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LUBRICATING OIL CONTAINING AN ANTIOXIDANT

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1

This invention relates to lubricants and other organic materials subject to deterioration in the presence of oxygen, and it relates more particularly to mineral lubricating oil compositions for use as crankcase lubricants for internal combustion engines containing addition agents suitable for retarding the deterioration of such oils and for lowering the pour point of the same.

In accordance with the present invention a new class of organic derivatives of boric acid are described which are particularly useful as additives for mineral lubricating oils used in internal combustion engines, in which they act as inhibitors of oxidation and deposition of varnish on hot metal surfaces and as agents for substantially reducing the pour point of the base oil. They are particularly useful in inhibiting the normal corrosiveness of the oil when in contact with copper-lead, cadmium-silver and other similar bearings now widely used in automotive engines. these compounds are likewise suitable as antioxidants in organic materials generally where the organic material is known to be susceptible to deterioration in the presence of oxygen.

It has been proposed in the art to use various esters of boric acid, such as tributyl borate, triamyl borate, trilauryl borate, triphenyl borate and the likes as additives for inhibiting the corrosiveness of lubricating oils toward hard metal alloy bearings. It has been found, however, that when alkyl borates or aryl borates with only short alkyl side chains are used as additives for oils, the ester is hydrolyzed by means of moist air, with the result that boric acid is precipitated in considerable quantities from the solution as a solid precipitate. By comparison, the additives of the present invention are practically free from a tendency to hydrolize in this manner.

The new class of antioxidant compounds are long chain alkylated aryl borates, and those which are especially effective are the wax-alkylated phenyl borates. The new class of additives may be defined more precisely by the general formula

$$(RAr)_mH_nBO_3$$

where Ar is any aryl nucleus, e. g., a benzene, biphenyl or naphthalene nucleus, R represents at least one open chain alkyl radical, all of such radicals containing a total of at least 16 carbon atoms, m is an integer from 1 to 3, n is 0, 1 or 2, and $m+n$ equals 3. The above formula is intended to include also compounds in which various substituent atoms or groups may be attached to the aromatic nucleus or to the side chain, such as alkyl, aryl, carboxyl, hydroxyl, alkoxy, aroxy, sulfhydryl, nitro, ester, keto, thioether, amino or aldehydo groups, halogen atoms, etc.

2

A highly preferred class of compounds are the wax-alkylated phenyl borates, which may be readily obtained by first preparing a wax-alkylated phenol, as by reacting phenol with a chlorinated wax, and then reacting the wax-alkylated phenol with boric acid. Compounds of this type which contain two or more wax chains on the phenyl nucleus are preferred. Various ratios of wax-alkylated phenol to boric acid may be used in the preparation, ranging from 1:2 to 3:1. It should be understood that more than one phenyl group may be attached to a single wax chain, as when a wax containing chlorine atoms at a number of points in the chain is reacted with phenol to produce a wax chain containing several phenol substituent groups, and that compounds so produced are intended to be included within the scope of the above general formula.

Alkyl phenols whose borate esters may be employed in the present invention include: wax alkylated phenol, wax alkylated naphthol, wax alkylated cresol, cetyl phenol, octadecyl phenol (stearyl phenol), di-tert.-octyl phenol, isohexadecyl phenol, and C_{16}–C_{20} branched chain alkyl phenols obtained by alkylating phenol or a cresol with a refinery butene polymer oil. Borates of the corresponding alkyl phenol sulfides may also be employed.

Generally, the additives of the present invention are most advantageously blended with lubricating oil base stocks in concentrations between the approximate limits of 0.02% and 5.0% and preferably from 0.5% to 2.0%, although larger amounts may be used for some purposes. The exact amount of addition agent required for maximum improvement depends to a certain extent on the particular products used, the nature of the lubricating oil base stock, and the general operating conditions of the engine in which the lubricant is to be used.

A number of examples of the preparation of the new compounds of the present invention and of the intermediates used in the preparation of such compounds will be described in detail, and data

showing the effect of these additives in lubricating oils when submitted to various test conditions will also be given. It should be understood that these examples are given for illustrative purposes only and are not to be construed as limiting the scope of the invention in any way.

PRODUCTION OF CHLORINATED WAX

Example 1

1 kg. of refined paraffin wax (M. P. 122° F.) was placed in a reaction flask and the wax melted over a hot plate. When the temperature of the melted wax reached 240° F. the hot plate was removed and the flask placed on a balance and chlorine gas passed into the wax at such a rate that the temperature remained about 200° F. throughout the entire chlorination process. When the weight had increased by a little more than 198 g. the flow of chlorine was stopped and dry nitrogen was passed in to remove the excess chlorine and HCl. This was continued for about 2 hrs. The resulting product (product I) was found to contain 17.46% chlorine.

Example 2

2 gallons of chlorinated wax, obtained by chlorinating semi-refined wax (M. P. 118° F.) at 200° F. by a process similar to that described in Example 1 and containing 13.5% chlorine when melted completely, was poured into a round bottomed flask. This was placed on a steam bath and nitrogen blown through for about 2 hours. The product was found to contain 12.83% chlorine (product IIA).

1 gallon of product IIA after standing for about 10 weeks was found to be mostly liquid at 131° C. The liquid portion was siphoned off into a separate vessel. This liquid portion was found to contain 13.60% chlorine (product IIB).

PRODUCTION OF WAX PHENOLS

Example 3

500 grams of chlorinated wax prepared as in Example 1 (product I) was placed in a 3-necked flask with stirrer, reflux condenser and thermometer. 70.5 grams of phenol was added, and a smaller flask containing 15 grams of $AlCl_3$ was attached to one neck of the reaction flask by means of Gooch tubing. The phenol-chlorinated wax mixture was heated to 65° C. and maintained at this temperature during the addition of the $AlCl_3$ over a 1 hour period. The mixture was then slowly heated to 150° C. over a period of 1¼ hours. During this heating HCl was evolved in large quantities. Heating was continued for 3 hours more at 150° C. and the mixture was then cooled to about 80° C. and 1 liter of petroleum naphtha (B. P. 160–240° F.) was added. The solution was poured into water and acidified with HCl. The mixture was shaken thoroughly to remove the $AlCl_3$. It was necessary to add isopropyl alcohol to break the emulsion. The mixture was washed several times with water and the upper layer was then distilled to remove the solvent. The distillation was begun at atmospheric pressure, then moderate vacuum was applied carefully when the vapor temperature rose above 100° C. After the bath temperature had risen to 250° C. the solution was distilled at about 1.5 mm. pressure until the temperature of the bath had reached 225° C. The residue weighed about 465 grams. (Product IIIA.)

312.3 grams of product IIIA was distilled to remove the unreacted chlorinated wax. The distillation was carried out at less than 1 mm. pressure and continued until the distillation temperature rose to 260° C. The residue weighed 276.8 grams. (Product HIB.)

Example 4

500 grams of chlorinated wax (product IIA) was placed in a reaction flask with stirrer and return condenser and 56.4 grams of phenol was added. The mixture was heated to 65° C. and then over a period of one hour 15 grams of $AlCl_3$ was gradually added from an Erlenmeyer flask connected to a side neck with Gooch tubing. The mixture was slowly heated at 150° C. and maintained at that temperature for 3 hours, after which it was partly cooled and 1 liter of naphtha was added. The naphtha solution was washed three times with water and dried over anhydrous $CaCl_2$. The solvent was stripped off at atmospheric pressure. The temperature was raised to 250° C., moderate vacuum being first applied and then high vacuum (less than 1 mm.) to remove the unreacted chlorinated wax as a distillate until a temperature of 260° C. was reached. The residue weighed 342 grams. (Product IV.)

Example 5

500 grams of chlorinated wax (product I) was placed in a reaction flask equipped with stirrer, return condenser, and thermometer and 67 grams of phenol was added. The mixture was heated to 65° C. and 15 grams of anhydrous $AlCl_3$ was added gradually over a period of 1 hour, employing the same technique as in previous examples. The flask was gradually heated to 150° C. and held between 150° and 160° C. for over 3 hours. The flask was allowed to cool partially and 1 liter of naphtha was added. The mixture was poured into a separatory funnel, allowed to stand overnight and washed twice with water. The emulsion which was formed was broken with a slow current of air. The solution was dried by stirring with $CaCl_2$ and the naphtha and remaining water were distilled off under moderate vacuum until a bath temperature of 250° C. was obtained. The residue was dissolved in naphtha and filtered through Hyflo (a diatomaceous earth filter aid). The solvent and unreacted material were distilled off under less than 1 mm. pressure until a distilling temperature of 240° C. was obtained. The residue weighed 419 grams. (Product V.)

Example 6

500 grams of chlorinated wax (product IIA) was placed in a reaction flask with stirrer, reflux condenser, and thermometer and 56.4 grams of phenol was added. The mixture was heated to 65° C. and 15 grams of anhydrous $AlCl_3$ was added in small proportions over a period of 1 hour. The mixture was gradually heated to 150° C. and held at 150°–160° C. for over 3 hours. The mixture was allowed to cool partially and 1 liter of naphtha added. The solution was poured into a separatory funnel, allowed to stand overnight and washed twice with water and dried over $CaCl_2$. The solvent and a small amount of water present were removed by distillation under moderate vacuum until a bath temperature of 250° C. was attained. The residue was dissolved in naphtha and filtered through Hyflo. The solvent and unreacted materials were distilled off under less than 1 mm. pressure up to a distilling temperature of 230° C. The residue weighed 400 grams. (Product VI.)

Example 7

500 grams of chlorinated wax (product IIB) was placed in a reaction flask with stirrer, return condenser, and thermometer, 60 grams of phenol was added and the whole heated to 65° C. To this solution 15 grams of anhydrous $AlCl_3$ was added over a period of ½ hour. The mixture was gradually heated to 150° C. and held at that temperature for 4 hours, after which 1 liter of naphtha was added. The solution was decanted to a separate flask and NH_3 gas passed in for ½ hour to decompose any $AlCl_3$ present. Air was blown in to remove the excess of NH_3. The solution was filtered and the volume of the filtrate then reduced by vacuum distillation until 605.8 grams of residual naphtha solution remained.

The residual naphtha solution was washed with dilute HCl and three times with water, and then dried by refluxing with a water trap. The solvent was removed by distilling in vacuum over a boiling water bath, the residue weighing 534 grams. (Product VII.)

PREPARATION OF WAX PHENYL BORATES

In Examples 8 to 15 will be described several preparations of wax phenyl borates, by reacting the wax phenols prepared as described above with boric acid in various proportions and under varying conditions of procedure.

Example 8

95.5 grams of wax phenol (product IIIA) was placed in a reaction flask and 500 cc. of xylene added. A stirrer, thermometer, and return condenser with trap were attached and the mixture refluxed several hours to remove any water which may have been present. The refluxing was stopped and 7 grams of powdered H_3BO_3 was added while the mixture was still hot. There was considerable reaction immediately with liberation of water. The mixture was refluxed overnight, then cooled and filtered. The solvent was removed from the filtrate by moderate vacuum and heated to 250 C. in a metal bath. The residue weighed 105 grams. (Product VIII.) This product was an amorphous, dark colored solid, somewhat gelatinous when cooled.

Example 9

100 grams of wax phenol (product IV) was dissolved in 500 cc. of toluene and placed in a reaction flask equipped with stirrer, return condenser and water trap. The solution was refluxed to remove any water which may have been present. 10 g. of H_3BO_3 was added and the mixture refluxed overnight. The solution was filtered from excess H_3BO_3 and the solvent distilled from the product at a pressure of 1 mm. until the bath temperature reached 190° C. The residue weighed 103.6 g. (Product IX.)

Example 10

100 g. of wax phenol (product IIIB) was dissolved in 500 cc. of toluene and placed in a reaction flask equipped with stirrer, return condenser and water trap. The solution was refluxed to remove any water which may have been present. 3.56 g. of H_3BO_3 was added and the mixture refluxed for 6 hours, water formed during the reaction being removed through the trap. All of the H_3BO_3 dissolved with the exception of a few crystals on the bottom of the flask. The solution was placed in a Claisen flask and the solvent

removed by distillation under moderate vacuum up to an oil bath temperature of 190° C. The residue weighed 101.1 g. (Product X.)

Example 11

In the same manner as in Example 9, 100 grams of wax phenol (product IV) was dissolved in 500 cc. of toluene and refluxed with 6.7 grams of powdered H_3BO_3 for 12½ hours. The clear liquid was decanted into Claisen flask and the solvent removed by distillation at 1 mm. pressure until a bath temperature of 175° C. was reached. The residue weighed 102 grams. (Product XI.)

Example 12

200 grams of wax phenol (product V) was dissolved in 750 cc. of mineral spirits having a boiling range of 300° to 410° F. and placed in a reaction vessel equipped with stirrer, thermometer, return condenser, and water trap. 14.3 grams of H_3BO_3 was added. The mixture was heated to 155° F. and held at this temperature overnight. The solution was filtered with the aid of Hyflo and the solvent partially removed by distillation under vacuum, then 800 grams of a refined paraffinic type mineral lubricating oil of S. A. E. 20 viscosity grade was added and the remainder of the mineral spirits removed by further distillation under house vacuum (150–200 mm. pressure) using a maximum bath temperature of 290° C. A maximum vapor temperature of 142° C. was reached. The residual oil solution was further treated by heating it for 4½ hours at 150° C. with 15 grams of boric acid, a stream of nitrogen being blown through the mixture at the same time to facilitate removal of water. A filter aid (Hyflo) was added and the mixture filtered to give a clear oil concentrate containing about 20% of wax phenyl borate. (Product XII.)

Example 13

200 grams of wax phenol (product VI) was dissolved in 1 liter of mineral spirits having a boiling range of 300° to 410° F. and placed in a reaction flask containing 12 grams of H_3BO_3. A stirrer, thermometer, and return condenser with water trap were attached and the mixture refluxed to remove water. The mixture was maintained at 150 C. overnight without refluxing and then filtered with the aid of Hyflo. The mineral spirits was partially removed by vacuum distillation (150–200 mm.). 600 grams of S. A. E. 20 mineral lubricating oil was added and the vacuum distillation was continued. The distilling temperature rose to a maximum of 130° C. with a bath temperature of 240° C.

The oil solution was further treated by heating it for 4½ hours at 150° C. with 15 grams of boric acid, a stream of nitrogen being blown through the mixture at the same time to facilitate removal of water. A filter aid (Hyflo) was added and the mixture filtered to give a clear oil concentrate containing about 25% of wax phenyl borate. (Product XIII.)

Example 14

300 grams of wax phenol (product VIIB) was placed in a reaction flask equipped with stirrer, thermometer, and return condenser with water trap. 1400 cc. of toluene was added and the mixture stirred while 50 grams of H_3BO_3 was added. The mixture was refluxed overnight and then filtered. Toulene was removed under house vacuum over a boiling water bath. The residue weighed 299 grams. (Product XIV.)

Example 15

200 grams of wax phenol (product VIIB) and 1 liter of toluene were placed in a reaction flask equipped with stirrer, thermometer, and return condenser with water trap. 10.3 grams of H_3BO_3 was added and the mixture stirred and refluxed over the week-end. All of the H_3BO_3 had disappeared. The toluene was removed by moderate vacuum distillation over a water bath and finally under high vacuum. The residue weighed 194.5 grams. (Product XV.)

In the following table are summarized some of the more pertinent data relating to the wax phenyl borate products whose preparation has been described above.

Table I

Product No.	Per cent Cl in Cl Wax	Wax/Phenol Ratio	Per cent Cl in Wax Phenol	Acetyl No. of Wax Phenol	Mol. Wt. from Acetyl No.	Wax Phenol/H_3BO_3, ratio (approx.)
VIII	17.46	3:1	1.00	56.30	955	1:1+
IX	12.83	3:1	0.54	54.30	992	1:1+
X	17.46	2:1	0.73	83.09	633	2.8:1
XI	12.83	3:1	0.54	54.30	992	1:1+
XII	17.46	3:1	0.78	61.70	867	1:1
XIII	12.83	3:1	1.33	48.90	1104	1:1+
XIV	13.60	3:1	0.68	40.40	1347	1:2+
XV	13.60	3:1	0.68	40.40	1347	1:1+

Example 16

Tertiary octyl phenol was prepared by alkylation of phenol with diisobutylene. 206 grams of tertiary octyl phenol was dissolved in 824 grams of S. A. E. 20 grade solvent refined paraffinic type mineral lubricating oil and treated with 61.8 grams of boric acid. The mixture was heated at 150° C. for 5 hours with stirring, nitrogen being blown through the mixture to facilitate water removal. The product was then filtered using Hyflo filter aid, to give a clear oil concentrate containing 25% of tertiary octyl phenyl borate. (Product XVI.)

Example 17

A solution of 270 grams (1 mol. proportion) of commercial stearyl alcohol (octadecyl alcohol) in 810 grams of S. A. E. 20 grade paraffinic type mineral lubricating oil was treated with 20.6 grams (3 mol. proportions) of boric acid. In essentially the same manner as in Example 16 the mixture was heated and stirred and blown with nitrogen for 5 hours at 150° C. and then filtered, giving a clear oil concentrate containing 25% of tri-octadecyl borate.

MOIST AIR TEST

Example 18

In the following series of tests, water-washed air was passed through oil solutions containing 1% each of various borate ester products to determine the effect of such moist air in hydrolyzing the ester and precipitating the boric acid from the oil solution. For each test 1% of the ester was dissolved in a base oil consisting of a refined paraffinic type lubricating oil of 20 viscosity grade, and 100 cc. of such solution was placed in a suitable vessel. Air was then bubbled through a bottle containing water and then through the oil solution at a rate of 4 to 7 cc. per second for a period of two days in each test, the apparatus being kept at room temperature. The results given in Table II show the amount of precipitate observed as the result of the hydrolysis of the ester. A number of alkyl and alkaryl esters of boric acid have thus been compared with the wax phenyl borates produced in the processes described above.

Table II

Borate Ester	Amount of Precipitation
Octadecyl borate (Product XVII).	A voluminous precipitate—small needles.
Tert.-Octylphenyl borate (Product XVI).	Voluminous precipitate in one day.
Product VIII	Slight precipitate.
Product X	Slightly hazy.
Product XI	No precipitate.
Product XII	Do.
Product XIII	Slightly hazy.
Product XIV	Slight powdery precipitate.
Product XV	Hazy solution and slight fine precipitate.
Triethyl borate	Immediate voluminous precipitate.
Triamyl borate	Do.

POUR POINT TESTS

Example 19

Measurement was made of pour points of the various wax phenyl borate products in a clay finished Pennsylvania neutral distillate light lubricating oil stock with a normal pour point of +30° F. 0.5% and 1% solutions were thus tested. The results are shown in Table III.

Table III

Product No.	Pour Point of Solution in Oil	
	0.5%	1.0%
VIII	<−35	<−35
IX	<−35	−5
X	−25	<−35
XI	+10	0
XII	−30	<−35
XIII	−5	+15
XV	−10	+15

INDIANA LIFE TESTS

Example 20

Blends of lubricating oils containing additives prepared in accordance with the present invention were submitted to the standard Indiana oxidation test, described in S. A. E. Journal, vol. 34, page 167, (1934). 0.5% of borate ester was present in each oil blend. The results are shown in Table IV. The values given represent the number of milligrams of sludge formed from 10 g. of oil at the end of various periods during which the test was run. The base oil used in each case was well refined, solvent extracted paraffinic type mineral lubricating oil of S. A. E. 20 grade.

During each test the varnish forming tendency of each oil blend was also determined in the following manner: In each oil sample tube a glass plate about 3" by 1" was placed. At the end of the 96 hour period the plate was removed, washed with naphtha, air dried and then weighed to determine the amount of varnish deposited. The milligrams of varnish obtained in each test are also given in Table IV.

Table IV

[Sludge (Mg/10 g. of oil)]

Oil	24 Hours	48 Hours	72 Hours	96 Hours	Indiana Life, Hours [1]	Mg. Varnish
Base Oil	0	0	16	55	63	3.6
Base Oil+Product VIII	0	0	0	Trace	>96	0.1
Base Oil+Product IX	0	Trace	Trace	43	78	2.3
Base Oil+Product X	0	0	Trace	57.8	76	0.8
Base Oil+Product XI	0	Trace	Trace	22.4	83	1.2
Base Oil+Product XII	0	Trace	8.1	68.7	73	3.1
Base Oil+Product XIII	0	0	Trace	48.4	77	3.3
Base Oil+Product XIV	0	Trace	Trace	66.0	76	2.5
Base Oil+Product XV	0	Trace	Trace	35.8	79	3.1

[1] Hours to form 10 mg. of sludge (determined by interpolation).

BEARING CORROSION TESTS

Example 21

Blends of the wax phenyl borate products prepared by the methods of the foregoing examples in a lubricating oil base consisting of a well refined solvent extracted paraffinic type mineral lubricating oil of S. A. E. 20 viscosity grade, the blends containing 0.5% and 1.0% of the additive, and a sample of the unblended base oil, were submitted to a corrosion test designed to measure the effectiveness of the products in inhibiting the corrosiveness of a typical mineral lubricating oil toward the surface of copper-lead bearings. The test was conducted as follows:

500 cc. of the oil was placed in a glass oxidation tube (13" long and 2⅝" diameter) fitted at the bottom with a ¼" bore air inlet tube perforated to facilitate air distribution. The oxidation tube was then immersed in a heating bath so that the oil temperature was mantained at 325° F. during the test. Two quarter sections of automotive bearings of copper-lead alloy of known weight having a total area of 25 sq. cm. were attacked to opposite sides of a stainless steel rod which was then immersed in the test oil and rotated at 600 R. P. M., thus providing sufficient agitation of the sample during the test. Air was then blown through the oil at the rate of 2 cu. ft. per hour. At the end of each four-hour period the bearings were removed and were washed with naphtha and weighed to determine the amount of loss by corrosion. The bearings were then repolished (to increase the severity of the test), reweighed, and then subjected to the test for an additional four-hour period. The cumulative weight losses of all the bearings used in a given test at the end of the various four-hour periods are given in Table V.

The lubricating oil base stocks employed in the blended lubricating oils of this invention may be straight mineral lubricating oils, or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichloro ethyl ether, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special application, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed, either alone or in admixture with mineral oils.

For the best results the base stock chosen should normally be that oil which without the new additives present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a

Table V

Oil Blend	Conc., percent	Cumulative Bearing Weight Loss (mg./25 sq. cm. surface)								
		4 Hours	8 Hours	12 Hours	16 Hours	20 Hours	24 Hours	28 Hours	32 Hours	36 Hours
Base Oil		5	181							
Base Oil+Product VIII	0.5	0	0	0	12	62	291			
Do	1.0	1	1	1	1	2	4	18	66	247
Base Oil+Product IX	0.5	0	0	0	2	164				
Do	1.0	0	0	1	1	1	3	14	94	332
Base Oil+Product X	0.5	2	2	20	276					
Do	1.0	1	1	2	15	47	221			
Base Oil+Product XI	0.5	0	0	0	2	11	369			
Do	1.0	0	0	0	1	2	3	11	34	215
Base Oil+Product XII	0.5	0	0	2	5	260				
Do	1.0	0	1	1	2	128				
Base Oil+Product XIII	0.5	0	1	12	365					
Do	1.0	0	0	3	151					
Base Oil+Product XIV	0.5	0	1	3	58	307				
Do	1.0	0	0	2	19	261				
Base Oil+Product XV	0.5	0	0	1	26	247				
Do	1.0	0	0	0	2	14	62	187		

satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of certain low and medium speed Diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of Diesel service, particularly with high speed Diesel engines, and in gasoline engine service, oils of higher viscosity index are often required, for example up to 75 or 100, or even higher, viscosity index.

In addition to the materials to be added according to the present invention, other agents may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, amides, nitriles, amines, aldehydes, halogenated or nitrated compounds and the like, may also be employed.

Assisting agents which are particularly desirable for reducing foam and for plasticizing concentrated oil solutions of the additives are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol, $C_8H_{17}OH$, lauryl alcohol, $C_{12}H_{25}OH$, cetyl alcohol, $C_{16}H_{33}OH$, stearyl alcohol, sometimes referred to as octadecyl alcohol, $C_{18}H_{37}OH$, and the like; the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols, such as naphthenic alcohols; and aryl substituted alkyl alcohols, for instance, phenyl octyl alcohol, or octadecyl benzyl alcohol or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes, the wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared synthetically by chemical processes may also be used, such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g., paraffin wax, petrolatum, etc. Other assisting agents include stearyl nitrile and stearyl amine.

In addition to being employed in crankcase lubricants and in extreme pressure lubricants, the additives of the present invention may also be used in industrial lubricants, process oils, engine flushing oils, turbine oils, insulating and transformer oils, steam cylinder oils, slushing and rust preventive compositions, and greases. Also their use in motor fuels, Diesel fuels and kerosene is contemplated. Since these additives exhibit antioxidant properties and are believed also to possess ability to modify surface activity, they may be employed in asphalts, road oils, waxes, fatty oils of animal or vegetable origin, soaps, and plastics. Similarly, they may be used in natural and synthetic rubber compounding both as vulcanization assistants and as antioxidants, and generally they may be used in any organic materials subject to deterioration by atmospheric oxygen.

The present invention is not to be considered as limited by any of the examples described herein, which are given by way of illustration only, but is to be limited solely by the terms of the appended claims.

We claim:

1. A composition of matter consisting essentially of a petroleum hydrocarbon product and an oxidation inhibiting proportion of a compound of the formula

$$(RAr)_mH_nBO_3$$

where Ar is an aryl nucleus, R represents at least one alkyl radical, the alkyl radicals containing a total of at least 16 carbon atoms, m is an integer from 1 to 3, n is 0, 1 or 2, and $m+n$ equal 3.

2. A composition of matter consisting essentially of a mineral lubricating oil and an oxidation inhibiting proportion of a compound of the formula

$$(RAr)_mH_nBO_3$$

where Ar is an aryl nucleus, R represents at least one alkyl radical, the alkyl radicals containing a total of at least 16 carbon atoms, m is an integer from 1 to 3, n is 0, 1 or 2, and $m+n$ equal 3.

3. A composition of matter according to claim 2 in which R of the formula is a wax radical and Ar is a benzene nucleus.

4. A composition of matter consisting essentially of a mineral lubricating oil and an oxidation inhibiting quantity of a wax alkylated phenyl borate.

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2,312,208	Clayton	Feb. 23, 1943
2,316,903	Van Ess	Apr. 20, 1943
2,326,496	Reiff	Aug. 10, 1943
2,333,871	Lincoln	Nov. 9, 1943
2,346,157	Farrington	Apr. 11, 1944
2,357,287	Reiff	Sept. 5, 1944
2,383,605	Lieber	Aug. 28, 1945