C. E. ACKER.

PROCESS OF PRODUCING NITROGEN COMPOUNDS.

APPLICATION FILED MAR. 23, 1909.

1,051,303.

Patented Jan. 21, 1913.

2 SHEETS—SHEET 1.

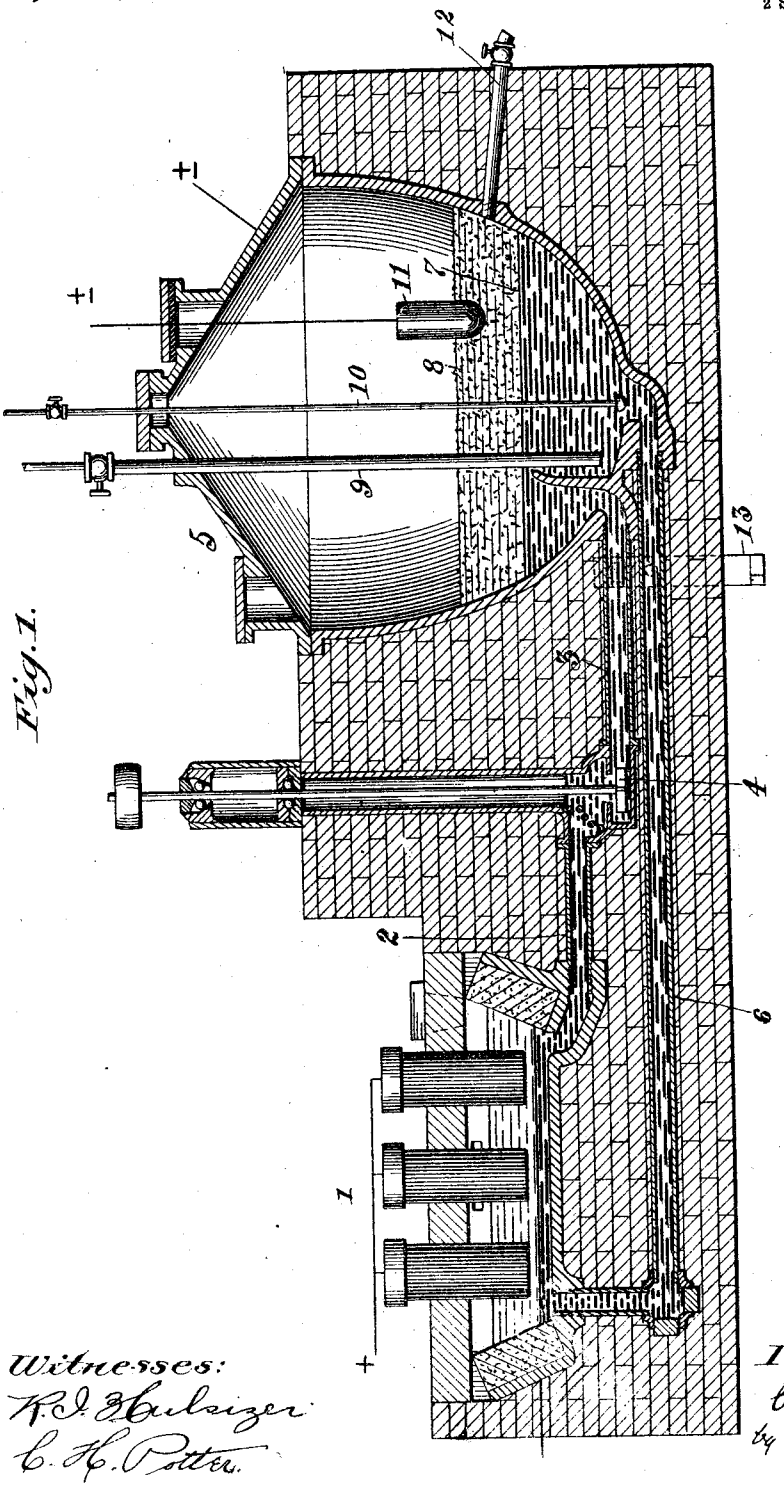

Fig. 1.

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2 SHEETS—SHEET 2.

Fig. 2.

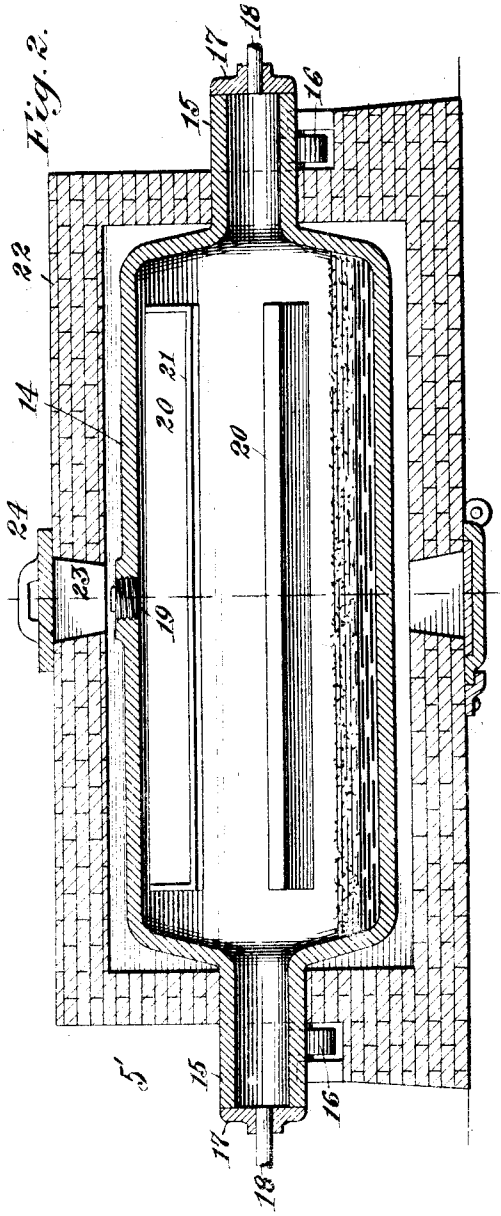
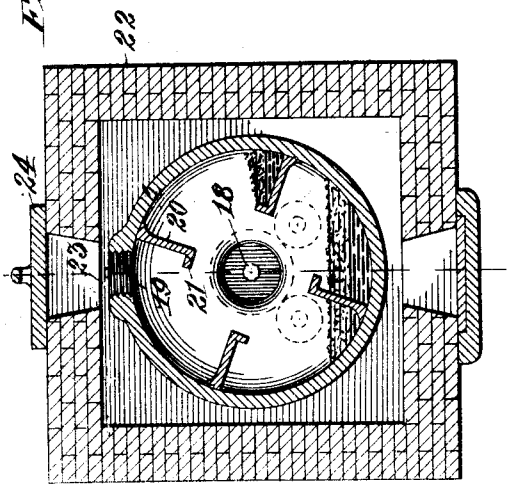


Fig. 3.



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UNITED STATES PATENT OFFICE.

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PROCESS OF PRODUCING NITROGEN COMPOUNDS.

1,051,303. Specification of Letters Patent. Patented Jan. 21, 1913.

Application filed March 23, 1909. Serial No. 485,344.

To all whom it may concern:

Be it known that I, CHARLES E. ACKER, a citizen of the United States, residing at New York, in the county of New York and State of New York, have invented certain new and useful Improvements in Processes of Producing Nitrogen Compounds, of which the following is a specification.

In my U. S. Letters Patent Nos. 914,214 and 914,100, dated March 2, 1909, I have described methods of fixing nitrogen and producing nitrogen compounds, such as nitrids, amids, cyanamids and cyanids, involving the electrolysis of a fused salt or compound, *e. g.*, sodium chlorid, in contact with a molten metallic cathode, *e. g.*, lead, whereby an alloy of sodium and lead is produced which is then reacted upon with nitrogen or a nitrogenous reagent, and in some cases, with an additional reagent, *e. g.*, carbon or a body containing carbon. In such processes the fixation of nitrogen may be indirectly effected by the use of one or more metals or metalloids intentionally added to the lead sodium, tin sodium, and other alloy employed, which act as carriers or "reactive metals" by initially but only temporarily fixing the nitrogen as a nitrid, or by first producing a carbid which in turn combines with the nitrogen. The sodium displaces the "reactive metal" after or simultaneously with some of the above reactions, to form sodium-nitrogen compounds, *e. g.*, sodium cyanid. In bringing about the synthesis of sodium cyanid in this manner, the "reactive metal" combines directly with carbon, even when sodium is present in the alloy, to form a carbid, and may likewise combine with nitrogen to form a nitrid, but these reactions are only intermediate and transitory, because the reaction proceeds further, in the presence of all the necessary elements and under the conditions of the process, to effect the synthesis of sodium cyanid.

The intermediate carbid may react with nitrogen: the intermediate nitrid may react with carbon: the nitrid and carbid may react together: and, finally, the alkali metal present in the alloy displaces and liberates the "reactive metal" at some point in the synthetic process, while in the form of either nitrid, carbid, cyanamid or cyanid of the "reactive metal," principally the latter, and the final result is alkali-metal cyanid. The "reactive metal" again becomes available, and is thus used over and over again.

The final result is much the same whether we start with certain previously-prepared metallic nitrids or carbids and react thereon with commercially pure sodium or potassium and the other element necessary to produce alkali-metal cyanid, to wit, carbon or nitrogen in reactive form, or start with a "reactive metal" free or alloyed with sodium or potassium, or alloyed with a mixture of metals containing sodium or potassium, which "reactive metal" will produce a nitrid or carbid under the conditions of operation, and which will, after effecting the synthesis of cyanid, be liberated by the alkali metal and thus become available for re-use.

Some nitrid-forming metals, and nitrids and carbids thereof, will not serve to combine nitrogen, carbon and sodium to form sodium cyanid. Such a metal is magnesium, for instance. Magnesium will decompose sodium cyanid when heated therewith into magnesium nitrid and sodium carbid, or sodium and carbon. In other words, the nitrid of magnesium is too strong a compound. Any other metal which will similarly, or in any way decompose sodium or potassium cyanid under the conditions of this process, will not serve the purpose of intermediary in this process. NaCN, "a body containing carbon," may be temporarily reduced by Ba, Li, etc., to Na_2CN_2 as a step, but afterward, when free carbon is added, is reconverted to cyanid.

The number of metals and metalloids capable of combining directly with carbon or nitrogen when heated therewith, under suitable conditions, is considerable: they are herein referred to as "reactive metals". The "reactive metals" are generally obtained from salts or oxids which are refractory or difficult to reduce by ordinary metallurgical processes. They are often difficult to handle, and special care must generally be taken to prevent abnormal oxidation, and

furthermore some of them are either so volatile or difficult to melt that they cannot be satisfactorily reacted upon in fluid condition. The most suitable "reactive metals" for the purposes of this process are lithium, calcium, barium, strontium, magnesium, aluminum, manganese, chromium, titanium, iron, vanadium, silicon, boron, phosphorus. Lithium is, of course, an "alkali metal", but for the purposes of this specification is included in the list of "reactive metals". These metals, and also the alkali metals, sodium and potassium may be made by any known methods, and some of them may be utilized in the process without being alloyed with another metal, that is, in a state of substantial purity, but in general I prefer to manufacture and utilize them in the form of alloys with relatively inert, heavy, solvent metals, such as tin, lead, antimony, zinc, aluminum or bismuth, which may be used as the cathode in an electrolytic process for producing the alloy. Such solvent metals should preferably have melting points below 800° C., and boiling points above 800° C. By thus combining or mixing "reactive metals" or alkali metals, with solvent metals, they are more easily manufactured, handled and reacted upon. The desirable percentage of "reactive metal" or metals present in such alloys is determined by: (1) economy and safety in manufacturing alloys containing relatively small or large percentages of the refractory metal; (2) relative ease with which such alloys may be handled and reacted upon; (3) relative efficiency in combining with either nitrogen or carbon, or both; (4) relative fusibility and fluidity at moderate temperatures.

The percentage of alkali metal present in alloys to be used in the process is to be determined by considerations (1) and (2) as above. By properly proportioning the constituent metals of the alloys, or mixture, which will be thinly fluid at a moderate temperature, and this is an important feature of the process.

The reaction between nitrogen or carbon and some of the reactive metals will take place at temperatures far below the range indicated above, so that it is not necessary in all cases to heat the metals or alloys to such an extent.

Metallic lithium will, if its surface be kept bright, absorb nitrogen at the ordinary temperature, but the absorption is much more rapid and complete if the metal is heated.

In carrying out the manufacture of alkali-metal cyanids and of the intermediate "reactive metal" cyanids, cyanamids, nitrids, carbids, etc., the general type of apparatus described in my specified patents may be employed, although it may be modified in any way desired, for instance by greatly changing the relative size of the two compartments there shown, by separating them widely and making them more distinct from each other, and by providing a number of electrolytic cells and a single or smaller number of separately-heated reaction-chambers, compartments, retorts or vessels, connected thereto by valved pipes, into which the alloy may be periodically or continuously introduced and there reacted upon, under pressure, if desired, and from which the partially depleted or impoverished metal may be periodically or continuously returned to the electrolytic cells to be again enriched with "reactive metal", alkali metal, or both. The reaction-chambers may be heated internally or externally, by the combustion of fuel or by electricity, and the temperature may be higher or lower than that of the electrolyte. The general range of temperature would be that known as a red heat, although this may vary from about 600° to 1100° C., which range I designate in this specification as a "moderate temperature". Alloys of tin or lead with sodium and other metals may be continuously or intermittently produced electrolytically in this apparatus up to 25% or more of sodium, and up to 15% or more of "reactive metal", or vice versa, that is to say, less of the former and more of the latter, which are suitable for the purposes of this process. Appropriate electrolytes for the purpose readily suggest themselves to one familiar with the art.

The mixed chlorids and fluorids of alkali, alkaline-earth and other metals may be employed as an electrolyte, and when the voltage and current density are sufficiently high, each salt in the mixed electrolyte will be regularly decomposed, the metals thereof becoming a part of the alloy when a suitable molten metallic cathode is employed. If fluorids are present in the bath, various oxids may be also dissolved therein, and regularly decomposed.

The reactive metals calcium, barium, strontium, and lithium, readily alloy with lead, and also with tin, zinc, antimony, bismuth, aluminum, and mixtures thereof, and will readily combine with nitrogen or carbon in one of their reactive forms over a considerable range of temperature to form nitrids or carbids, and with both nitrogen and carbon to form cyanids, *e. g.*, barium cyanid, lithium cyanid, calcium cyanid, etc. If the alkali metal, sodium or potassium, is also present in the alloy, the above-mentioned cyanids will be decomposed with liberation of the base metal, *e. g.*, barium, lithium, calcium, etc., and production of sodium or potassium cyanid.

The "reactive metals" manganese, chromium, titanium, aluminum, vanadium, etc.,

and the metalloids boron, silicon and phosphorus, readily alloy or mix or combine with tin, and also with antimony, zinc, aluminum, bismuth, and mixtures thereof, in which lead may also be present, and will then combine with nitrogen or carbon in one of their reactive forms, over a considerable range of temperature, preferably in the neighborhood of a good red heat, to form nitrids or carbids. The alkali metals, sodium and potassium, may be present in these alloys.

The nitrogen is preferably injected into the molten mass in such manner that the progress upward through the alloy is impeded by friction against solid surfaces such as refractory brick, stone-ware, metals, or, if cyanid is being made, charcoal or coke in lumps so disposed that the gas in rising through the same will be held in contact with the other reagents as long as is necessary to effect the combination.

The nitrogen is preferably obtained from the air, although ammonia or other nitrogenous gas may be used for special purposes. If ammonia is employed in whole or in part, the temperature of the alloy may be held considerably below that required for nitrogen. The nitrogen gas may be dry and pure, or diluted and mixed with one or more other gases, such as ammonia, hydrogen, carbon monoxid, etc., and may be heated or superheated previous to its introduction into the hot mass. Uncombined nitrogen, alone or carrying other gases or solids mixed therewith or in suspension, escaping from one reaction-chamber, may be reintroduced into the same chamber, or carried to a condenser or scrubber to catch the gas, fumes, or solid material in suspension. Water, acids, alkali, iron salts, etc., may be employed in the condenser or scrubber to dissolve or catch such residual gas or fumes. Several such scrubbers may be used in series, to dissolve or catch different constituents of the gas or fume.

In the patents above referred to, the nitrogen was injected into the molten metal under some pressure, due to the column of metal which had to be overcome. I have found that it is desirable in reacting on some of the alloys with nitrogen or carbon, or both, to employ a greater pressure than that involved in the above, and I may employ pressure as high as 75 pounds per square inch.

The steel or other metal pipes for injecting nitrogen into some molten alloys must be protected by refractory tubes, sleeves or coating. In some cases carbon or graphitized carbon tubes are necessary, which wear away slowly and gradually and are then renewed. Tubes for use in the process may also be made of porcelain, china, fused quartz, or other refractory material.

The carbonaceous reagent may be in the form of coke, charcoal, lampblack, soot, pitch, tar, gas-carbon, acetylene, hydrocarbon oils, crude petroleum, or any suitable body containing carbon.

When granular charcoal or coke is employed, the carbid is generally formed as a mere superficial layer on the surface of the carbon, but when the reagent is employed in the form of a gas, hydrocarbon oil, or lampblack, the resulting carbid is generally a finely-divided apparently amorphous product, which rises to the surface of the alloy and mixes with the cyanid. The carbids thus produced with few exceptions are not fused, and they are not produced in lumps or masses easily removable.

The carbid produced by this process is, as a rule, of much greater purity than the ordinary commercial carbid.

If nitrogen alone (without carbon) is introduced into the alloy, the product will be a nitrid of the "reactive metal," and if carbon alone (without nitrogen), is introduced, the product will be a carbid of the "reactive metal."

The primary intention is to react with nitrogen upon the carbid, *in situ*, while still hot and while in contact with or submerged in the moving or circulating alloy. The molten alloy may, however, be withdrawn from the chamber containing the carbid-coated charcoal or coke, or carbid-containing mass, which may then be reacted upon under pressure with nitrogen or other reagent, or the carbid may be otherwise treated, after which the molten metal, containing one or more alkaline metals, or both, may be again run into the chamber.

A different type of apparatus from that referred to in the foregoing may be employed in which to carry out the process, for instance:—The "reactive metal," alkali metal, or both, as well as alloys thereof, may be reacted upon in molten condition by nitrogen, carbon, nitrid, carbid, cyanamid, cyanid, etc., under pressure, in heavy closed, revolving retorts or cylinders provided on the inside with shelves, pockets, ledges or arms which will lift a portion of the metal or alloy as the cylinder revolves and afterward spill or discharge the same in such a manner that the clean metal surfaces will be continually or intermittently exposed to the reagent.

The product formed in my process by the interaction of the "reactive metal," and both carbon and nitrogen, without the alkali metal, is a cyanid of the "reactive metal," if such "reactive metal" cyanid is stable at the temperature of the operation. More or less cyanamid may also be formed in some cases. These intermediate cyanids may be reacted upon and utilized *in situ*, if desired, in several different ways for different purposes. The cyanid or cyanamid

of the "reactive metal" may be treated subsequent to its formation at a moderate temperature with an alkali metal or an alloy containing it, whereby alkali metal cyanid is formed and the original metal of the carbid is generally set free and becomes a part of the surrounding body of molten metal at the moment of its liberation, but I prefer to react immediately and simultaneously or practically so, on the carbid of the "reactive metal" with nitrogen and with the alkali metal, in order to produce at once alkali metal cyanid, *e. g.*, sodium cyanid, in molten condition, which will rise through the molten reactive metal, if in the form of an alloy with a heavy metal, and may be continuously, or intermittently, withdrawn from the reaction chamber.

It will, of course, be understood that it is not necessary to first or separately make the carbid referred to in the preceding paragraph. This carbid may be formed practically at the same moment that it is reacted upon with nitrogen or both nitrogen and sodium. And finally it will be understood that both nitrid and carbid in varying proportions may be initially formed and further reacted upon at the moment of their production or at any time afterward.

In making alkali metal cyanid by this process, it is advisable in effecting the reactions with alkali metal, reactive metal, or both, to employ an excess thereof, and this is also true of the carbonaceous reagent.

The alloys containing certain of the "reactive metals," such as calcium, barium, strontium, lithium, or either of the alkali metals, sodium or potassium, or mixtures thereof, will absorb and combine with hydrogen if that gas is substituted for nitrogen in the process hereunder and the temperature is maintained generally lower than a red heat, with the formation of the hydrids of calcium, barium, etc. These hydrids, and others, may thus be produced in the identical apparatus and by the same process described herein, and in U. S. Patent No. 914,214, for the manufacture of nitrids, by employing hydrogen as the reagent instead of nitrogen.

Suitable apparatus for carrying out the process is shown in the accompanying drawing, in which—

Figure 1 is a vertical longitudinal section of one complete apparatus; and Figs. 2 and 3 are a vertical axial section and a transverse vertical section, respectively, of a modified reaction-chamber.

The apparatus illustrated in Fig. 1 comprises an electrolytic cell 1 of the type illustrated in my specified patents, having a cathode of molten metal, and 2, 3, are delivery pipes for the alloy, with an intermediate centrifugal pump 4, for delivering alloy to the reaction-chamber 5. A pipe 6 serves to return the depleted cathode metal to the cell. A body 7 of the alloy is shown in the reaction-vessel, and, superincumbent thereupon, a body 8 of the molten product, shown as containing pulverulent carbon. A pipe 9 serves for the introduction of mineral oil, if used to supply carbon, and a pipe 10 for the introduction of hydrogen. An electrode 11, depending into the molten cyanid or other product, may be used to pass an electrolytic current therethrough to the metal within the vessel, to supply further heat. A valved pipe 12 serves to withdraw the molten product. The pipes 3 and 6 may be closed by a cock or cocks 13, if desired, to enable superatmospheric pressure to be maintained in the reaction-chamber.

The modified reaction-chamber 5′ shown in Figs. 2 and 3 consists of a revoluble horizontal drum 14, having at its ends hollow trunnions 15 supported on rollers 16. The trunnions are closed at their ends by caps 17 containing gas-pipes 18. A screw-plug 19 in the side of the vessel serves for the introduction of desired ingredients, and shelves 20, having marginal flanges 21, projecting from the inside of the vessel, serve to lift and agitate the contents. The vessel is shown surrounded by a brickwork 22, having an opening 23 registering with the screw-plug 19 and closed by a cover 24.

I claim:

1. The process of producing alkali metal cyanogen compounds, which consists in subjecting a metal capable when heated of combining directly with carbon or nitrogen, to the action of heat and a carbonaceous reagent for the purpose of producing a carbid, reacting on said carbid with a nitrogenous reagent in the presence of an alkali metal thereby producing an alkali metal cyanogen compound, and liberating the first-mentioned metal.

2. The process of producing alkali metal cyanogen compounds, which consists in subjecting a metal capable when heated of combining directly with carbon or nitrogen, to the action of heat and a carbonaceous reagent for the purpose of producing a carbid, reacting on said carbid with a nitrogenous reagent to produce an intermediate nitrogen compound, and reacting on said intermediate compound with an alkali metal and thereby producing an alkali metal cyanogen compound and liberating the first-mentioned metal.

3. The cyclic process of producing alkali metal cyanogen compounds, which consists in subjecting a "reactive metal" to the action of heat and a carbonaceous reagent to produce a carbid of the "reactive metal" and reacting on said carbid in the presence of an alkali metal with a nitrogenous reagent to produce an intermediate cyanogen compound having the "reactive metal" as

a base, the intermediate compound being then decomposed by the alkali metal with production of an alkali metal cyanogen compound and liberation of the "reactive metal" which again becomes available for reuse.

4. The cyclic process of producing alkali metal cyanogen compounds, which consists in subjecting a "reactive metal" to the action of heat and a carbonaceous reagent to produce a carbid of the "reactive metal," reacting on said carbid with a nitrogenous reagent to produce an intermediate cyanogen compound having the "reactive metal" as a base, and finally reacting on said compound with an alkali metal, whereby an alkali metal cyanogen compound is formed and the "reactive metal" again becomes available for reuse.

5. The process of producing alkali metal cyanogen compounds, which consists in subjecting an alloy containing a metal capable when heated of combining directly with carbon or nitrogen, to the action of heat and a carbonaceous reagent for the purpose of producing a carbid, and reacting on the carbid with a nitrogenous reagent in the presence of an alkali metal, thereby producing an alkali metal cyanogen compound and liberating the first mentioned metal.

6. The process of producing alkali metal cyanogen compounds, which consists in subjecting a metal capable when heated of combining directly with carbon or nitrogen to the action of heat and a carbonaceous reagent for the purpose of producing a carbid, reacting on said carbid with a nitrogenous reagent to produce an intermediate nitrogen compound, and reacting on said intermediate compound with an alkali metal alloy, thereby producing an alkali metal cyanogen compound and liberating the first mentioned metal.

7. The cyclic process of producing alkali metal cyanogen compounds, which consists in subjecting a "reactive metal" to the action of heat and a carbonaceous reagent to produce a finely-divided carbid of the "reactive metal", reacting on said carbid with a nitrogenous reagent to produce an intermediate cyanogen compound having the "reactive metal" as a base, finally reacting on said compound with an alkali metal alloy, whereby an alkali metal cyanogen compound is formed and the "reactive metal" again becomes available for reuse, supplying fresh alkali metal to the alloy and repeating the process as described.

8. The cyclic process of producing alkali metal cyanogen compounds, which consists in subjecting barium to the action of heat and a carbonaceous reagent to produce finely divided barium carbid, reacting on said carbid with a nitrogenous reagent to produce a cyanogen compound of barium, reacting on said barium compound with an alkali metal alloy, whereby an alkali metal compound is formed and the barium again becomes available for reuse, supplying fresh alkali metal to the alloy and repeating the process as described.

9. The process of producing nitrogen compounds, which consists in reacting with nitrogenous and carbonaceous reagents on an alloy of an inert metal, an alkali metal, and a third element having greater activity toward carbon and nitrogen than said alkali metal.

10. In a process for producing nitrogen compounds, the step which consists in reacting with nitrogen on a mixture of three elements, one of which is an inert diluent and two of which are capable of forming cyanids which are stable at a red heat.

11. The process of producing sodium cyanid, which consists in reacting with nitrogenous and carbonaceous reagents on an alloy of lead, sodium, and barium.

12. The herein described process, which consists in electrolyzing a molten compound containing two metals, alloying the separated metals with a cathode metal, removing the alloy and reacting on the alloyed metals with nitrogenous and carbonaceous reagents, and returning the residual metal to the cathode.

13. The herein-described process of producing alkali metal cyanogen compounds, which consists in electrolyzing a molten compound containing the alkali metal and another metal having greater activity toward carbon and nitrogen than said alkali metal, alloying the separated metals with a cathode metal, removing the alloy and subjecting it to the action of a nitrogenous gas and a carbonaceous reagent, and returning the residual metal to the cathode.

14. The herein-described process which consists in electrolyzing a molten compound of a metal, alloying the separated metal with a cathode metal, removing the alloy and reacting with nitrogenous and carbonaceous substances on the alloyed metal with production of an intermediate compound, supplying a separate reagent and reacting therewith on the intermediate compound, with production of the desired compound, and returning the residual metal to the cathode.

15. The process of producing cyanogen compounds, which consists in electrolyzing a molten compound of a "reactive metal," alloying the separated metal with a cathode metal, removing the alloy and reacting on the alloyed metal with nitrogenous and carbonaceous reagents, and returning the residual metal to the cathode.

16. The process of producing alkali metal cyanogen compounds, which consists in electrolyzing a molten compound containing the

alkali metal and a "reactive metal," alloying the separated alkali and "reactive metals" with a cathode metal, removing the alloy and reacting on the alloyed metals with a nitrogenous gas and a carbonaceous reagent, and returning the residual metal to the cathode.

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

CHARLES E. ACKER.

Witnesses:
SUSIE E. SAMPSON,
ETHEL R. HARRISON.