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LUBRICANTS CONTAINING ALKALI METAL DITHIOPHOSPHATES

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No Drawing. Continuation-in-part of application Ser. No. 444,424, Mar. 31, 1965. This application Jan. 26, 1967, Ser. No. 611,830

3 Claims. (Cl. 252—32.7)

ABSTRACT OF THE DISCLOSURE

Novel lubricants containing alkali metal dithiophosphates, more particularly lubricating oil compositions containing ashless detergents in combination with alkali metal dihydrocarbyl dithiophosphates.

CROSS REFERENCES

This applictaion is a continuation-in-part of application Ser. No. 444,424, filed Mar. 31, 1965, now abandoned.

BACKGROUND

Lubricant compositions commonly contain detergents to help prevent the deposit of solid materials on engine surfaces coming in contact with the lubricant composition. Such deposits tend to interfere with normal circulation of the lubricant composition and act as abrasives causing excessive wear of engine parts. A substantial proportion of modern engine deposits is attributable to the additives commonly present in lubricant compositions, particularly in the case of metal-containing detergents. As a lubricant composition is consumed by combustion on cylinder walls and the like in the engine, such metal-containing detergents may form an ash which deposits out on the engine surfaces coming into contact with the composition.

Lubricating oil compositions have been developed containing metal-free detergents to eliminate the formation of ash deposits from metals. Several types of such ashless detergents have been developed, as for example the high molecular weight polymeric detergents described in U.S. Patent No. 2,892,783. Briefly, these ashless detergents are oil-soluble polyglycol substituted polymers of at least one oil-solubilizing monomer and a polyglycol monomer. A relatively new class of nonmetallic ashless detergents is the amine salts, amides and imides of carboxylic acids containing basic amino groups.

The control of bearing corrosion is especially important in lubricating oil compositions containing detergent additives such as the metal sulfonates, metal phosphonates and metal phenates. The newer nonmetallic ashless detergents in lubricating oil compositions tend to aggravate the problem of bearing corrosion.

Zinc organic thiophosphates have been employed in lubricating oil compositions for the purpose of controlling bearing corrosion. However, it has been found that in the case of the newer nonmetallic ashless detergents, particularly those containing basic amino groups, that the zinc salts of organic substituted dithiophosphoric acids tend to cause undesirably high engine wear.

SUMMARY

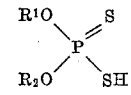
In accordance with the present invention, a superior new ashless detergent lubricating oil composition is provided which comprises a major proportion of an oil of lubricating viscosity, a minor proportion of metal-free detergent sufficient to enhance the detergent characteristics and a minor proportion of alkali metal dihydrocarbyl dithiophosphate sufficient to inhibit corrosion and wear.

It has been found that the lubricating oil compositions of the present invention possess outstanding detergent and corrosion inhibiting properties. At the same time, it has been found that the problem of high engine wear ordinarily associated with lubricant compositions containing ashless detergents in combination with zinc dithiophosphates has been avoided.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The metal-free detergents of the present invention are preferably the basic amino detergents selected from the class consisting of amine salts, amides and imides of aliphatic carboxylic acids containing basic amino groups. Such basic amino detergents are illustrated by the products obtained when polyamines are acylated with substantially aliphatic carboxylic acids, for example, where tetraethylene pentamine is reacted with oleic acid or polyisobutenyl succinic anhydride accompanied by the removal of water in case of amides and imides.

The alkali metal dihydrocarbyl dithiophosphate is the alkali metal salt of a hydrocarbon substituted dithiophosphoric acid, preferably containing from about 8 to about 60 carbon atoms in the hydrocarbon portion. These thiophosphates are also known as phosphorodithioates. They are also described as the alkali metal salts of thiophosphoric acids or phosphorodithioic acids having the formula



in which R_1 and R_2 are hydrocarbyl groups containing a total of from about 8 up to about 60 carbon atoms, preferably up to about 50 carbon atoms.

The preferred alkali metal thiophosphates are the lithium, sodium and potassium, preferably sodium salts of thiophosphoric acids of the above formula in which R_1 and R_2 are selected from the group consisting of alkyl radicals of at least 4 carbon atoms, preferably primary alkyl radicals, and mixtures thereof, and alkaryl radicals containing at least 12 carbon atoms and mixtures thereof. For present purposes, the alkaryl radicals derived from alkyl phenols having at least 6 carbon atoms in the alkyl group are preferred.

Illustrative alkyl, alkaryl and aralkyl radicals for the thiophosphates in accordance with the foregoing are derived from straight-chain or branched-chain primary, secondary or tertiary alcohols, preferably alcohols containing at least 4 carbon atoms, including isobutanol, trimethylcarbinol, 2-ethylbutanol, methylpentanol, methylisobutylcarbinol, 2-propylpentanol, n-decanol, dodecanol, octadecanol, hexylphenol, dodecylphenol, hexadecylphenol, octadecylphenyl, etc., and mixtures thereof.

The alkali metal salts of esters of dithiophosphoric acids are prepared by methods known heretofore. For example, a mixture of the desired alcohol or alkylphenol and phosphorus pentasulfide is reacted with or without a suitable solvent (for example, petroleum naphtha) at temperatures at about 100° to about 200° F., until the dithiophosphoric acid (phosphorodithioic acid) is formed. The crude acid mixture is then filtered to remove unreacted phosphorus pentasulfide, after which the resulting acid is neutralized with a base alkali metal compound, such as lithium hydroxide, sodium hydroxide, sodium carbonate or potassium hydroxide, in alcohol or aqueous solution, followed by the removal of the solvents. The re-

action can be carried out in a base lubricating oil as solvent if desired by first dissolving the dithiophosphoric acid in the oil and then neutralizing with the aqueous or alcoholic solution of the base.

Suitable basic amino ashless detergents of the amine salt type for use in lubricating oil compositions in accordance with the present invention include the amine salts, amides and imides of polyamines having the formula

$$H_2N(ANR')_x[AN(CH_2CH_2)_2N]_y(ANR')_zR'$$

wherein A is an alkylene radical containing from about 2 to 6 carbon atoms, R' is a member of the group consisting of hydrogen and alkyl radicals containing from about 1 to 5 carbon atoms, x is a number from 0 to 10, y is a number from 0 to 2, z is a number from 0 to 10, the total of $x+y+z$ being a number from 1 to 10, reacted with aliphatic carboxylic acids having at least 8 carbon atoms in the aliphatic group.

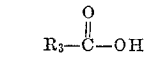
Preferred polyamines have the general formula

$$H_2N(ANH)_zH$$

wherein A is an alkylene radical of from 2 to 3 carbon atoms and z is an integer from 1 to 10, more particularly from 1 to 6.

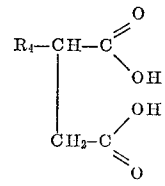
Illustrative alkylene amines and polyalkylene amines of the foregoing types are ethylene diamine, diethylene triamine, triethylene tetramine, dipropylene triamine, dimethylaminopropylamine, tetraethylene pentamine, N-aminoethyl piperazine, pentaethylene hexamine, nonaethylene decamine, etc.

Suitable aliphatic monocarboxylic acids from which the amine salts and amides may be derived are illustrated by the general formula

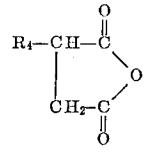


wherein R_3 is an aliphatic hydrocarbon radical, preferably alkyl, of from about 8 to 30 carbon atoms.

Suitable aliphatic dicarboxylic acids and anhydrides thereof are illustrated by the general formulae



and

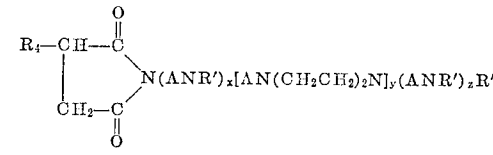


wherein R_4 is an aliphatic hydrocarbon radical, preferably an alkenyl radical, of from about 20 to about 400 carbon atoms.

The R_3 and R_4 radicals of the above formulae, that is, the aliphatic hydrocarbon radicals, are readily obtainable by polymerizing olefins of from 2 to 5 carbon atoms such as ethylene, propylene, isobutylene, pentene, etc., and mixtures thereof. Methods of polymerization are well known in the art, for example, U.S. Patents Nos. 3,024,237, 3,024,195 and 3,018,291.

The preferred aliphatic carboxylic acid compounds from which the amine salt detergents are derived are the alkenyl succinic anhydrides in which the alkenyl group contains from about 30 to about 300, more particularly from about 50 to about 200 carbon atoms, and is preferably derived from polyisobutylene.

The preferred basic amino ashless detergents of the lubricating oil compositions in accordance with the invention are the alkenyl succinimides which have the following general formula



wherein R is an alkenyl radical of from about 20 to 400 carbon atoms, A is an alkylene radical containing from about 2 to 6 carbon atoms, R' is a member of the group consisting of hydrogen and alkyl radicals containing from about 1 to 5 carbon atoms, x is a number from 0 to 10, y is a number from 0 to 2, z is a number from 0 to 10, the total of $x+y+z$ being a number from 1 to 10, the preferred polyamine portion being as described above.

The acylation of the polyamines with the aliphatic carboxylic acids is readily effected by heating the polyamines with the acid. In the formation of amides and imides, water is removed. In such reactions, the temperature will generally be from about 200° to 500° F., more particularly from about 225° to 400° F. The preferred polyamine-anhydride mole ratio will generally be in the range of from about 0.5:1 to about 1:1.5, more particularly from about 0.8:1 to about 1.2:1. The time for the reaction will generally be from about ½ hour to 24 hours or more, usually in the range of about 1 to 12 hours. If desired, the reactants may be employed with an inert reaction medium, such as a hydrocarbon, for example, mineral lubricating oil. In such case, the concentration of the reaction may range from about 1 to 90% by weight, but will usually be from about 25 to 75% by weight of the total reaction mixture. During the reaction, it may be desirable to remove water formed from the reaction, as for example by distillation. Subatmospheric pressures may be used for this purpose with advantage.

In the finished lubricating oils in accordance with the invention, the basic amino ashless detergent is employed in amounts sufficient to improve the detergent characteristics. Ordinarily, amounts of from about 0.1 to about 15% by weight are satisfactory for this purpose. In view of the excellent solubility characteristics of the basic amino detergent and alkali metal thiophosphate combination, a further feature of the invention lies in the preparation of lubricating oil concentrates containing higher percentages of the detergent and thiophosphate active ingredients up to about 75% by weight.

The alkali metal thiophosphate is present in finished lubricating oils in amounts sufficient to inhibit corrosion. Usually, amounts of from about 0.1 to about 10% by weight are satisfactory. Stated in other terms, the amounts of phosphate may be expressed as millimoles per kilograms of finished oil, based on the phosphorus content. That is, the amount of alkali metal phosphate is expressed as millimoles of phosphorus per kilogram of oil (i.e., "mM./kg."). Expressed in such terms, the amount of the alkali metal salts of dihydrocarbon esters of dithiophosphoric acid used in lubricating oils can be from about 1 mM. to about 50 mM. of phosphorus per kilogram of finished oil, preferably from about 4 to about 25 mM.

The base oil in the lubricant composition of the invention is any oil of lubricating viscosity. Thus, the base oil can be a refined paraffin-type base oil, a refined napthenic-type base oil, or a synthetic hydrocarbon or synthetic nonhydrocarbon oil of lubricating viscosity. As synthetic oils, suitable examples include oils obtained by polymerization of lower molecular weight alkylene oxides, such as propylene oxide and/or ethylene oxide employing alcohol or acid initiators, such as lauryl alcohol or acetic acid. Still other synthetic oils include esters, e.g., di-(2-ethyl-

hexyl)-sebacate, tricresylphosphate and silicate esters, such as tetra-(2-ethylhexyl)-orthosilicate and hexa-(2-ethylbutoxy)-disiloxane. For present purposes the mineral lubricating oils are preferred, since they show the greatest improvement.

Lubricant compositions within the scope of the present invention may also contain still other additives of conventional types, such as pour point depressants, oiliness and extreme pressure agents, antixoidants, dyes, blooming agents and the like.

Illustrative lubricant compositions of the aforementioned types containing additives other than the present ashless detergent and phosphate combination may include, for example, from about 0.1 to about 10% by weight of alkaline earth metal higher alkyl phenate detergent and wear reducing agents, such as the calcium alkylphenate having mixed alkyl groups of 12 to 15 carbon atoms. They may also include from about 0.1 to 10% by weight of organic thiophosphate corrosion and high-temperature oxidation inhibitors, such as the reaction product of pinene and P_2S_5, the reaction product of polybutene and P_2S_5, and the bivalent metal dihydrocarbon dithiophosphates, zinc butyl hexyl dithiophosphate. Metal salt detergents in amounts from about 0.1 to 10% which may also be used are the calcium petroleum sulfonates of the oil-soluble mahogany type and the calcium naphthenates.

The following examples are given as illustrations of the improved new lubricating oil compositions in accordance with the present invention. The proportions are on a weight basis unless otherwise specified.

Example 1.—Compositions containing alkenyl succinimide and zinc di(tetradecylphenyl)dithiophosphate

Lubricating oil compositions containing alkenyl succinimides and zinc thiophosphates were observed to cause undesirably high engine wear, apparently due to chemical reaction between the detergent containing free amino groups and the zinc thiophosphate. In a vessel, a 0.01 molar solution of polyisobutenyl succinimide of N-aminoethyl piperazine in which the polyisobutenyl radical had a molecular weight of about 850 was prepared in xylene and brought to a temperature of 78° F. In another vessel, a 0.01 molar solution of zinc di(tetradecylphenyl)dithiophosphate in xylene was also brought to a temperature of 78° F. Equal volumes of the two solutions were mixed in a Dewar flask, and the temperature was observed to rise to about 80° F. showing that a chemical reaction occurred with the evolution of considerable heat.

Example 2.—Compositions containing alkenyl succinimide and barium di(tetradecylphenyl)dithiophosphate

In this example, the procedure of the foregoing example was followed, except that the barium salt of di(tetradecylphenyl)dithiophosphoric acid was employed in combination with the polyisobutenyl succinimide of N-aminoethyl piperazine. There was a 4° F. rise in temperature as evidence of chemical reaction.

Example 3.—Compositions containing alkenyl succinimide and sodium di(tetradecylphenyl)dithiophosphate

In this example, the same procedure as in the foregoing examples was employed, except that the sodium salt of di(tetradecylphenyl)dithiophosphoric acid was employed in combination with the polyisobutenyl succinimide of N-aminoethyl piperazine. There was essentially no rise in temperature. This shows that there was no chemical reaction between the ingredients.

In further verification of the foregoing discovery of the combination of basic amino ashless detergent and alkali metal dihydrocarbyl dithiophosphate, the inhibition of bearing corrosion and high temperature performance in a gasoline engine were determined in a standard Chevrolet L–38 engine test. The base oil was a typical solvent refined SAE 30 grade paraffin type mineral lubricating oil. It contained 1% by weight of polyisobutenyl succinimide of tetraethylene pentamine in which the polyisobutenyl group had a molecular weight of about 850. The succinimide was obtained by reacting about equal molar proportions of polyisobutenyl succinic anhydride and tetraethylene pentamine. The polyisobutenyl group contained about 64 to 68 carbon atoms. In addition, the oil contained 24 mM./kg. of sodium salt of di(tetradecylphenyl) dithiophosphoric acid. The engine test resulted in a bearing weight loss of 117 mg., a total varnish rating of 49.9, a total sludge rating of 50, and a piston varnish number of 9.9, showing that the oil performed excellently from the standpoint of both detergency and bearing weight loss.

The piston ring wear performance of the improved new lubricating oil compositions of the invention was measured in a Caterpillar diesel engine run under the standard 1–H procedure for 60 hours. The sum of the loss in weight of all of the rings was recorded and is reported in the following table. Oils containing the following inhibitors in combination with the polyisobutenyl succinimide of N-aminoethyl piperazine as described above were tested:

A=Zinc butyl amyl dithiophosphate
B=Zinc di(tetradecylphenyl)dithiophosphate
C=Barium di(tetradecylphenyl)dithiophosphate
D=Sodium di(tetradecylphenyl)dithiophosphate

Since sodium is monovalent, while barium and zinc are divalent, twice the molar concentration of the sodium salt inhibitor D was used to give a comparable amount of thiophosphate.

TABLE

	1	2	3	4
Additives:				
Succinimide, percent by weight	0	1.75	1.75	1.75
Inhibitor A, mM./kg.	0	9	0	0
Inhibitor B, mM./kg.	0	3	0	0
Inhibitor C, mM./kg.	0	0	12	0
Inhibitor D, mM./kg.	0	0	0	24
Ring Wear: Weight loss, mg.	450	1,900	1,414	734

From the foregoing test results, it is seen that the conventional zinc and barium dithiophosphates cause high ring wear while the wear due to the sodium dithiophosphate is only slightly greater than that of the base oil.

Additional tests on the lubricating oil compositions of the invention in comparison with conventional compositions were carried out in the standard Falex testing apparatus. The base oil of the compositions was a typical mineral lubricating oil as described above. The oils contained 1% by weight of polyisobutenyl succinimide of tetraethylene pentamine as already mentioned, in combination with 24 mM./kg. of sodium di(2-ethylhexyl) dithiophosphate. For comparison, a similar oil composition containing 12 mM./kg. of zinc di(2-ethylhexyl) dithiophosphate was tested. The results of the Falex test showed that the wear with the zinc thiophosphate was 13.4 mg., whereas with the sodium thiophosphate the wear was reduced to 7.3 mg.

While the character of this invention has been described in detail with numerous examples, this has been done by way of illustration only and without limitation of the invention. It will be apparent to those skilled in the art that numerous modifications and variations of the illustrative examples may be made in the practice of the invention within the scope of the following claims.

We claim:

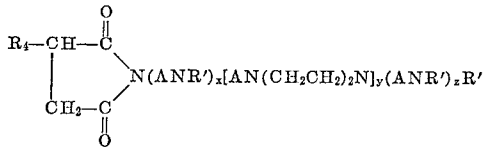
1. An ashless detergent lubricating oil composition comprising a major proportion of oil of lubricating viscosity, a minor proportion sufficient to improve the detergent characteristics thereof of the salt, amide or imide of alkenyl succinic acid or alkenyl succinic anhydride of a polyamine having the formula

$$H_2N(ANR')_x[AN(CH_2CH_2)_2N]_y(ANR')_zR'$$

wherein A is an alkylene radical containing from about 2 to 6 carbon atoms, R′ is a member of the group con-

sisting of hydrogen and alkyl radicals containing from about 1 to 5 carbon atoms, x is a number from 0 to 10, y is a number from 0 to 2, z is a number from 0 to 10, the total of $x+y+z$ being a number from 1 to 10, said polyamine being reacted with alkenyl succinic acid or alkenyl succinic anhydride in which the alkenyl group contains from about 20 to about 400 carbon atoms, in combination with a minor amount sufficient to improve the corrosion and wear resistant properties of an alkali metal salt of dihydrocarbyl dithiophosphoric acid containing from about 8 to about 60 carbon atoms in the hydrocarbon portion.

2. An ashless detergent lubricating oil composition comprising a major proportion of oil of lubricating viscosity, a minor proportion sufficient to improve the detergent characteristics thereof of an alkenyl succinimide having the formula



wherein R_4 is an alkenyl radical of from about 20 to 400 carbon atoms, A is an alkylene radical containing from about 2 to 6 carbon atoms, R' is a member of the group consisting of hydrogen and alkyl radicals containing from about 1 to 5 carbon atoms, x is a number from 0 to 10, y is a number from 0 to 2, z is a number from 0 to 10, the total of $x+y+z$ being a number from 1 to 10, in combination with a minor amount sufficient to improve the corrosion and wear resistant properties of an alkali metal salt of di(alkylaryl)dithiophosphoric acid of up to about 60 carbon atoms.

3. An ashless detergent lubricating oil composition comprising a major proportion of oil of lubricating viscosity, a minor proportion sufficient to improve the detergent characteristics thereof of an alkenyl succinimide of tetraethylene pentamine having from about 50 to about 200 carbon atoms in the alkenyl group in combination with a minor amount of sodium di(tetradecylphenyl) dithiophosphate sufficient to improve the corrosion and wear resistant properties.

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