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2,850,442

## BATH FOR THE MANUFACTURE OF SODIUM

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This application, a continuation-in-part of our copending application Serial Number 376,982, filed August 27, 1953, relates to the electrolytic production of metallic sodium and more particularly to a novel and useful bath and process for such production.

Metallic sodium is usually obtained from the electrolysis of sodium chloride. This is the cheapest and most abundant salt of the metal but melts at too high a temperature for convenient use alone in electrolytic baths. As a consequence, it is generally employed in admixture with calcium chloride. The resultant mixtures melt at a temperature sufficiently low for commercial acceptance and, upon electrolysis, yield sodium primarily. The mixtures generally contain a small percentage of barium chloride added as an impurity in the sodium chloride. As electrolysis proceeds, the concentration of this impurity increases until an equilibrium is reached. A typical conventional bath consists principally of 56–60% of calcium chloride, 1–5% of barium chloride and a remainder of sodium chloride.

The fused salt baths of prior practice have given good results. One disadvantage they possess, however, is that they codeposit some calcium at the cathode along with the sodium. In the conventional Downs cell of U. S. Patent 1,501,756, for example, a solution of calcium in liquid sodium is formed and rises into a sodium receiver. As this solution cools, some of the calcium precipitates and drops back into the bath. Since the precipitated calcium tends to block the pipe leading to the receiver, it is necessary to operate a stirring device to maintain sodium flow. Precipitated calcium also tends to cause short-circuits between the diaphragm and cathodes, decreasing diaphragm life and cell efficiency.

Another difficulty arises from the fact that all the calcium does not precipitate, as its solubility in sodium is still significant at the lowered temperature. The sodium produced from the conventional baths therefore contains a relatively high percentage of calcium metal, in some cases almost 1% by weight. Such a percentage of calcium cannot be tolerated in some modern applications of sodium and expensive procedures have been necessary to remove it.

Suggestions have been made from time to time as to the use of alternative bath compositions avoiding some of the disadvantages mentioned above but these baths have not found much favor. The Seward and Von Kugelgen U. S. Patents 841,724 and 868,670 and the Grabau Patent 464,097, for example, show several alternative baths. Although these patents are quite old, the baths disclosed therein have found no commercial acceptance as far as we are aware.

Filtration of the sodium contaminated with calcium as by a micrometallic filter can remove some of the impurity but undesirable quantities remain. Other methods are also available to reduce the calcium content but add an expensive step to the manufacturing process.

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An object of this invention is therefore provision of a new method for producing metallic sodium.

Another object is provision of a method for producing electrolytic sodium of a purity hitherto unattainable commercially.

A further object is provision of a novel and useful composition of matter suitable, in the fused state, for the electrolytic production of sodium.

The above-mentioned and still further objects are achieved in accordance with this invention by electrolysis of a fused bath consisting principally of strontium chloride. In practice a ternary salt mixture is formed containing strontium chloride, barium chloride and sodium chloride, and electrolyzed with direct current.

The preferred strontium-containing bath for producing sodium is one of a composition lying in the neighborhood of the  $\text{SrCl}_2\text{-BaCl}_2\text{-NaCl}$  eutectic mixture, i. e., about 60% by weight  $\text{SrCl}_2$ , 14%  $\text{BaCl}_2$ , and 26%  $\text{NaCl}$ . The equivalent molar percentages are about 42.5, 7.5, and 50.0 respectively. The melting point of this mixture is  $560^\circ\text{C}$ . For the purposes of this invention, the bath should contain between about 55 and 65% by weight of  $\text{SrCl}_2$ , about 10–20% by weight of  $\text{BaCl}_2$ , and a remainder of  $\text{NaCl}$ . The ternary system is discussed at some length by Vortisch, Neues Jahrb. Min. Geol. Palaeontol., 38, 201–217 (1914–15).

The preferred operating temperature of the bath is between about  $560^\circ\text{C}$ . and  $625^\circ\text{C}$ . Higher temperatures can be used but are unnecessary.

The sodium obtained from the present ternary baths is the purest yet produced commercially. It usually contains less than about 0.1% by weight of metallic impurities, largely strontium. If the sodium is cooled to about  $115^\circ\text{C}$ . and filtered or settled, i. e. allowed to stand, and decanted, the quantity of metallic impurities present can be reduced to less than 25 p. p. m. Filtration of sodium produced from the calcium-containing bath of a conventional Downs cell does not reduce the metallic impurities to less than about 0.04% by weight (400 p. p. m.).

Production of sodium from the strontium baths has other advantages than the elimination of impurities. Two of the most important of these are increase in current efficiency and increase in the life of the cell, particularly of the diaphragms interposed between the electrodes. A Downs cell normally operates at a current efficiency of about 83–85%. The ternary strontium bath improves this efficiency to about 85–89%. The life of the diaphragm is more than doubled in the calcium-free strontium baths.

Still further improvements in current efficiency can be obtained by adding about 1–2% by weight of sodium (or potassium) fluoride to the bath, the ratios of the other components remaining substantially unchanged. Thus a preferred bath contains about 60% by weight of  $\text{SrCl}_2$ , about 15%  $\text{BaCl}_2$ , 1–2%  $\text{NaF}$  and a remainder of  $\text{NaCl}$ . Baths of this composition will readily yield sodium with a current efficiency of about 90–95%. This high current efficiency is believed due to the effect of the sodium fluoride in suppressing the formation of a metallic sodium fog in the bath. The fluoride also lowers the eutectic melting point of the bath to a slight extent, i. e., to about  $550^\circ\text{C}$ . The purity of sodium obtained from and the diaphragm life in the quaternary bath are about the same as in the ternary bath discussed above. A disadvantage of the quaternary baths is that they attack the brickwork present in most commercial sodium cells.

There follow some examples which illustrate the practice of the invention in more detail. In these examples all percentages are by weight unless otherwise noted.

*Example 1*

This example shows the use of a ternary mixture of strontium, barium and sodium chlorides in producing sodium.

A salt mixture was formed consisting essentially of 58-60% strontium chloride ( $\text{SrCl}_2$ ) 18-20% barium chloride ( $\text{BaCl}_2$ ) and a remainder of sodium chloride. This mixture was melted at 560-570 C. in a substantially conventional Downs cell and electrolyzed at a potential varying between 6.2 and 7.4 volts.

Sodium was produced from this cell for several months. This sodium was exceptionally pure, generally containing less than 0.1% of foreign matter. Settling the liquid sodium at about 115° C. and decanting off the top portion reduced the content of metallic impurities in the decanted liquid to less than 25 p. p. m. Such pure sodium has never been obtained from a calcium chloride bath.

The life of the diaphragm in this bath was more than double that in a conventional fused-salt mixture.

Additions of sodium chloride and of small quantities of strontium and barium chlorides were employed to maintain the bath composition.

Stirring was employed occasionally but much less often than in the calcium-containing cells.

*Example 2*

The procedure of Example 1 was substantially repeated except that the salt mixture electrolyzed was the  $\text{SrCl}_2$ - $\text{BaCl}_2$ - $\text{NaCl}$  eutectic mixture consisting of 60%  $\text{SrCl}_2$ , 14%  $\text{BaCl}_2$ , and 26%  $\text{NaCl}$ . The results obtained were essentially the same as those of the previous example.

*Example 3*

This example shows the use of a quaternary mixture according to the practice of this invention.

An anhydrous salt mixture was made up containing about 55-60% strontium chloride, about 17-21% barium chloride, about 2% sodium fluoride ( $\text{NaF}$ ) and a remainder of sodium chloride. This mixture was melted in a Downs type cell at a steady temperature of 550-555° C. and electrolyzed at about 600° C. with direct current supplied at a potential of 6.4 volts. The chlorine liberated at the anode was almost free of fluorine. The sodium generally contained less than 0.1% strontium.

The bath composition was maintained approximately constant by regular additions of sodium chloride and occasional additions of small amounts of strontium and barium chlorides and sodium fluoride.

The test cell produced sodium with a current efficiency of 87-88% for periods totaling several weeks. The average current efficiency of fourteen cells operating with the conventional calcium chloride bath but otherwise comparable was 82-84% during these periods.

The cell diaphragm, renewed periodically, had a life at least double that in conventional Downs baths.

*Example 4*

Tests similar to those of Example 3 were repeated. For a 45-day period the current efficiency in the test cell averaged 90%, with a maximum of 94%. The sodium, after filtration, contained less than 25 p. p. m. of alkaline earth metal impurities. Current efficiencies of 94% and

purities of the figure given have never been obtained with calcium chloride baths.

It may be noted that the cell voltage is generally not much increased over that required for comparable operation in calcium chloride baths and in some cases has actually been lower. Thus over-all power efficiency may be improved with the present bath.

Having described our invention, we claim:

1. The method of producing metallic sodium containing less than 0.1% by weight of impurities which comprises electrolyzing with direct current a fused salt mixture comprising, by weight, 55-65% of strontium chloride, 10-20% of barium chloride and a remainder consisting essentially of sodium chloride.

2. The method of claim 1 in which the fusion temperature is about 560-625° C.

3. The method of claim 2 in which the bath consists essentially of about 60% by weight of strontium chloride, about 14% by weight of barium chloride and about 26% by weight of sodium chloride.

4. The method of claim 1 to which is added the additional step of filtering the metallic sodium to reduce the content of impurities to less than 25 p. p. m.

5. The method of claim 1 to which is added the additional step of settling the metallic sodium to reduce the content of impurities to less than 25 p. p. m.

6. The method of producing metallic sodium which comprises electrolyzing with direct current a fused salt mixture containing, by weight, about 60% of strontium chloride, about 20% of barium chloride, about 2% of sodium fluoride and a remainder consisting essentially of sodium chloride.

7. The method of claim 6 in which the temperature of the fused salt mixture is between about 550-625° C.

8. The process of continuously producing high purity metallic sodium which comprises (1) electrolyzing with direct current a fused salt mixture at about 560-625° C. containing by weight about 55-65% of strontium chloride, 10-20% of barium chloride, and a remainder consisting essentially of sodium chloride, (2) withdrawing sodium from the mixture as it is formed and (3) replenishing the mixture by additions thereto of sodium chloride and smaller additions of strontium chloride and barium chloride.

9. The process of claim 8 in which the salt mixture contains up to about 2% by weight of sodium fluoride.

10. A composition of matter comprising, by weight, about 55-65% of strontium chloride, about 10-20% of barium chloride, about 1-2% of fluoride of an alkali metal and a remainder consisting essentially of sodium chloride.

11. A composition of matter comprising, by weight, about 60% of strontium chloride, about 20% of barium chloride, about 2% of sodium fluoride and a remainder consisting essentially of sodium chloride.

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