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LUBRICANTS

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This invention relates to improved hydrocarbon lubricants and more particularly to hydrocarbon lubricants stabilized by a liquid alkylene baborate. This application is a continuation-in-part of my previous application, Serial No. 584,438, filed May 14, 1956, now abandoned.

Hydrocarbon lubricants deteriorate when subjected to the elevated temperatures encountered in lubrication service. This deterioration leads to deleterious deposits of carbonaceous material on the lubricated surfaces which greatly reduce the effectiveness of the lubricant.

Certain boron compounds have been proposed heretofore as lubricating oil additives. These boron compounds suffer the disadvantage that they are solids or gases. Even though such compounds may possess antioxidant effectiveness, they are not suited for commercial use as lubricating oil additives. This is because of their state of aggregation. Being solids or gases, their rate of solubility in lube oil is so low that they have prohibitively long dispersion times. Also their blending into the oil must be done by tedious methods. Moreover, they tend to crystallize or separate out from the oil when it is exposed for prolonged periods to quite low temperatures such as outdoor winter temperatures in Canada and the northern United States.

Liquid antioxidants, on the other hand, do not have these inherent disadvantages. Being liquids they are subject to ready blending into the lube oil base by such simple means as piping, pumping and the like. Moreover, they are subject to ready metering so that the exact predetermined amount of additive can be blended into the oil without difficulty. Once blended into the oil such additives possess the additional advantage that they are readily, thoroughly and almost instantaneously dispersed throughout the oil substrate so that a homogeneous blend is swiftly attained. Finally, such blends are capable of being subjected to extremely low temperatures for prolonged periods of time without any settling, crystallization or separation of the additive taking place. It is therefore very important to the art to have effective liquid additives available.

Various boron compounds have also been proposed as additives to leaded gasoline to alleviate certain problems associated with combustion chamber deposits. These problems are different from the problems encountered in lubricating oil and the purpose for which such compounds are added to leaded gasoline is different from the purpose for which such compounds are added to lubricating oil.

As the art recognizes, the deposit problem in the combustion chamber is an aggravated one. The presence of tetraethyllead in the fuel causes the deposits to be no longer essentially carbonaceous material. Despite the fact that one or more organic halides are included in the fuel with the tetraethyllead to serve as scavenging agent, not all of the lead is removed. A carbonaceous deposit with lead is often more tenacious and troublesome than a pure carbonaceous deposit. The fact that this deposit is partially metallic in character is thought to give it a catalytic activity which modifies the action of the deposit in affecting engine operation. Furthermore, since the lead is intimately mixed with the carbonaceous material, the lead in the deposit is difficult to reach by means of scavengers to eliminate or modify it, especially in engines which have been in operation and which have such deposits built up in them over a long period of time.

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These deposits have a number of adverse effects upon engine operation, but with available fuels they cannot be avoided and are inherent in present day operation of internal combustion engines. One adverse effect of the deposits is manifested most clearly to the operator of the engine, particularly an automobile engine, by the fact that the presence of the deposits in the engine requires a fuel having a higher octane rating in order not to knock than is required by a new or clean engine. This requirement for a fuel of higher octane number, as the engine becomes progressively dirtier, persists until the deposits reach equilibrium, and is known as octane requirement increase (ORI). Another factor to be considered is the reduction in the volume of the combustion zone equivalent to the volume of the deposits and the consequent increase in compression ratio which aggravates the above manifestation.

Another adverse effect of the deposits is characterized by uncontrolled ignition, either pre-ignition or post-ignition. This is explained by the fact that the deposits, or portions of them become heated to incandescence and ignite the hydrocarbon either before or after the portion in the cycle at which the charge would be ignited by the spark of the spark plug. This manifests itself in various ways characterized as "roughness," "rumble," various forms of knocking, and a general lack of smoothness in engine operation.

Another adverse effect of the deposits is on the spark plug, particularly when the deposits contain lead which results in spark plug fouling with resultant loss in power or reduced spark plug life.

Still another adverse effect of the deposits is the result of their thermal insulating property. They are poorer conductors than the metal parts of the engine and as a result they interfere with proper cooling and temperature maintenance of the engine parts. This is particularly true in the case of the exhaust valves which become overheated and burn or otherwise deteriorate as the result of the deposits. A serious adverse effect of the deposits is the channeling of exhaust valves. This is explained by the fact that the deposits flake off as fast as they are formed once the deposit equilibrium is reached, and the flakes leave through the exhaust valves. The glowing deposits exiting from the muffler have been seen by all who drive at night. As these deposits leave through the exhaust valve they may lodge between the valve and the seat, thereby interfering with the proper closing of the valve. The hot exhaust gases passing between the valve and the seat result in channeling. Failure of the valve to seal the combustion chamber properly results in loss of acceleration, power and mileage. Somewhat analogous results occur in connection with the inlet valves, but because these valves are cooler the character of the deposits is often different, and while not as severe, is nevertheless a problem in engine operation. The action of fuel and the deposits on valve life and condition has been largely overlooked or minimized in evaluating fuels, and since the valve action is vital to proper engine operation, this phase of the matter deserves special attention.

The problems with lubricating oil deposits are quite different from these. With oils we are not concerned with the problems of lead-containing deposits, e.g., ORI, pre-ignition, post-ignition, rumble, roughness, spark plug fouling, exhaust valve deterioration, etc. Instead, we are concerned with stability of the lube oil itself. Summertime operation of passenger cars at sustained high speeds, and operation of commercial vehicles in heavy-duty inter-city hauling result in high crankcase oil temperatures. It is not uncommon to encounter temperatures in the neighborhood of 275° F. Here oil deterioration is mostly the result of oxidation at elevated temperatures rather than

contamination by water and fuel decomposition products. When thoroughly mixed with air, oil tends to oxidize even at moderate temperatures, and this tendency is accelerated with increased temperature. Oxidation tendency is also accelerated by certain metallic contaminants which act as catalysts to further the oxidation reaction. The minute particles of iron, for instance, that are scraped from the cylinder walls by the piston rings seem to hasten oil oxidation at high temperatures.

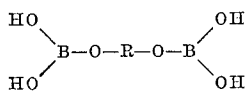
Under high temperature operating conditions, oxidation of the oil causes the formation of many compounds which have not hitherto been mentioned. Such compounds include oil-soluble acids, and asphaltic and varnish-like materials. The resulting products tend to adhere to hot metallic surfaces, producing the coatings frequently seen on piston skirts. Under extreme conditions of temperature these varnish-like materials may completely plug piston ring grooves. Instances have also occurred where piston skirt varnish has been heavy enough to interfere with operation of the engine. Another class of high-temperature operation products are the materials formed when oil strikes metal parts which are hot enough to cause the oil to "crack." These materials do not dissolve in the oil, and tend to form the so-called "coffee ground" type of sludge.

The amount of oil deterioration through oxidation and the formation of undesirable compounds depends on many factors including oil type, operating temperature, engine design, and oil drain interval.

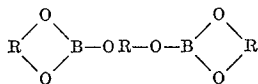
Thus it is clear that the problem of adding boron or other additives to lubricating oil is entirely different from the problem of adding boron or other additives to leaded gasoline. It is the former and not the latter problem with which the present invention is concerned.

It is, therefore, an object of this invention to provide improved hydrocarbon lubricants. Another object is to provide improved hydrocarbon lubricants containing stable esters of boric acid. A further object of this invention is to provide improved hydrocarbon lubricants having a high degree of thermal stability. Another object is to provide an improved crankcase lubricating oil containing alkylene bborate, sometimes known as tri(alkylene)borate. A further object is to provide lube oil containing a liquid boron additive.

The above and other objects of this invention are accomplished by providing a hydrocarbon lubricant containing a stabilizing amount of boron as a liquid alkylene baborate. The resulting lubricant has a greatly enhanced thermal stability. Biboric acids may be represented by the formula



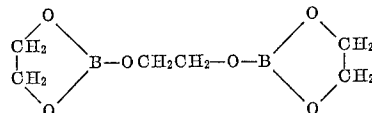
and the corresponding alkylene biborate esters have the formula



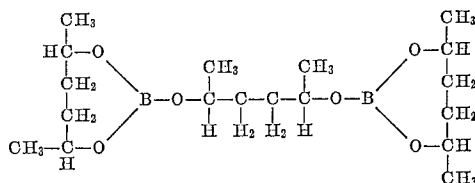
where R in both formulae is an alkylene group of from 2 to 6 carbon atoms in length and which contains from 2 to about 20 carbon atoms. Thus, R can represent a substituted alkylene group of from 2 to 6 carbon atoms in length which contains alkyl, aryl, cycloalkyl, aralkyl, alkaryl, halogen, ketone, carboxyl, or other substituents. These substituents may contain up to 18 carbon atoms when the alkylene group contains two carbon atoms, but substituents having up to about 8 carbon atoms are preferred as they give an ester of lower molecular weight, and thus more boron per mole. Alkyl substituents of from 1 to 6 carbon atoms are particularly preferred because the esters containing these groups are more easily prepared.

The baborates of this invention are clear mobile liquids of moderate viscosity. They are capable of ready blending in a wide variety of petroleum products, including all basic types of lubricating oils. They disperse quickly in such oils to provide lube oil compositions formed. Crystallization or separation do not occur on prolonged exposure to low ambient temperatures.

The nomenclature used in the biborate ester series is to name the glycol or the radical derived from the glycol in parentheses prefixed by the expression "tri" followed by the word "biborate." Thus, for example, the compound having the formula



can be referred to as tri(ethylene glycol)baborate or as tri(1,2-ethylene)baborate. Similarly, the baborate having the following formula



can be referred to as tri(2,5-hexylene glycol)baborate or tri(2,5-hexanediol)baborate or as tri(2,5-hexylene)baborate. The nomenclature of other esters of this invention follows the same pattern. Nomenclature of esters formed from more than one glycol (mixed esters) is similar except that the prefixes "di" and "mono" are used to indicate the number of each alkylene radical present.

When an alkylene biphosphate is compounded with a crankcase lubricating oil, it is desirable to add a small amount, i.e., sufficient liquid alkylene biphosphate to form a composition containing from 0.001 to 1.0 weight percent of boron. However, a preferred embodiment of this invention comprises a crankcase lubricating oil containing from about 0.01 to about 0.15 weight percent boron as a liquid alkylene biphosphate as it has been found that these amounts of boron effectively increase the thermal stability. A particularly preferred embodiment of this invention comprises a liquid hydrocarbon crankcase lubricating oil containing from 0.01 to 0.15 weight percent boron as tri(hexylene glycol) biphosphate.

The additives of this invention can be conveniently prepared by heating boric acid or boric oxide with the appropriate glycol as defined above in the ratio of substantially two moles of boric acid or one mole of boric oxide to three moles of the glycol. The reaction is preferably conducted at temperatures under which the water of esterification is driven off as vapor and not permitted to return to the reaction mixture, thus hastening the reaction to completion. It is convenient to use an azeotropic agent such as an aromatic hydrocarbon (benzene, toluene, etc.) to facilitate water removal. This method, using boric acid, is described in the Journal of the American Chemical Society, volume 67, pages 879-880 (1945).

The ratios of boric acid or oxide to glycol are very important. When the ratio is varied to any substantial degree, different and inferior products are obtained.

The following example illustrates preparation of a typical biborate of this invention starting with boric oxide.

EXAMPLE I

Boric oxide B_2O_3 , 8 parts) and 2-methyl-2,4-pentane-diol (39.5 parts were heated together in toluene medium in a system provided with a reflux condenser to which was attached a water trap. Heating was continued for a period of 30 minutes during which time 5.6 parts of water were taken off in the trap. The residual reaction mixture

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was then freed of toluene by distillation at about 3 millimeters. The tri(2-methyl-2,4-pentanediol)baborate product was recovered as residue from this distillation. Analysis of the material showed a boron content of 5.70 percent (calculated 5.85 percent). The product is a clear mobile colorless liquid boiling at 314–326° C./760 mm. and at 143–149° C./2 mm. It has a refractive index of 1.4381 (25° C.) and a density of 0.982 (21° C.). It is soluble in lube oil and in hydrocarbon solvents.

The other baborate esters of the invention are prepared by the above two methods, varying only the starting materials and the reaction temperature in order to operate preferably at the reflux temperature of the system at the pressure employed.

The lubricants which are beneficially enhanced by the practice of this invention include those fractions or blends of fractions from mineral oils which are used for lubricating and related purposes. Lubricating oil stock is usually considered to include all the distillate obtainable from crude oils after the lower boiling fractions and gas oils have been expelled, as well as some of the residues that are left in the still when non-asphaltic crudes are distilled.

Generally, lubricating oils are made from distilled fractions of a crude, but often these distilled fractions are combined with refined residuum, such as bright stocks, to yield oils having excellent lubricating qualities.

Lubricating oils are made into literally thousands of products which may consist of the pure mineral oil or blends containing one or more other ingredients. Among these products are motor oils, aviation oils, machine oils, transformer oils, cable oils, turbine oils, cutting oils, loom oils, textile oils, etc. Greases are lubricating oils which have been rendered solid or semi-solid by the addition of soaps or similar materials. Typical embodiments of this invention comprising an alkylene baborate and a hydrocarbon lubricant are illustrated by the following examples.

EXAMPLE II

To 500 parts of a commercially available neutral crankcase lubricating oil was added 2.8 parts of liquid tri(2-methyl-2,4-pentanediol)baborate, a quantity sufficient to produce a composition containing about 0.05 weight percent boron. The mixture was agitated until the baborate was completely dispersed in the oil.

EXAMPLE III

To 10,000 parts of a wholly-distilled mixed base, solvent refined lubricating oil having a gravity of 28.9° API, a viscosity grade of SAE 10W–20 and a viscosity index of 135.7 is added 2.75 parts of liquid tri(1,5-hexadecanediol)baborate and the mixture is stirred until the baborate is dissolved in the oil.

EXAMPLE IV

To 1000 parts of a mixed base solvent-refined lubricating oil containing bright stock and which has an SAE viscosity grade of 20, an API gravity of 30.5° and a viscosity index of 107.4, is added 16.75 parts of liquid tri(1,5-pentanediol)baborate.

EXAMPLE V

To 2162 parts of a wholly-distilled lubricating oil having an API gravity of 30.3°, a viscosity index of 154.2 and an SAE number of 5W–20, is added 1.6 parts of liquid tri(ethylene glycol)baborate and the mixture is stirred until the ester is dissolved.

EXAMPLE VI

To 216 parts of a wholly-distilled lubricating oil having an API gravity of 29.1, an SAE number of 10W–30 and a viscosity index of 138.9 is added 21.4 parts of liquid tri(3-methyl-1,3-butanediol)baborate. The mixture is agitated until the ester has dissolved.

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EXAMPLE VII

To 1000 parts of the oil described in Example II is added 15 parts of liquid tri(1,2-eicosanediol)baborate and the mixture is agitated until the ester is dissolved.

EXAMPLE VIII

To 1000 parts of the oil described in Example III is added 10 parts of liquid tri(1,6-hexylene glycol)baborate.

EXAMPLE IX

To a lubricating grease consisting of 11 parts of aluminum stearate, 1 part of lithium stearate and 88 parts of an oil having a viscosity of 100 seconds Saybolt Universal at 100° F. is added 2 parts of liquid tri(2-methyl-2,4-pentanediol)baborate and the mixture is blended until the ester is completely dispersed through the grease.

To demonstrate the superiority of a crankcase lubricating oil of this invention containing a liquid baborate of this invention, comparative tests were run on the oil prepared according to Example II and the identical oil which did not contain any baborate. These oils were compared by the panel coker test which measures the oxidative stability of a lubricating oil at a hot metal surface. This test is described in the Aeronautical Standards group of the departments of Navy and Air Force specification MIL–L–7808c, dated November 2, 1955. In this instance, the tests were run at 550° F. The results of such tests show (Table I) that a lubricating oil containing a small amount of a liquid alkylene baborate has a reduced coking tendency at elevated temperature when compared to an identical oil containing none of the baborate esters. Thus, the oil containing a liquid baborate ester has a greatly enhanced thermal stability and a superior resistance to oxidative deterioration.

Table I

PANEL COKER TEST

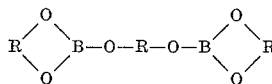
Additive:	Milligrams of deposit
None	468
0.05 percent boron as tri(hexylene glycol)baborate	300

In addition to the liquid baborates, the hydrocarbon lubricants of this invention may contain other additives. These other additives may include, for example, viscosity index improvers, detergents, corrosion inhibitors, metal deactivators, rust inhibitors, color stabilizers, pour depressants, emulsifiers, dyes, etc., and in the case of greases, metallic soaps, fillers, etc.

The diols suitable for use in preparing the liquid baborate esters of this invention include those wherein the hydroxyl groups are separated by from 2 to 6 carbon atoms. Further examples of the baborate esters which are prepared from these diols include: tri(ethylene glycol)baborate, tri(1,2-propylene glycol)baborate, tri(1,3-propyleneglycol)baborate, tri(1,2-butylene glycol)baborate, tri(1,3-butylene glycol)baborate, tri(1,4-butylene glycol)baborate, tri(1,6-hexylene glycol)baborate, tri(2,4-dimethyl-2,4-pentanediol)baborate, tri(2,3-dibutyltetramethylene glycol)baborate, tri(2,3-diphenyl tetramethylene glycol)baborate, and the like.

I claim:

1. Liquid hydrocarbon crankcase lubricating oil normally subject to oxidative deterioration to which has been added from about 0.001 to about 1.0 weight percent of boron as a liquid tri(alkylene)baborate having the formula



wherein R is an alkylene group of from 2 to 6 carbon atoms in length and contains from 2 to about 20 carbon atoms.

2. The composition of claim 1 wherein each alkylene group of said baborate is hexylene.
3. The composition of claim 1 wherein each alkylene group of said baborate is ethylene.
4. The composition of claim 1 wherein each alkylene group of said baborate is propylene.
5. The composition of claim 1 wherein each alkylene group of said baborate is butylene.
6. The composition of claim 1 wherein each alkylene group of said baborate is pentylene.

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