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## ADDITION AGENT FOR LUBRICATING OIL AND METHOD OF MAKING SAME

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6 Claims. (Cl. 260—461)

This invention relates to the treatment of hydrocarbon products such as mineral oils to improve their characteristics, and particularly to the addition to petroleum lubricating oils of certain materials which improve their ability to resist the deteriorating effect of oxidation and their ability to lubricate bearing surfaces which are subjected to extreme pressures such as are now commonly encountered in the newer types of machinery.

This application is a division of my application Serial No. 319,839, filed February 20, 1940, entitled Lubricant.

Moderately refined oils, such as motor oils and other moderately refined lubricating oils and moderately refined turbine oils normally used under conditions of exposure to oxidation in the presence of metals, oxidize, giving rise to sludge and/or acidic oxidation products frequently corrosive to the metals which they encounter in use, as for example bearing metals in automotive use, and copper and copper alloys in turbine use. It has now been found that stabilization of these oils against such oxidation effects may be conveniently accomplished by addition to the oils of certain materials which substantially retard the oxidation of the oils, whether or not metal is present, and which apparently have the ability to inhibit the catalytic effect of metals in promoting oxidation reactions and thus prevent the formation of sludge and/or acidic constituents and the like under normal conditions of use.

Recent changes in automotive engine design, tending toward higher bearing pressures, higher rotative speeds, higher engine temperatures, and the like, have occasioned departure from the use of the usual bearing metals such as babbitt. The newer bearing metals are of different nature, than those less recently developed and while harder, are in general more susceptible to destructive agencies of a corrosive nature. Typical of these newer bearings are those composed of a cadmium-silver alloy supported upon a steel back, which are now widely installed in certain makes of automobiles. Others of these relatively new bearing metals which may be mentioned are copper-lead alloys, copper-lead-tin alloys, cadmium-nickel alloys, cadmium-zinc alloys, cadmium-zinc alloys modified by the presence of lead, antimony, or both, and a general class of alloys consisting mainly of lead and hardened with calcium, barium, potassium, antimony, and the like, known generically as "high lead babbitts."

These changes in engine design have been concurrent with marked advances in methods of refining lubricant oils for automotive use. The demand for oils having lesser changes in viscosity with temperature change; i. e., higher viscosity index (frequently designated as V. I.), has been met by refining lubricants intended for motor oils by certain solvent refining or solvent extraction processes, wherein advantage is taken of the selective solvent power for hydrocarbons of various types which is possessed by certain liquid reagents, for example, dichlorodiethylether, cresylic acid, phenol, chloraniline, chlorophenol, phenetidine, benzyl alcohol, nitrobenzene, benzonitrile, furfural, aniline, benzyl acetate, liquid sulphur dioxide, mixtures of liquid sulphur dioxide or aniline with benzol, and the like. Those solvent refining processes are designed to concentrate in the desired lubricant fraction those compounds of a "paraffinic" nature possessed of the ability to suffer only a small change of viscosity with change of temperature, and to reject the compounds of "naphthenic" nature which do suffer such change of viscosity to a marked degree. These refining processes have provided a supply of oil of quite desirable general characteristics, definitely far superior to any oil previously produced from mixed base or asphaltic crudes, and superior to a like, though lesser, degree over oils previously produced from paraffin base crudes.

It has been found that the solvent refined motor oils referred to above are definitely corrosive to the newer bearing metals referred to above under extreme conditions of automotive use, due to oxidation during use, sometimes resulting in bearing failure after only a few thousand miles of driving. Difficulties are frequently encountered due to bearing corrosion in automotive equipment operated at sustained high speeds of the order of 60 to 90 M. P. H., or under other conditions conducive to high crankcase temperatures of the order of 275° F. or higher. It is further known that the same reaction, viz., corrosion of alloy bearing metals such as cadmium-silver, also occurs in good paraffinic base oils which have not been subjected to solvent refining. The higher the V. I. of the lubricating oil, the more pronounced is the tendency to corrosion of the kind referred to above. Generally speaking, the problem is encountered in oils having a V. I. of 100 or higher, particularly at elevated temperatures of engine operation.

Furthermore, the present trend in automotive design toward lower body styles, rapid acceleration, and the use of hypoid gears has increased the unit loadings on rear axles. In some cases

the unit pressures encountered become great enough to rupture the oil film of ordinary mineral oil lubricants, with consequent metal to metal contact. In other lines of power transmission and the like, there is a similar tendency toward the use of high unit pressures of a degree which are near or beyond the limit at which mineral oils, alone, will maintain effective lubrication. This invention is therefore specifically concerned with the production of lubricants capable of withstanding the high unit loadings which occur in such instances. Such lubricants are generally spoken of as extreme pressure lubricants.

Extreme pressure lubricants are normally produced by adding to a hydrocarbon lubricant a small amount of some characterizing substance which enables it to maintain a lubricant film unruptured under conditions which would cause the breakdown of a film formed of oil alone. Such additive substances are spoken of as E. P. (extreme pressure) bases, or E. P. ingredients. Many commonly used E. P. bases are composed of sulphur dissolved in mineral oil, sulphurized vegetable or animal oils, chlorinated compounds, metallic soaps, and the like. This invention is specifically concerned with the use as E. P. characterized ingredients, of compounds new and novel for this purpose, and not heretofore so used or known to be useful for this purpose.

It is an object of this invention to provide an extreme pressure lubricant, which lubricant is superior to lubricants of this class heretofore commonly known, particularly in load-carrying capacity, stability, and maintenance of extreme pressure lubricating properties under sustained conditions of high loading. It is an object of this invention to prepare novel and valuable ingredients and to combine them with hydrocarbon lubricant oils to produce lubricants having high load bearing capabilities, to prepare such ingredients which have good characteristics of stability, which are less corrosive, and which impart a greater influence when present in much smaller amounts than are required with extreme pressure ingredients now commercially available. Further objects are the provision of methods of making the ingredient or ingredients, methods of preparing lubricants containing these novel characterizing ingredients, and methods of lubrication making use of the lubricants so produced.

It is an important object of this invention to provide means for satisfactorily inhibiting or preventing corrosion from taking place to a serious degree particularly in oils of relatively high viscosity index. It is also an object of this invention to alter or modify a highly refined motor oil, normally corrosive, by the use of additive ingredient capable of substantially inhibiting this corrosion. It is a further object of this invention to provide a substantially non-corrosive motor oil of high V. I. Still another object of this invention is to provide an additive reagent or ingredient capable of inhibiting the corrosive properties of these oils. The production of solvent refined oils of low corrosive properties under conditions of automotive use is a major object of this invention, as well as the method of production of such oils which combine a relatively high viscosity index with a relatively low tendency to produce such corrosion.

A further object of this invention is the provision of lubricating oils, particularly oils for use in internal combustion engines, which do not deposit gummy or resinous films or "lacquers" upon pistons, rings, valves, and cylinder walls of engines, and especially those operated at relatively high temperatures and/or for long periods of time.

I have found that hydrocarbon oils of the classes defined above can be stabilized against the formation of acidic and/or corrosive and/or sludge bodies by the addition to said oils of a relatively small amount of a substantially stable, oil-soluble, water-insoluble reaction product of an ester of phosphorous acid and an alkyl aroxy alkanol. I have also found that novel lubricants having extreme pressure lubricating characteristics can be produced by adding to oil a sufficient quantity of said reaction product. Among the esters of phosphorous acid which may be suitably employed in the production of my reaction products are the aryl phosphites such as triphenyl phosphite, trinaphthyl phosphite, trianthryl phosphite; the alkylated aryl phosphites such as the tricresyl phosphites, trixylenyl phosphites, triethyl phenyl phosphites, tripropyl phenyl phosphites, tributyl phenyl phosphites, triamyl phenyl phosphites, and the isomers and higher homologs thereof. While I prefer to employ the aryl phosphites in the production of my reaction products, I may also utilize the alkyl phosphites such as trimethyl phosphite, triethyl phosphite, tributyl phosphite, triamyl phosphite, and the like. Mixed alkyl-aryl phosphites and hydroaromatic phosphites, as well as aryl or alkyl mono and diphosphites and the esters of hypophosphorous, pyrophosphorous, and thiophosphorous acids may also be employed.

The substituted alkanols which I utilize in the preparation of my reaction products are preferably the alkyl aroxy alkanols having the general formula $R.C_nH_{2n-x}.O.R'.OH$, wherein R comprises hydrogen or one or more alkyl or substituted alkyl groups, preferably alkyl groups having at least 3 carbon atoms in the chain, $C_nH_{2n-x}.O$ comprises an aroxy or substituted aroxy group. R' comprises one or more methylene or substituted methylene groups, and $x$ is at least 8. Typical of the substituted alkanols are phenoxymethanol, propyl phenoxymethanol, butyl phenoxymethanol, amyl phenoxymethanol, hexyl phenoxymethanol, heptyl phenoxymethanol, and the higher homologues decyl, lauryl, cetyl, oleyl, and stearyl phenoxymethanols. In lieu of the phenoxy group, other aroxy groups such as naphthoxy and anthroxy may be utilized, and in lieu of the methanol group, other alkanol groups such as ethanol, propanol, butanol, pentanol, and the like may be used. The substituted alkyl group R and the substituted methylene group R' may contain as substituents halogen and/or sulfur.

The above mentioned substantially stable oil-soluble, water-insoluble reaction products are adapted, as I have discovered, to be added directly to or dissolved in a hydrocarbon oil for the purpose of inhibiting or eliminating the normal tendency of said oils to corrode the metal bearings and parts hereinbefore mentioned, to stabilize said oils against the accelerating action of metals on the deteriorating effects of oxidation reactions under normal conditions of use and/or handling and/or storage and to increase the ability of the oil to withstand high unit loadings. By substantially stable, I mean stable under the normal conditions of use and/or handling and/or storage to which these corrosion inhibitors and oxidation inhibitors are ordinarily subjected, after manufacture, either before they are added to the hydrocarbon oil to be stabilized or after they are added to such an oil.

In preparing the reaction product to be employed in accordance with my invention, I prefer to admix the ester of phosphorous acid with the alkyl aroxy alkanol and thereafter bring the mixture to a temperature sufficient to cause reaction of the ingredients, whereby there is introduced into the ester of phosphorous acid at least one alkyl aroxy alkanol group. The mol ratio of ester to alkanol employed may vary from about 1:1 to about 1:2.5, and is preferably of the order of about 1:14. The admixture of ester and alkanol may be heated at atmospheric pressure under a reflux condenser to a temperature sufficient to effect reaction, for example, temperatures of the order of from about 200° F. to about 500° F., and the resulting oil-soluble, water-insoluble reaction product may be separated from the by-products of the reaction by distillation under reduced pressure, or by recrystallization from a suitable solvent, or by washing with a solvent having selective solvent power for either the reaction product or the undesirable by-products. Or, if the ester and the alkanol are relatively high boiling, the reaction may be carried on at elevated temperatures of the order of from about 200° F. to about 350° F., under reduced pressures of the order of 10 m. m. or less. On the other hand, if the ester and the alkanol are not relatively high boiling, the reaction may be carried on at elevated temperature and under a suitable superatmospheric pressure. Depending upon the ratio of ester to alkanol employed, and upon the temperature and time of reaction, at least one and in some instances two alkanol groups may be introduced into the ester of phosphorous acid. In general, it is preferred that the alkyl aroxy alkanol have a boiling point higher than that of the alcohol or phenol employed initially in the manufacture of the ester of phosphorous acid. The reaction products so produced may be regarded as complex esters of phosphorous acid which may or may not contain unreacted alkanol. Such reaction products have a wider range of utility and effectiveness as inhibitors and the like than the simple esters from which they are prepared.

Alternatively, my reaction product may be produced directly in hydrocarbon oil by adding thereto suitable quantities of ester and alkanol, and then heating the mixture to a temperature sufficient to cause the reaction of the ester with the alkanol, undesirable by-products of the reaction being removed by distillation or by washing with a suitable solvent.

The reaction products produced in accordance with my invention may be added to hydrocarbon oils in varying amounts, depending upon the qualities it is desired to impart to the oil. For example, in order to inhibit oxidation of hydrocarbon oils such as lubricating oil, turbine oil, or electrical insulating oil such as transformer or cable oil, I may incorporate in the oil from about 0.05% to about 0.5% of my reaction products. In the case of lubricating oils for internal combustion engines, quantities of reaction product of the order of 0.1% to about 0.7% will inhibit the formation of color bodies and acidity, and will inhibit corrosion of bearing metals such as cadmium-silver and copper-lead alloys. My reaction products, when employed in quantities of the order of 0.4% to about 0.7%, will inhibit the formation of sludge, resinous bodies, or "lacquers," and will impart to the oils moderate degree of film strength or extreme pressure characteristics. Where a considerable degree of improvement in film strength or extreme pressure characteristics is required, my products may be employed in amounts of the order of 1% to 2%, or more. In those cases where it is desirable, from an economic point of view, to employ only sufficient quantities of my reaction products to inhibit oxidation of the oil, and to obtain a high degree of film strength by the addition of other agents, I may add to the oil, for example, 0.4% of my reaction products and 0.6% of a film strength agent such as tricresyl phosphate. Other film strength agents, of course, may be employed in lieu of or in addition to tricresyl phosphate, and the quantities of such agents may be varied, as desired.

The reaction products of my invention may be utilized not only as inhibitors or film strength agents for hydrocarbon oils, but also for similar purposes in other products such as thickened oils or greases, cutting oils, petrolatums, waxes, animal and vegetable oils, or mixtures thereof with hydrocarbon oils.

What I claim is:

1. The method of producing an addition agent for hydrocarbon oils, which comprises reacting an ester of phosphorous acid with an alkyl aroxy alkanol at such temperature and for such period of time as to introduce into said ester at least one alkyl aroxy alkanol group.

2. The method of producing an addition agent for hydrocarbon oils, which comprises reacting an aryl ester of phosphorous acid with an alkyl aroxy alkanol at such temperature and for such period of time as to introduce into said ester at least one alkyl aroxy alkanol group.

3. The method of producing an addition agent for hydrocarbon oils, which comprises heating an ester of phosphorous acid with an alkyl aroxy alkanol at a temperature within the range of from about 200° F. to about 500° F. for a period of time sufficient to introduce into said ester at least one alkyl aroxy alkanol group.

4. The method of producing an addition agent for hydrocarbon oils, which comprises heating an aryl ester of phosphorous acid with an alky aroxy alkanol at a temperature within the range of from 200° F. to about 500° F. for a period of time sufficient to introduce into said ester at least one alkyl aroxy alkanol group.

5. The method of producing an addition agent for hydrocarbon oils, which comprises heating at least one mol of an ester of phosphorous acid with from about 1 to 2.5 mols of an alkyl aroxy alkanol at a temperature within the range of from about 200° F. to about 500° F. for a period of time sufficient to introduce into said ester at least one alkyl aroxy alkanol group.

6. An addition agent for hydrocarbon oils consisting of an ester of phosphorous acid corresponding to the formula



wherein R is an aryl radical, R' is an alkyl aroxy alkyl radical, and R'' is of the group consisting of aryl and alkyl aroxy alkyl radicals.

RAYMOND REUTER.

CERTIFICATE OF CORRECTION.

Patent No. 2,349,462. May 23, 1944.

RAYMOND REUTER.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 26-27, for the word "characterized" read --characterizing--; page 3, first column, line 11, for "about 1:14" read --about 1:1.4--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 8th day of August, A. D. 1944.

Leslie Frazer

(Seal) Acting Commissioner of Patents.