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FIXATION OF NITROGEN.

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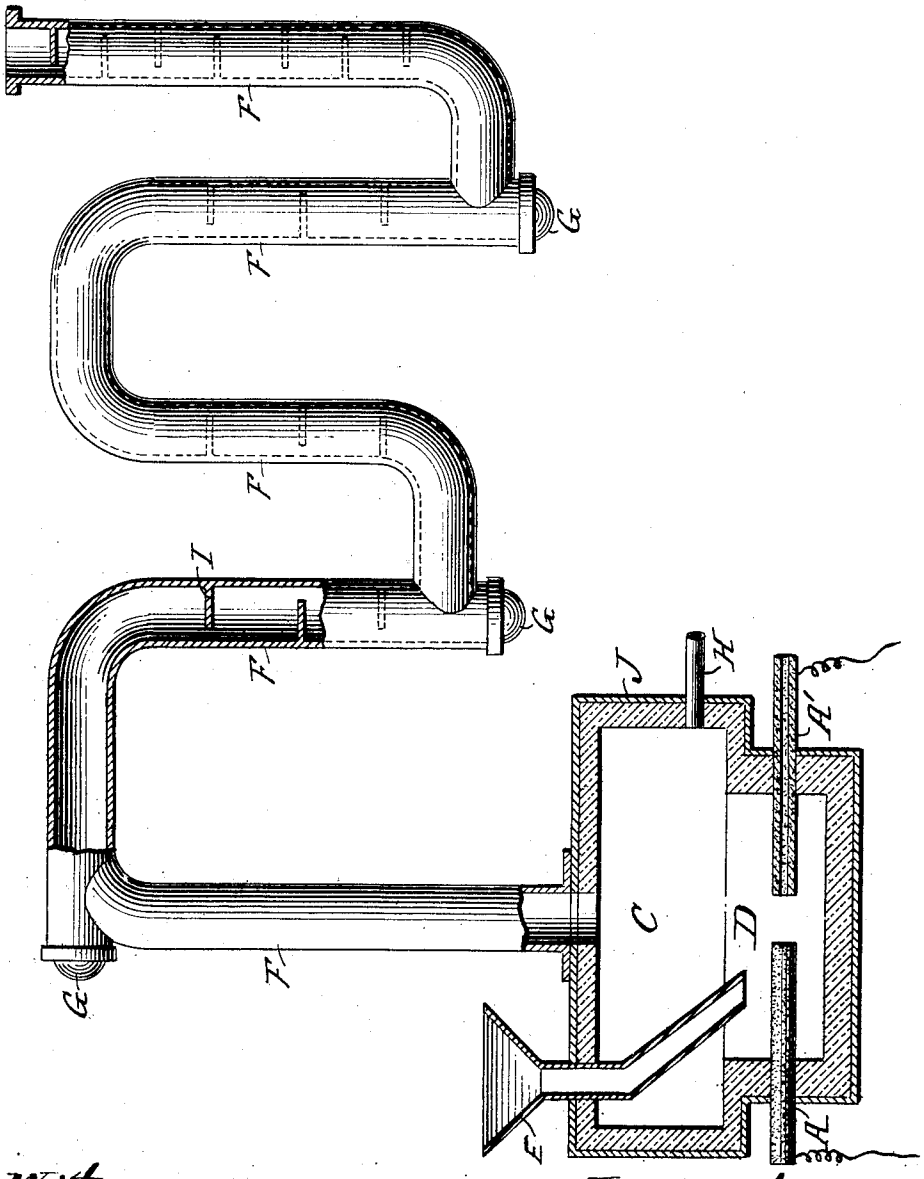
**1,175,007.** Patented Mar. 14, 1916

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# UNITED STATES PATENT OFFICE.

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## FIXATION OF NITROGEN.

1,175,007. Specification of Letters Patent. Patented Mar. 14, 1916.

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*To all whom it may concern:*

Be it known that we, HERBERT RAYMOND MOODY and SAMUEL AUCHMUTY TUCKER, citizens of the United States, both residing at New York city, county of New York, State of New York, have invented certain new and useful Improvements in Fixation of Nitrogen; and we do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

Our invention is based upon the discovery that if carbid-forming alkaline earth metals and lithium are received in a nascent vaporous condition into an atmosphere of nitrogen, at a temperature at or near that at which the said nascent metallic vapors were formed, they will combine with the nitrogen to form nitrogen compounds of economic value. We have particularly established the fact that this combination will take place when the carbid-forming metals referred to are released, at a high temperature, by dissociation from their carbids, and also when they are released from furnace charges adapted to produce such carbids but heated to temperatures above the dissociation points thereof.

Where the interacting atmosphere of nitrogen and nascent metallic vapor contains carbon under suitable conditions a greater or less proportion of the carbon will associate itself with the metallic nitrogen compounds, as, for instance, in the form of cyanamid or dicyanamid. The atmosphere of nitrogen may be obtained in any suitable and convenient way, as, for instance, by passing atmospheric air through highly heated copper for the purpose of removing the oxygen therefrom. So also, it may be obtained from producer gas, either used as such, or after having been first deprived of its carbon dioxid by passing it through or in contact with calcium oxid.

It is desirable that the atmosphere of nitrogen should contain no large amount of free oxygen, and it is even desirable that both carbon monoxid and carbon dioxid be present in but small proportion, although larger quantities, (even up to what is present in commercial producer gas) may be tolerated.

Although, as hereinbefore indicated, our invention may be practised by the dissociation of carbids that have been already formed, we prefer, for commercial purposes to proceed from a charge made up of suitable ingredients, in suitable proportions, appropriate to the usual production of carbids, and we recommend for the purpose such charges as would be appropriate for the making of carbids of the alkaline earth metals or carbid of lithium. For instance, in such case, it would be appropriate in making up the charge, to use an oxid or a carbonate of an alkaline earth metal (as calcium or barium) or the oxid or carbonate of lithium, or similar compounds of carbid-forming metals, together with carbon in equal or other suitable proportions by weight, as is well understood in the making up of charges for the production of carbids in the usual carbid manufacture. The mixture thus obtained and which should be charged dry, is heated, preferably electrically, as by arc or resistance heating, and with the employment of a direct or alternating current, in a closed heating chamber provided with or connected with a re-action chamber, and the latter, in its turn, being connected to a suitable condenser.

The heating is carried on at a temperature higher than the dissociation point of the carbid which the charge is adapted to produce, and for a sufficient length of time to form an atmosphere in which the metal is present in a finely divided condition, probably by reason of the formation of the carbid and its immediate decomposition, although it is at least conceivable that under the prevailing conditions, the high temperature of the furnace may actually prevent the formation of the carbid which would otherwise be produced. In any event, upon the introduction of nitrogen into the heating chamber or the reaction chamber, or both, as is found most expedient, there will be a rapid evolution of volatile products and an immediate fixation of nitrogen.

The entire process may be carried on continuously, or intermittently, as preferred.

It will, of course, be understood, as hereinbefore indicated, that instead of the carbid-forming charge, the furnace may be supplied with carbid that has already been formed in some prior operation, as, for instance, calcium carbid, barium carbid, or lithium carbid, the operation being otherwise the same, that is to say, the carbid being heated to a temperature above its dissociation point, so as to release the carbid-

forming metal and permit the subsequent reaction with the nitrogen supplied to the apparatus.

The presence of carbon in the reaction space brings about the formation of nitrogen compounds in which, in addition to the carbid-forming metal, carbon is present; such as, for instance, $CaCN_2$, $Ca(CN)_2$, $Ca(C_2N_3)_2$, in addition to the nitrid of the carbid-forming metal, as, for instance, $Ca_3N_2$, although in general, it will be found that the proportion of nitrid is notably less in amount than the other nitrogen compounds of the reaction.

In the accompanying drawing, we have illustrated diagrammatically and in section a form of apparatus appropriate to the practice of the invention.

Referring to the drawing, J indicates a furnace structure, suitably lined with refractory brick, and provided with a heating chamber D containing the charge, and a supplemental chamber C for the introduction of the nitrogen and for reaction between the nitrogen and the volatile products given off from the charge.

H indicates a suitable pipe through which the atmosphere of nitrogen is supplied to the reaction chamber, and E indicates a hopper for the introduction of the charge.

A A′ indicates the electrodes for supplying the electric current (direct or alternating) to the furnace, and one of these electrodes, as, for instance, the electrode A′ may be provided with a central passage which may be utilized for the introduction of the atmosphere of nitrogen into the heating chamber D, when preferred.

The reaction chamber C may itself constitute the condenser for the products of reaction, but it will usually be preferable to supply the reaction chamber with a supplemental condenser which may conveniently consist of a series of connected pipes F, provided with baffles I, said pipes being accessible at suitable places, as at G for the removal of the condensed products.

It will, of course, be understood that any suitable form of furnace may be employed for the treatment of the charge, and particularly any of the usual commercial furnaces for the intermittent or continuous manufacture of calcium carbid.

It has been heretofore proposed to effect the fixation of nitrogen, by introducing nitrogen into a heated body of calcium carbid. In such case, however, it was found more desirable, in practice, in many works, to introduce the nitrogen under pressure, and, for that purpose to employ a furnace structure of corresponding strength and one which is difficult of maintaining gas-tight under the conditions of use.

In the practice of our invention, although we do not exclude the employment of superatmospheric pressure, we find it unnecessary to employ it, inasmuch as an entirely satisfactory output is obtainable under the conditions specified, and with the additional advantage that the apparatus can be made of lighter construction and therefore cheaper and more readily maintained in operative condition.

Our method has the further advantage that carbid formation, carbid decomposition and nitrogen fixing, are all carried out in a single apparatus and in a single heating operation, whereby the process is capable of being carried on as a continuous process, involving no reheating and no secondary furnace apparatus.

The process has the further advantage that the heat energy evolved by the dissociation of the carbid becomes available to maintain the high temperature necessary for the procedure, and furthermore the products evolved by the dissociation of the carbid and which are carried into the atmosphere of nitrogen are in an exceedingly fine state of division so that a most intimate mixture of the said products of carbid dissociation and the nitrogen gas is obtained, and consequently a rapid and efficient reaction results.

The presence of carbon in the atmosphere of the furnace, in the practice of the invention, is, as we conceive it, due to the vaporization of carbon in the charge, and the mechanical upward propulsion of the freed carbon of the charge, due, in part, to the blowing action of the arc, and in part to the lifting action of the hot ascending gases and vapors.

We find it feasible and desirable to add to the carbid charge in the furnace an amount of calcium chlorid equal to about 5% of the weight of the calcium carbid producible from the charge. By so doing, we find that although the product is no richer in percentage of nitrogen content, yet the total amount of nitrogenous product obtained is approximately doubled, thus doubling the efficiency.

What we claim is:

1. The method of fixing nitrogen, which comprises introducing a carbid-forming metal of the alkali or alkali-earth groups in a vaporous condition into an atmosphere containing nitrogen at a temperature appropriate to the fixation of nitrogen; substantially as described.

2. The method of fixing nitrogen, which comprises introducing a carbid-forming metal in a vaporous condition in the presence of free carbon, into an atmosphere containing nitrogen, at a temperature appropriate to the fixation of the nitrogen; substantially as described.

3. The method of fixing nitrogen which comprises introducing into an atmosphere containing nitrogen the volatile constituents of a metal carbid at a temperature appro-

priate to the fixation of the nitrogen; substantially as described.

4. The method of fixing nitrogen, which comprises introducing into an atmosphere containing nitrogen, the volatile products given off from a furnace charge suitable for the production of a metal carbid but heated higher than the dissociation point of the carbid, the temperature prevailing being sufficient for the fixation of the nitrogen; substantially as described.

5. The method of fixing nitrogen, which comprises introducing into an atmosphere containing nitrogen the volatile products given off from a furnace charge suitable for the production of a metal carbid and likewise containing calcium chlorid but heated higher than the dissociation point of the carbid, the temperature prevailing being sufficient for the fixation of the nitrogen; substantially as described.

6. The method of fixing nitrogen, which comprises introducing calcium in a vaporous condition into an atmosphere containing nitrogen at a temperature appropriate to the fixation of nitrogen; substantially as described.

7. The method of fixing nitrogen, which comprises introducing calcium in a vaporous condition, in the presence of free carbon, into an atmosphere containing nitrogen, at a temperature appropriate to the fixation of the nitrogen; substantially as described.

8. The method of fixing nitrogen, which comprises introducing into an atmosphere containing nitrogen, the volatile compounds given off from a furnace charge suitable for the production of calcium carbid, and likewise containing calcium chlorid, but heated higher than the dissociation point of the calcium carbid, the temperature prevailing, being sufficiently for the fixation of the nitrogen; substantially as described.

In testimony whereof we affix our signatures, in presence of two witnesses.

HERBERT RAYMOND MOODY.
SAMUEL AUCHMUTY TUCKER.

Witnesses:
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