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LUBRICATING OIL COMPOSITION

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This invention relates to lubricating oils and methods of preparing the same, and more particularly to mineral lubricating oil compositions for use as crankcase lubricants in internal combustion engines.

Because in recent years the requirements for lubricating oils for gasoline and Diesel engines have steadily been made more stringent, it has been proposed to add various ingredients to these oils to improve their behavior in such service. One purpose of these ingredients is to impart detergency to the oils, thus bringing about greater engine cleanliness and avoiding ring sticking, carbon formation and varnish deposition. Certain of these ingredients also impart oxidation resistant properties to oils, thereby tending to inhibit the development of corrosive ingredients in such oils. Corrosion-preventing addition agents are particularly required when the oil is to come in contact with the newer type of alloys of silver and cadmium and of copper and lead, which are now widely used as bearing metals.

Various metal containing organic compounds, particularly metal salts, exhibit detergent properties by inhibiting the formation of varnish, lacquer, and sludge deposits and in promoting general cleanliness in the engine, and a very valuable class of such salts is the metal salts of inorganic acids having substituent oil-solubilizing organic groups. For example, 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.

While the above described metal salts are uniformly satisfactory as detergent agents, they vary somewhat in their ability to prevent corrosion, and some even increase the corrosive properties of the oil with which they are blended. Moreover, in the use of the salts the effectiveness of these compounds is gradually spent. The detergent capacity becomes exhausted as deterioration products, soot, dirt, varnish, etc., accumulate in the lubricant and saturate the adsorptive power of the additive. In engines equipped with a filter, the latter tends to remove the additive, particularly when the additive is adsorbed on contamination products which are strained out by the filter. The oxidation processes which are underway in an oil during use operate upon the antioxidant functions of the additive and thus also contribute to its exhaustion. The oxidation of the oil also creates insoluble substances which

the detergent is called upon to absorb, thus lessening its capacity for dispersing contamination products which enter the oil, and acidic substances are also formed which may react directly with the detergent to destroy its efficacy. When the detergent is employed also to impart corrosion resistant properties to the oil, the above degradation phenomena all hasten to break down this corrosion resistance.

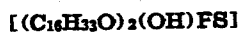
It is an object of this invention to provide an ingredient which, added to the metallic detergent, will provide the continued corrosion inhibiting effect desired. Such an ingredient is an alkylation product of p-cresol, as defined more particularly in the description which follows. This combination of addition agents provides for detergent action in the earlier stages of the use of the oil as well as continued corrosion inhibiting effect after the metallic detergent compound has been removed to some degree by the filter or otherwise weakened in its action. Furthermore, the presence of the second additive prevents any positive corrosive action by the metal compound, which may have been selected particularly because of its effective detergent action.

The present invention consists, then, in the use in mineral lubricating oils of a combination of two additives, the first being a metallic salt of an inorganic acid having at least one substituent oil-solubilizing organic group and the second being an alkylated reaction product of p-cresol, as defined in the description which follows.

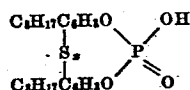
The salts used in the lubricating compositions of the present invention may, in general, be any metallic salts of inorganic acids containing at least one organic group which serves to render the salt soluble in mineral oil. This organic group may appear as a substituent for one of the hydrogen atoms 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 ($C_{18}H_{37}O(OH)_2PO_4$), dodecyl

phosphoric acid ($C_{12}H_{25}O(OH)_2PO$), diisobutyl-phenyl phosphorous acid [$C_6H_5C_4H_9O_2(OH)P$], oleyl sulfuric acid ($C_{18}H_{35}O(OH)SO_2$), amyl phenyl sulfonic acid ($C_5H_{11}C_6H_4(OH)SO_2$), mahogany acids, especially those obtained as a by-product in white oil manufacture, tetradecyl phosphoric acid ($C_{14}H_{29}O(OH)_2PO$), naphthenyl phosphinic acids, hexadecyl tetrathio phosphoric acid ($C_{16}H_{33}S(SH)_2PS$), dodecyl monothio ester of phosphoric acid ($C_{12}H_{25}S(OH)_2PO$), dicetyl ester of monothio phosphoric acid



decyl monothio ester of propyl phosphonic acid ($C_{10}H_{21}S(OH)(C_3H_7)PO$), octadecyl ester of butyl phosphonic acid ($C_{18}H_{37}O(OH)(C_4H_9)PO$), diisobutyl diphenoxy sulfide ester of phosphoric acid, which in its simplest form may be represented as



amyl benzyl sulfurous acid



and dioctyl sulfamic acid [$(C_8H_{17})_2N(OH)SO_2$], as well as comparable substituted arsenic, arsenious, arsinic, arsonic, boric, stannic, stannous, chromic, chromous, plumbous, 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 organo group. Especially preferred salts are the phosphates and thiophosphates, also sulfates and sulfonates, particularly those derived from petroleum.

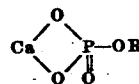
In the foregoing discussion, as well as elsewhere in this specification, the diisobutyl radical forming part of various compounds is to be understood as being derived from diisobutylene, and such radical may also be designated as tetramethyl butyl.

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, IV and VIII of the periodic table. Salts of group II, such as magnesium, calcium, and barium salts, have been found to be particularly effective.

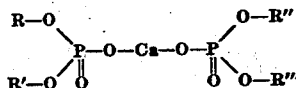
The oil-solubilizing substituent organic group which appears as part of the salt structure may be of any type, providing only that it imparts appreciable oil solubility to the salt. Thus, the substituent groups may be alkyl, alkoxy, aryl, aralkyl or heterocyclic groups, and such groups may, furthermore,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

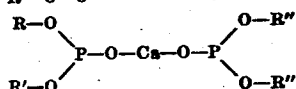
believed to possess, R, R', R'', etc., in the formulas designating organic groups:



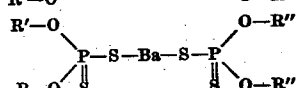
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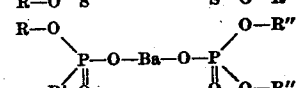
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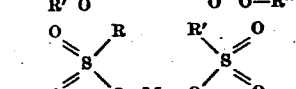
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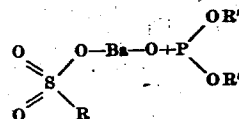


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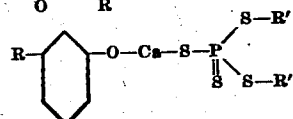


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When polyvalent metals are used, their valences may be satisfied with like radicals as depicted above or the metals may be joined to different radicals, as, for example, in the following compounds:



(8)



(9)

Also mixtures of salts may be used, as, for example, calcium diisobutylphenyl phosphite and barium octadecyl phosphate.

The substituted inorganic salts to be added to lubricating oils in accordance with this invention include the following: calcium cetyl phosphate, barium oleyl phosphate, aluminum lauryl phosphate, barium di(amylphenyl) thiophosphate, chromium octadecyl phosphate, barium cetyl phenyl phosphate, barium wax phosphate (in which the wax radical is derived from petroleum wax), calcium dioctyl dithiophosphate, and the magnesium, zinc, cobalt, calcium, barium and tin salts of mahogany acids (petroleum sulfonic acids). More particularly preferred are zinc dioctyl monothiophosphite, calcium dioctyl monothiophosphite, barium dioctyl monothiophosphite, the zinc and barium salts of mahogany acids, calcium diisobutyl phenyl phosphate and calcium cetyl phosphate.

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 emulsifying 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.

The second additive which is to be introduced into the lubricating oil compounds in accordance with the present invention is a product obtained by alkylating p-cresol with a tertiary alkyl group in the presence of a suitable alkylation catalyst. The source of the tertiary alkyl group may be a tertiary olefin, e. g., isobutene. A satisfactory method for the preparation of one of the preferred additives consists in reacting p-cresol with isobutene in the presence of sulfuric acid as a catalyst at about 70° C., in accordance with the method of preparation described below in Example 4. The product has a molecular weight of about 220, a chemical composition corresponding to the empirical formula $C_{15}H_{24}O$, and is, when purified, a white crystalline solid having a melting point of about 69.2° to 69.4° C.

The lubricating oil base stocks of this invention may be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichloro ethyl ether, propane, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed, either alone or in admixture with mineral oils.

For the best results, however, the base stock chosen should usually be that oil which without the additive present gives the optimum performance in the service contemplated. Since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of medium and high speed Diesel engines the general practice has been 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, in certain types of Diesel service, and in gasoline engine service, oils of higher viscosity index are often required, for example, up to 75 or 100, or even higher, viscosity index.

In addition to the materials to be added according to the present invention, other agents may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like, may also be employed.

Assisting agents which are particularly desirable are the higher alcohols having 8 or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol, $C_8H_{17}OH$, lauryl alcohol, $C_{12}H_{25}OH$, cetyl alcohol, $C_{16}H_{33}OH$, stearyl alcohol, sometimes referred to as octadecyl alcohol, $C_{18}H_{37}OH$, and the like; the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols, such as naphthenic alcohols; and aryl substituted alkyl alcohols, for instance, phenyl octyl alcohol, or octadecyl benzyl alcohol or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use 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 those materials, for some purposes the wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared synthetically by chemical processes may also be used, such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g. paraffin wax, petrolatum, etc.

Generally, the amounts of the substituted inorganic salt and of the alkylated p-cresol product 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% of each ingredient, the exact amount to be used depending to a certain extent on the particular compounds used, the character of the mineral oil base and the operating conditions of the engine in which the lubricant is to be employed.

The following are typical lubricating oil compositions suitable for use in internal combustion engines in accordance with this invention.

Oil A:

Mid-Continent base oil (S. A. E. 20), plus
1.0% barium octadecyl phosphate, and
0.25% tert. butyl ether of o-tert. butyl
p-cresol

Oil B:

Naphthenic base oil (S. A. E. 30), plus
0.2% zinc dioctyl monothiophosphite, and
0.3% tert. butyl ether of o-tert. butyl p-cresol

Oil C:

Highly refined Mid-Continent base oil (S. A. E. 20), plus
1.0% calcium diisobutylphenyl phosphate, and
0.25% tert. butyl ether of o-tert. butyl
p-cresol

75 Compositions in which two or more metal com-

pounds are used with one or more p-cresol products or in which one metal compound is used with two or more p-cresol products are also contemplated in this invention.

In the following examples there are described in detail methods of preparing a number of the preferred addition agents of the present invention. In Examples 1 to 3 are described methods of preparing certain organo substituted metallic salts of inorganic acids, and in Example 4 is described a method of preparing a typical example of a reaction product of p-cresol with a tertiary olefin. These examples are to be considered as illustrative only and not as limiting the scope of the invention in any way.

EXAMPLE 1

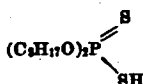
Preparation of calcium octyl thiophosphate

A mixture of 444 grams of phosphorous 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 2

Preparation of barium octyl thiophosphate

520 grams of octyl alcohol (2-ethyl hexanol) and 222 grams of powdered phosphorous 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 phosphorous 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 3

Preparation of barium soap of mahogany acids

For the preparation of this compound 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% of isopropyl alcohol and 40% of water, by volume. 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 4

Preparation of a reaction product of p-cresol and isobutene

324 grams of technical p-cresol and 16 grams of 95.5 to 96% commercial sulfuric acid were agitated at 70° C. in a suitable reaction vessel while isobutene was bubbled through the mixture. After about four hours the reaction was substantially complete, as indicated by the flow of isobutene from the gas exit of the reaction vessel. The reaction mixture was then blown with steam and washed with hot water and then with dilute alkali until neutral. The crude product (89% yield) was an oily material which readily crystallized when cooled. When the product was recrystallized from hot alcohol, it was obtained in the form of white crystals melting at 69.2 to 69.4° C.

In addition to being employed in crankcase lubricants for Diesel and automotive engines, the additives of the present invention may also be used in light mineral oils such as spindle oils and textile oils, metal cutting oils, turbine oils, insulating and transformer oils, steam cylinder oils and greases. Also, since these additives achieve their detergent effect by modifying surface activity, their use in asphalt, road oils, and waxes to improve wetting and adhesive properties is also contemplated. Likewise, they may be added to liquid fuels to increase their wetting ability for metals, enabling them to displace moisture which might otherwise cause corrosion of containers, fuel lines, pump parts, and the like.

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 is to be limited solely by the terms of the appended claims.

We claim:

1. A lubricant comprising a major proportion of a mineral oil base stock, about 0.02% to about 2.0% of a salt of a polybasic inorganic acid which contains at least one oil-solubilizing substituent organic group, said salt being a salt of a metal selected from groups I, II, III, IV and VIII of the periodic table and having a tendency to cause corrosion of metal surfaces during use in said lubricant, and about 0.02% to about 2.0% of an alkylation product obtained by reacting p-cresol with isobutene in the presence of a catalytic

amount of sulfuric acid, said product having a molecular weight of about 220, a chemical composition corresponding to the empirical formula $C_{15}H_{24}O$, and being, when purified, a white crystalline solid having a melting point of about 69.2° to about 69.4° C. 5

2. A lubricant comprising a major proportion of a mineral oil base stock, about 0.2% to about 2.0% of a barium salt of a petroleum sulfonic acid, and about 0.2% to about 2.0% of an alkylation product obtained by reacting p-cresol with isobutene in the presence of sulfuric acid as a catalyst, said product having a molecular weight of about 220, a chemical composition corresponding to the empirical formula $C_{15}H_{24}O$, and being, when purified, a white crystalline solid having a melting point of about 69.2° to 69.4° C. 10

3. A lubricant comprising a major proportion of a mineral oil base stock, about 0.2% to about 2.0% of zinc dioctyl monothiophosphite, and about 0.2% to about 2.0% of an alkylation product obtained by reacting p-cresol with isobutene in the presence of sulfuric acid as a catalyst, said product having a molecular weight of about 220, a chemical composition corresponding to the empirical formula $C_{15}H_{24}O$, and being, when purified, a white crystalline solid having a melting point of about 69.2° to 69.4° C. 25

4. A lubricant comprising a major proportion of a mineral oil base stock, about 0.2% to about 2.0% of calcium diisobutylphenyl phosphate, and about 0.2% to about 2.0% of an alkylation product obtained by reacting p-cresol with isobutene in the presence of sulfuric acid as a catalyst, said product having a molecular weight of about 220, a chemical composition corresponding to the empirical formula $C_{15}H_{24}O$, and being, when purified, a white crystalline solid having a melting point of about 69.2° to 69.4° C.

5. A lubricant according to claim 1 in which the metal salt is a salt of a metal of group II of the periodic table.

6. A lubricant according to claim 1 in which the metal salt is a salt of a metal of group II of the periodic table and a petroleum mahogany sulfonic acid.

7. A lubricant according to claim 1 in which the metal salt is a salt of a metal of group II of the periodic table and an acid of phosphorus containing an oil-solubilizing alkyl group.

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