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**007 c-87/02**

**PROCESS FOR THE ELECTROCHEMICAL PREPARATION OF ALKYLARYL-  
AMINES BENZYLAMINE AND BETA-PHENYLETHYLAMINE**

**Council of Scientific & Industrial Research,  
Rafi Marg, New Delhi-1, India, an Indian  
Registered body incorporated under the  
Registration of Societies Act (Act XVI of 1960)**

**The following specification describes the nature of this invention.**

**PRICE : TWO RUPEES**

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This is an invention by Handady Venkatakrishna Udyppa, Director, Venkatasubramanian Krishnan, Scientist, and Arunachalam Muthukumaran and Kanakasabapathy Ragupathy, Junior Scientific Assistants. They are Indian nationals, employed in the Central Electrochemical Research Institute, Karaikudi, Tamil Nadu.

This invention relates to the electrochemical preparation of benzylamine and beta-Phenylethylamine from benzonitrile and benzylcyanide respectively by electroreduction using deposited grey nickel cathode over graphite or copper base, under stationary conditions.

Hitherto, the above <sup>two</sup> amines have been prepared by catalytic hydrogenation of the nitriles under high Pressure. An electrochemical method for the Preparation of the above two amines was then developed by the above authors using deposited palladium black cathodes. But this electrochemical method was found to be costly due to very high price of Palladium salts. Hence, a simultaneous development of the Present invention.

To these ends, the invention broadly consists first in the deposition of grey nickel over graphite or copper base using a solution of nickel chloride, nickel sulphate and ammonium sulphate in appropriate concentrations. Aqueous sulphuric acid was used as the anolyte in a ceramic porous pot. a lead strip was

used as the anode. The current density employed for the deposition was critical.

The next stage consists in reducing the nitriles in ethanolic sulphuric acid medium using deposited, grey nickel cathode. A ceramic porous pot containing aqueous sulphuric acid as anolyte was used as the diaphragm into which a lead strip was placed as the anode. The temperature of the catholyte was maintained around 20°C. A current density of 5 amperes per sq.dm. was found to be the most advantageous current density taking into account various factors of electrolysis. As the theoretical charge was found to be insufficient extra current was passed to obtain a maximum yield. At the end of the electrolysis, the catholyte was distilled to recover alcohol and then the reaction mixture was diluted with water and extracted with benzene to remove the unreacted and other side-products. The aqueous portion was then neutralised with alkali to liberate the free base, which was then extracted with benzene. The benzene portion was distilled to recover benzene and the remaining viscous brown liquid was distilled to collect amines at their appropriate boiling points. The amines thus obtained were very pure as confirmed by spectral methods.

The following are the typical examples:

Deposition of Grey nickel

Catholyte = 4 litres of water containing 40 g nickel chloride, 80 g nickel sulphate and 80 g ammonium sulphate.  
Cathode = Graphite or copper base  
Anolyte = 10% Aqueous sulphuric acid (200 ml)  
Anode = Lead strip of area 0.77 dm<sup>2</sup>  
Current density employed for deposition: 5 A/dm<sup>2</sup> to 15 A/dm<sup>2</sup>  
Duration of deposition = Approximately an hour

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### Preparation of benzylamine

#### Experiment No.1

Catholyte = Ethanol (550 ml) and conc.  $H_2SO_4$  (50 ml)  
Anolyte = 10% Aqueous sulphuric acid (175 ml)  
Cathode = Deposited grey nickel of area 1.2 sq.dm.  
Anode = Lead strip of area 0.84 dm<sup>2</sup>  
Current density employed = 5 A/dm<sup>2</sup>  
Current passed = 6 amps  
Cell voltage = 6.5 V  
Temperature = Around 20°C  
Benzonitrile taken = 70 ml  
Pure Benzylamine = 51 ml obtained  
Yield efficiency = 73%  
Current efficiency = 36.5%  
Energy consumption = 17.84 Kwh/kg

#### Experiment No.2

Cathode = The deposited grey nickel from the above experiment was reused.  
All the conditions are same as above.  
Benzonitrile taken = 75 ml  
Current passed = 6 amps  
Cell voltage = 6.5 V  
Pure benzylamine obtained = 45 ml  
Yield efficiency = 60%  
Current efficiency = 30%  
Energy consumption = 21.71 Kwh/kg

## Preparation of Beta-phenylethylamine

### Experiment No.1

Catholyte = 550 ml ethanol + 55 ml conc.  $H_2SO_4$   
Anolyte = 10% aqueous sulphuric acid (175 ml)  
Cathode = Deposited grey nickel of area  $1.2 \text{ dm}^2$   
Anode = Lead strip of area  $0.84 \text{ dm}^2$  placed inside a ceramic porous pot.  
Current density employed =  $5 \text{ A/dm}^2$   
Current passed = 6 amps  
Cell voltage = 6.5 V  
Temperature = Around  $20^\circ\text{C}$   
Benzoyl cyanide taken = 100 ml  
Pure Beta-phenylethylamine isolated = 56.5 ml  
Yield efficiency = 70.00%  
Current efficiency = 28.0%  
Energy consumption = 12.68 Kwh/kg

### Experiment No.2

Catholyte = 550 ml of ethanol + 55 ml of conc.  $H_2SO_4$   
Anolyte = 10% aqueous sulphuric acid (175 ml)  
Cathode = Deposited grey nickel (Reuse from the above) of area  $1.2 \text{ sq.dm.}$   
Anode = Lead strip of area  $0.84 \text{ sq.dm.}$  placed inside a ceramic porous pot  
Current density employed =  $5 \text{ A/sq.dm.}$   
Current passed = 6 Amps  
Cell voltage = 7 V  
Temperature = Around  $20^\circ\text{C}$   
Benzyl cyanide taken = 70 ml  
Pure Beta-phenylethylamine isolated = 40 ml  
Yield efficiency = 57.1%  
Current efficiency = 28.5%  
Energy consumption = ~~XXXXX~~ 21.76 Kwh/kg

The following are the advantages of the invention:

- (i) Small amounts of nickel is sufficient to carry out the reduction of nitrile and moreover nickel salts are very cheap compared to palladium salts. This advantage has brought down the production cost of amines considerably.
- (ii) Copper also could be used as a base for grey nickel deposition; whereas in the case of palladium black deposition, only graphite could be used to get an adherant deposit.

Dated this 4th day of Sept. '75

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|----|-------------------------|------------------|
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Dated this 17th day of December, 1975

*[Signature]*

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**THE PATENTS ACT. 1970**

**COMPLETE SPECIFICATION**

(Section-10)

PROCESS FOR THE ELECTROCHEMICAL PREPARATION OF  
ARYL ALKYLAMINES SUCH AS BENZYLAMINE AND BETA -PHENYLETHYLAMINE

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH,  
Raf1 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  
is to be performed.

This is an invention by Handdy Venkatakrishna Udupa, Director,  
Wenkatasubramanian Krishnan, Scientist; Arunachalam Muthukumar,  
Junior Scientific Assistant and Kanakasabapathy Regupathy, Junior  
Scientific Assistant, all of the Central Electrochemical  
Research Institute, Karaikudi, 6, Tamil Nadu, India, all Indian  
citizen.

This invention relates to the electrochemical preparation of aryl alkylamines such as benzylamine and beta-phenylethylamine from benzonitrile and benzyloxyanide respectively. The above amines can also be prepared by reducing the nitriles with lithium aluminium hydride or sodium and ethanol and also by catalytic hydrogenation of nitriles in presence of precious metal oxides. The yields in the chemical reduction processes are less satisfactory. The catalytic method involves the use of costly equipments and chemicals. Benzylamine is used in the manufacture of powerful explosives and also as a corrosion inhibitor. It also finds use as an efficient corrosion inhibitors.

The main object of the invention is to prepare benzylamine and beta-phenylethylamine using nickel black cathode, by an electrochemical route. Both these are aryl alkylamines of a homologous series and this invention is a single process which can be exploited for the preparation of any aryl alkylamines - such as benzylamine and beta-phenylethylamine. Moreover this is the first time that such deposited nickel black cathode has been prepared and successfully employed for the electro reduction of nitriles.

This invention consists of three stages. In the first stage nickel black is deposited over graphite plate. In the second stage the electro reduction of nitriles is carried out with nickel black deposited over graphite plate as cathode either in ammoniacal or acid medium. In the third stage, amines are isolated from the electrolyte.

In the first stage, nickel black is deposited over graphite or copper plate by electrodeposition from a bath containing nickel sulphate, nickel chloride and ammonium sulphate. The nickel black deposited graphite electrodes have been used for 10 times in ammoniacal medium without much loss in yield efficiency and current efficiency of the product. In acid medium, the nickel dissolves slowly during electrolysis and thus restricting its use to three times only.



In the second stage, the reductions of nitriles have been carried out with nickel black deposited over graphite plate which is hitherto unknown. In the ammoniacal medium experiments, the catholyte contains ammonium sulphate dissolved in ethanol-water-ammonia mixture. In acid medium experiments, ethanolic sulphuric acid is used as the catholyte. In both these media, aqueous sulphuric acid taken in a ceramic porous pot, is used as the anolyte. More than the theoretical current required is passed for effecting maximum conversion of the reactants.

In the third stage, the amine is isolated from the catholyte as follows: In the ammoniacal medium experiments, after the electrolysis is over, the catholyte is distilled to recover alcohol. The residue obtained after the removal of alcohol is allowed to cool and is then extracted with benzene to remove any unreduced nitrile present in the catholyte. After the removal of unreduced nitrile from the residue, it is neutralised with excess of sodium hydroxide to liberate the amine.

In the acid medium experiment, the alcohol is removed from the catholyte after electrolysis is over. The residue is then neutralised with excess of sodium hydroxide to liberate the amine. The examples of the experiments of the reductions of benzonitrile and benzyloxyamide are given below. In the case of benzonitrile, it undergoes reduction only in the acid medium. The reduction efficiency of benzonitrile in ammoniacal medium is very poor. In the case of benzyloxyamide it undergoes reduction both in the acid and ammoniacal media most efficiently.

#### EXAMPLE 1

##### 1. Electrochemical reduction of benzonitrile in acid medium

Cathode	:	Black nickel deposited over 2 sq.dm area of the graphite plate
Anode	:	Lead plate placed inside porous pots
Catholyte	:	1.1 litre of 10% ethanolic sulphuric acid
Anolyte	:	500 ml of 30% aqueous sulphuric acid

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Current passed	:	10 ampe
Cell voltage	:	6.5 to 7 V
Temperature of the cell	:	Around 25°C
Benzonitrile taken	:	40 gms
Benzylamine got	:	22.5 gm
Current passed	:	1½ times the theoretical current
Yield efficiency	:	56.5%
Current efficiency	:	37.5%
Energy consumption	:	18.3 kwh/kg

### 2. Electrochemical reduction of benzonitrile in acid medium

Cathode	:	Black nickel deposited over 2 sq.dm area of the graphite plate
Anode	:	Lead plate placed inside porous pots
Catholyte	:	1.1 litre of 10% ethanolic sulphuric acid
Anolyte	:	600 ml of 30% aqueous sulphuric acid
Current passed	:	10 ampe
Cell voltage	:	7V
Temperature of the cell	:	Around 25°C
Benzonitrile taken	:	50 gm
Benzylamine got	:	28 gm
Current passed	:	1½ times the theoretical current
Yield efficiency	:	56%
Current efficiency	:	38%
Energy consumption	:	19.0 Kwh/kg

### 3. Electrochemical reduction of benzyl cyanide in acid medium

Cathode	:	Black nickel deposited over 2 sq.dm area of the graphite plate
Anode	:	Lead plate placed inside porous pots
Catholyte	:	1.1 litre of 10% ethanolic sulphuric acid
Anolyte	:	600 ml of 30% aqueous sulphuric acid
Current passed	:	10 ampe
Cell voltage	:	7V
Temperature of the cell	:	20 to 25°C

Benzoyl cyanide taken	:	50 gm
Beta-phenylethylamine got	:	32 gms
Current passed	:	Two times the theoretical current
Yield efficiency	:	64%
Current efficiency	:	32%
Energy consumption	:	11.2 kWh/kg

#### 4. Electrochemical reduction of benzoyl cyanide in ammoniacal medium

Cathode	:	Black nickel deposited over 5 sq. dm area of the graphite plate
Anode	:	Lead plate placed inside porous pots
Catholyte	:	$(\text{NH}_4)_2\text{SO}_4$ dissolved in (1:1) alcohol-water mixture containing aqueous ammonia (Total volume = 3 litres, 6% $(\text{NH}_4)_2\text{SO}_4$ )
Analyte	:	10% aqueous sulphuric acid
Current passed	:	25 amps
Cell voltage	:	9 to 12 V
Temperature of the cell	:	20 to 25°C
Benzoyl cyanide taken	:	200 gms
Beta-phenylethylamine got	:	104 gms
Nitrile recovered	:	18 gms
Diphenylethylamine got	:	34.5 gms
Current passed	:	1½ times the theoretical current
Yield efficiency	:	57.1%
Current efficiency	:	34.6%
Energy consumption	:	31.1 kWh/kg

The main advantages of the inventions:

- 1) The use of the deposited nickel black cathode is expected to bring down the cost of production of benzylamine and beta-phenylethylamine.
- 2) The deposited nickel black cathode has been reused atleast three times in ethanolic sulphuric acid medium and 10 times in aqueous ethanolic ammonium sulphate medium.

In an ethanolic sulphuric acid medium, both benzonitrile and benzylcyanide have been reduced using a deposited nickel black cathode. The amines benzylamine and beta-phenylamine are isolated from the reaction solution by neutralisation and extraction with benzene.

Benzylcyanide was also reduced in aqueous ethanolic ammonium sulphate medium using deposited nickel black cathode. The product namely beta-phenylethylamine was isolated from the reaction solution by neutralisation and extraction with benzene.

The novelty of the process is the preparation and use of deposited nickel black cathode for the first time in electrochemical preparation of amines, mentioned above. The use of such cathodes bring down the cost of production of amines. This technique can be employed for the preparation of other arylalkylamines.

**WE CLAIM:**

1. Process for the electrochemical preparation of arylalkylamines such as benzylamine and beta-phenylethylamine by electrolytic reduction of nitriles like benzonitrile and benzylcyanide in ethanolic sulphuric acid medium characterised in using a deposited nickel black cathode.
2. Process as claimed in claims 1 ~~and 2~~ wherein the deposited nickel black cathode is prepared by electrodeposition of nickel black on a graphite base plate in a bath containing nickel sulphate, nickel chloride and ammonium sulphate.
3. Process as claimed in claim 1 wherein the electrolytic reduction may be carried out in an aqueous ethanolic ammonium sulphate medium.
4. The process as claimed in claim 3 wherein the electrodeposition of nickel black is effected on a copper base plate.
5. The process as claimed in any of the preceding claims wherein aqueous sulphuric acid in a ceramic pot is used as anolyte.

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6) The process as claimed in any of the preceding claims wherein the catholyte obtained is distilled to recover alcohol, cooled and then extracted with benzene to remove any unreduced nitrils, the residue is then neutralised with excess of alkali to liberate the amines.

Dated this 22nd day of December 1976

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I. M. S. MAMAK

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**Scientist E (Patents)**  
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