

IMPROVEMENTS IN AND/OR RELATING TO THE ELECTROLYTIC REDUCTION OF *m*-DINITROBENZENE TO 2 : 4 DIAMINOPHENOL

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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 Venkatakrishna Udupa, Gobichetti-Palayam Srinivasan Subramanian and Kodethoor Shrivara Udupa, all of the Central Electro-Chemical Research Institute, Karaikudi, India, all Indian citizens.

This invention relates to improvements in or relating to the electrolytic reduction of *m*-dinitrobenzene to 2 : 4-diaminophenol.

Hitherto it has been proposed to employ an amalgamated cathode for the above reduction (Indian Patent No. 60865).

This is open to the objection that the overall yield of 2 : 4-diaminophenol is only of the order of 50 per cent.

The object of this invention is to obviate these disadvantages.

We have found that the total yield of 2 : 4-diaminophenol can be improved by the use of dual cathode technique for the reduction. To these ends, the invention broadly consists in subjecting *m*-dinitrobenzene to reduction at an amalgamated cathode followed by reduction at a copper cathode or *vice versa* but preferably the former. The use of such a dual cathode technique for the reduction of *m*-dinitrobenzene to 2 : 4-diaminophenol is the novel step whereby the total yield of 2 : 4-diaminophenol is improved.

The reduction is carried out in sulphuric acid at a temperature above 90°C but preferably at 95° ± 3°C.

Thus for the electrolytic reduction of *m*-dinitrobenzene to 2 : 4-diaminophenol by the use of 'dual cathode technique', an amalgamated monel cathode is used in the first stage of reduction till a current of 4 F/mol is passed, followed by the use of copper cathode in the second stage of reduction till a current of 6 F/mol is passed or *vice versa*, but preferably the former, using 50 per cent. sulphuric acid and a depolariser ratio of 1 : 18 and a temperature of 95°C.

Thus, in this technique, the first stage of the reduction of *m*-dinitrobenzene is carried out with an amalgamated monel cathode, using 50 per cent. sulphuric acid as catholyte and a depolariser ratio of 1 : 18 (1 gm of dinitrobenzene for every 18 cc of catholyte). After passing a quantity of current equal to 4F for every molecule of dinitrobenzene, electrolysis was continued changing over to a copper cathode and the required six Faradays of current passed. During the second stage of reduction 0.1 per cent. (wt/volume) of copper sulphate was added to the catholyte. On cooling the electrolyte with a mixture of ice and salt, 2 : 4-diaminophenol sulphate crystallised out. It is filtered and the electrolyte vacuum concentrated and cooled again so as to get a further crop of solids; filtered and the filtrate was made upto 50 per cent. strength and reused again. It is found that the overall yield of 2 : 4-diaminophenol by this technique is considerably higher than that in the process covered by Indian Patent No. 60865. Therefore the present investigation is a distinct improvement over the previous patent. We claim the technique of dual cathode reduction of *m*-dinitrobenzene to 2 : 4-diaminophenol as a novel feature of the process. The use of dual cathode technique does not appear to have been reported so far.

On a laboratory scale, the reduction was studied by using a disc-type monel and a disc-type copper rotating cathodes as well as a perforated cylindrical monel and copper stationary cathodes. 50% sulphuric acid has been used as the catholyte and 40% sulphuric acid as anolyte. Lead was used as anode. A wide range of current density

was employed, preferably 30 amp/dm² for rotating cathodes and 3 amp/dm² for stationary cathodes.

Procedure : The catholyte is heated to about 100°C and the *m*-dinitrobenzene added. For the first stage of reduction, an amalgamated disc-type monel cathode was used and rotated at 2000 r.p.m. After the 4 Faradays for every mole of *m*-dinitrobenzene are passed, the cathode is changed to a disc-type copper which is also rotated at about 2000 r.p.m. and the reduction carried out to the theoretical time of 6 Faradays for every mole of *m*-dinitrobenzene thus making the total current equal to 10 Faradays for every mole of *m*-dinitrobenzene. On cooling the catholyte, crude 2:4-diaminophenol sulphate is precipitated and this is filtered. The filtrate was concentrated under reduced pressure and on cooling, further separation of crude 2 : 4-diaminophenol sulphate takes place. This is also filtered and the combined precipitate is recrystallised and estimated as oxalate. The filtrate is then made up again to 50% and reused. The yields obtained for the three runs are given below :

Yield of 2 : 4-diaminophenol sulphate

	%
I use	63.3
II use	65.8
III use	64.7

This is a distinct improvement in the yields obtained as reported in the Indian Patent No. 60365.

The same reduction is also carried out using the same technique—'Dual Cathode Technique'—under stationary electrode conditions. Here the cathodes employed are perforated monel (amalgamated) and perforated copper each made out of 0.16 cm thick sheet and bent in the form of an open and cut cylinder concentric with a glass beaker. A glass stirrer was used for stirring the catholyte. The current densities employed are of the order of 1.5 amp/dm². The results obtained for the 3 runs are given below :

Yield of 2 : 4-diaminophenol sulphate

	%
I use	64.1
II use	64.7
III use	62.8

EXPERIMENTAL

(a) *Rotating cathode*.—The cell consists of 1 litre spoutless beaker into which is taken 500 cc of 50% sulphuric acid. The anolyte is 40% sulphuric acid contained in a porous pot. The cathodes are disc-type amalgamated monel and disc-type pure copper; made of 2.5 cms dia. × 0.16 cm thick discs each cathode having 6 discs and 5 spacers with a total area of nearly 0.60 sq.dm. The cathodes are rotated by a fractional horse power motor through a glass bush at 1800-2000 r.p.m. The anode is perforated lead cylinder 2.5 cm dia × 20 cm high in a porous pot. A wide range of current densities are employed but preferably a current density of 30 amp/dm² was used *m*-dinitrobenzene in the ratio of 1gm for every 18 cc of the catholyte was used. The temperature was kept at 95° ± 3°C. When an amount of current equal to 4F for every molecule of *m*-dinitrobenzene is passed, the cathode is changed from amalgamated monel to copper and the reduction is carried to completion with an amount of current equal to 6F for every mole of dinitrobenzene. It is possible to use the copper cathode first for 6F current

and then changed to amalgamated monel for the next 4F current. But the former is preferable than the latter for better yields. When copper cathode is used, 0.1% copper sulphate is also added to the catholyte.

The catholyte is then cooled, the precipitated crude 2 : 4 diaminophenol sulphate filtered and the filtrate is concentrated under reduced pressure and cooled. The precipitated crude sulphate recrystallised along with the first crop of crystals and estimated as oxalate.

EXAMPLE I

Catholyte	530 cc of 50 % sulphuric acid.
Anolyte	150 cc of 40% sulphuric acid.
m-dinitrobenzene	30 g.
Current employed	18 amp.
Voltage	4.5—5 volts.
Time of reduction with monel cathode	1 hour-4 mts.
Time of reduction with copper cathode.	1 hour-36 mts.

Results :

Yield of 2 : 4-diaminophenol sulphate	
	%
I use	63.33
II use	65.80
III use	64.70
Average current efficiency	<u>64.6%</u>

(b) *Stationary cathode.*—The cell consists of a 2 litre beaker cut to a height of 15 cms. The cathodes are perforated sheets of 0.16 cm thick monel and copper bent to a cylinder of 10 cms. dia. with a segmental gap of 5 cms. The perforations are 0.64 cms dia. at a spacing of 2.5 cms. The total effective area of immersion is nearly 4 sq. dm. The anode is similar to the one used in (a) and a porous pot is used as diaphragm and was concentric to the cathode. A range of current densities from 1 amp/dm² to 5 amp/dm² is employed but preferably 3 amp/dm². The conditions like the quantity of m-dinitrobenzene employed, the temperature of reduction, etc., are similar to (a). Here also the amalgamated monel cathode is used for an amount of current equal to 4F for every molecule of m-dinitrobenzene used and then changed to copper for the remaining period of 6F of current for every mole of dinitrobenzene. 0.1% copper sulphate is added when copper cathode is employed. A glass stirrer is used to keep the molten dinitrobenzene in a state of emulsion. Either amalgamated monel can be used first followed by copper or *vice versa* but the former is preferred for better yields of 2 : 4-diaminophenol.

EXAMPLE II

Catholyte	800 cc of 50% sulphuric acid.
Anolyte	200 cc of 40% sulphuric acid.
m-dinitrobenzene	44 g.
Current employed	12 amp.
Voltage	4.5 to 5 volts.
Time of reduction for amalgamated monel.	2 hours 24 minutes.
Time of reduction for copper cathode.	3 hours 36 minutes.

Results :

Yield of 2 : 4-diaminophenol sulphate

	%
I use	64.1
II use	64.70
III use	62.80
Average current efficiency	<u>63.9%</u>

We claim :

1. A process for the electrolytic reduction of m-dinitrobenzene to 2 : 4-diaminophenol which consists in subjecting m-dinitrobenzene to reduction at an amalgamated cathode followed by reduction at a copper cathode or *vice versa* but preferably the former.

2. A process as claimed in Claim 1, wherein an amalgamated monel cathode is used in the first stage of reduction till a current of 4 F/mol is passed, followed by the use of copper cathode in the second stage of reduction till a current of 6 F/mol is passed or *vice versa*, but preferably the former, using 50 per cent sulphuric acid and a depolariser ratio of 1 : 18 and a temperature of 95°C.

3. A process as claimed in Claim 1, or 2 wherein the reduction in sulphuric acid is carried out at a temperature above 90°C but preferably at 95±3°C.

4. A process as claimed in any of the above claims wherein an amalgamated monel cathode is used for first stage of the reduction till an amount of current equal to 4F for every molecule of m-dinitrobenzene is passed, the cathode being either rotated or kept stationary and the next stage of reduction is carried out with a copper cathode till an amount of current equal to 6F for every molecule of m-dinitrobenzene is passed, the cathode being either rotated or kept stationary.

5. A process as claimed in Claim 4, wherein the first stage of the reduction can be carried out either with an amalgamated monel or pure copper cathode and the second stage of the reduction carried out with a pure copper or an amalgamated monel cathode, both being either rotated or kept stationary but preferably the first stage is carried out with amalgamated monel followed by pure copper.

6. A process as claimed in any one of the above claims in which a wide range of current densities can be employed but preferably at 30 amp/dm² for rotating cathodes and 3 amp/dm² for stationary cathodes.

7. A process as claimed in any one of the above claims in which an anolyte of a wide range of concentration from 20 to 40% but preferably 40% sulphuric acid and perforated lead anodes are employed.

8. A process as claimed in any one of the above claims in which an addition of 0.1% copper sulphate is used in the stage of reduction with a pure copper cathode.

9. A process as claimed in any one of the above claims wherein 2 : 4 diaminophenol is recovered as sulphate on cooling the catholyte and subsequent concentration under reduced pressure and further cooling.

10. A process as claimed in Claim 9, above wherein the spent electrolyte is reused in order to economize on the use of sulphuric acid.

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