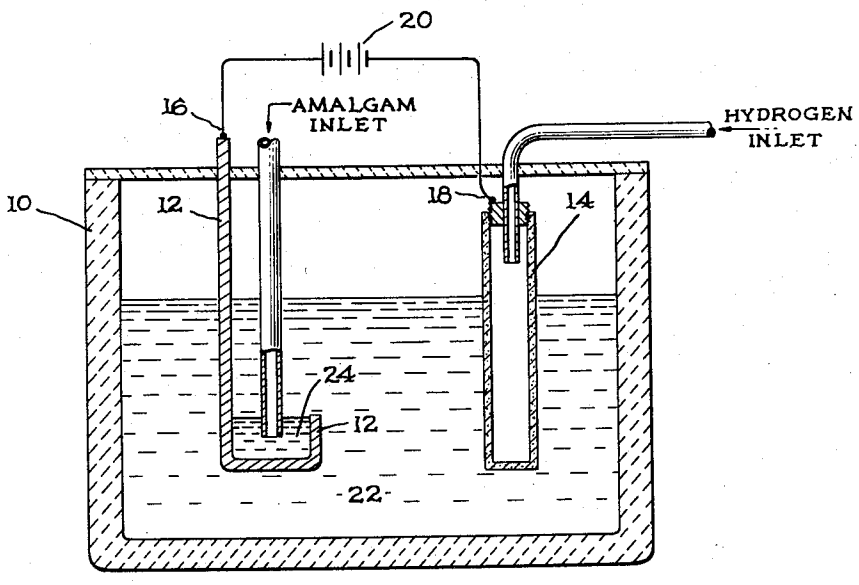
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ELECTROLYTIC PRODUCTION OF HYDRIDES

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INVENTOR.

GEORGE L. CUNNINGHAM

BY Lawrence I Field

ATTORNEY

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ELECTROLYTIC PRODUCTION OF HYDRIDES

George L. Cunningham, Cleveland Heights, Ohio, assignor to Horizons Incorporated

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This invention relates to the production of alkali metal hydrides and of useful compositions containing alkali metal hydrides. The principal object of the invention is the provision of a process in which an alkali metal amalgam anode is electrolytically decomposed in a substantially anhydrous fused salt bath and hydrogen is caused to react with the alkali metal, as it is deposited at the cathode, whereby the desired alkali metal hydride is formed. An additional object of the invention is the provision of a process wherein compositions containing alkali metal hydrides are produced in a form in which they may be readily utilized for metal cleaning, descaling or pickling, or for the formation of alkali metal borohydrides. A further object of this invention is to improve the operation of an installation of electrolytic cells operated at a higher temperature and a lower temperature by recovering heat from the products of the higher temperature cell and employing same to improve the operation of the lower temperature electrolytic cell. These and other objects will become readily apparent to those skilled in the art from the following description.

Numerous industrial uses exist for the alkali metal hydrides. At present they are extensively employed for the pickling of metals in a process involving the use of a fused salt bath. Another expanding use is in the production of various types of boron compounds such as the alkali metal borohydrides and trimethoxyhydrides which because of their high heat of combustion are being evaluated as potential fuels for rockets and the like.

Alkali metal hydrides have been prepared by various processes. For purposes of illustration in the following specification, the reactions will be described for sodium, although it will be understood by those skilled in the art that the description applies with equal force and effect to the other alkali metals and that my invention is not to be construed as applicable to only one member of the class. The simplest, and perhaps the most widely investigated, is the direct reaction of the alkali metal with elemental hydrogen at somewhat elevated temperatures. The reaction between sodium and hydrogen is moderately rapid at temperatures as low as about 200° C. and quite rapid at temperatures between 300° and 400° C. At these temperatures, the hydrogen appears to be absorbed on the surface of the sodium, forming sodium hydride as a solid film which prevents the hydrogen present from reacting further with the hydride covered sodium metal. In the past various expedients have been proposed to overcome this difficulty, among which may be mentioned: dispersing the sodium to be reacted as fine liquid droplets in a suitable hydrocarbon such as kerosene; or distributing the sodium to be reacted as a thin film coating solid salts such as sodium chloride; or the use of activators to speed up the reaction. None of these methods has been entirely successful in permitting the reaction to be rapidly effected at relatively low temperatures.

Instead of employing metallic sodium which is relatively expensive and the handling of which is somewhat hazardous, I have developed a process in which sodium in the form of an inexpensive amalgam is electrolytically

decomposed to yield the metal in highly reactive state under conditions such that it may be rapidly reacted with hydrogen to produce sodium hydride in a readily recoverable form.

Preferably the amalgam employed in the carrying out of the process is one which is commonly prepared by the electrolysis of an aqueous solution of sodium chloride in a cell having a mercury or sodium amalgam cathode in a manner well known in the art. One such arrangement is known as the Castner cell. In the cell, chlorine is liberated at the graphite anode and sodium is liberated at the liquid cathode with which it unites to form a product richer in sodium than that entering the cell. In present day commercial cells the sodium content of the amalgam withdrawn from the cell may vary from about 0.1% by weight to about 0.8% by weight. The operating temperature is usually in the range of 80 to 90° C. and this temperature determines the practicable upper limit of sodium content, since when greater than about 0.8% sodium is present, the formation of solid sodium-mercury compounds turns the amalgam from a liquid to a mushy solid and interferes with the flow of the liquid amalgam, necessary to the operation of the cell.

The liquid amalgam product leaving this first cell is led to a second cell in which the amalgam is employed as an anode very much in the manner described in U. S. Patent 2,148,404, issued Feb. 21, 1939. However, in order to recover the sodium content, in the form of sodium hydride, I have radically modified the second electrolysis.

In the single figure of the drawing, there is schematically shown one apparatus for carrying out the second electrolytic step of my invention.

In my process the second cell comprises a refractory container **10** fabricated from a ceramic material and is provided with a flowing amalgam anode **12** and a metal cathode **14**. The cell is provided with the usual means (not shown) for controlling the temperature of the bath, for admitting any desired atmosphere to the cell, for charging and discharging the contents of the cell, and with suitable electrical connections **16**, **18** to a source of potential **20** in order to effect the desired electrolysis. Such apparatus is well known in the art. For reasons which will hereinafter become apparent, the cathode **14** is preferably formed of porous metal, and is preferably fabricated of nickel, iron, or alloys which are based on iron or nickel such as steel or stainless steel.

Once a suitable cell has been provided, a fused salt bath **22** is established therein. The bath composition is selected from mixtures of alkali metal hydroxides and alkali metal halides. The fused bath composition chosen is one which melts at a relatively low temperature to form an electrolyte which is compatible with the reactants and the reaction products. When the hydride of a single alkali metal is to be prepared the bath is comprised of a halide of that alkali metal and either at least one additional halide of the same metal or the hydroxide of the same alkali metal preferably in proportions which form a eutectic. Where a mixture of alkali metal hydrides is desired, the bath may consist of a mixture of at least two alkali metal salts of the group consisting of alkali metal hydroxides and halides in which at least two alkali metals are included. The following bath compositions are exemplary:

Mol percent	Mol percent	M. P. °C.	Operating Temperature, °C.
75 LiI 55 NaOH 55 KOH	25 KI 45 NaI 45 NaOH	250 225 168	255–260 230–240 175–190

At these low temperatures the vapor pressure of mercury is quite low, and hence contamination of the freshly formed sodium is minimal.

Once an appropriate fused salt bath has been established, relatively dilute amalgam of the alkali metal is fed into the bath to establish a pool 24 which will function as an anode. Hydrogen is then fed into the bath, adjacent to the cathode, or preferably through the pores in the porous cathode. Excess hydrogen fed into the bath passes up through the electrolyte and is confined in the volume above the bath to form a protective atmosphere. As the electrolysis proceeds, the desired alkali metal hydride forms at the cathode by combination of the alkali metal (stripped from the amalgam anode) with the hydrogen passed into the bath in the region of the cathode. Since the alkali metal hydride dissolves in the fused salt electrolyte as it forms, and the sodium is reacted with as it is evolved at the cathode, formation proceeds at an undiminished rate as long as reactants are available.

The solubility of the alkali metal hydrides in fused salt baths such as those described is increased with increase of temperature, but the contamination of the cathode product by the mercury vapor formed in the second cell, as a result of decomposition of the amalgam, also increases with temperature and hence it is desirable to operate the second cell at a temperature not appreciably higher than 375° C. By operating the second cell at temperatures between about 250° C. and 350° C. until the fused salt is practically saturated with respect to the alkali metal hydride, and then cooling the fused salt, it is possible to precipitate the desired alkali metal hydride and to recover same from the melt by filtering or other suitable procedure. However, many of the contemplated uses for the alkali metal hydrides do not require separation of the hydride from the fused bath. For instance, to practice a pickling process of the type set forth in Gilbert Patent 2,377,876, issued June 12, 1945, the fused salt from my second electrolytic cell may be withdrawn when the desired hydride concentration has been reached and employed as the cleaning medium. Alternatively, the cell may be operated at a temperature of about 350° C. until almost saturated with the desired hydride, then cooled slightly to precipitate some of the hydride which is separated and recovered, and the remaining bath may then be used as a less concentrated fused salt hydride-containing cleaning bath. The exact amount of alkali metal hydride dissolved in a salt melt will depend upon the melt composition, temperature and the particular hydride. For example, in excess of 20% by weight of sodium hydride may be dissolved in sodium hydroxide at about 375° C.

For purposes of illustration, I will now describe one manner of carrying out my process for producing sodium hydride.

An aqueous solution of sodium chloride is electrolyzed in a cell having a flowing stream of mercury or sodium amalgam as cathode, e. g., a conventional Castner cell. As is well known in the art, sodium released at the cathode unites with the mercury to form an amalgam so that the liquid flowing from the cell is richer in sodium than the mercury or amalgam entering the cell. (See for example Moulton Patent 1,961,160 for a detailed description of a suitable cell.) The amalgam leaving the cell is relatively dilute and contains up to about 0.1% and 0.2% and cell temperatures between about 80° and 90° C. have been found to be particularly suitable.

The amalgam which preferably continuously flows out of the first cell, is preferably introduced into a second cell containing a fused salt mixture of appropriately low melting point, for example, one of the eutectic mixtures previously described. The amalgam introduced into the second cell serves as an anode. The cathode of the second cell is, in this preferred embodiment, formed of porous nickel. Hydrogen is continuously flowed into the second cell, through the porous cathode. The electrolysis in the second cell constantly removes sodium from the amalgam and results in the release of nascent sodium at the cathode, where it combines with the hydrogen to form sodium hydride. The sodium hydride dissolves readily in the fused salt bath. Any excess hydrogen flowing out of the bath serves to protect the fused bath and cell products from oxidation. The second cell is preferably provided with a cover to exclude moisture and oxygen from the air and the hydrogen flowing out of the bath is usually maintained at a pressure slightly in excess of atmospheric to prevent ingress of air into the cell. In some cases, where the presence of small amounts of alkali metal oxide is not detrimental, the second cell need not be rigorously protected against oxidizing influences.

A further feature of my invention lies in the recovery of heat from the reactants to improve the efficiency and economics of the process.

Heretofore, in the operation of a commercial amalgam cell the sodium chloride brine used was approximately 90% saturated with sodium chloride and when the brine concentration falls to about 75% the brine was circulated through solid sodium chloride crystals to bring the concentration back to about 90% saturated. If the sodium chloride concentration fell much below about 75% saturation the electrical conductivity of the brine decreased with an increase in the cell voltage. This meant that solid sodium chloride must be provided for the operation of mercury cells. Sodium chloride as a solid is considerably more expensive than sodium chloride in the form of a substantially saturated brine. This has previously been one of the big disadvantages of the mercury type cell in comparison with the diaphragm type electrolytic cells.

In the process of this invention the first cell wherein sodium chloride is electrolyzed is operated at about 80 to 90° C. while the second cell is operated at much higher temperatures in the range of 250 to 350° C. Thus the mercury could transport considerable heat from the hot cell to the cooler cell with the possibility of the cooler cell becoming overheated. This defect is overcome in the following manner. Brine, withdrawn intermittently or continuously from the first cell is aerated to remove chlorine gas and the dilute brine is passed into a heat exchanger located between the two cells. Mercury leaving the second cell at a temperature of about 300° C. will come into heat exchange contact with cooler dilute brine from the first cell, and with the necessary amount of incoming brine from the brine wells. This will cause evaporation of the dilute brine, cool the mercury, and will at the same time serve to concentrate the dilute brine back to saturation. Thus in the operation of the cell it is not necessary to use solid salt which is the conventional practice. Instead the sodium is furnished in the form of brine, and concentrated by means of heat which would otherwise cause overheating of the brine cell.

In operating the cell in a continuous manner over extended periods of time, it has been found that there is substantially no decomposition of the fused electrolyte. The composition of the bath remains substantially unchanged over extended periods of time and there is no evidence of anodic oxidation of the halide. Hence, the cell may be operated practically indefinitely without changing or replacing the electrolyte or readjusting the composition thereof, when the alkali hydrides are separated and recovered. Of course, any fused bath withdrawn for use as a pickling agent must be replaced in order for the process to continue.

One further point should be noticed concerning the operation of the second cell in my process. By introducing hydrogen adjacent the cathode, it has been found that the overall voltage of the cell is diminished, presumably because the voltage at the cathode is reduced.

I claim:

1. A process for the production of an alkali metal hydride which comprises electrolyzing a fused salt bath

consisting essentially of at least one alkali metal compound selected from the group consisting of alkali metal hydroxides and alkali metal halides in an electrolytic cell provided with an alkali metal amalgam anode and a porous metal cathode, composed of metal from the group consisting of iron, nickel and alloys based on at least one of said metals, introducing hydrogen into the bath through the pores of said porous cathode for reaction with the alkali metal as it forms during the electrolysis, and recovering the alkali metal hydride from said fused salt bath.

2. A process for the production of sodium hydride from a sodium amalgam which comprises electrolyzing a fused salt bath having a melting point below about 400° C. and consisting essentially of at least one sodium compound selected from the group consisting of sodium hydroxide and sodium halides in which the sodium amalgam is the anode and in which hydrogen is introduced into the bath during the electrolysis through the pores of a porous nickel cathode to react with sodium liberated at the cathode.

3. The process of claim 2, in which the sodium hydride is recovered from the bath by cooling the bath to precipitate the hydride and separating the precipitate from the fluid bath constituents.

4. A process for producing an alkali metal hydride from a crude alkali metal salt brine which comprises: electrolyzing an aqueous solution of the alkali metal salt brine with a mercury cathode to obtain a liquid dilute alkali metal amalgam, withdrawing said amalgam from the zone of electrolysis, introducing the dilute amalgam into a second electrolytic cell containing a fused salt bath consisting essentially of at least one alkali metal compound of the group consisting of alkali metal hydroxides and alkaii metal halides, electrolyzing the fused salt bath with the dilute amalgam as the anode in said second cell while introducing hydrogen into said second cell through the pores of a porous metal cathode composed of metal selected from the group consisting of iron, nickel and alloys based on at least one of said metals, recovering the resulting alkali metal hydride produced by reaction between the alkali metal electrolytically liberated and the hydrogen introduced through the pores of the metal cathode, withdrawing amalgam depleted in alkali metal from the second cell, passing the hot withdrawn amalgam in countercurrent heat exchange relationship with aqueous cell feed material for the first cell, thereby cooling the amalgam and heating the aqueous cell feed, and charging the heated cell feed into the first cell as electrolyte and the cooled amalgam into the first cell as a liquid cathode.

5. A process for producing sodium hydride from a crude sodium salt brine which comprises: electrolyzing an aqueous solution of the salt brine in a first cell with a mercury cathode to obtain a liquid dilute sodium amalgam containing between about 0.1% and 0.8% by weight of soduim, withdrawing said amalgam from the zone of electrolysis in said first cell, introducing the dilute amalgam into a second electrolytic cell containing a fused salt bath melting below about 400° C. and consisting essentially of at least one sodium compound of the group consisting of sodium hydroxide and sodium halide, electrolyzing the fused salt bath with the dilute amalgam as the anode in said second cell while introducing hydrogen into said second cell through the pores of a porous metal cathode of metal selected from the group consisting of iron, nickel and alloys based on at least one of said metals and recovering the resulting sodium hydride produced by reaction between the sodium electrolytically liberated and the hydrogen introduced through the pores of the porous metal cathode.

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