

**GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, ACHARYA JAGDISH BOSE ROAD,
CALCUTTA-17.**

Specification No. 130295, Application and Provisional Specification filed on 17th February 1971.

Complete Specification filed on 15th November 1971. (Acceptance advertised on 2nd June 1973)

Index at acceptance—32F2a[IX(1)]; 70C6+7[LVIII(5)]

**"AN ELECTROCHEMICAL PROCESS FOR THE PRODUCTION OF PARA-AMINO-DIMETHYL ANILINE FROM
PARA-NITROSO DIMETHYL ANILINE FOR MAKING METHYLENE BLUE"**

**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)**

**This is an invention by Handady Venkatakrishna Udupa, Director, Mysore Seshaiyer Venkatachalapathy, Scientist,
Ramanujam Kanakam, Senior Scientific Assistant, and Sivaprakasam Balagopalan, Junior Scientific
Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3, Tamil
Nadu, India, all Indian citizens.**

PROVISIONAL

The following Specification describes the nature of this invention.

This invention relates to the discovery of a new electrochemical process for the production of methylene blue from dimethyl aniline.

Hitherto it has been proposed to produce methylene blue chemically by employing generally zinc or iron powder for the reduction of p-nitroso dimethylaniline which was subsequently converted to methylene blue.

This is open to objection that the reducing agents employed in the preparation of methylene blue is costly and involves the tedious separation of unconverted iron or zinc dust.

The object of this invention is to obviate the disadvantages by the use of an elegant electrochemical method. According to the present invention, dimethyl aniline is first converted to p-nitroso dimethylaniline which was subsequently reduced electrolytically and used for the production of methylene blue.

To these ends, the invention broadly consists first in the preparation of p-nitroso dimethylaniline, by the use of sodium nitrite. Then it is reduced electrolytically and converted to methylene blue, the details of which are given in the example.

The following typical example is given to illustrate the invention.

Example I

A cooled solution of 16 g. of pure dimethylaniline in 30 ml of 30% hydrochloric acid is mixed with ice and a 20% solution containing 7 g. of NaNO_2 is added over a period of one hour. The nitrosodimethylaniline formed is filtered and reduced electrolytically using copper cathode at a current density of 5-10 amp/dm². The temperature of electrolysis is 20 to 25°C. An assay yield of 95% for the formation of p-amino dimethylaniline is obtained based on the dimethylaniline. The catholyte is 19 g. of p-nitrosodimethylaniline in 10% sulphuric acid containing 19 g. of p-nitrosodimethylaniline. A porous pot is used to separate the anolyte from the catholyte. The anolyte is 5% sulphuric acid and lead is used as anode.

After reduction, the catholyte is removed and 50 cc of 50% ZnCl_2 is added. A solution of 19 g. aluminium sulphate in 30 ml of water is added and stirred well at room temperature. Then sodium thiosulphate 26.2 g. in 25 cc of water is added. After two seconds, a solution containing

11 g. of potassium dichromate in 15 cc of water is added. The temperature of the mixture is raised to 40°C and a solution of 10 g. of dimethylaniline in 14 g. of concentrated hydrochloric acid is added, followed by a solution containing 22 g. of potassium dichromate in 30 cc of water. The mixture is heated to 70°C and 12.5 g. of MnO_2 is added and the temperature is raised to 85°C. After half an hour, the mixture is allowed to cool to 50°C and 25 ml of sulphuric acid is added. The dye is filtered at 20°C and washed with 10% salt solution. This crude product is dissolved in 500 ml of water at 100°C. The solution is filtered and the dye is precipitated by the addition of zinc chloride and common salt. The yield is 22 g.

Example II

12 g. of dimethylaniline are dissolved in a mixture of 40 ml of water and 65 g. of concentrated HCl and the solution cooled to 12-15°C. This solution is stirred mechanically and a solution of 7.1 g. of sodium nitrite run in slowly taking care that the temperature does not rise above 15°C. This nitroso compound is reduced electrolytically using copper electrode at a current density of 5-10 amp/dm². The temperature of electrolysis is 20 to 25°C. An assay yield of 95% for the formation of p-aminodimethylaniline is obtained based on the dimethylaniline. The catholyte is 14.2 g. of p-nitrosodimethylaniline in 5% sulphuric acid. Anolyte is 5% sulphuric acid and lead is used as anode.

After reduction the catholyte is neutralised with soda ash diluted with water to 500 ml. Added 12 g. of dimethylaniline in 10 ml of concentrated hydrochloric acid and 50 g. of sodium thiosulphate in little water. The mixture is oxidised by adding a concentrated solution of 25 g. of potassium dichromate and boiled for two hours. 53 g. of sulphuric acid diluted with 100 ml of water are now added and the solution boiled to expel SO_2 . The leuco methylene blue is oxidised by adding 8 g. of neutral sodium dichromate and the resulting dye is precipitated by adding salt.

The crude product is dissolved in minimum amount of water and the dye is precipitated by the addition of zinc chloride and common salt and the yield is about 17 g.

The main advantage of the invention is that the costly reducing agents like zinc dust and iron powder is avoided and the tedious step of separation of the unconsumed iron and zinc dust is eliminated.

Price : TWO RUPEES.

COMPLETE

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to an electrochemical process for the production of para-aminodimethylaniline from para-nitrosodimethylaniline for making methylene blue.

Hitherto it has been proposed to produce methylene blue chemically by employing zinc or iron powder for the reduction of p-nitrosodimethylaniline which was subsequently converted to methylene blue.

The processes hitherto known suffer from the following draw-backs namely that the use of metals like zinc and iron employed for reduction results in the increased cost of the final product and also involves the tedious separation of unconverted iron or zinc dust.

The main object of the invention is to obviate the draw-backs mentioned earlier by the modifications and improvements now effected by us.

According to the present invention, there is provided a process for the preparation of p-aminodimethylaniline by electrolytic reduction of p-nitrosodimethylaniline characterised in that the electrolytic reduction is carried out using a copper cathode, either stationary or rotating and an anode as herein described which is separated by means of a porous diaphragm.

Lead or antimonial lead or lead silver alloy is used as anode material.

A current density of 2.5 to 5.0 amp/dm², but preferably 3 amp/dm² in the case of stationary cathode and 10-30 amp/dm² in the case of rotating cathode is employed to reduce p-nitrosodimethylaniline.

The concentration of the electrolyte is varied between 5% and 20%, but preferably 15%.

The temperature range is 20-25°C preferably 25°C.

Thus, dimethylaniline is first converted to p-nitrosodimethylaniline which was subsequently reduced electrolytically and used for the production of methylene blue. The present process is superior to the processes hitherto described in literature since it does not involve the use of expensive reducing agents like zinc dust or iron powder. This also saves foreign exchange since zinc dust is imported. The product isolation is simplified since it does not involve the tedious separation of unconverted zinc or iron dust. P-nitrosodimethylaniline is thus prepared from dimethylaniline by the use of sodium nitrite, reducing it electrolytically and then converting to methylene blue, the details of which are given in examples.

Example 1

A cooled solution of 16 g. of pure dimethylaniline in 30 ml of 30% hydrochloric acid is mixed with ice and a 20% solution containing 7 g. of sodium nitrite is added over a period of one hour. The nitrosodimethylaniline formed is filtered and reduced electrolytically using rotating copper cathode at current density of 5-10 amp/dm². The temperature of electrolysis is 20 to 25°C and an assay yield of 95% for the formation of p-dimethylphenylenediamine is obtained based on the dimethylaniline. The catholyte is 19 g. of p-nitrosodimethylaniline in 250 cc of 10% sulphuric acid. Anolyte is 10% sulphuric acid and lead used as anode. A porous pot is used to separate the anolyte from the catholyte.

After reduction, the catholyte is removed and 50 cc of 50% zinc chloride is added. A solution of 19 g. of aluminium sulphate in 30 ml of water is added and stirred well at room temperature. Then 26.2 g. of sodium thiosulphate in 25 cc of water is added. After 2 seconds, a solution containing 11 g. of potassium dichromate in 15 cc of water is added. The temperature of the mixture is raised to 40°C and a solution of 10 g. of dimethylaniline in 14 g of concentrated hydrochloric acid is added, followed by a solution containing 22 g. of potassium dichromate in 30 cc of water. The

Adarsh Bharat Printers, Meerut.

mixture is heated to 70°C and 12.5 g. of manganese dioxide is added and the temperature is raised to 85°C. After half-an-hour, the mixture is allowed to cool to 50°C and 25 ml of sulphuric acid is added. The dye is filtered at 20°C and washed with 10% salt solution. This crude product is dissolved in 500 ml of water at 100°C. The solution is filtered and the dye is precipitated by the addition of zinc chloride and common salt. The yield is 22 g.

Example 2

12 g. of dimethylaniline are dissolved in a mixture of 40 ml of water and 65 g. of concentrated hydrochloric acid and the solution cooled in ice to 12-15°C. This solution is stirred mechanically and a solution of 7.1 g. of sodium nitrite is added slowly, taking care that the temperature does not rise above 15°C. This nitroso compound is reduced electrolytically using copper electrode at a current density of 5-10 amp/dm². The temperature of electrolysis is 20-25°C. An assay yield of 95% for the formation of p-dimethyl phenylene diamine is obtained based on the dimethyl aniline. The catholyte is 14.2 g. of p-nitrosodimethylaniline in 250 cc of 10% sulphuric acid. Anolyte is 10% sulphuric acid and lead is used as the anode.

After reduction, the catholyte is neutralised with soda ash and diluted with water to 500 ml. Added 12 g. of dimethylaniline in 10 ml of concentrated hydrochloric acid and 50 g. of sodium thiosulphate in a little water. The mixture is oxidised by adding a concentrated solution of 25 g. of potassium dichromate and boiled for 2 hours. 53 g. of sulphuric acid diluted with 100 ml of water is now added and the solution boiled to expel SO₃. The leuco methylene blue is oxidised by adding 8 g. of neutral sodium dichromate and the resulting dye is precipitated by adding salt.

The crude product is dissolved in minimum amount of water and the dye is precipitated by the addition of zinc chloride and common salt and the yield is 17 g.

The main advantages of the invention is that the costly reducing agents like zinc dust and iron powder is avoided and the tedious step of separation of the unconsumed iron and zinc dust is eliminated.

We claim:

1. A process for the preparation of p-aminodimethylaniline by electrolytic reduction of p-nitrosodimethylaniline characterised in that the electrolytic reduction is carried out using a copper cathode, either stationary or rotating and an anode as herein described which is separated by means of a porous diaphragm.
2. A process as claimed in claim (1) wherein lead or antimonial lead or lead silver alloy is used as anode material.
3. A process as claimed in claim (1) wherein a current density of 2.5 to 5.0 amp/dm², but preferably 3 amp/dm², in the case of stationary cathode and 10-30 amp/dm² in the case of rotating cathode is employed to reduce p-nitrosodimethylaniline.
4. A process as claimed in claim (1) wherein the concentration of the electrolyte is between 5% and 20% but preferably 15%.
5. A process as claimed in claim (1) wherein the temperature range is from 20-25°C, preferably 25°C.
6. A process for the preparation of p-aminodimethylaniline, by electrolytic reduction of p-nitrosodimethylaniline substantially hereinbefore described.

Dated this 12th day of November 1971.

Patents Officer,

Council of Scientific and Industrial Research