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International Classification - C 07 d 31/42

" ELECTROCHEMICAL PROCESS FOR THE PREPARATION OF 3-AMINO METHYL PYRIDINE DIHYDROCHLORIDE FROM 3-CYANOPYRIDINE "

Council of Scientific & Industrial Research, Rafi Marg, New Delhi-1, India, an Indian Registered Body incorporated under the Registration of Societies Act (ACT XXI of 1860)

The following specification describes the nature of this invention:-

This is an invention by Mandady Venkatakrishna Udupa, Director, Venkatasubramanian Krishnan, Scientist and Kanakasabapathy Ragupathy, Junior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi-6, Tamil Nadu, India and all Indian Citizens.

PRICE Rs 2.00

This invention relates to the preparation of 3-amine methyl Pyridine dihydrochloride from 3-cyano black graphite electroreduction using deposited palladium black graphite cathodes (both stationary and rotating).

Hitherto the following methods have been proposed for the preparation of 3-amine methyl pyridine dihydrochloride: (i) Hydrogenation of 3-cyano pyridine in methylamine - methanol medium using Raney Nickel catalyst under high pressure. (ii) Reduction of Nicetinohydroxamic acid using $LiAlH_4$ in tetrahydrofuran. In the first method a high pressure generating equipment is necessary and moreover the yield of the primary amine is lowered due to the for mation of secondary amine. In the second method the yield of primary amine is very poor.

The method developed by us at present is a simple Electrochemical route which gives a good yield of 3-amine methyl pyrdine dihydrochloride in pure state. This

invention consists of two stages. The first stage involves the deposition of palladium black over graphite cathode using a bath containing palladium chloride and ammonium chloride in aqueous hydrochloric acid medium. The current density employed for the deposition is very low. Aqueous hydrochloric acid contained in the porous pot is used as the anolyte, the anode being a graphite plate.

The second stage involves the electroreduction of 3-cyano pyridine in aqueous hydrochloric acid medium using deposited palladium black over graphite cathode both under stationary and rotating conditions. A graphite anode is kept inside a ceramic porous pot, aqueous hydrochloric acid being the anolyte. The reduction is carried out in the temperature range of 8° to 12°C. In these cases where the cathode is kept stationary, the catholyte is vigorously stirred using a glass stirrer. A current density of 2 to 4 A/sq.dm. is employed for the reduction of both stationary and rotating systems. Nearly twice the theoretical time has been found to be necessary to obtain a good yield. After the electrolysis is over, the catholyte is distilled under vacuum to complete dryness when a pale yellow solid was obtained. This was purified by macerating with methanol when a light yellow solid of 3-amino methyl pyridine dihydrochloride was obtained.

The following are the typical examples to illustrate the invention:

PART I - Deposition of palladium black over graphite plate (stationary)

Cathode	: Graphite plate
Anode	: Graphite placed inside a diaphragm
Catholyte	: A dilute solution of palladium chloride (1 gpl) in aqueous HCl 6% (w/v) containing 0.5 to 2% ammonium chloride (Total volume 350 ml)

Anolyte	:	6% aqueous HCL (w/v) (75ml)
Cathode current density	:	50 mA/sq.dm.
Anode current density	:	75 mA/sq.dm.
Cell voltage	:	1.5 V
Temperature	:	30 - 35°C

The deposition is continued till the catholyte becomes colourless. The same procedure is adopted for the deposition of palladium black over rotating cylindrical graphite rod.

PART II(A) - Reduction of 3-cyano pyridine using staticnary cathode

Cathokyte	:	10% aqueous hydrochloric acid (500 ml)
Anolyte	:	10% aqueous hydrochloric acid (230 ml)
Cathode	:	Palladium black deposited over graphit plate (effective area 2 sq.dm.)
Anode	:	Graphite plate (0.6 sq.dm.)
Current passed	:	4 amperes
Cell voltage	:	2.4 V
Temperature of the cell	:	10 - 15°C
3-cyano pyridine taken	:	8 gms
3-amino methyl pyridine dihydrochloride isolated:		9.5 gms
Yield efficiency	:	68%
Current efficiency	:	34%
Energy consumption	:	4.204 kWh/kg

PART II(B) - Reduction of 3-cyanopyridine under rotating conditions

Catholyte	:	10% aqueous hydrochloric acid (500 ml)
Anolyte	:	10% aqueous hydrochloric acid (230 ml)
Cathode	:	Palladium black deposited over rotating cylindrical graphite rod (effective area = 2 sq.dm.)
Anode	:	Graphite rod (0.6 sq.dm.)
Current passed	:	4 amps
Voltage	:	2.4 V
Temperature of the cell	:	10 to 15°C
3-cyano pyridine taken	:	8 gms
3-amino methyl pyridine dihydrochloride isolated	:	9 gms
Yield efficiency	:	65%
Current efficiency	:	32.5%
Energy consumption	:	4.4 kWh/kg

The following are the main features of the invention:

1. This invention opens up a new and simple route for the electrochemical synthesis of 3-amino methyl pyridine.
2. A thinly deposited palladium black surface was found to be enough for carrying out the reduction of 3-cyano pyridine.
3. This method avoids the use of solvents like ethanol and high pressure generating equipments which are essential for catalytic methods.

Dated this 18th day of April, 1975.

Sd/-
Asstt. Patents Officer,
Council of Scientific & Industrial Research.

144403

THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section—10)

* ELECTROCHEMICAL PROCESS FOR THE PREPARATION OF 3-AMINOMETHYL PYRIDINE DIHYDROCHLORIDE FROM 3-CYANOPYRIDINE *

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian Registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:-

This is an invention by Handady Venkatakrishna Udupa, Director, Venkatasubramanian Krishnan, Scientist and Kanakasabapathy Ragupath, Junior Scientific Assistant, all of Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India and all Indian citizens.

~~e following specification particularly describes and ascertains the nature of this invention d the manner in which it is to be performed :—~~

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an electrochemical process for

This invention relates to the preparation of 3-aminomethylpyridine dihydrochloride. This chemical has been so far prepared by the following methods: (1) Hydrogenation of 3-cyanopyridine in methylamine-methanol medium using Raney nickel catalyst under high pressure. (2) Reduction of Nicotinehydroxamic acid using $LiAlH_4$ in tetrahydrofuran.

The process described in the ~~patent~~ specification is a new method and gives a pure product.

The main object of the invention is to prepare pure 3-aminomethylpyridine dihydrochloride in fairly good yields. The first stage of the process is the deposition of palladium black over graphite cathode using an aqueous acid solution containing palladium chloride and ammonium chloride. Thus, this electro-reduction technique involves the use of only small amounts of palladium.

The second stage of the process deals with the preparation of 3-aminomethylpyridine dihydrochloride from 3-cyanopyridine. In this method, deposited palladium black over graphite acts as the cathode. 3-cyanopyridine in aqueous hydrochloric acid solution is electrolytically reduced using the above said cathode. After the electrolysis is over, the catholyte is distilled under reduced pressure, when 3-aminomethyl-pyridine dihydrochloride crystallises out from the residue. This is an electrocatalytic reaction and the deposited palladium black acts as a cathode-cum-catalyst.

The invention is a process for the production of 3-aminomethylpyridine dihydrochloride and the accompanying drawing (Fig.1) is a scheme for the preparation of the same. In the diagram, the cell(1) is made up of either glass-lined vessel or vessel made of PVC. Deposited palladium black over graphite substrate is the cathode(2). Graphite rod(3) acts as anode. Ceramic porous pot(4) acts as the diaphragm separating the catholyte(5) from the anolyte(6). The catholyte after the electrolysis is transferred to the glass-lined distillation unit(7) for vacuum distillation to recover the amine salt(8) and ethanol(9) which can be reused in subsequent experiments.

Deposition of palladium black over graphite cathode

Cathode	Graphite plate (effective area of deposition = 0.6 sq.dm.)
Anode	Graphite placed inside a diaphragm
Catholyte	A dilute solution of palladium chloride(1 gpl) in aqueous HCl(6% w/v) containing 0.5 to 2% ammonium chloride (Total volume 350 ml).
Anolyte	6% aqueous HCl (w/v) (75 ml)
Cathode current density	50 mA/sq.dm.
Anode current density	75 mA/sq.dm.
Cell voltage	1.5 V
Temperature	30 - 35°C

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Reduction of 3-cyanopyridine

Example I

Catholyte	10% aqueous hydrochloric acid(500 ml)
Anolyte	10% aqueous hydrochloric acid(230 ml)
Cathode	Palladium black deposited over graphite plate (effective area 2 sq.dm.)
Anode	Graphite plate (0.6 sq.dm.)
Current passed	4 amperes
Cell voltage	2.4 V
Temperature of the catholyte	10 - 15°C
3-cyanopyridine taken	8 gms
3-aminomethylpyridine dihydrochloride obtained	9.5 gms
Yield efficiency	68%
Current efficiency	34%
Energy consumption	4.204 kwh/kg

Example II

Catholyte	10% aqueous hydrochloric acid (500 ml)
Anolyte	10% aqueous hydrochloric acid (230 ml)
Cathode	Palladium black deposited over graphite plate (effective area = 2 sq.dm.)
Anode	Graphite rod (0.6 sq.dm.)
Current passed	4 amps
Voltage	2.4 V
Temperature of the catholyte	10 - 15°C
3-cyanopyridine taken	8 gms
3-aminomethylpyridine dihydrochloride obtained	9 gms
Yield efficiency	65%
Current efficiency	32.5%
Energy consumption	4.4 kwh/kg

The 3-amino-methyl pyridine dihydrochlorides are useful as corrosion inhibitors & drug intermediate for preparation of vaso dilators.

Advantages of this invention are as follows:

(1) In the present case, the thinly deposited palladium black cathode has been used for four experiments and it is expected to be active for few more reduction experiments. Thus the thinly deposited palladium can be reused. But in the catalytic process, the catalyst has to be purified which leads to the loss of precious catalyst.

(2) The present process is a simple route and does not involve the use of high pressure generating equipment and other facilities which are normally required for catalytic hydrogenation process.

We claim:-

(1) An electrochemical process for the production of 3-aminomethyl pyridine dihydrochloride from 3-cyanopyridine which comprises of finding electro deposition of palladium black over graphite cathode and subsequent electro-reduction of 3-cyanopyridine in aqueous ethanolic hydrochloric acid medium to 3-aminomethyl pyridine dihydrochloride using the said cathode.

(2) A process as claimed in claim 1 wherein electroreduction of 3-cyanopyridine is carried out at a temperature of 10-15°C.

Dated this 4th day of May, 1976.

(I.M.S. MAMAK)
SCIENTIST 'E'(PATENTS)
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COMPLETE SPECIFICATION

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Nº OF SHEETS :- 1
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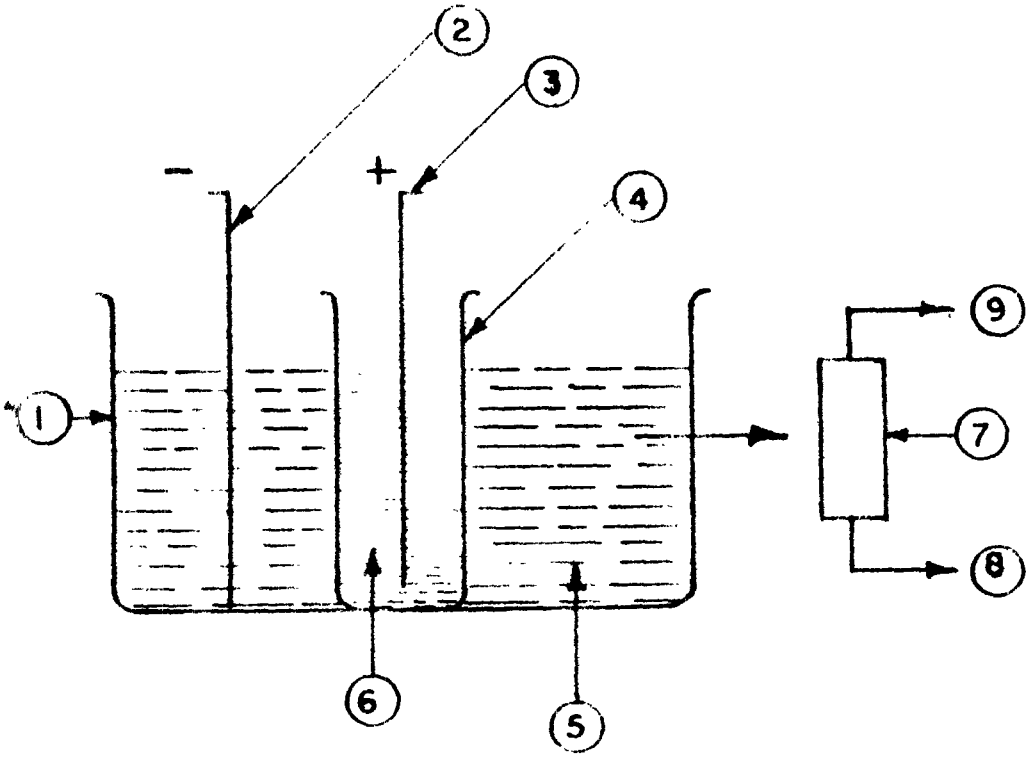

FIG. 1

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