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PROVISIONAL SPECIFICATION

“IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC REDUCTION OF p-NITROPHENOL TO A p-AMINOPHENOL

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJI 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 Handady Venkatakrishna Udupa, Director, Gobichettipalayam Srinivasan Subramanian, Scientist, Payyallur Narayanan Anantharaman, Scientist and Annamalai Pourasamy, Senior Laboratory Assistant, all of Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India and all Indians.

This invention relates to the improvements in or relating to the electrolytic reduction of p-nitrophenol to p-aminophenol.

Hitherto it has been proposed to reduce p-nitrophenol to p-aminophenol by chemical methods by the Bechamp method using iron and hydrochloric acid. The electrochemical methods so far employed use nitrobenzene as the raw material for the reduction of p-aminophenol. Although for the production of p-aminophenol the direct reduction of the nitrobenzene is more economical from the point of view of the cost of raw material and power the reduction of p-nitrophenol can be considered when large quantities of p-nitrophenol is available so that p-aminophenol free from aniline can be produced to meet the needs of the pharmaceutical industries.

The electrochemical methods so far employed for the production of p-aminophenol from p-nitrophenol use only stationary cathodes operating at low current densities and high amperage cells require larger floor space and considerable time was taken for completing the reduction.

The object of this invention is to obviate these disadvantages by reducing nitrophenol electrochemically using the rotating cathode technique. By this technique, the design of high amperage cell is made easier. The reduction proceeds smoothly even at high current density ranges employed.

To these ends, the invention broadly consists in reducing a suspension of p-nitrophenol in a catholyte of sulphuric acid or sodium sulphate but preferably the former upto a concentration of 10% using a rotating cathode of copper or zinc or tin but preferably copper in a divided cell. 0.1% copper sulphate is added to catholyte in order to give a fine deposit of copper over the cathode. The reduction is further carried out at temperature range between 45-70°C but preferably between 50-55°C using a range of current density range between 10 amp/dm² to 30 amp/dm² but preferably at 20 amp/dm². The anolyte is dilute sulphuric acid upto 30% strength but preferably 10%. A ceramic porous pot is used as a diaphragm material and lead is the anode. After the reduction is over, the catholyte is cooled to room temperature and filtered. Thus the unreduced nitro compound is recovered. The filtrate is treated with animal charcoal until the solution is clear. About 1 to 2 gms of sodium bisulphite is added to make the solution resistant towards the attack of oxygen. The solution is neutralised with ammonia or ammonium bicarbonate till the pH is 7. The solution is cooled over ice when all p-aminophenol separates out. It is then filtered. The filtered cake is treated with a gelatin solution containing sodium bisulphite. The p-aminophenol thus obtained is

dried in a vacuum desiccator. The gelatin solution can be prepared by adding 1% sodium bisulphite to 1% gelatin solution.

The following typical examples are given to illustrate the invention.

Example I

Catholyte	1000 ml of 10% H ₂ SO ₄ v/v
Cathode	Cylindrical copper (rotating)
Nitrocompound taken	200 gms
Temperature	50-60°C
Anolyte	180 ml 10% H ₂ SO ₄ v/v
Diaphragm	Unglazed ceramic
Current density	20 amp/dm ²
Voltage	4.5 - 6 V
Duration	14.5 hours
Weight of CuSO ₄ ·5H ₂ O added to catholyte	1 gm
Yield	85.2%
Current efficiency	85.2%
Energy consumed	10.85 kwh/kg of p-aminophenol

Example II

Catholyte	1000 ml 10% H ₂ SO ₄ v/v
Cathode	Cylindrical copper (rotating)
Nitrocompound taken	200 gms
Temperature	50 - 60°C
Anolyte	180 ml 10% H ₂ SO ₄ v/v
Diaphragm	Unglazed ceramic
Current density	25 amp/dm ²
Voltage	4.5 - 6 V
Duration	11.6 hours
Weight of CuSO ₄ ·5H ₂ O	— gm
Yield	78.4%
Current efficiency	78.4%
Energy consumed	11.47 kwh/kg of p-aminophenol

The following are the main advantages of the invention :

1. The use of rotating cathode enables employment of high current densities which increases the cell capacity.
2. The reduction proceeds smoothly with high efficiency.
3. No other product other than p-aminophenol is formed during the course of reduction.
4. Isolated product is extremely pure.

Dated this 22nd day of January, 1972.

Sd./-

(R. BHASKAR PAI)

Patents Officer,

Council of Scientific and Industrial Research.

Price: TWO RUPEES.

COMPLETE SPECIFICATION

IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC REDUCTION OF p-NITROPHENOL TO p-AMINOPHENOL

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 Dr. HANDADY VENKATKRISHNA UDUPA, Director, GOBICHETTIPALAYAM SRINIVASAN SUBRAMANIAN, Scientist-in-Charge, CSIR Complex Adyar, Madras-20, PAYYALAR NARAYANAM ANANTHARAMAN, Scientist, and ANNAMALAI POURASAMY, Senior Laboratory Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India, all Indian citizens.

This invention relates to "Improvements in or relating to the electrolytic reduction of p-Nitrophenol to p-Aminophenol".

The invention consists in improvements in or relating to reduction of p-nitrophenol to p-aminophenol by electrolytic method using either stationary or rotating cathode. Aminophenol is mostly used as a raw material for the manufacture of p-acetamol which is an important pharmaceutical. p-Aminophenol is also used as a raw material for the manufacture of photographic developers. Hence it is directly related to pharmaceutical and photographic industries.

p-Aminophenol can be obtained from p-nitrophenol by Bechamp reduction using iron and hydrochloric acid. Product obtained by this method will be contaminated with iron which is not desirable from the point of view of pharmaceutical as well as photographic industries.

p-Aminophenol is also obtained by reduction of nitrobenzene by chemical as well as electrochemical method.

In both the cases it will be contaminated with aniline which is not desirable from other point of view of the abovementioned industries. p-Aminophenol obtained from p-nitrophenol by electrochemical method gives a product of high purity.

The main object of the invention is to finalise the optimum conditions for the electrolytic reduction of p-nitrophenol to aminophenol using stationary or rotating cathode.

The main finding (the new principle) underlying the inventions:

Electrolytic reduction of p-nitrophenol to p-aminophenol is done by suspending p-nitrophenol in a solution of 10% sulphuric acid using a stationary or rotating copper cathode anode being lead kept in an anolyte of 10% sulphuric acid which is separated from catholyte by an unglazed ceramic diaphragm. After reduction the catholyte is neutralised and free base p-aminophenol is isolated.

To these ends, the invention broadly consists in reducing a suspension of p-nitrophenol in a catholyte of sulphuric acid upto a concentration of 10% V/V using a stationary or rotating cathode of copper or zinc or tin but preferably copper in a divided cell. The reduction is further carried out at temperature upto 70°C but preferably between 50-60°C using a range of current density upto 40 amps/dm² but preferably at 20 amp/dm². The anolyte is dilute sulphuric acid of 10% strength V/V. A ceramic porous pot is used as a diaphragm material and lead as the anode. The filtrate is treated with ammonia or ammonium bicarbonate till the pH is 7. sodium bisulphite is added to make the solution resistant towards the attack of oxygen. The solution is neutralised with ammonia or ammonium bicarbonate till the pH is 7. The solution is cooled over ice when all the p-aminophenol separates out. It is then filtered. The filtered cake is treated with a gelatin solution containing sodium bisulphite. The p-aminophenol thus obtained is dried in a vacuum desiccator. The gelatin solution can be prepared by adding 1% bisulphite to 1% gelatin solution.

p-Aminophenol of purity 99.9% was obtained by the above method. This was confirmed by estimation by nitrite method.

The present invention consists of a process relating to the electrolytic reduction of p-nitrophenol to p-aminophenol in a supporting electrolyte of sulphuric acid upto a concentration of 10% (by volume) using stationary or rotating electrode of copper.

The reduction is further carried out at a temperature upto 70°C but preferably between 50-60°C using a range of current density upto 40 amp/dm² but preferably at 20 amp/dm². The anolyte is dilute sulphuric acid of 10% strength (V/V). A ceramic porous pot is used as diaphragm and lead as anode.

Details of the unit processes involved are given in the flow sheet attached with the specification.

Two typical examples to illustrate the yields are given for stationary as well as rotating cathode.

Example I

Conditions

Catholyte	1000 ml of 10% H ₂ SO ₄ (V/V)
Cathode	Sheet copper (Stationary)
p-Nitrophenol taken	100 g
Temperature	50-60°C
Anolyte	180 ml of 10% H ₂ SO ₄ (V/V)
Diaphragm	Unglazed ceramic
Current density	18 amp/dm ²
Voltage	4.5 to 6 V
Wt. of CuSO ₄ ·5H ₂ O	1 g
Yield	89.3%
Current efficiency	89.3%
Energy consumed	10.85 kWhr/kg of p-aminophenol

Example II

Catholyte	1000 ml of 10% H ₂ SO ₄ (V/V)
Cathode	Cylindrical copper (rotating)
p-Nitrophenol taken	200 g
Temperature	50-60°C
Anolyte	180 ml of 10% H ₂ SO ₄ (V/V)
Diaphragm	Unglazed ceramic
Current density	20 amp/dm ²
Voltage	4.5 to 6 V
Wt. of CuSO ₄ ·5H ₂ O	1 g
Yield	90.6%
Current efficiency	90.6%
Energy consumed	10.85 kWhr/kg of p-aminophenol

The advantages of the invention are its simplicity, ease of scaling up to any desired capacity, isolation of the product in the purest form and its high yield.

The invention consists in reducing a suspension of p-nitrophenol in a supporting electrolyte of dilute sulphuric acid preferably 10% concentration (V/V) using a stationary or rotating cathode of copper. The temperature is kept between 50-60°C and the reduction is carried out at current density of 20 amps/dm². By this technique high yield of p-aminophenol is obtained. The product isolation is simple and the process does not require any complicated equipment.

WE CLAIM:

1. A process for the manufacture of p-aminophenol which comprises in electrolytically reducing a suspension of p-nitrophenol to p-aminophenol in a supporting electrolyte of mineral acid preferably sulphuric acid upto a concentration of 10% V/V using stationary or rotating electrode of copper, and employing a current density upto 20 amp/dm² and temperature between 50 and 60°C.

2. A process as claimed in claim (1) wherein 0.1% copper sulphate is added to the catholyte, so that a thin spongy deposit of copper is obtained.

3. A process for the production of p-aminophenol which consists in reducing p-nitrophenol which is characterised in that electrolyte reduction using stationary or

rotating cathode is used, with the same conditions as stated under claim 1.

4. A process as claimed in any of the preceding claims wherein the catholyte consists of sulphuric acid solution with 0.1% copper sulphate which is required to give a fine deposit of copper over the electrode.

Dated this 22nd day of August 1972.

Sd./-

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