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ELECTROLYTIC PRODUCTION OF ALKALI METALS

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Fig. 1.

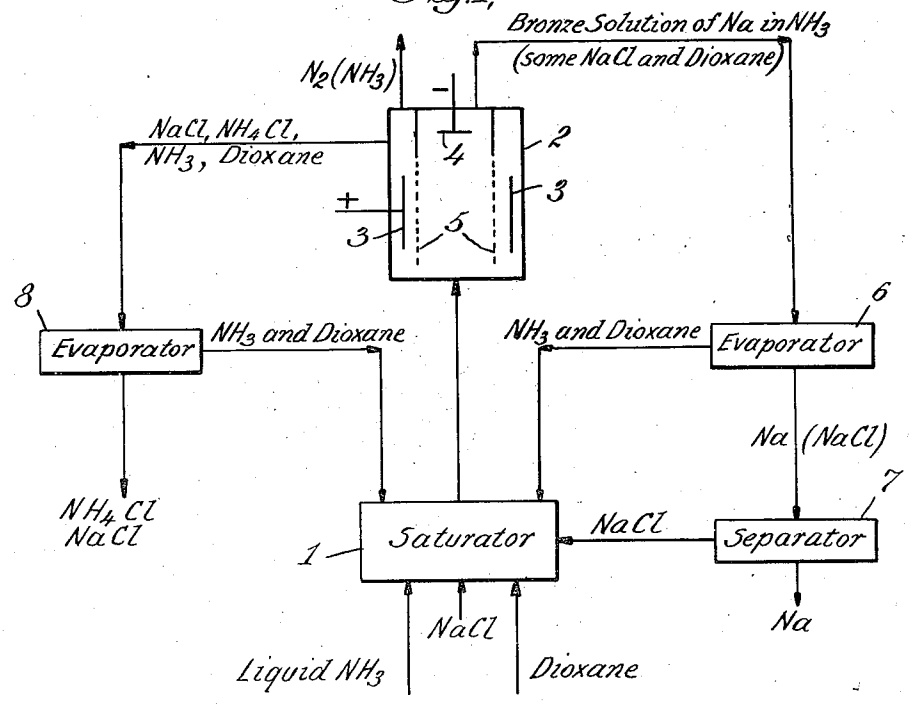
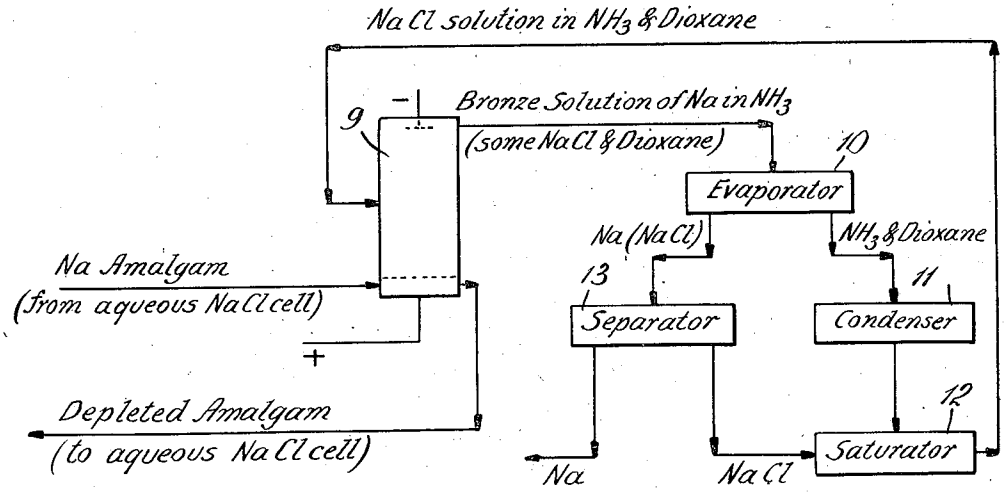


Fig. 2.



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ELECTROLYTIC PRODUCTION OF ALKALI METALS

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14 Claims. (Cl. 204—59)

This invention relates to the production of alkali metals.

Metallic sodium or potassium is ordinarily produced by the electrolysis of either the fused alkali chloride or the fused alkali hydroxide. The electrolysis of the fused chloride presents several serious difficulties, among which are severe corrosion of equipment and the necessity for employing very high temperatures to maintain the chloride in a fused condition. The electrolysis of fused alkali hydroxide also requires the employment of relatively high temperatures to maintain the hydroxide in a fused condition. Furthermore, the anode reaction in the electrolysis of the hydroxide results in the formation of oxygen and water; the water thus formed tends to diffuse through the fused alkali hydroxide electrolyte and to react with the metal product, thereby diminishing the yield of metal and generating hydrogen. The evolution of hydrogen and oxygen causes frequent explosions to occur, which are obviously objectionable.

It has been proposed to prepare metallic sodium by the electrolysis of a solution of sodium chloride in liquid ammonia. However, as stated by Ewan in United State Patent 1,538,389, the solubility relationships of the sodium chloride-sodium-liquid ammonia system are such that the sodium product formed at the cathode dissolves to a substantial extent in the electrolyte and diffuses toward the anode where it reacts with the anode products, or, if an amalgam anode is used, is absorbed in the mercury. Moreover, an electrolyte solution containing an appreciable amount of dissolved free alkali metal causes shorting of the cell due to the high conductivity of the free electrons in such solutions. It has been proposed to employ cells having diaphragms of asbestos cloth or the like in the electrolysis of solutions of sodium chloride in liquid ammonia to prevent diffusion of the sodium product through the NaCl-liquid ammonia solution. However, since the catholyte (consisting of liquid NH_3, NaCl and Na) and anolyte consisting of liquid NH_3, NaCl and anode products) in such a cell are mutually miscible, the diaphragm is not effective to keep the Na from diffusing to the anode unless the Na concentration in the catholyte is maintained quite low; under such conditions the electrolytic efficiency of the cell is low and recovery of metallic sodium from the cathode liquor is difficult because of the low concentration of sodium therein.

Ewan has described in United States Patents 1,538,389 and 1,538,390 methods for the production of metallic sodium involving the electrolysis of solutions of sodium cyanide or sodium iodide in liquid ammonia in a cell employing a sodium amalgam anode, whereby a layer of liquid ammonia rich in metallic sodium product separates at the cathode and is withdrawn. However, for the reasons pointed out above, Ewan states that sodium chloride is not suitable in the practice of his process. Obviously, a process for the manufacture of metallic sodium permitting the employment of relatively inexpensive sodium chloride would be highly desirable; such a process has not, however, been attainable commercially by the methods known to the prior art.

It is the object of this invention to provide a simple and efficient process for the production of metallic sodium or potassium, preferably from the corresponding chloride, or, if desired, from more soluble salts such as the bromide, iodide, or cyanide.

We have found that by electrolyzing a sodium or potassium chloride solution in liquid ammonia containing an inert organic solvent in which the free metal is substantially insoluble, a separate layer of a solution of sodium or potassium in liquid ammonia rich in the desired metal product is formed at the cathode, from which the free metal may be readily recovered. By operating in accordance with our invention, metallic sodium or potassium may be obtained in excellent yields, since diffusion of the metal to the anode and consequent loss thereof is substantially avoided. Solvents which may be used in the practice of our invention are dioxane; ethers, particularly alkyl ethers of molecular weight not exceeding 75, such as diethyl ether; amines, particularly lower alkyl amines of molecular weight not exceeding 75 such as ethylamine; benzene and other organic solvents in which ammonia is soluble but in which sodium is substantially insoluble; we prefer to use dioxane since we have found this solvent to be highly suitable for carrying out our novel process.

In producing sodium, for example, in accordance with our invention, a solution of sodium chloride in liquid ammonia containing an inert organic solvent in which sodium is insoluble is formed in any suitable manner. Preferably, the liquid ammonia and organic solvent are first mixed and the mixture then agitated with sodium chloride. The proportions of liquid ammonia and organic solvent employed may vary widely depending upon the solvent used and the relative volumes of the two liquid phases maintained in the cell; generally the amount of organic solvent will vary between about 25% and about 100% of the liquid ammonia. When using dioxane, we have found that about 40% by weight of dioxane to about 60% by weight of ammonia forms a suitable solvent mixture. The amount of sodium chloride dissolved in the solvent mixture may likewise vary; we have found, however, that it is advantageous substantially to saturate the solvent mixture with sodium chloride. Sodium chloride may be dissolved in the above sol-

vent mixture at any suitable temperature and pressure so long as the liquid ammonia solvent is maintained in the liquid phase; thus, for example, sodium chloride may be dissolved in the solvent mixture at room temperatures, e. g., 25° C., and at a pressure of about 9 atmospheres, though it has been found advantageous to operate at lower temperatures, e. g., —10° C., from the standpoint of higher salt solubility, higher cell conductivity, and lower pressures.

The solution thus formed is then introduced into a cell of any suitable design and electrolyzed. The electrolysis is preferably carried out as a continuous process, the electrolyte being thus continuously introduced into the cell and the products of the electrolysis being continuously withdrawn. The electrodes of the cell may be constructed of inert metallic compositions, such as chrome iron or platinum, in which case nitrogen and an ammonium salt (e. g., ammonium chloride, when an alkali chloride is being electrolyzed) are continuously formed at the anode. The nitrogen gas thus formed is vented from the cell carrying with it a little ammonia and, after recovery of the ammonia, may be used as desired; e. g., in an ammonia synthesis plant. The ammonium chloride should be removed from the anode to prevent its diffusion through the cell and resulting reaction thereof with sodium in the neighborhood of the cathode, as the sodium would react therewith to form sodium chloride, hydrogen, and ammonia. To minimize diffusion of the ammonium chloride towards the cathode, a porous diaphragm (e. g., formed from asbestos or porous ceramic ware) may be positioned between the anode and cathode. A solution containing sodium chloride, ammonium chloride, liquid ammonia, and dioxane is preferably continuously withdrawn from the neighborhood of the anode, the solvents volatilized, and the resulting mixture of ammonium chloride and sodium chloride treated as desired; e. g., the mixture may be treated in an ammonia-soda process to convert the sodium chloride to sodium carbonate and the ammonium chloride, if desired, to calcium chloride and ammonia.

Sodium amalgam, which may be produced by the electrolysis of an aqueous sodium chloride solution in a cell employing a mercury cathode and which may contain from about 0.1% to about 1.5% sodium, may be used with advantage as the anode in accordance with our invention, since in this case the only anode product is the depleted amalgam which may be continuously withdrawn and replenished with sodium. Cells having sodium amalgam anodes are preferably used in the electrolysis of iodide, bromide or cyanide solutions, hereinafter described.

Upon electrolysis of the sodium chloride solution, a bronze layer which comprises a solution of sodium in liquid ammonia forms at the cathode. The sodium chloride solution is more dense than the bronze sodium solution and hence the latter floats on the sodium chloride solution. Therefore, the cell should be so arranged that the cathode is above the anode, whereby the bronze sodium solution may form a liquid layer surrounding the inert metal cathode and thereafter the sodium solution may serve as cathode in the cell. The organic solvent generally tends to blend with the lower liquid layer, the solution of sodium chloride in ammonia upon which the bronze sodium solution floats. It has been found advantageous to avoid an excess of organic solvent such that it forms in the cell a third liquid layer composed largely of organic solvent, because the conductivity of such third layer is undesirably low.

The temperature at which the electrolysis is carried out in accordance with our invention may vary between about —20° and about 30° C. The pressure within the cell will depend upon the temperature and should be sufficient to maintain the ammonia in the liquid phase; thus the pressure may vary between about 1.5 and about 10 atmospheres. The current density may vary depending somewhat upon the design of the cell, but generally the current density should be between about 0.01 and about 0.04 ampere per sq. cm. The voltage applied to the cell depends somewhat upon the current density, somewhat upon the design of the cell, and also upon the cell resistance, which may vary with the nature of the electrolyte solution; the voltage may vary between about 0.5 and about 20 volts for cells with amalgam anodes, and from about 3 to 25 volts for cells with inert anodes.

The bronze solution of sodium in ammonia formed at the cathode in accordance with the process of our invention is continuously withdrawn and the free metal recovered therefrom by evaporation of the ammonia solvent. Any dioxane present in the solution is also removed by evaporation. The metal thus obtained may be finished as desired. Small amounts of alkali chloride are usually present in this solution, from which the free metal may easily be separated by heating the mixture of metal and metal chloride to melt the metal and separating the molten metal from the solid residue.

Figures 1 and 2 illustrate preferred embodiments of our invention, as applied to production of sodium from sodium chloride, Figure 1 illustrating the embodiment in which a cell having an inert anode is employed, and Figure 2 illustrating the embodiment employing a cell using a sodium amalgam anode.

In Figure 1, liquid ammonia and dioxane are introduced into saturator 1 and thoroughly mixed; sodium chloride is then introduced into saturator 1 to form a substantially saturated solution of sodium chloride in the solvent mixture. This solution is then introduced into a cylindrical cell 2 provided with an annular platinum anode 3 concentric with the cell, and a centrally located chrome iron cathode 4, separated from the anode by a cylindrical shell 5 of porous ceramic ware, the cathode being disposed in the upper part of the inner cathode chamber formed by the ceramic shell. Upon electrolysis of the sodium chloride-liquid ammonia-dioxane solution, a bronze solution of liquid ammonia rich in sodium and containing small quantities of sodium chloride and dioxane is continuously formed at the cathode, where it separates as a liquid layer which thereafter serves as cathode in the cell, and wherefrom it is withdrawn to evaporator 6. In evaporator 6 the ammonia and dioxane are removed and returned to saturator 1. The mixture of sodium and sodium chloride thus formed is then passed to separator 7, wherein the sodium is melted and withdrawn as product, the sodium chloride residue being returned to saturator 1. At the anode, nitrogen and ammonium chloride are continuously formed. The nitrogen is vented from the system along with a little ammonia. A solution containing sodium chloride, ammonium chlo-

ride, liquid ammonia, and dioxane is continuously withdrawn from the upper part of the annular anode chamber and passed to evaporator 8, wherein the ammonia and dioxane are evaporated and returned to saturator 1; the mixture of sodium and ammonium chlorides thus obtained is used as desired.

In Figure 2, sodium amalgam produced by the electrolysis of an aqueous solution of sodium chloride in a cell employing a mercury cathode is continuously introduced into cell 9, forming a layer at the bottom thereof. A solution of sodium chloride in ammonia containing dioxane formed as hereinafter described is introduced into cell 9, forming a layer above the sodium amalgam anode. Cell 9 is provided with a chrome iron cathode disposed above the anode. Upon passage of an electric current through the cell, a bronze solution of sodium in ammonia containing some dioxane and sodium chloride is continuously formed at the cathode and withdrawn to evaporator 10. In evaporator 10, ammonia and dioxane are removed, passed to condenser 11, and thence to saturator 12. The sodium residue containing some sodium chloride is withdrawn from evaporator 10 to separator 13, wherein the mixture is heated and molten sodium withdrawn as product. The sodium chloride residue from separator 13 is introduced into saturator 12, wherein it dissolves in the ammonia and dioxane present in saturator 12, and is returned to cell 9. Depleted amalgam is continuously withdrawn from the anode and returned to the aqueous sodium chloride cell.

The following examples are illustrative of the practice of this invention. Amounts are given in parts by weight.

Example 1.—Liquid ammonia and dioxane were mixed in the proportions of about 60 parts of ammonia per 40 parts of dioxane and the solvent mixture then saturated by agitation with about 3 parts of sodium chloride per 100 parts of solvent mixture at 25° C. and a pressure of about 9 atmospheres. The solution was continuously introduced into a cell maintained at a temperature of about 25° C. and a pressure of about 9 atmospheres, provided with a chrome iron cathode and a platinum anode, the cell being arranged with the cathode at the top thereof. A potential of about 18 volts was applied to the cell. At the commencement of the electrolysis the solution became blue near the cathode due to the dissolution of the sodium product therein. Shortly, however, a bronze solution was continuously formed at the cathode and floated on the surface of the blue solution. The bronze solution was continuously removed from the cathode, and the ammonia and small amounts of dioxane evaporated therefrom, leaving a residue of sodium containing small amounts of sodium chloride. The sodium was recovered by heating the residue and withdrawing molten sodium product. Nitrogen and ammonium chloride were continuously formed at the anode, the nitrogen being vented from the cell. A solution containing ammonium chloride, sodium chloride, liquid ammonia, and dioxane was continuously withdrawn from the neighborhood of the anode, the ammonia and dioxane evaporated therefrom, and the residue discarded.

Example 2.—Liquid ammonia and dioxane were mixed in the proportions of about 60 parts of ammonia per 40 parts of dioxane and the solvent mixture then saturated by agitation with about 12 parts of sodium chloride per 100 parts of solvent mixture at a temperature of about −10° C. and a pressure of about 1.5 atmospheres. The solution thus formed was continuously introduced into a cell maintained at a temperature of about −10° C. and a pressure of about 1.5 atmospheres, provided with a chrome iron cathode and a platinum anode, the cell being arranged with the cathode at the top thereof. A potential of about 18 volts was applied to the cell. In a short time a bronze solution continuously separated at the cathode and floated on the surface of the electrolyte. The bronze solution was continuously withdrawn, the ammonia and small amounts of dioxane evaporated therefrom, leaving a residue of sodium containing small amounts of sodium chloride. The sodium was recovered by heating the residue and withdrawing molten sodium product. Nitrogen and ammonium chloride were continuously formed at the anode; the nitrogen was vented from the cell along with a little ammonia. A solution containing ammonium chloride, sodium chloride, liquid ammonia, and dioxane was continuously withdrawn from the anode. The ammonia and dioxane were evaporated, condensed, and mixed with the condensed ammonia and dioxane recovered from the bronze sodium solution. Additional quantities of sodium chloride were dissolved in the mixture and the solution returned to the cell. The residue of sodium chloride and ammonium chloride was discarded.

Example 3.—Liquid ammonia and dioxane were mixed in the proportions of about 60 parts ammonia per 40 parts dioxane and the solvent mixture was then saturated by agitation with about 3 parts of sodium chloride per 100 parts of solvent mixture at a temperature of about 25° C. and a pressure of about 9 atmospheres. The solution was continuously introduced into a cell maintained at a temperature of about 25° C. and a pressure of about 9 atmospheres and electrolyzed between a sodium amalgam anode containing about 1.0% sodium and a chrome iron cathode, the cathode being disposed above the anode. A potential of about 18 volts was applied to the cell. A bronze solution continuously separated at the cathode and was continuously withdrawn. Ammonia and small amounts of dioxane were evaporated from this solution, leaving a residue containing sodium and small quantities of solium chloride. The sodium was recovered by heating the residue and withdrawing molten sodium. Depleted amalgam was continuously withdrawn from the anode.

Example 4.—Liquid ammonia and dioxane were mixed in the proportions of about 60 parts ammonia per 40 parts dioxane and the solvent mixture was then saturated by agitation with about 12 parts of sodium chloride per 100 parts of solvent mixture at a temperature of about −10° C. and a pressure of about 1.5 atmospheres. The solution was then continuously introduced into a cell maintained at a temperature of about −10° C. and a pressure of about 1.5 atmospheres, and electrolyzed between a sodium amalgam anode containing about 1.0% sodium and a chrome iron cathode, the cathode being disposed above the anode. A potential of about 18 volts was applied to the cell. A bronze solution continuously separated at the cathode and was continuously withdrawn therefrom. Ammonia and small amounts of dioxane were evaporated from this solution and condensed, leaving a residue of sodium and sodium chloride. The sodium was recovered from the

residue by heating the residue to melt the sodium and withdrawing molten sodium product. The sodium chloride was mixed with the condensed ammonia and dioxane and returned to the cell. Depleted amalgam was continuously withdrawn from the anode.

It is to be understood that while the above examples describe the use of dioxane as the organic solvent used in accordance with our invention, other inert organic solvents in which sodium is insoluble, such as ether and benzene, may also be used.

While our invention is particularly directed to the production of sodium from sodium chloride, it will be understood that it is also applicable to the production of sodium or potassium using instead of sodium chloride salts such as sodium bromide, sodium iodide, sodium cyanide, potassium bromide, potassium cyanide and potassium iodide. Of these salts, potassium bromide and cyanide, like the chlorides of sodium and potassium, are only moderately soluble in liquid ammonia. Hence, by use of an organic solvent, in accordance with our invention, a separate liquid phase rich in dissolved potassium forms at the cathode. Sodium bromide, sodium cyanide and the iodides of sodium and potassium are more soluble in liquid ammonia. However, electrolysis of these more soluble salts in ammonia-organic solvent solutions also results in advantages in operation as compared with the electrolysis of these salts in ammonia alone in that addition of the organic solvent decreases the solubility of the free metal in the liquid ammonia electrolyte and thus avoids short-circuiting of the cell by the metal dissolved in the electrolyte as well as the undesirable anode reactions which occur when the dissolved metal diffuses to the anode.

It will be seen from the above description that the process of our invention permits the production of metallic sodium or potassium from relatively inexpensive sodium or potassium chloride by a process which employs convenient operating temperatures and which does not involve serious problems of corrosion.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. A process for the production of a metal from the group sodium and potassium which comprises electrolyzing a solution of the corresponding metal chloride dissolved in a solvent mixture including liquid ammonia and an inert organic liquid in which liquid ammonia is soluble but in which the metal is substantially insoluble selected from the group consisting of dioxane, alkyl ethers of molecular weight not exceeding 75, alkyl amines of molecular weight not exceeding 75 and benzene, said organic liquid being present in such amount that a separate alkali-metal-rich liquid phase is formed upon solution of alkali metal in said solvent mixture.

2. A process for the production of metallic sodium which comprises electrolyzing a solution of sodium chloride dissolved in a solvent mixture including liquid ammonia and dioxane, said dioxane being present in such amount that a separate sodium-rich liquid phase is formed upon solution of metallic sodium in said solvent mixture.

3. A process for the production of metallic sodium which comprises electrolyzing a solution of sodium chloride dissolved in a solvent mixture including liquid ammonia and an alkyl ether of molecular weight not exceeding 75, said ether being present in such amount that a separate sodium-rich liquid phase is formed upon solution of metallic sodium in said solvent mixture.

4. A process for the production of metallic sodium which comprises electrolyzing a solution of sodium chloride dissolved in a solvent mixture including liquid ammonia and benzene, said benzene being present in such amount that a separate sodium-rich liquid phase is formed upon solution of metallic sodium in said solvent mixture.

5. A substantially continuous process for the production of metallic sodium which comprises forming a mixture of liquid ammonia and an inert organic liquid in which liquid ammonia is soluble but in which sodium is substantially insoluble selected from the group consisting of dioxane, alkyl ethers of molecular weight not exceeding 75, alkylamines of molecular weight not exceeding 75, and benzene, said organic liquid being present in such amount that a separate sodium-rich liquid phase is formed upon solution of metallic sodium in the solvent mixture, dissolving sodium chloride in the solvent mixture, continuously introducing the sodium chloride solution into a cell provided with inert electrodes, the cell being arranged so that a porous diaphragm is interposed between the cathode and the anode, electrolyzing the solution, continuously withdrawing a solution containing sodium dissolved in liquid ammonia from the cathode portion of the cell, recovering metallic sodium therefrom, continuously removing from the cell nitrogen gas generated at the anode, and continuously withdrawing a solution containing ammonium chloride, sodium chloride, and liquid ammonia from the anode portion of the cell.

6. A substantially continuous process for the production of metallic sodium which comprises forming a mixture of liquid ammonia and dioxane in the proportions of between about 25 and about 100 parts of dioxane per 100 parts of ammonia, dissolving sodium chloride in the solvent mixture, continuously introducing the sodium chloride solution into a cell provided with inert electrodes, the cell being arranged so that the cathode is disposed in the upper part of the cell, electrolyzing the solution, continuously withdrawing a solution containing sodium dissolved in liquid ammonia from the cathode portion of the cell, recovering metallic sodium therefrom, continuously removing from the cell nitrogen gas generated at the anode, and continuously withdrawing a solution containing ammonium chloride, sodium chloride, liquid ammonia, and dioxane from the anode portion of the cell.

7. A substantially continuous process for the production of metallic sodium which comprises forming a mixture of liquid ammonia and an alkyl ether of molecular weight not exceeding 75 in the proportions of between about 25 and about 100 parts of ether per 100 parts of ammonia, dissolving sodium chloride in the solvent mixture, continuously introducing the sodium chloride solution into a cell provided with inert electrodes, the cell being arranged so that the cathode is disposed in the upper part of the cell, electrolyzing the solution, continuously withdrawing a solution containing sodium dissolved in liquid ammonia from the cathode portion of

the cell, recovering metallic sodium therefrom, continuously removing from the cell nitrogen gas generated at the anode, and continuously withdrawing a solution containing ammonium chloride, sodium chloride, liquid ammonia, and ether from the anode portion of the cell.

8. A substantially continuous process for the production of metallic sodium which comprises forming a mixture of liquid ammonia and benzene in the proportions of between about 25 and about 100 parts of benzene per 100 parts of ammonia, dissolving sodium chloride in the solvent mixture, continuously introducing the sodium chloride solution into a cell provided with inert electrodes, the cell being arranged so that the cathode is disposed in the upper part of the cell, electrolyzing the solution, continuously withdrawing a solution containing sodium dissolved in liquid ammonia from the cathode portion of the cell, recovering metallic sodium therefrom, continuously removing from the cell nitrogen gas generated at the anode, and continuously withdrawing a solution containing ammonium chloride, sodium chloride, liquid ammonia, and benzene from the anode portion of the cell.

9. A substantially continuous process for the production of metallic sodium which comprises forming a mixture of liquid ammonia and dioxane in the proportions of about 40 parts dioxane to about 60 parts ammonia, saturating the solvent mixture with sodium chloride by agitating the mixture with about 3 parts of sodium chloride at a temperature of about 25° C. and a pressure of about 9 atmospheres, continuously introducing the saturated sodium chloride solution into a cell provided with inert metallic electrodes consisting of an annular anode and a centrally located cathode, a porous diaphragm being interposed therebetween, electrolyzing the solution at a temperature of about 25° C. and a pressure of about 9 atmospheres, continuously withdrawing a solution containing sodium dissolved in liquid ammonia from the cathode portion of the cell, recovering metallic sodium therefrom, continuously removing from the cell nitrogen gas generated at the anode, and continuously withdrawing a solution containing ammonium chloride, sodium chloride, liquid ammonia, and dioxane from the anode portion of the cell.

10. A substantially continuous process for the production of metallic sodium which comprises mixing liquid ammonia and an inert organic liquid in which liquid ammonia is soluble but in which sodium is substantially insoluble selected from the group consisting of dioxane, alkyl ethers of molecular weight not exceeding 75, alkylamines of molecular weight not exceeding 75, and benzene, said organic liquid being present in the mixture in such amount that a separate sodium-rich liquid phase is formed upon solution of metallic sodium in said mixture, dissolving sodium chloride in the solvent mixture, continuously introducing the sodium chloride solution into a cell provided with a sodium amalgam anode and an inert cathode, the cell being arranged so that the cathode is disposed above the anode, electrolyzing the solution, continuously withdrawing depleted amalgam from the anode portion of the cell, continuously withdrawing a solution containing sodium in liquid ammonia from the cathode portion of the cell, and recovering sodium from said solution.

11. A substantially continuous process for the production of metallic sodium which comprises mixing liquid ammonia and dioxane in the proportions of between about 25 and about 100 parts of dioxane per 100 parts of ammonia, saturating the solvent mixture with sodium chloride, continuously introducing the saturated sodium chloride solution into a cell provided with a sodium amalgam anode and an inert cathode, the cell being arranged so that the cathode is disposed above the anode, electrolyzing the solution, continuously withdrawing depleted amalgam from the anode portion of the cell, continuously withdrawing a solution containing sodium in liquid ammonia from the cathode portion of the cell, and recovering sodium from said solution.

12. A substantially continuous process for the production of metallic sodium which comprises mixing liquid ammonia and an alkyl ether of molecular weight not exceeding 75 in the proportions of between about 25 and about 100 parts of an alkyl ether of a molecular weight not exceeding 75 per 100 parts of ammonia, saturating the solvent mixture with sodium chloride, continuously introducing the saturated sodium chloride solution into a cell provided with a sodium amalgam anode and an inert cathode, the cell being arranged so that the cathode is disposed above the anode, electrolyzing the solution, continuously withdrawing depleted amalgam from the anode portion of the cell, continuously withdrawing a solution containing sodium in liquid ammonia from the cathode portion of the cell, and recovering sodium from said solution.

13. A substantially continuous process for the production of metallic sodium which comprises mixing liquid ammonia and benzene in the proportions of between about 25 and about 100 parts of benzene per 100 parts of ammonia, saturating the solvent mixture with sodium chloride, continuously introducing the saturated sodium chloride solution into a cell provided with a sodium amalgam anode and an inert cathode, the cell being arranged so that the cathode is disposed above the anode, electrolyzing the solution, continuously withdrawing depleted amalgam from the anode portion of the cell, continuously withdrawing a solution containing sodium in liquid ammonia from the cathode portion of the cell, and recovering sodium from said solution.

14. A substantially continuous process for the production of metallic sodium which comprises mixing liquid ammonia and dioxane in the proportions of about 60 parts ammonia to about 40 parts dioxane, saturating the solvent mixture with sodium chloride by agitating the mixture with about 3 parts of sodium chloride at a temperature of about 25° C. and a pressure of about 9 atmospheres, continuously introducing the saturated sodium chloride solution into a cell provided with a sodium amalgam anode containing about 1.0% sodium and an inert metallic cathode and maintained at a temperature of about 25° C. and a pressure of about 9 atmospheres, the cell being arranged so that the cathode is disposed above the anode, electrolyzing the solution, continuously withdrawing depleted amalgam from the anode portion of the cell, continuously withdrawing a solution containing sodium in liquid ammonia from the cathode portion of the cell, and recovering sodium from said solution.

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