J. E. BUCHER.

PROCESS OF FIXING NITROGEN AND ELECTRIC FURNACE FOR EFFECTING THE SAME.

APPLICATION FILED JUNE 25, 1914.

1,174,667.

Patented Mar. 7, 1916.

2 SHEETS—SHEET 1.

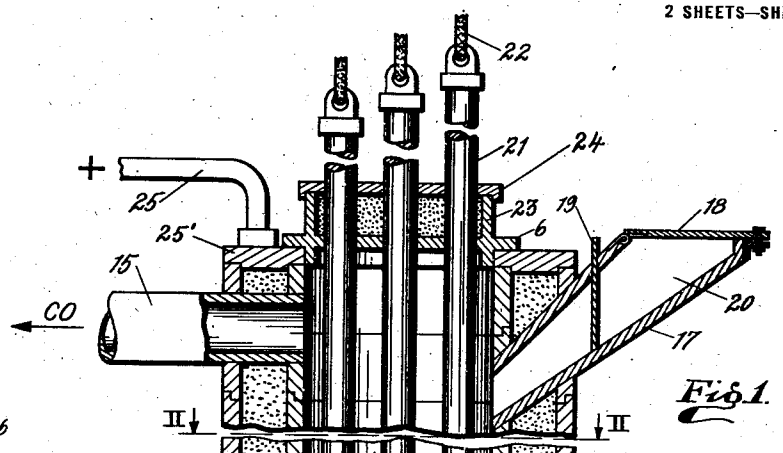


Fig. 1.

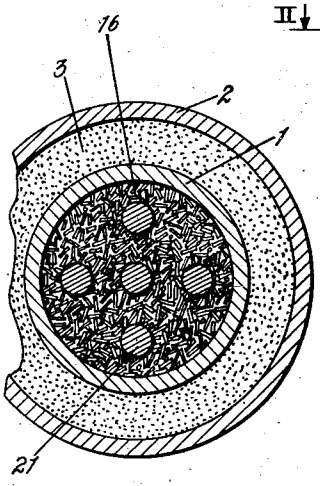


Fig. 2.

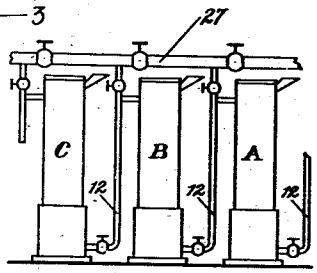
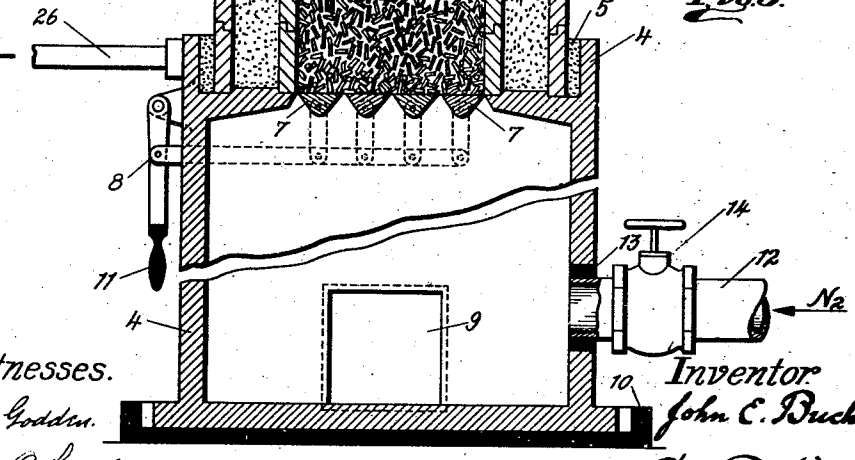


Fig. 3.



Witnesses.

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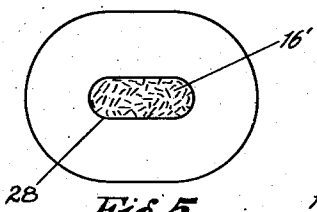


Fig. 5.

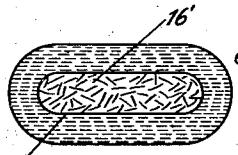


Fig. 6.

Fig. 4.

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UNITED STATES PATENT OFFICE.

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PROCESS OF FIXING NITROGEN AND ELECTRIC FURNACE FOR EFFECTING THE SAME.

1,174,667. Specification of Letters Patent. Patented Mar. 7, 1916.

Application filed June 25, 1914. Serial No. 847,337.

To all whom it may concern:

Be it known that I, JOHN E. BUCHER, a citizen of the United States, residing at Coventry, in the county of Kent and State of Rhode Island, have invented certain new and useful Improvements in Processes of Fixing Nitrogen and Electric Furnaces for Effecting the Same, of which the following is a specification.

This invention relates to a process and means for the fixation of atmospheric nitrogen; the free nitrogen being caused to combine with carbon and with a suitable base forming element such as an alkali or alkaline earth metal, to form a cyanogen compound. This combination is effected through the intermediacy of a suitable catalyzer which is capable of rendering the carbon reactive, and the cyanogen-compound-forming reaction is in the hereindescribed process effected in a suitable receptacle or furnace, heated either directly, or in part at least directly, by passing electric current through the mass of material which supplies preferably all of the constituents of the cyanogen compound to be formed other than the nitrogen.

The preferred process is especially characterized by the fact that the electrical heating is employed in such a manner that the charge itself acts, either entirely, or in part, as the electrical resistor.

A charge of the preferred material, or rather mixture of materials, conducts heat rather slowly and, if it be attempted to heat the mass thereof exteriorly, heat has to penetrate the interior portions by being conducted through the walls of the retort and the outer layers of the charge.

Owing to the extremely efficient mixture and the rapidity with which the nitrogen may be supplied, especially to briqueted materials of the character in question, the rapidity of the process is very seriously retarded by this relatively slow heat penetration; and it has been one of the principal objects of the present invention to surmount this difficulty. Furthermore, where external heating is resorted to, the retorts and furnaces must be so designed that the heat has to penetrate but a comparatively short distance into the charge and even then the temperature outside has to be kept much higher than that necessary for economical cyanid formation, to the end that a reasonably rapid heat penetration may be assured. This involves the additional serious disadvantages that the retorts, if of iron as they preferably are, soon becomes highly carburized and are more likely to melt or become injured by oxidation; that the exterior portions of the charge may be heated so as to melt or sinter the catalyzer, which is preferably pulverulent, at least initially; and that in the hotter exterior portions there may occur such a volatilization of the alkali compounds or their equivalents as to completely disintegrate the briquets with consequent tendency to flood other portions of the charge with such an excess of alkali material as to make such portions partially or entirely inactive. I have found that these disadvantages, which are practically inherent in substantially all methods of external heating can be overcome completely by internal electrical heating through the use of the charge itself as a resistor.

Nitrogen fixation, by the use of an electrical resistor made up of such materials as a mixture of finely divided iron, carbon and sodium carbonate has not heretofore been accomplished, and its accomplishment presented some apparently serious difficulties. For example, while such a resistor is, largely by reason of the presence of the solid alkali carbonate, virtually an insulator, I have found that its resistivity may be so enormously diminished upon heating, as to convert it to a fairly good conductor which becomes plastic while at the same time ingredients thereof participate powerfully in the endothermic cyanid-forming reaction.

By way of exemplifying the preferred mode of conducting my process, it may be here stated that iron and carbon, both finely divided, may be mixed with, for example, alkali carbonate and briqueted under pressure after the addition of suitable quanti-

ties of water; or, the mixture may be heated slightly above the melting point of the alkali carbonate while substantially excluding air, and briqueted under suitable pressure. In the latter case the briquets are already at the temperature of the cyanid formation and this preheating is of great advantage.

If the briquets are prepared moist, they are best dried quickly so that they may be firm and even this slight heating is of great advantage, not only because of the heat thus supplied to the briquets, but also on account of the increase in electrical conductivity due to this preheating.

The briquets may be made in many shapes but the ones preferably used in this process were pressed through a die and were made cylindrical in shape, being each one quarter of an inch in diameter and about one inch long. A resistor of such briquets presents large interstices through which the nitrogen current can flow to all portions of the resistor, after which it quickly penetrates by diffusion through the very small interstices or pores between the particles of iron and carbon.

The briquets are in general only in contact with each other at points and hence at first offer very poor electrical contact; and the same must be true to some extent of the very small irregular fragments of iron and carbon of which the briquets are formed, which are, in addition, more or less separated by the powdered sodium carbonate; the latter being an insulator when cold. The entire resistor is hence almost a nonconductor when cold and even 500 volts E. M. F. may send but a very slight current through a five-foot column in a one-inch tube.

The very slight current soon reaches a maximum when the heat loss by radiation counterbalances the heating effect of the current and it would hence require an excessively high voltage to bring the heating action to the critical point and a still more impractical voltage to do this expeditiously. Increasing the pressure on the mass increases the conductivity somewhat but not to the desired extent. This initial resistance can be overcome by using a shorter column which permits of the use of a more reasonable voltage and when the current flows freely, the electrodes may be partly withdrawn and more briquets added after which the current may be again allowed to act until it flows freely. This procedure may be repeated easily and quickly in a furnace of the character shown in Figure 1 of the accompanying drawings until the resistor is of the desired length. The current is then allowed to flow until the entire mass shows a uniformly bright incandescence and the conductivity of the resistor has increased over a thousandfold, in some cases. It is also possible to avoid the use of currents of high voltage by preheating the briquets or using them hot as they come from the drier in which their moisture is removed. When a mass of briquets is used as a resistor, the conductivity of the carbon and soda ash increases while that of the iron decreases, and, as the temperature rises heat is developed at the points of poorer contact, but as the temperature continues to rise the briquets soften at first at such points and the weight of the column then presses them together so as to produce a surface contact with comparatively good conductivity whereupon excessive heating at such surfaces ceases automatically and other portions in turn, become heated; thus equalizing the heating of the resistor. Also if the resistor is of such a shape that the current may flow in channels, producing excessive heating, this may be equalized by reducing the voltage of the current or shutting it off entirely until the heat has been conducted away to the cooler parts; thus again equalizing the resistance and consequently the heating.

Injurious local heating in such a resistor is further counteracted by the latent heat of fusion of the alkali carbonate which is present, and even more effectively by the very rapid volatilization of such alkali compounds, where the temperature temporarily gets too close to the melting point of the carburized iron. The condensation of this volatilized matter on the neighboring colder parts heats such neighboring parts; and thereby again tends to equalize heat throughout the mass. The gas current through the coarse interstices of the resistor greatly increases this favorable heat distributing action both by convection and increasing volatility. The heat changes due to vaporization and condensation not only act directly as a safety device to secure uniform heat distribution in the resistor, but, also effectively, by thus controlling the heat generation itself, effect a consequential automatic adjustment of resistance.

In addition to the equalization and control of temperature, effected by reason of the nature of the resistor employed, the powerfully endothermic reaction which takes place within the resistor mass: (1) $Na_2CO_3+4C+N_2=2NaCN+3CO-138{,}500$ cal. affords another very effective means for aiding in the equalization of temperature through the resistor mass. For example, when a portion of the resistor becomes hotter than the rest, cyanid formation will occur much more rapidly at such places; thus causing rapid heat absorption with simultaneous readjustment of resistance to equalize heat production.

The enormous change of conductivity with temperature makes such a resistor an

excellent thermostat for the process, as it is only necessary to determine for given conditions what amperage is necessary and then insert the proper fuses, circuit breakers and transformers into the circuit. Thus the current may be safely and automatically controlled even when heat is generated very rapidly in the charge. A 100 ampere current at 104 volts can readily be passed through a cylindrical column of briquets 1½ inches in diameter by 10 inches in length, which current will supply enough heat to complete the above reaction in about thirty seconds. On a small scale with properly prepared briquets I have actually converted the carbonate into cyanid in less than one minute. Such a very rapid generation of electrical energy in the resistor allows comparatively little time for loss by radiation and hence gives very high heating efficiency. This resistor contains an extremely active catalytic solution surface which renders the carbon more active thereat by presenting it while in solution in, for example, iron, to the elements which are to react therewith. It also provides for very free access of nitrogen to the reacting surface, and permits rapid heating of the interior portions of the charge. The preferred resistor, further, permits of very free circulation of alkali metals or compounds through its interstices by reason of its porosity, and of the absence therefrom of injurious binders and supports. Because of these and other advantages it permits cyanid formation more rapidly and efficiently than has heretofore been possible.

The resistor may be made in many different forms. For example, it may be pressed through a die in one piece, with suitable perforations to conduct the gases therethrough. The iron-carbon-sodium carbonate mixture may even be used in the powdered form without briqueting; but in any case the resistor should be so prepared and used as to provide and maintain an enormous catalytic solution surface at which the cyanid-forming reaction may take place, while at the same time providing for free access of alkali metal or compounds thereof or equivalents of such metal or compounds, together with nitrogen, thereto.

In the accompanying drawings which form a part hereof I have exemplified a preferred furnace; but as I am aware of very many changes and modifications which may be made herein without departing from the spirit of my invention and while yet affording means suitable for the effectuation of the herein described process, I desire in no way to be restricted to the form of apparatus shown nor indeed to the specifically described steps of my process other than as set forth in the claims appended hereto.

Referring to the drawings: Fig. 1 is a vertical median section of a furnace in which my process may be carried out. Fig. 2 is a section through said furnace taken on line II—II of Fig. 1. Fig. 3 is a diagrammatic representation of a group of furnaces. Fig. 4 is a somewhat diagrammatic section of a modified construction adapted for continuous operation of the process. Fig. 5 is a section taken on line V—V of Fig. 4, and Fig. 6 is a section taken on line VI—VI of said figure.

In the apparatus shown in Fig. 1 the furnace comprises inner and outer cylindrical portions respectively designated 1 and 2. The inner one may be built of superposed magnesia brick and the space 3 therebetween may be filled with kieselguhr, or even ashes or some like refractory material. These telescoped chimney-like sections may be sustained by a base 4 of cast-iron or the like and the base may further be sealed, as at 5, by kieselguhr or other suitable material; the top of the furnace being provided with a cover 6, preferably of cast-iron which is capable of being rotated so that, if desired, the electrodes may thereby be made to contact with the resistor at different places to counteract the tendency of the current to flow in channels when the length of the resistor is too short as compared with its cross-section. This method of working and applying the electrodes also insures positive contact and suitable pressure on the resistor, under all conditions, thus preventing the formation of arcs.

The base 4 has pivotally mounted therein a series of grate-bars 7 provided with suitable means 8 for rotating these bars to permit of a discharge of the whole or of a portion of the material within the furnace, into the chamber provided below said bars in the base 4. This chamber may have an air-tight closure 9 at an opening therein through which the treated and cooled material deposited in said chamber, may be removed. The base 4 is insulatedly mounted, as at 10, and the operating parts of the grate are preferably provided with an insulated or insulating handle 11. Nitrogen may be introduced through a pipe 12 which leads into the chamber below the grate, and said pipe may be insulated from the base, as at 13, in any suitable manner, and is further preferably provided with a valve 14 for regulating the inflow of nitrogen. The gaseous products of the reaction effected in this furnace, which are principally carbon monoxid, pass off from the upper portion of the furnace through a pipe 15, which may be of magnesia brick or other suitable material; and the briqueted charge 16, which in the preferred construction constitutes the resistor for the furnace, may be introduced through a hopper or chute 17. The latter has an air-tight cover or closure 18, and is also prefer-

ably provided with a slide or gate 19, so that when gate 19 is closed a determined quantity of briquets can be introduced into the space or chamber 20 between gates 18 and 19; cover 18 being thereupon closed and the gate 19 raised to permit of this charge sliding down into the interior of the furnace.

In the present instance, in the furnace shown, there are provided five electrodes 21, of iron or other suitable material, which are insulatedly suspended by wire ropes 22 and pass downwardly through apertures in the cover 6, so that their lower extremities rest upon the upper surface of the briqueted charge. The apertures in said cover through which these electrodes extend may be sealed by means of asbestos 23, or in any other suitable manner, a cap 24 being provided to retain the asbestos against upward displacement when the electrodes are elevated. Electrical connections are made to these electrodes either directly, or, through the cover 6 which engages said electrodes, and a lead 25 from a suitable source of current is connected to the frame 25′ of the cover 6. In the present case the five electrodes 21 are of course in parallel. Assuming that the lead 25 is positive, current passes down through the electrodes and enters the resistor mass 16 at the top thereof, traverses the same downwardly and passes out through the grate-bars 7, base 4 and returns to negative lead 26.

As above intimated, unless the briquet charge or resistor be preheated, its resistivity is so great that it is a comparatively good insulator and hence in starting a furnace of the type shown, it is preferable to preheat the briquets, at least moderately, and to further introduce but a portion of the mass, initially, into the furnace, so that for example, but a few inches of charge may rest upon the bars 7; the electrodes 21 being allowed to descend well into the furnace until they make contact with this shallow charge. Thereupon current is allowed to flow through the resistor which gradually heats up and as its temperature rises its conductivity is enormously increased, permitting additional briqueted matter to be introduced through the hopper 20 from time to time. The electrodes are then successively raised, with or without rotation, by turning the cover through a suitable angle, and allowed to drop back into contact with the upper surface of the resistor, until a charge of sufficient depth has been introduced into the furnace, after which the nitrogen current is turned on and flows up through the interstices between the bars 7 and between the briquets, effecting the cyanid-forming reaction according to the previously given equation. Of course the nitrogen may be turned in, if desired, even when the column of briquets is short or shallow and with substantially equally good results. In practice the current is allowed to become of sufficient density to heat the resistor to from about 800° up to 1000° C.; although the cyanid-forming reaction may take place at a materially lower temperature if suitable provision be made for effecting adequate volatilization, or in some cases liquefaction, of the alkali compound or its equivalent which constitutes the source of the metal which is to become the base of the cyanogen compound formed. For example, by mixing potassium and sodium carbonate, in lieu of using but a single one of these substances, the operating temperature may be materially lowered and if other similar compounds be judiciously mixed the operating temperature may be made as low as 650° C., or thereabout. However, on account of the cheapness of the alkaline compounds, above specified, I prefer to use sodium carbonate alone, or in certain cases to use a mixture of sodium carbonate and potassium carbonate. If the temperature of the operation be sufficiently high the cyanid formed will be vaporized and will pass off together with the carbon monoxid through the tube 15, to condense as soon as the rapidly lowering temperature permits, The cyanid formed may thus be separated from the resistor by electrical heating either with or without the passage of a gas current along with the cyanid vapor, or, it may even be distilled under diminished pressure. This use of the resistor for distilling cyanid from the reaction mixture, therein, materially aids in avoiding the great difficulty of supplying heat from the outside of the retort to the interior of the poorly conducting charge.

As the charge settles fresh briquets may be introduced from time to time through the hopper 20 and when the mass has been sufficiently treated, the current is turned off and the briquets are allowed to cool and harden, after which the grate bars are rotated and the now no longer plastic briquets will hence drop through readily.

By reason of the peculiar properties of the resistor above referred to the electric heating of the mass may be made economically effective and far more uniform throughout than is possible when a similar mass of like bulk is heated by external means.

The rather remarkable change in the resistivity of such a resistor as the temperature approximates that at which the cyanid is formed, is one of the most striking features of the present process and in certain cases the difference in resistance between the briqueted charge when cold and the same charge when heated, let us say, to about 1000° C. may even reach a thousandfold or more. This permits of the use of a current of such low voltage that an ordinary lighting circuit may be used. Indeed it is possible by properly preheating the

mass to employ a current of 50 volts or even lower E. M. F. It will be found advantageous in many cases, and particularly in this latter, to also preheat the nitrogen which is supplied to the furnace.

The electrical heating of the above described resistor which contains metal (resistivity 12) carbon (resistivity 1200 or more) and soda ash which is practically a fusible insulator, was at first considered impossible of practical accomplishment; but I have proven that it can be done very efficiently when the above described measures are observed. In the carrying out of my present process there is involved, therefore, a movable chemical resistor, which is in large measure automatically self-regulating by enormous change in conductivity by volatilization of one of its constituents, by internal endothermic chemical change, and by fusion of its internal insulator (soda ash, etc.); this fusion of the soda ash, or the equivalent thereof, producing a tremendous change in contact conditions between the metallic and carbon portions of the mass, as well as relatively great electrical conductivity as compared with the conductivity of the resistor when comparatively cold, and, hence, also a correspondingly great increase in heat conductivity at high temperatures. I believe that is hard to over-estimate the value of these changes which so intimately concern the heat regulation of the reacting mass and which in effect, and in combination with suitable fuses and circuit breakers, constitute a means for practically limiting the rise in temperature at any one point in the mass beyond that temperature at which it is undesirable to conduct the process. In this connection it may be noted that when a catalyzer such as iron is used in the solid phase, it is preferably very finely divided and the eutectic point of the carbon saturated catalyzer should, in such cases, never be exceeded since the catalytic solution surface would be thereupon seriously impaired by fusion or sintering of the iron particles, which would result in a material decrease in the extent of the catalytic surface and a consequent decrease in the effectiveness of the chemical resistor at such points therein as might be subject to such excessive temperatures. The catalyzer used is preferably iron or a carbon dissolving metal; but it may also form nitrids to aid in the process.

I may here point out that it is highly desirable in preparing the briquets, that the catalyzer be most intimately associated with the carbon, and that during the cyanid-forming operation the current of nitrogen be directed into contact with the catalytic material while the base-forming element, or source of the same, *e. g.* sodium carbonate, is also in contact therewith, whether said element or compound be in the gaseous phase or otherwise.

Free oxygen should be carefully excluded from the reaction zone in the furnace and indeed from contact with the cyanid, after formation of the latter, so long as said cyanid or equivalent cyanogen compound is hot. Obviously also the escape of cyanogen compound fumes should be prevented, these latter being poisonous; while any material waste of such material or of the volatilized sodium carbonate is costly. It should here be noted also that the columnar disposition of the mass of porous briquets is greatly to be preferred to any horizontal arrangement of the same, owing to the tendency of the mass under the influence of gravity, to compact itself, to prevent the formation of any large channel or channels therein through which the free nitrogen might pass without effectively participating in the cyanogen-compound-forming reaction. Again, it is by no means necessary that all of the heating current should be passed through the briqueted mass as a resistor, since I am aware of various other electrical heating arrangements which may be made reasonably effective for the effectuation of my process. I prefer that shown, however, on account of its simplicity and economy.

A series of furnaces of the type shown in Fig. 1 may be arranged as diagrammatically indicated in Fig. 3, so that a hot charge in furnace A, for example, which has been treated to form cyanid therein, may be cooled by passing cold nitrogen from the gas main 27 up through the treated charge in furnace A before delivering it through pipes covered with kieselguhr or the like to furnace B or C; suitable valves being provided to permit of any desired disposition of the gaseous current. Thus the treated briquets may be rapidly cooled preparatory to dropping them out of the reaction zone of the furnace while at the same time the nitrogen to be delivered to some other furnace in the series is highly preheated and heat is conserved. This also serves to preheat the briquets in furnaces B and C as well as to condense the poisonous alkali and cyanid fumes. It, further, permits the maintenance of a heat zone in the resistor at such temperatures that a deposit of carbon may occur therein under the influence of the catalyzer according to the equation:

$$(2)\quad 2CO \rightleftarrows CO_2 + C + 38{,}960 \text{ calories.}$$

In so far as this takes place, it produces ashless carbon together with the simultaneous internal heating in the resistor itself, and saves both carbon and grinding of the same.

In Fig. 4 I have diagrammatically represented a furnace which may be continuously

operated. Herein, a briquet resistor column 16′ is fed more or less continuously through a preferably flattened channel 28, portions of which, not between electrodes, may be of wrought iron pipe or the like, which further may flare for a portion of the length thereof, as at 29. The channel walls between the electrodes may be of magnesia brick or some like non-conductive material. I prefer to water-cool the flared part 29 so as to quickly reduce the plasticity of the descending briquets before the latter reach the revolving table 30 or equivalent charge shifting or conveying device. A screw conveyer 31 or the like may deliver the charge in a continous stream, if desired, from a suitable hopper or receptacle 32, and the briquets before entering the reaction zone may be preheated as by burning the carbon monoxid, formed during the course of the reaction, in the pre-heater indicated. The ascending gaseous reaction products help to internally preheat the moving resistor and may emerge from the furnace at 33. Electrodes 34, connected to bus bars 35, are suitably disposed around the channel 28 to establish the location of the reaction zone therein; said electrodes being preferably annuli of iron or other conductive material; and in the present case the electric current flows down through the chemical resistor from the upper to the lower of these electrodes. Around the pipe 28 at the reaction zone and respectively above and below the electrodes, are rings or blocks of magnesia brick, and a layer of kieselguhr is suitably retained around the outside of these rings and around the electrodes to insulate the furnace as far as practicable against loss of heat. The channel 28 is flattened as indicated in Fig. 5 to favor the preheating of the briquets, while the subsequent cooling of the charge is greatly favored by the flattening of the pipe at 29, as indicated in Fig. 6.

In operating a furnace of this type, or one of the form previously considered, it may at times be found desirable to shut off or reduce the electric current in order to enable the heat in the charge to more uniformly distribute itself; but the novel resistor employed in very large measure obviates the necessity for so doing and usually permits of a practically continuous operation of the furnace. Also, when external preheating is used, it is desirable to heat the briquets in such a manner that the hotter briquets become mixed with the cooler ones to get an average uniform heat distribution in the resistor. This may be done in a rotary furnace, or even by having a pre-heater at 36 around the horizontal pipe through which the briquets are conveyed to the furnace, or in other suitable manner.

If the part of the furnace between *a* and *b* is not filled with briquets, this empty space will serve as a mixing chamber as the briquets fall to the bottom. In this way, the initial formation of a comparatively good conducting annular layer of briquets on the outside of the resistor, with a subsequent tendency to conduct too large a part of the current (thus leaving a comparatively cold core on the inside), may be avoided in continuously acting furnaces.

I particularly desire to point out the value of the columnar disposition of the moving charge, not only in preventing wasteful gas channels such as I have found are apt to form when the charge is stationary and horizontally disposed, but further in preventing arcing at the electrodes; since gravity causes the briquets in the vertical column to always flow into proper contact with the electrodes and gaps across which arcing might occur are thus obviated.

If the furnace is to be operated with gases such as those containing nitrogen mixed with carbon monoxid, they are introduced, preferably highly preheated, into the reaction zone in the hot resistor at 37. By thus causing a more or less continuous advance of the resistor column through the heat or reaction zone, to the already mentioned advantages of the stationary resistor, we add those of returning the upwardly escaping volatilized (but subsequently condensed) alkali metal and compounds to the heat zone of the moving resistor, to thus produce circulation without flooding the colder portions with alkali compounds, while at the same time introducing extra heat and ash-free carbon from without according to the equation (2) and avoiding the destructive action, on the cooling cyanid containing mass, of the CO_2 produced coincidentally with the deposition of said carbon in said mass. Finally on account of the high resistance of the charge when cold, in starting a continuous furnace of the type shown, the preheating of the charge is very desirable unless some such provision as that of the movable electrodes shown in the first described construction be resorted to; and whether the furnace be of the continuous or discontinuous type ash free carbon may, if desired, be deposited from carbon monoxid in the preheating zone.

In the appended claims the term "cyanogen compound" is to be regarded as of sufficient breadth to cover not only cyanid but other cyanogen containing substances, such, for example, as cyanamid, etc.; since I am aware that, for example, by providing insufficient carbon for the cyanid forming reaction, cyanamid will be formed.

Finally, in this application I desire to direct attention to the division of the present case, Ser. No. 864,690, filed Oct. 2, 1914.

Having thus described my invention what I claim is:

1. Means for fixing nitrogen comprising

an electrically heated furnace having therein a resistor which includes a catalyzer of low resistivity, carbon and material capable of supplying the base of a stable cyanogen compound to be be formed in said resistor, said resistor being adapted to permit of the passage of nitrogen therethrough in contact with said catalyzer, and said catalyzer holding a portion at least of said carbon in solution therein.

2. Means for fixing nitrogen comprising an electrically heated furnace having therein a resistor which includes a catalyzer of low resistivity, carbon and material capable of supplying the base of a stable cyanogen compound to be formed in said resistor, said resistor being adapted to permit of the passage of nitrogen therethrough in contact with said catalyzer, and said catalyzer being intimately associated with said carbon.

3. Means for fixing nitrogen comprising an electrically heated furnace having therein a resistor which includes a catalyzer of low resistivity, carbon and material capable of supplying the base of a stable cyanogen compound to be formed in said resistor, said resistor being adapted to permit of the passage of nitrogen therethrough in contact with said catalyzer, and said base supplying material having, when in the solid phase and at temperatures materially below those at which said cyanogen compound may be formed, a high resistivity as compared with that of said catalyzer, the resistivity of said resistor being variable through wide limits by a change in phase of said base supplying material.

4. An electric furnace for fixing nitrogen which comprises a resistor which itself includes material capable of catalytically participating in a cyanogen-compound-forming reaction during the course of which reaction free nitrogen is combined with carbon and with an element capable of acting as the base of said cyanogen compound, said furnace further comprising means for directing said free nitrogen into contact with said catalytic material while said base forming element and carbon are also in contact therewith, electrical connections for passing current through said resistor to heat the same, and means to conduct away from the reaction zone in said furnace gaseous products of said reaction.

5. An electric furnace for fixing nitrogen which comprises a resistor which itself includes carbon and material capable of catalytically participating in a cyanogen-compound-forming reaction during the course of which reaction free nitrogen is combined with said carbon and with an element capable of acting as the base of said cyanogen compound, said furnace further comprising means for directing said free nitrogen into contact with said catalytic material while said base forming element and carbon are also in contact therewith, and electrical connections for passing current through said resistor to heat the same.

6. An electric apparatus for fixing nitrogen which comprises an intersticed resistor which itself includes a compound of a metal which is capable of acting as the base of a cyanogen compound carbon, and material capable of catalytically participating in a reaction effected within the interstices of said resistor to form said cyanogen compound by combining the carbon present in said resistor with said metal and free nitrogen through the instrumentality of said catalytic material, said apparatus including electrical connections for passing current through said resistor, and provisions for directing said free nitrogen into the interstices of said resistor.

7. The combination of a resistor comprising a mass of briquets in which are present in intimate association, a carbon containing catalyzer presenting an extended solution surface, and a compound of a metal capable of acting as the base of a stable cyanogen compound to be formed in said briqueted mass, said mass being porous to permit of the flow of a current of free nitrogen over and in contact with said solution surface, means for introducing said nitrogen current into said mass and means for passing electric current in part at least through said resistor to internally heat the same.

8. The combination of a resistor comprising a mass of briquets in which are present in intimate association, a carbon containing catalyzer presenting an extended solution surface, and a compound of a metal capable of acting as the base of a stable cyanogen compound to be formed in said briqueted mass, said mass being porous to permit of the flow of a current of free nitrogen over and in contact with said solution surface, means for introducing said nitrogen current into said mass and means for passing electric current in part at least through said resistor to internally heat the same, said catalyzer being solid and finely divided and said compound of said metal being initially in the solid phase but being subject to a change in phase as the temperature of the resistor is raised, whereby the resistivity of said resistor is greatly lessened as the cyanid forming temperature is approximated.

9. The combination of a resistor comprising a mass of briquets in which are present, in intimate association, finely divided carbon, finely divided catalytic material, and a compound of an alkali metal capable of acting as the base of a stable cyanogen compound to be formed in said briqueted mass, said mass being porous to permit of the flow of a current of free nitrogen over and in

contact with the extended surface of said catalytic material, means for introducing said nitrogen current into said mass, and means for passing electric current in part at least through said resistor to internally heat the same.

10. The combination of a resistor comprising a mass of briquets in which are present, in intimate association, finely divided carbon, finely divided catalytic material, and an oxygen containing compound of an alkali metal capable of acting as the base of a stable cyanogen compound to be formed in said briqueted mass, said mass being porous to permit of the flow of a current of free nitrogen over and in contact with the extended surface of said catalytic material, means for introducing said nitrogen current into said mass, and means for passing electric current in part at least through said resistor to internally heat the same.

11. The combination of a resistor comprising a mass of briquets in which are present, in intimate association, finely divided carbon, finely divided catalytic material, and a carbonate of an alkali metal capable of acting as the base of a stable cyanogen compound to be formed in said briqueted mass, said mass being porous to permit of the flow of a current of free nitrogen over and in contact with the extended surface of said catalytic material, means for introducing said nitrogen current into said mass, and means for passing electric current in part at least through said resistor to internally heat the same.

12. In means for fixing atmospheric nitrogen, an electric furnace having a catalytic resistor constituents of which are capable of participating in a cyanid forming reaction, and means for passing free nitrogen through said resistor to promote said reaction.

13. The process of fixing nitrogen which comprises briqueting a mass comprising a compound of a metal capable of acting as the base of a stable cyanogen compound carbon and a catalyzer capable of rendering said carbon reactive to combine with said metal and with free nitrogen to form said cyanogen compound, using the briqueted mass as a resistor in an electric circuit to heat said mass to a temperature at which the cyanogen-compound-forming reaction may take place, and passing free nitrogen through the briqueted mass at said temperature to effect said reaction.

14. The process of fixing nitrogen which comprises preparing a mass comprising a compound of an element capable of acting as the base of a cyanogen compound, carbon and a catalyzer intimately associated with said carbon and capable of rendering it reactive to combine with said element and with free nitrogen to form said cyanogen compound, subjecting said mass to the action of an electric current, and passing free nitrogen through said mass to form said cyanogen compound.

15. The process of fixing nitrogen which comprises preparing a mass comprising a compound of an element capable of acting as the base of a cyanogen compound, carbon and a catalyzer intimately associated with said carbon and capable of rendering it reactive to combine with said element and with free nitrogen to form said cyanogen compound, subjecting said mass to the direct action of a dense electric current, and passing free nitrogen through said mass to form said cyanogen compound.

16. The process of fixing nitrogen which comprises preparing a mass comprising a compound of an element capable of acting as the base of a cyanogen compound, carbon and a catalyzer intimately associated with said carbon and capable of rendering it reactive to combine with said element and with free nitrogen to form said cyanogen compound, preheating said mass preparatory to the passage therethrough of a dense electric current, subjecting said mass to the action of said electric current, and passing free nitrogen through said mass to form said cyanogen compound.

17. The process of fixing nitrogen which comprises preheating a porous briqueted mass comprising a compound of an element capable of acting as the base of a cyanogen compound, carbon and a catalyzer intimately associated with said carbon and capable of rendering it reactive to combine with said element and with free nitrogen to form said cyanogen compound, subjecting said mass to the action of an electric current, and passing free nitrogen through said mass to form said cyanogen compound.

18. The process of fixing nitrogen which comprises preheating a porous briqueted mass comprising a compound of an element capable of acting as the base of a cyanogen compound, carbon and a catalyzer intimately associated with said carbon and capable of rendering it reactive to combine with said element and with free nitrogen to form said cyanogen compound, preheating said mass preparatory to the passage therethrough of a dense electric current, subjecting said mass to the action of said electric current, and passing free nitrogen through said mass to form said cyanogen compound.

19. The process of fixing nitrogen which comprises preparing a mass comprising a compound of an alkali metal capable of acting as the base of a stable cyanogen compound, carbon and a catalyzer intimately associated with said carbon and capable of rendering it reactive to combine with said element and with free nitrogen to form said

cyanogen compound, subjecting said mass to the action of an electric current, and passing free nitrogen through said mass to form said cyanogen compound.

20. The process of fixing nitrogen which includes preparing a mass comprising carbon intimately associated with an element of the iron group which is capable of dissolving carbon and of thereby rendering said carbon reactive to combine with free nitrogen and a metallic base to form a cyanogen compound of said metallic base, and subjecting said mass to the action of an electric current and to free nitrogen and material which includes said base while said element contains said carbon in solution, whereby to form said cyanogen compound.

21. The process of fixing nitrogen which includes preparing a mass comprising carbon intimately associated with an element of the iron group in the solid phase which is capable of dissolving carbon and of thereby rendering said carbon reactive to combine with free nitrogen and a metallic base to form a cyanogen compound of said metallic base, and subjecting said mass to the action of an electric current and to free nitrogen and material which includes said base while said element contains said carbon in solution whereby to form said cyanogen compound.

22. The process of fixing nitrogen which includes preparing a mass comprising carbon intimately associated with a finely divided element of the iron group which is capable of dissolving carbon and of thereby rendering said carbon reactive to combine with free nitrogen and a metallic base to form a cyanogen compound of said metallic base, and subjecting said mass to the action of an electric current and to free nitrogen and material which includes said base while said element contains said carbon in solution whereby to form said cyanogen compound.

23. The process of fixing nitrogen which includes preparing a porous briqueted mass comprising carbon intimately associated with an element of the iron group in the solid phase which is capable of dissolving carbon and of thereby rendering said carbon reactive to combine with free nitrogen and a metallic base to form a cyanogen compound of said metallic base, and subjecting said mass to the action of an electric current and to free nitrogen and material which includes said base while said element contains said carbon in solution, whereby to form said cyanogen compound.

24. The process of fixing nitrogen which includes preparing a mass comprising carbon intimately associated with an element of the iron group which is capable of dissolving carbon and of thereby rendering said carbon reactive to combine with free nitrogen and a metallic base to form a cyanogen compound of said metallic base, and subjecting said mass, while in columnar form, to the action of an electric current and to free nitrogen and material which includes said base while said element contains said carbon in solution, whereby to form said cyanogen compound.

25. The process of fixing nitrogen which includes preparing a porous briqueted mass comprising carbon intimately associated with an element of the iron group in the solid phase, which is capable of dissolving carbon and of thereby rendering said carbon reactive to combine with free nitrogen and a metallic base to form a cyanogen compound of said metallic base, subjecting said mass to the action of an electric current and to free nitrogen and material which includes said base while said element contains said carbon in solution whereby to form said cyanogen compound, and extending the length of the columnar mass during the operation as the decreasing resistivity of said mass, due to the heating thereof, permits.

26. The process of making cyanid which comprises subjecting a resistor in an electric furnace to the action of an electric current of high density whereby to heat said resistor to a temperature sufficient to cause at least one of the ingredients of the resistor itself to actively and another to catalytically participate in a cyanid forming reaction while supplying an additional participant for said reaction in gaseous form from a source extraneous to said resistor.

27. The process of making cyanid which comprises subjecting a resistor in an electric furnace to the action of an electric current of high density whereby to substantially uniformly heat said resistor to a temperature sufficient to cause at least one of the ingredients of the resistor itself to actively and another to catalytically participate in a cyanid forming reaction while supplying an additional participant for said reaction in gaseous form from a source extraneous to said resistor.

28. The process of making cyanid which comprises subjecting a resistor in an electric furnace to the action of an electric current of high density whereby to heat said resistor to a temperature sufficient to cause at least one of the ingredients of the resistor itself to catalytically participate in a cyanid forming reaction while supplying an additional participant for said reaction in gaseous form from a source extraneous to said resistor.

29. The process of making cyanid which comprises subjecting a resistor in an electric furnace to the action of an electric current of high density whereby to heat said resistor to a temperature sufficient to cause at least one of the ingredients of the resistor itself to actively participate, and a second and carbon dissolving ingredient to catalyti-

cally participate, in a cyanid forming reaction while supplying an additional participant for said reaction in gaseous form from a source extraneous to said resistor.

30. The process of forming cyanid which comprises electrically heating a catalytic porous mass of material, constituents of which themselves participate in a cyanid forming reaction which in part at least regulates the temperature conditions in said mass by removing heat from portions thereof at which the reaction is proceeding with excessive violence, and further making provision for temperature regulation by providing in said mass as one of the aforesaid constituents a material which is subject to a change in phase as the predetermined temperature limit is approximated.

31. In means for fixing atmospheric nitrogen, an electric furnace having a catalytic resistor, constituents of which are capable of participating in a cyanogen compound forming reaction, said resistor being substantially free from supports or binders for said constituents which are foreign to said reaction, and means for passing free nitrogen into contact with said resistor to promote said reaction.

32. In means for fixing atmospheric nitrogen, an electric furnace having a catalytic resistor, constituents of which are capable of participating in a cyanogen compound forming reaction, said resistor being substantially free from substances which would impede said reaction, and means for passing free nitrogen into contact with said resistor to promote said reaction.

33. In means for fixing atmospheric nitrogen, an electric heating apparatus having a resistor, constituents of which are capable of participating in a cyanogen compound forming reaction, one of said constituents being a catalyzer for said reaction, and means for passing free nitrogen into contact with said resistor.

34. In means for fixing atmospheric nitrogen, an electric heating apparatus having a resistor, constituents of which are capable of participating in a cyanogen compound forming reaction, one of said constituents being a catalyzer and another being substantially ash-free carbon, and means for passing free nitrogen into contact with said resistor.

35. In means for fixing atmospheric nitrogen, an electric heating apparatus having an intersticed resistor, constituents of which are capable of participating in a cyanogen compound forming reaction, one of said constituents being a catalyzer and another being substantially ash-free carbon, and means for passing free nitrogen into contact with said resistor.

36. In means for fixing atmospheric nitrogen, an electric heating apparatus having an intersticed resistor, constituents of which are capable of participating in a cyanogen compound forming reaction, one of said constituents being a catalyzer and another being substantially ash-free carbon deposited in the interstices of said resistor from carbon monoxid, in part at least through the intermediacy of said catalyzer, and means for passing free nitrogen into contact with said resistor.

37. In means for fixing atmospheric nitrogen, an electric heating apparatus having an intersticed resistor, constituents of which are capable of participating in a cyanogen compound forming reaction, one of said constituents being a catalyzer for said reaction, means to pass nitrogen through the interstices of said resistor and means to establish a reaction zone in said resistor, said apparatus having provisions for effecting a relative movement between said zone establishing means and said resistor.

38. In means for fixing atmospheric nitrogen, an electric heating apparatus having a resistor, constituents of which are capable of participating in a cyanogen compound forming reaction, one of said constituents being a catalyzer for said reaction, means to supply nitrogen to said resistor, means to establish a reaction zone in a part only of said resistor, and means to dispose said zone successively in different parts of said resistor.

39. In means for fixing atmospheric nitrogen, an electric heating apparatus having a resistor, constituents of which are capable of participating in a cyanogen compound forming reaction, one of said constituents being a catalyzer for said reaction, means to supply nitrogen to said resistor, means to establish a reaction zone in a part only of said resistor, and means to dispose said zone successively in different parts of said resistor by the action of gravity upon said resistor.

40. In means for fixing atmospheric nitrogen, an electric heating apparatus having a resistor, constituents of which are capable of participating in a cyanogen compound forming reaction to be effected within said resistor, one of said constituents being volatilizable during the course of said reaction, and another being a solid catalyzer for said reaction, said apparatus having provisions to co-act with its resistor to prevent such an accumulation of said volatilizable constituent in the liquid phase thereof, as would flood the surface of said catalyzer in parts of said resistor and thereby impede said reaction.

41. In means for fixing atmospheric nitrogen, an electric heating apparatus having a resistor, constituents of which are capable of participating in a cyanogen compound forming reaction to be effected within said resistor, said resistor having conduits there-

through for the passage of gaseous matters and having the interior surfaces thereof which are in communication with said conduits, greatly extended to favor said reaction and the volatilization of the product formed, and means co-acting with said resistor to electrically heat the latter to cause said reaction and to volatilize said product.

42. The process of fixing nitrogen which comprises incorporating ash-free carbon in a catalytic mass in part at least through the action of the catalyzer in said mass upon carbon-monoxid, and treating said mass with nitrogen and as a resistor in an electric furnace to combine said nitrogen with said carbon.

43. The process of fixing nitrogen which comprises incorporating ash-free carbon in a catalytic mass in part at least through the action of the catalyzer in said mass upon carbon-monoxid while at the same time preheating said mass through the conversion of the carbon-monoxid to carbon dioxid, and treating said mass with nitrogen and as a resistor in an electric furnace to combine said nitrogen with said carbon.

44. The method of operating an electric furnace for the production of a cyanogen compound, which includes supplying free nitrogen to a reaction zone in a resistor in said furnace, which resistor comprises a catalytic mass in which are present carbon, a solvent for said carbon and a substance which is capable of being volatilized by the heat generated in said resistor and when thus volatilized of supplying the base of the cyanogen compound to be formed in said reaction zone, and effecting a relative movement between said resistor and parts of said furnace whereby to subject escaped volatilized portions of said substance to said reaction in said zone.

45. The method of operating an electric furnace for the production of a cyanogen compound, which includes supplying free nitrogen to a cyanogen compound forming reaction zone in a resistor in said furnace, which resistor comprises a moving mass in which are present carbon, a catalyzer capable of promoting a cyanogen compound forming reaction, and a substance which is capable of being volatilized by the heat generated in said reaction zone, the movement of said mass being made such as to return to said zone escaped portions of said substance.

46. The method of operating an electric furnace for the production of a cyanogen compound which includes using as a resistor in said furnace a mass of material constituents of which participate in the cyanogen compound forming reaction, one of said constituents participating catalytically and effecting a circulation of one of said constituents through said mass, in part at least by moving said resistor through a part of said furnace.

47. The method of operating electric heating apparatus to effect the formation of a cyanogen compound in a reaction zone in said apparatus, which comprises using as a resistor in said apparatus, a mass which includes a catalyzer for said reaction, and incorporating ash-free carbon in a porton of said mass, previous to effecting said reaction in said portion, by passing carbon-monoxid, which escapes from the reaction zone, through said portion while lowering the temperature of said carbon-monoxid to convert the same to carbon-dioxid.

48. The method of operating electric heating apparatus to effect the formation of a cyanogen compound in a reaction zone in said apparatus, which comprises using as a resistor in said apparatus a mass which includes a catalyzer for said reaction, which catalyzer is also capable of converting carbon-monoxid to carbon-dioxid at temperatures below that at which said cyanogen compound is formed, supplying a mixture of nitrogen and carbon-monoxid directly to said reaction zone, combining said nitrogen with constituents of said resistor to form said cyanogen compound, and subsequently converting said carbon-monoxid to carbon-dioxid while depositing carbon, through the intermediacy of said catalyzer.

49. The method of operating an electric furnace which comprises treating a catalytic resistor for said furnace, to be used in the production of a cyanogen compound, with carbon monoxid to deposit carbon thereupon, and subjecting said resistor to the action of nitrogen to combine said carbon and nitrogen.

50. The method of operating an electric furnace which comprises treating a catalytic resistor for said furnace with carbon monoxid to deposit carbon thereupon and to aid in preheating said resistor, elevating the temperature of said resistor to a temperature sufficient to effect a cyanogen forming reaction in which said carbon participates, and subjecting said resistor to the action of nitrogen to combine said carbon and nitrogen.

51. The method of producing a cyanogen compound which comprises treating a porous catalytic resistor one at least of the constituents of which participates in a reaction to form said cyanogen compound with gaseous material to supply the remaining constituent or constituents for said compound, and removing said compound, when formed, from a part at least of said resistor in the gaseous phase.

52. The process of fixing nitrogen which comprises preheating a catalytic resistor the parts of which are movable with respect to each other and which parts are relatively poor conductors of heat, and mixing said

parts to effect a relatively uniform distribution of said heat through the mass, and subjecting said resistor to the action of an elective current and free nitrogen to combine said nitrogen with at least one constituent of said resistor.

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

JOHN E. BUCHER.

Witnesses:

NORMAN E. HOLT,

THOMAS H. ROBERTS.