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HYDROCARBON OIL COMPOSITIONS

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This invention relates to hydrocarbon oil compositions and more particularly to hydrocarbon compositions highly resistant to undesirable oxidation changes.

The compositions of my invention constitute superior hydrocarbon oil compositions possessing increased resistance to oxidation and sludge formation. These compositions comprise in combination a major proportion of a hydrocarbon oil and minor proportions of each of an alkyl substituted phenol antioxidant and an orthoboric acid triester. The orthoboric acid triester is of the general formula $(RO)_3B$ in which R represents an organic radical in which at least 2 carbon atoms are joined to the carbon atom attached to the oxygen. In the preferred embodiment of my invention an alkyl phenol antioxidant such as 2,6-di-tertiary-butyl-4-methylphenol constitutes the alkyl substituted phenol antioxidant and the orthoboric acid triester is a trialkyl orthoborate ester derived from orthoboric acid and a secondary aliphatic alcohol having 3 to 18 carbon atoms. Best results are secured when the concentration of the orthoboric acid triester is about 0.0001 to about one percent by weight, and preferably about 0.0005 to about 0.5 percent by weight, and the concentration of the alkyl substituted phenol antioxidant is about 0.01 to about 10 percent by weight, and preferably about 0.1 to about 2 percent by weight. The optimum amount of each additive may vary depending upon the particular oil and the severity of the conditions to which it is subjected. The additive constituents are present in the hydrocarbon oil in an amount sufficient to produce a composition having an induction period longer than the sum of the induction periods of two compositions produced by incorporating each of the additive constituents alone in portions of the same hydrocarbon oil.

The hydrocarbon oil employed in the compositions of my invention comprises any of the conventional hydrocarbon oils utilized for the lubrication of metal surfaces, as heat transfer fluids, transformer oils, insulating oils, or switch oils. Thus, the hydrocarbon oils can be derived from mineral lubricating oil fractions such as those secured from the refining of paraffinic oil stocks, naphthenic oils, and also from oil-bearing shale. In addition, the hydrocarbon oil can be derived from synthetic hydrocarbon oils such as those secured from the "Fischer-Tropsch" synthesis. The exact grade of hydrocarbon oil to be used in the compositions of my invention is dependent upon the ultimate use to which the composition is put. Thus, if the compositions of my invention are employed for the lubrication of automobiles, the hydrocarbon oil constituent of the composition will consist of a refined mineral lubricating oil of lubricating viscosity for the particular point of application. In other words a conventional gear oil may be used where the composition is used for the lubrication of the gears, and generally a less viscous, more highly refined oil, will be used in the crankcase.

The finished compositions of my invention may also contain other "additive" agents including oiliness and extreme pressure agents, such as aromatic chlorine-contain-

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ing compounds, stabilized chlorinated paraffins, sulfurized fatty oils and high molecular weight ketones and esters; viscosity index improvers, such as high molecular weight polymers of isobutylene and the polymers of methacrylic esters; pour point depressants, such as a condensation product of chlorinated wax and naphthalene and a condensation product of chlorinated wax and phenol followed by further condensation of this reaction product with organic acids; detergents, such as nickel naphthenate, metal salts of ethylhexyl salicylate, and metal salts of alkyl substituted phenol sulfides; and foam inhibitors, such as organo-silicon oxide condensation products, and organo-silicol condensation products.

The alkyl substituted phenol antioxidants of the type herein involved comprise the class of phenol derivatives which confer resistance to oxidation when added to a hydrocarbon oil. The term "phenol" as used herein and in the appended claims includes phenol and its methyl homologues such as the cresols and xylenols as well as the corresponding bis-phenols. Particularly suitable alkyl phenols are those wherein the sum of the number of carbon atoms present in the alkyl groups occupying the positions ortho to the hydroxyl group is four or more. Particularly suitable alkyl substituents are those containing from four to eight carbon atoms, such as the butyl, amyl, hexyl, heptyl and octyl groups. While the phenol may contain only one such substituent, good results are obtained when using a phenol antioxidant containing two or three of such substituents. The alkyl substituents can be either normal, secondary or tertiary alkyl groups.

Examples of some of the alkyl substituted phenol antioxidants which can be used in the compositions of the invention are 2,6-di-tertiary-butyl-4-methylphenol; bis(2-hydroxy-3-tertiary-butyl-5-methylphenyl)methane; 1,1-bis(2-hydroxy-3-tertiary-butyl-5-methylphenyl)ethane; 1,1-bis(2-hydroxy-3-tertiary-butyl-5-methylphenyl)propane; 2,4-di-tertiary-butyl-5-methylphenol; 2,4,6-tri-tertiary-butylphenol; 2-tertiary-butyl-4-methylphenol; butylated hydroxy-anisole; 2,6-di-tertiary-butyl-4-phenylphenol; 2,6-di-secondary-amylphenol; 4-octylphenol; etc.

The orthoboric acid triesters of this invention are of the general formula $(RO)_3B$ in which R represents an organic radical in which at least 2 carbon atoms are joined to the carbon atom attached to the oxygen. Examples of these orthoboric acid triesters include the triesters of boric acid with phenols, tertiary alcohols, and secondary alcohols such as tri-para-tertiary-butyl-phenyl-borate; tri-tertiary-butyl-borate; tricyclohexyl-borate; and tribornyl-borate. In the preferred embodiment of my invention the orthoboric acid triester has the general formula $(XO)_3B$ in which X represents a secondary aliphatic alkyl radical having 3 to 18 carbon atoms and thus comprises a triester of orthoboric acid and a secondary aliphatic alcohol having 3 to 18 carbon atoms. The preferred secondary alcohols are those having 2 or 3 carbons joined to either or both of the carbon atoms adjacent to the hydroxyl-bearing carbon atom. Examples of secondary alcohols that are useful for the preparation of orthoboric acid triesters include diisopropylcarbinol, diethylcarbinol, methylisobutylcarbinol, diisobutylcarbinol, 3,9-diethyl-6-hydroxytridecane.

The orthoboric acid triesters used in the compositions of the invention were prepared by reacting boric acid and the corresponding alcohol, with the alcohol being employed as a solvent in several instances, and with benzene or toluene as the solvent in others; and then refluxing the mixture in an apparatus equipped with a water trap. The preparation of the trialkyl orthoboric acid esters of pentanol-3, diisopropylcarbinol, methylisobutylcarbinol, 3,9-diethyl-6-hydroxytridecane and diisobutylcarbinol is given below.

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Example I

The reaction to prepare the trialkyl orthoboric acid ester of pentanol-3 was carried out in a suitable reaction vessel equipped with a mechanical stirrer, a water trap fitted with a water-cooled condenser, and a dropping funnel. 20.6 parts by weight of orthoboric acid and 100 parts by weight of pentanol-3 were added to the flask and the mixture heated. After approximately one hour, the reflux temperatures reached 92° C., the vessel temperature reached 115° C., and 10 parts by weight of water had collected in the water trap. 20 parts by weight of pentanol-3 were then added slowly from the dropping funnel to the mixture. After another two hours of heating, the reflux temperature reached 98° C., the reaction vessel temperature reached 130° C. and a total of 18 parts by weight of water had collected in the trap. The reaction mixture was clear and remained clear after standing for 18 hours. The mixture was then distilled and the fraction boiling between 232.5° C. and 239° C. at a pressure of 750 mm. of mercury was collected. This fraction constituted 74 parts by weight of tris(3-pentoxy)-boron or a yield of about 81.5 percent of the theoretical.

Example II

Similar type apparatus to that mentioned in Example I was utilized in the preparation of tri-(diisopropylcarbinyl)-borate. Thus, 20.6 parts by weight of boric acid and 156 parts by weight of diisopropylcarbinol were refluxed together for approximately two hours, at a reflux temperature of 102° C. 18 parts by weight of water were collected in the trap and then 61.7 parts by weight of unreacted alcohol were recovered. The reaction mixture was cooled and the crystalline product separated by filtering. 80.1 parts by weight of crude tris(2,4-dimethyl-3-pentoxy)boron were obtained constituting a 67.7 percent theoretical yield. This product was dissolved in ether and filtered to remove any unreacted boric acid. The product was then recovered by evaporation of the ether and was recrystallized from 95 percent ethyl alcohol. A total of 59.6 parts by weight, equivalent to a 50.3 percent theoretical yield, of a white crystalline compound having a melting point of 57.5° to 58.5° C. was recovered.

Example III

Similar type apparatus to that mentioned in Example I was utilized in the preparation of the triester of boric acid and methylisobutylcarbinol. Thus, 20.6 parts by weight of boric acid and 122.2 parts by weight of methylisobutylcarbinol were refluxed together for approximately 2¾ hours at a vessel temperature of approximately 200° C. 17.7 parts by weight of water were collected in the trap. The reaction mixture was cooled and then distilled under vacuum. 94.7 parts by weight of crude tris(4-methyl-2-pentoxy)boron equivalent to a 90.5 percent theoretical yield were collected at a pressure of 0.8 mm. of mercury.

Example IV

Similar type apparatus to that mentioned above was utilized in the preparation of the triester of boric acid and 3,9-diethyl-6-hydroxytridecane. Thus, 7.5 parts by weight of boric acid and 93.4 parts by weight of 3,9-diethyl-6-hydroxytridecane were refluxed together for approximately 2½ hours at a vessel temperature of about 250° C. 86 parts by weight of toluene were added to the mixture to facilitate removal by azeotropic distillation of the water formed during the reaction. 5.5 parts by weight of water were recovered. Upon distillation under vacuum at a pressure of 1 mm. of mercury and a temperature of between 255° and 265° C., 76.3 parts by weight of crude tris(3,9-diethyl-6-tridecoxy)boron were obtained constituting 81 percent theoretical yield.

Example V

Similar type apparatus to that mentioned above was utilized in the preparation of the triester of boric acid and diisobutylcarbinol. 20.6 parts by weight of boric

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acid and 144 parts by weight of diisobutylcarbinol were refluxed together and 14 parts by weight of water were collected in the trap. The crude tris(2,6-dimethyl-4-heptoxy)boron was recrystallized from ether and pentane, and yielded 70.8 parts by weight or a 48.3 percent theoretical yield of crystalline material having a melting point of 98-99° C.

Tests were run to determine the induction period for sludge formation for a transformer-type mineral oil base having the following typical inspections:

Gravity, ° API	28.3
Viscosity @ 100° F., SUV	54.4
Viscosity @ 210° F., SUV	33.6
Flash point, C. O. C. ° F.	275
Flash point, C. O. C. ° F.	310
Pour point, ° F.	55
Neutralization No.	0.01
Sulfur (B) percent	0.10

In addition, the induction periods for sludge formation of mixtures of this oil base with an alkyl phenol, and of the oil base plus a trialkyl orthoborate were also determined. These were then compared with the induction period of the composition containing the mineral oil base plus both the alkyl phenol and the trialkyl orthoborate.

The induction period for sludge formation was determined by the time required until sludge began to form under the conditions set forth in A. S. T. M. D670-42T, method A, as described in "A. S. T. M. Standards on Electrical Insulating Materials," January 1950, modified as follows. Instead of subjecting three samples to the test and determining the amount of sludge formed at the end of the three given periods of time, five samples of each composition tested were placed in the apparatus. After starting the test, the samples were periodically checked and the time prior to the first evidence of sludge formation was determined.

Example VI

	Oil	Oil+0.3 wt. percent 2,6-di-tertiarybutyl-4-methyl-phenol	Oil+0.05 wt. percent tri-(methylisobutylcarbinyl) borate	Oil+0.3 wt. percent 2,6-di-tertiarybutyl-4-methyl-phenol+0.05 wt. percent tri (methylisobutylcarbinyl) borate
Induction period in days	0	10	0	24

Example VII

	Oil	Oil+0.3 wt. percent 2,6-di-tertiarybutyl-4-methyl-phenol	Oil+0.01 wt. percent tri-(methylisobutylcarbinyl) borate	Oil+0.3 wt. percent 2,6-di-tertiarybutyl-4-methyl-phenol+0.01 wt. percent tri (methylisobutylcarbinyl) borate
Induction period in days	0	10	0	21

Example VIII

	Oil	Oil+0.3 wt. percent 2,6-di-tertiarybutyl-4-methyl-phenol	Oil+0.05 wt. percent tri-(diisobutylcarbinyl) borate	Oil+0.3 wt. percent 2,6-di-tertiarybutyl-4-methyl-phenol+0.05 wt. percent tri-(diisobutylcarbinyl) borate
Induction period in days	0	10	0	22

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Example IX

	Oil	Oil+0.3 wt. percent 2,6-di-tertiary-butyl-4-methyl-phenol	Oil+0.01 wt. percent tri-(diisobutyl-carbinyl) borate	Oil+0.3 wt. percent 2,6-di-tertiary-butyl-4-methyl-phenol+0.01 wt. percent tri-(diisobutyl-carbinyl) borate
Induction period in days.....	0	10	2	18

Example X

	Oil	Oil+0.3 wt. percent 2,6-di-tertiary-butyl-4-methyl-phenol	Oil+0.05 wt. percent tri-(diethyl-carbinyl) borate	Oil+0.3 wt. percent 2,6-di-tertiary-butyl-4-methyl-phenol+0.05 wt. percent tri-(diethyl-carbinyl) borate
Induction period in days.....	1	15	5	22

Example XI

	Oil	Oil+0.3 wt. percent 2,4,6-tri-tertiary-butylphenol	Oil+0.05 wt. percent tri-(diisobutyl-carbinyl) borate	Oil+0.3 wt. percent 2,4,6-tri-tertiary-butylphenol +0.05 wt. percent tri-(diisobutyl-carbinyl) borate
Induction period in days.....	1	2	0	4

Example XII

	Oil	Oil+0.3 wt. percent di-secondary-amyphenol	Oil+0.05 wt. percent tri-(diisobutyl-carbinyl) borate	Oil+0.3 wt. percent di-secondary-amyphenol +0.05 wt. percent tri-(diisobutyl-carbinyl) borate
Induction period in days.....	1	2	0	5

Example XIII

	Oil	Oil+0.3 wt. percent p-octylphenol	Oil+0.05 wt. percent tri-(diisobutyl-carbinyl) borate	Oil+0.3 wt. percent p-octylphenol +0.05 wt. percent tri-(diisobutyl-carbinyl) borate
Induction period in days.....	1	2	0	4

Example XIV

	Oil	Oil+0.3 wt. percent butylated hydroxyanisole	Oil+0.05 wt. percent tri-(diisobutyl-carbinyl) borate	Oil+0.3 wt. percent butylated hydroxyanisole +0.05 wt. percent tri-(diisobutyl-carbinyl) borate
Induction period in days.....	1	2	0	6

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Example XV

	Oil	Oil+0.3 wt. percent bis-(2-hydroxy-3-t-butyl-5-methyl-phenyl) methane	Oil+0.05 wt. percent tri-(diisobutyl-carbinyl) borate	Oil+0.3 wt. percent bis-(2-hydroxy-3-t-butyl-5-methyl-phenyl)-methane +0.05 wt. percent tri-(diisobutyl-carbinyl) borate
Induction period in days.....	1	4	0	7

15 It can be seen from the foregoing that the induction period for the combination of phenol and borate in the oil is much greater than that of the phenol alone or of the borate alone, and that a true synergistic action is effected between the two. I have found that not only do the additive combinations of my invention confer improved sludge-suppressing and antioxidant characteristics upon hydrocarbon oils but also these compositions possess improved lubricating properties as indicated by Falex Wear Test data, and in addition the corrosive effect of the oil base on bearing metals is inhibited. Moreover, the triesters of orthoboric acid with phenols, secondary alcohols, or tertiary alcohols are exceptionally resistant to hydrolysis. In this respect these esters are very superior to orthoboric acid triesters of primary alcohols, which were found to readily hydrolyze under normal working conditions when employed as an additive for a lubricant or transformer oil.

I do not wish to be bound by any explanation for the synergistic effect of the phenol antioxidant and orthoboric acid triester within the hydrocarbon oil compositions of my invention. However, it is possible that this synergistic effect is due to the simultaneous action of the phenol antioxidant and orthoboric acid triester on separate portions of the sludge-forming constituents of the hydrocarbon oil. As a result the striking synergistic effect of my invention is obtained.

While the character of the invention has been described in detail, and examples of the compositions given, this has been done by way of illustration only and with the intention that no limitation should be imposed upon the invention thereby. It will be apparent to those skilled in the art that numerous modifications and variations of the illustrations and examples may be effected in the practice of the invention, and accordingly these modifications and variations should be construed as included within the scope of the claims appended hereto. By way of example, in place of the hydrocarbon oils which have been disclosed, other hydrocarbon oils having similar properties may be utilized. In addition, various relative concentrations of phenol antioxidant to orthoborate ester within the compositions of my invention may be employed.

The compositions of my invention comprise useful transformer oils, switch oils, insulating oils, lubricating oils, turbine oils, and the like. They are possessed of superior sludge-suppressing characteristics and of superior anti-corrosive and lubricating properties.

This application is a continuation-in-part of my co-pending application, Serial No. 227,937, filed May 23, 1951 and now abandoned.

I claim:

1. A composition consisting essentially of a major proportion of a hydrocarbon oil and minor proportions of each of an alkyl phenol antioxidant wherein the alkyl group contains 4 to 8 carbon atoms and a trialkyl orthoborate having the general formula (XO)₃B in which X represents a secondary alkyl radical having 5 to 9 carbon atoms, the additive constituents being present in an amount sufficient to produce a composition having an induction period longer than the sum of the induction

periods of two compositions produced by incorporating each of the additive constituents alone in portions of the same hydrocarbon oil.

2. A composition in accordance with claim 1 in which the alkyl phenol comprises from between about 0.1 to 2 percent by weight, and the trialkyl orthoborate comprises between about 0.0005 to about 0.5 percent by weight.

3. A composition consisting essentially of a major proportion of a hydrocarbon oil and minor proportions of each of 2,6-di-tertiary-butyl-4-methylphenol and a trialkyl orthoborate having the general formula $(XO)_3B$ in which X represents a secondary aliphatic alkyl radical having 5 to 9 carbon atoms, the additive constituents being present in an amount sufficient to produce a composition having an induction period longer than the sum of the induction periods of two compositions produced by incorporating each of the additive constituents alone in portions of the same hydrocarbon oil.

4. A composition in accordance with claim 3 in which the 2,6-di-tertiary-butyl-4-methylphenol comprises between about 0.1 to 2 percent by weight, and the trialkyl orthoborate comprises between about 0.0005 to about 0.5 percent by weight.

5. A composition consisting essentially of a major proportion of a hydrocarbon oil and minor proportions of each of an alkyl phenol antioxidant wherein the alkyl group contains 4 to 8 carbon atoms and tris(2,6-dimethyl-4-heptoxy)boron, the additive constituents being present in an amount sufficient to produce a composition having an induction period longer than the sum of the induction periods of two compositions produced by incorporating each of the additive constituents alone in portions of the same hydrocarbon oil.

6. A composition consisting essentially of a major proportion of a hydrocarbon oil and minor proportions of each of 2,4,6-tri-tertiary-butylphenol and tris(2,6-dimethyl-4-heptoxy)boron, the additive constituents being present in an amount sufficient to produce a composition having an induction period longer than the sum of the induction periods of two compositions produced by incorporating each of the additive constituents alone in portions of the same hydrocarbon oil.

7. A composition consisting essentially of a major proportion of a hydrocarbon oil and minor proportions

of each of 2,6-di-tertiary-butyl-4-methylphenol and tris(2,6-dimethyl-4-heptoxy)boron, the additive constituents being present in an amount sufficient to produce a composition having an induction period longer than the sum of the induction periods of two compositions produced by incorporating each of the additive constituents alone in portions of the same hydrocarbon oil.

8. A composition consisting essentially of a major proportion of a hydrocarbon oil and minor proportions of each of bis(2-hydroxy-3-tertiary-butyl-5-methylphenyl)methane and tris(2,6-dimethyl-4-heptoxy)boron, the additive constituents being present in an amount sufficient to produce a composition having an induction period longer than the sum of the induction periods of two compositions produced by incorporating each of the additive constituents alone in portions of the same hydrocarbon oil.

9. A composition consisting essentially of a major proportion of a hydrocarbon oil and minor proportions of each of di-secondary-amyphenol and tris(2,6-dimethyl-4-heptoxy)boron, the additive constituents being present in an amount sufficient to produce a composition having an induction period longer than the sum of the induction periods of two compositions produced by incorporating each of the additive constituents alone in portions of the same hydrocarbon oil.

10. A composition consisting essentially of a major proportion of a hydrocarbon oil and minor proportions of each of 2,6-di-tertiary-butyl-4-methylphenol and tris(4-methyl-2-pentoxy)boron, the additive constituents being present in an amount sufficient to produce a composition having an induction period longer than the sum of the induction periods of two compositions produced by incorporating each of the additive constituents alone in portions of the same hydrocarbon oil.

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