

UNITED STATES PATENT OFFICE.

COURTLAND F. CARRIER, JR., OF ELMIRA, NEW YORK.

PROCESS OF MANUFACTURING CHEMICAL COMPOUNDS.

No. 910,498.

Specification of Letters Patent.

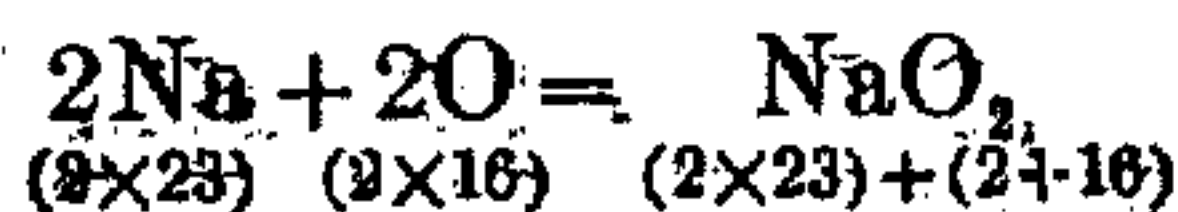
Patented Jan. 26, 1909.

Application filed June 5, 1906. Serial No. 320,284.

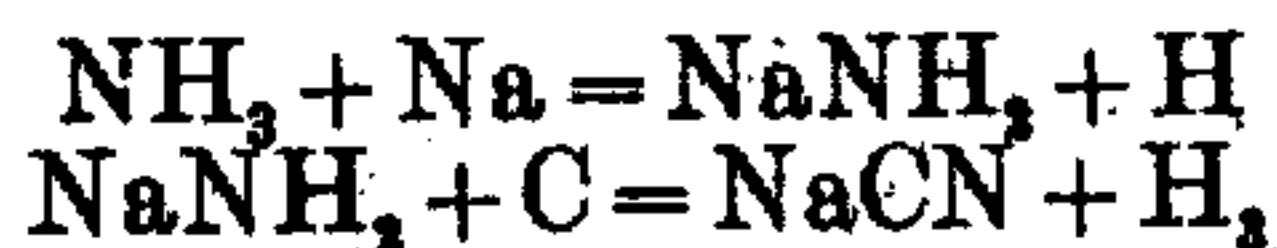
To all whom it may concern:

Be it known that I, COURTLAND F. CARRIER, JR., a citizen of the United States, residing at Elmira, in the county of Chemung and State of New York, have invented a new and useful Improvement in Processes of Manufacturing Chemical Compounds, of which the following is a specification.

This invention relates to an improved process for the production of compounds of the alkali and alkaline earth metals which require the use of the free metal in their preparation; and my object is to accomplish such production in a manner more economical than has been hitherto attained. For example, the present process of producing peroxid of sodium (Na_2O_2) consists in oxidizing metallic sodium by means of the oxygen of the atmosphere, under proper conditions. The reaction is as follows:



This shows that forty-six (46) grams of sodium unite with thirty-two (32) grams of oxygen to form seventy-eight (78) grams of sodium peroxid; or in other words, the production of one (1) gram of sodium peroxid requires at least 0.59 + gram of metallic sodium. The consumption of this valuable raw material, sodium, makes the price of sodium peroxid so high that its use in the arts is greatly restricted. If, then, any chemical reaction can be devised which will reduce the relative consumption of sodium as a metal, the market price of sodium peroxid will be relatively reduced. Similarly, there is the possibility of economy in the production of sodium cyanid. One of the processes now in technical use is based on the following reactions:

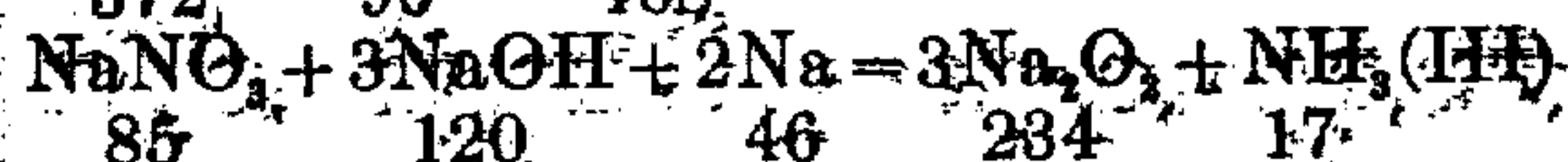
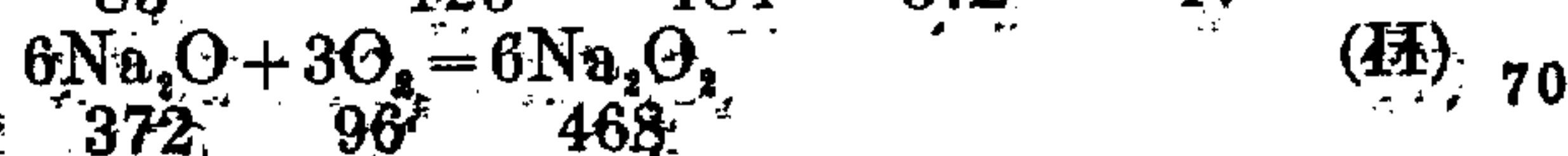
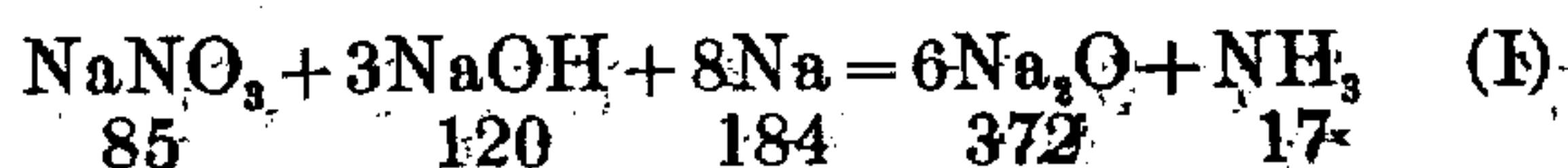


From this it will be seen that all the sodium which is recovered as sodium cyanid enters the process as metallic sodium.

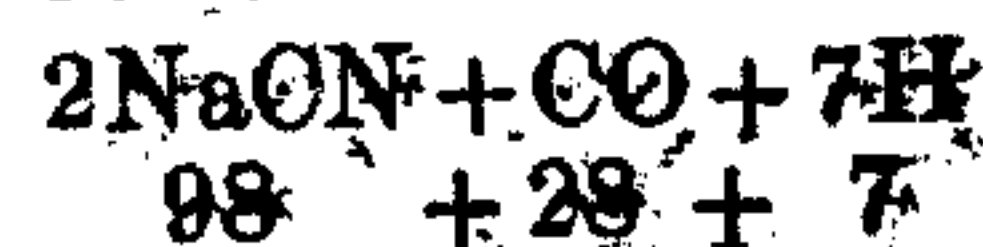
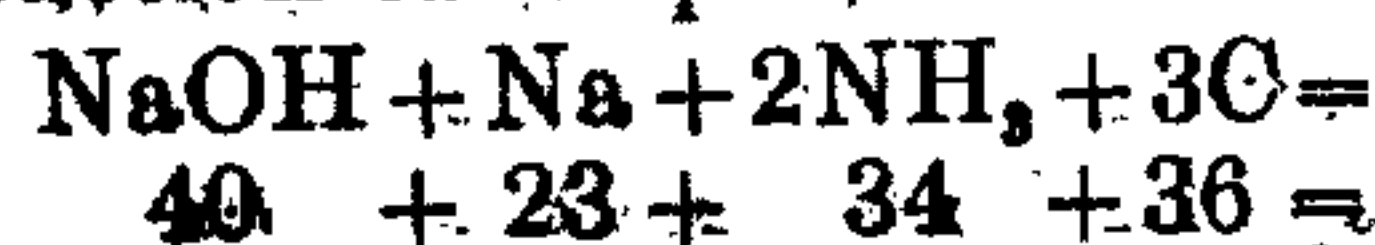
The amount of metallic sodium consumed in the two above mentioned examples may be reduced by using a fused bath containing sodium salts, which will be decomposed by sodium, or sodium alloy, in such a manner as to render the combined sodium of the bath

available as a source of sodium atoms for the end product; and adding sodium, or sodium alloy, to this fused bath. This general principle may be made clearer by application in the two cases already cited.

If sodium be added to a mixed fusion of sodium hydroxid (NaOH) and sodium nitrate (NaNO_3) in the proper proportions, namely, approximately two parts by weight of the latter to three parts of the former, there are numerous possible reactions the final state of which may be expressed by the following reactions:



Reactions I and III take place at the same time, the preponderance of either reaction depending upon the condition of the operation and the law of mass action. The actual amount of sodium peroxid produced will therefore lie between the results of reaction I + reaction II and reaction III. In I + II, 468 grams of Na_2O_2 are produced by the use of 184 grams of metallic Na, or 1 gram of Na_2O_2 requires the use of 0.393 + gram Na. In reaction III, 234 grams of Na_2O_2 are produced by use of 46 grams of metallic sodium, or 1 gram Na_2O_2 requires 0.196 + gram metallic sodium. As all three of the above reactions will take place in the process as carried out on a commercial scale, the amount of sodium required per gram of Na_2O_2 produced will vary between the limits 0.393 and 0.196, or a saving in sodium consumption of from 33.4% to 66.7%. This same principle may be applied to the production of sodium cyanid. If metallic sodium be added to a fused bath of NaOH in which carbon is suspended and NH_3 gas be bubbled through the melted mass at the same time, the following reaction takes place:



In this way only 23 grams of metallic Na are required to produce 98 grams of NaCN ,

whereas by previous known methods, it would require 46 grams of metallic Na, thus saving 50% in the consumption of metallic sodium.

5 Sodium peroxid and sodium cyanid may be made as outlined above by the addition of previously prepared metallic sodium to suitable melted baths, but there is still further advantage to be gained if sodium can be applied in a form, or under conditions, more economical than previously prepared metallic sodium. It is obvious that, in the above outlined process, or in that about to be described, the substances available for the fused baths need not necessarily be confined to those which produce only the product desired and gaseous products, for the formation of solid by-products will not interfere with the process if such solid products can be readily separated from the finished product. It has been suggested frequently that in the manufacture of this class of sodium products, sodium alloys might be used in place of sodium. This, however, seems not to have been done in practice, either because such alloys are not strong enough in their action, or because no practical method has hitherto been devised for making use of this vague suggestion. The simple addition of lead-sodium alloy in place of sodium to such a bath as was specified above for making oxids of sodium is not practicable because lead would be oxidized as well as sodium and the sodium oxid would be contaminated with sodium plumbate. Likewise the alloy could not be used in the formation of sodium cyanid because the alloy produced in practice has not sufficient reducing power to give the desired result. To make practicable the use of a lead-sodium alloy, it is necessary to devise a continuous process under such conditions that the reaction with the Na can be obtained without interference of the lead. The following description is a specific application of this principle which will enable one skilled in the art to obtain oxids of sodium by such a method.

In carrying out my improved process, lead-sodium alloy is first produced by any of the well known methods. This is most practically done by electrolyzing a molten bath of sodium chlorid (NaCl) with a graphite anode and a molten lead cathode. The lead-sodium alloy is caused to circulate, by any convenient mechanical means, and is conveyed to and from a second compartment adjoining the one in which the decomposition of the sodium chlorid was effected. The lead-sodium alloy in this second compartment is covered to a convenient depth with a fused bath of sodium hydroxid. This bath of NaOH is then electrolyzed using iron, nickel or other suitable metal for the cathode and the lead-sodium alloy as a soluble anode. Upon passing the current, Na would be dis-

solved from the sodium-lead anode and deposited at the cathode. If, however, NaNO₃ is added, at intervals in amount proportional to the number of amperes used the sodium of the lead-sodium alloy will be consumed as fast as liberated according to the following reaction:



The relative values of the factors a , b , c and x , y , z will depend upon the condition of the operation as previously explained. This mixture of Na₂O + Na₂O₂ can be entirely converted into Na₂O₃ by solidifying, pulverizing and heating the powder to over 300° C. in air free from CO₂ and H₂O. The lead-sodium alloy which has been partly depleted of its sodium is continuously returned to the first compartment, by means of the circulating device, where it again acts as cathode and takes up more sodium to be in turn removed in the second compartment. The production of cyanid of sodium is conducted in the same way, except that a different electrolyte must be used in the second compartment. In this case the fused NaOH holds carbon in suspension. The bath is electrolyzed as before and ammonia gas is bubbled through the electrolyte, in place of the NaNO₃ used when sodium oxid was desired. From these two concrete examples, it will be seen that the successful use of lead-sodium alloy, as a substitute for pure sodium, rests on the use of that alloy as a soluble anode in the electrolysis of a fused bath, which is consumed in the process, thus economizing in the theoretical quantity of metallic sodium consumed and yielding only the desired product; or by-products that are readily separated therefrom. It is also obvious, to one skilled in the art, that other compounds than those of sodium can be prepared in a similar manner, the only requisite being that such metal will alloy with a less positive metal, such alloy being capable of acting as a soluble anode in a manner substantially as described. The inert metal is also not limited to lead. It is also evident that this process does not apply to any salts of the above class of metals which depend upon the action of water for their formation, for the above reactions take place only in the dry, or fused state. The scope of the invention is also limited by the small number of possible electrolytes that melt within practicable limits.

An apparatus designed for carrying out the above described process on a commercial basis, is described by me in a co-pending application, filed June 9, 1906, Serial No. 320,987. The value of this process lies in the production of more of the final product than could be produced from the actual quantity of the metal entering into the reaction as metal or alloy only. That is, I make the

metal contained in the fused salt of the second compartment available as a substitute for a portion of the metal which would otherwise have to be supplied in full quantity.

5 What I claim as my invention and desire to secure by Letters-Patent is:

1. The process of producing compounds of the alkali and alkaline earth metals which consists in subjecting a fused bath containing a salt of said metal which will react with the metal to form the desired product to electrolysis with a soluble anode comprising a fused alloy of the metal with a metal which is electro-negative thereto.

15 2. The process of producing compounds of the alkali and alkaline earth metals which consists in continuously producing a fused alloy, of which said metal is the more electro-positive constituent, by the electrolysis of a fused bath containing said metal with a fluid cathode comprising a metal which is electro-negative to said metal, and continuously utilizing the said more electro-positive constituent of said alloy in electrolysis with a fused bath containing a salt of said metal which will react with the metal to form the desired product.

3. The process of producing compounds of the alkali and alkaline earth metals, which consist in subjecting a fused soluble anode which contains the metal to electrolysis with a fused bath containing a salt of said metal which will react with the metal to form the desired product, said bath being consumed in producing the compound.

4. The process of manufacturing sodium oxids, which consists in adding metallic sodium to a bath consisting of melted NaNO_3

and NaOH , in the proportions of approximately two parts of NaNO_3 to three parts of NaOH , substantially as herein set forth.

5. The process of manufacturing sodium oxids, which consists in continuously producing an alloy of sodium by the electrolysis of a fused bath containing sodium with a fluid cathode comprising a metal which is electro-negative to sodium, and using the alloy so produced as a fused soluble anode in a bath containing a melted salt of sodium which will re-act with the sodium of the alloy to form the desired oxid.

6. The process of manufacturing sodium oxids, which consists in continuously producing an alloy of sodium by the electrolysis of a fused bath containing sodium with a fluid cathode comprising a metal which is electro-negative to sodium, and utilizing the alloy so produced as a fused soluble anode in a bath composed of melted NaOH and NaNO_3 , to which more NaOH and NaNO_3 are added from time to time, as the bath is consumed.

7. The process of manufacturing sodium peroxid, which consists in the continuous production of sodium oxids by the electrolysis, with a fused soluble anode containing sodium, of a bath containing melted salts of sodium which will react with metallic sodium to produce sodium oxids, and heating the oxids so produced to over 300°C . in purified air or oxygen.

In testimony whereof I have affixed my signature, in presence of two witnesses.

COURTLAND F. CARRIER, JR.

Witnesses:

J. H. O'BRIEN,

A. S. DIVEN.