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70B [LVIII(5)]

Improvements in or relating to the electrochemical preparation of para aminobenzoic acid.

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 describes the nature of this invention.

This is an invention by Handady Venkatakrishna Udapa, Scientist, Mysore Seshaiyer Venkatachalopathy, Scientist, Angiya Parthasarathy Shakunthala, Junior Scientific Assistant and Ramamujam Kanakam, Senior Laboratory Assistant, all of Central Electrochemical Research Institute, Karaikudi-3, Madras State, India, all Indians.

Price Rs.2/-

This invention relates to improvements in or relating to the electrochemical preparation of para-amino benzoic acid.

Hitherto it has been proposed to employ chemical reducing agent like ferrous sulphate and catalytic hydrogenation of p-nitrobenzoic acid for the preparation of p-aminobenzoic acid from p-nitrobenzoic acid.

Next

This is open to the objection that the processes reported in literature suffer from the following drawbacks.

- 1) It is rather tedious and laborious to separate the product from the reactants like ferrous sulphate while employing chemical reducing agents.

ii) Further purification of the product is essential in a process employing chemical reducing agents.

iii) High pressure reaction equipments are essential for the catalytic reduction technique and the unit processes are expensive as catalysts have to be imported.

iv) Information available on the cathodic preparation of para-aminobenzoic acid is not adequate enough for setting up a practical scale unit.

The object of this invention is to obviate these disadvantages by the improvements now effected in the process.

According to the present invention, expensive high pressure catalytic reduction units are avoided by using cathodic reduction of p-nitrobenzoic acid for the production of p-aminobenzoic acid. The present process is superior to the chemical processes hitherto described in literature since it not only eliminates the tedious and laborious process of separating the product from the reactants but also gives a very pure product and thereby renders the process more easy to operate without economic drawbacks. Additional advantage in the process now established by us is that by using a rotating cathode, high current density and high concentration of p-nitrobenzoic acid could be employed without adversely affecting the energy economics of the process.

To these ends, the invention broadly consists in reducing cathodically p-nitrobenzoic acid to give p-aminobenzoic acid in an electrolytic cell, fitted with either a rotating tin, or tinned or tin plated cathode. The catholyte was separated from anolyte by means of a porous diaphragm. A 35% solution of sulphuric acid was used as anolyte and the anode was made of lead or lead alloy. The catholyte employed was hydrochloric acid of density 1.054 and the concentration of the depolarizer was kept

between 2 and 15% but a solution of 10% would give the maximum current efficiency and yield. A current density of 2.5 - 5 amp/dm² in the case of stationary cathode and 10-25 amp/dm² with a rotating cathode could be employed. The temperature of the catholyte could vary from 50-70°C, but a temperature of 65-70°C was employed for most of the experiments. A current efficiency of 88-90% and an yield of 85-90% was obtained.

The following typical examples are given to illustrate the invention:

EXAMPLE I

Electrolytic reduction of p-nitrobenzoic acid using a stationary tin cathode:

125 g of p-nitrobenzoic acid was suspended in 2500 cc of hydrochloric acid of density 1.03. Tin was employed as cathode. A 35% aqueous solution of sulphuric acid was employed as anolyte and lead was used as anode. The catholyte was separated from the anolyte by means of a ceramic diaphragm. During the electrolysis, the temperature of the catholyte was kept between 65°-70°C by means of a water bath. A current density of 10 amp/dm² was employed. The cell voltage was 4.20. After passing 120 amp-hrs, 78 g of p-aminobenzoic acid was obtained with a current efficiency of 76.1% and an yield of 80%. Para-aminobenzoic acid was isolated from the electrolyte by neutralising to pH 2-3 with soda ash solution.

EXAMPLE II

Electrolytic reduction of p-nitrobenzoic acid using a rotating tin cathode:

10 g of p-nitrobenzoic acid was suspended in 200 cc of hydrochloric acid of density 1.03. A rotating cylinder of tin was employed as cathode. The r.p.m. was kept between 1500-2000. The cell voltage was 3.8 to 4.0. During the electrolysis, the temperature of the catholyte was kept

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between 65°-70°C. A current density of 10 amp/dm² was employed and after passing 9.60 amp-hr, 8.1 g of p-aminobenzoic acid was obtained. No unreduced nitro-compound could be detected after electrolysis. A current efficiency of 99% and an assay yield of 90% was obtained. The mode employed was the same as that given in Example I.

EXAMPLE III

Electrolytic reduction of p-nitrobenzoic acid using a stationary tin plated cathode:

10g of p-nitrobenzoic acid was suspended in 250 cc of 20% sulphuric acid containing 0.5% stannous chloride. Tin plated copper was employed as cathode. A 30% aqueous solution of sulphuric acid was employed as anolyte and lead was used as anode. The cell voltage was 3.6 - 4.0. During the electrolysis, the temperature of catholyte was kept between 65-70°C. A current density of 10 amp/dm² was employed. Excess current was passed to reduce p-nitrobenzoic acid completely. 3.10 g of p-aminobenzoic acid was obtained with a current efficiency of 52.5% for an assay yield of 90.3%.

The following are among the main advantages of the invention:

- 1) The process does not involve the use of any chemical reagent and as such its removal does not arise.
- 2) Isolation of the product is simplified, thereby also giving a product which is pure.
- 3) The employment of a rotating cathode would very much help in the design of high amperage cells in order to adopt the process for large scale preparation.

Dated this fourteenth day of December 1966

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Signature: M. S. Kamath Designation: Scientist B
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108573

This invention relates to Improvements in or relating to the Electrochemical preparation of Para Amino Benzoic Acid.

The invention also relates to the field of organic chemical industry with special reference to production of pharmaceutical chemical and drugs on an industrial scale by this electrochemical method.

Hitherto it has been proposed to employ chemical reducing agents like ferrous sulphate and catalytic hydrogenation employing either costly catalysts, or ordinary catalysts under pressure.

The processes hitherto reported in literature suffer from the following drawbacks:

i) It is rather tedious and laborious to separate the product from the reactant like ferrous sulphate while employing chemical reducing agents.

ii) Further purification of the product is essential in a process employing chemical reducing agents.

iii) High pressure reaction equipments are essential for the catalytic reduction techniques and the unit processes are expensive as catalysts have to be imported.

The main object of the invention:

The main object of the invention is to obviate the drawbacks mentioned earlier by the modification and improvements now effected by us.

The main finding underlying the invention:

Expensive high pressure catalytic reduction units are avoided by using a rotating cathode for the reduction of p-nitrobenzoic acid for the production of p-aminobenzoic acid.

The present process is superior to the chemical processes hitherto described in the literature since it not only eliminates the tedious and laborious process of separating the product from the reactants but also gives a very pure product and thereby renders the process more easy to operate

Indian Patents and Designs, Act, 1911

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COMPLETE SPECIFICATION

Section 4

IMPROVEMENTS IN OR RELATING TO THE ELECTROCHEMICAL PREPARATION OF PARA AMINO BENZOIC ACID

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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 VENKATKRISHNA UDUPA, Scientist, MYSORE SESHAIYER VENKATACHALAPATHY, Scientist, ANGIYA PARTHASARATHY SHAKUNTHALA, Junior Scientific Assistant and RAMANUJAM KANAKAM, Senior Laboratory Assistant, all of the Central Electro-chemical Research Institute, Karaikudi-3, Madras State, all Indian citizens.

without economic drawbacks. Additional advantage in the process now established by us is that by using a rotating cathode, high current density and high concentration of p-nitrobenzoic acid could be employed without adversely affecting the energy economics of the process.

The invention broadly consists in cathodic reduction of p-nitrobenzoic acid to give p-aminobenzoic acid in an electrolytic cell fitted with either a rotating tin or tin plated cathode. The catholyte was separated from anolyte by means of a porous diaphragm. A 35% solution of sulphuric acid was used as anolyte and the anode was made of lead or lead alloy. The catholyte employed was hydrochloric acid of density 1.034 and the concentration of the depolariser was kept between 3 and 15% but a solution of 5% could give the maximum current efficiency and yield. A current density of 2.5 - 5 amp/dm² in the case of stationary cathode and 10-25 amp/dm² with a rotating cathode could be employed. The temperature of catholyte could vary from 50-70°C but a temperature of 65-70°C was employed for most of the experiments. A current efficiency of 88-90% and an yield of 85-90% was obtained.

Typical examples:

EXAMPLE I

Electrolytic reduction of p-nitrobenzoic acid using a stationary tin cathode: 125 g of p-nitrobenzoic acid was suspended in 2.5 litres of hydrochloric acid of density 1.03. Tin was employed as cathode. A 35% aqueous solution of sulphuric acid was employed as anolyte and lead was used as anode. The catholyte was separated from the anolyte by means of a ceramic diaphragm. During the electrolysis, the temperature of the catholyte was kept between 65 and 70°C by means of a water bath. A current density of 10 amp/dm² was employed. The cell voltage was 4.2.

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After passing 120 amp.hrs., 78 g of aminobenzoic acid was obtained with a current efficiency of 76.1% and an yield of 80%. The energy consumption comes to 6.6 Kwh/Kg.

EXAMPLE II

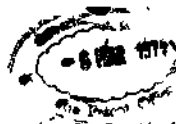
Electrolytic reduction of p-nitrobenzoic acid using a rotating tin cathode: 10 g of p-nitrobenzoic acid was suspended in 200 cc of hydrochloric acid of density 1.03. A rotating cylinder of tin was employed as cathode. The r.p.m. was kept between 1500-2000. The cell voltage \bar{E} was 3.8 to 4.0. During the electrolysis, the temperature of the catholyte was kept between 65-70°C. A current density of 10 amp/dm² was employed and after passing 9.60 amp.hr. 8.1 g of p-aminobenzoic acid was obtained. No undreduced nitro compound could be detected after electrolysis. A current efficiency of 99% and an assay yield of 93% was obtained. The anode employed was the same as that given in Example I. The energy consumption comes to 5.8 Kwh/Kg.

Summary:

A process has been invented for the electrolytic production of p-aminobenzoic acid from p-nitrobenzoic acid. This process eliminates the use of conventional methods which require further purification of the product and also high pressure reaction equipment. High amperage could be employed in the cell by the use of rotating cathode which renders the process more easy to operate without any economic drawbacks.

WE CLAIM:

1. A process for the electrochemical preparation of p-aminobenzoic acid from p-nitrobenzoic acid using a tin or tin plated cathode either stationary or rotating and having a lead anode which has been separated from the cathode by means of a porous diaphragm.



2. A process as claimed in claim (1) wherein perforated lead strips are used as anodes

3. A process as claimed in claim (1) wherein sulphuric acid of concentration between 30 and 40% is used as anolyte, but preferably 35%.

4. A process as in claim (1) wherein hydrochloric acid is used as catholyte and the density of it could be varied between 1.02 and 1.06 but preferably be 1.035.

5. A process as in claim (1) wherein a current density upto 10 amp/dm² in the case of stationary cathode and 5-30 amp/dm² in the case of rotating cathode are employed.

6. A process as in claim (1) wherein the temperature range could be 50-75°C but preferably 70°C.

7. A process as claimed in claim (1) wherein the cathode is stationary or rotating and while stationary and auxiliary stirrer is employed.

Dated this 27th day of September, 1967


Asst. PATENT OFFICER
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