

GOVERNMENT OF INDIA : THE PATENTS OFFICE, 214, ACHARYA JAGDISH BOSE ROAD,
CALCUTTA-17.

Specification No. 127059, 15th June 1970. (Accepted 22nd September 1971)

Index at acceptance—32F2C[IX(I)]; 70C7[LVIII(5)]

“IMPROVEMENTS IN/OR RELATING TO THE ELECTROLYTIC REDUCTION OF NITROGUANIDINE TO AMINOGUANIDINE”

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BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT, (ACT XXI OF 1860).

This is an invention by Handady Venkatakrishna Udupa, Gobichettipalyam Srinivasan Subramanian, Kodethoor Shrivara
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Karaikudi-3, & Rly., India, all Indian citizens.

PROVISIONAL

The following Specification describes the nature of this invention.

This invention relates to improvements in/or relating to the electrolytic reduction of nitroguanidine.

Hitherto it has been proposed to reduce nitroguanidine to aminoguanidine, by rotating/or stationary cathodes of copper or stainless steel or m.s. having a deposit of zinc, as a suspension in a supporting electrolyte of ammonium sulphate using ceramic porous pots as a diaphragm.

This is open to objection that by such a method the dissolution of zinc from the cathode takes place during the reduction and a part of the zinc is deposited back on the cathode and part is collected as metal powder in the solution. The use of ceramic porous pot limits the scale up size of the cells since high amperage cells for commercial production are somewhat difficult to be fabricated since bigger size porous pots are not readily available and even when available such pots are fragile and have poor mechanical strength.

The object of this invention is to obviate these disadvantages by suitable modification of the cell operation by which the nitroguanidine is added in instalments instead of one whole lot, the instalments depending upon the ampere-hours passed. This minimises the dissolution of zinc from the substrate and the given cathode surface can be used any number of times without requiring further deposition of zinc. The diaphragm is also modified by using terylene cloth in combination with microporous rubber sheet, so that the design of high amperage cells are simplified and diaphragms of any desired shape and size can be fabricated.

To these ends, the invention broadly consists in reducing nitroguanidine in a supporting electrolyte of ammonium sulphate preferably of 30% strength. The nitroguanidine is added in regular instalments depending on the amount of current passed. A rotating/or stationary electrode of copper, brass, stainless steel or m.s. having a deposit of zinc preferably to a thickness of 10 thou is used. A diaphragm of terylene cloth in combination with a microporous rubber sheet supported in a wooden frame is used and a perforated lead sheet is used as anode. The anolyte is dilute sulphuric acid up to 30% strength but preferably 20%. The reduction is done at a current density up to 20 amp/dm² but preferably 12 to 15 amp/dm². The temperature is maintained up to 25°C but preferably below 18°C. The reduction is carried out to theoretical time corresponding to 1.5 amp/hr per gm of nitroguanidine reduced. The catholyte is then treated with carbon dioxide till the pH becomes 8 and reacted with ammonium bicarbonate added in stoichiometric proportion to the aminoguanidine formed. The solution is allowed to remain over-night and aminoguanidine bicarbonate is filtered and the solution can be recycled after making it neutral.

By the addition of nitroguanidine in instalments, the dissolution of the zinc from the cathode is minimised and

there is no loss of zinc from the cathode which can be used a number of times without requiring further deposition.

The following examples are given to illustrate the invention:

EXAMPLE I

Cathode : M.S. Cylinder having
a 10 thou deposit of zinc } area 0.5 dm²
Current : 6 amps—voltage: 8-10 V
Catholyte : 390 ml of 30% ammonium sulphate
Anolyte : 50 ml of 20% sulphuric acid
Picrite (nitroguanidine added) : 18 gm in 3 instalments of 6 gm each
Temperature : 15-18°C
Aminoguanidine bicarbonate isolated = 17.5 gms
Assay yield = 74.4%

At the end, there was no zinc present in the solution.

EXAMPLE II

Repetition of the above Experiment—Conditions same as in Example I
Nitroguanidine added = 18 gms in 3 instalments of 6 gm each
Aminoguanidine bicarbonate isolated = 17 gms
Assay yield = 72.3%
No zinc present in solution at the end.

EXAMPLE III

Repetition of the above Experiment - Conditions same as in Example I.
Nitroguanidine added = 12 gms in 2 instalments
Aminoguanidine bicarbonate isolated = 11.2 gms
Assay yield = 72.4%
No zinc present in solution at the end.

The following are among the main advantages of the invention:

- (a) The addition of picrite in instalments in the catholyte minimises the dissolution of zinc from the cathode and the same cathode surface can be used a number of times without further deposition of zinc.
- (b) the use of terylene cloth in combination with microporous sheets as diaphragm has the advantage of ease of fabrication and good mechanical strength.
- (c) the precipitation of aminoguanidine bicarbonate with CO₂ and ammonium bicarbonate makes it possible to recycle the electrolyte a number of times.

Price : TWO RUPEES.

COMPLETE

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to improvements in/or relating to the electrolytic reduction of nitroguanidine to aminoguanidine, which is largely used for synthesis of weedicides.

Hitherto it has been proposed to reduce nitroguanidine to aminoguanidine, by rotating/stationary cathode of copper or stainless steel or mild steel having a deposit of zinc as a suspension in a supporting electrolyte of ammonium sulphate using ceramic porous pots as a diaphragm.

This is open to objection that by such a method the dissolution of zinc from the cathode takes place during the reduction and a part of the zinc is deposited back on the cathode and part is collected as metal powder in the solution. The use of ceramic porous pot limits the scale up size of the cells since high amperage cells for commercial production are somewhat difficult to be fabricated since bigger size porous pots are not readily available and even when available, such pots are fragile and have poor mechanical strength.

The object of this invention is to obviate these disadvantages by suitable modifications of the cell operation by which the nitroguanidine is added in instalments instead of one whole lot, the instalments depending upon the ampere hours passed. This minimises the dissolution of zinc from the substrate since the concentration of nitroguanidine being low, the cathode potential soon reaches above the dissolution potential of zinc and the given cathode surface can be used any number of times without requiring further deposition of zinc. The diaphragm is also modified by using terylene cloth in combination with microporous rubber sheet, so that the design of high amperage cells are simplified and diaphragms of any desired shape and size can be fabricated.

The invention consists in reducing nitroguanidine in a supporting electrolyte of ammonium sulphate preferably of 30% strength. The nitroguanidine is added in regular instalments depending on the amount of current passed. A rotating/stationary electrode of copper, brass, stainless steel or mild steel having a deposit of zinc preferably to a thickness of 10 thou is used. Terylene cloth in combination with a microporous rubber sheet supported in a wooden frame is used as diaphragm.

As a result of the invention, the dissolution of zinc from the cathode is minimised and the same cathode surface can be used for a number of times without requiring any further deposition of zinc. The use of terylene cloth in combination with a microporous rubber sheet supported in a wooden frame as diaphragm simplifies the scale up of cells to any large capacity.

The present invention consists of a process which comprises in reducing nitroguanidine in a supporting electrolyte of ammonium sulphate preferably of 30% strength. The nitroguanidine is added in regular instalments depending on the amount of current passed. A rotating/stationary electrode of copper, brass, stainless steel or mild steel having a deposit of zinc preferably to a thickness of 10 thou is used. The aminoguanidine is recovered as bicarbonate outside the cell by double decomposition with sodium/ammonium bicarbonate or heating with carbon dioxide.

A diaphragm of terylene cloth in combination with a microporous rubber sheet supported in a wooden frame is used and a perforated lead sheet is used as anode. As a result of this invention, the dissolution of zinc from the cathode is minimised and the same cathode surface can be used a number of times without requiring further deposition. As a result of the use of terylene cloth in combination with microporous rubber supported in a wooden frame as a diaphragm the scale up to any desired size has been simplified.

The subsidiary novel features are:

- (i) good mechanical strength of the diaphragm

- (ii) easy fabrication to any desired shape and size,
(iii) lowering of the operating voltages of the cell.

The investigation broadly consists in reducing nitroguanidine in a supporting electrolyte of ammonium sulphate preferably 30% strength. The nitroguanidine is added in regular instalments depending on the amount of current passed. A rotating/stationary cathode of copper, brass, stainless steel or mild steel having a deposit of zinc preferably to a thickness of 10 thou is used. A diaphragm of terylene cloth in combination with a microporous rubber sheet supported in a wooden frame is used and a perforated lead sheet is used as anode. The anolyte is dilute sulphuric acid up to 30% strength but preferably 20%. The reduction is done at a current density up to 20 amp/dm² but preferably 12 to 15 amp/dm². The temperature is maintained up to 25°C but preferably below 18°C. The reduction is carried out to theoretical time corresponding to 1.5 amp hr/gm of nitroguanidine reduced. The catholyte is then treated with carbon dioxide till the pH becomes 8 and reacted with ammonium bicarbonate added in stoichiometric proportions to the aminoguanidine formed. The solution is allowed to remain overnight and aminoguanidine bicarbonate is filtered and the solution can be recycled after making it neutral.

By the addition of nitroguanidine in instalments, the dissolution of the zinc from the cathode is minimised and the same can be used a number of times without requiring further deposition.

Figure 1 of the accompanying drawings represents the flow sheet for the process.

The following examples are given to illustrate the invention:

EXAMPLE I

Cathode	Mild steel cylinder having a 10 thou deposit of zinc—area of cathode 0.5 dm ² —Rotating
Current	6 amps
Cell voltage	8-10 V
Catholyte	390 ml of 30% ammonium sulphate solution
Anolyte	50 ml of 20% sulphuric acid
Nitroguanidine added	18 gm in 3 instalments of 6 gms each
Diaphragm	Terylene cloth along with microporous rubber supported in a wooden frame
Anode	Lead
Temperature	15-18°C
Aminoguanidine bicarbonate isolated	15 gms
Assay yield	63%
	No zinc is present in solution

EXAMPLE II

Conditions same as above and the same cathode and catholyte are reused.	
Aminoguanidine bicarbonate isolated—	14.8 gm
Assay yield	—62.4%
No zinc is present in solution	

The following are the main advantages of the invention:

- (a) The addition of picrite in instalments in the catholyte minimises the dissolution of zinc from the cathode and the same cathode surface can be used a number of times without further deposition of zinc.
- (b) The use of terylene cloth in combination with microporous sheets as diaphragm has the advantage of ease of fabrication and good mechanical strength.

- (c) The precipitation of aminoguanidine bicarbonate with CO_2 and ammonium bicarbonate make it possible to recycle the electrolyte a number of times.

We claim:

1. A process for the production of aminoguanidine bicarbonate which consists in electrolytically reducing a suspension of nitroguanidine added in regular instalments in a supporting electrolyte of ammonium sulphate in a divided cell using a rotating/stationary cathode of copper, brass, stainless steel or mild steel having a deposit of zinc up to thickness of 10 thou and recovering the aminoguanidine as bicarbonate outside the cell by double decomposition with sodium/ammonium bicarbonate or heating with carbon dioxide.
2. A process as claimed in claim 1 wherein aminoguanidine bicarbonate is recovered from the supporting electrolyte by bubbling carbon dioxide till the pH becomes 8 and precipitating with ammonium bicarbonate added in stoichiometric proportion to the aminoguanidine formed.
3. A process as claimed in claim 1 or 2 wherein the steps are reducing nitroguanidine added in regular

instalments in a supporting electrolyte of ammonium sulphate preferably of 30% strength using a rotating/stationary electrode of copper, stainless steel or mild steel having a deposit of zinc preferably to a thickness of 10 thou and employing a diaphragm of terylene cloth in combination with microporous rubber sheet supported in a wooden frame.

4. A process as claimed in any of the preceding claims wherein terylene is used in combination with microporous rubber supported in a wooden frame and aminoguanidine bicarbonate is recovered by bubbling carbon dioxide in the catholyte till the pH becomes 8 and then precipitating with ammonium bicarbonate.

Dated this 24th day of March 1971.

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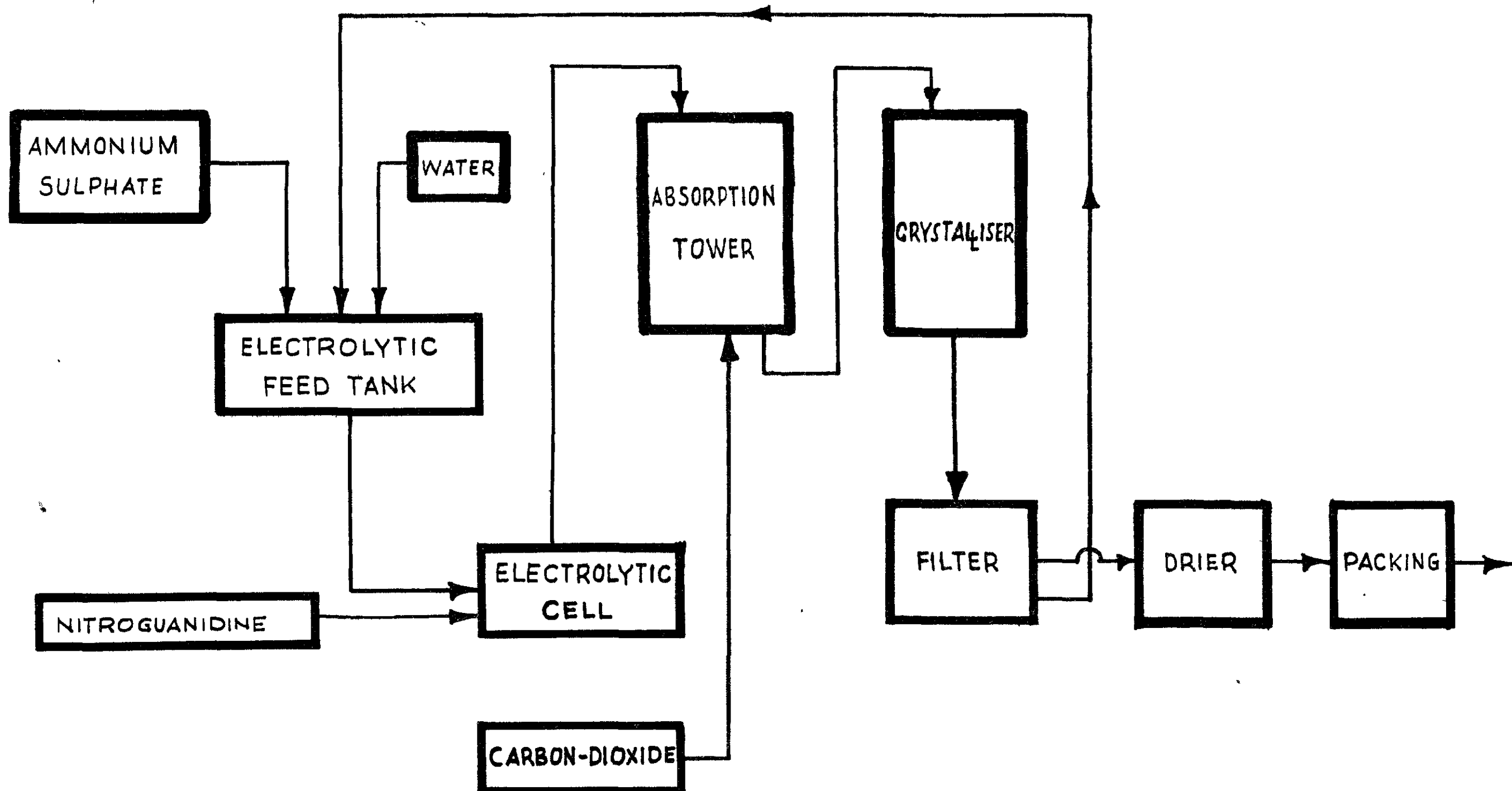


FIG. 1 FLOW SHEET FOR AMINO GUANIDINE BICARBONATE

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