

# UNITED STATES PATENT OFFICE.

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## PROCESS OF MAKING AMMONIA.

957,843.

Specification of Letters Patent.

Patented May 10, 1910.

No Drawing.

Application filed March 26, 1908. Serial No. 423,451.

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 Making Ammonia, of which the following is a specification.

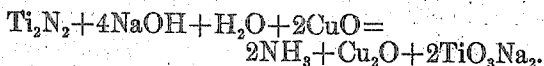
In the *Comptes Rendus* (82, page 974) it is stated by Friedel and Guerin that a titanium nitrid ( $Ti_2N_2$ ) on being boiled with concentrated sulfuric acid gives rise to ammonia and titanitic acid. I have now discovered that titanium nitrids can be made to yield ammonia by oxidation in the presence of water, under which term I include water both in the liquid state and in the form of vapor or steam. Of course the oxidation of the titanium nitrids should be carried out under such conditions that none, or practically none, of the ammonia formed becomes 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. 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 nitrid with steam in the presence of an oxygen carrier (for instance, a metallic salt, or oxid, or hydroxid, such as sodium carbonate, caustic soda, and calcium chlorid) which, by itself, under the conditions used as to temperature and quantity, has no oxidizing action, or practically no oxidizing action, on the titanium nitrid. Steam by itself does not react upon the titanium nitrid 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 nitrid with a bisulfate, provided water be present and the temperature employed be not too high. If desired, the treatment with the oxidizing agent may be made to take place 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 process 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 nitrid, making use of atmospheric 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.

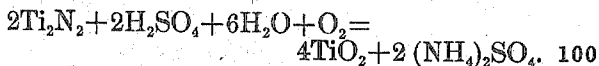
The following examples will serve to illustrate further the nature of my invention, which, however, is not confined to these examples. The parts are by weight.

Example 1: Heat together, in an autoclave, at about  $180^{\circ} C.$ , 1 part of finely divided titanium nitrid, 15 parts of 30 per cent. caustic soda solution, and 2 parts of copper oxid. On opening the valve of the autoclave ammonia escapes. The reaction which takes place can be represented by the equation



In this example instead of copper oxid, an equivalent quantity of iron oxid, or manganese peroxid, or chromic acid, can be employed.

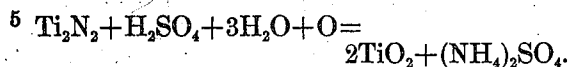
Example 2: Heat together at from  $100^{\circ} C.$ , to  $140^{\circ} C.$ , in an autoclave, 1 part of titanium nitrid, 20 parts of 20 per cent. sulfuric acid, and one part of 30 per cent. ferrous sulfate solution, and pump in air, while stirring well, until the oxidation is complete. The reaction which takes place can be represented by the equation



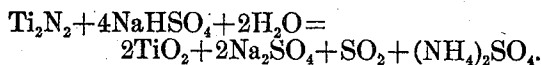
If the ferrous sulfate be omitted, the reaction proceeds more slowly.

Example 3: Suspend 1 part of titanium nitrid in 20 parts of 50 per cent. sulfuric acid, add one part of chromium sulfate or ferrous sulfate to the suspension and oxidize it electrolytically, at  $100^{\circ} C.$ , in a cell pro-

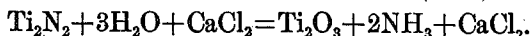
vided with a diaphragm. The reaction which takes place can be represented by the equation



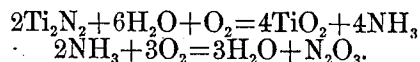
Example 4: Introduce 1 part of finely divided titanium nitrid ( $\text{Ti}_2\text{N}_2$ ) into 10 parts of molten sodium bisulfate, and raise the temperature gradually to from  $350^\circ \text{C}$ . to  $400^\circ \text{C}$ ., until a quiet melt is obtained. Then allow the melt to cool somewhat, and add a small quantity of water, and heat again to from about  $350^\circ \text{C}$ . to about  $400^\circ \text{C}$ . Repeat this operation until the melt is white, or until the nitrid has disappeared, when the nitrogen is all obtained in the form of ammonia. If desired, instead of adding small portions of water as aforesaid, steam can be passed through the melt at a temperature of about from  $350^\circ \text{C}$ . to  $400^\circ \text{C}$ ., but in this case the reaction takes a longer time. The reaction which takes place can be represented by the equation



Example 5: Heat a mixture of 1 part of titanium nitrid with 3 parts of calcium chlorid in a current of steam at a temperature of  $500^\circ \text{C}$ ., whereupon ammonium chlorid passes over. The reaction which takes place can be represented by the equation



Example 6: Soak titanium nitrid in 40 platinum chlorid solution until it contains from 2 to 3 parts per 1,000 of platinum, and then heat it at from  $300^\circ \text{C}$ . to  $400^\circ \text{C}$ . 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. The reaction which takes place can be represented by the equations



Now what I claim is:

1. The process of producing ammonia by 55 heating titanium nitrid with an oxidizing agent in the presence of water while maintaining the temperature so low that the production of free nitrogen is practically avoided.
2. The process of producing ammonia by 60 heating titanium nitrid with an oxidizing agent in the presence of water and an oxygen carrier.
3. The process of producing ammonia by 65 heating titanium nitrid with air and steam in the presence of an oxygen carrier.
4. The process of producing ammonia by 70 heating titanium nitrid 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.