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LUBRICANT COMPOSITION

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10 Claims. (Cl. 252—32.7)

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The present invention relates to improvements in lubricants and especially to the improvement of lubricating oils principally useful for internal combustion engines operating under severe conditions. The invention will be fully understood from the following description.

Lubricating oils which exhibit improved performance under all types of operating conditions when used for the lubrication of heavy duty gasoline engines and for Diesel engines are coming into greater and greater demand. It has been proposed to add various ingredients to these oils to improve their behavior in such service. In accordance with the present invention, certain ingredients are added to bring about greater engine cleanliness and to avoid ring sticking, varnish formation and carbon deposition, also to avoid corrosion of metal parts. It is therefore an object of the present invention to provide addition agents for lubricating oils of the type described which not only exhibit such detergent and corrosion inhibiting properties, but which will not increase the pour point of the oil and will blend readily with the oil to form a solution which will remain homogeneous both during storage and during use.

It is known that various salts, particularly metal salts, have a beneficial effect on lubricating oils to which they are added, that is, these salts exhibit detergent properties by inhibiting the formation of sludge deposits and in promoting general cleanliness in the engine; and they have the further very valuable property of preventing the normal deterioration of oils which results in the corrosion of metal parts, particularly the cadmium-silver and copper-lead alloys which are now widely used in bearings. Many metallic salts have been proposed for use in lubricants, and among the most valuable of these are the metallic salts of inorganic acids having substituent oil-solubilizing organic groups. For example, the alkaline earth salts of substituted orthophosphoric acids, such as calcium cetyl phosphate, calcium (cetyl phenyl) phosphate, aluminum octadecyl phosphate and chromium oleyl phosphate, and the cadmium, tin and cobalt mahogany sulfonates are among those which have been disclosed as addition agents.

It has been found, however, that there is one drawback to the use of such salts, and that is

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their tendency to promote the deposition of varnish on the engine parts with which the oil containing the salt comes in contact. Such varnish formation is very objectionable, since it contributes to ring sticking, and when the deposits become sufficiently heavy on piston skirts the pistons may "freeze" to the cylinder walls. It has been found, in accordance with the present invention, that this tendency to form varnish can be materially reduced and often entirely eliminated if a small amount of a high molecular weight alcohol is added to the oil containing the metallic salt. The action of the alcohol is not understood, since the addition of alcohol alone to uncompounded oils sometimes actually increases the amount of varnish formed. It is evident, therefore, that the alcohol and salt cooperate with each other in some way to mutually inhibit the normal tendency of each to produce a certain amount of varnish.

The invention may be defined in its broadest terms as the use in mineral lubricating oils of a higher alcohol together with a salt of an inorganic acid which contains at least one oil-solubilizing substituent organic group.

The higher alcohols suitable for use in conjunction with the metal salts are preferably those having 8 carbon atoms or more, though in general alcohols falling in the C_{12} to C_{20} range are preferred. These alcohols include the saturated, straight or branched chain aliphatic alcohols, such as octyl alcohol, lauryl alcohol, cetyl alcohol, stearyl alcohol and the like; the corresponding olefinic alcohols, such as oleyl alcohol; cyclic alcohols, such as naphthenic alcohols; and aryl substituted alkyl alcohols, for example, phenyl octyl alcohol, or octadecyl benzyl alcohol; or mixtures of these alcohols, which may be pure or substantially pure synthetic alcohols. There may also be used mixed naturally occurring alcohols, such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from these materials, for some purposes the wool fat, sperm oil or other natural products rich in alcohols may be used as such. Products prepared synthetically by chemical processes may also be used, such as al-

cohols prepared by the oxidation of petroleum hydrocarbons, e. g., paraffin wax, petrolatum, etc. In general, the effectiveness of the alcohol increases with its molecular weight and straight chain alcohols have been preferred in view of their greater availability.

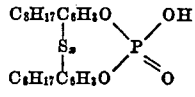
The amount of higher alcohols to be used may vary between the approximate limits of 0.01 to 5.0%, though generally from 0.1 to 1.0% is preferred, the exact amount to be used depending upon the severity of the operating conditions and upon the type of lubricating oil base stock used.

The salts used in the lubricating compositions of the present invention may, in general, be any metallic salts of inorganic acids containing at least one organic group which serves to render the salt soluble in mineral oil. This organic group may appear as a substituent for one of the hydrogen atoms of the inorganic acid from which the salt was derived, or the group may even appear as a substituent for a hydroxyl group of such acid, as in the case of salts of organic sulfonic acids which may be considered as sulfuric acid in which one hydroxyl group is substituted by an organic group. Since there must be at least one metal atom or equivalent radical and at least one solubilizing organic group in the salt, such salt must necessarily be derived from a polybasic inorganic acid.

The organo substituted inorganic acids of which the preferred salts of the present invention may be considered as derivatives may be any organo substituted inorganic acids capable of forming oil soluble metallic salts, such, for example, as octadecyl phosphoric acid ($C_{18}H_{37}O(OH)_2PO$), dodecyl phosphoric acid ($C_{12}H_{25}O(OH)_2PO$), diisobutylphenyl phosphorous acid

$$[(C_8H_{17}C_6H_4O)_2(OH)P]$$

oleyl sulfuric acid ($C_{18}H_{35}O(OH)SO_2$), amyl phenyl sulfonic acid ($C_5H_{11}C_6H_4(OH)SO_2$), tetradecyl phosphoric acid ($C_{14}H_{29}(OH)_2PO$), naphthenyl phosphinic acids, hexadecyl thiophosphoric acid ($C_{16}H_{33}S(SH)_2PS$), diisobutyl diphenyl sulfide phosphoric acid, which in its simplest form may be represented as



amyl benzyl sulfurous acid

$$[(C_5H_{11}C_6H_4CH_2O)(OH)SO]$$

and dioctyl sulfamic acid $[C_8H_{17})_2N(OH)SO_2]$, as well as comparable substituted arsenic, arsenious, arsinic, arsonic, stannic, stannous, chromic, chromous, plumbic, aluminic and silicic acids and the like, also the corresponding acids in which sulfur, selenium or tellurium is substituted for oxygen. Included also are the derivatives of the above named acids in which halogen, oxygen, nitrogen and sulfur substituents appear in the organic group. Especially preferred salts are the phosphates and thiophosphates, also sulfates and sulfonates, particularly those derived from petroleum.

In the foregoing discussion, as well as elsewhere in this specification, the diisobutyl radical forming part of various compounds is to be understood as being derived from diisobutylene, and such radical may also be designated as tetramethyl butyl.

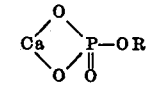
The metals which may appear in the salts which are added to the mineral lubricating oils

may be any metals, and the salts may include salts of amines, pyridine and similar basic nitrogen compounds, ammonium (NH_4—) or salts of ammonium containing one to four substituent organic radicals, such as the quaternary ammonium salts, and the corresponding salts of phosphonium, sulfonium, arsonium, and stibonium bases. Especially preferred are the metals of groups I, II, III and VIII of the periodic table. Salts of group II, such as magnesium, calcium and barium salts, have been found to be particularly effective.

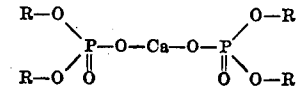
The oil-solubilizing substituent organic group which appears as part of the salt structure may be of any type, providing only that it imparts appreciable oil solubility to the salt. Thus, the substituent groups may be alkyl, alkoxy, aryl, aralkyl or heterocyclic groups, and such groups may, furthermore, contain substituent groups and atoms, for example, amino, nitro, hydroxy or mercaptan groups, or halogen atoms.

Typical of the metallic salt compounds preferred for use in accordance with the present invention are the following, which are illustrated by structural formulas showing the structures which a few of the most preferred compounds are believed to possess, R in the formulas designating an organic group:

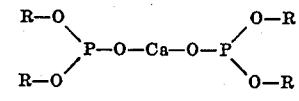
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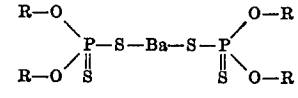
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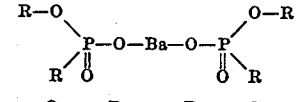
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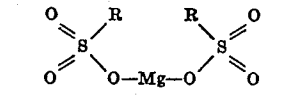
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Among the most preferred substituted inorganic salts, to be added to lubricating oils in conjunction with the higher alcohols described above, are the following, which are given by way of illustration only: calcium cetyl phosphate, barium dioctyl dithiophosphate, diisobutyl di(triamylammonium phenolate) sulfide and magnesium petroleum sulfonate.

The substituted inorganic salts described above may be prepared in various ways. One typical method, such as that described in U. S. Patent No. 2,228,659, consists in reacting an appropriate inorganic oxide or sulfide, for example, an oxide or sulfide of phosphorus, with an aliphatic alcohol to form an alkyl substituted inorganic acid, which is subsequently reacted with an alkali to form the alkali salt, and the desired metal salt is formed by precipitating from a solution of the alkali salt on adding the appropriate metal ion. In the case of the preparation of salts of sulfonic acids, such as the calcium or barium salts, alkali salts of sulfonic acids, well-known as emulsify-

ing agents and obtained from petroleum fractions or other hydrocarbon materials by means well known to the art, may be reacted in appropriate solutions with calcium or barium salts to form the corresponding calcium or barium soaps of the sulfonic acid.

Generally, the amount of the salt to be used in the compositions of the present invention should be between the approximate limits of 0.02 and 2.0%, and preferably from 0.1 to 1.0%, the exact amount to be used depending to a certain extent on the particular compound, the amount of higher alcohol used, the character of the mineral oil base and the operating conditions of the engine in which the lubricant is to be used.

The lubricating oil base stock for this invention, in its broadest aspect, may be any mineral oil distillate or blend and may contain a residual oil, or it may be a fraction resulting from various physical and chemical refining treatments, such as solvent extraction, precipitation, etc. For the best result, however, the base stock chosen should usually be that oil which, without the additives present, gives the optimum performance in the service contemplated. For the lubrication of medium and high speed Diesel engines it is general practice to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, preference is often expressed for oil of very high viscosity index (100 or higher) and such oils are to be considered as within the scope of the present invention. The oils may be free from other addition agents or they may contain other materials for particular purposes, for example, thickeners, sludge dispersing agents, dyes, pour depressants, viscosity index improvers, solvents, oiliness agents and antioxidants.

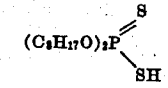
In the following examples there are described in detail methods of preparing a number of the preferred addition agents of the present invention and tests showing their use in a typical Diesel oil, together with the results obtained in the test of the amount of varnish film formation resulting from the use of the prepared blends. These examples are to be considered as illustrative only and not as limiting the scope of the invention in any way.

Example I

For the preparation of calcium octyl thiophosphate, a mixture of 444 grams of phosphorus pentasulfide, 1170 grams of octyl alcohol, and 250 grams of sodium carbonate was heated gradually to 70° C. and finally to 110° C. with agitation until evolution of carbon dioxide and hydrogen sulfide had ceased. The reaction mixture was filtered and then diluted with 500 cc. of absolute ethyl alcohol. A solution of 2 mols of calcium nitrate in 1 liter of ethyl alcohol was added and the mixture filtered to remove the sodium nitrate formed. The ethyl alcohol was removed from the filtrate under vacuum and the residue diluted with 1.5 liters of petroleum ether and again filtered to remove the unreacted calcium nitrate. The latter filtrate was contacted with metallic mercury to remove active sulfur as mercuric sulfide and again filtered. The petroleum ether was stripped from the product and the latter was heated to 135°–140° C. under 3–4 mm. pressure for about 30 minutes to remove unreacted octyl alcohol.

Example II

For the preparation of barium octyl thiophosphate, 520 grams of octyl alcohol (2-ethyl hexanol) and 222 grams of powdered phosphorus pentasulfide were placed in a reaction flask and heated to 80° C. with agitation. Evolution of hydrogen sulfide began at about 50° C. and the reaction was practically complete after 3–4 hours at 80° C., but the mixture was agitated at 40–50° C. overnight with a slow stream of air passing through the flask. Titration of the crude product showed that 90.2% of the theoretical amount of octyl thiophosphoric acid,



had formed. The crude product was filtered to remove unreacted phosphorus pentasulfide, and 392 grams of the filtrate (containing 1 mol or 354 grams of octyl thiophosphoric acid) were neutralized with alcoholic sodium hydroxide. After removing the alcohol under vacuum, 422 grams of a clear, straw colored, rather viscous oil were obtained. 75 grams of the sodium octyl thiophosphate thus formed were dissolved in 150 cc. of absolute alcohol.. A mixture of 100 cc. of the alcohol and 36 grams of barium bromide was added with stirring. The alcohol was removed by evaporation and the residue dissolved in ether and filtered. Upon removal of the ether from the filtrate 63 grams of a straw colored, semi-solid material (barium octyl dithiophosphate) were obtained.

Example III

For the preparation of a barium soap of petroleum sulfonic acids a commercially available alcoholic solution of sodium salts of mahogany sulfonic acids was employed, containing 12.75% of salts, 2.25% of mineral oil and 57.9% of isopropyl alcohol, the remainder being water. To 400 grams of this solution was added an aqueous solution of 25 grams of barium chloride. The mixture was boiled with stirring for one hour and then evaporated to dryness. The residue was taken up with 250 cc. of a mixture of one part of naphtha to one part of a solution containing 60%, by volume, of isopropyl alcohol and 40%, by volume, of water. The naphtha layer was separated and washed free of chlorides with water. Evaporation of the naphtha yielded 77 grams of barium sulfonates which contained about 20% of mineral oil remaining from the original alcohol solution.

Example IV

Mineral oil blends were prepared by adding in each case 1% of calcium octyl thiophosphate, barium octyl thiophosphate or barium soap of petroleum sulfonic acids, prepared as described above, to a base lubricating oil consisting of a distilled Coastal oil of 55 Saybolt seconds viscosity at 210° F., also by adding 0.5% of stearyl alcohol to portions of each of these blends and to a blank oil sample. These oil blends, as well as a blank oil sample, were submitted to the Indiana oxidation test (Ind. Eng. Chem., Anal. Ed., v. 6, p. 419 (Nov. 15, 1934)), modified as described below so that varnish film formation could be measured. In each oil sample tube a glass plate approximately 3 inches by 1 inch was placed. At the end of 24 hours, using the conventional Indiana oxidation test procedure, the plate was removed, washed with naphtha, air dried and weighed. From the known weight of the glass plate at the beginning of the test the

weight of varnish formed was calculated. The results of the tests are given in the following table:

Oil or oil blend	Varnish formed in 24 hrs., mg.
Base oil	0.0
Base oil+0.5% stearyl alcohol	0.9
Base oil+1% calcium octyl thiophosphate	4.2
Base oil+1% calcium octyl thiophosphate+0.5% stearyl alcohol	0.0
Base oil+1% barium octyl thiophosphate	2.5
Base oil+1% barium octyl thiophosphate+0.5% stearyl alcohol	1.8
Base oil+1% barium soap of petroleum sulfonic acids	2.4
Base oil+1% barium soap of petroleum sulfonic acids+0.5% stearyl alcohol	0.0

The above test is intended to indicate the extent to which various lubricating oils will tend to cause the deposition of varnish-like materials on piston skirts and other engine parts. As mentioned earlier in the specification, such varnish formation is undesirable.

It will be seen from the above data that in each instance when the alcohol was added to the blend of mineral oil and metal additive, varnish formation was reduced considerably and in most cases the amount was less than that obtained with either the alcohol or the metal derivative alone.

The present invention is not to be considered as limited by any of the examples described herein, which are given by way of illustration only, but it is to be limited solely by the terms of the appended claims.

We claim:

1. A machinery lubricant suitable for use at high temperatures comprising a major proportion of a mineral oil base stock, a minor proportion, sufficient to impart substantial detergent properties to said lubricant, of a metal salt of a polybasic inorganic acid which contains at least one oil-solubilizing organic group, and a minor proportion, sufficient to inhibit varnish formation, of a higher alcohol.

2. A lubricant according to claim 1 in which the metal of the metal salt is selected from the class consisting of the metals of groups I, II, III, and VIII of the periodic table.

3. A lubricant according to claim 1 in which the metal of the metal salt is a metal of group II of the periodic table and in which the alcohol contains at least 8 carbon atoms per molecule.

4. A lubricant according to claim 1 in which the metal salt is a salt of an alkylated acid of phosphorus and in which the alcohol contains at least 8 carbon atoms.

5. A lubricant according to claim 1 in which the metal salt is a barium salt of petroleum sulfonic acid and in which the alcohol contains from 12 to 20 carbon atoms per molecule.

6. A machinery lubricant suitable for use at high temperatures comprising a major proportion of a mineral oil base stock, about 0.02% to about 2% of a salt of a metal of group II of the periodic table and a polybasic inorganic acid containing at least one oil-solubilizing substituent alkyl group, and about 0.01% to about 5% of an alcohol having at least 8 carbon atoms per molecule.

7. A lubricant according to claim 6 in which the salt is an alkaline earth metal salt of an octyl thiophosphoric acid and in which the alcohol is stearyl alcohol.

8. A lubricant according to claim 6 in which the salt is a barium soap of petroluem sulfonic acid and in which the alcohol is stearyl alcohol.

9. A machinery lubricant suitable for use at high temperatures comprising a major proportion of a mineral oil base stock, about 1% of an alkaline earth metal salt of an octyl thiophosphoric acid and about 0.5% of stearyl alcohol.

10. A machinery lubricant suitable for use at high temperatures comprising a major proportion of a mineral oil base stock, about 1% of a barium soap of petroleum sulfonic acid and about 0.5% of stearyl alcohol.

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