PROVISIONAL SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC REDUCTION OF P-NITROPHENOL TO A P-AMINOPHENOL

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJ 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 Harshad Venkatarkrishna Udupa, Director, Golchetalipalyam Srinivass Subramaniam, Scientist, Payalal Narayan Anandharasan, Scientist and Annapurna Purusha, 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 use the amylplied nitrobenzene as the raw material for the reduction of p-nitrophenol. Although the production of p-aminophenol by 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 are available so that p-aminophenol free from aminol 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 upon 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 and preferably between 50-55°C using a range of current density range between 10 amp/cm² to 30 amp/cm² but preferably at 20 amp/cm². The anolyte is dilute sulphuric acid up to 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. The anode is removed and p-nitrophenol 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-nitrophenol 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% H₂SO₄, v/v |
| Cathode | Cylindrical copper (rotating) |
| Nitrocompound taken | 200 gms |
| Temperature | 50-60°C |
| Anolyte | 180 ml 10% H₂SO₄, v/v |
| Diaphragm | Unplated ceramic |
| Current density | 20 amp/cm² |
| Voltage | 4.5 - 6 V |
| Duration | 14.5 hours |
| Weight of CuSO₄.5H₂O added to catholyte | 1 g |
| Yield | 85.2% |
| Current efficiency | 85.2% |
| Energy consumed | 10.85 kWh/kg of p-aminophenol |

Example II

| Catholyte | 1000 ml 10% H₂SO₄, v/v |
| Cathode | Cylindrical copper (rotating) |
| Nitrocompound taken | 200 gms |
| Temperature | 50-60°C |
| Anolyte | 180 ml 10% H₂SO₄, v/v |
| Diaphragm | Unplated ceramic |
| Current density | 25 amp/cm² |
| Voltage | 4.5 - 6 V |
| Duration | 11.6 hours |
| Weight of CuSO₄.5H₂O | 8 g |
| 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.

R. BHASKAR PAI
Patent Officer, Council of Scientific and Industrial Research,

Price: TWO RUPEES.
The following specification particularly describes and avowes the nature of this invention and the manner in which it is to be performed:

This is an invention by Dr. HANANDY VENKA-TAKRISHNA UDUPA, Director, GOVINDIPET- LAYAM SRINIVASAN SUBRAMANIAM, Scientific-in-Charge, CSIR Complex Adyar, Madras-30, FAYYA- LUR NARAYANAM ANANTHARAMAN, Scientist, and ANANJAYAL 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 the 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-aminophenol 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 means similar to the one described above. The 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 nitrophenol by chemical as well as electrochemical method.

In both the cases it will be contaminated with aniline which is not desirable from the 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 invention:

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 and leading a direct current of 40 amperes/dm² but preferably 20 amperes/dm². The current is then passed through the electrolyte by the anode, which is a copper tube with a platinum wire. The product obtained is then purified by washing with water and drying in an oven.

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 up to 10% (by volume) using stationary or rotating electrode of copper.

The reduction is further carried out at a temperature up to 70°C but preferably between 50-60°C using a range of current density up to 40 amperes/dm² but preferably at 20 amperes/dm². The anolyte is dilute sulphuric acid of 10% strength (V/V). A ceramic porous pipe is used as a 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% H₂SO₄ (V/V)
  - **Cathode**: Surgical copper (Stationary)
  - **Temperature**: 50-60°C
  - **Anolyte**: 100 ml of 10% H₂SO₄ (V/V)
  - **Diaphragm**: Unglazed ceramic
  - **Current density**: 10 amperes/dm²
  - **Voltage**: 4.5 to 6 V
  - **Wt. of CuSO₄.5H₂O**: 1 g
  - **Yield**: 89.3%
  - **Current efficiency**: 89.3%
  - **Energy consumed**: 10.35 kWh/kg of p-aminophenol

**Example II**

- **Catholyte**: 1000 ml of 10% H₂SO₄ (V/V)
- **Cathode**: Cylindrical copper (rotating)
- **p-Nitrophenol taken**: 200 g
- **Temperature**: 50-60°C
- **Anolyte**: 100 ml of 10% H₂SO₄ (V/V)
- **Diaphragm**: Unglazed ceramic
- **Current density**: 20 amperes/dm²
- **Voltage**: 4.5 to 6 V
- **Wt. of CuSO₄.5H₂O**: 1 g
- **Yield**: 90.6%
- **Current efficiency**: 90.6%
- **Energy consumed**: 10.85 kWh/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 amperes/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 upon 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./-

(R. BHASKAR PAI)

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