

## UNITED STATES PATENT OFFICE

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PROCESS OF MANUFACTURING  
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mington, Del., a corporation of DelawareNo Drawing. Application May 3, 1932,  
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13 Claims. (Cl. 260—125)

This invention relates to the manufacture of substituted and unsubstituted aminoguanidine and more particularly to the catalytic reduction of substituted and unsubstituted nitroguanidine.

It has been the practice to prepare aminoguanidine by reducing nitroguanidine by means of zinc dust and acetic acid. (Thiele Ann. 270, 20 (1898); 302, 333 (1898)). In such a method a large excess of zinc dust is used and for the reason that only 5 50% yields are obtainable this method has been regarded as unsatisfactory. Aminoguanidine has also been prepared from hydrazine and methylisothiourea but this method is also unsatisfactory because of the expensive reagents that are 10 used.

An object of this invention is an improved process of making substituted and unsubstituted aminoguanidines. A further object is to improve generally upon the manufacture of substituted 20 and unsubstituted guanidines. Other objects will appear hereinafter, as the description proceeds.

According to this invention these aminoguanidines can be produced very satisfactorily by the catalytic reduction of nitroguanidines. Although 25 in the following discussion nitroguanidine is described in detail, the invention is applicable to substituted nitroguanidines in general, e. g., ditolylnitroguanidine, unsymmetrical diphenylnitroguanidine, xylolnitroguanidine, naphthylnitroguanidine, ethylnitroguanidine, butylnitroguanidine, triphenylnitroguanidine and like compounds.

According to this invention the reduction should be carried out with hydrogen in the presence of a 35 catalyst at a relatively low temperature. It is advantageous to operate the process at temperatures such that the aminoguanidine will not be pyrolytically decomposed. It has been found also that if the hydrogenation is carried too far de- 40 composition of the aminoguanidine results with consequent formation of urea and ammonia.

For the purpose of this invention a nickel catalyst and hydrogen are preferred for the reduction of the nitroguanidine. Other hydrogenating 45 catalysts may, however, be used, for example metallic catalysts prepared in a finely divided condition. Suitable catalysts may be selected from the group of metals known as the hydrogenating metals, comprising the elements copper, nickel, iron and cobalt and the noble metals of the 8th group of the periodic table such as platinum and palladium, rhodium, or alloys of two or more of these metals. In this process it has been 50 found desirable to keep the temperature as low

as possible to prevent decomposition, e. g., below 125° C. Temperatures between 25° C. and 85° C. are satisfactory and preferably the temperatures should be between 70° and 85° C. Also it is preferred to operate the process at such pressures as will permit the hydrogenation to proceed at a rate in excess of the rate of decomposition of the products. Suitable results may be obtained at a hydrogen pressure above 400 lbs. per sq. in. Lower pressures lead to incomplete conversion 10 and the excessive formation of by-products. Good results have been obtained when operating the process at a pressure of about 1100 lbs. per sq. in., although higher pressures even as high as 3000 lbs. /sq. in. may be used in some cases. For 15 the reason that acids and bases catalyze the decomposition of aminoguanidine it has been found that this may be overcome by the addition of a buffering material, such as magnesium sulfate, mixtures of alkaline phosphates, or mixtures of 20 borax with boric acid and sodium chloride, which serves to reduce the decomposition. While carbondioxide neutralizes the aminoguanidine it is sufficiently acid in reaction to decompose it.

The following examples are given as specific 25 embodiments which further illustrate my invention:

## Example 1

A hydrogenation catalyst is prepared by suspending kieselguhr in a solution of nickel nitrate. 30 Basic nickel carbonate is precipitated on the kieselguhr by adding sodium carbonate solution. The mass of kieselguhr and basic nickel carbonate is washed several times by decantation and filtered. The catalyst is then activated by reducing the basic nickel carbonate by means of hydrogen.

Ten and four tenths grams of nitroguanidine, 5 grams of the above catalyst, and 200 grams of water are placed in a steel reaction vessel capable 40 of being heated. The reaction vessel is sealed, attached to a source of hydrogen, and heated to 80° C. with good agitation under a hydrogen pressure of 1200 lbs. per sq. in. until the calculated amount of hydrogen has been absorbed. The reaction vessel is then unloaded. The aminoguanidine is recovered by filtering off the catalyst, evaporating the neutralized solution and precipitating the aminoguanidine as aminoguanidine bicarbonate by addition of sodium 50 bicarbonate.

## Example 2

Ten and four tenths grams of nitroguanidine and 5 grams of the catalyst described in Example 1 are suspended in 200 grams of water solution 55

containing 7 grams of magnesium sulfate. The mixture is placed in a steel reaction vessel capable of being heated. The reaction vessel is sealed, attached to a supply of hydrogen, and heated to 5 80° C. with good agitation under a hydrogen pressure of 800 lbs./sq. in. After the calculated amount of hydrogen has been absorbed, the reaction vessel is unloaded and the aminoguanidine isolated as described in Example 1.

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*Example 3*

Ten and four tenths grams of nitroguanidine and 5 grams of the catalyst described in Example 1 are suspended in 200 grams of ethyl acetate. The mixture is placed in a steel reaction vessel capable of being heated. The reaction vessel is sealed, attached to a supply of hydrogen, and heated to 80° C. with good agitation under a 15 hydrogen pressure of 800 lbs./sq. in. After the calculated amount of hydrogen has been absorbed, the reaction vessel is unloaded and the aminoguanidine isolated as described in Example 1.

20 25 The resulting aminoguanidine may be isolated by filtration and neutralizing with dilute sulfuric acid. To the solution, after evaporation, is added potassium bicarbonate to precipitate the aminoguanidine. The solution may then be cooled, 30 filtered, and the product dried.

The statements inserted in the claims "in the substantial absence of acids" and "in the absence of any substantial amount of acids" are used to define the invention yet not limiting it as to the 35 presence of small amounts of acid inadvertently present as impurities in the nitroguanidine. The presence of some acid would be expected, at least in some instances, since the nitroguanidine used is separated from a solution high in sulphuric 40 acid.

I claim:

1. The process of producing an aminoguanidine which comprises the reduction of nitroguanidine with hydrogen at a temperature between 25° C. 45 and 125° C. in the presence of a hydrogenation metal catalyst, and in the absence of any substantial amount of acids.

2. The process of claim 1, in which the metal catalyst is a nickel catalyst.

3. The process of claim 1, in which the metal catalyst is taken from a group consisting of copper, nickel, iron, and cobalt.

4. The process of claim 1, in which the catalyst is taken from the eighth group of the periodic table.

5. The process of producing aminoguanidine which comprises the reduction of unsubstituted 10 nitroguanidine with hydrogen at a temperature between 25° C. and 125° C. in the presence of a hydrogenation metal catalyst and in the absence of any substantial amount of acids.

6. The process of producing aminoguanidine 15 which comprises reducing nitroguanidine by means of hydrogen in the presence of a hydrogenation metal catalyst and in the absence of any substantial amount of acids, operating the process at a pressure above 400 pounds per square 20 inch, and maintaining the temperature of the reaction between 25° C. and 125° C.

7. The process of claim 6, in which the pressure is maintained between 400 pounds and 1200 25 pounds per square inch.

8. The process of claim 6, in which the pressure is maintained between 400 pounds and 3000 pounds per square inch.

9. The process of producing an aminoguanidine which comprises reducing nitroguanidine by 30 means of hydrogen in the presence of a hydrogenation metal catalyst, and in the absence of any substantial amount of acids, operating the process in the presence of a buffering material and at a pressure above 400 pounds per square 35 inch.

10. The process of claim 9, in which the buffering material is an alkaline material.

11. The process of claim 9, in which the buffering material is magnesium sulfate.

12. The process of claim 9, in which the buffering material is a mixture of phosphates of the alkali metals.

13. The process of claim 9, in which the buffering material is a mixture of borax with boric acid 45 and sodium chloride.

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