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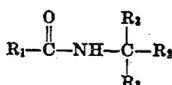
## LIQUID HYDROCARBONS CONTAINING A BORON ADDITIVE

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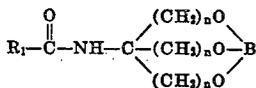
This invention relates to novel boron compounds and to liquid hydrocarbons containing the same. More particularly, this invention relates to a class of boron compounds which may find use as additives for motor fuel, fuel oil, and lubricating oil compositions.

The boron compounds of this invention are prepared by reacting boric acid or boric oxide with a N-acylated amino hydroxy compound having the following general formula:

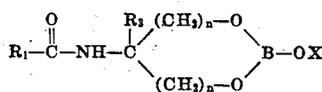


wherein R<sub>1</sub> represents a radical selected from a group consisting of an alkyl, alkenyl, or arylalkyl radical containing 7 to 21 carbon atoms, R<sub>2</sub> represents the radical  $-(\text{CH}_2)_n\text{OH}$  where  $n$  is a small whole number such as 1 to 3, and R<sub>3</sub> represents a radical selected from the group consisting of R<sub>2</sub> or an alkyl radical containing 1 to 8 carbon atoms where R<sub>3</sub> may be the same or different for the two positions of R<sub>3</sub> on the molecule.

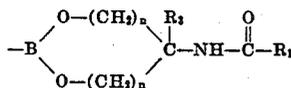
When both positions of R<sub>3</sub> are the same as R<sub>2</sub>, the boron compounds will have the general structure:



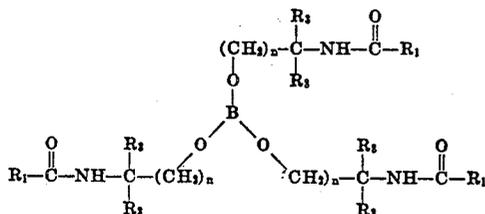
When one position for R<sub>3</sub> is the same as R<sub>2</sub> and the other position for R<sub>3</sub> is an alkyl radical, the boron compounds will have the general structure:



where X is hydrogen or



When both positions for R<sub>3</sub> are alkyl radicals, the boron compounds will have the general structure:



The above-mentioned class of boron compounds have been found to be excellent multi-functional additives for motor fuel when one or more of the same are incorporated therein in only small amounts. In common with other boron-containing compounds, these materials are highly effective in controlling troublesome conditions caused by deposit buildup in the combustion chamber of an internal combustion engine.

It is well known that the continued operation of the internal combustion engine results in the formation of combustion chamber deposits. This deposit problem is

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particularly aggravated when tetraethyl lead is contained in the fuel for the purpose of increasing the octane number of the fuel to a desired level for modern high-compression engines. The use of leaded fuels leaves combustion chamber deposits which are no longer essentially carbonaceous in chemical nature, but comprise appreciable quantities of lead compounds generally mixed in the carbonaceous material. The fact that such deposits are partially metallic in character is believed to give it a catalytic activity which modifies the action of the deposit in affecting engine operation. Despite the fact that one or more volatile organic halides such as ethylene dichloride and/or ethylene dibromide are included in the fuel as scavenging agents, not all the lead is removed.

Combustion chamber deposits, and particularly deposits resulting from the burning of leaded fuels, produce a number of adverse effects in engine operation, notable among which is a tendency for these deposits to become heated to incandescence, developing one or more hot spots in the combustion chamber. These spots ignite the fuel either before or after the position in the cycle at which fuel would normally be ignited by the spark of the spark-plug. This condition, referred to commonly as surface ignition, manifests itself in various ways characterized as different forms of knocking or engine roughness, and usually resulting in appreciable power loss.

Organo boron compounds have been previously proposed for use in gasoline to overcome at least in part the adverse effects of combustion chamber deposits and to thereby provide smoother engine operation and greater engine efficiency. The presence of boron in the fuel is believed to eliminate the amount of deposits and/or in some manner beneficially modify the chemical nature of these deposits. However, although boron compounds are well known to offer such advantages, many of the boron compounds proposed for use in gasoline are not satisfactory for use in large scale marketing due to their characteristic instability toward hydrolysis while in gasoline. Contact with small amounts of water and moist atmospheric conditions during prolonged storage causes many of these compounds to hydrolyze to solid insoluble products which precipitate out of the gasoline phase so that the boron content never reaches the engine where it might be effective. In contradistinction to this failing, the boron compounds of the present invention are surprisingly stable toward hydrolysis, both in their pure form and in solution in gasoline, and hence these compounds are very acceptable for use in gasoline for large scale marketing operations.

Gasolines containing one or more of the boron compounds of this invention are also highly effective in preventing carburetor deposits. Such deposits are believed to accumulate from contaminated intake air which the carburetor must breathe in tremendous volume and are responsible for rough idling of the engine and in many cases the occurrence of frequent stalling. This condition is commonly experienced in the operation of most cars, particularly those vehicles operated in urban areas where the air is heavily contaminated with combustion products exhausted from the large population of other cars operating in the same immediate area. The condition is, of course, aggravated by any blowby fumes from the operation of the car's own engine, in addition to any industrial fumes present in the air which the carburetor breathes. These sources of contamination are additive in nature and may cause the rapid buildup of deposits on the carburetor of the engine.

Gasolines containing one or more of the boron compounds of this invention are further characterized as to their improved anti-rust protection, thereby eliminating the requirement of a special additive to provide this important property to the fuel. The motor fuel re-

ferred to hereinabove consists essentially of one or more hydrocarbon base stocks which may be any of those conventionally used in preparing a motor gasoline for a spark-ignited internal combustion engine, such as catalytic distillate, motor polymer, alkylate, catalytic reformat, isomerate, naphthas, etc. The motor fuel may also contain tetraethyl lead in amounts up to 6 ml., generally up to 3 ml., but at least ½ ml. per gallon and a scavenging agent. This definition permits the inclusion, in addition to the lead anti-detonant and scavenging agent, of other common additives such as anti-oxidants, stabilizers, solvent oils, dyes, phosphorus compounds, and the like.

The amount of boron compound or compounds to be used in motor fuel may vary. Generally the smallest amount that will give significant results will be in the order of 0.001% by weight. Amounts greater than approximately 1% by weight usually cannot be justified economically.

Due to the excellent anti-rust characteristics which the boron compounds of this invention impart and since the same are readily soluble and compatible in most liquid hydrocarbons, these compounds may find broad utility as an anti-rust agent in various hydrocarbon products, such as fuel oils and motor fuels other than gasoline, i.e., diesel fuels and jet engine fuels. The boron compound may be added directly to the hydrocarbon product or, if desired, the boron compound may be dissolved in a solvent or a combination of solvents such as toluene, catalytic reformat, neutral oil, xylene, benzene, etc. to produce a liquid concentrate and then the concentrate may be blended into the desired liquid hydrocarbon product to offer the desired concentration of boron compound. For anti-rust protection, the concentration of the boron compound in the liquid hydrocarbon should be at least 0.001% by weight. The upper limit to be used will be dictated largely by economics.

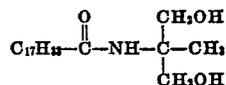
The boron compounds of the present invention have also been found to be excellent additives for lubricating oils. Only small concentrations of one or more of these compounds is required to significantly improve the dispersancy power of the oil stock. The lubricating oil comprises a base stock of a mineral oil or a synthetic oil, or mixtures thereof, and may contain any other known oil additives, such as detergents, anti-oxidants, and anti-wear agents. The mineral oil may be any petroleum hydrocarbon oil of lubricating viscosity. The S.A.E. viscosities for lubricating oil range from No. 10 to No. 70. Oils having S.A.E. Nos. 10 to 40 have a viscosity within the range from 90 to 225 SSU at 130° F., and those oils having S.A.E. Nos. 40 to 70 have a viscosity within the range from 80 to 150 SSU at 210° F. Acid-treated or solvent-extracted oils are equally useful in the compositions of the invention. No attempt will be made 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 various types of lubricating oils are discussed fully. Any of the oils mentioned therein can be employed with the boron compounds of the invention. The synthetic oils may be the polyalkylene oxide liquid oils; the dicarboxylic acid esters, examples of which are dihexyl azelate, di-2-ethyl hexyl azelate, di-dodecyl sebacate; the liquid esters of acids of phosphorus; or the silicone-type lube oils.

The amount of boron compound to be added to the lubricating composition may vary. Best results are obtained when amounts of at least 1% by weight are used. Amounts greater than 10% will usually not be justified economically.

The N-acylated amino hydroxy compounds used in preparing the boron compounds of this invention may

be prepared from amino hydroxy compounds containing a primary or secondary amine functional group by the N-acylation of the amine group of the compound with a long-chain acid or acid-chloride containing from 8 to 22 carbon atoms, and such materials are well known in the trade and are commercially available.

Any of the compounds having the general formula offered hereinbefore are suitable for the invention. The preferred compounds, however, are the N-acylation products of amino dihydroxy compounds so that one position for R<sub>2</sub> is the same as R<sub>1</sub> and the other position for R<sub>2</sub> is an alkyl radical, and where R<sub>1</sub> as defined heretofore contains from 11 to 17 carbon atoms for maximum solubility in the liquid hydrocarbon. The amino dihydroxy compounds are preferred since they are more readily soluble in hydrocarbons than are the amino trihydroxy compounds where R<sub>2</sub> for both positions on the molecule are the same as R<sub>1</sub> and because the amino dihydroxy compounds such as of the type derived from 2-amino-2-alkylpropanediol-1,3 form a six-membered ring upon boration with boric acid or boric oxide which is believed to offer optimum stability toward hydrolysis. Mixtures of the amino hydroxy compounds may be used. Mixtures of radicals may also be used for R<sub>1</sub>, and this frequently will be the case since the R<sub>1</sub> radicals are preferably derived from fatty acids found in naturally occurring fats and oils, and hence R<sub>1</sub> will correspond to the fatty acid radicals derived from fats and oils such as tallow, cottonseed oil, soybean oil, tall oil, etc. The nature of R<sub>1</sub> does not affect the results appreciably, it has been found, and therefore its selection will be dictated largely by economics. The commercial grade of the compounds, including small amounts of impurities or by-products, are suitable. A particularly desirable starting compound for purposes of the invention is the N-oleoylamide of 2-amino-2-methylpropanediol-1,3:

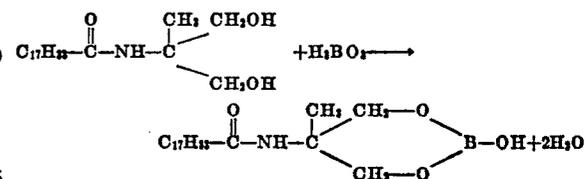


These N-acylated amino hydroxy compounds readily undergo reaction with boric acid under conditions in which the water of reaction may be removed from the reaction mixture as it is formed. This removal of water may be accomplished by simple boiling, but it is preferable to remove the water by means of azeotropic fractional distillation using, preferably, benzene or toluene as the solvent. Boric oxide may be used in place of boric acid as the boron source in these reactions with only the requirement for making the appropriate weight adjustment in order to maintain the molar relationship with the N-acylated amino hydroxy compounds.

The preparation of these compounds will be better understood in connection with the following examples.

#### Example 1

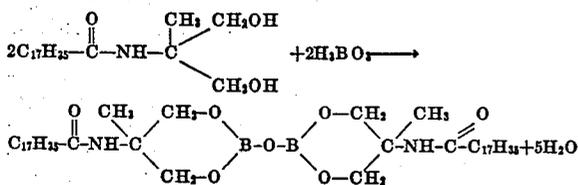
74.4 grams of N-oleoylamide of 2-amino-2-methylpropanediol-1,3 was placed in a flask with 12.4 grams boric acid (a 1:1 molar ratio) and 120 milliliters (ml.) of benzene. The mixture was stirred and refluxed together until 7.3 ml. of water was azeotropically distilled off overhead. The reaction mixture was then filtered and the filtrate evaporated down to produce a transparent plastic material which was readily soluble in gasoline. The reaction proceeds in accordance with the following equation:



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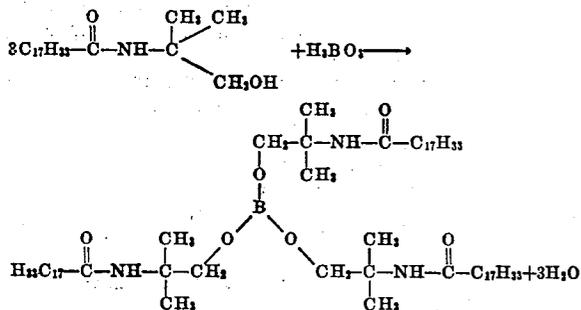
## Example 2

To 74.2 grams of N-stearoylamide of 2-amino-2-methylpropanediol-1,3 contained in a flask was added 300 grams of benzene and 12.4 grams of boric acid (a 2:2 molar ratio). The mixture was refluxed together for several hours until 8.0 ml. of water was azeotropically distilled off overhead. The remainder of the benzene was then distilled off, leaving a plastic solid which was readily soluble in gasoline. The reaction may be represented by the following equation:



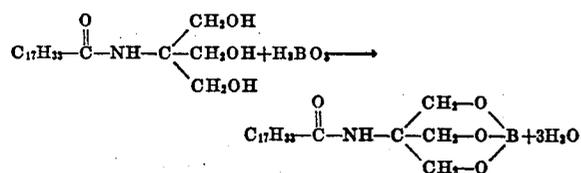
## Example 3

105.9 grams of the N-oleoylamide of 2-amino-2,2-dimethyl propanol was placed in a flask with 6.2 grams of boric acid (3:1 molar ratio) and 300 ml. of benzene. The mixture was stirred and refluxed together until 5.4 ml. of water was azeotropically distilled off overhead. The remaining benzene was then distilled off, leaving a plastic product readily soluble in gasoline. The reaction proceeds as follows:



## Example 4

38.5 grams of the N-oleoylamide of tris(hydroxymethyl) aminomethane was dissolved in 300 ml. of benzene. 6.2 grams of boric acid was then added (a 1:1 molar ratio) and the mixture was refluxed at the azeotropic distillation temperature for the removal of the theoretical amount of water with benzene overhead. The remainder of the benzene was distilled off. The reaction proceeds according to the following equation:



As illustrative of the benefits derived from the use of motor fuels containing one or more of the boron compounds mentioned, the following tests with respect to surface ignition suppression and carburetor cleanliness were conducted.

To determine the effectiveness of the gasoline of this invention to suppress surface ignition, an ASTM-CFR single cylinder engine having the compression ratio adjusted at 12:1 was employed. Preparatory to the test cycle, the engine was run open throttle at 900 r.p.m. for thirty minutes to stabilize the engine conditions for the test period. Following this, the engine was continued at open throttle continuously for three hours, during which time the total surface ignition count was observed electronically. All experimental conditions were the same for each test except the gasoline.

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The base fuel in each test was the same and had the following composition and specifications.

## Composition:

5	30.3% saturates	
	15.3% olefins	
	54.4% catalytic reformat	
5	Tetraethyl lead (motor mix).....cc./gal.	2.5
	API gravity.....	58.0
10	Engler distillation, ° F.:	
	I.B.P.....	91
	10%.....	122
	30%.....	170
	50%.....	229
15	70%.....	281
	90%.....	370
	E.P.....	426
	Reid vapor pressure.....	11.6

20 The number of surface ignitions in the additive fuel is expressed as percentage of the surface ignitions of the blank fuel with the results as follows:

25	Additive	Concentration, percent by weight	SI rating of fuel	
			Total SI	Audible SI
30	None.....	None	100	100
	Compound of Example 1.....	0.059	59	39

To determine the effectiveness of the gasoline of the invention to avoid carburetor deposits, a contamination system was developed to simulate the conditions which contribute to carburetor deposits in the urban operation of motor vehicles. The system comprises the operation of a slave engine and a test engine. The exhaust gases from one bank of the slave engine (four cylinders) is metered to the crankcase of the test engine at a rate of 1.5 cubic feet per minute. All gases from the crankcase of the test engine are passed to the air intake of the carburetor of the test engine including, therefore, the exhaust gases from the slave engine and the blowby fumes of the test engine. The 1.5 cubic feet per minute rate of exhaust gases from the slave engine under these conditions constitutes approximately 8% of the total air intake of the test engine at idle manifold vacuum and speed. The operating conditions for the two engines are as follows:

	Test engine	Slave engine
Engines.....	'54 Olds., 10:1 C.R.....	'55 Chrys., 11:1 C.R.
55 Spark plugs.....	Champion J-12.....	Champion N-8B.
Carburetion.....	Standard 4-barrel Rochester carburetor.	Standard 4-barrel Carter carburetor.
Engine speed.....	Set up initially for each test at 850 r.p.m., except for accelerations to 3,000 r.p.m., unloaded.	700 r.p.m. ± 20.
Jacket temp.....	160° F. ± 5°.....	165° F. ± 5°.

The test cycle was 2 hours in time, which included four acceleration periods conducted on the unloaded test engine spaced at ½ hour intervals, the first acceleration period being 30 minutes after the test cycle was commenced. During each acceleration period the throttle was moved quickly to a wide open position and then quickly closed again to an idle position five separate times to permit a surge of carburetted gasoline to come into contact with the carburetor parts. The carburetor at the start of each test was in spotless condition. All experimental conditions were the same for the two test cycles except for the gasoline.

The base fuel in each test was the same and had the following composition and specifications.

## Composition:

75% cat. distillate	
25% SR naphtha	
API gravity	62.4
Engler distillation, ° F.:	
I.B.P.	98
10%	130
30%	163
50%	204
70%	262
90%	365
E.P.	424
Reid vapor pressure	8.75

At the end of each test the carburetor was removed and disassembled and a numerical rating was assigned for amount of deposits and discoloration by a number of observers rating independently and uninformed of the gasoline they were rating. The rating assigned was based on a standardized scale ranging from 100 to 0, wherein 100 would be a rating of a perfectly clean carburetor throttle plate and barrel, and 0 rating would represent a throttle plate and barrel loaded with deposits.

The results below represent the average rating by the observers:

Additive	Concentration, percent by weight	Rating
None	None	35
Compound of Example 1	0.01	57
Compound of Example 2	0.05	60

To demonstrate the anti-rust activity of the boron compounds of the invention, three clean 12-penny nails were placed upright in each of two beakers containing a standard diesel fuel so as to be completely immersed therein. The diesel fuel in each beaker contained 5% by volume water to accelerate the incidence of rusting. The diesel fuel in the first beaker contained 0.1% concentration of the compound of Example 1. The fuel in the second beaker contained no anti-rust agent. The nails in the two beakers were observed daily and the test discontinued after 14 days. After 2 days had passed there was definite evidence of rust formation on the nails in the second beaker containing no additive, whereas no rust had formed on the nails in the first beaker containing the compound of Example 1. After 2 weeks the nails in the second beaker were badly rusted while the nails in the first beaker still showed no sign of rust formation. This test was repeated for a distillate fuel oil with and without the compound of Example 1, and the same results were observed.

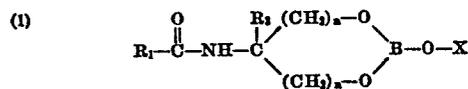
To illustrate the improvement in the dispersancy power of a lubricating oil obtainable by the use of these compounds, the following test was run which is a measure of the ability of the oil to hold carbon black in suspension. The oil tested was a petroleum hydrocarbon oil having a viscosity of 140 SSU at 100° F. and viscosity index of 100 with and without a boron compound as an additive. For the test 5% solution of the oil in dry benzene is first prepared. A 100 ml. of the solution is placed in a glass stoppered graduate. Carbon black in increments of 0.2 gram is added to the solution which after each increment is then shaken for fifteen seconds and permitted to stand for five minutes in front of a light source and the contents observed for a "break point." This point is seen as a thin upper layer of completely transparent liquid containing no carbon black particles. The largest amount of carbon black which does not produce a break point is recorded as the result of the test. The results are shown below:

Composition	Percent by weight additive concentration (in base oil)	Gm. carbon added to break point
Base oil only	None	0.4
Base oil+borated N-stearoylamide of 2-amino-2-methyl-1,3-propanediol	6	1.6
Base oil+borated N-oleoylamide of 2-amino-2-methyl-1,3-propanediol	6	1.4

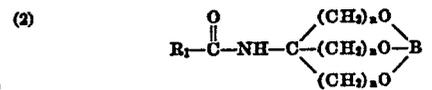
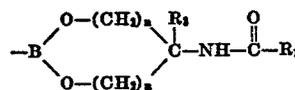
As stated heretofore, the boron compounds of this invention are stable toward hydrolysis and particularly so when dissolved in gasoline. It has been found that small amounts of these compounds may be added to gasoline as a means of improving the hydrolytic stability of other organo boron compounds which, when present in gasoline alone, have limited commercial value due to their tendency to hydrolyze in the presence of moisture. In this manner, it is possible to introduce a desired amount of elemental boron into a gasoline by utilizing a major amount of an organo boron compound offering a high elemental boron content but otherwise undesirable due to its hydrolytic stability in conjunction with minor amounts of one or more of the boron compounds of the present invention, thereby lowering the total amount of additive required in the fuel and insuring adequate hydrolytic stability. It has been found that the addition of as little as 5 to 10% of the boron additive as a compound of the class set forth hereinbefore can significantly improve the hydrolytic stability of various organo boron compounds.

## I claim:

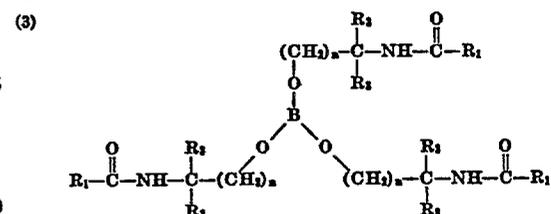
1. A liquid hydrocarbon selected from the group consisting of a motor fuel, fuel oil, and a lubricating oil containing from 0.001% to 1% by weight a boron compound selected from the group consisting of



where X is selected from the group consisting of hydrogen and



and



wherein R<sub>1</sub> represents a radical selected from the group consisting of an alkyl, alkenyl, and arylalkyl radical containing 7 to 21 carbon atoms, n is a small whole number from 1 to 3, and R<sub>2</sub> represents an alkyl radical containing 1 to 8 carbon atoms which may be different alkyl radicals when R<sub>2</sub> is present for more than one position on the molecule.

2. A motor fuel containing from 0.001% to 1% by weight a boron compound selected from the group consisting of

