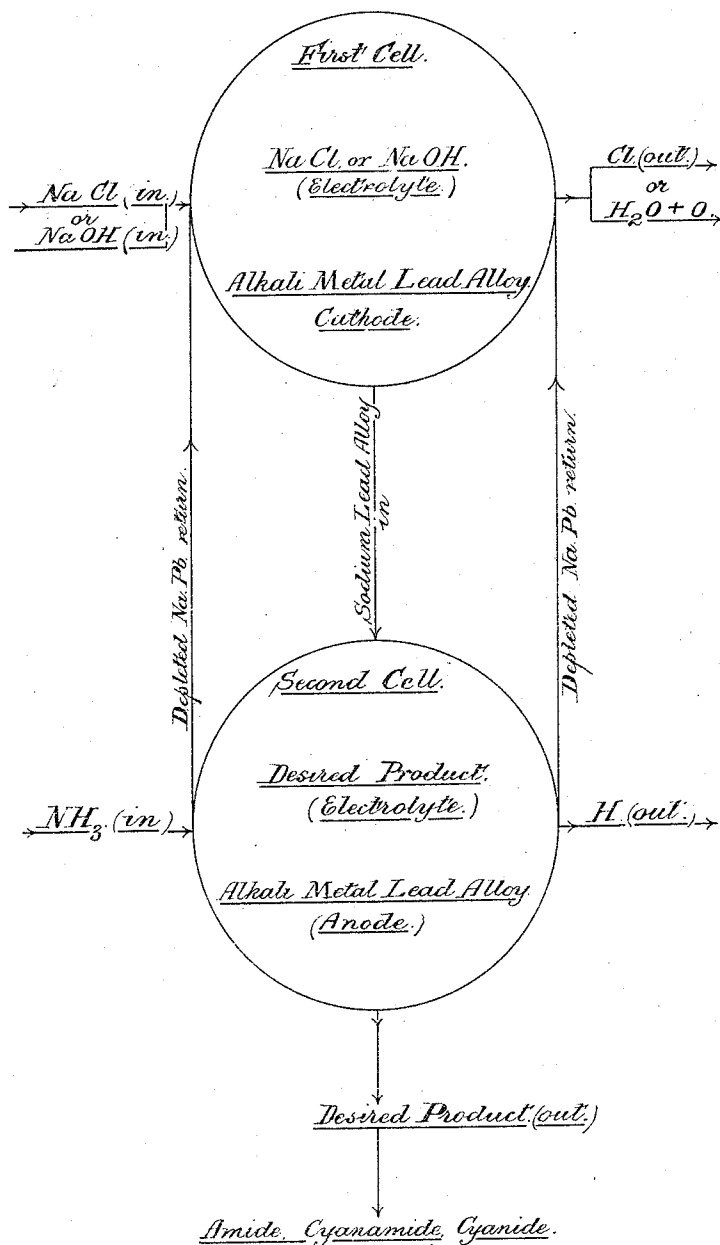


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 MANUFACTURE OF METALLIC AMIDS, CYANAMIDS, AND CYANIDS.  
 APPLICATION FILED APR. 14, 1910.

1,163,498.

Patented Dec. 7, 1915.



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# UNITED STATES PATENT OFFICE.

EDGAR ARTHUR ASHCROFT, OF LONDON, ENGLAND.

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1,163,498.

Specification of Letters Patent.

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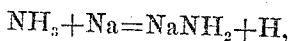
Application filed April 14, 1910. Serial No. 555,530.

*To all whom it may concern:*

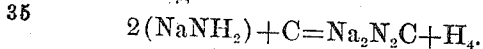
Be it known that I, EDGAR ARTHUR ASHCROFT, a subject of the King of Great Britain and Ireland, of 99 Buckingham Palace road, in the county of London, England, have invented new and useful Improvements in the Manufacture of Metallic Amids, Cyanamids, and Cyanids, of which the following is a specification.

My invention relates to the direct production, by electrolysis, of amids, cyanamids, and cyanids, of the alkali metals, such for example as sodium, or potassium, from raw materials, (such as the chlorids, or hydrates, of alkali metals) and nitrogenous matter or both nitrogenous matter and carbon, or carbonaceous gas, according to whether amids, cyanamids, or cyanids, are to be produced.

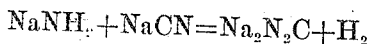
It has long been known that if nitrogenous matter, such as ammonia gas, be brought into contact with metallic sodium, at a temperature above the melting point of sodium amid (120° centigrade), and below its decomposition point (about 440° centigrade), fused sodium amid will readily be produced, the reaction being



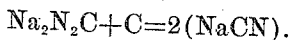
and that this amid, if brought into contact with carbon, or carbonaceous gas, such as acetylene, or coal gas, at a temperature above 350° centigrade and below 600° centigrade, will yield disodium cyanamid, the reaction being



It is also known that sodium amid in contact with sodium cyanid at a temperature just above 400° centigrade will react and yield disodium cyanamid according to the reaction



and that disodium cyanamid will react with carbon at a temperature of about 800° centigrade and form cyanid, the reaction being



It is known that all these reactions may be made nearly quantitative and that similar reactions take place with potassium and some other metals. I am aware that it has been suggested to substitute, for metal sodium, sodium-lead and other alloys in the produc-

tion of sodium amid by injecting ammonia into the molten alloy, and also to produce the said alloy continuously by electrolysis, but this method has hitherto had serious practical disadvantages, and, in consequence, has not been adopted in practice.

I have discovered that either amids, cyanamids, or cyanids, of the alkali metals, can be economically and conveniently produced according to a new process based upon the process described in the specification of United States Patent 801199 dated the 10th October 1905 granted to me.

In carrying the process according to my present invention into effect (taking the production of sodium derivatives as an example), I employ a double cell apparatus and an intermediate electrode of a molten metal, such, for example, as lead, mercury, or tin, or an alloy of any of these, (and I may add any other suitable metal), with which is alloyed the sodium produced in the first cell, and then this intermediate electrode is conveyed to the second cell where it is subjected to anode reactions, as described in the specification of my aforesaid Patent No. 801199, but, in carrying out my present invention, I may use, in the first cell, other raw materials than the chlorid of the desired metal, such, for instance, as the hydrate of sodium (caustic soda), or the sulfid of sodium, either alone, or in any suitable admixture with fluxing material, such as sodium, or potassium, chlorid, iodid, or the like, and in the second cell I substitute for the electrolytes recommended for the production of alkali metals in accordance with my aforesaid Patent No. 801,199, an electrolyte consisting of fused amid, cyanamid, or cyanid, or the like, of the metal under consideration, for instance, sodium amid alone, or in various admixtures, according to the product which it is desired to obtain. When mercury is employed for the intermediate electrode, I may use a solution of the raw material, such as chlorid of sodium, or the like, as the electrolyte in the first cell. If sodium amid, for example, be the product which is to be obtained by the process of my present invention, anhydrous ammonia in the form of gas is conducted into the second cell through any convenient pipe, or through a hollow cathode, and this ammonia gas, by coming

in contact with the nascent sodium produced, forms more  $\text{NaNH}_2 + \text{H}$  (the hydrogen escaping) and thus continuously augments the electrolyte which is periodically  
5 tapped off for use for any desired purpose.

In the operation it is desirable, in order to secure maximum efficiency and avoid loss of ammonia, to keep the temperature of the second cell as low as possible consistent with  
10 the free movement of the anode alloy, a temperature of, say, between  $250^\circ$  and  $350^\circ$  centigrade being suitable, the higher temperatures being necessary when a fused electrolyte is used in the first cell and an  
15 intermediate electrode of lead alloy, the lower temperatures being preferable when a solution of the raw materials is used in the first cell and mercury is used for the intermediate electrode.

If cyanamid is to be produced, a similar procedure is followed, except that carbon, in any suitable form is added to the electrolyte in the second cell and allowed to react with the amid as fast as it is formed, thus producing the cyanamid, and that a fused electrolyte, and not a solution of the raw materials, must be used in the first cell, and mercury is not suitable for the intermediate electrode. At the start, the electrolyte may  
20 be introduced into the cell as cyanamid, or the cyanamid may be formed in the cell by means of ammonia and carbon. The temperature employed in the second cell in this case will be somewhat higher (say  $500^\circ$  centigrade), especially toward the end of the  
25 reaction and previous to drawing a charge, so that the produced cyanamid remains fused and mobile and can be tapped off periodically.

When cyanid is to be produced, the procedure is the same as in making the cyanamids, except that the temperature is raised to or about  $800^\circ$  centigrade, preferably toward the end of the reaction and before  
30 drawing off a charge, and that more carbon is added. In starting the process, the electrolyte may be introduced into the cell as cyanid, or the cyanid may be formed in the cell by causing carbon and ammonia to react  
35 with the nascent sodium.

It will be evident that the process according to my present invention presents great economical advantages over the hitherto known methods of producing amids, cyanamids, and cyanids, as it constitutes a continuous process for the manufacture of the said products direct from the raw materials (such, for example, as sodium chlorid, or caustic soda) with ammonia, or ammonia  
40 and carbon.

Considering the present industry as a whole whereby sodium metal, for example, is first produced electrolytically and afterward employed according to the known  
45 methods for making the desired products,

my present invention avoids all the labor and other costs of collecting and packing the metal and re-treating it in separate apparatus heated externally.

Even when, in carrying out my present invention, caustic soda is employed as the raw material in the first cell, the desired products can be obtained far more economically than by the methods hitherto employed, partly because of the greater electrical efficiency obtained, in the process according to my invention, in the first cell, (the contained water of the caustic soda escaping freely at the upper part of the cell being eliminated largely as steam and not decomposed by the current), and partly because of the avoidance, as aforesaid, of much labor and other items of cost in separate sodium production, and collection, packing, and the like.  
50

In the accompanying diagrammatic illustration, the first cell may contain as electrolyte sodium chlorid or sodium hydroxid, the cathode being alkali metal lead alloy. The alkali metal lead alloy which may be sodium-lead passes during the operation of the process into the second cell where it becomes the anode, the electrolyte in the second cell being the desired product.  
55

As will be seen from the illustration, chlorin, or watery vapor (steam) plus oxygen escapes from the first cell while hydrogen escapes from the second cell, ammonia being introduced into the second cell to obtain the required reaction and the depleted sodium-lead alloy being continuously returned to the first cell.  
60

When a fused halogen salt is the raw material used in the first cell, anodes of graphite or carbon, are most suitable for this cell, chlorin, escaping. When caustic soda is the raw material employed, anodes of nickel are most suitable. When I use solutions of the raw materials, such as a solution of sodium chlorid, the anodes may be of graphite, or of platinum, which may, for instance, be in the form of gauze. The cathode in the second cell may be of copper, or nickel, or other suitable material, and the containing vessel may be made of copper, nickel, iron, or the like.  
65

Although I have described the invention as being carried out from the raw materials, it will be understood that, if desired, the alloy constituting the aforesaid intermediate electrode may be taken from any other source and used as the anode in carrying out the process of the production of amid, cyanamid, or cyanid, as described with regard to the action in the aforesaid second cell.  
70

It will be evident that, in place of using ammonia I may employ other suitable nitrogenous matter.

It is to be understood that, in the following  
75

ing claims, I include, in mentioning the compounds of alkali metals especially those of sodium, potassium, and mixtures thereof.

What I claim is:—

1. The process of producing nitrogen-containing compounds of the alkali and alkali-earth metals which consists in subjecting a fused bath consisting substantially entirely of the desired nitrogen-containing product to electrolysis over an anode consisting of an alloy of said metal and in the presence of an agent reacting with the nascent metal at the cathode to form the desired nitrogen-containing product.
2. A cyclic process for producing nitrogen-containing compounds of the alkali and alkali-earth metals, which consists in subjecting suitable raw material to electrolysis in a first cell over a metal cathode adapted

to become alloyed with the said metal yielded by the raw material, electrolyzing said alloy as anode in a second cell having as its electrolyte substantially solely the desired nitrogen-containing product and introducing into said second cell a nitrogen-containing radical to react with the nascent metal produced at the cathode to form the desired nitrogen-containing compound, and returning the depleted alloy to the first cell for reuse.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

EDGAR ARTHUR ASHCROFT.

Witnesses:

EDWARD GEORGE DAVIES,  
H. D. JAMESON.

Copies of this patent may be obtained for five cents each, by addressing the "Commissioner of Patents, Washington, D. C."