UNITED STATES PATENT OFFICE.

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PROCESS OF PRODUCING AMMONIA.

990,191. Specification of Letters Patent. Patented Apr. 18, 1911.

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To all whom it may concern:

Be it known that I, CARL BOSCH, doctor of philosophy and chemist, subject of the King of Prussia, residing at Ludwigshafen-on-the-Rhine, Germany, have invented new and useful Improvements in Processes of Producing Ammonia, of which the following is a specification.

My invention relates to the production of ammonia from the so-called titanium cyanonitrid, which can easily be obtained for instance by heating a mixture of titanic acid and carbon in the presence of nitrogen (Deville and Wöhler, *Annalen der Chemie*, vol. 103, p. 230 *et seq.*).

It is stated in the literature on the subject that titanium cyanonitrid is unattacked by boiling concentrated sulfuric acid and that by melting it at a red heat with potassium bisulfate (*Annalen der Chemie*, 73, p. 38) the nitrogen is evolved as such, and it is also stated (Dammer "*Handbuch d. anorg. Chemie*," II, part 1, page 597) to be soluble in a mixture of nitric acid and hydrofluoric acid. In this case also nitrogen is set free. On the other hand, by melting titanium cyanonitrid with caustic alkali, or by passing steam over it at a red heat, ammonia is obtained, but these reactions are not suitable for carrying out on a large scale since the first reaction is too costly and the second reaction does not yield sufficient ammonia.

I have now discovered that titanium cyanonitrid can be made to yield ammonia in a manner which allows the reaction to be carried out on a commercial scale by oxidizing it under such conditions that none, or practically none, of the ammonia formed becomes further oxidized to free nitrogen. Provided that this condition be maintained, many different oxidation agents and methods may be employed, for instance the reaction can be carried out in alkaline, or neutral, or acid solution, or suspension, or even in a melt. In all cases of course some body containing hydrogen such for instance as water, or steam, or sulfuric acid, must be present. As examples of oxidizing agents I mention chromic acid, manganese dioxid, iron oxid, copper oxid, cerium oxid, mercury oxid, and salts corresponding to these oxids. The oxidation may also be caused to take place by treating the titanium cyanonitrid with steam in the presence of an oxid or hydroxid or salt of an alkali or alkaline earth metal (such, for instance, as sodium carbonate, caustic soda, and calciumchlorid) which, by itself, under the conditions used as to temperature and quantity, has no oxidizing action, or practically no oxidizing action, on the titanium compound but which in the presence of steam favors the oxidation. Steam by itself does not react upon titanium cyanonitrid until such a temperature is reached that the ammonia formed is decomposed again to a greater or lesser extent. Or the oxidation may be carried out by heating the titanium cyanonitrid with a bisulfate, provided the temperature employed be not too high, and by boiling it with concentrated sulfuric acid. If desired, the treatment with sulfuric acid or with a bisulfate can be caused to take place in the presence of water and under pressure. Electrolysis with or without the use of so-called oxygen carriers can also be employed to effect the oxidation, and even air can be used in the presence of steam or water (if necessary under pressure, and using an oxygen carrier) to bring about oxidation.

When carrying out the processes of my invention, the titanium is obtained in the form of its oxid, or of a salt thereof, and can then easily be reconverted into titanium cyanonitrid making use of atmosphere nitrogen.

If, when carrying out the oxidation in the presence of air and steam as hereinbefore described, a contact body, such for instance as finely divided platinum be present the ammonia produced is wholly or partially oxidized to oxids of nitrogen.

During the reaction which takes place according to this invention, the titanium cyanonitrid is oxidized so that the nitrogen is converted into ammonia, the titanium is converted into titanic acid (TiO_2), and the carbon either remains as such, or it may be oxidized according to the vigor with which the oxidizing agent acts. For instance if

boiling sulfuric acid be employed as the oxidizing agent, the carbon is converted into carbon dioxid. Of course if the oxidizing agent is capable of combining with the ammonia formed or with the titanic acid, this will lead to the formation of salts. Thus, when boiling sulfuric acid is employed for oxidizing purposes according to this invention, the ammonia is obtained in the form of ammonium sulfate and the titanium oxid will also combine with sulfuric acid to form titanium sulfate. On the other hand if the titanium cyanonitrid be treated with caustic soda solution and copper oxid, the ammonia is produced in the free form, while the copper oxid is reduced. When titanium cyanonitrid is heated with sodium carbonate in the presence of steam, ammonia is produced, generally partly as such and partly in the form of ammonium carbonate while the titanium is obtained in the form of titanium oxid or sodium titanate, and some hydrogen and some carbon monoxid are also formed. On the other hand, when titanium cyanonitrid is heated with platinum chlorid in the presence of air and steam, ammonia is formed and in the presence of the platinum is partially oxidized into nitric oxid, while the titanium is converted into titanium oxid and the carbon is oxidized to carbon dioxid.

The following examples will serve to illustrate further the nature of my invention, which, however, is not confined to these examples. The parts are by weight and the temperatures in degrees centigrade.

Example 1: Boil 1 part of titanium cyanonitrid with 10 parts of concentrated sulfuric acid. Sulfur dioxid is evolved and in from 15 to 30 minutes the oxidation is complete. The nitrogen of the titanium cyanonitrid has been converted into ammonium sulfate, which can be worked up in any desired manner.

Example 2: Melt 1 part of finely divided titanium cyanonitrid with 5 parts of potassium bisulfate at from 300 to 400 degrees. After from 30 to 60 minutes, dissolve the melt in water, digest for a considerable time at 100 degrees, until the titanic acid has separated out, filter, add excess of lime to the filtrate, and drive off the ammonia by means of heat.

Example 3: Heat together in an autoclave, for from 2 to 3 hours, at a temperature of from 350 to 400 degrees, 1 part of finely divided titaniumf cyanonitrid, 3 parts of sodium bisulfate, and 3 parts of water, and work up the product as described in the foregoing Example 2.

Example 4: Heat together, in an autoclave, at about 180 degrees, finely divided titanium cyanonitrid, 30 per cent. caustic soda solution and sufficient copper oxid to effect oxidation. On opening the valve of the autoclave ammonia escapes. In this example instead of copper oxid, an equivalent quantity of iron oxid or manganese peroxid or chromic acid can be employed.

Example 5: Heat together, for from 2 to 3 hours, on the water bath, titanium cyanonitrid and ferric sulfate solution. Ferrous sulfate is formed and the solution also contains ammonia.

Example 6: Heat together at from 100 to 140 degrees, in an autoclave, titanium cyanonitrid, dilute sulfuric acid and a little ferrous sulfate solution, and pump in air, while stirring well, until the oxidation is complete. If the ferrous sulfate be omitted, the reaction proceeds more slowly.

Example 7: Suspend titanium cyanonitrid in dilute sulfuric acid, add some chromium sulfate, or ferrous sulfate, to the suspension and oxidize it electrolytically at 100 degrees, in a cell provided with a diaphragm.

Example 8: Heat a mixture of 1 part of titanium cyanonitrid with 3 parts of sodium carbonate in a current of steam at a temperature of from 400 to 500 degrees. Ammonia passes over either in the free state or in the form of its carbonate.

Example 9: Heat a mixture of 2 parts of titanium cyanonitrid with 1 part of caustic soda in a current of steam at a temperature of from 300 to 400 degrees. In a short time the evolution of ammonia is complete.

Example 10: Soak titanium cyanonitrid in platinum chlorid solution until it contains from 2 to 3 parts per 1,000 of platinum and then heat it at from 300 to 400 degrees in a current of mixed air and steam. By the catalytic action of the platinum in the presence of an excess of oxygen more or less of the ammonia is converted into oxids of nitrogen.

Now what I claim is:

1. The process of producing ammonia by oxidizing titanium cyanonitrid in the presence of a body containing hydrogen while maintaining the temperature so low that the production of free nitrogen is practically avoided.

2. The process of producing ammonia by heating titanium cyanonitrid with an oxidizing agent in the preser e of a body containing hydrogen while maintaining the temperature so low that the production of free nitrogen is practically avoided.

3. The process of producing ammonia by heating titanium cyanonitrid with an oxidizing agent in the presence of an oxid or hydroxid or salt of an alkali or alkaline earth metal and in the presence of a body containing hydrogen.

4. The process of producing ammonia by heating titanium cyanonitrid with air and steam in the presence of an oxid or hydroxid or salt of an alkali or alkaline earth metal.

5. The process of producing ammonia by heating titanium cyanonitrid with air in the presence of ferric sulfate and water.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

CARL BOSCH.

Witnesses:
J. ALEC. LLOYD,
JOS. H. LEUTE.