C. E. ACKER.

PROCESS OF PRODUCING CYANOGEN COMPOUNDS AND THE LIKE.

APPLICATION FILED AUG. 30, 1910.

1,072,373.

Patented Sept. 2, 1913.

3 SHEETS—SHEET 1.

Fig. 1.

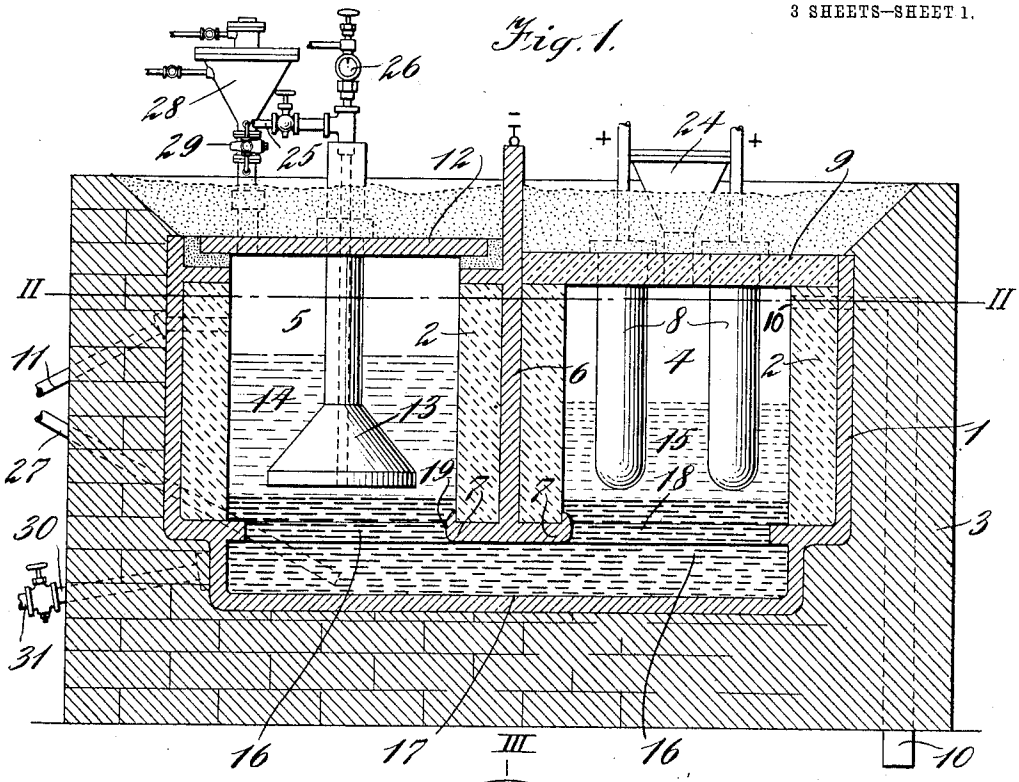
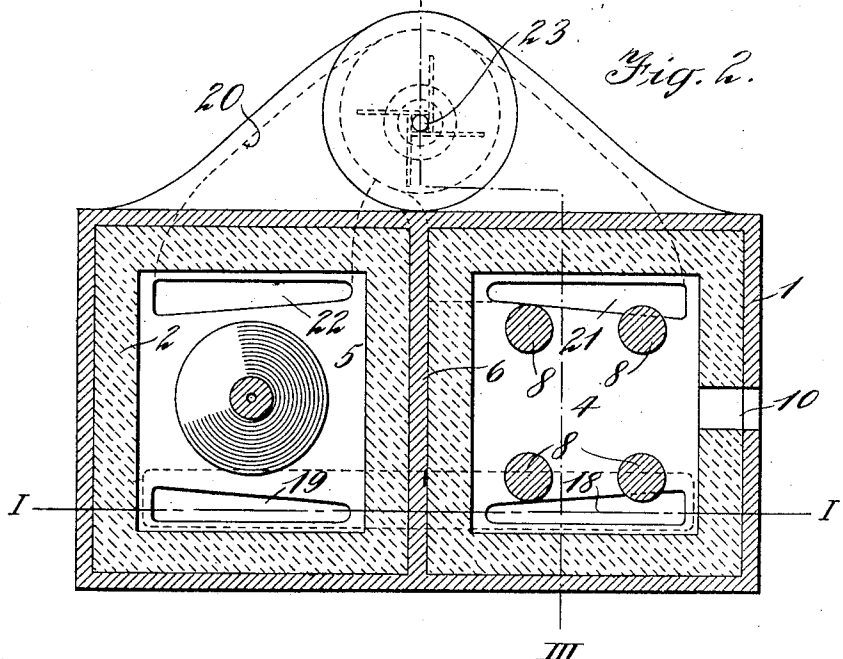


Fig. 2.



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3 SHEETS—SHEET 2.

Fig. 3.

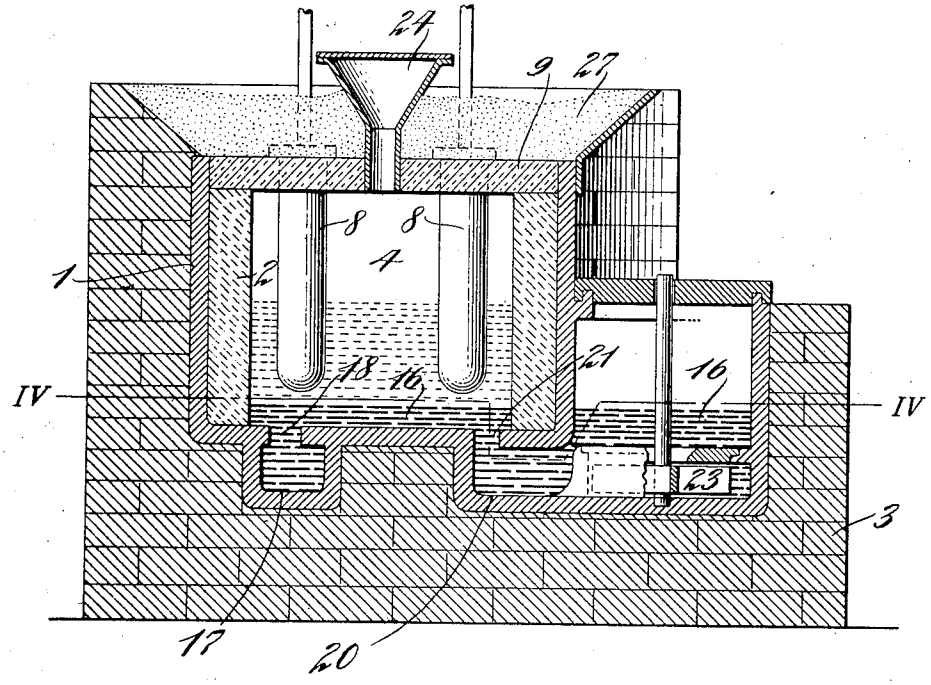
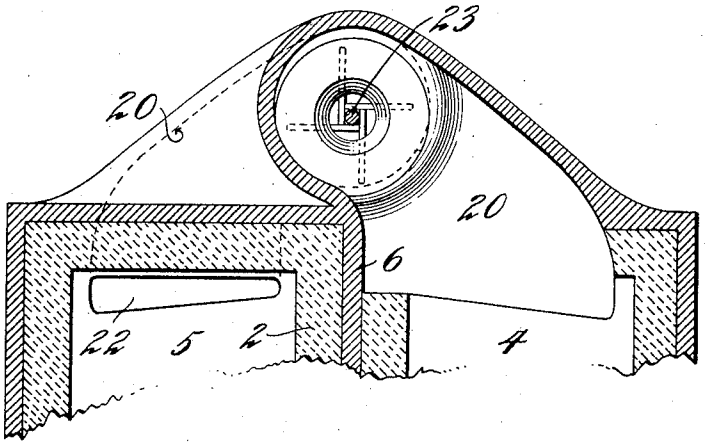


Fig. 4.



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3 SHEETS—SHEET 3.

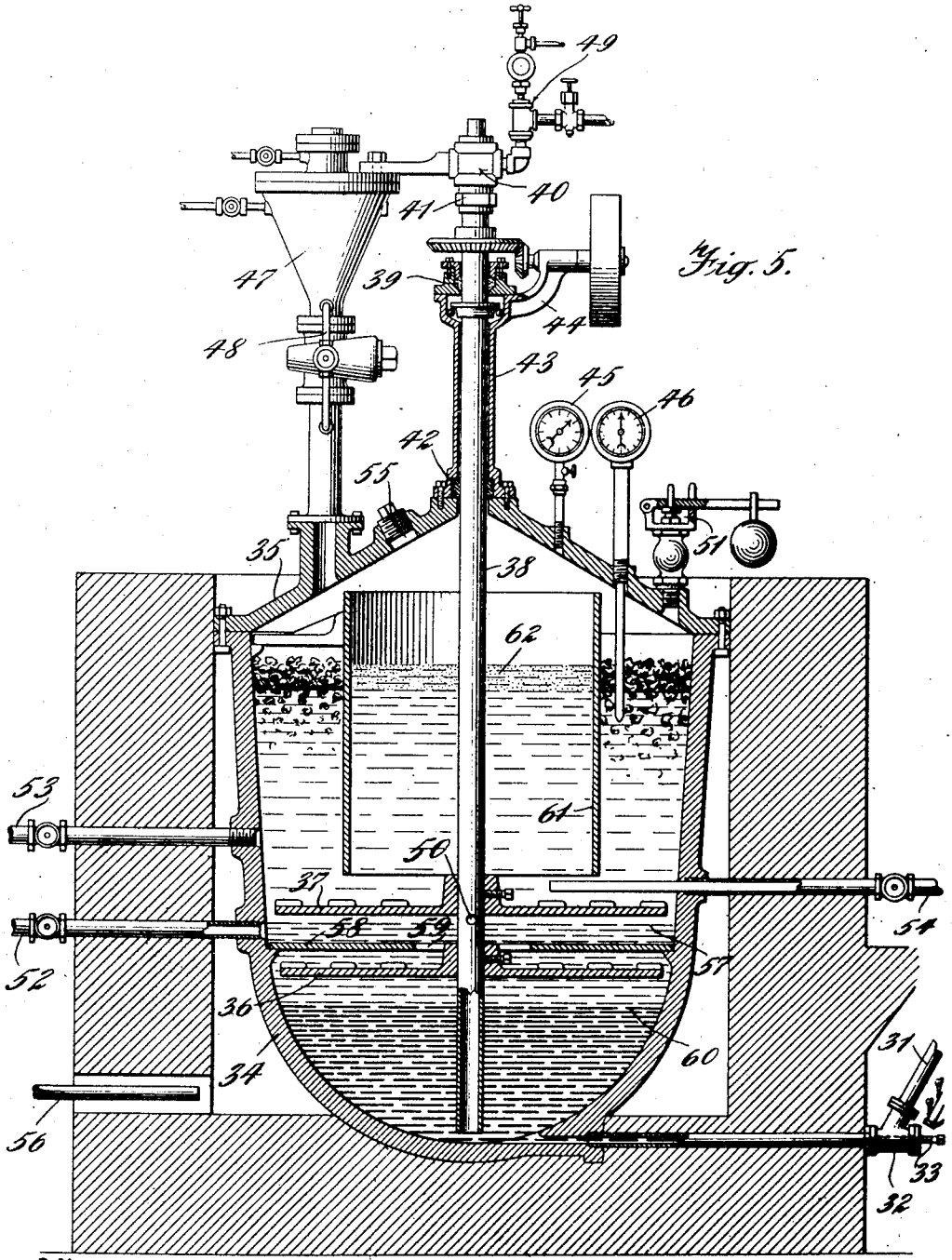


Fig. 5.

Witnesses:

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UNITED STATES PATENT OFFICE.

CHARLES E. ACKER, OF OSSINING, NEW YORK, ASSIGNOR TO THE NITROGEN COMPANY, A CORPORATION OF NEW YORK.

PROCESS OF PRODUCING CYANOGEN COMPOUNDS AND THE LIKE.

1,072,373. Specification of Letters Patent. Patented Sept. 2, 1913.

Application filed August 30, 1910. Serial No. 579,763.

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 Processes of Producing Cyanogen Compounds and the Like, of which the following is a full, clear, and exact description.

This invention relates to a process for the manufacture of alkali metal cyanids, cyanamids and the like, and more particularly to certain improvements in the process described in my United States application Serial No. 485,344, filed March 23, 1909, the process therein disclosed consisting in initially reacting on a particularly "reactive metal", such as barium, lithium, calcium, strontium, manganese, etc., with carbon or a carbonaceous reagent, for the purpose of producing a carbid of such metal, *e. g.*, barium carbid; in then treating this carbid with nitrogen or a nitrogenous reagent, for the purpose of producing the cyanid of such metal, in this case barium cyanid; and in finally reacting on the barium cyanid with an alkali metal, *e. g.*, sodium with the consequent production of sodium cyanid and metallic barium. It was stated in the application aforementioned that the "reactive metal" *e. g.*, barium, might combine directly with nitrogen to form barium nitrid, which would then react with the carbonaceous reagent to form barium cyanid; and that this cyanid would in turn be decomposed by sodium as above with formation of sodium cyanid and metallic barium. It was further stated that both carbid and nitrid might be formed under the conditions of the process, and that these products might in turn then react together to form "reactive metal" cyanid, *e. g.*, barium cyanid, which would then be similarly decomposed by metallic sodium.

While it is possible to bring about the reactions substantially as hereinabove described, I find, as a result of further investigation of the phenomenon, that in practice by far the greater part of the final product is produced as the result of the initial formation of "reactive metal" carbid, in what seems to be a particularly favorable physical condition, such carbid when in such condition readily absorbing and combining with nitrogen; and that as a consequence, but a comparatively small proportion of the final product is obtained as a result of the initial formation of reactive metal "nitrid"; this small proportion of course combining with carbon in the manner above described to form the cyanid, etc. Sufficient free carbon being present, I consider that the principal reactions are as follows:

$$(1)\ Ba+2C=BaC_2$$
$$(2)\ BaC_2+N_2=Ba(CN)_2$$
$$(3)\ Ba(CN)_2+2Na=Ba\ (\text{free metal})+2NaCN.$$

If anhydrous ammonia is employed instead of free nitrogen, the second of the above equations will be as follows:

$$(4)\ BaC_2+2NH_3=Ba(CN)_2+6H.$$

The "reactive metal" *e. g.*, barium, and the alkali metal, *e. g.*, sodium, may be employed in the manner then stated, to wit, either in the pure state, in the form of an alloy with each other, or in the form of an alloy with certain relatively inert metals, such as lead, tin, etc. The nitrogen may be employed in the form of pure or diluted gas, ammonia, or other nitrogenous reagent; while the carbonaceous reagent may be employed in the form of finely divided, granular, or lump charcoal, coal, coke, or a hydrocarbon gas, fuel oil, lamp black, or cyanids or cyanamids. If the source of carbon is a gas, fuel oil or lamp black, the resultant carbid produced by the combination of the "reactive metal" with carbon as pointed out in the patent application above referred to, is found to be present solely in finely divided form.

I have discovered that the carbid produced in the present process is apparently amorphous and impalpable, which is evidently a result of the very low temperature at which it is produced, generally below 900° C. and under most radically different conditions from the impure, hard, iridescent, crystalline carbids which are pro-

duced at temperatures ranging from 1400° to 1800° C., or more. The terms amorphous and impalpable particularly well describe this substance since the separate particles of it which are produced, if indeed they may be termed particles, are so minute that they cannot be seen by the naked eye; and are non-crystalline and probably porous. They are non-crystalline by reason of the fact that the temperature at which this form of carbid is formed, under the conditions of the process, is sufficient to permit the formation thereof; but is not sufficient to fuse or liquefy the same; as a result of which fact the molecules of the material have no opportunity to arrange themselves to form crystals, and the resultant substance is amorphous. In so far as I am aware, it has never been possible to produce this form of carbid up to the time of my invention and discovery thereof.

It is obvious that the physical characteristics above referred to promote the reactions whereby the cyanid is formed. I desire now to differentiate the particular process herein described and that set forth in the aforementioned patent application. The particular methods originally described, involved the interaction of various substances (1) within the mass of molten metals or alloy,—or in other words when partly or wholly submerged therein; (2) when brought into intimate contact with each other and with the changing surfaces of the molten reactive metal, alkali metal, or alloy, while contained in a revolving retort or cylinder,—and under pressure, if desired; (3) and by first reacting on the alloy with carbon to produce carbid; then withdrawing the alloy from a chamber containing carbid coated charcoal or coke, or carbid containing masses, introducing nitrogen or other reagent into the chamber under pressure so that the same may intimately contact with the carbid, and in finally returning the molten alkali metal alloy to the chamber. I have discovered, however, that greatly increased efficiency and speed in carrying out the process may be had by causing or permitting both carbon and carbid in very finely divided form to rise from the surface of the alloy and from thence become diffused throughout the accumulated molten cyanid itself. In other words, I have now discovered that it is possible and most desirable to induce most of the reactions in question to occur outside of the mass of alloy in contradistinction to the process originally described, wherein the reactions occur principally at or below the surface of the alloy, with the primary object of there effecting the synthesis of sodium cyanid. When the original process was carried out the sodium cyanid by reason of its low specific gravity flowed through and accumulated on the surface of the alloy, and it was this action that led to the discovery that both the carbon and carbid would, if in sufficiently finely divided form, rise to the surface and become diffused in the manner above described.

Certain matter related to the present invention is set forth and claimed by me in my divisional Patent No. 1,019,002, granted February 27, 1912.

Referring to the accompanying drawings, which form a part hereof: Figure 1 is a vertical cross section of an apparatus adapted for the carrying out of my improved process; said section being taken on line I—I of Fig. 2. Fig. 2 is a horizontal section through the said apparatus taken on the line II—II of Fig. 1. Fig. 3 is a transverse vertical section of said apparatus taken on the line III—III of Fig. 2. Fig. 4 is a fragmentary section taken on line IV—IV of Fig. 3. Fig. 5 is a central vertical section of a reaction vessel or pot which is especially well adapted for carrying out the latter steps of my process.

Like parts are designated by the same reference sign throughout the respective views.

Referring now to the first four figures, the furnace or inner container 1 should preferably be made of cast iron or cast steel, and the inner walls of such chamber should preferably be lined with refractory material 2, such as alumina or magnesia. The furnace casting is inclosed at the bottom and on all sides by heat insulating material 3, preferably brick or the like. The furnace comprises two principal chambers, an electrolytic chamber 4 and a reaction chamber 5, these chambers being separated by a septum or wall 6; the bottom flanges 7 of this wall serving to support the adjacent side linings 2. A set of anodes 8 extend into the electrolytic chamber and are preferably made of some form of carbon. The electrolytic chamber 4 is covered with a slab 9 of suitable refractory material; and the gases liberated at the anodes are conducted away through flues 10. The reaction chamber 5 is fitted with a spout 11 for conducting off the final product, such compartment having a cover 12 spaced from the container by an air tight gasket to prevent the admission of air into the reaction chamber. A casting 13, called a plunger, preferably provided with a flattened lower face, projects through the cover into the mass of a fluid salt 14 disposed in the reaction chamber; the electrolyte in the electrolytic chamber being designated 15.

A body of heavy metal or alloy 16 is disposed in the bottom of the respective compartments or chambers, and a plurality of conduits, filled by said alloy, afford means for effectively circulating the heavy metal or alloy through and sealing the respective chambers. In the form of furnace in ques-

tion, one of such conduits is shown in section in Fig. 1 and has been designated 17; a passage 18 leading down into it from chamber 4 and a corresponding passage 19, leading from it to chamber 5. The second conduit 20 is in communication with the further sides of the respective chambers through passages 21, 22, the conduit 20 leading therefrom to a suitable pump 23. This pump is preferably of the centrifugal type, but any suitable apparatus may be employed for this purpose. The movement of the mass of fluid alloy through the chambers, results in stirring up the respective molten salts, since such bodies float upon the surfaces of the alloy in the respective chambers. The circulation of this alloy may be effected either intermittently or continuously by mechanical means or otherwise, and suitable means, such as a hopper 24, may be provided for permitting the continuous or intermittent introduction of the salt required in the electrolytic chamber. The "plunger" is adjustable in the air tight cover 12 and has a hole extending through its shank, the upper part of which is fitted with a valved pipe 25 for introducing nitrogen or ammonia into the molten mass in the reaction chamber; and is also fitted with an oil feed device 26, through which fuel oil or other hydrocarbon may be introduced in carefully regulated quantities into the reaction chamber. An auxiliary supply pipe 27 extends through the side of the reaction chamber, which pipe may be used to introduce nitrogen or hydrocarbon, or both, directly into the mass of molten metal, when desired. The cover 12 is also fitted with a specially constructed hopper 28, which has an air tight cover and is so arranged that it may be filled with charcoal and then subjected to a vacuum for the purpose of exhausting the air from the hopper and the charcoal contained therein, before it is charged into the reaction chamber, the connections for exhausting the air being indicated at 29. The molten cyanid is produced in the reaction chamber and normally rises to a relatively high level before it is permitted to run off through the spout 11; this spout being temporarily closed, when desired, to permit the cyanid to accumulate in the chamber before being tapped off.

In starting the apparatus the electric current is passed through the electrolyte in the electrolytic chamber, such electrolyte consisting, for example, of barium chlorid and sodium chlorid, at a sufficiently high voltage and current density to simultaneously liberate both metallic barium and sodium on the surface of the molten lead constituting the cathode and in electrical contact with flange 7 of wall 6. The liberated metals combine with the lead to form an alloy of barium, sodium and lead, which is conducted into or circulated through the reaction chamber by means of the centrifugal pump. The entire mass of molten metal in the apparatus soon becomes of practically uniform composition and temperature, and increases in volume to a considerable extent. Carbon in the form of charcoal, from which the air and moisture have been removed is then introduced through the hopper 28 and falls into the reaction chamber. If a large quantity of the charcoal is so introduced its weight will be sufficient to submerge a part of it in the molten alloy. The piston-shaped casting or plunger may be lowered to a point where its lower surface or "face" is submerged in the molten alloy. Fuel oil under pressure may then be introduced through the oil feed device and will come in contact with the red hot alloy below the surface of the plunger, at which temperature the oil will be broken up into finely divided carbon (lamp black) and hydrogen, the latter of which will escape through the overflow spout 11. If there is sufficient barium in the alloy it will combine with the carbon of the charcoal or with the carbon produced by the decomposition of the oil to form barium carbid, some of which will be held submerged in the alloy against the lower surface of the plunger, and some of which will be forced out by the escaping hydrogen. Nitrogen may be introduced through pipe 25 and will then pass down through the hollow shank of the plunger to the lower surface thereof, and then spread out in the form of a thin layer between the face of the plunger and the molten alloy and thus come into more or less effective contact with the carbids which will have been produced in accordance with the reaction hereinbefore referred to. That portion of the nitrogen which comes into reactive contact with some of the barium carbid then combines therewith to produce barium cyanid. The barium in the barium cyanid is then displaced by metallic sodium in the alloy with the consequent production of sodium cyanid and metallic barium; the barium immediately becoming available for the production of more carbid. As soon as a sufficient proportion of barium (or other "reactive metal") has been incorporated into the alloy to react readily with the carbon it becomes unnecessary to supply more for the reason that the "reactive metal" is used over and over again and therefore no more barium chlorid need be added to the electrolyte. If any loss of available barium occurs in the alloy or of barium carbid or cyanid in the melt through any unavoidable or inadvertent circumstance; or if as in some cases, a certain proportion of the barium cyanid is allowed to be drawn off together with the sodium cyanid produced, or for any other reason, the deficiency may be

supplied from time to time by adding barium chlorid to the electrolyte or by supplying it in any other manner.

Sodium cyanid is very fusible at the temperature of the operation and raises to and accumulates on the surface of the alloy. I have found that the presence of a considerable body of molten cyanid on the surface of the alloy is highly beneficial, in that the presence of this fluid mass permits the amorphous barium carbid and finely divided carbon to become diffused therein; being mixed and suspended to a considerable extent and thus much more easily brought and held in reactive contact with the nitrogen or nitrogenous reagent. The entire mass of cyanid is practically saturated with impalpable carbid and if a sample of the molten cyanid be withdrawn during the process, and moistened with water, the presence of carbid is very evident from the odor of the evolved acetylene, although no lumps or crystals of carbids whatsoever may be visible. The carbid is therefore present in a very fine state of division, and is probably entirely amorphous, although it is possible that it may in part, at least, be in actual solution.

When the cyanid is examined under the microscope the pure colorless crystals of cyanid loom up very large and clear, and squeezed in between the crystals is the dark gray or black carbid apparently in the form of a film. The moisture in the air attacks this film of carbid between the crystals at the exposed edges of the film and minute bubbles of gas are constantly given off all along the exposed edges.

Evidently the carbid is in very soft condition since it is squeezed into the thin spaces between the crystals of the cyanid in the manner described; but it is impossible to examine it directly in the open air on account of the minute bubbles of gas which instantly cover its surface.

The specific gravity of some carbids, *e*, *g*., barium carbid, is considerably greater than that of molten sodium cyanid, but owing to the fact that these carbids are apparently in amorphous condition, very little agitation is required to maintain them in suspension. A little fuel oil injected into the alloy or into the molten cyanid and used primarily as a source of carbon, suffices to produce all the agitation required to maintain both the carbon and amorphous carbid in suspension in the molten cyanid; and if there is then escaping around the edge of the plunger and passing up through the alloy an excess of nitrogen or ammonia, I find that such gases arising in the form of bubbles into the superimposed body of molten cyanid, also keep the carbon and carbid in suspension and that nitrogen or ammonia there advantageously reacts with the suspended and impalpable, or possibly even dissolved barium carbid, to form barium cyanid. The latter compound, dissolving in the molten sodium cyanid, is then or afterward easily brought into contact with the necessary alkali metal or alkali metal alloy and transformed into sodium cyanid and metallic barium. This liberated barium soon seizes upon more carbon to reform amorphous barium carbid which again becomes suspended in the molten cyanid ready to combine with more nitrogen, ammonia, or other nitrogenous reagent; this cycle being indefinitely repeated. I have discovered, furthermore, in employing either free nitrogen or ammonia as the nitrogenous reagent, that it is not necessary at any time to bring the gas into actual contact with the molten metal, either at the surface of the molten alkali metal, "reactive metal", when used in a pure state, or molten alloy, containing either of them; nor to inject it into the mass, *i. e.*, below the surface thereof, provided there is present on the surface of the alloy a sufficient body of molten cyanid. The plunger may, hence, in such case, be raised so that its lower surface is entirely above the molten alloy, but still submerged in the cyanid.

The absorption of free or molecular nitrogen by the pure suspended barium carbid, formed under the conditions of the process, when heated, may be attributed to either one or both of two things; namely, the amorphous condition of such carbid, in which respect it is radically different from the hard crystalline pure carbid which Moissan stated (*Comptes Rendus* 1894, page 503) would not absorb free nitrogen; and because the molten cyanogen compound in which the carbid is suspended apparently assists the absorption in a way not as yet understood.

The temperature of the lower end of the plunger when submerged in the red hot alloy, is of course, substantially equal to that of the molten metal itself; but if the face of the plunger be raised above this efficient metallic heat conductor, I find that sufficient heat may be conducted away through the shank of the plunger, to the outside of the furnace, to materially reduce the temperature of the face and entire lower end of the plunger and of the molten cyanid in immediate contact therewith; and this is a fact of great importance when ammonia is employed as the nitrogenous reagent. The combination of the nitrogen of the ammonia with the amorphous carbid suspended in the molten cyanid takes place with great rapidity and efficiency owing to the fact that the nitrogen is liberated in nascent form directly in contact with the carbid, whereas if the ammonia were first introduced into the red hot alloy, it would be partly decomposed into free nitrogen and hydrogen, and this free nitrogen rising into the molten cyanid does not combine with the carbid with anything like the

same degree of avidity as it does when in a nascent state. The absorption of free nitrogen, in other words, is effected much more slowly than the absorption of nascent nitrogen. While it is prejudicial for this reason to first introduce ammonia into the molten metal, this objection does not hold with free or molecular nitrogen, which may in fact be advantageously introduced in the molten metal, for the purpose of pre-heating such nitrogen before it comes in contact with the carbid, whether the carbid is suspended in the molten metal or in the molten cyanid, or both. It may hence be desirable, in some cases, to introduce nitrogen through the pipe 27 directly into the body of the molten alloy while simultaneously introducing ammonia into the cyanid mass thereabove through the instrumentality of the hollow plunger.

In practicing this process of effecting reactions within a body of the molten cyanid itself, I prefer to introduce the necessary cyanid in the reaction chamber at the outset instead of building it up carefully as described.

After the process has been carried on for some time and the reaction vessel is sufficiently full of cyanid, the flow of gas should be stopped and the alloy should be circulated a short time longer in order to insure the decomposition of all of the barium cyanid by sodium, after which the mass should be allowed to settle.

For certain purposes, as for example in the extraction of gold from ores, it is not always essential that the sodium cyanid be absolutely pure; and a small percentage of barium cyanid which will react in substantially the same manner as the sodium cyanid may be permitted to remain. In such case it is not necessary to allow the mass to settle in the manner above described. Barium carbid, which has a specific gravity somewhat greater than sodium cyanid will settle out together with the excess carbon to the surface of the alloy in the course of time, after which the clear sodium cyanid or part of it may be tapped off at one of the spouts above the sodium alloy.

The apparatus which I have just described is adapted to the more or less continuous utilization of the alkali metal in the alloy, and while in practically free communication with the alloy in the electrolytic chamber.

In my previous application, above referred to, I pointed out that the reaction chamber might be quite distinct and widely separated from the electrolytic chamber, and adapted to the continuous or intermittent treatment of a very large body of alloy, the product, for instance, of several large electrolytic furnaces. In this connection therefore it is obvious that the alloy produced in the apparatus shown in Figs. 1, 2, 3 and 4, need not be utilized *in situ;* but a portion of it may be tapped off from time to time through the valved pipe 30, and conducted in fluid condition directly to a separate reaction vessel. The alloy will accumulate in the furnace and will constantly expand and rise in the chamber; which in this case will therefore simply be used as a storage reservoir for the alloy, preparatory to tapping off a portion thereof; and not as a reaction chamber. The alloy may be run from a number of such furnaces into a single reaction vessel, such as that shown in Fig. 5, which is adapted to treat several tons of alloy at one time; and suitable removable pipe connections 31 may be provided for this purpose between the valved pipe 30 and the Y, or like connection 32, shown in Fig. 5. The connection 32 is disposed adjacent a section of pipe, the opening leading from which may be closed by any suitable means, such as that indicated at 33. The alloy may be conducted through the pipe sections 30 by gravity or it may be impelled by vacuum, gas pressure, or suitable mechanical means from one vessel to the other.

The reaction vessel or pot shown in Fig. 5 consists of a large cast iron pot 34 which is flanged at the top and fitted with a gas tight cover 35 which is bolted thereto; the pot being provided with a mixing or stirring device comprising one or more flat disks or plates 36 and 37; such plates having ribbed projections on their upper sides and being mounted on a vertical hollow shaft 38 which passes through a stuffing box 39, preferably located at some distance above the cover so as to be out of the hot zone. This hollow shaft connects above the bearings with a stationary supply pipe 40 by means of a gas tight slip-joint 41. The shaft is steadied within the pot by means of a carbon bearing ring 42 which is held in position upon the cover by means of a suitable sleeve 43, this sleeve carrying a bracket 44 wherein is journaled suitable driving mechanism for rotating the said shaft.

The pot and all its fittings should be adapted to withstand heat; and pressure as high as 75 pounds per square inch may be employed. The pot should be fitted with a pressure gage 45, a pyrometer 46, a hopper 47, such hopper having a valved pipe 48 for permitting the exhaustion of air from the hopper, and an oil feed device 49, connecting with the stationary supply pipe 40, for introducing nitrogen, ammonia, or a mixture thereof, and oil, which will pass downwardly through the hollow shaft escaping from the lower end thereof near the bottom of the pipe. If, however, a plug be removed from the orifice 50, which is disposed just below the disk 37, the gas will be discharged at a much higher level and above the surface of the alloy. The nitrogenous gas and fuel oil may be either simultaneously or alternately

introduced through the hollow shaft; or in any other suitable manner.

The residual hydrogen gas from fuel oil or ammonia, or any residual nitrogen gas which may accumulate in the pot and tend to raise the pressure above the working limit, may escape from a safety valve 51. Such gas may, obviously, if desired, be collected and further utilized. The pot may be fitted with valved pipes near the bottom thereof and at different levels, as shown at 52, 53, and 54; which devices together with pipe 30 may be used for receiving and discharging the materials required and produced in the process. An opening 55 may be provided for permitting examination of the interior of the pot before starting the process. Air must in all cases, however, be excluded while operating.

The reaction vessel or pot may be heated electrically; or externally by the combustion of suitable fuel, to a working temperature approximating a red heat; a fuel oil burner being indicated at 56 which may be used for external heating.

The barium-sodium alloy, or the like, may be charged in the reaction vessel up to the level designated 57; and charcoal in finely divided or lump form, or both, may then be charged through the hopper 47. The air must be exhausted from the pot in all cases before starting in order to eliminate oxygen, and for the same reason air and moisture should also be removed from the charcoal. If the charcoal has been stored after preparing it, it is advisable to heat it under a vacuum in order to thoroughly remove moisture and occluded gases; and such charcoal should be charged into the reaction pot without again coming into contact with the air.

Instead of using charcoal, fuel oil, which does not contain oxygen, may be used to advantage; the oil being broken up into its constituents at the temperature and under the conditions of the process and thus supplying the necessary carbon. The mechanical stirring device may then be started and the contents of the pot treated with nitrogen or ammonia, or both. Nitrogen or ammonia gas may be introduced either below or above the surface of the molten alloy, depending on whether the opening 50 be opened or closed; and sufficient gas may be introduced at one time to produce a pressure of 75 pounds or less, per square inch, within the vessel. The barium or other reactive-metal, *e. g.*, lithium in the alloy will combine directly with both the nitrogen and carbon and the action will proceed in the presence of metallic sodium to produce sodium cyanid, which will then accumulate above the alloy; but in starting the operation in a separate reaction vessel it is desirable, and more convenient, to introduce a sufficient charge of alkali metal cyanid directly into the reaction pot at the beginning of the operation instead of gradually building it up by reacting with carbon and nitrogen on the alloy; such latter operation being both inefficient and tedious.

After a sufficient body of molten cyanid has been introduced or accumulated the gaseous nitrogen or ammonia may be simply injected into the body of molten cyanid itself through the orifice 50; or may even be simply brought in contact with the surface of the cyanid and not injected into the alloy at all in order to react efficiently when the barium or lithium carbid, or other finely divided carbids in suspension, solution, or both. If, however, the gaseous nitrogen or ammonia escapes at the lower extremity of the hollow shaft, orifice 50 being plugged, the bubbles of gas will then rise through the alloy and strike the lower surface of the plate 36, which at first will be submerged in the rich bulky alloy. The bubbles of gas can only escape by passing along the under surface of this plate to the periphery thereof, after which they will rise and strike the underside of the baffle plate 58, and will then pass along to the center of this plate in intimate contact with the alloy. Any uncombined gas will then bubble up through the surface of this alloy passing through the orifice 59 in the center of plate 58, and strike the under surface of plate 37, which is preferably submerged in the molten cyanid from the beginning action of the operation. The nitrogen introduced on the under side of plate 37, is thus held submerged in the molten cyanid by this plate or disk which insures most favorable conditions for absorption. Any unabsorbed nitrogenous gas or residual hydrogen may then pass around the periphery of the plate 37 and escape to the upper part of the vessel. If the orifice 50 is open the gaseous nitrogen or ammonia will obviously not pass through the bottom of the shaft, but will pass through the cyanid below the plate 37. The impoverished alloy in the pot which extends up to the line 60 may be returned to the electrolytic furnace by means of compressed gases such as hydrogen, nitrogen, ammonia, or oil gas, acting on the surface of the alloy, or of the superimposed cyanid in the pot. Pressure then forces the fluid alloy up through the discharge pipe 31 from the bottom of the pot. The pipe 31, which extends outside of the brick-work of the pot and of the electrolytic furnace, may be inclosed in any suitable manner so as to leave a passage-way or flue therearound to permit independent heating of such pipe by a gas flame, or the like. The alloy may, however, be returned by any suitable lifting device for fluid metal if desired. Such device may be located somewhat near, but below, the reaction vessel so that molten metal will flow to it by gravity.

When the reaction pot is sufficiently full of cyanid, the flow of gas should be stopped and the agitator should run a short time longer in order to insure decomposition of all of the barium cyanid by sodium, after which the agitator should be stopped and the mass allowed to settle. The clear molten sodium cyanid or a part of it may be tapped off at one of the openings above the surface of the alloy, which latter, after the abstraction of the light metals therefrom will have greatly diminished in volume so that its surface may be as low as level 60. It will be observed by considering reactions No. 1 to No. 4 (representing the principal steps of the process) that the "reactive metal" *e. g.* barium passes from the metallic state, to carbid, from carbid to cyanid, and from cyanid back to the metallic state, and then over the same course again and again during numberless cycles. If there is insufficient free carbon present, some of the "reactive metals" *e. g.*, barium, lithium, etc., will combine with a portion of combined carbon in the sodium cyanid itself to form barium carbid and sodium cyanamid (dialkali cyanamid) probably according to the following equation:

(5) $4NaCN+Ba=2Na_2CN_2+BaC_2$

but the cyanamid thereafter on the introduction of free carbon into the molten mass, is promptly reconverted into cyanid. If, however, free carbon is not supplied the reduction of the cyanid to cyanamid by the barium or other "reactive metal" will proceed until the entire mass of cyanid is converted into cyanamid, and for this reason the process may be used for the production of alkali cyanamids, as well as cyanids.

I regard it as likely, in view of the fact that barium does reduce molten sodium cyanid to sodium cyanamid by combining with some of its combined carbon, and in view of the fact that molten sodium cyanid is in intimate and close contact with the barium at the moment of its liberation,—pressed against it in fact by the weight of the supernatant fluid cyanid, and in view of the impalpable and amorphous character of the barium carbid produced in the process at so low a temperature (below 900° C.) that the greater part of the barium carbid, which is concerned in the synthesis of sodium cyanid by this process is produced by barium combining with a portion of carbon in the cyanid itself,—it being understood, of course, that but a very small proportion of the whole mass of cyanid would be thus momentarily reduced,—and that the free carbon floating around therein quickly reconverts the reduced portion back to cyanid.

The element lithium may be regarded as being characterizable both as a reactive metal and as an alkali metal, since it is usable in the process in either capacity. Indeed, it may be used in the process in both capacities, as for example, when the alloy contains lithium as the reactive metal and the molten bath comprises lithium cyanid or cyanamid.

It will be apparent that a carbid, nitrid, cyanid, or cyanamid, if of sufficient purity and in suitable physical condition, may be employed at the outset instead of the "reactive metal" itself; that being possible by reason of the fact that the initial carbid or nitrid, under the conditions of the process, will be converted into either cyanamid or cyanid of the "reactive metal," and that the alkali metal sodium, or potassium will thereupon liberate or set free the "reactive metal" in metallic form.

Other "reactive metal" salts may be similarly introduced and decomposed with consequent liberation of a free "reactive metal" but the method is slightly objectionable for the reason that it introduces an impurity or diluent, *e. g.*, sodium chlorid into the final cyanid. Thus barium chlorid, lithium chlorid, etc., if introduced into the molten cyanid will melt and dissolve therein and come into contact with the sodium or potassium in the alloy, which will then decompose such chlorids with the formation of sodium or potassium chlorid and metallic barium or metallic lithium, which latter will be liberated according to the following equation:

(6) $LiCl+Na=$
$NaCl+Li$ (free "reactive metal").

It will be apparent from a consideration of the above reactions, that a free "reactive metal" must be employed at some point in the cycle or in lieu thereof a compound which will yield a free "reactive metal" at some point in the cycle, and that the use of any salt or compound which when introduced into the molten mass or employed under any of the conditions of the process, will yield such "reactive metal" at some point in the process, is within the scope of my invention. Other "reactive metals" may be employed instead of barium,—notably lithium, strontium and calcium, in which event the reactions will be quite similar to those indicated for barium.

The "reactive metals" manganese, cerium, chromium, titanium, vanadium, etc., have the property when heated of combining directly with carbon to form carbids, and with free nitrogen to form stable nitrids, and although they do not themselves form the base metal of stable cyanids under the conditions of the process, they will nevertheless bring about the synthesis of sodium or potassium cyanid under the process—the mechanism of some of the intermediate reactions being necessarily different from those

for which equations are given in this specification,—and being in fact, not clearly understood. The process also works somewhat more slowly when manganese, cerium, etc., are employed instead of barium, lithium, etc. Pure iron will also combine with carbon to form a carbid in the process, but it will not combine with free nitrogen to form a stable nitrid and will not accomplish the synthesis of alkali cyanid under the process.

If finely divided or amorphous manganese is brought into contact with carbon in a cyanid bath, manganese carbid will be readily formed and nitrogen or ammonia will react therewith to form a manganese nitrid, that will settle to the surface of the sodium-lead alloy, and there in contact with sodium and carbon will be formed sodium cyanid and finely divided manganese, the latter probably in amorphous condition. The manganese will not melt at the temperature of the operation and will not alloy with the lead. The same steps may be followed with chromium, cerium, etc. If the alkali-metal is employed in the pure state, instead of in the form of an alloy with a heavy metal, or if both pure alkali-metal and alloy be used, the reactions and the final result will be substantially the same as those already described. The pure sodium or potassium will float on the surface of molten cyanid, however, or on a portion of the surface, which may be restricted for instance inside of a cylindrical casing 61 shown in the large pot in Fig. 5. The ascending nitrogen or ammonia will in such case pass upwardly into the cyanid adjacent the walls of the pot and outside of the cylinder, and may hence pass entirely through the mass of cyanid, if not completely absorbed thereby, without passing through the molten alkali metal 62. If ammonia be employed instead of pure nitrogen and some of it comes in physical contact with pure sodium, thus floating on the surface of the molten cyanid, another set of very transitory intermediate reactions may come into play to a small extent and likewise result in the production of sodium cyanid; but the free carbon suspended in the cyanid will continue to react with the "reactive metal" as in equation 1, and the process will proceed substantially according to equations 1, 4 and 3.

I wish to define that in the claims the scope of the term "nitrogenous reagent" includes any reagent which will yield nitrogen under the conditions of the process, as, for example, either nitrogen, nitrids, or ammonia; and similarly, that "carbonaceous reagent" includes any reagent which will yield carbon under such conditions, as, for example, charcoal, fuel oil, coal, cyanids, cyanamids, etc.

In conclusion I desire to call attention to the fact that iron when heated does not combine directly with free or molecular nitrogen to produce a stable nitrid, hence certain of the claims which define the metal referred to therein as one which belongs to that class of metals which are capable when heated of directly combining with free nitrogen to form nitrids, exclude potassium ferro-cyanids, etc., but do cover the use of manganese, chromium, titanium cerium, etc., which combine with free nitrogen to form stable nitrids, although they do not form cyanids like the alkaline earth and alkali metals.

What I claim, is:

1. In a process of producing cyanogen compounds and the like, the step which consists in reacting on an impalpable amorphous carbid with a nitrogenous reagent, at a temperature above 500° C.

2. The process of producing cyanogen compounds and the like, which comprises effecting a chemical reaction between a nitrogenous reagent and a quantity of non-crystalline carbid at a temperature below the fusing point of said carbid but above 500° C.

3. The process of producing cyanogen compounds and the like, which comprises reacting with a nitrogenous reagent on a carbid held in suspension in and diffused through a fused bulk of a compound the radical forming constituents of which constitute a considerable percentage of said compound and which constituents are the same as those of the compound which is to be produced while substantially excluding oxygen from participation in the reaction.

4. The process of producing cyanogen compounds and the like, which comprises reacting with a nitrogenous reagent on a carbid held in suspension in and diffused through a fluid compound the radical forming constituents of which constitute a considerable percentage of said compound and which constituents are the same as those of the compound which is to be produced, at a temperature above 500° C.

5. The process of producing cyanogen compounds and the like which comprises effecting a reaction between a nitrogenous reagent and the carbid of a "reactive-metal," the latter being in impalpable non-crystalline condition and held in suspension in and diffused through a mass of non-aqueous fluid comprising a compound the radical forming constituents of which are the same as those of the compound which is to be produced.

6. A process of producing cyanogen compounds and the like, which comprises forming an amorphous carbid by bringing together carbid forming elements at a temperature insufficiently high to fuse the carbid as formed, and reacting on said amorphous carbid with a nitrogenous reagent.

7. The process of producing alkali-metal

cyanogen compounds and the like, which includes reacting with a nitrogenous reagent on a carbid of a "reactive-metal" while said carbid is contained in a fused mass which contains carbon and nitrogen, the fused mass being in contact with a fused body of alloy containing an alkali-metal as one of the constituents thereof.

8. The process of producing alkali-metal cyanogen compounds and the like, which includes reacting with a nitrogenous reagent on a carbid of a "reactive-metal" while said carbid is contained in a fused salt which contains carbon and nitrogen, and dissociating the product of such reaction, in the presence of an alkali metal thereby causing the carbon and nitrogen to unite with said alkali-metal to form the product sought.

9. The process of producing alkali-metal cyanogen compounds and the like, which includes reacting with nitrogen on a carbon compound of a "reactive-metal" while said compound is contained in a nitrogenous salt, the nitrogenous salt being in contact with a fused body of alloy, containing an alkali-metal as one of the constituents thereof, said salt being maintained at a lower temperature than that of the alloy.

10. In a process of producing cyanogen compounds and the like, the steps which consist in forming a carbid of a "reactive-metal" at a temperature below that at which such carbid will fuse, thereby substantially avoiding subsequent crystallization thereof, and effecting a reaction between such carbid and a nitrogenous reagent within a mass of nitrogenous salt.

11. In a process of producing cyanogen compounds and the like, the steps which consist in forming a carbon compound at a temperature below that at which such compound will fuse, and effecting a reaction, between such compound and a nitrogenous reagent within a mass of fluid nitrogenous salt.

12. A process of producing cyanogen compounds and the like, which comprises forming an amorphous carbid by bringing together carbid forming elements at a red heat, and reacting on said amorphous carbid with a nitrogenous reagent.

13. A process of producing cyanogen compounds and the like, which comprises forming an amorphous carbid at a temperature below the fusing point of said carbid, and reacting on said carbid with a nitrogenous reagent at a temperature also below that at which said carbid will fuse.

14. A process of producing cyanogen compounds and the like, which comprises forming a carbid at a given temperature within a fused bulk of a compound having radical forming constituents which constitute a considerable percentage of said compound, and which constituents are the same as those of the compound which is to be produced, and reacting on said carbid at a temperature substantially the same as that of the given temperature aforesaid.

15. In a process of producing cyanogen compounds and the like, the step which comprises reacting on amorphous lithium carbid with a nitrogenous reagent.

16. In a process of producing cyanogen compounds and the like, the step which comprises reacting on lithium carbid with a nitrogenous reagent.

17. In a process of producing cyanogen compounds and the like, the step which includes reacting on a substance which comprises lithium, with free nitrogen in the presence of carbon.

18. In a process of producing cyanogen compounds and the like, the step which includes effecting a reaction in which the elements lithium, nitrogen and carbon participate, in a mass of molten matter comprising said elements.

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

CHARLES E. ACKER.

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

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