C. KRAUSS & P. STAEHELIN.

PROCESS OF PREPARING NITROGEN COMPOUNDS.

APPLICATION FILED DEC. 6, 1913. RENEWED DEC. 8, 1916.

1,212,504.

Patented Jan. 16, 1917.

2 SHEETS—SHEET 1.

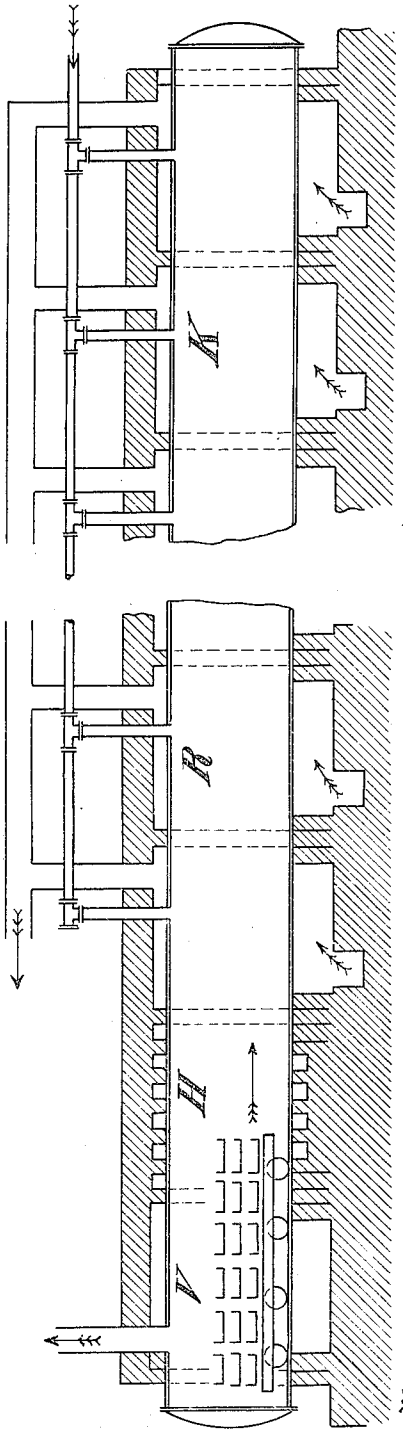


Fig. 1.

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2 SHEETS—SHEET 2.

Fig. II.

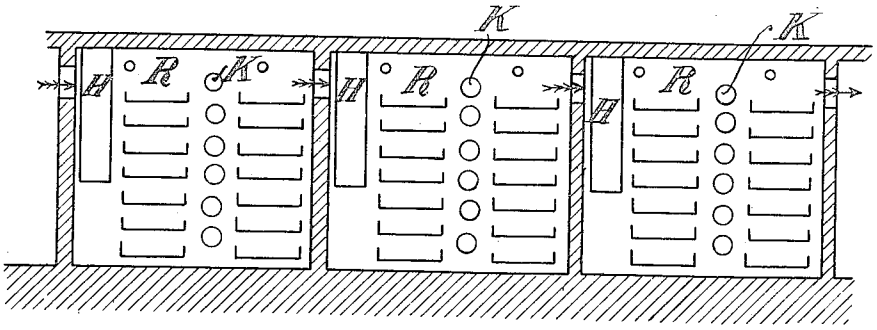
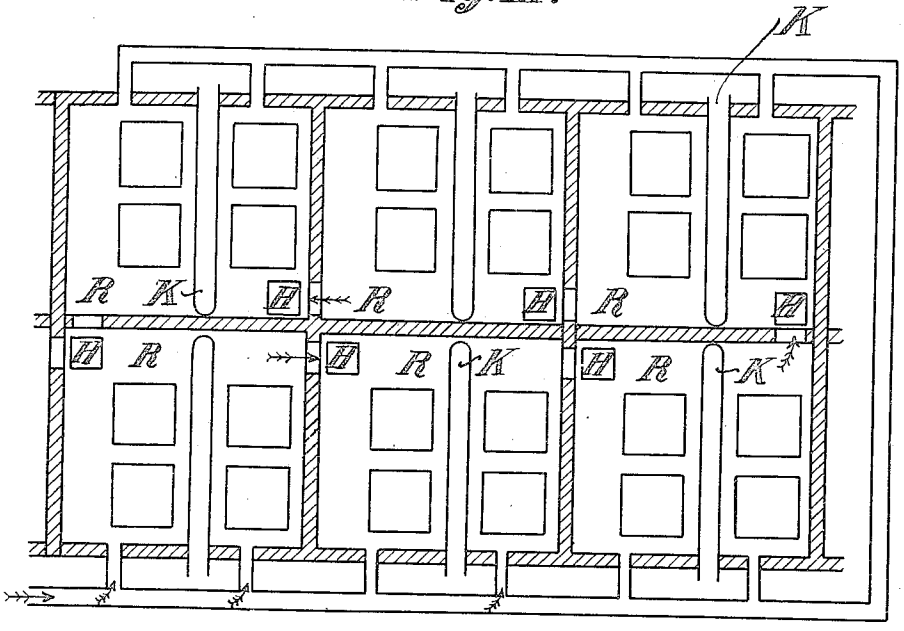


Fig. III.



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UNITED STATES PATENT OFFICE.

CONSTANTIN KRAUSS, OF COLOGNE-BRAUNSFELD, AND PAUL STAEHELIN, OF KNAPSACK, NEAR COLOGNE, GERMANY.

PROCESS OF PREPARING NITROGEN COMPOUNDS.

1,212,504. Specification of Letters Patent. Patented Jan. 16, 1917.

Application filed December 6, 1913, Serial No. 805,130. Renewed December 8, 1916. Serial No. 135,900.

To all whom it may concern:

Be it known that we, CONSTANTIN KRAUSS and PAUL STAEHELIN, subjects of the King of Prussia, German Emperor, and residents at Cologne-Braunsfeld and Knapsack, near Cologne, respectively, in the Province of the Rhine, Kingdom of Prussia, German Empire, have invented a certain new and useful Process of Preparing Nitrogen Compounds, of which the following is a specification.

This invention relates to a process and apparatus for the production of nitrogen compounds.

It is already known: (1) To produce nitrogen compounds from metallic carbids or carbid mixtures and nitrogen in a continuous operation (see Norwegian Patent No. 20777, Italian Patents Nos. 112336 and 101994, also German Patents Nos. 7911 and 149594 and so forth). (2) That on the reaction of nitrogen upon the carbid, certain limits of temperature must be maintained because the reaction is reversible (see Caro and others, *Zeitschrift für Elektrochemie* 1909, S. 1179; Le Blanc, *Zeitschrift für Elektrochemie* 1911–20; Bredig, *Zeitschrift für Elektrochemie*). (3) That the reaction between ordinary nitrogen and carbid can be hastened quite materially, if the reaction takes place in the presence of certain chemical reagents especially the halogens (see Patent Polzenius 163320). (4) That the reaction of nitrogen with metallic carbid is strongly exo-thermic. Efforts have therefore been made either by cooling or by a particular manner of the supply of nitrogen to regulate the reaction temperature (see Norwegian Patent No. 20777, United States Patent No. 1004509, German Patents Nos. 149594 and 228925. It is moreover the desire of every technician to arrange his manufacture as continuous as possible. All the above named patents have by themselves not yet been able to attain any conspicuous success in the technical industry, in this regard, for they are all of them troubled with more or less serious drawbacks. Especially there are two points which have hitherto greatly hindered the technical availability according to the processes above proposed namely (1) the method of the transport of the reaction mass through the apparatus and (2) the regulation of the correct temperature.

Most inventors have overlooked that on the reaction of nitrogen upon a metallic carbid, the reaction product does not remain pulverulent, but sinters together whereby stoppages of the apparatus are inevitable; and those inventors who have grasped the importance of the regulation of the temperature have remained quite unclear over the point as to the amount of energy liberated in the reaction. The applicants for both the Norwegian Patent No. 20777 and the United States Patent No. 1004509 which have most completely developed the temperature regulation hitherto, remain far from their goal. The Norwegian patent endeavors to regulate the reaction heat, by conducting the nitrogen around the outside of the double walled apparatus, heating it thereby and then first allowing it to act upon the hot carbid. Consequently, it brings together at the moment when the reaction mass possesses the highest temperature, the hottest nitrogen to react upon it, a process which must create the opposite of the purpose in view. In addition thereto, there is the fact that the released quantities of heat very greatly exceed what the quantities of nitrogen necessary for the process under normal conditions are capable of taking up. The United States patent endeavors to regulate the temperature by shutting off the supply of nitrogen from time to time either partially or entirely by automatic means. That such a method of working is only a technical trick is obvious, because with the shutting off of the supply of nitrogen, the entire apparatus is brought to a standstill, because otherwise under the circumstances, the carbid which is not yet treated with nitrogen would be moved by the rotation of the cylinder toward the exit, whereby neither a uniform production in regard to quantity nor yet in regard to quality could be attained without regard to the fact that the apparatus will technically not be fully utilized. The mistake which both these inventors have made is to be seen in the first instance in that they—as above stated—are not aware of the large quantites of heat which are liberated during the reaction. Both the aforesaid processes have moreover the further drawback that the reaction product escapes in a brightly incandescent condition from the apparatus and must be prepared by means of special cooling devices for further treatment. Moreover, both the inventors

overlook the fact that the brightly incandescent nitrogen product which is produced sinters together fast and the apparatus must be stopped up in a very short time.

In the following specification, we describe a process and apparatus which according to our experience, avoids the aforesaid drawbacks and enables a continuous working to take place with the most economical utilization of the technical constructions. Our process is also based on the principle of the reaction of the nitrogen upon the carbid in counter current, and in addition the regulation of the reaction temperature at those parts of the apparatus where increases of temperature are developed.

The reaction of the nitrogen can take place in two different ways. (1) By causing both the material and also the nitrogen to move. (2) By causing nitrogen gas to act in counter current upon the stationary material.

The accompanying drawing shows a simple apparatus for carrying out the process herein described, in which—

Figure 1, shows a longitudinal section of a channel furnace. Fig. 2 shows a modification of the apparatus shown in Fig. 1, and Fig. 3, is a plan view on the line *x*—*x*, of Fig. 2.

For the first mode of working, there is employed a horizontal channel furnace (Fig. 1). This furnace consists of four parts: 1 A preliminary heating space. 2 A full heating space. 3 A reaction space, and 4 A cooling space.

In the preliminary heating space V the reaction product (finely pulverized carbid or carbid mixtures with or without additions which facilitate the reaction) is warmed by means of the gases escaping from the other spaces. In the heating chamber H, the carbid is heated up to the temperature necessary for the carrying out of the reaction. In the reaction space R the treatment with nitrogen is effected: in the cooling space K, the finished product is cooled down until it can be withdrawn without special precautions and can be further utilized.

The method of working is as follows:— The finely pulverized material, to which substances facilitating the reaction can be added, is transported by mechanical means, such as trucks, transporting bands or the like through the furnace. In the contrary direction to that in which the material to be treated with nitrogen is transported, there is admitted cold nitrogen gas. In the preliminary heating space the excess escaping gases give up part of their heat to the material and are drawn off comparatively cool. The material then passes somewhat warmed into the heating space, where it is heated up to the reaction temperature, either by means of an electric heating device or by outside fire. The consumption of heat energy is thus very small, because the nitrogen gas coming from the cooling and reaction spaces is already so hot, that it reacts upon the material to be nitrogenized, causing further reaction heat to be liberated which again supports the reaction. The heating space serves therefore properly only as a heat regulator. From the heating space, the reaction mass passes into the reaction space. There is here an interchange between the cool inflowing nitrogen gas and the reaction masses proceeding out of the heating space of such a kind that under all circumstances, the reaction mass before cooling must exceed the critical temperature which assures the quantitative nitrogenizing and prevents any reformation of the carbid.

As above stated, it is necessary to work with a quite extraordinarily great surplus of cold nitrogen in order to overcome by this means the masses of heat liberated. This would, however, render the process very costly and moreover enable no certain working reaction because under certain circumstances, during short interruptions of the operation, local heating can take place which might injure the material in the furnace or the transporting mechanism. We have therefore in addition to the regulatable internal supply of the cool nitrogen current also devised a regulation of the furnace by outward cooling. For this purpose, we have surrounded the channel furnace with an outer cooling mantle and have constructed the inner mantle from material which conducts heat. By this arrangement it becomes possible whenever the various measuring instruments inserted in the reaction space indicate an undesirable rise of temperature, to act immediately upon the temperature by passing cold air between the channel furnace and the outer mantle. In this manner therefore, a double temperature regulation takes place, firstly by the nitrogen in the interior of the channel furnace and secondly by air and cooling gases at the outside. As the overheating (as already stated) is chiefly local, we have arranged to allow the cold nitrogen gas to flow into the reaction space at various points to regulate temperatures. Moreover, we have divided the cooling space between the channel furnace and the outer mantle in various divisions, as may be seen in the drawing, whereby we are in the position to cool certain parts of the channel furnace according to requirement. From the reaction space the reacting material passes into the cooling space and is also capable of being cooled down by surrounding air so that the reaction mass can be so far cooled that its removal from the furnace and its further treatment is not hindered.

For the second method of working in which the material absorbing the nitrogen

is not moved but remains at the same position in the furnace until it is completely used up, a kind of ring furnace is provided, the operation of which is as follows:—In the various chambers of the furnace (Figs. 2 and 3) the carbid or the carbid mixture is spread out on stages in layers. The separate chambers R, R are provided with suitable heating devices H for electric internal heating. The nitrogen inlet takes place at various points, of the separate chambers. For the commencement of the process, there is first heated one chamber to the reaction temperature, then cooled nitrogen is passed in and in such a quantity that the same suffices to prevent the reaction temperature rising beyond the best point. For this there are obviously required much greater quantities of gas than are needed for the saturation of the carbid which is in the chamber. The unconsumed highly heated nitrogen is introduced in the second chamber and reacts upon the carbid there. Here again, reaction heat is liberated which would lead to the overheating of the reaction product. In order to prevent this cooled nitrogen is introduced in such quantities that again the best reaction temperature is not exceeded. The nitrogen is passed through the first chamber until the mass is sufficiently cooled. This hot nitrogen passes as already stated, from the first into the second chamber. The temperature of the nitrogen passing in is lowered however in the degree that the reaction product is cooled in the first chamber, consequently the introduction of fresh cold nitrogen in the second chamber must be gradually reduced.

The same operation takes place in the third chamber again and so forth. The heating of the chambers will therefore only need to be undertaken when for some industrial reason or other, a chamber has not attained to the necessary reaction temperature or when a furnace is being newly started. As even in this mode of working, local overheatings are not impossible, we have constructed in the separate reaction chambers cooling tubes or cooling boxes K of material which easily conducts heat, through which cold air can be passed, as soon as the measuring instruments indicate an undesirable rise of temperature.

It will be obvious without further explanation that firstly a choking of such apparatuses is rendered impossible, whereby a uniform action of the nitrogen is secured, and that secondly, an injurious overheating of the reaction product and a redecomposition of the nitrogen compound already formed is rendered impossible, because in the attaining of the most suitable reaction temperature, no overheating but rather a gradual cooling takes place in the nitrogen current, and because moreover the reaction product leaves the apparatus cooled.

According to our process there arises in the action of nitrogen on carbid, a mixture of nitrogen compounds and, in fact, chiefly calcium cyanamid, also dicyandiamid and cyanid. By proper additions we are in a position to increase the production of one of the latter products at the expense of the cyanamid.

Finally, the saving of heat is the most favorable possible because both the heat which is stirred up in the product left in the furnace is absorbed by the current of cold nitrogen gas and also the heat of the nitrogen gas which is drawn off is continuously transferred to the newly charged reaction mass, and also the reaction heat liberated during the reaction is so controlled that it coöperates to assist and not to injure the process. Saving of heat according to our process is actually so favorable that the reaction process proceeds almost entirely without the addition of heat from without when once the mass in the furnace has been brought to the requisite temperature. The heating devices then serve simply as regulators of the temperature.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the continuous production of nitrogen compounds which consists in subjecting the material to be combined with nitrogen in pulverized state, to a preliminary heating, passing the material through a heat of reaction temperature, then passing the material to a point of critical temperature, and subsequently cooling the resultant mass, all in the path of a current of nitrogen gas flowing in a direction opposite to that of the travel of the material.

2. A process for the continuous production of nitrogen compounds which consists in subjecting carbid, in pulverized state, to a preliminary heating, passing the partially heated carbid through a heat of reaction temperature, then passing the mass to a point of critical temperature, and subsequently cooling the resultant mass, all in the path of a current of nitrogen gas flowing in a direction opposite to that of the travel of the carbid.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

CONSTANTIN KRAUSS.
PAUL STAEHELIN.

Witnesses:
LOUIS VANDORY,
OSCAR DAPNER.