steam-heated funnel. The product had a neutralization number of 6.0 and is a 1:1 blend in mineral oil. Fifty grams of the aforesaid reaction product, 4 grams of barium hydroxide octahydrate, 25 grams of mineral oil (S. U. V. at 45 seconds at 210° F.) and 75 ccs. of methanol were heated at 70° C. in order to effect reaction of the barium-containing reagent in the aforesaid reaction product. Most of the methanol distilled out at this temperature, 70° C., and final traces thereof were removed together with water of reaction when the temperature was raised slowly to 150° C. for 30 minutes. Hydrogen sulfide was also evolved. The reaction mixture was then filtered through Hi-Flo clay on a steam heated funnel. The filtrate was a dark green oil having a neutraliza-

tion number of 1.4. Sixty-one grams out of a total of 70 grams of this product and 20 grams of the original para-dodecyl aniline-P_2S_5 product were further treated with 3.5 grams of barium hydroxide octahydrate in the same procedure. The reaction product (product II) is a barium salt in a 1:2 mineral oil blend. This product is non-corrosive to copper, as evidenced by a copper strip test at 100° C. for 24 hours.

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

CORROSION TEST

In this test metal salts were blended with a Pennsylvania solvent-refined oil having a S. U. V. 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 each 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 differences between the losses in weight of the two bearing sections demonstrated conclusively the effectiveness of the metal salts contemplated herein as corrosion inhibitors.

Table I

Addition Agent	Conc., Wt. Per cent	Bearing Loss, mgms.	
		Inhibited Oil	Uninhibited Oil
Product I	1/10	0	23
Product II	1/20	0	28

OPERATION TEST

To demonstrate the effectiveness of the metal salts under actual operating conditions of an automotive engine, unblended oils and improved oils, containing the metal salts, 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 36 hours with a 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 a viscosity of 45 seconds S. U. V. at 210° F.

Table II

Addition Agent	Conc., Wt. percent	Kv. @ 210° F.	N. N.
None		8.8	9.59
Product I	1	6.5	8.39

The amount of improving agent which may be used in an oil varies with the type of oil fraction with which it is blended and with the properties desired in the final oil compositions. In general, satisfactory improvement is realized when amounts from about 0.10 per cent to about 10 per cent of the metal salts are used in viscous mineral oil fractions, with amounts of the order of 2 per cent being preferred.

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

I claim:

1. A mineral oil fraction containing a minor proportion, from about 0.1 per cent to about 10 per cent, of an oil-soluble, metal salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction, at a temperature within the range varying between about 100° C. and about 175° C., of a phosphorus sulfide and an amine selected from the group consisting of an alkyl-nuclear-substituted primary and secondary aromatic amine and an alkyl-N-substituted secondary aromatic amine, said alkyl substituent being characterized by at least about 10 carbon atoms.

2. A mineral oil fraction containing a minor proportion, from about 0.1 per cent to about 10 per cent, of an oil-soluble, metal salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction, at a temperature within the range varying between about 100° C. and about 175° C., of phosphorus pentasulfide and an amine selected from the group consisting of an alkyl-nuclear-substituted primary and secondary aromatic amine and an alkyl-N-substituted secondary aromatic amine, said alkyl substituent being characterized by at least about 10 carbon atoms.

3. A mineral oil fraction containing a minor proportion, from about 0.1 per cent to about 10 per cent, of an oil-soluble, metal salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction, at a temperature within the range varying between about 100° C. and about 175° C., of phosphorus pentasulfide and an alkyl - nuclear - substituted primary aromatic amine, said alkyl substituent being characterized by at least about 10 carbon atoms.

4. A mineral oil fraction containing a minor proportion, from about 0.1 per cent to about 10 per cent, of an oil-soluble, metal salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction, at a temperature within the range varying between about 100° C. and about 175° C., of phosphorus pentasulfide and an alkyl-nuclear-substituted secondary aromatic amine, said alkyl substituent being characterized by at least about 10 carbon atoms.

5. A mineral oil fraction containing a minor proportion, from about 0.1 per cent to about 10 per cent, of an oil-soluble, metal salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction, at a temperature within the range varying between about 100° C. and about 175° C., of phosphorus pentasulfide and an

alkyl-N-substituted secondary aromatic amine, said alkyl substituent being characterized by at least about 10 carbon atoms.

6. A viscous mineral oil fraction containing therewith a minor proportion, from about 0.1 per cent to about 10 per cent, of an oil-soluble, barium salt of an acidic, phosphorus- and sulfur-containing reaction product obtained by reaction, at a temperature within the range varying between about 100° C. and about 175° C., of phosphorus pentasulfide and di-octadecenyl aniline.

7. A viscous mineral oil fraction containing a minor proportion, from about 0.1 per cent to about 10 per cent of an oil-soluble, barium salt of an acidic, phosphorus- and sulfur-containing

reaction product obtained by reaction, at a temperature within the range varying between about 100° C. and about 175° C., of phosphorus pentasulfide and para-dodecyl aniline.

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

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