GOVERNMENT OF INDIA, THE PATENT OFFICE
214, ACHARYA JAGADISH BOSE ROAD
CALCUTTA-700017.

Complete Specification No. 143906 **dated** 7th May 1976
Application and Provisional Specification No. 748/Cal/1975 **dated** 14th April 1975.
Acceptance of the complete specification advertised on 25th February 1978.

Index at acceptance— 32F2a [IX(1)]
70C7 [LVIII(5)]
International Classification— C 07 c 85/12

"Process for electrochemical preparation of beta-phenyl ethylamine hydrochloride from benzyl cyanide".

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH,
Rafi Marg, New Delhi-1, India, an Indian Registration of Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention.

This is an invention by Handady Venkatakrishna Udupa, Director, Venkatasubramanian Krishnan, Scientist and Kanakasabapathy Ragupathy, Junior Scientific Assistant, all employed at the Central Electrochemical Research Institute, Karaikudi, Tamil Nadu and all are Indian nationals.

PRICE : TWO RUPEES

This invention relates to the preparation of Beta-phenyl ethylamine hydrochloride from benzylcyanide. In the method invented, Beta-phenyl ethylamine hydrochloride is prepared from benzyl cyanide by electrolytic reduction using deposited palladium black graphite cathodes (both stationay and rotating). Hitherto, the following methods have been proposed for the preparation of Beta-phenyl ethylamine; (1) Reduction of benzyl cyanide using palladium adsorbed over carbon under high pressure; (2) Reduction of cyanide using sodium and ethanol, Raney Nickel and lithium aluminium hydride. The method proposed by us at present is a simple electrochemical route.

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 and is critical. Aqueous hydrochloric acid contained in the porous pot is used as the anolyte, the anode being a graphite plate.

In the second stage, Beta-phenyl ethylamine hydrochloride is prepared from benzyl cyanide by electrochemical reduction in ethanolic hydrochloric acid medium using deposited palladium black graphite cathode either under stationary or under rotating conditions. A graphite plate is used as the anode and is kept inside a ceramic porous pot, contianing aqueous hydrochloric acid which is the anolyte. The reduction is carried out in the temperature range of 15 to 25°C. In cases where cathode is kept stationary, the catholyte is vigorously stirred using a glass stirrer. A current density of 2 to 8 A/sq. dm. can be employed for the reduction for both stationary and rotating cathodes. 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. When most of the alcohol is removed, a dark brown coloured liquid (identified as phenyl acetaldehyde) separates out. After the removal of the dark brown coloured liquid, the distillation is continued when a dard brown coloured mass is outained. This solid is crystallised to get a pure and crystalline Beta-phenyl ethylamine hydrochloride.

The following are the typical examples to illustrate the inventions:-

Part I

Deposition of Palladium Black over graphite plate (Stationary)

Cathode	: Graphite plate
Anode	: Graphite plate 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 of the catholyte = 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 to 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 benzyl cyanide using stationary cathode

Experiment No.1

Catholyte	: 3 N ethanolic hydrochloric acid (350 ml)
Anolyte	: 3 N aqueous hydrochloric acid (75 ml)
Cathode	: Palladium black deposited over graphite plate (effective area 0.8 sq.dm.)
Anode	: Graphite plate of 0.5 sq.dm. area
Current passed	: 6 amps
Cell voltage	: 4.5 V
Temperature of the catholyte	: 10 to 15°C
Benzyl cyanide added	: 10 gms
Phenyl ethylamine hydrochloride isolated	: 8.5 gms
Phenylacetaldehyde got (byproduct)	: 2 ml
Yield efficiency(with respect to phenyl ethylamine hydrochloride)	: 63%
Current efficiency with respect to the product	: 31.5%
Energy consumption	: 9.75 kWh/kg

Experiment No.

Catholyte	: 3N ethanolic hydrochloric acid (350 ml)
Anolyte	: 3N aqueous hydrochloric acid (75 ml)
Cathode	: Deposited palladium black graphite plate (effective area 0.5 sq.dm.)
Anode	: Graphite plate of 0.5 sq.dm.
Current passed	: 3 amps
Cell voltage	: 3.5 V
Temperature of the catholyte	: 10 to 15°C
Benzyl cyanide added	: 5 gms
Phenyl ethylamine hydrochloride isolated	: 3.5 gms
Phenylacetaldehyde got (Byproduct)	: 1.5 ml
Yield efficiency (with respect to phenylethylamine hydrochloride)	: 52%
Current efficiency with respect to the main product	: 26%
Energy consumption	: 9.19 kWh/kg

Part II(B)

Reduction of Benzyl cyanide using rotating cathode

Experiment No. 1

Catholyte	: 3N ethanolic hydrochloric acid (350 ml)
Anolyte	: 3N aqueous hydrochloric acid 75 ml
Cathode	: Palladium black deposited over rotating cylindrical graphite rod of 0.5 sq. dm. area
Anode	: Graphite plate of 0.5 sq.dm.
Current passed	: 4 amps
Cell voltage	: 4.5 V
Temperature of the catholyte	: 10 to 15°C
Benzyl cyanide added	: 15 gms
Phenyl ethylamine hydrochloride isolated	: 12 gms
Phenylacetaldehyde got (byproduct)	: 2 ml
Yield efficiency(with respect to phenylethylamine hydrochloride)	: 60%
Current efficiency with respect to the main product	: 30%
Energy consumption	: 10.24 kWh/kg

The following are the main features of the invention:

1. This inventions opens up a new and simple route for the electrochemical synthesis of Beta-phenyl ethylamine.
2. A minimum amount of deposited palladium is sufficient for carrying out the reduction experiment.
3. Isolation of amine hydrochloride is easy.
4. This method avoids the use of high pressure generating equipments.

Dated this 5 th day of April, 1975

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

143906

THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section-10)

"Electrochemical preparation of beta-phenyl-ethylamine hydrochloride from benzyl cyanide".

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 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, Venkatasubraminian Krishnan, Scientish and Kanakasabapathy Ragupathy, Junior Scientific Assistant, all employed at the Central Electrochemical Research Institute, Karaikudi, Tamil Nadu and all are Indian citizens.

This invention relates to the preparation of beta-phenylethylamine hydrochloride, a drug intermediate. This chemical can be prepared by any one of the following methods: (i) Catalytic hydrogenation of benzyl cyanide using palladium absorbed over carbon (ii) Reduction of benzyl cyanide using sodium and ethanol or Raney nickel or lithium aluminium hydride. The present electro-reduction technique is a simple process where the operation and working up of the product are easy.

The main object of the invention is to prepare pure beta-phenylethylamine hydrochloride in 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. These deposited palladium black cathodes were used for a few reduction experiments with periodic replenishment of the deposit. Thus, this electroreduction technique involves the use of only small amount of palladium.

The second stage of the process deals with the preparation of beta-phenylethylamine hydrochloride from benzyl cyanide. In this method, deposited palladium black over graphite acts as the cathode. Benzyl cyanide in aqueous alcoholic hydrochloric acid solution is electrolytically reduced using the above said cathode. After the electrolysis is over, the catholyte is distilled under reduced pressure when beta-phenylethylamine hydrochloride crystallises out from the residue. This is an electrocatalytic reduction and the deposited palladium black acts as a cathode-cum-catalyst.

The present invention first consists of thin deposition of palladium black over graphite cathode. The second stage of the invention consists of a process for the preparation of beta-phenylethylamine hydrochloride. This involves the electroreduction of benzyl cyanide using a deposited palladium black cathode in an aqueous alcoholic acid medium.

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

<u>Deposition of palladium black over graphite cathode</u>

Cathode	Cylindrical graphite vessel closed at one end
Anode	Graphite placed inside a diaphragm
Catholyte	A dilute solution of palladium chloride (2.5 gms) in aqueous HCl (6% w/v) containing around 0.4 to 0.8% ammonium chloride. The solution was vigorously stirred using a glass stirrer. Total volume = 1.5 litres
Anolyte	6% aqueous HCl
Cathode current density	50 mA/sq.dm.
Anode current density	75 mA/sq.dm.
Voltage	1.5 V
Temperature	30 - 35°C

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Reduction of benzyl cyanide

Example 1

Catholyte	3N ethanolic hydrochloric acid (1.3 litres)
Anolyte	3N aqueous hydrochloric acid(800 ml)
Cathode	Palladium black deposited in the inner portion of the cylindrical graphite vessel closed at the bottom (effective area = 8 sq.dm.)
Anode	Graphite (area 6 sq.dm.) placed inside a diaphragm
Current passed	50 amps
Cell voltage	4.5 V
Temperature of the catholyte	10 - 15°C
Benzyl cyanide taken	125 gms
Beta-phenylethylamine hydrochloride obtained	115 gms
Yield efficiency	73%
Current efficiency	36.5%
Energy consumption	8.65 kwh/kg

Example 2

Catholyte	3N ethanolic hydrochloric acid (1.3 litres)
Anolyte	3N aqueous hydrochloric acid(800 ml)
Cathode	Palladium black deposited in the inner portion of the cylindrical graphite vessel closed at the bottom(effective area = 8 sq.dm.)
Anode	Graphite (area = 6 sq.dm.) placed inside a diaphragm
Current passed	50 amps
Cell voltage	3.5 V
Temperature of the catholyte	25 - 30°C
Benzylcyanide taken	125 gms
Beta-phenylethylamine hydrochloride obtained	90 gms
Yield efficiency	55%
Current efficiency	27.5%
Energy consumption	8.69 kwh/kg

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Advantages of this invention are as follows:-

(i) 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 experiments. Thus the thinly deposited palladium black can be reused. But in the catalytic process, the catalyst has to be purified which leads to the loss of precious catalyst.

(ii) 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) A process for the electrochemical production of beta-phenylethylamine hydrochloride from benzylcyanide characterised in that palladium black is deposited over a graphite cathode and subsequent electro-reduction of benzylcyanide in aqueous ethanolic hydrochloric acid medium using the said graphite cathode to beta-phenylethylamine hydrochloride is carried out.

(2) A process as claimed in claim 1 wherein the electroreduction of benzylcyanide is carried out at a temperature of 10 to 30°C.

Dated this 30th day of April, 1976.

(I.M.S. MAMAK)
SCIENTIST 'E' (PATENTS)
COUNCIL OF SCIENIFIC AND INDUSTRIAL RESEARCH.

COMPLETE SPECIFICATION

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

Nº OF SHEETS :-1
SHEET Nº. 1

No. 748/Cal/75

NO. 143906

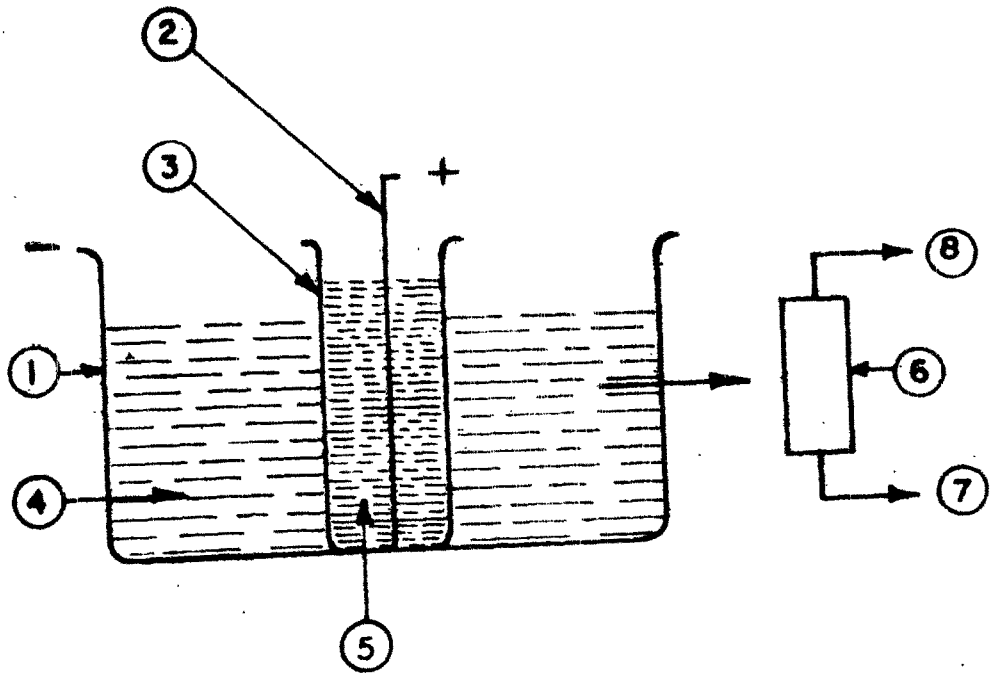

FIG. 1

R B Shastri Bai

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