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LUBRICANT

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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.

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 such 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. characterizing 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 an 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 a relatively high boiling aliphatic alcohol. 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 homologues 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, and triamyl phosphite. 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 relatively high boiling aliphatic alcohols which I utilize in the preparation of my reaction products include the mono and polyhydric alcohols, preferably those having boiling points above about 200° C. Representative examples of such compounds are octyl alcohol, nonyl alcohol, decyl alcohol, undecyl or lauryl alcohol, oleyl alcohol, stearyl alcohol, ceryl alcohol, ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, triethylene glycol, and glycerol. I may likewise employ high boiling ether alcohols such as diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, and the like.

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 relatively high boiling alcohol 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 high boiling alcohol group. The mol ratio of ester to alcohol employed may vary from about 1:1 to about 1:2.5, and is preferably of the order of about 1:1.4. The admixture of

ester and alcohol 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 byproducts 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 byproducts. Or, if both the ester and the alcohol 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 mm. or less. On the other hand, if the ester is relatively low boiling and the alcohol is 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 alcohol employed, and upon the temperature and time of reaction, at least one and in some instances two alcoholic groups may be introduced into 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 high boiling alcohol. 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 high boiling alcohol, and then heating the mixture to a temperature sufficient to cause the reaction of the ester with the alcohol, undesirable byproducts 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.

My invention may be further illustrated by the following examples, which, however, are not intended as limiting the scope thereof.

1 mol of tricresyl phosphite and 1.3 mol of cetyl alcohol were admixed and introduced into a vacuum still. Heat was applied to the still and the admixture was brought to a temperature of about 150° F., whereupon the pressure within the still was reduced to about 5 mm. by means of a vacuum pump connected to the condensing system associated with the still. The admixture was then heated, under the reduced pressure aforesaid, to a temperature of the order of about 240° F., at which temperature reaction between the tricresyl phosphite and the cetyl alcohol was initiated. The temperature of the reaction mixture was then progressively raised to about 340° F. and the mixture was maintained at such temperature until substantially all of the cresol liberated during the reaction (about 1 mol of cresol or 30.7% by weight of the tricresyl phosphite initially charged) has been distilled from the reaction mixture. Traces of residual cresol may be removed from the heated reaction mixture, while under reduced pressure, by bubbling a small quantity of air or inert gas such as carbon dioxide or nitrogen through the reaction mixture. The cresol distilled from the mixture may be condensed and disposed of as desired. The reaction product obtained by the above process appears to be a complex ester of phosphorous acid containing at least one cetyl alcohol group.

The inhibiting effect of the above described reaction product upon the formation of sludge due to oxidation of lubricating oil is illustrated by the data presented in the following table. The blank oil and the oil containing various percentages of my reaction product was subjected to an oxidation test which comprised heating a 100 cc. sample of the oil at a temperature of 340° F. for a period of 96 hours, while bubbling air through the heated sample at a rate of 3 liters per hour. The insoluble sludge was separated from the oil, washed with a solvent to remove adhering oil, and dried to constant weight. The amount of sludge is reported as milligrams per 10 grams of oil. The oil employed was a solvent refined S. A. E. 20 motor oil having a Sabolt universal viscosity of 313 seconds at 100° F. and an A. P. I. gravity of 29.3°.

Oil composition	Sludge
	Milligrams
Blank oil	197
Blank oil+0.1% by vol. of reaction product	99
Blank oil+0.3% by vol. of reaction product	78
Blank oil+0.7% by vol. of reaction product	59
Blank oil+1.5% by vol. of reaction product	42

To demonstrate the inhibiting action of my reaction product upon corrosion of bearing metals by refined lubricating oil, the following data is presented. The test utilized comprised submerging in the oil samples to be tested a weighed cadmium-silver bearing, and heating the samples at a temperature of 340° F. for 24 hours while bubbling air through the samples at the rate of 3 liters per hour. At the completion of the heating period the bearings were removed from the oil samples, washed, dried and weighed. The loss in weight, due to corrosion, is reported in milligrams. The oil employed in this test was a selective solvent refined oil having a Saybolt

universal viscosity of 313 seconds at 100° F., and an A. P. I. gravity of 29.3°.

Oil composition	Weight loss of bearings
	Milligrams
Blank oil	42
Blank oil+0.1% by vol. of reaction product	12
Blank oil+0.3% by vol. of reaction product	8
Blank oil+0.7% by vol. of reaction product	0
Blank oil+1.5% by vol. of reaction product	0

The effectiveness of my reaction product in increasing the film strength or load-bearing capacity of lubricating oil is illustrated by the results tabulated below. The blank oil and the oils containing various percentages of my reaction product were tested in an Almen extreme pressure lubricant testing machine operated at 200 R. P. M. The pressures are expressed as lbs./sq. in. projected bearing area sustained before seizure of the test bearing. The lubricating oil employed was the same as used in the preceding test for corrosion inhibition.

Oil composition	Film strength
	Lbs./sq. in.
Blank oil	4,000
Blank oil+0.3% by vol. of reaction product	12,000
Blank oil+1.5% by vol. of reaction product	17,000

To further demonstrate the effectiveness of my novel reaction product, under actual conditions of use, tests were made employing a Chevrolet engine. The Chevrolet engine was run for 32 hours at 3,000 R. P. M., at a crankcase oil temperature of 280° F., samples of the test oils being withdrawn and examined at 8 hour intervals. The results of the Chevrolet engine tests are presented in the following table.

Properties	Oil (new)	Oil (used), hours				Oil+0.7% reaction product (used), hours			
		8	16	24	32	8	16	24	32
A. P. I. gravity, degrees	28.9				25.2				26.1
S. U. vis./100° F. seconds	325	356	418	440	521	395	437	471	500
S. U. vis./210° F. do	53				63				61
Viscosity index	93				89				84
Neut. number (mgs. KOH/gm.)	.02	2.0	3.8	4.9	5.5	1.6	2.8	4.1	4.1
Carbon residue	.01	.42	.83	.95	1.08	.38	.59	.83	.97
Asphaltenes	.00	.11	.22	.42	.85	.18	.06	.18	.16
Sediment	.00	.10	.07	.23	.18	.03	.09	.05	.19
Piston ring weight loss in mgs.					6,002				2,677

From the results of the tests above set forth, it will be apparent that in all respects the oils containing small amounts of my reaction product are markedly superior to oils to which no reaction product has been added.

The reaction product of my invention may be utilized not only as an inhibitor or film strength agent 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. A hydrocarbon oil composition comprising a relatively large proportion of a refined hydrocarbon oil normally tending to deteriorate by oxidation under normal conditions of use and in intimate admixture therewith a relatively small amount sufficient to inhibit such deterioration, of an oil-soluble, water-insoluble reaction product of an ester of phosphorous acid and a relatively high boiling aliphatic alcohol, said reaction product containing at least one and not more than two aliphatic radicals corresponding to said high boiling alcohol.

2. A hydrocarbon oil composition comprising a relatively large proportion of a refined hydrocarbon oil normally tending to deteriorate by oxidation under normal conditions of use and in intimate admixture therewith a relatively small amount sufficient to inhibit such deterioration, of an oil-soluble, water-insoluble reaction product of an aryl ester of phosphorous acid and a relatively high boiling aliphatic alcohol, said reaction product containing at least one and not more than two aliphatic radicals corresponding to said high boiling alcohol.

3. A hydrocarbon oil composition comprising a relatively large proportion of a refined oil, normally tending to deteriorate by oxidation under normal conditions of use, and in intimate admixture therewith a relatively small amount sufficient to inhibit such deterioration of an oil-soluble, water-insoluble reaction product of tricresyl phosphite and a relatively high boiling aliphatic alcohol, said reaction product containing at least one and not more than two aliphatic radicals corresponding to said high boiling alcohol.

4. A hydrocarbon oil composition comprising a relatively large proportion of a refined oil, normally tending to deteriorate by oxidation under normal conditions of use, and in intimate admixture therewith a relatively small amount sufficient to inhibit such deterioration of an oil-soluble, water-insoluble reaction product of tricresyl phosphite and cetyl alcohol, said reaction product containing at least one and not more than two cetyl radicals.

5. A lubricant comprising hydrocarbon lubricating oil and a small amount of an oil-soluble, water-insoluble reaction product of an ester of phosphorous acid and a relatively high boiling aliphatic alcohol, said reaction product containing at least one and not more than two aliphatic radicals corresponding to said high boiling alcohol.

6. A lubricant comprising a selective solvent refined hydrocarbon lubricating oil having a relatively high viscosity index and a small amount of an oil-soluble, water-insoluble reaction product of an aryl ester of phosphorous acid and a relatively high boiling aliphatic alcohol, said reaction product containing at least one and not more than two aliphatic radicals corresponding to said high boiling alcohol.

7. A lubricant comprising hydrocarbon lubricating oil and from about 0.05% to about 2.0% of an oil-soluble, water-insoluble reaction product of an aryl ester of phosphorous acid and a relatively high boiling aliphatic alcohol, said reaction product containing at least one and not more than two aliphatic radicals corresponding to said high boiling alcohol.

8. A lubricant comprising hydrocarbon lubricating oil and from about 0.4% to about 0.7% of an oil-soluble, water-insoluble reaction product of an aryl ester of phosphorous acid and a relatively high boiling aliphatic alcohol, said reaction product containing at least one and not more than two aliphatic radicals corresponding to said high boiling alcohol.

9. A lubricant comprising hydrocarbon lubricating oil, a small quantity of a reaction product of tricresyl phosphite and cetyl alcohol, and a small quantity of tricresyl phosphate, said reac-

tion product containing at least one and not more than two cetyl groups.

10. The method of lubricating bearing surfaces, which comprises maintaining between bearing surfaces, one of which is an alloy selected from the class consisting of cadmium-silver, cadmium-nickel, cadmium-zinc, cadmium-zinc-lead-antimony, copper-lead, copper-lead-tin, and high lead babbitts, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid alloy, and maintaining the effectiveness of the lubricating oil by incorporating therein a small amount, sufficient to substantially retard corrosion, of an oil-soluble, water-insoluble reaction product of an ester of phosphorous acid and a relatively high boiling aliphatic alcohol, said reaction product containing at least one and not more than two aliphatic radicals corresponding to said high boiling alcohol.

11. The method of lubricating bearing surfaces which comprises maintaining between bearing surfaces, one of which is an alloy selected from the class consisting of cadmium-silver, cadmium-nickel, cadmium-zinc, cadmium-zinc-lead-antimony, copper-lead, copper-lead-tin, and high lead babbitts, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid alloy, and maintaining the effectiveness of the lubricating oil by incorporating therein a small amount, sufficient to substantially retard corrosion, of an oil-soluble, water-insoluble reaction product of an aryl ester of phosphorous acid and a relatively high boiling aliphatic alcohol, said reaction product containing at least one and not more than two aliphatic radicals corresponding to said high boiling alcohol.

12. A lubricant comprising hydrocarbon oil and a small quantity of an ester of phosphorous acid corresponding to the formula:



wherein R is a cetyl radical, R' is a cresyl radical, and R'' is of the group consisting of cetyl and cresyl radicals.

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