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AN ELECTROCHEMICAL PROCESS FOR THE PREPARATION OF
2- AMINO -m- XYLENE FROM 2 - NITRO-m- XYLENE.

Council of Scientific and Industrial Research,
Rafi Marg, New Delhi - 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 :
Payyallur Narayanan Anantharaman, Scientist and Michael Noel,
Junior Scientific Assistant, all of Central Electrochemical
Research Institute, Karaikudi 623 006, India - an Indian citizen.

PRICE: TWO RUPEES

This invention relates to the improvement in or relating to the electrolytic reduction of 2-nitro-m-xylene to 2-amino-m-xylene.

Hitherto it has been proposed to reduce 2-nitro-m-xylene to 2-amino-m-xylene with iron and hydrochloric acid. Since aniline has got a tendency to complex with iron the product may not be isolated quantitatively with high purity. Moreover disposal of iron oxide sludge causes a problem. The yield in this process is reported to be between 34 and 43, percent.

Electrochemical method can give high purity product with good yield. Many nitro compounds have been reduced successfully and products of high purity have been isolated with good yield. Yields over 90% have been reported in the case of aniline, p-aminophenol, o-aminophenol, m-phenylene diamine, p-chloro aniline and 2,4 diamino toluene in this laboratory from their respective nitro compounds. Same procedure was adopted for the reduction of 2-nitro-m-xylene to 2-amino-m-xylene. In this case, under similar conditions the yield was less than 50% and the current efficiency was less than 20%. Hence a surface active agent cetyl trimethyl ammonium bromide (CTAB) was added and it was found that it improves both the yield efficiency. 79% yield and 73% current efficiency were obtained for 2 amino-m-xylene.

The invention broadly consists in reducing a suspension of 2 nitro-m-xylene in a catholyte of sulphuric acid upto a concentration of 20% (V/V) with about 0.1% copper sulphate using stationary or rotating cathode of copper between 30-90°C but preferably between 50-60°C using a range of current density upto 25 A/dm² but preferably 5 A/dm². The anolyte is sulphuric acid solution upto 40% but preferably 20% (V/V). As diaphragm ceramic or blue asbestos but preferably ceramic is used. Lead in the pure form or alloy form either as lead antimony or lead lead. silver is used as the anode. Addition agents like titanous sulphate or titanous sulphate of concentration equivalent to 10 g TiO₂ in one litre catholyte is used. CTAB is also used as addition agent of concentration equivalent to 0.01% w/v of the catholyte. ~~Copper sulphate upto 0.1% (W/V) of catholyte is added to the catholyte.~~ Copper sulphate upto 0.1% (W/V) of catholyte is added to the catholyte and electrolysis

is carried out prior to addition of 2-nitro-m-xylene so that the copper gets deposited on the cathode and hence increases the surface area.

Experiments were carried out on both stationary and rotating cathodes. Since lower current density ($5A/dm^2$) leads to better efficiency stationary cathodes which is simpler to use must be sufficient. In this cases as indicated in the examples stationary cathode gives better yield (79%) compared to the rotating cathode(64.8%).

The reduction is carried out for theoretical time(6 Faradays for 1 gram mole) and afterwards 10% extra quantity is passed if needed to see that no smell of nitro compound is left afterwards. Later the solution is either neutralised with ammonia or ammonium bicarbonate till the pH is seven. If the electrolyte is to be reused the solution is cooled to room temperature when 2-amino-m-xylene sulphate separates out as solid. The solution is estimated for total sulphuric acid by estimation with standard sodium hydroxide with phenolphthalein indicator. 2-Amino-m-xylene in solution is estimated with standard sodium nitrite with starch iodide paper as indicator. Sulphuric acid taken by 2 amino-m-xylene is thus estimated. For the next use of electrolyte sulphuric acid is added to make the free acid content 20% (V/V). Thus the reduction is continued for the next charge also in the same manner as above. In this way the catholyte may be reused, thus bringing down the cost of production. After neutralising the solution of 2 amino-m-xylene sulphate solution with ammonia or ammonium bicarbonate it is filtered so that all solid matter like hydrolysed titanium salts or copper powder will be removed and the solution will contain only aqueous solution and oil, the 2 amino-m-xylene. The oil can thus be separated out using a separating funnel. The isolated oil can be distilled to remove water which is present as impurity. After removal of oil the aqueous solution is saturated with sodium chloride and the oil is extracted with benzene. The benzene layer is removed and subjected to evaporation over a water bath when the 2 amino m-xylene remains behind. Afterwards the 2 amino-m-xylene can be purified by distillation as mentioned earlier.

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Conditions :

Example 1

Catholyte : 400 ml 20% H_2SO_4 (V/V) containing
1% TiO_2 as titanlic sulphate + 0.1%
copper sulphate + 0.01% CTAB

Anolyte : 100 ml 20% H_2SO_4 (V/V)

Cathode : Rotating copper of area 0.85 dm^2

Current : 5 A

C.D. : 5.8 A/ dm^2

Anode : Lead

Diaphragm : Ceramic porous pot

Temperature : 40 - 50°C

Voltage : 3.5 - 4V

Wt of 2 nitro m-xylene added : 68.4 g

Wt of 2 nitro m-xylene recove-: Nil
red

Wt. of 2 amino m-xylene recove-: 31.2 g
red

Yield : 64.8%

No. of amp hrs passed : 55

Current efficiency : 51.5%

Energy consumption : 7.05 kwh/kg amine produced.

Example 2

Conditions:

Catholyte : 250 ml 20% H_2SO_4 (V/V) containing 1%
 TiO_2 titanlic sulphate + 0.1%
copper sulphate + 0.1%CTAB

Anolyte : 100 ml 20% H_2SO_4 (V/V)

Cathode : Stationary copper of area 2.26 dm^2
(Copper vessel of 9 cm diameter and
9 cm height).

Current : 10 A

Current density : 4.4 A/ dm^2

Anode : Lead

Diaphragm : Ceramic porous pot

Temperature : 50 - 60°C

Voltage : 3.5 - 4.5V

wt of 2 nitro m-xylene added : 136.8 g

Wt of 2 nitro m-xylene recovered : NIL

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Wt of 2 amino m-xylene sulphate : 10 g
recovered as solid

Total 2 amino m-xylene recovered : 85 g
as oil

Yield : 79%

No. of amp hrs passed : 155

Current efficiency : 73%

Energy consumption : 8.2 kwh/kg amine produced

~~energy consumption~~

Analysis was done by estimation with standard sodium nitrite in the usual manner (Vide Laboratory Manual of Organic Chemistry - B.B.Dey and M.V.Sitaraman) Purity was confirmed by B.P.also. Redistilled 2 amino m-xylene has a B.P.216°C. The product was found to be more than 99% pure.

The following are the main advantages of the invention:

- 1) The reduction proceeds smoothly with high efficiency so that repeated reuse can be made
- 2) No other product other than 2 amino m-xylene is formed during the course of reduction
- 3) Use of addition agents like copper sulphate, titanitic sulphate and CTAB have made the electrolytic reduction simpler as this reduction can be carried out even under the stationary electrodes.
- 4) Isolated product is extremely pure. Product of purity over 99% was obtained.

Dated the 22nd day of February 1978.

Sd/-
Asstt. Patents Officer,
Council of Scientific & Industrial Research

COMPLETE SPECIFICATION

(Section-10)

AN ELECTROCHEMICAL PROCESS FOR THE PREPARATION OF
2 AMINO m - XYLENE FROM 2 - NITRO m - XYLENE

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 :—

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This is an invention by Handady Venkatakrishna Udupa, Director; Payyallur Narayanan Anantharaman, Scientist and Michael Noel, Junior Scientific Assistant all of Central Electrochemical Research Institute, Karaikudi - 623 006, India - all Indian citizens.

This invention relates to the improvement in or relating to the electrolytic reduction of 2 nitro m-xylene to 2 amino m-xylene.

Hitherto it has been proposed to reduce 2 nitro m-xylene to 2 amino m-xylene with iron and hydrochloric acid. This is open to the following objections. Since the amine has got a tendency to complex with iron the product is not isolated quantitatively with high purity. Moreover disposal of iron oxide sludge causes a problem. The yield efficiency in the chemical method is also low (35-40%).

The object of the present investigations is to obviate these disadvantages by an electrochemical method which can give high purity product with good yield and current efficiency. In the new process developed for the reduction of 2 nitro m-xylene to 2 amino m-xylene yield upto 80% and current efficiency upto 73% are obtained.

The 2-amino-m-xylene obtained by the process of this ^{Invention} are important intermediates in the production of azo-dyes, aviation gasoline additive, use as a rubber accelerator, ^{Wetting} ~~wetting~~ agent for textiles, antioxidant for paint pigments and frothing agent in ore dressing.

AN 1081 According to the invention an electrochemical process for the preparation of 2 amino m-xylene from 2 nitro m-xylene comprises electrolytically reducing a suspension of 2 nitro m-xylene in a supporting electrolyte of sulphuric acid using an electrolytic cell with electrodes of copper as cathode, a strip of lead as anode and a porous pot as diaphragm.

The process consists in reducing a suspension of 2 nitro m-xylene in a catholyte of sulphuric acid upto a concentration of 20% (V/V) using stationery or rotating cathode of copper between 30-90°C using a range of current density 1-7 A/dm². The anolyte is sulphuric acid solution upto 40% (V/V) As diaphragm ceramic or blue asbestos is used. Lead in the pure form or alloy form either lead antimony or lead silver is used. 2-3% titanium sulphate, 0.01 - 0.1% CTAB and 0.1 - 0.5% DuSO₄ 5H₂O are used as addition agents in the catholyte to improve the electrochemical process.

In this process both stationary and rotating copper may be used as the cathode. But as shown in the examples (Examples 1 and 3) stationary cathode gives better results.

The reduction is carried out for theoretical time (6 faradays for 1 g mole) and afterwards 10% extra quantity is passed if needed to see that no smell of nitro compound is left afterwards. Reduction is carried out till more than 20 gms of nitro compound for each 100 ml of catholyte is reduced and the solution is cooled below the room temperature say 20°C when 2 amino m-xylene sulphate separates out as solid. For recycling the electrolyte, sulphuric acid is added to make the free acid content 20% (V/V). Thus the reduction is continued for the next charge also in the same manner as above. After neutralising the 2 amino m-xylene sulphate solution with ammonia or ammonium bicarbonate till the pH is brought between 7 and 8 it is filtered so that the solid hydrolysed titanium salt will be removed and the solution will contain only aqueous solution and the oily 2 amino m-xylene. The oil is separated out using a separating funnel. After removal of oil the aqueous solution is saturated with sodium chloride and the small amount of remaining oil in aqueous layer is extracted with benzene. The benzene layer is removed and subjected to evaporation over a water bath when the 2 amino m-xylene remains behind. Afterwards the whole sample of 2 amino m-xylene is purified by steam distillation.

Example 1

Conditions:

Catholyte	: 400 ml 20% H ₂ SO ₄ (V/V) + 2.4% titanitic sulphate + 0.1% copper sulphate + 0.01% CTAB
Anolyte	: 100 ml 20% H ₂ SO ₄ (V/V)
Cathode	: Rotating copper of area 0.85 dm ²
Current	: 5A.

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Current density : 5.8 A/dm²

Anode : Lead

Diaphragm : Ceramic porous pot

Temperature : 40 - 50°C

Voltage : 3.5 - 4V

Wt of 2 nitro m-xylene added : 68.4 g

Wt of 2 nitro m-xylene recovered : Nil

Wt of 2 nitro m-xylene recovered : 31.2 g

Yield : 64.8%

No. of amp hours passed : 55

Current efficiency : 51.5%

Energy consumption : 7.05 kwh/kg amine produced

Example 2

Conditions:

Catholyte : 250 ml 20% H₂SO₄ (V/V) + 2.4% titanitic sulphate + 0.1% copper sulphate + 0.01% CTAB

Anolyte : 100 ml 20% H₂SO₄ (V/V)

Cathode : Stationary copper of area 2.26 dm² (copper vessel of 9 cm diameter and 9 cm height)

Current density : 4.4 A/dm²

Current : 10 A

Anode : Lead

Diaphragm : Ceramic porous pot

Temperature : 50-60°C

Voltage : 3.5 - 4.5V

Wt of 2 nitro m-xylene added : 136.8 g

Wt of 2 nitro m-xylene recovered : Nil

Wt of 2 amine m-xylene sulphate recovered : 10 g

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Total 2 amino m-xylene recovered : 85 g
as oil
Yield : 79%
No. of amp hrs passed : 155
Current efficiency : 73%
Energy consumption : 8.2 kwh/kg amine produced

Example 3

Conditions:

Catholyte : 250 ml of 20% H_2SO_4 (V/V) + 2.4%
titanic sulphate + 0.1% $CuSO_4 \cdot 5H_2O$
0.01% CTAB.
Anolyte : 100 ml of 20% H_2SO_4 (V/V)
Cathode : Cu cathode of area 1.6 dm^2 stationary
Cathode current density : 6.25 A/ dm^2
Anode : Lead silver alloy (1% silver)
Diaphragm : Ceramic porous pot
Temperature : 45 - 50°C
Cell voltage : 4.6 - 5.0V

First electrolysis:

Wt of 2 nitro m-xylene added : 56 gms
No. of amp hrs passed : 70 A hrs
Temperature to which the catholyte : 20°C
was cooled
Amount of 2 amino m-xylene sulphate: 4.4 gms
separated out as solid

First reuse:

Amount of H_2SO_4 added : 45.0 gms
Wt of 2 nitro m-xylene added : 33.6 gms
No. of amp hrs passed : 45 A hrs
Temperature to which the catholyte : 20°C
was cooled
Amount of 2 amino m-xylene sulphate: 13.1 gms
separated out as solid

Overall result :

Total amount of 2 amino m-xylene isolated	: 55.0 gms
Yield	: 76.6%
Current efficiency	: 63.7%
Energy consumption	: 10.45 Kwh/kg

Analysis was done by estimation with standard sodium nitrite in the usual manner (Vide Laboratory Manual of Organic chemistry - B.B.Dey and M.V.Sitaraman) and found to be of 99% purity. Purity was confirmed by B.P.also. Redistilled 2 amino m-xylene has a B.P. 216°C.

The following are the main advantages of the invention:

- 1) The reduction proceeds smoothly with high efficiency so that reuse of catholyte can be made to the extent of about two.
- 2) No product other than 2 amino m-xylene is formed during the course of reduction.
- 3) Use of addition agents like copper sulphate, titanilc sulphate and CTAB have made the electrolytic reduction simpler as this reduction can be carried out even under the stationary electrodes.
- 4) The yield and efficiency are comparatively higher than the chemical method.

We Claim :

1. An electrochemical process for the preparation of 2 amino m-xylene from 2 nitro m-xylene comprises electrolytically reducing a suspension of 2 nitro m-xylene in a supporting electrolyte of sulphuric acid using an electrolytic cell with electrodes of copper as cathode, a strip of lead as anode and a porous pot as a diaphragm.
2. Process as claimed in claims 1 wherein the electrolyte when used as catholyte has a sulphuric acid concentration of 20%(V/V) and a concentration of upto 40%(V/V) when used as anolyte.
3. Process as claimed in claim 2 wherein the anolyte used has a concentration of 20% H_2SO_4 (V/V).
4. Process as claimed in any of claims 1 to 3 wherein the stationary or rotating cathode is used.
5. Process as claimed in any of the claims 1-4 wherein the porous diaphragm used is ceramic or blue asbestos.
6. Process as claimed in any of the preceding claims wherein there are added 2-3% of titanitic sulphate, 0.01 -0.1% cetyl trimethyl ammonium bromide and 0.1-0.5% of $CuSO_4 \cdot 5H_2O$ to W/V of the catholyte.
7. Process as claimed in any of the preceding claims wherein the electrochemical reduction is carried out using a current density range of 1-7A/Dm² at a temperature between 30 to 90°C preferably at 40-60°C.
8. Process as claimed in any of the preceding claims wherein anode used is of pure lead or an alloy of lead-antimony or lead silver.

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9. An electrochemical process for the preparation of 2 amino m-xylene from 2 nitro m-xylene substantially as herein described and illustrated in examples 1, 2 and 3.

Dated this 7th day of March 1979.

Sd/-
(I.M.S.MAMAK)
Scientist-in-charge(Patents)
Council of Scientific and Industrial Research.