

Specification No. 97002. Application No. 97002, dated 14th December 1964. Complete specification left on 14th September 1965. (Application accepted 12th September 1966.)

Index at acceptance—32F2a [IX(1)].
PROVISIONAL SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC REDUCTION OF
NITROBENZENE TO P-PHENETIDINE.

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 describes the nature of this invention.

This is an invention by Handady Venkatakrishna Udupa, Gobichettipalayam Srinivasan Subramanian and Paramakudi Subbiah, all of Central Electrochemical Research Institute, Karaikudi-3, India, all Indians.

This invention relates to improvements in or relating to the electrolytic reduction of nitrobenzene to p-phenetidine.

Hitherto it has been the practice to reduce p-nitrophenetole which is itself prepared by a round about way.

This is open to objection in that p-nitrophenetole is a costlier raw material and has to be prepared involving a number of unit processes.

The object of this invention is to obviate these disadvantages by a direct electrochemical synthesis from a cheaper raw material, namely nitrobenzene by reducing nitrobenzene with a rotating amalgamated copper or monel or brass cathode in alcoholic sulphuric acid bath.

To these ends, the invention broadly consists in reducing nitrobenzene with a rotating amalgamated copper or monel but preferably monel cathode in alcoholic sulphuric acid bath preferably a strength of 30 per cent acid. The reduction is carried out at a current density upto 40 amp/dm² but preferably at 10 amp/dm² at a temperature between 50-60° C. After the reduction is completed, phenetidine sulphate precipitating is separated and a fresh charge of nitrobenzene is added and reduced. The electrolyte is further reused after making up the strength of free acid upto 30 per cent, and adding further quantity of ethyl alcohol. The p-phenetidine sulphate is neutralised with alkali and steam distilled to recover any aniline formed. The residue is then salted out and p-phenetidine is separated as a thick red oil. It is purified by distilling under reduced pressure.

The following typical example is given to illustrate the invention:

EXAMPLE 1.

Catholyte: 300 ml containing 36 ml of conc. sulphuric acid and 264 ml of ethyl alcohol. 60 ml of nitrobenzene added in 3 lots of 20 ml each.

Anolyte: 30 per cent sulphuric acid.
Current density: 25 amp/dm².
Cathode: Rotating amalgamated monel
—Area 0.4 dm².
Anode: Lead.
p-Phenetidine obtained: 35.4 g.
Current efficiency: 49.2 per cent.

The following are among the main advantages of the invention:

(1) The electrolytic reduction of nitrobenzene in alcoholic sulphuric acid gives p-phenetidine thereby making it possible to carry out simultaneously the transformation and ethoxylation in the same set-up.

(2) The use of rotating cathode technique has simplified the design of high amperage cell and good current efficiencies are obtained even at high current densities.

(3) Because of the simultaneous transformation and ethoxylation taking place, the number of steps involved in preparing p-phenetidine by other methods are reduced to the minimum.

(4) The electrolyte is used three times when p-phenetidine sulphate separates out and it is possible to make the process continuous by separating the sulphate and cycling the electrolyte.

(5) The reduction is carried out with a cheaper raw material namely, nitrobenzene while p-nitro phenetole will be costlier raw material in the usual technique.

(6) The technique could be employed generally for the preparation of different aromatic ethers having an amino-group in the p-position.

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Patents Officer,

COUNCIL OF SCIENTIFIC & INDUSTRIAL
RESEARCH.

Dated this 11th day of December 1964.

COMPLETE SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC REDUCTION OF
NITROBENZENE TO P-PHENETIDINE.

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 Handady Venkatakrishna Udupa, Gobichettipalayam Srinivasan Subramanian and Paramakudi Subbiah, all of the Central Electrochemical Research Institute, Karaikudi-3, India, all Indian citizens.

This invention relates to improvements in or relating to the electrolytic reduction of nitrobenzene to p-phenetidine.

Hitherto it has been the practice to reduce p-nitrophenetole which is itself prepared by a round about way.

This is open to objection in that p-nitrophenetole is a costlier raw material and has to be prepared involving a number of unit processes.

The object of this invention is to obviate these disadvantages by a direct electrochemical synthesis from a cheaper raw material, namely nitrobenzene by reducing nitrobenzene with a rotating amalgamated copper or monel or brass cathode in alcoholic sulphuric acid bath.

To these ends, the invention broadly consists in reducing nitrobenzene with a rotating amalgamated copper

Price : TWO RUPEES.

or monel but preferably monel cathode in alcoholic sulphuric acid bath preferably a strength of 30 per cent. acid. The reduction is carried out at a current density upto 40 amp/dm² but preferably at 10 amp/dm² at a temperature between 50-60° C. After the reduction is completed, phenetidine sulphate precipitating is separated and a fresh charge of nitrobenzene is added and reduced. The electrolyte is further reused after making up the strength of free acid upto 30 per cent. and adding further quantity of ethyl alcohol. The p-phenetidine sulphate is neutralised with alkali and steam distilled to recover any aniline formed. The residue is then salted out and p-phenetidine is separated as a thick red oil. It is purified by distilling under reduced pressure.

The following typical example are given to illustrate the invention:

EXAMPLE I.

Catholyte:	2 litres containing 360 ml of concentrated sulphuric acid and 1640 ml ethyl alcohol. 420 ml nitrobenzene added.
Anolyte:	30% sulphuric acid (500 ml)
Current density:	10 amp/dm ² .
Cathode:	Rotating amalgamated monel-Area=1.4 dm ² .
Anode:	Lead.
p-Phenetidine obtained:	242 g.
Current efficiency:	42%.

EXAMPLE II.

Catholyte:	2 litres containing 360 ml of concentrated sulphuric acid and 1640 ml of ethyl alcohol. Further 165 ml of nitrobenzene added.
Anolyte:	30% sulphuric acid 500 ml.
Current density:	10 amp/dm ² .
Cathode:	Rotating amalgamated monel-Area=1.4 dm ² .
Anode:	Lead.
p-Phenetidine obtained:	275 g.
Current efficiency:	47%.
Anolyte:	30 per cent. sulphuric acid.
Current Density:	25 amp/dm ² .
Cathode:	Rotating amalgamated monel—Area 0.4 dm ² .
Anode:	Lead.
p-Phenetidine obtained:	35.4 g.
Current efficiency:	49.2 per cent.

The following are among the main advantages of the invention:

1. The electrolytic reduction of nitrobenzene in alcoholic sulphuric acid gives p-phenetidine thereby making

it possible to carry out simultaneously the transformation and ethoxylation in the same set-up.

2. The use of rotating cathode technique has simplified the design of high amperage cell and good current efficiencies are obtained even at high current densities.

3. Because of the simultaneous transformation and ethoxylation taking place, the number of steps involved in preparing p-phenetidine by other methods are reduced to the minimum.

4. The electrolyte is used three times when p-phenetidine sulphate separates out and it is possible to make the process continuous by separating the sulphate and cycling the electrolyte.

5. The reduction is carried out with a cheaper raw material namely, nitrobenzene while p-nitro phenetole will be costlier raw material in the usual technique.

6. The technique could be employed generally for the preparation of different aromatic ethers having an amino-group in the p-position.

We claim:

1. A process for the electrolytic reduction of nitrobenzene to p-phenetidine which consists in reducing nitrobenzene with a rotating amalgamated copper or monel but preferably monel cathode in alcoholic sulphuric acid bath preferably a strength of 30 per cent. acid.

2. A process as claimed in Claim 1, wherein the reduction is carried out at a current density upto 40 amp/dm² but preferably at 10 amp/dm² at a temperature between 50-60° C.

3. A process as claimed in Claim 1 or 2, wherein after the reduction is completed, phenetidine sulphate precipitating is separated and a fresh charge of nitrobenzene is added and reduced.

4. A process as claimed in any of the preceding claims wherein the electrolyte is further reused after making up the strength of free acid upto 30 per cent. and adding further quantity of ethyl alcohol.

5. A process as claimed in any of the preceding claims wherein the p-phenetidine sulphate is neutralised with alkali and steam distilled to recover any aniline formed.

6. A process as claimed in any of the preceding claims wherein the electrolyte is used three times when p-phenetidine sulphate separates out and it is possible to make the process continuous by separating the sulphate and cycling the electrolyte.

7. A process for the electrolytic reduction of nitrobenzene to p-phenetidine substantially as described in the example.

8. p-Phenetidine whenever obtained by the electrolytic reduction of nitrobenzene substantially as hereinbefore described.

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Dated this 7th day of September 1965.