C. E. ACKER.

METHOD OF PRODUCING NITROGEN COMPOUNDS.

APPLICATION FILED OCT. 27, 1910.

1,018,802. Patented Feb. 27, 1912.

Fig. 1.

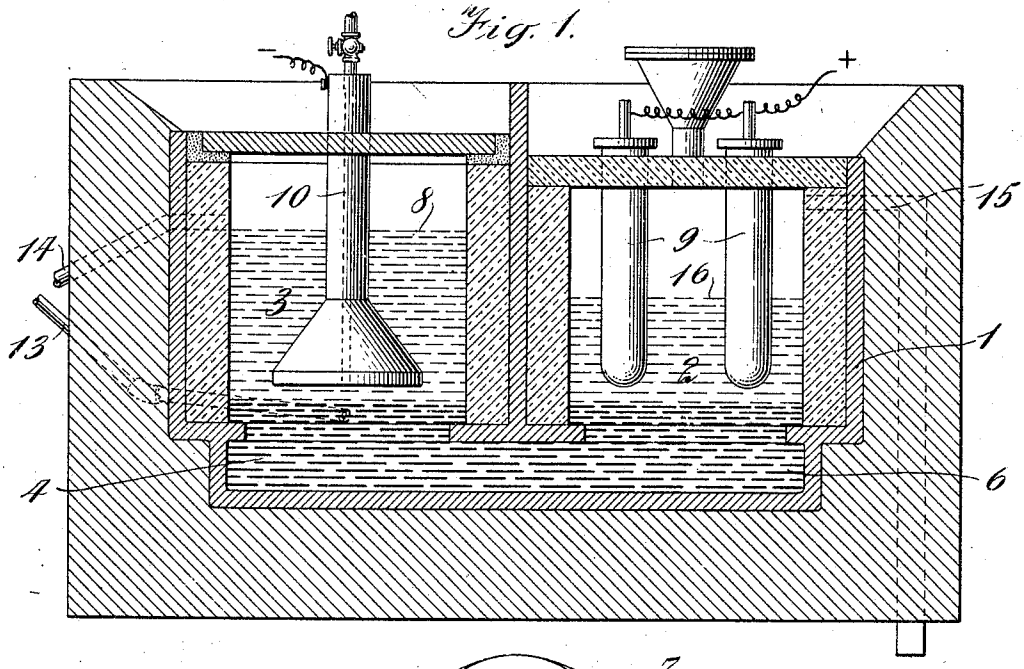


Fig. 2.

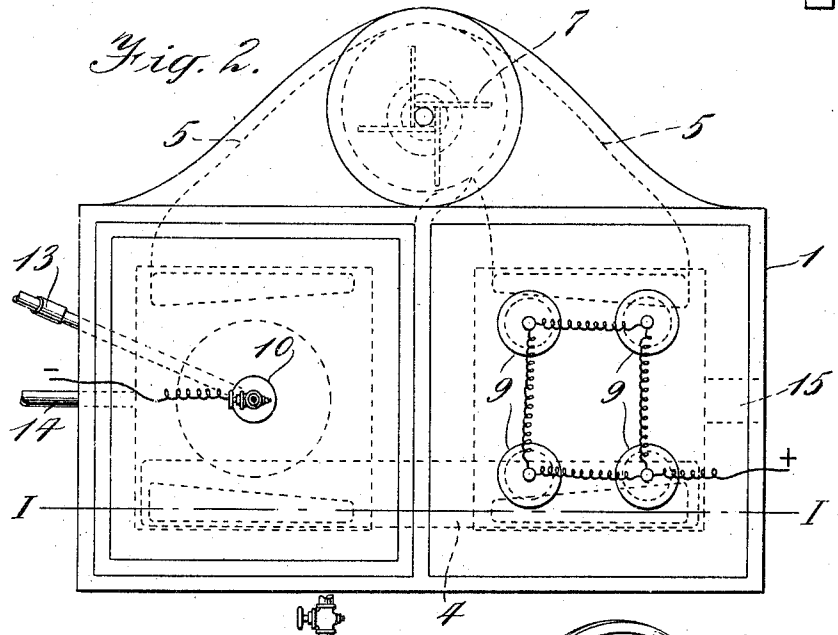


Fig. 3.

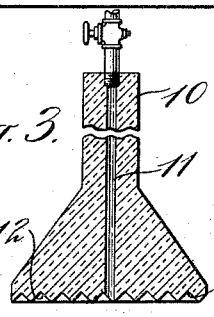
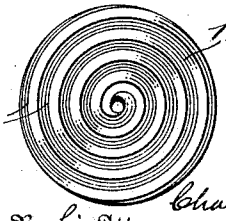


Fig. 4.



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UNITED STATES PATENT OFFICE.

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METHOD OF PRODUCING NITROGEN COMPOUNDS.

1,018,802. Specification of Letters Patent. Patented Feb. 27, 1912.

Application filed October 27, 1910. Serial No. 589,292.

To all whom it may concern:

Be it known that I, CHARLES E. ACKER, a citizen of the United States, residing at Ossining, in the county of Westchester and State of New York, have invented certain new and useful Improvements in Methods for Producing Nitrogen Compounds, of which the following is a full, clear, and exact description.

In my United States Patent No. 914,214, dated March 2, 1909, I described a process relating to the electrolytic production of nitrogen compounds, such as nitrids, amids, cyanamids and cyanids of the alkali and alkaline-earth metals. This process comprised the steps of electrolyzing a molten compound of a metal capable of forming nitrogen compounds, alloying the separated metal with a cathode metal, removing the alloy, and reacting on it with a nitrogenous reagent, separating the products of reaction, and returning the residual metal to the cathode. Incidental steps comprised cooling the alloy before treatment with the gas, particularly when ammonia was employed as the nitrogenous reagent. This is of considerable importance, because the ammonia would to a certain extent be decomposed into its elements nitrogen and hydrogen, if injected into the alloy at the same temperature at which the alloy would ordinarily be produced, and this free nitrogen in the case of a sodium-lead alloy would pass through unabsorbed. It is further of importance since the initial product of the reaction between the alkali or alkaline-earth metal and ammonia, would be an amid, *e. g.*, sodium amid ($NaNH_2$) which, if formed at all at such temperature, would quickly decompose, in which case, in the absence of carbon, the nitrogen would be set free. It was pointed out that sodium amid produced at a relatively low temperature could subsequently be converted into alkali cyanid or alkali cyanamid, by treating it in the same chamber, but at a higher temperature, with carbon or a carbonaceous reagent, in the presence of the residual metal. Alkali amid and possibly cyanamid (Na_2CN_2) would thus be produced as intermediate compounds in the production of the cyanid. Certain specific features relating to the production of these intermediate compounds, and their conversion into final compounds, including the methods of effecting changes in the temperature, were described in my U. S. Patent 914,100, also bearing date of March 2, 1909; this latter patent being a division of the original case above referred to. In this patent, I described a method of producing the desired alloy by electrolyzing molten sodium chlorid and alloying the liberated sodium with a cathode metal; thereafter conducting the alloy into a "reaction" chamber containing molten cyanid resting on the surface of the alloy. The reaction chamber was described as being heated by means of an alternating current which was passed through the molten products of reaction between a carbon electrode, which extended into the cyanid, and the surface of the alloy or the pot itself; the molten products acting as a liquid resistor. In Patent 914,100, I further stated that ammonia could be introduced directly into the molten alloy, and it will be evident from an examination of the original drawing, Figure 2, that unabsorbed portions of such gas would pass up through the molten cyanid and so come into contact with the carbon electrodes therein.

I have now discovered that by passing a direct current of electricity from the surface of an alkali-metal alloy, *e. g.*, sodium-lead alloy, in the reaction chamber, through for example, molten sodium cyanid, to the carbon electrode serving as cathode, the alkali metal may be liberated in the pure state on the surface of such cathode; and that if ammonia, hydrocarbon amins, their decomposition products or mixtures of any of the foregoing reagents, or other suitable nitrogenous reagent be brought into contact with the surface of this cathode, while the current is passing, such reagent will instantly combine with the liberated alkali metal and carbon of the cathode, to form more sodium cyanid; this product being immediately commingled with the mass of molten cyanid previously provided or formed. It should be noted that in the present method it is unnecessary to bring the ammonia or other nitrogenous reagent directly into contact with the alloy and this is a distinct advantage in that all decomposition of the reagent by contact with the considerable mass of diluent metal, *e. g.*, lead, in the alloy is avoided. The reagent may advantageously be introduced through a hole or conduit in the carbon cathode directly to the surface where the sodium is liberated. Another ad-

vantage of this process over the earlier patents referred to, lies in the fact that all of the reactions involved in the manufacture of alkali metal cyanid from alkali metals, carbon and ammonia or other suitable nitrogenous reagent may be effected at one temperature, and this temperature may be substantially the same as that required to produce the alloy by the electrolysis of molten sodium chlorid,—of mixed chlorids of sodium and potassium, or of mixtures of other haloid salts, in connection with a molten metallic cathode such as lead, thus permitting the utilization of the alloy as fast as it is produced; economizing energy and permitting the return of the residual metal to the primary furnace without undue loss of heat.

In the foregoing matter, reference has been made to nitrogenous reagents other than ammonia and in this connection I desire particularly to direct attention to a class of substances that I have found well adapted for the purpose in question, to wit, hydrocarbon bodies containing nitrogen, obtained from the distillation of "vinasses" of the beet sugar refineries, etc., the hydro-carbon-amins, such as methylamin, di- and trimethylamin, the corresponding ethylamins, and particularly the compound- trimethylamin (C_3H_9N), or the products resulting from heating to a red heat or higher, simultaneously with or previous to their use as a source of nitrogen, of any of the foregoing hydro-carbons.

When the alkali metal is liberated on the surface of a carbon cathode in an electrolyte consisting of molten alkali cyanid, and ammonia is brought into contact with this carbon, and with the alkali metal at the moment of its liberation, the conditions are ideal for the complete and rapid absorption of the ammonia, and since all of the elements entering into the composition of the alkali metal cyanid are present, the action proceeds with great rapidity, and alkali metal cyanid is formed,—the hydrogen of the ammonia escaping, and carrying with it practically no uncombined nitrogen or unused ammonia. The hydro-carbon-amins or their breaking down products, or mixtures of any of the foregoing with ammonia may be substituted for ammonia in effectuating the process.

The temperature most suitable for the production of the alloy through the electrolysis of a molten mixture consisting principally of sodium chlorid, may vary from 800° down to, say 625° C., and the temperature in the chamber in which the sodium cyanid is produced, in accordance with this process, may be substantially the same. When operating at such temperatures, and under the conditions named it is a matter of great uncertainty as to just what intermediate reactions actually take place in this process between ammonia, or an amin, *e. g.*, trimethylamin, alkali metal, at the moment of its liberation, and carbon; the latter element being supplied by the carbon cathode, by the amin, or by the cyanid itself—a body containing carbon.

A notable advantage, useful under certain conditions, possessed by the hydro-carbon amins resides in the fact that such bodies contain carbon and hence it is not essential that an additional supply of that element be afforded. In fact, in methylamin both nitrogen and carbon are present in the exact proportion required in the cyanid, whereas in di- and tri- methylamin the carbon is in excess; the nitrogen present being insufficient to combine with all of the carbon to form the product sought. In case di- or tri-methylamin be used therefor as the nitrogenous reagent, nitrogen or some compound, such as ammonia, capable of supplying additional nitrogen may be introduced or injected into the molten mass in sufficient quantity to make up the deficiency. A hydro carbon amin *e. g.*, trimethylamin may hence be regarded as both a carbonaceous and nitrogenous reagent; and the previously formed or supplied cyanogen compound may be regarded as the electrolyte.

In the U. S. patent to Castner, No. 541,066, June 18, 1895, "Process of making cyanids," Castner claims:—

"The improvements in the manufacture of alkali cyanids, consisting in treating previously, or separately made alkali metal with nascent nitrogen and carbon, as described."

Castner states that the best temperature is "just below a dull red heat, which is equivalent to just above the melting point of the cyanid," and explains the reaction involved in his process as follows:

$$NH_3+C+Na=NaCN+H_3$$

In the U. S. patent to Castner, No. 543,643, July 30, 1895, the statement occurs with reference to the process described in said Patent 541,066, that,—

"While the ultimate product is alkali cyanid, several intermediate reactions take place, and these at times render it difficult to carry on the manufacture without considerable care to avoid loss of nitrogen. I have found by experiment that such loss can be avoided if I carry on the process in two separate steps, or reactions."

The first step of the process consisted in passing anhydrous ammonia over metallic sodium, at a temperature between 300° and 400° C., thereby producing sodium amid,—the reaction being:

$$NH_3+Na=NaNH_2+H$$

In the second step the sodium amid is

fused in contact with carbon at a higher temperature, to wit, "a dull red heat," whereby sodium cyanid is formed in accordance with the following reaction:

$$NaNH_2+C=NaCN+H_2$$

Castner states in this specification that he was aware that sodium amid had been previously produced in accordance with the first reaction, and also that sodium cyanid had been previously produced by heating sodium amid with charcoal; but he claimed that the essential novelty in his process consisted in pre-heating the carbon before the amid was brought into contact with it.

A series of patents was taken out by Johannes Pfleger, in the year 1901, as follows:—671,709, process of making dialkalicyanamid; 682,741, method of making cyanids; 686,949, method of making cyanids; 686,950, method of making cyanamids, all of which relate in one way or another, to the reactions involved in the manufacture of alkali cyanid, or intermediate compounds, by the treatment of "previously or separately made" alkali metal, as described in Castner's Patent No. 541,066, with ammonia, etc. A patent was also taken out by Ewan and Pfleger, No. 674,295, May 14, 1901, "Process of making alkali amids," which claimed as a novel feature,—the introduction of ammonia down into a mass of alkali metal. With all of these patents, I am familiar, and now wish to strongly differentiate the process disclosed in this specification from all of the above enumerated patents, directing special attention to the fact that the sodium, in my process, may be reacted upon with, for example, ammonia, affording nascent nitrogen, and carbon, substantially at the moment of the liberation of the alkali metal by the current on the surface of the cathode; said metal being thus in peculiarly reactive condition—*i. e.*, in the nascent state.

The cathode itself may be of carbon and may, as aforesaid constitute the source of carbon; or finely divided carbon may be suspended in the electrolyte; carbon in lump form or in the form of a hydro carbon gas or oil may be charged into the cyanid; a hydro-carbon amin, or the products obtained by heating such amins to a red heat or higher may be employed as a source of both nitrogen and carbon; and finally the cyanid itself may, in the absence of free carbon, supply such element to the reacting ammonia and alkali metal. The product formed in the latter case will be dialkalicyanamid; and the cyanid electrolyte will itself be gradually reduced to dialkali cyanamid if no free carbon is supplied in the meantime. The production of dialkalicyanamid would, however, require a cathode made of material other than carbon.

The present process need not be carried out in steps; nor does it require one constituent to be first formed and then reacted with another constitutent at a higher temperature. Further, the operation may with advantage be continuously carried out at a temperature substantially exceeding the melting point of cyanid, (although it may, if desired, be also continuously carried out at the same temperature) and in a separate compartment of the same apparatus in which the alloy is produced; and the residual alloy or metal may be continuously or intermittently circulated between the two compartments and replenished without substantial change in the temperature.

In my co-pending U. S. application, Serial No. 575,819, filed Aug. 5, 1910, I described a method of producing alkali and alkaline-earth metals by electrolyzing a molten bath containing cyanid or cyanamid compounds, in connection with an anode consisting of a molten alloy containing the desired metal; the collected or accumulated metal formed in the apparatus by means of the process therein described being normally run off from such apparatus and separately utilized. This requires handling of the metal and involves labor.

Each of the metals referred to in that specification may be produced as described; but in accordance with the present process, at the instant of their liberation by the current and while still in the nascent state, they may be reacted upon with ammonia and carbon, or with other reagents as stated—*e. g.*, trimethylamin, the latter preferably with nitrogen or ammonia, to produce cyanids of potassium, sodium, lithium, barium, strontium, or calcium, and also such cyanamids of the foregoing metals as are fusible below 900° C., notably the alkali cyanamids. Mixed cyanids or cyanamids may be produced in the same way by providing an alloy containing two or more metals which it is desired to convert into mixed cyanids or cyanamid salts.

When hydrocarbon amins, *e. g.*, trimethylamins are heated to a temperature which is apt to be required on the ground of economy such a body does not break up until the instant that it combines with the alkali metal; hence its valuable constituent elements, carbon and nitrogen are also in a nascent state at such instant and a reaction of maximum efficiency is the result. As previously stated, some of the hydrocarbon amins contain an excess of carbon over that necessary for the production of cyanids and in order to utilize such excess of carbon while in the nascent state, it is convenient and desirable to introduce simultaneously with the amin a predetermined quantity of ammonia, the nitrogen of which will also be liberated in the nascent state and therefore be present in

condition to combine with such excess carbon and the alkali metal to form alkali metal cyanid.

In my U. S. application Serial No. 580,190, filed Sept. 1, 1910, I described a process somewhat resembling that herein set forth, but with the essential difference that the nitrogen or ammonia in such process reacted directly with a "reactive metal" carbid instead of with the alkali metal.

In the present process the cathode may be of metal instead of carbon, and owing to the heat conducting properties of metal, said cathode may, if desired, be made to serve as a means for maintaining the temperature of the cathode and of the electrolyte in immediate contact therewith, considerably lower than that of the molten alloy beneath.

In the accompanying drawing I have somewhat diagrammatically illustrated one form of apparatus adapted for carrying out the process herein described.

Fig. 1 is a vertical section taken through the respective primary and secondary cells on line I—I of Fig. 2. Fig. 2 is a plan of the apparatus. Fig. 3 is a detail section of the secondary cathode. Fig. 4 is a bottom view of said cathode.

Like reference characters designate like parts throughout the respective views.

Referring to Fig. 1, a suitably lined and covered casing 1 is partitioned into a primary compartment 2 and a reaction chamber or secondary cell 3. These cells are connected by conduits 4 and 5, so that a body of molten alloy 6 may be circulated therethrough by a suitable pump 7.

The superposed mass of molten cyanid or the like, hereinbefore referred to is shown at 8. The primary anodes 9 may be of any suitable description; but the secondary cathode or "plunger" 10, which may be of carbon or metal, *e. g.*, cast iron, as above described, is axially apertured at 11 for the passage of the nitrogenous reagent or reagents therethrough. Such reagents may be gaseous ammonia, trimethylene or the like and pass down through the said aperture to the lower face of the cathode. I prefer to provide a long spiral groove 12 which starts from the opening in the center of the face of the cathode and winds outwardly toward the periphery, so that when a gaseous reagent is introduced through the hollow shank of the cathode or plunger, it will be forced to follow the course of the spiral groove, and thus be made to travel a distance of several feet in contact with alkali metal, the electrolyte, and the suspended or dissolved material in the electrolyte. The sides of the groove preferably are angularly disposed as shown and form a spiral ridge on the face of the plunger. I have found, when the ammonia is thus made to move or travel along an open bottom groove or conduit in contact with alkali metal, the electrolyte, finely divided suspended carbon in the latter, etc., while continuously submerged in the molten cyanid, that a notable advantage results, in that this procedure permits the introduction and complete reaction of the ammonia, trimethylamin, etc., far more expeditiously and perfectly than is possible when employing merely a flat cathode surface.

If a supplementary nitrogenous reagent such as ammonia be employed in addition to such a reagent as trimethylamin, it may either be introduced through the hollow shank of the cathode together with the trimethylamin, or through a separate pipe 13. An overflow and withdrawal pipe 14 is provided for the product, and a vent 15 for the gas evolved in the primary cell. Current is led in through the electrodes 9, passes thence through the molten sodium chlorid 16 or the like, through the molten alloy 6, molten cyanogen mass 8 and thence out through the cathode 10.

The terms "direct reaction" and "directly reacting" as used in the appended claims are intended to differentiate from intermediate or step-by-step reactions.

In the present process the elements, being for the most part in the nascent state, immediately and directly react to form the resultant product.

The present process may also be substantially, although not so efficaciously, effected by liberating the alkali metal from the alloy by electrolytic deposition, for example, as described in my application 575,819, above referred to; permitting said metal to accumulate on the surface of the cyanid or like electrolyte, and there reacting upon said metal with ammonia, hydrocarbon amins, their decomposition products, (*e. g.* trimethylamin) or the like, or the mixtures of any of the foregoing. Said process may hence be conducted either continuously or intermittently; and obviously the primary and secondary furnaces may, if desired, be entirely separate and distinct from each other.

With reference to the term "nascent" as applied to alkali metals in the appended claims, I desire to point out that it is barely possible that a freshly deposited or freed metal of this class may not be in exactly the condition to which this term is generally applied (as to nitrogen, for example); but such metals are at the moment of liberation, and possibly for a short while thereafter, more active chemically than at other times, and hence this term is applied to said metals when in such condition.

What I claim is:—

1. The process of producing cyanogen compounds, which comprises electrolytically depositing an alkali metal and effecting a

direct reaction between such metal, while in the nascent state, and a gaseous nitrogenous compound associated with a carbonaceous substance, said reaction taking place at a temperature approximating a red heat.

2. The process of producing cyanogen compounds, which comprises effecting a direct reaction in a heated medium free from water and water forming constituents between an alkali metal in the nascent state and a gaseous nitrogenous compound associated with a carbonaceous substance.

3. The process of producing cyanogen compounds which comprises effecting a direct reaction in a mass of molten cyanogen compounds, between an alkali metal in the nascent state and a nitrogenous reagent associated with a carbonaceous substance, said reagent including hydrogen as one of the constituents thereof, and the said mass being free from water and water forming constituents.

4. The process of producing an alkali-metal cyanogen compound which comprises directly reacting with trimethylamin on electrolytically-deposited, nascent alkali metal at the instant of its deposition from, and while within, a bath of fused cyanogen salt.

5. The process of producing cyanogen compounds which involves reacting on an electrolytically deposited metal with a hydrocarbon-nitrogen compound while said metal is still in the nascent state due to its electrolytic deposition.

6. The process of producing cyanogen compounds which involves reacting on an electrolytically deposited metal with a hydrogen-carbon-nitrogen compound which is free from oxygen while said metal is still in the nascent state due to its electrolytic deposition.

7. The process of producing cyanogen compounds which comprises reacting on a metal while in the nascent state with a hydrogen-carbon-nitrogen compound which is free from oxygen and with a supplementary nitrogenous reagent.

8. The process of producing cyanogen compounds which comprises effecting a direct reaction between a metal while in the nascent state, carbon and nitrogen, both of said last mentioned elements being also nascent at the instant of such reaction while excluding oxygen from the vicinity of such reaction.

9. The process of producing cyanogen compounds which comprises electrolytically depositing an alkali metal by a direct electric current, and effecting a direct reaction between the so deposited metal, carbon and nitrogen, the latter element and the metal being in the nascent state at the instant of such reaction.

10. The process of producing cyanogen compounds, which comprises electrolytically depositing an alkali metal from a mass of molten salt, and immediately and directly reacting on the so deposited metal with gaseous nitrogenous and carbonaceous reagents, to form the product sought.

11. The process of producing cyanogen compounds, which comprises electrolytically depositing an alkali metal from a mass of molten salt by passing a direct current through said salt from a mass of alloy comprising said alkali metal, and directly reacting on the so deposited metal with a reagent other than the said salt, to form the product sought by a single reaction.

12. The process of producing cyanogen compounds, which comprises reacting on a metal while in the nascent state by passing a stream of gaseous nitrogenous reagent over a surface of such metal in the presence of a carbonaceous reagent, said stream being maintained in intimate contact with said surface until substantially all of the molecules of the nitrogenous reagent have been involved in the reaction.

13. The process of producing cyanogen compounds, which comprises reacting on a metal while in the nascent state by passing a stream of gaseous carbonaceous reagent over a surface of such metal in the presence of a nitrogenous reagent, said stream being maintained in intimate contact with said surface until substantially all of the molecules of the carbonaceous reagent have been involved in the reaction.

14. The process of producing cyanogen compounds, which comprises reacting on an electrolytically deposited metal by passing a stream of gaseous reagent over a surface of such metal, said reagent comprising both carbon and nitrogen.

15. The process of producing cyanogen compounds, which comprises directly reacting on an electrolytically deposited metal with a non-salt nitrogenous compound associated with a carbonaceous substance, at a temperature substantially exceeding the melting point of sodium cyanid and in a mass of molten material.

16. The process of producing cyanogen compounds, which comprises directly reacting on an electrolytically deposited metal with a non-salt carbonaceous compound associated with a nitrogenous substance, in a mass of molten material.

17. The process of producing cyanogen compounds, which comprises directly reacting on an electrolytically deposited metal with a gaseous carbonaceous compound associated with a nitrogenous substance, in a mass of molten material.

18. The process of producing cyanogen compounds, which comprises reacting on a metal while said metal is in the nascent state with a non-salt compound comprising car-

bon and nitrogen, in a mass of molten material, to thereby immediately form a cyanogen compound.

19. The process of producing cyanogen compounds, which comprises forming an alloy of an inert metal and an alkali metal at a temperature exceeding the melting point of sodium cyanid, electrolytically depositing said alkali metal out of said alloy, and directly reacting on the so deposited metal with a gaseous nitrogenous compound in the presence of a carbonaceous reagent to thereby form the product sought.

20. The process of producing cyanogen compounds, which comprises forming an alloy of an inert metal and a relatively light metal at a temperature exceeding the melting point of sodium cyanid, electrolytically depositing said light metal out of said alloy, and directly reacting on the so deposited metal with a non-salt reagent to form the product sought, the temperature at which the reaction occurs being substantially that at which the alloy is formed.

21. The process of producing cyanogen compounds, which comprises forming an alloy of an inert metal and a relatively light metal at a temperature exceeding the melting point of sodium cyanid, electrolytically depositing said light metal out of said alloy, and reacting on the so deposited metal with trimethylamin to form the product sought, the temperature at which the reaction occurs being substantially that at which the alloy is formed.

22. The process of producing cyanogen compounds, which comprises forming an alloy of an inert metal and a relatively light metal, electrolytically depositing said light metal out of said alloy, and reacting on the so deposited metal with trimethylamin to form the product sought.

23. The process of producing an alkali-metal cyanogen compound which comprises directly reacting with a hydrocarbon amin on electrolytically-deposited, nascent alkali-metal, at the instant of its deposition from, and while within, a bath of fused nitrogenous salt.

24. The process of producing cyanogen compounds which comprises reacting on a metal while in the nascent state with a hydrocarbon-nitrogen compound and a supplementary nitrogenous reagent.

25. The process of producing cyanogen compounds which comprises reacting on a metal while in the nascent state with a hydrocarbon-nitrogen compound and a supplementary reagent, one constituent element of which is a constituent element of the said hydrocarbon-nitrogen compound.

26. The process of producing cyanogen compounds which involves reacting on a metal capable of acting as the base of a cyanogen compound, and while said metal is in the nascent state, with a hydrogen-carbon-nitrogen compound, portions of whose carbonaceous and nitrogenous constituents are capable of combining to form a radical comprising carbon and nitrogen, when the said compound is reacted upon by said nascent metal.

In witness whereof, I subscribe my signature, in the presence of two witnesses.

CHARLES E. ACKER.

Witnesses:
WALDO M. CHAPIN,
WILLIAM C. LARY.