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3,076,013

PROCESS FOR PREPARING A COMPLEX MIXTURE OF ALIPHATIC GLYCOL BORATES

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9 Claims. (Cl. 260—462)

This invention relates to a novel process for preparing boron compositions which will remain stable against hydrolysis in gasoline, comprising the reaction product obtained by the oxidation of certain refinery olefins in the presence of boric acid.

One of the most serious problems encountered in the operation of internal combustion engines is the deposits which form progressively and accumulate on the surfaces within the combustion zone, on the cylinder head, piston top, sparkplugs and the intake and exhaust valves. These deposits are made more stubborn by the tetraethyl lead present in most gasoline fuels, because this not only contributes to the deposit but it also converts it from an essentially carbonaceous deposit to one comprising appreciable quantities of lead and lead compounds mixed therewith, such as lead sulfate, and lead oxide. The carbonaceous deposits act as a cementing agent for the lead deposits, and the lead deposits are more difficult to remove than the carbon deposits. Thus, a deposit of this sort is more tenacious and troublesome than a purely carbonaceous deposit.

The nature of the lead-carbonaceous deposits is such that they are quite difficult to remove, once they have been built up. They are not attacked by the scavenging agents which are included in the fuel with the tetraethyl lead. Despite the fact that the amount of the deposits eventually levels off, after which there is no appreciable further increase, the presence of the built-up deposits interferes considerably with the operation of the engine, and it would be desirable both to prevent formation of deposits and to remove them after they have been formed. The disadvantageous effects of these deposits are well discussed in U.S. Patent No. 2,741,548 to Samuel M. Darling, Philip S. Fay and Lorraine M. Szabo.

It has been proposed to attack such deposits by incorporating in the liquid leaded motor fuel an organic boron compound which is soluble in the fuel. The boron compound is thought to modify the action of the fuel in the engine, and to react with the deposits so that the adverse effects due to the deposits are eliminated or markedly reduced.

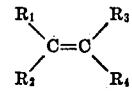
In application Serial No. 705,481 filed December 27, 1957, now abandoned, by one of us and owned by our assignee, there is described and claimed a two-step process of first converting refinery olefins to α-alkylene glycols and then reacting the glycols with boric acid.

This invention relates to a process of forming moisture-stable high boiling boron-containing reaction products by the simultaneous oxidation and boration of refinery olefins. These products are useful in gasoline and lubricating oils as a source of boron. The refinery olefins are oxidized primarily to α-alkylene glycols in the presence of the boric acid, and the boron additives of the invention are formed simultaneously by the reaction of the boric acid with the α-alkylene glycols. This process has the advantage of combining all of the reactions in a single step.

The borated reaction products of the invention are gasoline-soluble, oil-soluble, moisture-stable, and have low volatility. Engines operated with gasolines and with lubricating oils containing such boron compounds have improved performance. The E.P. (Extreme Pressure) and

wear properties of lubricating oils containing these additives also are improved. No adverse effects for either gasolines or oils containing these additives have been observed.

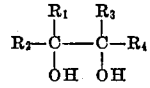
The term "refinery olefin" as used in the specification and claims refers to the complex mixtures obtained by the polymerization and copolymerization of propylene and/or butylenes. These refinery olefins are generally quite highly branched and have a high proportion, preferably at least 80%, of nonterminal double bonds, i.e., olefinic bonds which have three or four alkyl radicals around the double bond. These olefins have from seven to thirteen carbon atoms. They can be defined by the following general structure:



I

where R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen and alkyl radicals having a total of five to eleven carbon atoms. No more than 20% of the olefins in the mixture have terminal double bonds, i.e., R_1 and R_2, or R_3 and R_4 are each hydrogen in no more than 20% of the olefins. At least 50% have three or four alkyl radicals. The alkyl radicals preferably are themselves highly branched. Exemplary alkyl radicals are methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-amyl, isoamyl, tert-amyl, neopentyl, hexyl, isohexyl, 2-ethyl hexyl, tert-hexyl, 1,2-dimethyl butyl, 1, methyl-2-propyl pentyl, n-heptyl, isoheptyl, n-octyl, isooctyl, tert-octyl, and 1,2,3-trimethyl pentyl. Typical examples of available refinery olefins as defined above are tetrapropylene, tripropylene, tri-isobutylene, di-isobutylenes, motor polymer and fractions thereof.

When these refinery olefins are oxidized by conventional procedures, α-alkylene glycols are obtained having the following general formula:



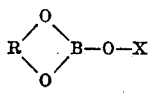
II

where R_1, R_2, R_3 and R_4 are the same as before. These are α-alkylene glyco's, inasmuch as the hydroxyl groups are on adjacent carbon atoms. These glycols can be regarded as ethylene glycol derivatives to which the remaining five to eleven carbon atoms consisting of R_1, R_2, R_3 and R_4 are attached as straight or branched alkyl radicals.

Four species of glycol borates can be formed by the reaction of boric acid with such α-alkylene glycols depending upon the relative proportions of the reactants. These species are designated as follows:

	Reaction products of α-alkylene glycol with boric acid in the proportion of
(*a*) Monoglycol borates	1:1
(*b*) Diglycol diborates	1:1
(*c*) Diglycol borate	2:1
(*d*) Triglycol diborate	1½:1

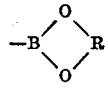
The above glycol borate compounds can be represented by the formula:



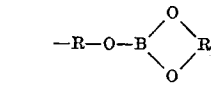
III

where X is selected from the group consisting of

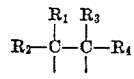
(*a*) Hydrogen Monoglycol borate 1:1

(*b*)  Diglycol diborate 1:1

(c) —R—OH Diglycol borate 2:1

(d)  Triglycol diborate 3:2

R in each case has the formula:



where R_1, R_2, R_3 and R_4 are as hereinbefore defined.

However, since the glycol formation, in accordance with the invention, is carried out in the presence of excess boric acid, it is unlikely that (*c*) diglycol borates or (*d*) triglycol diborates are formed. The product will consist almost entirely of (*a*) monoglycol borates and (*b*) diglycol diborates.

It is apparent that when a mixture of two or more diols is used there is a possibility of two or more species. Very complex mixtures can be obtained from mixtures of three or more diols. Inasmuch as the refinery olefins utilized as starting materials for the α-alkylene glycols are complex mixtures, it will be understood that the actual compositions having the general formulae above are complex mixtures of the various possible species.

The glycol borate compounds of the invention are solids or liquids which are stable to moisture. The liquids and the solutions of the compounds in oil remain homogeneous and clear when stored in a moisture-saturated chamber for forty-eight hours at room temperature (25° C.). They are quite soluble in gasoline and in petroleum lubricating oils, and were tested in oil in a concentration of 0.1% boron.

The glycol borate compounds of the invention are prepared in one stage in which there occurs simultaneously the hydroxylation of the olefin and the reaction with the borating reagent. This procedure permits the preparation of relatively complex glycol borate mixtures, composed principally of the glycol borate compounds, with other oxidized olefin derivatives which are obtained in the course of the oxidation, such as aldehydes, acids and ketones, which are also borated to the extent that they react with the borating reagent.

The reaction can be carried out at super-atmospheric or at atmospheric pressure.

The oxidation under super-atmospheric pressure with air or oxygen is carried out by heating the olefin and a stoichiometric excess of a source of boron such as boric acid or boric oxide, with a small amount of an oxidation catalyst, if desired, at a temperature within the range of about 100° to about 200° C. The excess of boric acid is not harmful. The reaction can be carried out at any air pressure above atmospheric, but preferably between the range of from 50 to 500 p.s.i.g. The desirable rate of flow of air or oxygen during the reaction mixture will depend upon the reaction temperature and the concentration of reactants. Usually an amount of oxygen within the range from about 1 to about 100 liters per hour per liter of reaction mixture will be adequate. When air is used, the rate should be increased proportionately. The reaction is carried out with stirring under reflux.

The reaction at atmospheric pressure is carried out under much the same conditions, using a lower reaction temperature, within the range of about 80 to 150° C., and a somewhat lower flow rate of oxygen within the range from about 0.5 to about 75 liters per hour per liter of reaction mixture, proportionately increased when air is used. The reaction time may vary from 1 to 50 hours. A preferred reaction time, using air as the oxidant, is about 5 to 30 hours at air flow rates of 35 to 45 liters per hour. A catalyst is not necessary, but can be employed if desired. The amount of the source of boron present will be stoichiometrically in excess of that required to form the desired product, and the source of boron can

be either boric acid or boric oxide. An excess of the boric acid is not harmful.

The catalyst is not critical and any one can be used that is conventional in the oxidation of hydrocarbons such as cobalt naphthenate or cumene hydroperoxide, as well as naphthenates or carboxylates of lead, copper, chromium, rare earth metals, iron and vanadium. The catalyst has little effect on the yield. The amount of the catalyst is 0.01% to 1.0% by weight based on the refinery olefin in the charge.

In either the atmosphere or super-atmospheric process a solvent for the borated compound may be present such as ethyl alcohol, acetone, methyl ethyl ketone, isopropanol, tridecanol, benzene, toluene, etc. The presence of the solvent shortens the reaction time.

The low boiling unreacted material and by-products can be removed by distillation, if desired, and the reaction mixture can be filtered and dried.

The experimental conditions used in carrying out these procedures are illustrated in the following examples, which, in the opinion of the inventors, represent the best embodiment of their invention.

Examples 1 to 3

A group of the representative refinery olefins listed below were oxidized and borated according to the following procedure: 300 g. of the olefin and 37.2 g. of boric acid were placed in a reactor. To this was added 0.6 ml. of Harshaw's Cobalt Uversol (cobalt naphthenate catalyst, containing 6 weight percent cobalt) in a hydrocarbon diluent. Oxygen gas was conducted through the mixture at a rate of 2 liters per hour at atmospheric pressure. The reaction temperature was held in the range of from 85 to 95° C. and the reaction time in each case was forty-six hours. The product was cooled, filtered and dried with a dehydrating agent, sodium sulfate. The reaction mixture is analyzed for boron.

0.02% solutions (based on the boron added) of the glycol borate compound in gasoline were prepared, and the hydrolytic stabilities of the glycol borates in these solutions determined. Samples were stored in moisture-saturated atmospheres at room temperature for 48 hours. Filtered exposed samples, as well as control (unexposed) samples then were analyzed for boron content. Stabilities were expressed as follows:

$$\text{Percent hydrolytic stability} = 100 \times \frac{\text{Percent B in solution after exposure}}{\text{Percent B in solution before exposure}}$$

The data on the boron content and stability are given in Table I.

TABLE I

Example No.	1	2	3
	Motor polymer cuts, B.P.		Tripropylene
	>110° C.	>135° C.	
B, Percent	0.8	0.7	0.9
Stability, Percent	>95	>98	100

Examples 4 to 6

Following the same procedure as Examples 1 to 3 but employing air instead of oxygen and utilizing the refinery olefins, the temperature, the reaction time and the flow rate indicated in Table II, products were obtained and the boron content together with their stabilities are also listed in Table II.

TABLE II

Ex. No.	Motor polymer cut, B.P. °/C.	Reaction temperature, °C.	Reaction time, hrs.	Air flow rate, l./hr.	Boron, percent	Stability, percent
4	>110	90–95	28	40	1.2	71
5	>135	90–95	22	40	0.8	60
6	>110	105	8	60	0.5	68

It will be noticed that the use of air gives products which do not have as high stability but this is counterbalanced by the much greater economy of the process in utilizing air instead of the relatively large amounts of oxygen acquired in Examples 1, 2 and 3.

Examples 7 to 13

In a further effort to utilize air instead of oxygen for the purpose of rendering the process more economical, a number of reactions were carried out utilizing air as the oxygen-supplying material. The reaction was carried out in a pressure reactor equipped with a stirrer. Heating and cooling means in the reactor provided temperature control which was measured by the thermocouple. The catalyst was mixed with the olefin and the boric acid slurried therein and introduced into the reactor, which was sealed and the reaction then conducted in the usual manner.

The olefin employed and the relative amount thereof in relation to the boric acid and the catalyst is indicated in Table III. The amount of air, the reaction time, the reaction pressure and the reaction temperature are also indicated in Table III. The products obtained were borated mixtures and the amount of boron and the stability are also indicated in Table III.

The gasoline of the invention also contains tetra-ethyl lead in amounts up to 6 cc., but usually from ½ cc. to 3 cc. per gallon, and a scavenging agent. The latter may be 1 theory of ethylene dichloride and ½ theory of ethylene dibromide (the so-called "motor mix" or MM) or 1 theory of ethylene dibromide, the so-called "aviation mix" or AM. Reference to MM and AM refered to a gasoline containing the scavenging agent in amount above recited. By "theory" is meant the stoichiometric amount of the ethylene dihalide for combination with all of the lead as lead halide. The AM is preferred since in combination with the boron compound there results a better overall effect in engine performance. The gasoline may contain any of the usual adjuncts such as antioxidants, dyes, solvent oils, alcohols, etc.

The amount of the boron compound added to the fuel may vary and the amount is preferably expressed in terms of boron. Generally an amount of the compound to provide 0.002% by weight of boron (based on the total fuel) is the smallest amount that will gve any significant effect. An amount of 0.004% is preferred. Use of amounts in excess of 0.1% usually do not give sufficiently superior results to justify the use of the larger amount.

The borate compounds of the invention can be used with any petroleum hydrocarbon oil of lubricating viscosity. The SAE viscosities for lubricating oils range from No. 10 to No. 70. Oils having SAE Nos. 10 to 40 have a viscosity within the range from 90 to 255 SSU at 130° F., and those oils having SAE Nos. 40 to 70 have a viscosity within the range from 80 to 150 SSU at 210° F. The acid-treated and solvent-extracted oils are equally useful in the compositions of the invention. The oils may be blended from suitable bright stocks and finished neutral oils of light and heavy viscosities. It is impossible here to give a complete description of the various methods used in the preparation of lubricating oils, but reference is made to the text by Georgi entitled Motor Oils and Engine Lubrication, published by Reinhold Publishing Corporation, New York (1950), chapter V, wherein the various types of lubricating oils are discussed fully. Any of the oils mentioned therein can be employed in the compositions of the invention.

TABLE III

Ex. No.	Olefin	Grams of olefin	H_3BO_3, grams	Catalyst	Grams of catalyst	Air, l./hr.	Time, hrs.	Temp., ° C.	Press., p.s.i.g.	Percent B	Stability percent
7	Tetrapropylene	654	37.1	Co naphthenate [1]	2	200	3	130–140	300	0.54	87
8	do	654	55.6	Pb naphthenate [2]	1.8	200	3	70–80	200	0.53	85
							2	135–145			
9	do	654	55.6	Cumene-hydroperoxide	5	200	8	95–105	200	0.60	48
10	Tripropylene	625	74.3	Co naphthenate [1]	2.2	200	2	60–82	200	1.08	91
							1	106–132			
							2	161–165			
11	Tetrapropylene [a]	654	74.3	do [1]	2.5	200	2	130–140	200	0.56	94
12	do	654	55.6	Fe naphthenate [3]	2.0	200	3	70–80	200	0.45	84
							2	135–145			
13	Tripropylene	654	74.6	Co naphthenate [1]	2.5	200	2	60–82	200	0.69	91
							1	106–132			
							2	161–165			

[1] Contains 6% Co. [2] Contains 24% Pb. [3] Contains 6% Fe.
[a] 10 g. methanol plus 10 g. tridecanol used as solubilizers and boration carriers.

In view of the above results it is possible to obtain products having good hydrolytic stability in a relatively short time as compared with an operation under atmospheric pressure using air.

In connection with all of the above data, it is to be noted that the poly-olefins which are derived or derivable from motor polymer are very inexpensive raw materials since their alternative use is in gasoline. While yields of the borate compounds are not as large as would be the case if a pure glycol were used as a starting material, nevertheless, the cost of the olefin is so small that the process is economically attractive, notwithstanding the lower yields. Furthermore, if the borated products are to be used as additives for oil and gasoline, which are the products of a petroleum refinery, the invention makes it possible to produce these additives from starting materials which are also available in a petroleum refinery. Thus, the refinery is not dependent on outside raw materials except the boric acid.

The gasoline base stocks to which the boron compounds are added may be any of those conventionally used in making motor gasoline (gasoline for use in an automobile internal combustion engine).

Very small amounts of the organic borate compounds of the invention will give a marked improvement in the engine performance of the lubricating oil. All proportions of the compounds are based on the amount of boron in the compound as a percent of the total oil composition, since it is the boron that is the active component in removing the deposit. As little as 0.05% is effective, and amounts between 0.125% and 0.25% are preferred. Use of amounts in excess of 0.5% usually cannot be justified economically.

The gasoline and oil compositions of the invention are prepared simply by mixing the boron compound with the gasoline or oil at room temperature. The boron compound is soluble and dissolves therein either instantaneously or after a short time. No solvents are required.

The following examples are illustrative of lubricating oil and gasoline compositions containing the glycol borate compounds of the invention.

Four lubricating oil compositions were prepared using a lubricating oil blend of 67% solvent-extracted neutral oil, 300 SSU at 100° F., and 33% of a solvent-extracted bright stock, 78 SSU at 210° F. To the oil was added 2% of the glycol borate compounds of the previous examples.

The compositions were subjected to the Falex E.P. test, run by the standard procedure, where the load on the bearing was increased automatically and the pressure reported was that registered at failure. The wear tests were run on the same equipment using a constant pressure on the bearing. The data show that the oils of the invention containing the boron compound tolerated higher pressure and produced less wear than the corresponding blend without boron or the base oil alone.

The procedure employed determining gum solvency consisted of accumulating gum by the use of the ASTM D525 air jet evaporation procedure. The beakers containing the gum were rinsed with pentane before adding the test oil. Thirty grams of test oil were placed in the beakers and these were stored at room temperature for fourteen hours. The oil was decanted and the beakers were rinsed with pentane and weighed. Loss of weight of the gum was expressed in terms of percent of the gum dissolved. At room temperature there was in indication of higher gum solvency at the 2% concentration of the boron compound than for the corresponding 4% concentration or the base oil alone.

To determine the effect of the boron on the ignition temperature of the carbon deposit, several synthetic carbon deposits and actual engine deposits were tested. The reactor consisted of glass tubing cemented into a glass tube 1¾" in diameter wrapped with Nichrome wire. The sample in the form of a pellet was placed on a porcelain insulator bead which was mounted on the end of a glass rod that entered the bottom of the tube. Loosely packed samples of the deposit in a porcelain crucible were used and were placed in position. An iron constantan thermocouple was inserted at the top of the reactor and was placed very close to the surface of the sample but not in contact with it. Synthetic carbon deposits were prepared by carbonizing about 200 g. of oil in a platinum crucible. Samples were made containing 6.4% by weight of lead bromide in order to study the effect of boron on the ignition temperature of carbon in the presence of lead.

In determining the ignition temperature of the deposit the apparatus was preheated to about 300° F. The sample was placed in the tube and oxygen flowed through it at the rate of 630 cc. per minute. A rate of temperature increase of about 30° per minute was employed in the ignition point range when testing the natural deposits. When testing the synthetic deposits, a heating rate of 11° per minute was used. Temperature rise was recorded and a short break in the curve indicated the ignition temperature. Since the apparatus was built to measure ignition temperatures in the 500 to 800° F. range, the test run was discontinued when ignition did not occur at 900° F. The carbonaceous deposits alone did not ignite below 850° F. Thus, the only comparison for synthetic deposits were those that were mixed with lead bromide. The ignition temperature of the deposit containing boron average almost 100° F. higher than those without boron.

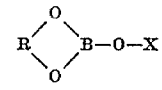
When the above-described oils are used to lubricate an internal combustion engine operating from 72 hours on non boron fuel and the engine is dismantled, it is found that the deposit contains boron which is derived from the lubricating oil finding its way into the combustion chamber with the resultant advantage of the boron in the deposits.

Gasoline fuels were prepared containing the glycol borate compounds of the previous examples. The base stock was the same in each, a mixture of straight run naphtha and catalytic distillate in the ratio of 1:3 with 3 cc. of tetraethyl lead per gallon to give an Octane No. of 94. The gasolines contained the so-called "aviation mix" scavenging agent which is 1 theory of ethylene dibromide. By "theory" is meant the stoichiometric amount of the ethylene dihalide for combination with all the lead as lead halide. This effect of boron is described in Industrial and Engineering Chemistry, 43 2841-4 (December 1951), and in U.S. Patent No. 2,741,548. The boron-containing gasoline gave the advantages there described.

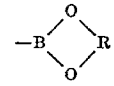
All parts and percentages in the specification and claims are by weight.

We claim:

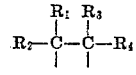
1. A process for preparing a complex mixture of organic glycol borate compounds having the formula



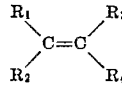
where X is selected from the group consisting of hydrogen, and



and R is



which compounds are soluble in gasoline and lubricating oil and stable against hydrolysis in the presence of moisture, which process comprises reacting a refinery olefin having from seven to thirteen carbon atoms of the formula



where R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen and alkyl radicals and no more than 20% have terminal double bonds, and at least 50% have at least three alkyl radicals, simultaneously with molecular oxygen and boric acid to form the above-mentioned glycol borates, said reaction taking place in the presence of an oxidation catalyst selected from the group consisting of naphthenates of cobalt, lead, copper, chromium, iron, vanadium, rare earth metals; carboxylates of lead, copper, chromium, iron, vanadium, rare earth metals; and cumene hydroperoxide.

2. A process for preparing a complex mixture of organic glycol borate compounds in accordance with claim 1, in which the refinery olefin is motor polymer.

3. A process for preparing a complex mixture of organic glycol borate compounds in accordance with claim 1, in which the refinery olefin is tetrapropylene.

4. A process for preparing a complex mixture of organic glycol borate compounds in accordance with claim 1, in which the refinery olefin is tripropylene.

5. The process of claim 1 in which the reaction is carried out at atmospheric pressure.

6. The process of claim 1 in which the reaction is carried out at a super-atmospheric pressure.

7. The process of claim 6 in which the molecular oxygen is obtained from air.

8. The process of claim 1 in which the simultaneous oxidation and boration is carried out in the presence of a solvent for the glycol borate.

9. The process of claim 8 in which the solvent is an alcohol.

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