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3,133,800

GLYCOL BORATE AMINE SALTS AS  
GASOLINE ADDITIVES

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5 Claims. (Cl. 44-69)

This invention relates to organic boron compounds as fuel additives and to motor fuels containing organic boron compounds. More particularly, the invention relates to motor fuel compositions containing minor quantities of a multi-functional additive in the form of a glycol borate amine compound, and to such compounds as fuel additives.

In United States Patent 2,497,521 to Charles G. Trautman, there is described and claimed hydrocarbon oil compositions containing minor amounts of an addition agent to improve the stability of the oil. The additive described in the Trautman patent is an amine salt of a boro-diol complex, and is prepared by reacting a molar excess of a 1:2 (molar) boro-alkylene glycol with an amine.

In accordance with the present invention, it has surprisingly been found that the reaction product of a 1:1 (molar) glycol borate with a stoichiometric amount of an amine, acts as a multi-functional additive for motor fuels. The addition of minor amounts of the reaction product to motor fuels imparts bactericidal and anti-rust properties to the fuel, inhibits the buildup of deposits in the carburetor, prevents carburetor icing, and modifies the action of the fuel on the engine to provide an overall improvement in smoothness of engine operation.

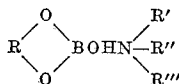
It is therefore an object of this invention to provide motor fuels having excellent bactericidal and anti-rust properties.

Another object is to provide a motor fuel which, in normal consumption, prevents carburetor icing and inhibits the buildup of deposits on carburetor internals.

A further object is to improve smoothness of operation by modifying the action of a fuel on an internal combustion engine.

Other objects and advantages will become apparent from the following detailed description of the invention.

The boron additives of the present invention are believed to have the following formula:



where R is a divalent alpha or beta, straight or branch chain saturated hydrocarbon radical having from 3 to 20 carbon atoms; and R', R'' and R''' are selected from the group consisting of hydrogen or alkyl, alkenyl, amino-alkyl and amino-alkenyl groups having from 3 to 20 carbon atoms, provided that at least one of the R', R'' or R''' is an alkyl or alkenyl group and not more than one of the R', R'', or R''' is an amino alkyl or an amino-alkenyl group. While compounds having R, R', R'' and/or R''' groups of more than 20 carbon atoms are suitable for use according to this invention, it will be recognized that the low percent weight of boron in such higher molecular weight compounds is a disadvantage. Furthermore, the higher molecular weight starting materials required to produce such compounds are not readily available and are therefore expensive.

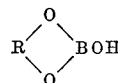
The present invention, however, is in no way limited

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by any theory concerning the structure of the glycol borate amine compounds.

Physical evidence in the form of calorimetric measurements indicates that a stoichiometric reaction takes place. A definite amount of heat is evolved, indicating a chemical reaction. A maximum of about 2 kilogram calories of heat per mole is evolved when a glycol borate and an amine are mixed. This indicates the formation of a relatively weak chemical bond when compared with the 13 kilogram calories per mole associated with the formation of a polar bond such as H—OH. These findings were helpful in interpreting infra-red analyses. The reaction product showed all the infra-red bands produced by the glycol borate and four new bands. These new bands were determined not to be solvent bands and did not make an appearance when a solution of glycol borate was examined. These new bands would indicate either (1), the presence of two starting materials plus a third compound, or (2), if one compound is indicated by physical evidence, the formation of a compound between the glycol borate and the amine with force loose enough not to disturb OH and NH vibrations. Since the physical evidence shows the stoichiometric formation of a compound, it would seem that alternative (2) is the proper interpretation of the infra-red analysis.

The organic boron compounds contemplated are those derived from the reaction of a 1:1 (molar) glycol borate having the formula:



and a primary, secondary, or tertiary mono- or diamine, having the formula:



where R, R', R'', and R''' are defined the same as above. To satisfy solubility requirements in gasoline, the reaction product must contain a minimum total of 14 carbon atoms; the glycol portion thereof, a minimum total of 3 carbon atoms. Both alpha and beta glycols are contemplated. The maximum number of carbon atoms is limited by economic factors and to some extent by the effect in the engine; to these ends, a maximum of 30 carbon atoms is recommended.

Motor fuels containing a glycol borate amine compound of the type described are effective in markedly reducing many of the adverse effects resulting from combustion chamber deposits which accumulate during the operation of an initially clean internal combustion engine running on a hydrocarbon fuel, and particularly a hydrocarbon fuel which contains a tetra-alkyl lead compound as an anti-knock agent. Despite the fact that one or more organic halides may be included in the fuel with the tetra-alkyl lead, as a scavenging agent, not all of the lead is removed. The adverse effect of residual deposits manifests itself in uncontrolled ignition and a general lack of smoothness in engine operation, caused principally by such deposits becoming heated to incandescence within the combustion chamber during engine operation, and igniting the fuel either before or after that portion of the cycle where normal spark plug discharge would cause ignition. It has been found that incorporating minor amounts of the compounds of this invention in gasoline modifies the action of the resulting fuel on an engine to provide an overall improvement in smoothness of engine operation.

Another prevalent operational difficulty alleviated by the motor fuels of this invention is carburetor icing. Vaporization of gasoline injected into a carburetor absorbs heat from incoming air and adjacent carburetor parts. On cool, humid days the temperature of the incoming air can be reduced below its dewpoint, resulting in condensation of moisture on cooled carburetor parts, which parts in turn have been reduced in temperature to below the freezing point of water. In a short period of time, sufficient ice can build up on carburetor walls, throttle valve and in the venturi to cause the engine to stall. This condition is most likely to occur when the engine is below its normal operating temperature, as for instance, during warm-up. It has been found that where higher molecular weight amines (about C 12 and above) are reacted in the manner disclosed, and a minor amount of the reaction product is added to gasoline, the resulting fuel, as normally consumed in an engine, prevents carburetor icing.

Fuels containing compounds formed from higher molecular amines (about C 12 and above) are also effective in preventing the formation of carburetor deposits. Such deposits are believed to accumulate from contaminants borne by the copious quantities of intake air an operating carburetor breathes. The situation is aggravated by prolonged engine operation in urban and industrial areas where the concentration of contaminants in the air is high. Since these deposits can result in rough idling and frequent stalling, their inhibition is distinctly advantageous.

The fuels of this invention also possess antirust and bactericidal activity. Bacteria and rust contaminate fuels, are believed to be the cause of unpleasant odors and may even accelerate fuel degradation. Sufficient rust and bacteria develop under normal fuel storage conditions to be troublesome, making their elimination highly desirable. The compounds of this invention depress the formation of rust and bacteria to below troublesome levels.

Specific additives which may be used according to this invention include:

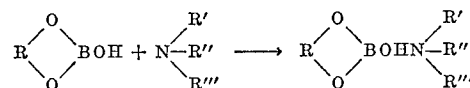
Propylene glycol borate dihexyl amine  
Propylene glycol borate di-2-ethyl hexyl amine  
Butylene glycol borate diamyl amine  
Butylene glycol borate decyl amine  
Neopentyl glycol borate diamyl amine  
Hexylene glycol borate tripropyl amine  
Hexylene glycol borate dibutyl amine  
Hexylene glycol borate octyl amine  
Hexylene glycol borate coconut oil amine  
Hexylene glycol borate oleyl amine

Gasoline base stocks to which the glycol borate amine compounds of this invention are added 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 gasoline will preferably contain a tetra-alkyl lead compound as in anti-knock agent and a scavenging agent. The amount of the anti-knock agent will be usually at a level of approximately 3 ml./gal., but may range from ½ ml./gal. up to 6 ml./gal. The base gasoline may also include other common additives such as anti-oxidants, stabilizers, solvent oils, dyes, and the like.

The amount of compound to be added to motor fuels for purposes of the invention may vary, and is conveniently expressed in terms of percent by weight of boron. Excellent results have been obtained where the amount of compound is within the range of 0.001 to 0.01% boron by weight. Usually amounts greater than 0.005% boron by weight cannot be economically justified.

The amine salts of this invention may be prepared in a variety of ways, the simplest of which is to mix with stirring, stoichiometric quantities of a 1:1 (molar) glycol

borate with an amine. The reaction is substantially spontaneous and is believed to proceed according to the following representation:



where R', R'', and R''' are defined the same as above.

The reaction may be carried out with or without a solvent. Where higher molecular weight borates and/or amines are employed, a solvent may be desirable to effect solution of the reactants. Preferred solvents are hydrocarbons and especially aromatics which are normal gasoline components, and therefore need not be removed from the reaction product.

The reaction is mildly exothermic, but external heat, while not required, may be desirable to melt higher molecular weight starting materials where, for some reason, the use of a solvent is to be avoided.

The glycol borate may be prepared by reacting one mol. of boric acid with one mol. of glycol. A detailed discussion of glycol borate preparations may be had by reference to United States Patent 2,741,548 to Darling et al. Any of the 1:1 (molar) glycol borates disclosed in this patent may be used.

Alternatively, the glycol borate amine compounds may be prepared by simultaneously mixing boric acid or boric oxide, a glycol, and an amine together in the presence of a solvent (such as toluene or xylene), removing the requisite amount of water to form a 1:1 glycol borate, whereupon the amine will spontaneously react with the glycol borate to form the desired product.

#### EXAMPLE I

##### Butylene Glycol Borate-Diamyl Amine

A mixture of 18.0 g. butylene glycol, 12.4 g. boric acid, and 100 ml. toluene were heated with stirring until 7.2 g. of water were removed by azeotropic distillation. The product was allowed to cool to room temperature, whereupon 31.4 g. of diamyl amine were added with stirring. The spontaneous reaction product was a pale, yellow liquid.

#### EXAMPLE II

##### Hexylene Glycol Borate-Dibutyl Amine

A mixture of 23.6 grams of hexylene glycol, 12.4 g. boric acid, and 100 ml. of toluene were heated with stirring until 7.2 g. of water were removed by azeotropic distillation. The product was allowed to cool to room temperature, whereupon 25.8 g. of dibutyl amine were added with stirring. The spontaneous reaction product was a clear, white liquid.

#### EXAMPLE III

##### Hexylene Glycol Borate Coconut Oil Primary Amine (HGB-COA)

8.64 g. of hexylene glycol borate was admixed with 13.38 g. of "Armeen C" (a coconut oil primary amine derived from a mixture of fatty acids comparable to that found in coconut oil). The materials with stirring spontaneously reacted to form a dark brown liquid.

#### EXAMPLE IV

##### Hexylene Glycol Borate Oleyl Amine (HGB-OA)

A mixture of 59.0 g. hexylene glycol, 30.9 g. boric acid, 100 ml. xylene and 143.5 g. "Armeen O" (oleyl primary amine was heated with stirring until the requisite 18.0 g. of water to produce a 1:1 (molar) glycol borate was removed by azeotropic distillation. The heating was stopped as the amine spontaneously reacted with the glycol borate to form an amber liquid reaction product.

#### Carburetor Icing

##### A. Test procedure:

A 1955 Plymouth V-8 engine was equipped with a

two-barrel carburetor. Air was supplied to the carburetor at a constant rate of 70 cu. ft. per minute by a specially designed air conditioner controlled at 45° F. and 85% relative humidity (conditions frequently found, and conducive to carburetor icing). All test conditions for each of the runs were the same save for the amine salt additive.

The test consisted of running five cycles on each fuel. During each cycle the engine was operated at 2200 r.p.m. for 10 seconds and then de-accelerated normally to an idle of 600 r.p.m. for a maximum of 30 seconds. Performance of the engine was observed during each idle period, and a numerical "merit rating" based on the degree of rough idling and engine stalling was assigned to each cycle. Merit ratings were chosen from a scale ranging from 100 to 0; an engine operating at a smooth idle over the idle period of a cycle would be entitled to a rating of 100, while an engine which stalled in less than 8 seconds of idle would get a 0 rating. The base fuel used had the following composition and specifications:

Composition	Percent Vol.	ASTM Distillation	
			° F.
Light catalytic distillate.....	40.0	IBP.....	85
Ultraformate.....	40.0	10%.....	111
Light naphtha.....	8.3	30%.....	141
Iso-pentane.....	8.3	50%.....	186
Butane.....	3.4	70%.....	243
		90%.....	310
TEL (cc./gal.).....	3.0	EP.....	366
API gravity (° 60/60).....	62.2		
Reid vapor Pressure (p.s.i.).....	12.0		
Octane No.:			
F-1.....	100.3		
F-2.....	90.0		

#### B. Test results:

TABLE I

Fuel	Boron (wt. percent) In Fuel	Merit Rating
Base.....	None	59
Base+HGB-OA <sup>1</sup> .....	0.001	71

<sup>1</sup> Hexylene glycol borate-oleyl amine.

It can be seen that the addition of a minor amount of glycol borate amine to the base fuel improved performance by 12 merit rating units.

#### Carburetor Deposits

##### A. Test procedure:

A 1954 Oldsmobile engine was equipped with a cleaned, standard 4 barrel Rochester carburetor and an air filter with the filter element removed. The air filter inlet was fed a mixture of exhaust gases from a slave engine, and blow-by gases from the crankcase of the test engine. Prior to running the test cycles, the carburetor was stabilized with the test fuel by running the engine unloaded at 1500 r.p.m. for 15 minutes, throttling back and running the engine unloaded at 850 r.p.m. for 5 minutes.

The test for each fuel ran about 2 hours during which time 4 cycles were run. Each cycle consisted of 30 minutes at idle followed by 5 full throttle accelerations to 3000 r.p.m. All test conditions for each of the runs were the same, save for the glycol borate amine additive. At the end of each test the carburetor was removed and disassembled. The primary throats were inspected and rated on an 0-10 scale; the higher the number, the cleaner the carburetor. After being rated the carburetor was cleaned, assembled, and remounted on the engine in preparation for the next test. The base fuel used consisted of 75% catalytic distillate and 25% straight run naphtha.

TABLE II

Fuel	Boron (wt. percent) in Fuel	Rating Base=4.5 (Improvement over Base)
Base+HGB-DBA <sup>1</sup> .....	0.002	+0.5
Base+HGB-DBA <sup>2</sup> .....	0.002	+0.0
Base+HGB-COA <sup>3</sup> .....	0.001	+2.5
Base+HGB-OA <sup>4</sup> .....	0.002	+4.5

<sup>1</sup> Hexylene glycol borate-dibutyl amine.

<sup>2</sup> Hexylene glycol borate-diamyl amine.

<sup>3</sup> Hexylene glycol borate-coconut oil amine.

<sup>4</sup> Hexylene glycol borate-oleyl amine.

It will be noted that the lower molecular weight additives, while not harmful, had little or no effect on the reduction of deposits; the coconut oil and oleyl amine compounds showed a substantial improvement.

In connection with the carburetor deposit test outlined above, it was found that the addition of from 20 to 100 weight percent hexylene glycol borate to a higher molecular weight amine compound (about C 12 and above) produced unexpected results. As shown in the table below, hexylene glycol alone had no effect on the amount of material deposited in the carburetor. When used alone in an amount equivalent to 0.002 and 0.001 weight percent boron, hexylene glycol borate oleyl-amine effected an improvement over the base fuel of 4.5 and 2.3 units, respectively. The 2.3 unit improvement was increased to 3.8 units by the addition of an amount of hexylene glycol borate, equivalent to 0.001 weight percent boron. This improvement was entirely unexpected since the hexylene glycol borate, by itself, was ineffectual against carburetor deposits. The carburetors were rated on an 0-10 scale; the higher the number, the cleaner the carburetor.

TABLE VI

Fuel	Boron (wt. percent) in Fuel	Rating Base=4.5 (Improvement over Base)
HGB <sup>1</sup> .....	0.003	0
HGB-OA <sup>2</sup> .....	0.002	+4.5
HGB-OA.....	0.001	+2.3
HGB-OA.....	0.001	+3.8
+HGB.....	0.001	-----

<sup>1</sup> Hexylene glycol borate.

<sup>2</sup> Hexylene glycol borate-oleyl amine.

#### Smoothness

##### A. Test procedure:

A 1956 Oldsmobile research engine with an 11:1 compression ratio was equipped with a vibration pick-up mounted on the engine block near the front main bearing, and pressure responsive pickups mounted in each of the combustion chambers. Crankshaft vibration and excessively high combustion chamber pressures are caused by surface ignition and manifest themselves in a rough running engine. By actual vibration and pressure count, it was possible to measure the effect of an additive in suppressing surface ignition, thereby providing a smoother running engine.

The signal generated from each of the pickups was amplified and fed to an electronic counter. By adjusting the gain on the amplifier, it was possible to count cycles of varying levels of roughness. For purposes of this test, the counters recorded only those manifestations which were sufficiently severe to be apparent to the operator.

Each test fuel was run in the engine at 1700 r.p.m. and 15" Hg manifold vacuum for 25 minutes. The engine was then adjusted at 1800 r.p.m. and 8" Hg manifold vacuum. The counters were turned on and for 70 seconds counted firing cycles of abnormal roughness. At the end of this period, the engine was throttled back and the carburetor was drained and flushed with

the next test fuel. The base fuel used had the following composition and specifications:

Composition	Percent Vol.	Engler Distillation	
			° F.
Saturates.....	57	IBP.....	102
Olefins.....	8	10%.....	140
Aromatics.....	35	30%.....	200
TEL (cc./gal.).....	2.2	50%.....	238
API gravity (° 60/60).....	55.64	70%.....	276
		90%.....	350
		EP.....	402

B. Test results:

The values for the base fuel were adjusted to zero so that a negative value represents a smoother burning fuel than the base, and a positive value, a rougher burning fuel.

TABLE III

Fuel	Boron (wt. percent) in Fuel	Pressure Counts (avg.)	Vibration Counts (avg.)
Base.....	none	0	0
Base+HGB-DBA <sup>1</sup> .....	0.002	-173	-24

<sup>1</sup> Hexylene glycol borate-dibutyl amine.

Anti-Rust

A. Test procedure:

12-inch lengths of 1-inch angle-iron were sanded on a belt sander. The specimens were placed in glass containers along with 400 ml. of test fuel, and the fuel in the containers was vigorously sloshed. After the addition of 4 ml. of water, the containers were sealed and mounted along radii of a large rotatable wheel. At a speed of 3 r.p.m., the wheel and specimens were rotated for 100 hours. At completion of the run, the metal specimens were observed and rated according to an arbitrary 0-10 scale. A rating of 0 would be given to a specimen that showed no rust after 100 hours. A rating of 10 would be given to a specimen that is completely covered by rust after 100 hours. The base fuel used had the following composition and specifications.

Composition:

Saturates .....	percent.....	60
Olefins .....	do.....	11
Aromatics .....	do.....	29
TEL (cc./gal.).....		282
Reid vapor pressure (p.s.i.).....		10.1
API gravity (° 60/60).....		59.0

Octane No.—

F-1 .....	99.1
F-2 .....	90.7

Engler distillation, ° F.:

IBP .....	84°
10% .....	125
30% .....	172
50% .....	229
70% .....	274
90% .....	342
EP .....	408

B. Test results:

TABLE IV

Fuel	Boron (wt. percent) in Fuel	Rating
Base.....	None.....	5.6
Base+HGB-DBA <sup>1</sup> .....	0.001.....	1.0-2.5
Base+HGB-COA <sup>2</sup> .....	0.001.....	1.75

<sup>1</sup> Hexylene glycol borate-dibutyl amine.

<sup>2</sup> Hexylene glycol borate-coconut oil amine.

Bactericidal Properties

A. Test procedure:

The initial procedure was the same used for the anti-rust

determination. At the end of 100 hours of rotation on the wheel, 1 ml. of fuel was removed from each container for bacteriological examination, and mixed with 20 mls. of sterile agar nutrient (at 45° C.) in Petri dishes. The mixture on the dishes was then allowed to cool to room temperature, whereupon the agar congealed. Each dish was then inverted and placed in an incubator maintained at 37° C. After incubation for 48 hours, the colonies were counted using an illuminated, cross-hatched field. The counts reported are in terms of bacteria per milliliter of sample. The base fuel used was ASTM iso-octane.

B. Test results:

Fuel	Boron (wt. percent) in Fuel	Count/ml.
Base (1).....	none	70,000,000
Base (2).....	none	8,000,000
Base (2) + HGB-DBA <sup>1</sup> .....	0.001	0
Base (1) + HGB-COA <sup>2</sup> .....	0.001	2
Base (2) + HGB-OA <sup>3</sup> .....	0.001	1

<sup>1</sup> Hexylene glycol borate-dibutyl amine.

<sup>2</sup> Hexylene glycol borate-coconut oil amine.

<sup>3</sup> Hexylene glycol borate-oleyl amine.

Because they possess an unusual combination of desirable properties, the compounds of this invention are tailor-made for use as gasoline additives. Insofar as we are aware, these compounds have no other utility.

It is to be understood that various modifications of the present invention will occur to those skilled in the art upon reading the foregoing disclosure. It is intended that all such modifications be covered which reasonably fall within the scope of the appended claims.

We claim:

1. A gasoline composition comprising a major proportion of gasoline, and the product of the reaction of a 1:1 molar glycol borate containing a minimum of 3 carbon atoms with a stoichiometric amount of an aliphatic hydrocarbyl amine selected from the group consisting of saturated and olefinically unsaturated amines, said product containing a minimum of 14 carbon atoms and being present in an amount to provide from 0.001 to 0.01 weight percent boron, based on the gasoline.

2. A gasoline composition comprising a major proportion of leaded gasoline and the product of the reaction of 1:1 molar hexylene glycol borate with a stoichiometric amount of an oleyl amine, said product being present in an amount to provide from 0.001 to 0.01 weight percent boron, based on the gasoline.

3. The composition of claim 2 which contains an additional, unreacted portion of hexylene glycol borate in an amount from 20 to 100 weight percent, based on said reaction product.

4. The composition of claim 2 which additionally contains an amount of a tetra-alkyl lead anti-knock agent within the range of from ½ ml. to 6 ml. per gallon of gasoline.

5. The composition of claim 2 which contains an amount of a tetra-alkyl lead anti-knock agent within the range of from ½ ml. to 6 ml. per gallon of gasoline.

References Cited in the file of this patent

UNITED STATES PATENTS

2,497,521	Trautman .....	Feb. 14, 1950
2,629,732	Schechter .....	Feb. 24, 1953
2,848,312	Liao .....	Aug. 19, 1958
2,883,412	Lowe .....	Apr. 21, 1959
2,937,932	Newman et al. ....	May 24, 1960
2,938,923	Schechter et al. ....	May 31, 1960
2,948,600	Larson .....	Aug. 9, 1960
2,990,423	Miller .....	June 27, 1961

OTHER REFERENCES

Kalichevsky and Kobe: 1956, Elsevier Pub. Co. (page 480).

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,133,800

May 19, 1964

Richard J. De Gray et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 53, for the claim reference numeral "2"  
read -- 1 --.

Signed and sealed this 20th day of October 1964.

(SEAL)  
Attest:

ERNEST W. SWIDER  
Attesting Officer

EDWARD J. BRENNER  
Commissioner of Patents