UNITED STATES PATENT OFFICE.

GEORG ERLWEIN AND KARL WARTH, OF BERLIN, GERMANY, ASSIGNORS TO SIEMENS & HALSKE A. G., OF BERLIN, GERMANY, A CORPORATION OF GERMANY.

PROCESS OF MAKING NITROGENOUS COMPOUNDS.

994,095. Specification of Letters Patent. Patented May 30, 1911.

No Drawing. Application filed November 15, 1910. Serial No. 592,474.

To all whom it may concern:

Be it known that we, GEORG ERLWEIN and KARL WARTH, subjects of the German Emperor, and residing at Berlin, Germany, have invented a certain new and useful Improved Process of Manufacturing Nitrogen Products Which when Treated with Water at a High Temperature Yield Ammonia, of which the following is a specification.

The subject-matter of our invention is a process of manufacturing nitrogen products which when treated with water at a high temperature yield ammonia. According to our invention the said nitrogen products are made by a carbid, *e. g.* calcium carbid, being changed in a manner known *per se* by heating it to a temperature between about 300° and 1000° C. so that when it is treated with water no hydrocarbon at all or only very small quantities thereof are generated. The product thus obtained is treated with nitrogen at a high temperature. During the first part of this process, namely the heating of the carbids, it is obviously a matter of a more or less complete decomposition with the separation of carbon. The treatment must, of course, take place with as perfect exclusion of air as possible, because otherwise oxidation or nitration products would be obtained, and it must be continued until no more hydrocarbon is generated when the product is treated with water, or until the decomposition of the carbid is complete. This requires, as a rule, several hours. When the product thus obtained is treated with dilute solvents, a residue of finely divided carbon is obtained approximately corresponding to the total quantity of the carbon which was contained in the carbid. It is true that to heat the carbid until it is completely decomposed requires, under certain circumstances, considerable quantities of heat. These can, however, be materially diminished when oxids, carbonates or halogen compounds of alkalis or of alkaline earths or of earths, or if iron, copper, aluminium, magnesium or titanium are added to the calcium carbid. These admixtures are preferably added in a state of very fine distribution. Even when employed in relatively small quantities the admixtures cause the decomposition to be considerably accelerated and, in certain cases, to commence at a low temperature. The product obtained by heating the carbids is heated in the presence of nitrogen in order to obtain nitrogen compounds, above all cyanamids, which when treated with water at a high temperature yield ammonia. Although a relatively low temperature, say up to dark red heat, suffices for this nitrogen treatment, it is preferable to raise the temperature to white heat.

It is well known *per se* that when the metals of the akalis, alkaline earths and earths are heated they absorb nitrogen, nitrids being formed. It is likewise well-known that when these metals are heated with carbon in a current of nitrogen, nitrogen compounds are obtained. Mallet (*Ann. Chem.* 186, p. 155) obtained aluminium nitrogen compounds by heating aluminium with soot in a graphite crucible in the presence of nitrogen. Further, it is very well-known that calcium cyanamid is produced when metallic calcium is heated with carbon in a current of nitrogen. It is generally stated that this is due to the previous formation of carbid which is then azotized. In our present opinion, the remainder of the mass is probably carbon and a kind of lower carbid or impure calcium. It is also well-known that carbids treated with nitrogen under the action of heat yield nitrogen compounds which when treated with hot water produce ammonia. In contradistinction to all such known processes the employment of the products of decomposition of the carbids obtained by heat, as described herein, as starting material for the manufacture of nitrogen compounds has very considerable advantages. On the one hand, the product of decomposition can be made very cheaply, and, on the other hand, it not only reacts exceedingly readily and rapidly with nitrogen, but results in a mass containing a high percentage of nitrogen compounds.

That the present process can be carried into practice at a small cost is due, firstly, to its not being necessary to use pure or substantially pure carbid, and, secondly, to its being possible to select the place of manufacture independently of that where the carbid is made, and consequently in a locality which affords specially favorable possibilities of manufacture and sale. This independence of the locality of manufacture results from its not being necessary, when employing the product of decomposition, to have regard, as when carbids are employed, to the influences of air and moisture, and

therefore the product of decomposition of the carbid can readily be conveyed everywhere without either special cars or sealed vessels. In addition it is to be noted that the finished final product contains no residue whatever of carbid and can therefore also be packed and conveyed without special precautions having to be taken. When lying in the air no unpleasant odor is emitted by the mass, and this also is a considerable advantage.

Our process may be carried into practice as follows:—50 kg. calcium carbid containing 75% carbid are heated, while excluded from the air, for five hours to about 1100° C. This may take place in ordinary muffle-furnaces such as are generally employed in the art. After being heated the product still contains about 0.7% carbid. Now if this product is heated again, but in the presence of nitrogen, a product is obtained which contains 12 to 15% nitrogen in a form such that, when the mass is treated with superheated steam, ammonia is obtained.

Instead of employing calcium carbid, as starting material, another carbid of the alkaline earths may be employed.

We claim:—

1. The herein described process which comprises heating a carbid, which with water yields hydrocarbon in an inert environment at from about 300° C. to about 1100° C. for such length of time that a decomposition product which no longer yields hydrocarbon when treated with water is obtained, and subsequently subjecting said decomposition product to the action of nitrogen at such temperature and for such length of time that a nitrogen product is obtained which will yield ammonia when treated at high temperature with water.

2. The herein described process, which comprises adding a halogen compound to a carbid, which with water yields hydrocarbon, heating the mixture in an inert environment at from about 300° C. to about 1100° C. for such length of time that a decomposition product, which no longer yields hydrocarbon when treated with water, is obtained, and subsequently subjecting said decomposition product to the action of nitrogen at such temperature and for such length of time that a nitrogen product is obtained which will yield ammonia when treated at high temperature with water.

3. The herein described process which comprises heating calcium carbid in an inert environment at from about 300° C. to about 1100° C. for such length of time that a decomposition product, which no longer yields hydrocarbon when treated with water, is obtained, and subsequently subjecting said decomposition product to the action of nitrogen at such temperature and for such length of time that a nitrogen product is obtained which will yield ammonia when treated at high temperature with water.

4. The herein described process which comprises heating a carbid, which with water yields hydrocarbon, in an inert environment at such a temperature and for such length of time that a decomposition product which no longer yields hydrocarbon when treated with water, is obtained, cooling said product and subsequently subjecting said decomposition product to the action of nitrogen at such temperature and for such length of time that a nitrogen product is obtained, which will yield ammonia when treated at high temperature with water.

5. The herein described process, which comprises adding a halogen compound to a carbid, which with water yields hydrocarbon, heating the mixture in an inert environment at such a temperature and for such length of time that a decomposition product, which no longer yields hydrocarbon when treated with water, is obtained, cooling said product and subsequently subjecting said decomposition product to the action of nitrogen at such temperature and for such length of time that a nitrogen product is obtained which will yield ammonia when treated at high temperature with water.

6. The herein described process which comprises heating calcium carbid in an inert environment at such a temperature and for such length of time that a decomposition product, which no longer yields hydrocarbon when treated with water, is obtained, cooling said product and subsequently subjecting said decomposition product to the action of nitrogen at such temperature and for such length of time that a nitrogen product is obtained which will yield ammonia when treated at high temperature with water.

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

GEORG ERLWEIN.
KARL WARTH.

Witnesses:
HENRY HASPER,
WOLDEMAR HAUPT.