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LUBRICATING COMPOSITION

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This invention relates to lubricating oil addition agents designed to improve the lubricating properties of lubricating oils for use under conditions of severe service such as those encountered in Diesel engines, and the like, and to lubricating oils containing these addition agents.

The primary object of this invention is to produce, for use under severe service conditions, lubricating oils which will be non-corrosive to corrosion-sensitive bearings, such as the copper-lead or cadmium-silver type, and which will also avoid the deposition of lacquer and varnish-like materials upon pistons and overcome carbon deposition behind the rings.

Other objects, features and advantages of this invention will be apparent from the description contained hereinafter.

It is well known that ordinary mineral lubricants are effective only within certain limits of engine operating conditions and when these limits are exceeded deterioration of the lubricating oils results causing undesirable ring sticking, bearing corrosion, sludge formation, piston lacquering, and the like. Addition agents have been developed and used in lubricating oils to minimize this deterioration and to reduce its deleterious effects if it does occur.

Addition agents which have been proposed for the improvement of lubricating properties of lubricating oils are many in number. In general these agents are designed to function in some specific manner; for example, an addition agent to which is attributed detergent properties is one which tends to keep pistons, rings and valves free of lacquer and varnish-like deposits. Oil-soluble metal salts of sulfonic acids are perhaps the addition agents most generally used to improve the detergent properties of a lubricating oil and their use is well known in the art. Prevention of bearing corrosion is another specific function for which lubricating oil addition agents have been designed. Addition agents which perform this function include phenolic compounds, metal salts of the reaction products of a sulfide of phosphorus and an alcohol, metal salts of the reaction products of a sulfide of phosphorus and metal sulfonates such as those disclosed in U. S. Patent No. 2,350,959 to Cook et al., and many others.

This invention resides in lubricating oils especially mineral lubricating oils containing oil-soluble metal salts of substituted sulfur-containing acids of phosphorus having an organic substituent, said organic substituent imparting oil solubility to said metal salt and said substituent being incorporated in said metal salt by reacting a

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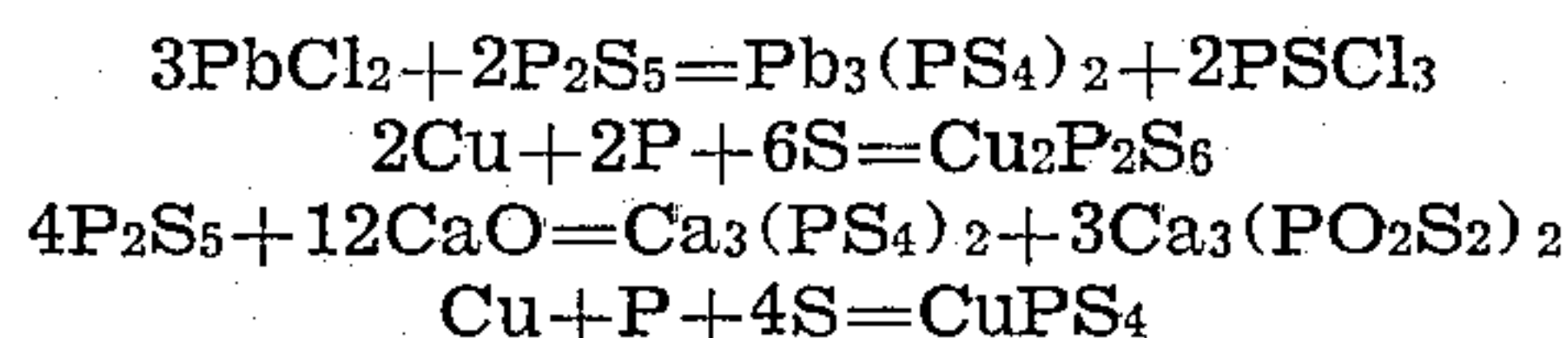
metal salt of a sulfur-containing acid of phosphorus with an organic compound having a reactive group capable of combining with said metal salt of a sulfur-containing acid of phosphorus.

I have discovered that the addition of a small amount of an oil-soluble product of the reaction between a metal salt of a sulfur-containing acid of phosphorus and an organic compound having a reactive group capable of combining with said metal salt, which compound may be selected from the group consisting of hydroxy organic compounds, metal sulfonates and hydrocarbons, to a mineral lubricating oil markedly improves the lubricating properties of the oil.

I have discovered also that the performance of internal combustion engines under severe service conditions such as those encountered in Diesel engines can be markedly improved by the use of a lubricating oil, especially a mineral lubricating oil, to which has been added a small amount of an oil-soluble metal salt of a substituted sulfur-containing acid of phosphorus having an oil-solubilizing organic substituent as described hereinabove together with small quantities of other lubricating oil addition agents. Such other addition agents which may be used in conjunction with the reaction products of the present invention include detergents, anticorrosion agents, antiwear agents, oiliness agents, and the like. Among detergents which are particularly desirable are: (1) oil-soluble metal sulfonates, (2) oil-soluble metal salts or soaps of fatty acids, halogenated fatty acids or substituted fatty acids such as dichlorostearic acid, phenyl-stearic acid, and the like, (3) oil-soluble metal salts or soaps of rosin acids or hydrogenated rosin acids such as abietic acid, hydrogenated abietic acid, and the like, (4) oil-soluble metal salts or soaps of acids produced by oxidation of high molecular weight paraffinic hydrocarbons or hydrocarbon fractions such as paraffin wax, highly paraffinic lubricating oil fractions, and the like. Among anticorrosion agents which are particularly desirable may be listed: (1) oil-soluble metal salts of phenols and particularly alkyl or cycloalkyl substituted phenols such as those having more than about 12 carbon atoms per molecule, (2) oil-soluble metal salts of phenol sulfides or alkyl or cycloalkyl substituted phenol sulfides and particularly those having alkyl substituents containing at least about 4 carbon atoms, (3) oil-soluble metal salts of the reaction products formed by reacting a sulfide or oxide of phosphorus with an alcohol or with a phenol, (4) oil-soluble metal salts of phosphonic or phosphinic acids obtained

by reacting elemental phosphorus with hydrocarbons.

The metal salts of sulfur-containing acids of phosphorus to be used in the practice of this invention may be prepared by a variety of methods. As examples of these methods I may cite: the reaction of sulfides of phosphorus upon metals, metal oxides, metal sulfides or metal halides; the reaction of elementary sulfur upon metal salts of oxygen acids of phosphorus; the reaction of oxides of phosphorus upon metal sulfides; the direct combination of the elements; the metathesis of aqueous alkaline solutions of sulfides of phosphorus with aqueous alkaline solutions of metal salts of other acids. The following equations are given as examples of some of the above methods for the preparation of metal salts of sulfur-containing acids of phosphorus:



These metal salts of sulfur-containing acids of phosphorus are oil-insoluble inorganic compounds and may be referred to as metal salts of inorganic acids of phosphorus or sulfur-containing inorganic acids of phosphorus.

Hydroxy organic compounds which may be reacted with metal salts of sulfur-containing acids of phosphorus according to the process of my invention include mono- and polyhydroxy aliphatic, alicyclic, alkaryl, aralkyl and aryl organic compounds. Thus aliphatic and alicyclic alcohols may be used, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, amyl, heptyl, octyl, decyl, lauryl, tetradecyl, octadecyl, cyclohexyl, methylcyclohexyl, benzyl, and the like, as well as alcohols or mixtures of alcohols obtained in various commercial processes such as the hydration of olefins, hydrogenation of oxides of carbon, hydrogenation of hydroxy aromatic compounds, and the like. Other hydroxy organic compounds which may be used include hydroxy aromatic compounds such as phenol, alpha-naphthol, beta-naphthol and alkyl substituted hydroxy aromatic compounds, for example, cresol, p-tertiaryamylphenol, p-octylphenol, and wax alkylated phenols or naphthols. Still other hydroxy organic compounds which may be employed in the practice of this invention are the polyhydroxy organic compounds of both the aliphatic and aromatic series. Among these compounds are included ethylene glycol, propylene glycol, butylene glycol, catechol, resorcinol, hydroquinone, pyrogallol, p-tertiarybutyl catechol, p-tertiaryoctyl catechol, and the like.

The metal sulfonates which may be used in the preparation of the oil-soluble reaction products of this invention are preferably oil-soluble metal salts of sulfonic acids having a molecular weight of about 300 to 500 or higher. Oil-soluble metal salts of the petroleum sulfonic acids known as mahogany acids are particularly desirable. Oil-soluble metal salts of petroleum sulfonic acids are obtainable on the market under various trade names. For example, "Petronate," sold by Sonneborn Sons, Inc. of New York city, contains about 40% by weight of oil-soluble sodium salts of petroleum sulfonic acids. These metal salts may be used as obtained or they may be converted into other metal salts by reaction of metathesis under con-

ditions well known in the art for effecting reactions of this type. Thus sodium petroleum sulfonates may be converted into calcium petroleum sulfonates by treating an oil solution of the sodium sulfonates with an aqueous solution of calcium chloride or calcium nitrate. Metal sulfonates may also be obtained by direct neutralization of sulfonic acids prepared by the sulfonation of a suitable petroleum fraction with a sulfonating agent such as fuming sulfuric acid, gaseous sulfur trioxide, chlorosulfonic acid, and the like. The direct neutralization of these sulfonic acids may be carried out by treating the acids with basically reacting metallic compounds, such as oxides, hydroxides, carbonates, sulfides, or, in some instances, the metal itself.

Many hydrocarbons may be reacted with metal salts of sulfur-containing acids of phosphorus according to the process of my invention. Petroleum fractions, such as extracts or raffinates obtained in the solvent refining of lubricating oils, may be employed as well as various other hydrocarbons such as olefins, olefin polymers, aromatic hydrocarbons, for example, alkyl or cycloalkyl substituted benzenes, naphthalenes, and the like, in which the substituent preferably contains at least about 10 carbon atoms, and in fact many others.

The oil-soluble reaction product of a metal salt of a sulfur-containing acid of phosphorus with hydroxy organic compounds, metal sulfonates or hydrocarbons may be prepared by agitating and heating a metal salt of a sulfur-containing acid of phosphorus, obtained by any of the methods described hereinabove, with one or more of the organic compounds mentioned above for a period of one to twelve hours, or until reaction has substantially ceased, at temperatures from about 100° F. to about 400° F. and preferably at about 200° F. The optimum temperature at which the reaction is to be carried out varies greatly with the particular metal salt of the sulfur-containing acid of phosphorus and with the type of organic reactant employed. In many instances it is found that hydrogen sulfide is evolved as a result of the reaction and in these cases reaction is considered complete when the evolution of hydrogen sulfide has substantially ceased. In some instances it is advantageous to carry out the reaction in the presence of a solvent or thinner in order to insure intimate contact of the reactants. When a low boiling gasoline or naphtha fraction, such as a fraction having a boiling point in the temperature range of about 100° F. to about 400° F., is employed as a solvent and the reaction carried out at the reflux temperature sufficient agitation of the reaction mixture is provided by the boiling solvent. The reaction may be carried out under pressure such as in an autoclave at pressures between ordinary atmospheric and 100 atmospheres or even higher.

Oil-soluble metal salts of substituted sulfur-containing acids of phosphorus having an organic substituent may be prepared by reacting a metal salt of a sulfur-containing acid of phosphorus with organic compounds other than hydroxy organic compounds, metal sulfonates and hydrocarbons and said oil-soluble metal salts are to be included within the scope of this invention. Thus, for example, a metal salt of a sulfur-containing acid of phosphorus may be reacted with a sulfonic acid having a molecular weight of about 300 to 500 or higher for one to

twelve hours at temperatures from about 100° F. to about 400° F. and preferably at about 200° F. The reaction product may then be neutralized with a basically reacting metal compound. The sulfonic acids to be employed may be prepared by direct sulfonation of a suitable material with a sulfonating agent, such as fuming sulfuric acid, gaseous sulfur trioxide, chlorosulfonic acid or the like, or they may be prepared from the hereinabove described metal sulfonates by any of several methods well known in the art for converting metal sulfonates to sulfonic acids. These methods include treating the metal sulfonates with a 60% by weight solution of sulfonic acid, treating the metal sulfonates with a suitable ion-exchange resin and treating the metal sulfonates with gaseous hydrogen chloride in an anhydrous medium, and the like.

The molar ratio of metal salt of a sulfur-containing acid of phosphorus to the hydroxy organic compound, sulfonic acid, metal sulfonate or hydrocarbon to be employed in the preparation of the oil-soluble reaction products of this invention is preferably about 0.2 to 1, but ratios between about 0.1 to 1 and about 2 to 1 can be employed with satisfactory results depending upon the particular phosphorus compound and hydroxy organic compound, sulfonic acid, metal sulfonate or hydrocarbon used in the reaction.

Oil-soluble metal sulfonates which may be used in conjunction with my reaction product as an auxiliary addition agent in the production of a high quality lubricating oil include the oil-soluble metal salts of substantially any sulfonic acid. Thus any of the oil-soluble metal sulfonates described hereinabove as suitable reagents for reaction with a metal salt of a sulfur-containing acid of phosphorus may be employed as an auxiliary additive.

Oil-soluble metal salts of phenols which may be used together with the additive of this invention include the oil-soluble metal salts of many phenolic materials such as those of alkyl or cycloalkyl substituted phenols having more than about 12 carbon atoms per molecule as well as phenol sulfides of the alkyl hydroxy phenyl thio ether type. Thus metal phenates such as those described in U. S. Patent No. 2,281,401 to Wilson and U. S. Patent No. 2,344,988 to Kavanagh et al. may be employed. Phenol sulfides of the above type which may be employed are described in U. S. Patent No. 2,139,766 to Mikeska et al. and similar compounds together with their method of preparation are described in U. S. Patent No. 2,139,321 to Mikeska et al.

Suitable oil-soluble metal salts of synthetic organic acids produced by oxidizing hydrocarbons or hydrocarbon fractions are described in U. S. Patent No. 2,270,620 to Bray. The synthetic organic acids used in the preparation of oil-soluble metal salts are preferably obtained by oxidizing relatively high molecular weight hydrocarbon fractions such as highly paraffinic lubricating oil fractions, paraffin wax, and the like. The acids so produced may be converted into the metal salts directly or they may be chlorinated and the chlorinated acids converted into their metal salts. Preferably the acids will contain in excess of 10 carbon atoms per molecule.

Suitable oil-soluble metal salts of acids produced by the reaction of a phosphorus sulfide or oxide with alcohol or with phenol are preferably those alkyl, aryl, or aralkyl phosphoric or thiophosphoric acid salts prepared by the re-

action of P_2S_5 or P_2O_5 with an alcohol or phenol. The method of preparing these salts is fully described in the Freuler U. S. Patent No. 2,364,284. These reaction products may be described as the reaction products of a sulfide or oxide of phosphorus with a monohydroxy organic compound.

Metals which may be used to form the desired metal salts of the sulfur-containing acids of phosphorus as well as the salts or soaps of each of the additive materials described hereinabove include the alkaline earth metals, calcium, strontium, barium and magnesium, and other metals such as zinc, nickel, aluminum, lead, manganese, mercury, copper, iron, tin, chromium, bismuth and thorium. In some instances the alkali metal, i. e., the sodium, potassium or lithium, salt or soaps may be employed.

The products of this invention may be employed to improve the lubricating qualities of any lubricating oil, but I prefer to use mineral lubricating oils, especially mineral lubricating oils having a viscosity index (defined by Dean and Davis, Chemical and Metallurgical Engineering, vol. 36, page 618 (1929)) above about 70, such as those produced by solvent treating paraffinic base stocks.

In preparing lubricating oils containing the reaction product of a metal salt or a sulfur-containing acid of phosphorus with hydroxy organic compounds, sulfonic acids, metal sulfonates or hydrocarbons either with or without the addition of auxiliary agents, such as detergents, anti-corrosion agents, and the like, the proportion of the reaction product employed should be such that the phosphorus content due to the presence of said reaction product will be in the order of from about 0.01% to about 0.5% by weight and preferably in the range of about 0.02% to 0.1% by weight. If an auxiliary agent, i. e., detergent, anticorrosion agent, etc., is present it should constitute between about 0.1% and 5.0% by weight and preferably between about 0.5% and 2.5% by weight of the finished oil.

The method used to determine the percentage of phosphorus in the reaction products and in the finished oils is a standard analytical procedure. The phosphorus, in a weighed quantity of the material to be analyzed, is first converted into the phosphate form by oxidation with sodium peroxide in a Parr bomb and the analysis is finished according to the procedure outlined in Kolthoff and Sandell, Textbook of Quantitative Inorganic Analysis, page 676 (1936) for the determination of phosphorus in steel. In this method of analysis the phosphorus is weighed as magnesium pyrophosphate.

The metal salts that I employ in the preparation of a high quality lubricating oil are oil-soluble and require only simple mixing with a lubricating oil to obtain solution. However, the blending is usually effected at slightly elevated temperatures in the range of 100° F. to 200° F. in order to facilitate solution and dispersion of the addition agents in the body of the lubricating oil.

Although the foregoing description has been limited to the use of those metal salts of acids of phosphorus which contain sulfur, it is to be distinctly understood that metal salts of acids of phosphorus which do not contain sulfur may also be employed. Thus, metal salts of oxy acids of phosphorus as well as the metal salts of acids of phosphorus containing selenium or tellurium may also be employed in place of the metal salts

of the sulfur-containing acids of phosphorus, although the latter compounds are the preferred type.

Metal salts of oxy-acids of phosphorus which may be employed include metal salts of phosphorous acid, hypophosphoric acid, orthophosphoric acid, pyrophosphoric acid and metaphosphoric acid. These are common phosphorous acids and methods for their preparation are well known. These acids may be converted into metal salts by neutralizing with a basic metal compound, such as an oxide, hydroxide, carbonate of the metal or, in some instances, the metal itself.

The following examples are presented to further illustrate some of the aspects of my invention, but it is to be understood that the invention is not limited to the methods or modes of operation described in these examples.

Example I

To a solution of 0.1 mol phosphorus pentasulfide in 250 ml. of cold 6-normal ammonium hydroxide was added an aqueous ammoniacal solution containing 0.3 mol zinc sulfate. The resulting white pasty precipitate, containing mixed zinc thio-phosphates, was filtered off. The wet precipitate cake was stirred into a solution containing 60 grams of calcium petroleum sulfonate, 140 grams of mineral lubricating oil in the SAE 20 range and 1000 ml. of a hydrocarbon solvent having a boiling range of 200° F. to 300° F. The mixture was refluxed, returning the reflux liquid through a water trap, for three hours after dryness was attained. The mixture was then filtered and the hydrocarbon solvent distilled off. The product remaining contained 0.42% phosphorus.

A lubricant having a phosphorus content of 0.03% by weight and consisting of 7.0% by weight of the product obtained hereabove and 93.0% by weight of a mineral lubricating oil of SAE 30 grade having a gravity of 29.1° API, a viscosity of 540 seconds Saybolt Universal at 100° F. and a viscosity index of 90 was subjected to a laboratory corrosion test in which air at 0.02 cubic feet per minute was passed through 150 ml. of the lubricant at 325° F. A copper-lead bearing having a surface area of approximately 4½ square inches was suspended in the solution and its loss in weight determined. After 93 hours the bearing in the solution containing my addition agent had suffered no loss in weight while under identical test conditions a similar bearing suspended in the hereabove described mineral oil without my addition agent lost 200 mgs. after 93 hours.

Example II

A mixture of 44.4 grams of P_2S_5 and 88 grams of zinc sulfide was heated in an atmosphere of nitrogen at a temperature between 600° F. and 800° F. for one hour. The product was cooled and ground to a powder. This product was reacted with 30 grams of methylcyclohexanol. The reaction was effected by heating the mixture in the presence of petroleum naphtha to a maximum temperature of 200° F. under refluxing conditions. Considerable evolution of hydrogen sulfide occurred beginning at about 130° F.-140° F. The reaction product was distilled to remove the naphtha and dissolved in 100 grams of a light, high V. I. mineral lubricating oil and the product filtered to remove insolubles. The product was found to contain 1.9% of phosphorus.

A lubricant having good anticorrosion characteristics and having a phosphorus content of

0.025% by weight was prepared by dissolving 13 grams of the agent prepared above in a 1000 grams of the SAE 30 grade mineral lubricating oil employed in Example I.

Example III

The calcium salt of sulfur-containing acids of phosphorus was prepared by heating a mixture of phosphorus pentasulfide and calcium oxide in a molar ratio of 4 mols of P_2S_5 to 12 moles of CaO at a temperature of 900° F. in an atmosphere of nitrogen. The reaction mixture was heated slowly to the required temperature, because the reaction is highly exothermic, and maintained at about 900° F. for one hour. The salts thus obtained were ground to a powder and heated with an alkylated benzene, obtained by treating benzene with chlorinated paraffin wax in the presence of anhydrous aluminum chloride, for three hours at a temperature of 400° F. The product was an oil-soluble calcium and phosphorus containing material.

A lubricant containing 3% of this product and 97% of the SAE 30 grade mineral lubricating oil employed in Example I was found to have good anticorrosion characteristics.

The foregoing description and examples of my invention are not to be taken as limiting since many variations may be made by those skilled in the art without departing from the spirit or scope of the following claims.

I claim:

1. A lubricating oil composition comprising a major proportion of a mineral lubricating oil and a small amount, sufficient to impart anti-corrosion properties to said oil, of an additive resulting from the reaction of a metal salt of a sulfur-containing inorganic acid of phosphorus with an oil-soluble metal sulfonate in the molar ratio of between about 0.1 to 1 and 2 to 1, at a temperature within the range of about 100° F. to about 400° F., to impart a phosphorus content to the lubricating oil composition of between about 0.01% and about 0.5% by weight of said composition.

2. A lubricating oil composition as set forth in claim 1 in which the metal salt of the sulfur-containing acid of phosphorus is the zinc salt.

3. A lubricating oil composition as set forth in claim 2 in which the metal sulfonate is a sulfonate of petroleum sulfonic acids having a molecular weight of at least 300.

4. A lubricating oil composition as set forth in claim 1 in which the sulfonate is a calcium sulfonate.

5. A lubricating oil composition as set forth in claim 4 in which the metal sulfonate is a sulfonate of petroleum sulfonic acids having a molecular weight of at least 300.

6. A lubricating oil composition as set forth in claim 1 containing also about 0.1% to about 5.0% by weight of an oil-soluble metal salt of the product of the reaction between a phosphorus compound of the class of phosphorus sulfides and phosphorus oxides and a monohydroxy organic compound.

7. A lubricating oil composition as set forth in claim 1 in which the metal sulfonate is a sulfonate of petroleum sulfonic acids having a molecular weight of at least 300.

8. A lubricating oil composition as set forth in claim 1 in which the metal of at least one of the metal compounds is an alkaline earth metal.

9. A lubricating oil composition as set forth in

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claim 1 in which the metal of at least one of the metal compounds is lead.

MARJORIE J. VOLD.

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Cook	Feb. 13, 1945
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Fischer	Sept. 27, 1949