Government of India, The Patent Office, 214, Acharya Jagadish Bose Road, Calcutta-17. Complete specification No.142233 dated 6th September 1975. Application and Provisional specification No.1239/Cal/1974 dated 6th June 1974. Acceptance of the complete specification advertised on 11th June 1977.

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" ELECTROCHEMICAL PREPARATION OF BENZYLAMINE HYDROCHLORIDE FROM BENZONITRILE "

Council of Scientific and Industrial Research, Rafi Marg, New Delhi-1, India, an Indian Registered body incorporated uuder 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 and Venkatasubramanian Krishnan, Scientist, both employed at the Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India and both are Indian citizens.

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This invention relates to the preparation of benzylamine from benzonitrile (an example for aromatic nitrile group) by electrolytic reduction using palladium black deposited over graphite cathodes, either stationary or rotating.

Hitherto, it has been proposed to prepare benzylamine by catalytic hydrogenation of benzonitrile, under high pressure. The catalytic hydrogenation method for the preparation of benzylamine is open to the following objections: (1) the benzonitrile has to be dissolved in absolute ethanol; (2) the reduction of the nitrile requires high pressure equipments; (3) elaborate purification procedure has to be carried out for the reuse of the catalyst.

To these ends, the invention broadly consists first in the deposition of palladium black over graphite cathodes using a bath containing palladium chloride and ammonium chloride in aqueous hydrochloric acid medium. The current density employed for 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.

The next stage consists in reducing benzonitrile in aqueous ethanolic hydrochloric acid medium using deposited palladium black cathode either under stationary or rotating conditions. A graphite plate is used as the anode and is kept inside a ceramic porous pot. The temperature of the catholyte is maintained around 15-25°C. The catholyte is given a vigorous motion using a glass stirrer under stationary conditions. A current density of 3-8 A/dm^2 can be used for the reduction for both the rotating and stationary systems. At the end of the electrolysis, the catholyte was distilled under vacuum to recover the alcohol completely when a pale yellow mass was obtained. This was crystallized to get a highly pure and crystalline benzylamine hydrochloride. It was also observed that the same cathode could be reused for further efficient reduction of benzonitrile under the above conditions.

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

PART I

DEPOSITION OF PALLADIUM BLACK OVER GRAPHITE PLATE

Cathode	..	Graphite plate
Anode	..	Graphite plate placed inside a diaphragm [illegible]
Catholyte	..	A dilute solution of palladium chloride (1 gpl) 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 = 350 ml
Anolyte	..	6% Aqueous HCl(w/v); 75 ml
Cathode current density		50 mA/dm^2
Anode current density		75 mA/dm^2
Voltage		1.5 V
Temperature		30-35°C

The deposition was continued till the catholyte became colourless.

PART II(A)

REDUCTION OF BENZONITRILE USING STATIONARY CATHODE

Experiment No.1

Catholyte	..	3N ethanolic hydrochloric acid (350 ml)
Anolyte	..	3N aqueous hydrochloric acid (75 ml)
Cathode	..	Palladium black deposited over graphite (effective area 0.5 dm^2
Anode	..	Graphite plate of 0.5 dm^2 area, placed inside a diaphragm
Current passed	..	3 Amps
Cell voltage	..	3.4 V
Temperature of catholyte	..	15-25°C
Benzonitrile added	..	6 gms
Benzylamine hydrochloride isolated	..	6.3 gms
Yield of efficiency	..	75%
Current efficiency	..	40%
Energy consumption	..	8.420 KwH/Kg

Experiment No.2

Catholyte	..	Aqueous ethanolic hydrochlori acid of 6% acid strength(w/v) (350 ml)
Anolyte	..	6% aqueous HCl (w/v) (75 ml)
Cathode	..	The same cathode which was used for the previous experiment
Anode	..	Graphite plate of area 0.5 dm^2 inside a diaphragm
Current passed	..	3 Amps
Cell voltage	..	3 V
Temperature of the catholyte	..	15-25°C
Benzonitrile added	..	9 gms
Benzylamine hydrochloride isolated	..	9 gms
Yield efficiency	..	71%
Current efficiency	..	39%
Energy consumption	..	8.247 Kwh/Kg

Experiment No.3

Catholyte	..	3N methanolic hydrochloric acid (350 ml)
Anolyte	..	3N aqueous hydrochloric acid(75 ml)
Cathode	..	The same cathode which was used for the experiment no.2
Anode	..	Graphite plate of area 0.5 dm^2 placed inside a diaphragm
Current passed	..	3 Amps
Cell voltage	..	3.4 V
Temperature of the catholyte	..	15-25°C
Benzonitrile added	..	4 gms
Benzylamine hydrochloride isolated	..	4.0 gms
Yield efficiency	..	70%
Current efficiency	..	35%
Energy consumption	..	10.29 Kwh/Kg

Deposition of palladium black over rotating cylindrical graphite

Cathode	..	Rotating cylindrical graphite
Anode	..	Graphite plate placed inside a diaphragm
Catholyte	..	A dilute solution of palladium chloride of known weight in aqueous HCl containing around 0.4 to 0.8% ammonium chloride.
Anolyte	..	Aqueous HCl
Cathode current density	..	50 mA/dm^2
Anode current density	..	100 mA/dm^2
Voltage	..	1.5 V
Temperature	..	30-35°C

The deposition was continued till the catholyte became colourless.

Experiment No.4

Catholyte	..	3N ethanolic hydrochloric acid
Anolyte	..	3N aqueous hydrochloric acid
Cathode	..	Palladium black deposited over rotating cylindrical graphite of 0.5 dm^2 area.
Anode	..	Graphite plate placed inside a diaphragm
Current passed	..	4 Amps

Cell voltage	..	4.8 V
Temperature of the catholyte	..	15-25°C
Benzonitrile added	..	4 gms'
Benzylamine hydrochloride isolated	..	4.2 gms
Yield efficiency	..	75%
Current efficiency	..	36%
Energy consumption	..	13.18 Kwh/Kg

The following are among the main advantages of the invention:-

1) The number of reuse of the thinly deposited palladium black cathode is the main advantage in the reduction studies. Under the above mentioned experimental conditions, the cathode can be reused for roughly 10 times.
2) This method avoids the use of high pressure generating equipments.
3) Absolute ethanol which is used in the catalytic reduction of benzonitrile is avoided here.

Dated this 28th day of

Dated this 28th day of May 1974

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Asstt. Patents Officer,
Council of Scientific & Industrial Research

THE PATENT ACT, 1970

COMPLETE SPECIFICATION

SECTION 10

ELECTROCHEMICAL PREPARATION OF BENZYLAMINE HYDROCHLORIDE FROM BENZONITRILE

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 and VENKATASUBRAMANIAN KRISHNAN, Scientist, both of the Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India, both Indian citizens.

This invention relates to the preparation of benzylamine hydrochloride, a drug intermediate. Benzylamine has been prepared by various chemical routes. Catalytic reduction of benzonitrile seems to be in vogue at present. One of the well-known chemical methods is the treatment of ammonia with benzyl chloride under high pressure. Reduction of benzyl nitrile and that of benzonitrile using LiAlH or Raney nickel are the other methods known. There is also a report on the electroreduction of benzonitrile using lead cathode in sulphuric acid medium. But from our work, we find that this observation is ill-founded. And so there is no electrochemical route known so far for the preparation of benzylamine. In the chemical methods employed, the inorganic impurities affect the purity of the product and the yield also has been found to be only moderate. Catalytic reduction technique involves the use of costly items like high pressure generating equipment and absolute alcohol. Moreover, the precious metal catalyst has to be purified before every reuse.

The main object of the invention is to prepare pure benzylamine hydrochloride in high yield. 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.

According to the present invention, there is provided a process for the production of benzylamine hydrochloride from benzonitrile in an ethanolic hydrochloric acid supporting catholyte using deposited palladium black over graphite cathode which consists of the following steps:

(i) deposition of palladium black over graphite substrate using an aqueous solution of palladium chloride in hydrochloric acid medium at a cathode current density of 50 mA/dm^2 and at a cell temperature of 30-35°C,

(ii) electroreduction of benzonitrile in ethanolic hydrochloric acid medium using deposited palladium black cathode at a catholyte temperature of 15-20°C, the anolyte being aqueous hydrochloric acid, and

(iii) vacuum concentration of the catholyte (ethanolic hydrochloric acid containing benzylamine hydrochloride which is the reduction product of benzonitrile) giving benzylamine hydrochloride as the residue.

Thus, this electroreduction technique involves the use of only small amount of palladium. The second stage of the process deals with the preparation of benzylamine hydrochloride from benzonitrile. In this method, deposited palladium black over graphite acts as the cathode. Benzonitrile in aqueous alcoholic hydrochloric acid solution is electrolytically reduced using the above said cathode. After the reaction is over, the catholyte is distilled under reduced pressure when benzylamine hydrochloride crystallises out from the residue. The principle involved in this process can generally be applied for the preparation of any primery amine. This is an electrocatalytic reaction and hence the deposited palladium black acts as a cathode-cum-catalyst. Moreover, this electroreduction technique involves the use of minimum amount of palladium and even this can be reused for a few subsequent reduction experiments without employing any purification procedures. In the catalytic method, there is a loss of precious metal catalyst during purification for reuse in addition to the loss during the reduction processes.

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 benzylamine hydrochloride. This involves the electroreduction of benzonitrile using a deposited palladium black cathode in an aqueous alcoholic acid medium.

The invention is a process for the production of benzylamine 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 deposited with palladium black which acts as the cathode. Ceramic porous pot acts as the diaphragm separating the catholyte from anolyte. The catholyte is then transferred to the glass-lined distillation unit for vacuum distillation to recover the amine salt and ethanol saturated with HCl. This recovered ethanol can be reused.

Deposition of palladium black over graphite cathode (Stationary)

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 (w/v) ; 800 ml
Cathode current density	: 50 mA/dm^2
Anode current density	: 75 mA/dm^2
Voltage	: 1.5 V
Temperature	: 30-35°C

Reduction of benzonitrile using stationary cathode

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 dm^2) placed inside a diaphragm
Current passed	: 50 Amps
Cell voltage	: 3.4 V
Temperature of the catholyte	: 15 - 20°C
Benzonitrile added	: 125 gms
Benzylamine hydrochloride obtained	: 120 gms
Yield efficiency	: 71%
Current efficiency	: 35%
Energy consumption	: 8.35 kwh/kg

Deposition of palladium black over rotating cylindrical graphite in a PVC cell container

Cathode	: Rotating cylindrical graphite rod
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. Total volume = 1.5 litres.
Anolyte	: 6% aqueous HCl (w/v) (800 ml)
Cathode current density	: 50 mA/dm^2
Anode current density	: 75 mA/dm^2
Voltage	: 1.5 V
Temperature	: 30 - 35°C

Reduction of benzonitrile using rotating cylindrical cathode in a PVC

Catholyte	: 3N ethanolic hydrochloric acid (1.4 litres)
Anolyte	: 3N aqueous hydrochloric acid(800 ml)
Cathode	: Rotating cylindrical deposited palladium black cathode(effective area 8 sq.dm.)
Anode	: Graphite (effective area 6 sq.dm.) placed inside a diaphragm
Current passed	: 50 Amps
Cell voltage	: 3.8 V
Temperature of the catholyte	: 10 - 20°C
Benzonitrile added	: 125 gms
Benzylamine hydrochloride obtained	: 110 gms
Yield efficiency	: 63%
Current efficiency	: 31.5%
Energy consumption	: 11.0 kwh/kg

Advantages of this invention are as follows:

(i) By using a proper ratio of palladium chloride and ammonium chloride, a thin deposit of palladium black is obtained over graphite cathode and this cathode can be reused for a few reduction experiments.

(ii) There is no need for the purification of the cathode surface and hence practically there is no loss of precious metal. Then this is highly advantageous over the catalytic method.

(iii) This reduction technique is a simple process and does not involve the use of high pressure generating equipment and other facilities for protecting the precious metal catalyst.

We claim:-

1. A process for the production of benzylamine hydrochloride from benzonitrile in an ethanolic hydrochloric acid supporting catholyte using deposited palladium black over graphite cathode which consists of the following steps:

(i) deposition of palladium black over graphite substrate using an aqueous solution of palladium chloride in hydrochloric acid medium at a cathode current density of 50 mA/dm^2 and at a cell temperature of 30-35°C,

(ii) electroreduction of benzonitrile in ethanolic hydrochloric acid medium using deposited palladium black cathode at a catholyte temperature of 15-20°C, the anolyte being aqueous hydrochloric acid, and

(iii) vacuum concentration of the catholyte (ethanolic hydrochloric acid containing benzylamine hydrochloride which is the reduction product of benzenitrile) giving benzylamine hydrochloride as the residue.

Dated this 4th day of September, 1975.

R Bhaskara Rao

Patents Officer,

Council of Scientific & Industrial Research.

30 MAR 1977

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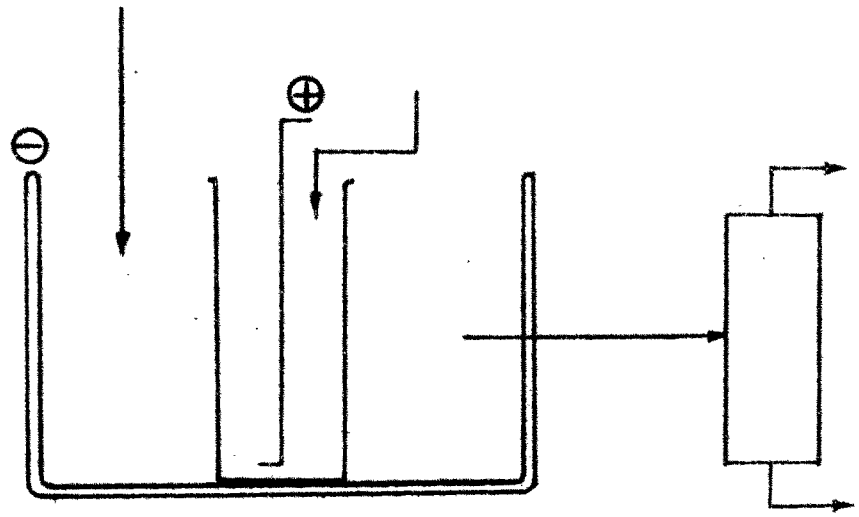
FIG. 1



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