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BORINE TRIALKYL AMINES

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The present invention relates to novel borine-alkyl amine addition compounds. In particular my invention relates to borine-trialkylamine addition compounds whose characteristics are such as to endow them with a number of varied utilities.

Addition compounds wherein an atom of one molecule contributes a pair of electrons for bond formation to an atom of another molecule are known to the art. An example of this type of coordinate linkage is the addition compound resulting from the donation of a pair of electrons by the nitrogen of an amine molecule to the boron of a borine compound. A number of such compounds have been prepared in the past. However, their utilities have been limited due to their instability and other unfavorable properties.

Certain boron-containing compounds have been suggested as ignition improvers in compression ignition engines. However, the compounds proposed in the prior art have a number of shortcomings. Some of them decompose too readily causing the fuel to flash at too low a temperature. Others are unstable in the presence of water and since commercial diesel fuel almost universally contains minor amounts of water, this instability results both in reduced ignition quality of the fuel and the formation of troublesome sediments, sludges and the like. Other potential ignition accelerators are colored and thus impart an undesirable coloration to the fuel to which they have been added even when employed in very low concentrations. Since the color of the fuel is generally used by the consumer as a criterion of its quality, it is highly desirable that the additive be colorless. Other boron-containing compounds are unstable in the presence of atmospheric oxygen and present a storage problem. Still other compounds are solids and therefore difficult to blend with the fuel. An ideal diesel fuel cetane improver should have the following properties:

(1) The additive should be readily soluble in all types of diesel fuel.

(2) The additive should be compatible with high sulfur fuels.

(3) The additive should be equally effective in both straight run and catalytically cracked fuels.

(4) The additive should have a boiling point not above that of the diesel fuel itself to prevent evaporation losses on storage.

(5) The additive should not materially reduce the flash point of the fuel in question.

(6) The viscosity and pour point of the additive should be such that no difficulty is experienced in blending procedures, regardless of temperature conditions.

(7) The additive should be non-hazardous to both personnel and equipment.

It is evident, therefore, that the state of the art would be greatly enhanced by a class of borine amine addition compounds which accelerate ignition due the energy liberated upon the rupture of the boron to nitrogen bond and subsequent reaction of borine with oxygen at the elevated temperature of the combustion chamber, and

which would in addition also fulfill the above enumerated requirements.

Consequently, it is an object of the present invention to provide new compositions of matter useful as cetane improvers for distillate fuels in the diesel fuel boiling range.

An additional object is to provide a cetane improver of enhanced stability in the presence of water.

Another object of my invention is to provide a fuel additive which is colorless and thus does not add an objectionable color to the fuel mixture.

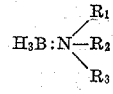
It is an additional object to provide a cetane improver which is in a liquid form at ordinary temperatures and therefore easily blended with fuels.

Another object is to provide an additive which is compatible with different types of fuels.

Another object is to provide a process for the preparation of the novel compounds of my invention.

Other objects of the present invention will become apparent from the subsequent discussion.

I have found that the above and other objects can be accomplished by practicing my invention which consists of providing as new compositions of matter addition compounds wherein one molecule of borine is bonded to one molecule of a trialkylamine, in which the total number of carbon atoms in the amine varies from four to about twelve. Such compounds may be defined by the general formula



in which R_1, R_2, and R_3 are alkyl groups and can be the same or different and wherein the total number of carbon atoms represented by $R_1+R_2+R_3$ varies from four to about twelve.

Typical compounds of the present invention are exemplified by such compounds as borine-dimethylethylamine, borine-methyldiethylamine, borine-dimethyl-n-propylamine, borine - methyldi - n - propylamine, borine - dimethylisopropylamine, borine - methyldiisopropylamine, borine - diethyl - n - propylamine, borine-ethyldi - n - propylamine, borine - diethylisopropylamine, borine - ethyldiisopropylamine, borine - diethylbutylamine, borine - ethyldibutylamine, borine - diethyl - t-butylamine, borine - ethyldi - t - butylamine, borine - diethylamylamine, borine - ethyldiamylamine, borine-triethylamine, borine - tributylamine, borine - dimethylbutylamine, borine - methyldibutylamine, and various other combinations and permutations of alkyl radicals attached to the nitrogen which yields a total number of carbon atoms from four to about twelve.

The compounds of my invention can be prepared by passing diborane into a slight excess of the appropriate trialkylamine which can be contained in a solvent nonreactive toward diborane. The reaction is conducted in an inert atmosphere, such as in nitrogen and the reaction vessel is cooled by means of an ice-salt bath or some other appropriate method. The addition product is best separated by fractional distillation. Several specific examples are given below.

Example I

Borine-triethylamine.—B_2H_6 was generated by adding dropwise 135 milliliters of BF_3 etherate (1.06 moles) to 200 milliliters of an ether solution containing 0.65 mole of $LiAlH_4$ according to the method of I. Shapiro et al., J. A. C. S. 74, 901 (1952). The diborane formed was bubbled into a solution of 180 milliliters (1.3 moles) of purified triethylamine (boiling between 88.5 and 89.0° C.) and 20 milliliters of ether contained under a nitrogen atmosphere. The glass reaction vessel was cooled with

an ice-water bath. The product was purified by fractional distillation in a vacuum line under a reduced pressure of the magnitude obtainable with a vacuum oil pump. The solution was distilled through a trap cooled with a salt-ice bath into a vessel cooled with liquid nitrogen. The ether and excess triethylamine were collected in the vessel cooled with liquid nitrogen, while the borine-triethylamine condensed in the salt-ice trap kept at —17° C. The product borine-triethylamine,

$$H_3B{:}N(C_2H_5)_3$$

melted at —4° C., forming a colorless liquid and had a vapor pressure of approximately 1 millimeter at 28° C. The rate of hydrolysis of this compound is very low. One milliliter of $H_3B{:}N(C_2H_5)_3$ allowed to stand in contact with 1 milliliter of water for three days produced only 2 milliliters of non-condensable vapor, which was presumed to be H_2.

Example II

Borine-tributylamine.—Tributylamine was purified by distillation at a reduced pressure of about 12.5 millimeters mercury. A fraction boiling at a constant temperature of 90° C. was collected for use in this synthesis. The borine-tributylamine was prepared in a manner similar to the preparation of borine-triethylamine by reacting diborane with tributylamine, with the exception that benzene was used as a solvent. The reaction was carried out at a temperature of 25° C. in a nitrogen atmosphere. The $H_3B{:}N(C_4H_9)_3$ was obtained in 84 percent yield based on the amount of B_2H_6 bubbled in.

The product, $H_3B{:}N(C_4H_9)_3$, had a melting point of —12° C., producing a colorless liquid of a very low vapor pressure. Heating the product to 70° C. at a pressure less than 1 millimeter mercury in a vacuum line did not result in any noticeable distillation to a cold trap.

Example III

Borine - dimethylethylamine.—The borine - dimethylethylamine was prepared in a manner similar to that used in the preparation of borine-triethylamine, by reacting diborane with dimethylethylamine in a nitrogen atmosphere. The product $H_3B{:}N(CH_3)_2C_2H_5$ was obtained in 84 percent yield based on the amount of B_2H_6 bubbled in. The $H_3B{:}N(CH_3)_2C_2H_5$ is a colorless liquid, melting at 17.7° C.

Example IV

Borine-diethylmethylamine.—The method of preparation of borine-diethylmethylamine was similar to that used in Example III by reacting diborane with diethylmethylamine in a nitrogen atmosphere. An 86 percent yield of $H_3B{:}N(C_2H_5)_2CH_3$ was obtained. The product melted at —38° to —40° C. yielding a colorless liquid.

While the examples given above illustrate a convenient method for the preparation of the compounds of my invention, it will be obvious to one skilled in the art that many variations and modifications are possible in adapting this method for alternate commercial processes. For example, while benzene and diethyl ether were found to be efficacious solvents in the synthesis of borine-trialkylamines, other solvents may be used. Illustrative examples of ether solvents are dimethyl ether, methylethyl ether, diethyl ether, ethyl-propyl ether, dipropyl ether, ethyl isopropyl ether, di-isopropyl ether, methylpropyl ether, dibutyl ether, amyl ether, hexyl ether, heptyl ether, octyl ether, dodecyl ether, anisole, phenylethyl ether, phenyl sulfide, and the like. These are but a few examples of the straight chain ethers, branched chain ethers, mixed aliphatic ethers, aromatic-aliphatic ethers in which the aromatic substituent may be alkyl substituted, aliphatic ethers with aromatic substituents, dioxane and other cyclic ethers, halogenated ethers, the glycol ethers such as β-ethoxy ethanol. The ethers may thus be either oxy- or thio-ethers. Ethers, other than those mentioned above will be apparent to those skilled in the art.

Other solvents that may be used are straight and branched chain aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, diethyldimethylmethane, triethylmethane, cyclohexane and the like; aromatic and substituted aromatic hydrocarbons such as benzene, toluene, the xylenes, ethyl benzene, propyl benzene, etc.; halogenated hydrocarbons such as chloroform, ethylene chloride, methylenebromide, carbon tetrachloride, ethyl bromide, propyl bromide, propyl chloride, the dibromopropanes, the dichloropropanes, the butyl bromides, the chloropentanes, bromobenzene, m-bromochlorobenzene, chlorobenzene, m - dichlorobenzene, p - dichlorobenzene, etc. Mixtures of various solvents can also be used. An example of mixed hydrocarbon solvent is a petroleum fraction such as that obtained by a cracking process or other well-known methods. Since it is not desirable to have a high concentration of olefinic material in the solvent, the petroleum fraction can be first subjected to a treatment well-known in the art for the reduction of the olefinic content thereof. The above are non-limiting examples of the various hydrocarbons and halogenated hydrocarbons that may be used as solvents.

While solvents were employed in the synthesis of the borine-trialkylamine compounds of the present invention, the reactions can be carried out equally well in the absence of solvent.

In the examples given above, the reaction mass was cooled by external means. Other means of cooling can be used. One method would be the use of cooling coils inside the reaction vessel. Another means of cooling is the use of a low boiling solvent which would absorb heat on vaporization. On the other hand, since the temperature of the reaction is not critical, the trialkylamine used in the synthesis may serve as a coolant by absorbing heat on vaporization. The vaporized substance can be condensed on the cooler parts of the apparatus or with the aid of condensers or equivalent means and returned to the reaction zone.

The manufacture of the borine-trialkylamines of the present invention may be carried out as a batch or continuous process. In a continuous process the diborane and the trialkylamine can be fed continuously into the reaction vessel. When so doing, a portion of the reaction mass can be continuously withdrawn and passed through a zone wherein the trialkylamine and the solvent, if one is used, can be distilled off and fed back into the reaction zone while the product, borine-trialkylamine is drawn off by conventional means.

In synthesizing these compounds one should observe the necessary precautions apparent to those familiar with the art. For example, since diborane cannot be exposed to air the reactions are preferably conducted under a nitrogen or other inert atmosphere. The product should be kept away from strong concentrated acid, since the strong acid decomposes the addition compound, forming borine which in turn recombines to form diborane with the liberation of heat. Hence, in the presence of air an explosive mixture of oxygen and diborane may result. The above precautions should therefore be taken in spite of the fact that the borine-amine addition compounds of my invention are more stable than alkylborine-trialkylamines.

The compounds of my invention are novel and have the unexpected property of being liquids at ordinary temperatures. For example, borine-dimethylethylamine, $H_3B{:}N(CH_3)_2C_2H_5$, melts at 17.7° C., whereas the trimethylamine derivative $H_3B{:}N(CH_3)_3$, is a solid melting at a relatively high temperature of 94° C. It is, therefore, unexpected and surprising that the replacement of an ethyl group for one of the methyl radicals on the nitrogen atom lowers the melting point by more than 76 degrees. It is not inconceivable, therefore, that my compounds possess a type of chemical bonding

or electron configuration different from superficially related addition compounds of the conventional type.

The unexpected property of being in the liquid state at ordinary temperatures makes the compounds of my invention useful as solvents. They are especially valuable in cases where the dielectric constant of the solvent is a critical factor in a specific operation since the dielectric property of the compounds of my invention may be varied and finely adjusted by a suitable choice of the alkyl groups attached to the nitrogen.

As agricultural chemicals the borine-trialkylamines of my invention can be used as fungicides, insecticides, miticides, herbicides and plant growth regulators, and as soil conditioners. The compounds in question also make excellent amine carriers.

It was also discovered that the compounds of the present invention are colorless liquids. As indicated, this is an exceptionally good quality in the use of these compounds, particularly when employed as cetane improvers since it is not desirable to change the color of a fuel upon admixture therewith of an additive.

Another important property inherent in the compounds of my invention is their remarkable stability against oxidation. Contrary to expectations they do not react or otherwise deteriorate in the presence of oxygen from the atmosphere. It would appear, therefore, that this characteristic of my novel borine-trialkylamine compounds further establishes their unusual and peculiar chemical bonding, which at least in part may explain their unexpected properties and hence utilities.

Another property the compounds possess is remarkable resistance to hydrolysis. By way of example borine-triethylamine was left in contact with water for three days and was found to yield only a small quantity of gas. This is indicative of the extreme resistance the compounds of this invention possess against hydrolytic decomposition notwithstanding other indications of their relatively low intramolecular cohesive forces.

All the above properties are essential in a good cetane improver. The effectiveness of the compounds of the present invention in improving the ignition qualities of a diesel fuel is shown by comparison with a standard reference fuel in a C. F. R. engine using the ignition delay method according to the method described in American Society for Testing Materials, volume 36, I, 418 (1936).

In blending the cetane improver with the fuel, either of the straight run or catalytically cracked variety, the components can be measured out by weight. Having weighed a volume of fuel or determined its weight from its volume and a knowledge of its specific gravity, an appropriate amount of the desired borine-trialkylamine or a mixture of various borine-trialkylamines of my invention to be used as an additive can be weighed or measured.

Since the compounds of my invention are liquids, advantage can be taken of their specific gravities to measure them out by volume in order to obtain the desired amount of the additive. The volume method is usually a much faster means of measurement than weighing and therefore the advantage of the liquid property of the compounds of my invention is herein displayed. The blending can be performed in storage tank, tank car, barrel, gallon or smaller lots. The borine-trialkylamines of the present invention can therefore be stored in tanks, barrels, or in smaller containers depending on the volume of fuel to be blended. After adding the borine-trialkylamine to the fuel, the liquid is stirred, or agitated by some other means, until a homogeneous mixture results. Here again the advantages of the liquid form of the compounds of my invention are exhibited since a liquid is more easily blended into a fuel while a solid would tend to settle out and would require more drastic methods to bring into solution. An alternative method of blending is to first dissolve the additive in a small amount of fuel and then adding the cetane improver in the form of a concentrate to the bulk of the fuel and stirring or agitating until a homogenous mixture results.

The amount of the borine-trialkylamines in the fuel can vary from 0.01 to about 5 weight percent depending on the fuel used and the improvement in the ignition qualities desired. For example, it has been found that varying the concentration of the additive in a straight run fuel from 0.1 to 1.0 weight percent results in an increase in the ignition rating of from about 3.2 to about 15.7 cetane numbers. The following examples are illustrative of the results obtained.

Example V

To 1980 parts by weight of straight run diesel fuel, was added 20 parts of borine-triethylamine and the mixture was stirred until a homogeneous solution resulted. This produced a diesel fuel composition in which the borine-triethylamine was present in 1.0 percent by weight.

Example VI

To 720 parts by weight of straight run diesel fuel, was added 80 parts of the composition of Example V. The blending was accomplished in the same manner as in the previous example. The resulting solution contained 0.1 percent of borine-triethylamine. In a similar manner, fuel compositions containing 0.2, 0.4 and 0.6 weight percent of borine-triethylamine were prepared.

The procedure as set forth hereinabove was repeated using catalytically cracked fuel in place of the straight-run diesel fuel to obtain fuel compositions containing 0.1, 0.2, 0.4, 0.6 and 1.0 weight percent borine-triethylamine in said catalytically cracked fuel.

Blends of borine-dimethyethylamine, borine-methyldiethylamine, and borine-tributylamine with straight-run diesel fuel were made up in an analogous manner to provide fuels with improved ignition qualities for use in compression ignition engines.

The table given below shows the cetane improvement obtained by an illustrative number of the novel compounds of my invention.

Additive	Fuel	Cetane Number	Increase in Cetane Number for Weight Percent Additive					
			0.1	0.2	0.4	0.6	0.7	1.0
$H_3B:N(CH_3)_2C_2H_5$	Straight run	33.1	4.3	6.0	9.4	------	12.6	15.7
$H_3B:N(C_2H_5)_2CH_3$	do	33.1	3.8	6.2	9.2	------	11.9	14.9
$H_3B:N(n\text{-}C_4H_9)_3$	do	33.1	3.2	4.7	6.0	7.9	------	11.4
$H_3B:N(C_2H_5)_3$	do	33.1	3.3	5.3	7.9	10.7	------	14.7
$H_3B:N(C_2H_5)_3$	Catalytically cracked.	25.5	4.0	5.8	7.4	9.3	------	12.5

Thus, it is seen from the above examples that a marked increase in cetane number of compression ignition fuel is obtained by the addition thereto of small amounts of borine-trialkylamine compounds.

Other advantages to be obtained by employing the compounds of the present invention as cetane improvers are increased engine cleanliness, increased storage stability, increased solubility, and the like.

Although my compounds have been shown to be useful

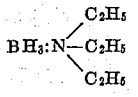
in improving the cetane rating and other properties of hydrocarbon fuels of the diesel fuel boiling range, they can be successfully utilized as additives to other hydrocarbon compositions. For example, minor proportions of these compounds can be blended with burner fuels to improve their combustion characteristics. Likewise, by blending minor proportions of the compounds of my invention with unctuous solvents such as natural and synthetic lubricating oils and greases the characteristics thereof can be materially increased. Similarly, the borine-trialkylamines are effective in improving the combustion characteristics of jet and rocket fuels as well as being especially effective as starting aids for diesel and jet engines.

In addition to the above uses the borine-trialkylamine compounds are valuable as chemical intermediates.

Having fully described the nature of the novel compounds of the present invention, I do not intend that my invention be limited except within the spirit and scope of the appended claims.

I claim:

1. Borine-triethylamine having the formula



2. Borine tributyl amine.

3. Borine dimethylethyl amine.

4. Borine methyldiethyl amine.

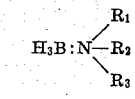
5. A process for the preparation of borine trialkyl amines wherein one molecule of borine is bonded to one molecule of a trialkyl amine in which the total number of carbon atoms varies from 4 to about 12; said process comprising reacting at substantially atmospheric pressure, under cooling, and in the presence of an inert gas and an inert solvent, diborane with a trialkyl amine corresponding to the general formula



wherein R_1, R_2 and R_3 represent alkyl groups and wherein the total number of carbon atoms in the three alkyl groups varies from 4 to about 12.

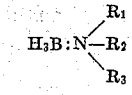
6. A process for the preparation of borine triethyl amine comprising reacting substantially one mole of diborane with substantially 1.3 moles of triethyl amine in ether solution under a nitrogen atmosphere at substantially atmospheric pressure with cooling, and recovering borine triethyl amine by distillation from the reaction mixture.

7. An addition compound wherein one molecule of borine is bonded to one molecule of a trialkyl amine corresponding to the general formula



wherein R_1, R_2 and R_3 represent alkyl groups and wherein the total number of carbon atoms in the three alkyl groups varies from 4 to 12.

8. An addition compound wherein one molecule of borine is bonded to one molecule of a trialkyl amine corresponding to the general formula



wherein R_1, R_2 and R_3 represent alkyl groups in which at least one R is different from the others and wherein the total number of carbon atoms in the three alkyl groups varies from 4 to 12.

References Cited in the file of this patent

UNITED STATES PATENTS

2,234,581	Rosen	Mar. 11, 1941
2,257,194	Rosen	Sept. 30, 1941
2,266,776	Leum	Dec. 23, 1941
2,267,701	Leum	Dec. 23, 1941
2,429,883	Johannson	Oct. 28, 1947
2,678,949	Banus et al.	May 18, 1954

OTHER REFERENCES

Krause: Ber., vol. 57, pp. 813–818 (1924).

Wieberg: Zeit. für Anorg. u. All. Chemie, vol. 256, pp. 285–306.

Schaeffer et al.: "Jour. Am. Chem. Soc.," 1949, vol. 71, pp. 2143–5.

Brown et al.: "Jour. Am. Chem. Soc.," 1952, vol. 74, pp. 2340–5.