PROCESS FOR THE PRODUCTION OF ALKALI METAL BOROHYDRIDES

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ABSTRACT OF THE DISCLOSURE

In the process for the production of sodium borohydride in which sodium borate or a mixture of sodium oxide and boron oxide is reacted with hydrogen and a reducing metal, the improvement which comprises effecting said reaction at a temperature between about 200 and 650° C. at a pressure of about 1 to 10 atmospheres in the presence of sodium and a member selected from the group consisting of aluminum metal and alloys thereof containing more than 50% aluminum as the reducing metal.

This invention relates to the production of alkali metal borohydrides.

The invention provides a method for making alkali metal borohydrides by reacting boron-oxygen compounds with metals and hydrogen.

The alkali metal borohydrides, and in particular sodium borohydride, are excellent reducing and hydrogenating agents having a very high reducing equivalent and selective action. For example, aldehydes and ketones can be reduced to primary and secondary alcohols. Metals and plastics can be chemically plated with nickel or cobalt by means of sodium borohydride. It has also been proposed to use alkali metal borohydrides in combination with bisulfite in vat dying and wood pulp bleaching (M. Lindhardt in Textilberichte, vol. 8 (1963), pp. 994-998). In addition, metal borohydrides which can be easily transported can be used in the generation of steam and, further, the alkali metal borohydrides can be used as starting material in the production of other boron and, in particular, boron-organic compounds.

The use of alkali metal borohydrides on a large scale has hitherto been handicapped by the high production costs of the known processes; that is, the alkali metal borohydrides have been produced in a variety of ways all characterized by low yields or that they require highly skilled operating techniques.

The primary object of the invention is to provide a simple and easily performed method for making alkali metal borohydrides which is efficient, may be practiced with readily available and inexpensive starting materials, is not dependent upon highly skilled operating technique, and is more direct and more easily practiced to provide these products at less expense than in the case with previously known methods.

Still other objects will be recognized from the following specification.

It is known from German patent specifications 1,036,222 and 1,067,005 and from a publication in Angew. Chemie 72, 1960, pp. 964-1000 that alkali metal borohydrides and, in particular, sodium borohydride, can be prepared by reacting alkali metal or alkaline earth metal borates with alkali metal hydrides, for example, sodium hydride or sodium and hydrogen, at a low pressure (approximately 3-6 atm.) and temperatures of about 400 to 550° C., possibly, in the presence of silicon dioxide. It is further known from German patent specification No. 1,053,476 that alkali metal borohydrides can also be produced by the reaction of metalborohydrides with hydrogen and aluminum or other metals the oxides of which are not reduced by hydrogen under the stated reaction conditions. In this reaction it is necessary to work with high hydrogen pressures (e.g., 60 atm.) in order to obtain good yields of metal borohydrides.

The advantages of reacting alkali metal or alkaline earth metal borates with alkali metal or alkaline earth metal hydrides, in the presence of silicon dioxide, in some cases consist in the relatively easy technical execution of the process since in this case continuous operation is possible, due to the low reaction pressure. The disadvantage of the process, however, is the relatively high cost of the alkali metal used as the reducing agent. Furthermore, relatively large amounts of starting and secondary products, as compared to the yield of metal borohydrides must be processed. Admittedly, the reaction of boronate with aluminum and hydrogen obviates the disadvantages described above; however, but because of the unfavorable reaction conditions and especially the technical conditions which arise from the very high reaction pressure, this process is impaired, and the continuous performance of the reaction is made extremely difficult.

According to the invention, there is provided a process for the production of alkali metal borohydrides comprising the reaction of a boron-oxygen compound with hydrogen, an alkali metal and/or alkali metal hydride, aluminum and/or alloy rich in aluminum, at temperatures between about 200 and 650° C. and pressures of about 1-15 atmospheres.

It has been found that the advantage of the low reaction pressure which is a characteristic feature of the reaction of borates with sodium and hydrogen can be combined with the great economic advantage of using aluminum as reducing agent if the reduction of the borates to sodium borohydride is carried out with a mixture of sodium and aluminum.

The process according to the invention may be illustrated in greater detail by taking the production of sodium borohydride as an example. If the process is carried out, for example, according to Equation 1

\[ 2\text{Na}_2\text{B}_4\text{O}_7 + 7\text{Al} + 11\text{Na} + 16\text{H}_2 \rightarrow 8\text{NaBH}_4 + 7/2\text{Al}_3\text{O}_3 + 7/2\text{Na}_2\text{O} \]  

then the reaction proceeds with excellent yields even at temperatures of about 330 to 350° C. and at hydrogen pressures between 2 and 5 atmospheres.

Suitable reactive boron-oxygen compounds for use according to the present invention include, if desired after dehydration, alkali metal boron minerals and alkaline-earth metal boron minerals, such as borax

\[ \text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{O} \]  

kernite \[ \text{Na}_2\text{B}_4\text{O}_7 + 4\text{H}_2\text{O} \]  

boronatrocacite \[ \text{Na}_2\text{B}_4\text{O}_7 + 6\text{H}_2\text{O} \]  

panendrite \[ \text{Ca}_2\text{B}_4\text{O}_9 + 3\text{H}_2\text{O} \]  

colemanite \[ \text{Ca}_2\text{B}_4\text{O}_7 + 5\text{H}_2\text{O} \]  

boracite \[ 2\text{MgB}_2\text{O}_4 + 2\text{MgCl}_2 \]  

In addition, borates and mixtures of metallic oxide and boracic oxide of any desired composition can be used, as, for example, those obtainable by contacting and optionally heating metallic oxides or compounds yielding metallic oxides and boracic oxide or acid or boracic oxide, such as sodium orthoborate \[ \text{Na}_2\text{B}_4\text{O}_5 \]  
sodium metaborate \[ \text{Na}_2\text{B}_4\text{O}_7 \]  
or higher borates such as \[ \text{Na}_2\text{B}_4\text{O}_10 \]  
and \[ \text{Na}_2\text{B}_4\text{O}_9 \]  
preferably mixtures with an \[ \text{Na}_2\text{O}/\text{B}_2\text{O}_3 \]  
and an \[ \text{MgO}/\text{B}_2\text{O}_3 \]  
ratio of about 3:1 and 1:4 are employed; however mixtures with other ratios can be used, since alkali metal oxides and \[ \text{B}_2\text{O}_3 \]  
are miscible in every proportion forming clear glasses (Gmelin No. 13, Vol. of Addition, p. 134); to some extent also the alkaline
earth metal oxide boron trioxide mixtures are concerned (loc. cit. p. 135). However it is not necessary to use the boron containing starting material in the form of a compound or metal oxide $\text{B}_2\text{O}_3$-solution. Also mixtures of the two components which are intimately mixed can be employed. For reason of economy however the naturally occurring borates are preferred.

A particularly advantageous method of producing sodium borohydride is by heating boron-oxygen compounds of sodium which are readily available, such as the previously mentioned minerals borax and kernite in accordance with the invention.

As the process of the invention is carried out in a hydrogen atmosphere to which an inert gas such as nitrogen or gases of the argon group may be added, the reduction can be effected with an alkali metal as well as with the corresponding alkali metal hydrides. In accordance with the above said conditions of temperature and pressure, the new process can be carried out in the range where sodium hydride exists as well as at temperatures and pressures at which sodium hydride is completely dissociated, as may be seen from the following table:

According to Gmelin, Handbuch der Anorganischen Chemie, Syst. No. 21, p. 162, the dissociation pressure of sodium hydride can be calculated from the following formula:

$$\log P_{NaH} = -\frac{5700}{T} + 2.5 \log T + 3.956$$

From this formula the following extrapolated dissociation pressures are obtained:

- 0 atmospheric excess pressure = 1 atmospheric pressure at 424°C.
- 1 atmospheric excess pressure = 2 atmospheric pressure at 447°C.
- 2 atmospheric excess pressure = 3 atmospheric pressure at 462°C.
- 3 atmospheric excess pressure = 4 atmospheric pressure at 472°C.
- 4 atmospheric excess pressure = 5 atmospheric pressure at 480°C.
- 5 atmospheric excess pressure = 6 atmospheric pressure at 487°C.
- 6 atmospheric excess pressure = 7 atmospheric pressure at 493°C.
- 7 atmospheric excess pressure = 8 atmospheric pressure at 498°C.

The aluminum is used in a state of fine subdivision and preferably in a particle size below 1 mm. diameter (aluminum bronze, aluminum grains, aluminum flakes, aluminum powder or aluminum turnings). Instead of pure aluminum there may be used aluminum-containing alloys, preferably those having a content of more than 50% Al. Suitable for use in the process of this invention are aluminum or alloys of aluminum with Si, Mg, Ca, Cu, Zn, Mn, Fe, Ni, etc., such as Magnalium, Duralumin, Lantal, Hydronalum as well as other readily available, technically used alloys. The purity requirements of the aluminum are not very high so that the process of the invention can be carried out with the waste material of the aluminum industry.

The ratio between the sodium and aluminum is preferably chosen so that, in addition to alkali metal borohydride the reaction product essentially consists of sodium aluminate. The process can also be accomplished with an excess of aluminum in such a manner that $\text{Al}_2\text{O}_3$ is obtained as a by-product according to the equation

$$3\text{Na}_2\text{B}_4\text{O}_7 + 6\text{Na} + 14\text{Al} + 24\text{H}_2 = 12\text{NaB}_2\text{H}_4 + 7\text{Al}_2\text{O}_3$$

With respect to the reaction of sodium and aluminum or sodium oxide and aluminum it is of course possible to use any reaction schemes falling between the Formulae I and II. It is further possible to use sodium in an amount exceeding that of Equation I.

The reaction can be accelerated by the addition of activating substances, such as, for example, alkali metal hydroxide, mercury, copper compounds as well as organic boron or aluminum compounds. Particular advantages in this regard are observed if the aluminum is used, a pretreatment step effecting activation of the surface may be of advantage.

The process is carried out at reaction temperatures above 100°C, preferably at temperatures between about 300 and 620°C. Especially good yields are achieved at temperatures of 300 to 550°C. The hydrogen pressure to be used (about 1–15 atm.) depends substantially upon the temperature conditions. At very low temperatures (below 200°C) it is necessary to apply high pressures, but above about 300°C the reaction proceeds with almost quantitative yields at hydrogen pressures of 1–10 atmospheres, preferably 2 to 6 atmospheres. The use of pressures higher than about 15 atm. is possible but does not appear to be expedient for the reasons mentioned above.

In the discontinuous performance of the process described herein, the reaction can be carried out by heating mixtures of alkali metal borates, sodium and finely divided aluminum to the reaction temperature at a hydrogen pressure of 4 atmospheres and maintaining this temperature until the reaction mixture no longer absorbs hydrogen. Alternatively, the process can be accomplished by heating an intimate mixture of the reaction components, i.e., sodium, aluminum, and hydrogen at pressures of 1 to 10 atmospheres, then adding the entire amount of borax at temperatures of about 350°C and slowly increasing the temperature to about 620°C. It is likewise possible to continuously add to the mixture of sodium, aluminum and hydrogen the required amount of borax at temperatures of 300 to 620°C.

The process can further be carried out in such a manner that a mixture of sodium, hydrogen and borax is used and the required amount of aluminum is subsequently added either totally or in portions or continuously. According to this embodiment a mixture of sodium hydride and borax can be prepared in a first step at temperatures below 350°C and the aluminum added thereto at temperatures of 300 to 620°C.

The continuous performance of the new process is preferably accomplished in mixing screws or similar devices. It is possible to use multistage screws wherein in the first step the starting products borax, sodium, aluminum and hydrogen are heated to temperatures of 350°C with intimate mixing. In the second step the reaction mixture which contains sodium hydride which has been formed in the first step is heated to temperatures up to 620°C while in the third step there may occur a secondary reaction and cooling of the reaction products.

The continuous performance of the new process can further be accomplished by continuously adding either the dehydrated borax and/or aluminum to the other reaction components.

During the course of the exothermic reaction it may be of advantage to add to the reaction mixture diluents, e.g., graphite, excess starting products such as borax or aluminum or sodium aluminate formed as by-product or mixtures of sodium aluminate and aluminum oxide.

The methods described above for the production of sodium borohydride from borate materials have also been applied to the production of other alkali metal borohydrides.

The finishing of the product obtained according to the process of the invention can be performed by an extraction with ammonium or alkyl amines such as isopropyl amine. If borax, aluminum, sodium and hydrogen have been used as starting materials, the mixture contains besides sodium borohydride sodium aluminate as by-product and non-reacted aluminum, borax and sodium hydride can be worked up on the other hand by pouring...
it into water, whereby temperatures of about 0–40° C., preferably 10–30° C. are used. The resulting suspension is then separated from the solids, e.g., by filtering through a finely meshed sieve and to the solution there is afterwards added an alkaline earth metal chloride such as calcium chloride, strontium chloride or barium chloride in an amount to precipitate the by-products or impurities as, e.g., calcium aluminate and calcium borate. The aqueous solution of sodium borohydride can now be used as such as reducing agent. Furthermore, the solution can be worked up to yield a solid borohydride-sodium chloride mixture. For this purpose the pH of the solution is adjusted to a value above 8, preferably to a pH between 10 and 11, by saturating the solution with calcium hydroxide; however, other alkaline earth metal hydroxides and alkali metal hydroxides can be used. Higher pH-values are not harmful, the higher the pH the more stable is the borohydride. The stabilized solution is then evaporated under moderate conditions, i.e., with low temperatures and short drying time, e.g., in a spray drier with a starting temperature of between 150–200° C. and an exit temperature of the gases of about 50–110° C.

Since in the process according to German published specification No. 1,035,476 the reaction with aluminum proceeds satisfactorily only with the application of high pressures, it is surprising that in the process according to the present invention the aluminum reacts smoothly at substantially lower pressures, for example at 2 to 5 atmospheres. A technical advance is achieved by the process according to the invention in that now the production of alkali metal borohydrides and in particular sodium borohydride can be carried out continuously under technical conditions which can be easily controlled with the use of economical reducing agents, whereas the known process using high pressures can be performed only batchwise.

The following examples are given for the purpose of illustrating the present invention:

**EXAMPLE 1**
A mixture of 201.5 grams of dehydrated borax, 127 grams of sodium and 105.5 grams of aluminum bronze (91% of aluminum) was heated to 480° C. within 2 to 3 hours with stirring in an autoclave of 2 liter capacity under a hydrogen pressure of 3 atmospheres and was further stirred at the same temperature for 5 hours under a hydrogen pressure of 5 atmospheres. When the absorption of hydrogen had terminated and the mixture had cooled down, a grey powder was obtained from which the sodium borohydride formed in almost quantitative yield could be isolated by means of liquid anhydrous ammonia or isopropylamine with a degree of purity of 96 to 98%.

**EXAMPLE 2**
A mixture of 202.5 grams of dehydrated borax, 130 grams of sodium and 110 grams of aluminum bronze was heated to about 300° C. under a hydrogen pressure of 4 atmospheres with stirring in an autoclave of 2 liter capacity and maintained at this temperature and this pressure until the NaH-formation was terminated, if necessary with cooling. The mixture was then heated to about 485° C. with further stirring and maintenance of the hydrogen pressure at 3 atmospheres and kept at this temperature, if necessary by cooling, until the hydrogen absorption had terminated (4 hours). After cooling there was obtained a grey powder from which the sodium borohydride formed in very good yield was extracted, e.g., with liquid ammonia.

**EXAMPLE 3**
A mixture of 130 grams of aluminum grains and 130 grams of sodium was heated to about 450° C. in a 2 liter autoclave with stirring at a hydrogen pressure of 4 atmospheres. 202.5 grams of dehydrated, coarse-grained borax were added within 2½ hours to the resulting mixture of sodium hydride and aluminum while slowly in-

creasing the temperature up to 510° C. and maintaining the hydrogen pressure of 4 atmospheres. Sodium borohydride was thereby obtained in very good yield.

**EXAMPLE 4**
A mixture of 202.5 grams of dehydrated finely divided borax and 130 grams of sodium was hydrogenated in a 2 liter autoclave with stirring at a hydrogen pressure of 3 atmospheres and a temperature of about 300° C., if necessary with cooling. To the mixture obtained, there were added, beginning at 440° C. and up to 540° C., 155 grams of aluminum bronze in measured quantities within 4 hours while maintaining the hydrogen pressure of 3 atmospheres. Sodium borohydride was thereby obtained in very good yield.

In the above described example an aluminum bronze with a content of 91.3% Al has been used with high yields. Similar results have been obtained with aluminum grit (96.8% Al) and aluminum dust (99.3% Al).

**EXAMPLE 5**
130 grams of sodium were heated to 500 to 510° C. in a 2 liter autoclave. At this temperature and a hydrogen pressure of 3 atmospheres a mixture of 202.5 grams of dehydrated borax and 130 grams of aluminum bronze was added within 6 hours with stirring. The sodium borohydride which was formed in very good yield was extracted with anhydrous liquid ammonia.

This example was repeated with an aluminum magnesium alloy containing 10–20% of Mg under otherwise equal conditions with high yields. The same results have been obtained also with an aluminum silica alloy containing 11.7% Si as well as with an aluminum nickel alloy containing about 8% of nickel.

**EXAMPLE 6**
Following the procedure of Example 3 a mixture of 120 grams of aluminum grains, 130 grams of sodium and 20 grams of potassium hydroxide were heated to 440° C. under a hydrogen pressure of 4 atmospheres with stirring. 230 grams of borax were then added within 1½ hours whereupon the temperature was increased to 600° C. Sodium borohydride was obtained in very good yield.

**EXAMPLE 7**
Following the procedure set out in Example 6, a mixture of 120 grams of aluminum grains, 130 grams of sodium and 14.5 grams of sodium hydroxide were heated with stirring to 450° C. under a hydrogen pressure of 4 atmospheres. 230 grams of borax were then added within 1 hour while the temperature was increased to 620° C. Sodium borohydride was thereby obtained in good yield.

**EXAMPLE 8**
Following the procedure prescribed in Example 2, a mixture of 138 grams of dehydrated borax, 78 grams of sodium, 100 grams of aluminum bronze and 100 grams of aluminum grains were heated with stirring to about 300° C. under a hydrogen pressure of 4 atmospheres. Formation of sodium hydride took place within about 15 minutes; care was taken where necessary by cooling that the temperature did not exceed 360° C. After completion of the hydride formation heating was continued while the hydrogen pressure of 4 atmospheres was maintained. Above 360° C. borohydride formation set in and rapidly increased as the temperature increased. The temperature was kept below 480° C. by cooling. Sodium borohydride was thereby obtained within 20 minutes in very good yield.

**EXAMPLE 9**
Following the procedure of Example 3, a mixture of 285 grams of aluminum grains and 130 grams of sodium were heated with stirring to about 400° C. under a hydrogen pressure of 4 atmospheres. While the temperature...
ture was increased up to 550° C. 200 grams of dehydrated borax were added within 45 minutes. Sodium borohydride was obtained in this manner in very good yield.

**EXAMPLE 10**

A mixture of 285 grams of aluminum grains and 130 grams of sodium were heated with stirring to 530° C. in a 2 liter autoclave under argon. The argon atmosphere was then replaced by hydrogen (4 atmospheres) and 200 grams of dehydrated borax were added within 45 minutes, while the temperature was allowed to slowly drop to 490° C. Sodium borohydride was recovered in very good yield.

**EXAMPLE 11**

Following the disclosure of Example 8, 78 grams of sodium were hydroxogenated in a mixture of 138 grams of dehydrated borax, 100 grams of aluminum bronze and 100 grams of aluminum grains with stirring at 300 to 350° C. under a hydrogen pressure of 4 atmospheres, yielding sodium hydride. The resulting mixture was then added with stirring within 1/4 hours at 455 to 480° C. and under a hydrogen pressure of 4 atmospheres to a mixture as set out in Example 8 after reaction of the latter. Sodium borohydride was obtained in very good yield.

**EXAMPLE 12**

78 grams of sodium and 138 grams of dehydrated coarse-grained borax were hydroxogenated at 300 to 350° C. under a hydrogen pressure of 4 atmospheres. 100 grams of aluminum bronze and 100 grams of aluminum grains were then added at about 350° C. and the temperature was increased up to 560° C. under a hydrogen pressure of 4 atmospheres within 30 minutes. Sodium borohydride was obtained in this manner in very good yield.

**EXAMPLE 13**

400 grams of a crude product, containing 22.5% sodium borohydride, sodium aluminite, unreacted aluminum, borax and sodium hydride and which had been prepared according to the equation

$$2Na_2B_4O_7 + 14Al + 11Na + 16H_2 \rightarrow 8NaBH_4 + 7NaAlO_2 + 7Al$$

were dissolved in a mixture of 500 grams ice and 700 ml. water, then filtered through a sieve of fine mesh size (640 mesh per cm²) to remove aluminum and was then filtered. The residue was washed on the filter with water. There were obtained 1880 ml. of a solution containing 88 grams of sodium borohydride NaBH₄ (97.8% of the theoretical). The borohydride solution was then mixed while stirring at room temperature with an aqueous solution of 362 grams calcium chloride hexahydrate. Following filtration, the precipitate was washed with 300 ml. water. There were obtained 3220 ml. of a filtrate containing 80.5 grams sodium borohydride. Thus, the total yield was 89.4% of the theoretical.

The solution can be used directly for reducing purposes.

The recovery of a mixture of solid sodium borohydride and sodium chloride was effected by mixing the borohydride solution with 5 grams calcium hydroxide followed by evaporation in a spray drier (gas inlet temperature: 180° C., outlet temperature: 85° C.). A loss of borohydride could not be detected.

**EXAMPLE 14**

A mixture of 2.025 grams dehydrated finely divided borax and 130 grams of sodium is heated in a 2 liter autoclave under a hydrogen pressure of 1 atmosphere to a temperature of 520° C. while stirring. To this mixture there are added with stirring 109 grams of aluminum bronze, whereby the hydrogen pressure of 1 atmosphere is kept constant, while heating the mixture to a temperature of 515° C. in 1¼ hours. Sodium borohydride is obtained with a good yield and extracted with anhydrous liquid ammonia.

**EXAMPLE 15**

A mixture of 200 grams of dehydrated sodium meta-borate, 70 grams of sodium and 90 grams of aluminum bronze is heated in a 2 liter autoclave to a temperature of 300° C. and under a hydrogen pressure of 3 atmospheres. The mixture is kept under this pressure and temperature with stirring until sodium hydride has been formed. Afterwards the mixture is heated to a temperature of 510° C., whereby stirring is continued and the hydrogen pressure is kept constant at 3 atmospheres. After 3 hours the mixture does not take up a further amount of hydrogen. The sodium borohydride formed with high yields is extracted with anhydrous liquid ammonia.

**EXAMPLE 16**

A mixture of 125 grams of aluminum bronze and 185 grams of sodium is heated in a 2 liter autoclave with stirring to a temperature of 460° C. under a hydrogen pressure of 3 atmospheres. To this mixture there are added 250 grams finely pulverized Na₂B₂O₇, whereby the temperature is increased slowly to 540° C. under a constant pressure of 3 atmospheres. The pentaborate is added in the course of 2½ hours. Sodium borohydride is obtained in good yields.

What is claimed is:

1. In the process for the production of sodium borohydride in which sodium borate or a mixture of sodium oxide and boron oxide is reacted with hydrogen and a reducing metal, the improvement which comprises effecting said reaction at a temperature between about 200 and 650° C. at a pressure of about 1 to 10 atmospheres in the presence of sodium and a member selected from the group consisting of aluminum metal and alloys thereof containing more than 50% aluminum as the reducing metal.

2. Improvement according to claim 1 in which said reaction is effected according to the following reaction scheme:

$$2Na_2B_4O_7 + 7Al + 11Na + 16H_2 \rightarrow 8NaBH_4 + 7/2Al_2O_3 + 7/2Na_2O$$

3. Improvement according to claim 1 in which said reaction is effected according to the following reaction scheme:

$$2Na_2B_4O_7 + 6Na + 14Al + 2H_2 \rightarrow 12NaBH_4 + 7Al_2O_3$$

4. Improvement according to claim 1 in which said group member is in finely divided form.

5. Improvement according to claim 4 in which said group member has a particle size of less than 1 mm. diameter.

6. Improvement according to claim 1 in which said group member is an alloy of aluminum with a member selected from the group consisting of silicon, magnesium, calcium, copper, zinc, manganese, iron, nickel, and mixtures thereof having an aluminum content of more than 50%.

7. Improvement according to claim 1 in which said group member is initially reacted with said sodium at a temperature above about 50° C. in the presence of hydrogen at a hydrogen pressure of about 4 atmospheres, and in which coarse-grained borax is thereafter introduced into the resulting reaction mixture and the reaction continued at a temperature of about 510° C. at a hydrogen pressure of about 4 atmospheres.

8. Improvement according to claim 1 in which said group member is initially reacted with said sodium in the presence of an alkali metal hydride activator at a temperature of between about 440 and 450° C. and a hydrogen pressure of about 4 atmospheres and thereafter borax is added to the resulting mixture and the reaction continued at a temperature above about 600° C.
9. Improvement according to claim 1 in which the reaction is effected according to the following equation:

\[ 2\text{Na}_2\text{B}_2\text{O}_3 + 14\text{Al} + 11\text{Na} + 16\text{H}_2 \rightarrow \]

\[ 8\text{NaBH}_4 + 7\text{NaAlO}_2 + 7\text{Al} \]

and which includes forming a solution of the product thus obtained containing sodium borohydride, sodium aluminate, unreacted aluminum, borax and sodium hydride, treating said solution to remove any solid material contained therein, thereafter adding to the solution an alkaline earth metal chloride whereby there is precipitated out from said solution the by-products obtained in the reaction, and separating the aqueous solution of said borohydride from said precipitated by-product.

10. Improvement according to claim 9 wherein said alkaline earth metal chloride is a member selected from the group consisting of calcium chloride, strontium chloride, and barium chloride.