

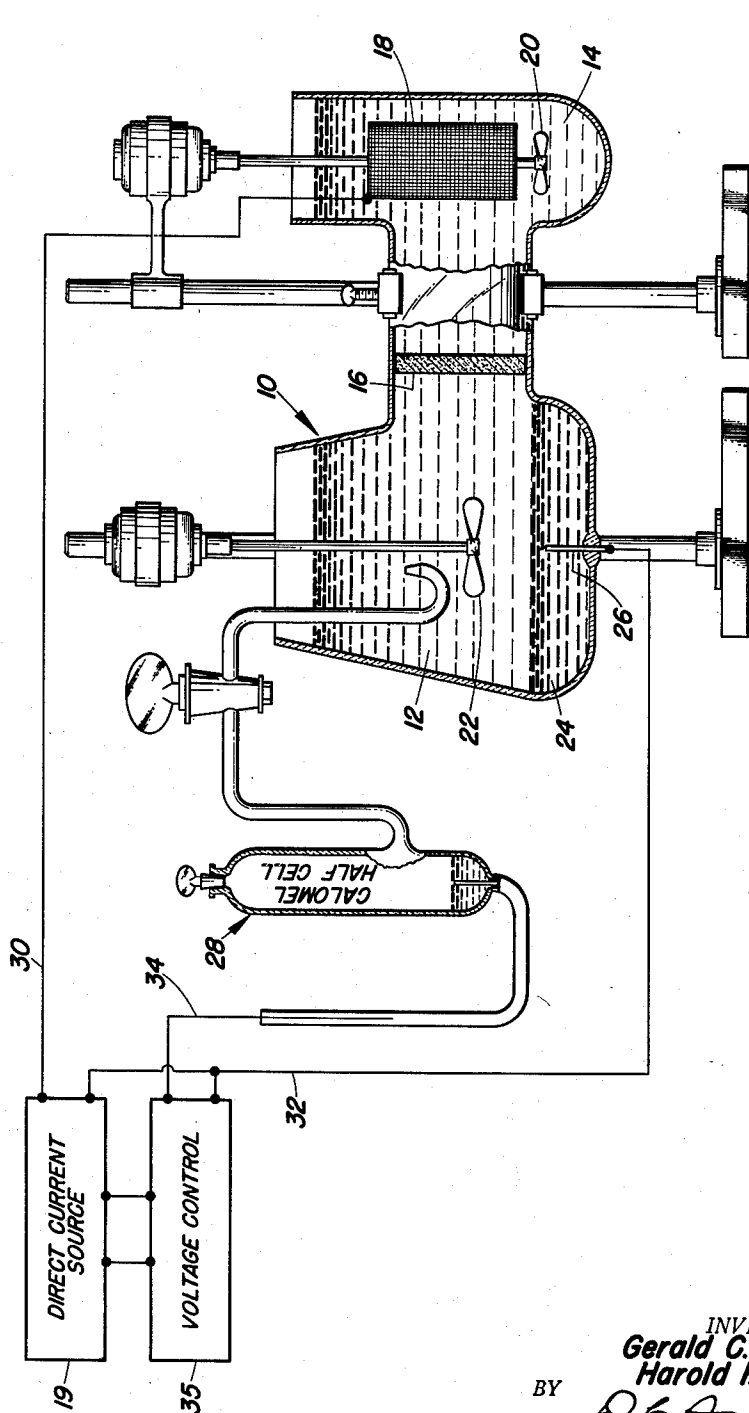
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ELECTRO-CHEMICAL PREPARATION OF NITROSOGUANIDINE

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ELECTRO-CHEMICAL PREPARATION OF NITROSOGUANIDINE

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1 Claim. (Cl. 204—74)

(Granted under Title 35, U. S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to the preparation of nitrosoguanidine, and more particularly to a process for preparing nitrosoguanidine by the electrolytic treatment of nitroguanidine at the cathode pole of an electrolytic cell.

Nitrosoguanidine has been prepared from nitroguanidine in the past by chemical reduction. Chemical reduction, however, is unsatisfactory due to low yields and to impurities in the desired product. Electrolytic methods have been used with some success in reducing aromatic nitro compounds to the corresponding amino and nitroso derivatives. However, the reduction of aliphatic nitro compounds has met with little success due to the fact that aliphatic nitro compounds are somewhat more difficult to reduce than the aromatic compounds, and also because they are very reactive, so that, under the conditions usually obtaining in the reducing atmosphere of an electrolytic cell, competing reactions take place and contaminating products are formed, along with minimum amounts of the desired reduction product. In the case of nitroguanidine, the reduction is rendered even more difficult by the fact that a partial reduction is required to form nitrosoguanidine since nitrosoguanidine itself can be reduced further to form aminoguanidine. It has been found, nevertheless, that nitroguanidine is reduced to nitrosoguanidine by a controlled voltage in a partitioned electrolytic cell. The product is crystalline and relatively pure as formed. The addition of nickel ions to the electrolyte solution in the cathode compartment of the cell brings about an increase in the yield of nitrosoguanidine.

An object of the invention is to provide a process for the electrolytic preparation of nitrosoguanidine.

A further object is to carry out the reductive electrolysis under such controlled conditions that undesired side reactions are suppressed and the main reaction involved in the reduction is favored.

Further objects will be apparent from the following description and claim.

The figure of the drawing illustrates a vertical sectional view of an apparatus that may be utilized to attain the above objects.

The apparatus comprises a reaction vessel 10 divided into compartments 12 and 14 by the porous fritted glass disk 16. The anode may conveniently be a platinum screen 18 in which stirrer 20 operates. Stirrer 22 agitates the solution in compartment 12. A pool of mercury 24 functions as cathode, and a platinum wire 26 sealed in the bottom of compartment 12 serves to connect the cathode 24 to a source of direct current. One side of a saturated calomel reference cell 28 makes contact with the electrolyte in compartment 12. Lead 30 connects anode 18 to the positive pole of the current source 19 which may be any one of a large number of controllable current sources known to workers in the art. Lead 32 connects cathode 24 to the negative pole of the current source. Lead 34 connects one terminal of the saturated calomel half cell 28 to the control element 35 of the current source, thus making it possible to maintain a cathode potential of precisely the desired voltage with reference to the calomel cell 28. The control element

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35 may be of the type disclosed by Sands, U. S. Patent 2,584,816; other suitable control elements are known to workers in the art.

In the operation of the process using the above described cell, 450 milliliters of 2 molar ammonium sulfate is placed in chamber 12, and 150 milliliters of the same solution is placed in chamber 14. Stirrers 20 and 22 are put into operation, and a direct current applied to leads 30 and 32 to the anode 18 and cathode 24 respectively. Cathode voltage with reference to the calomel half cell is maintained at minus 1 volt plus or minus 5% by means of the voltage control 35. Nitroguanidine is added to the cathode chamber of the cell. The solution becomes yellow as nitrosoguanidine is formed, and when the electrolyte becomes saturated, pure crystals of nitrosoguanidine precipitate out upon the surface of the mercury cathode. These crystals are recovered by filtration. The yield is over 20% based on the weight of nitroguanidine added to the cell.

When an excess of nickel sulfate is added to the 2 molar ammonium sulfate electrolyte in compartment 12 of the described cell, or a 0.5 molar nickelous acetate solution is used as the electrolyte in compartment 12 the described cell, the yields of nitrosoguanidine are substantially increased and approach values predicted from theoretical considerations. A bright red precipitate of nickel nitrosoguanidine settles out on the surface of the mercury cathode when nickel ions are present to react with nitrosoguanidine as it is formed. This nickel nitrosoguanidine complex may be recovered by filtration and then broken down to yield the nitrosoguanidine. The addition of some heavy metal salts to the electrolyte or the use of a heavy metal salt as the electrolyte has the advantage of increasing the yields of nitrosoguanidine in the process. In the presence of these salts, side reactions and decomposition of the nitrosoguanidine are held to a minimum during the process.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claim the invention may be practiced otherwise than as specifically described.

What is claimed is:

In a process for the preparation of nitrosoguanidine in an electrolytic cell having a mercury cathode connected to a source of negative current and positioned in a cathode compartment which is separated by a porous member from an anode compartment containing a platinum anode connected to a source of positive current, the steps comprising adding a 2 molar solution of ammonium sulfate to the anode and cathode compartments of said cell, placing a calomel half cell junction in said solution in said cathode compartment, dissolving nitroguanidine in said solution in said cathode compartment, agitating the solutions in said compartments, passing an electric current through said cell from said anode to said cathode, maintaining a voltage of minus 1.05 volts to minus 0.95 volts on said cathode with reference to said calomel cell, and recovering the resulting nitrosoguanidine thereby produced.

References Cited in the file of this patent

UNITED STATES PATENTS

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