

PROVINCIAL SPECIFICATION.

IMPROVEMENTS IN AND RELATING TO THE ELECTROLYTIC REDUCTION OF M-DINITROBENZENE TO 2:4-DIAMINOPHENOL.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, 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 the invention.

THIS IS AN INVENTION BY GOBICHETTIPALAYAM SRINIVASAN SUBRAMANIAN, HANDADY VENKATAKRISHNA UDUPA AND BIMAN BIHARI DEY, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, ALL INDIAN CITIZENS.

The electrolytic reduction of m-dinitrobenzene to 2:4-diaminophenol using strong sulphuric acid has been known for a considerable time. Recently Japanese workers have described the use of 80 per cent. sulphuric acid. The use of 40 per cent. sulphuric acid and amalgamated monel or copper cathode to obtain nearly 45 per cent. yield of 2:4-diaminophenol has been patented earlier (Indian Patent No. 35328). The conditions described therein are use of stationary electrodes and low current densities. The present investigation was aimed at improving the yield and the improvements made are (i) the rotation of the cathode and consequent employment of high current densities, (ii) the use of acid concentration of fairly wide range between 30 to 50 per cent. and (iii) the reuse of the spent electrolyte so as to economise the cost of acid. The process described below gives a higher yield of aminophenol and the time of electrolysis is considerably reduced by the use of high current densities. It is not possible to pass high current densities under stationary electrode conditions. For example an yield of 14.5 per cent. only of 2:4-diaminophenol was obtained by passing 30 amp/dm.<sup>2</sup> current density when stationary cathode gave an yield of 55.9 per cent. aminophenol. We claim the rotation of the cathode as a novel feature of the process. The use of rotating cathodes in the electrolytic reduction of m-dinitrobenzene to 2:4-diaminophenol does not seem to have been reported so far.

On a laboratory scale the reduction was studied using a cylindrical cathode and the different variables investigated in order to arrive at the optimum conditions of electrolysis. Lead was the material used and in some of the experiments 1 per cent. copper sulphate was incorporated in the catholyte, so that a copper coated lead cathode was used in some reductions. Amalgamated copper and monel have also been used as rotating cathodes and the yield of 2:4-diaminophenol calculated in each case. 50 per cent. sulphuric acid has been used as the catholyte.

Procedure.

The catholyte is heated to 100° C., the m-dinitrobenzene added and the current passed for the theoretical period of time. The unreduced m-dinitrobenzene is recovered by cooling and filtering and the catholyte concentrated under reduced pressure. On cooling, the crude diaminophenol sulphate is separated and purified by recrystallisation. The actual diaminophenol content is estimated by precipitation as diaminophenol oxalate. The spent electrolyte from which the Crude diaminophenol sulphate is separated is made up again to 50 per cent. strength and reused for further electrolysis. The average yield obtained after using the acid three times for the different types of cathodes used are given below:

(1) Lead cathode with addition of copper sulphate	48.5%
(2) Amalgamated copper cathode	50.0%
(3) Amalgamated monel cathode	56.8%

EXAMPLE I.

50 per cent. sulphuric acid catholyte. 1 per cent. copper sulphate was taken in the catholyte. Cathode current density was 30 amp/dm.<sup>2</sup>. Temperature was 100° C. Depolarizer ratio (weight/vol. of catholyte) was 1:18. 100 cc. Catholyte was taken and 5.6 g. m-dinitrobenzene added. 2:4-diaminophenol sulphate was isolated as reported above. In the first run the yield was 38 per cent. The yields in the second and third runs were 52.3 per cent. and 55.3 per cent. respectively, giving an overall yield of 48.5 per cent. for the three trials using the same acid.

EXAMPLE II.

The cylindrical copper cathode used had the same dimensions as above. The copper was amalgamated by dipping it into acidic mercuric sulphate solution. 1 per cent. mercuric sulphate was also taken in the catholyte and the reduction carried out as above. The yields obtained in 3 experiments on successive use of the same catholyte were 42 per cent., 54.6 per cent. and 51.7 per cent. respectively, thereby giving an overall yield of 50 per cent. 2:4-diaminophenol.

EXAMPLE III.

Rotating monel cylindrical cathode was employed, other conditions being the same as in Example I. The yields obtained in 3 successive experiments were 52.3 per cent., 58.4 per cent. and 59.8 per cent. thereby giving an overall yield of 56.8 per cent.

The results obtained on a large scale laboratory unit will be reported in the complete specifications to be filed later.

The following are among the noteworthy features of this process:

1. A process for the electrolytic reduction of m-dinitrobenzene to 2:4-diaminophenol using 30 to 60 per cent. sulphuric acid as catholyte but preferably sulphuric acid of 50 per cent. strength.
2. A process as in 1, wherein a rotating lead cathode is used along with the addition of 1 per cent. copper sulphate in the catholyte, so that copper plated-lead acts as the effective cathode.
3. A process as in 1, wherein a rotating amalgamated copper or monel cathode is used.
4. A process as above wherein the electrolyte is heated to a temperature above the melting point of m-dinitrobenzene and preferably to 100° C.
5. A process as above wherein a wide range of cathode current density is employed but preferably 30 amp/dm.<sup>2</sup>.
6. A process as above wherein the 2:4-diaminophenol is recovered as sulphate by concentrating the catholyte under reduced pressure and cooling.
7. A process as in 6, wherein the spent electrolyte is made up to 50 per cent. sulphuric acid and reused so as to economise the use of acid and to increase the overall yield of 2:4-diaminophenol.
8. A process as in any of the above wherein 20 to 40 per cent. sulphuric acid is used as anolyte but preferably 40 per cent. sulphuric acid.

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TO 2:4-DIAMINOPHENOL.

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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 GOBICHETTIPALAYAM SRINIVASAN SUBRAMANIAN, HANDADY VENKATA-  
KRISHNA UDUPA AND BIMAN BIHARI DEY, ALL OF THE CENTRAL ELECTROCHEMICAL 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.

The electrolytic reduction of m-dinitrobenzene to 2:4-diaminophenol using strong sulphuric acid has been known for a considerable time. Recently Japanese workers have described the use of 80 per cent. sulphuric acid. The use of 40 per cent. sulphuric acid and amalgamated monel or copper cathode to obtain nearly 45 per cent. yield of 2:4-diaminophenol has been patented earlier (Indian Specification No. 35328). The conditions described therein are use of stationary electrodes and low current densities.

The present investigation was aimed at improving the yield and the improvements made are (i) the rotation of the cathode and consequent employment of high current densities, (ii) the use of acid concentration of fairly wide range between 30 to 60 per cent. and (iii) the reuse of the spent electrolyte so as to economise the cost of acid.

The present invention consists in the electrolytic reduction of m-dinitrobenzene to 2:4-diaminophenol using 30 to 60 per cent. sulphuric acid as catholyte but preferably sulphuric acid of 50 per cent. strength, and wherein a rotating cathode is employed. The process described below gives a higher yield of aminophenol and the time of electrolysis is considerably reduced by the use of high current densities. It is not possible to pass high current densities under stationary electrode conditions. For example an yield of 14.5 per cent. only of 2:4-diaminophenol was obtained by passing 30 amp/dm.<sup>2</sup> current density when stationary cathode was used and the use of a rotating cathode gave an yield of 55.9 per cent. aminophenol. We claim the rotation of the cathode as a novel feature of the process: the use of rotating cathodes in the electrolytic reduction of m-dinitrobenzene to 2:4-diaminophenol does not seem to have been reported so far.

On a laboratory scale the reduction was studied using a cylindrical cathode and the different variables investigated in order to arrive at the optimum conditions of electrolysis. Lead was the material used and in some of the experiments 1 per cent. copper sulphate was incorporated in the catholyte, so that a copper coated lead cathode was used in some reductions. Amalgamated copper and monel have also been used as rotating cathodes and the yield of 2:4-diaminophenol calculated in each case. 50 per cent. sulphuric acid has been used as the catholyte.

#### Procedure.

The catholyte is heated to 100° C., the m-dinitrobenzene added and the current passed for the theoretical period of time. The unreduced m-dinitrobenzene is recovered by cooling and filtering and the catholyte concentrated under reduced pressure. On cooling, the crude diaminophenol sulphate is separated and purified by recrystallisation. The actual diaminophenol content is estimated by precipitation as diaminophenol oxalate. The spent electrolyte from which the crude diaminophenol sulphate is separated is made up again to 50 per cent. strength and reused for further electrolysis. The average yield obtained after using the acid three times for the different types of cathodes used are given below:

- |   |       |
|---|-------|
| (1) Lead cathode with addition of copper sulphate | 48.5% |
|---|-------|

#### EXAMPLE I.

A cylindrical cathode of lead  $\frac{1}{2}$ " diameter and 5" long was used and rotated by means of a fractional horse power motor inside a porous pot which acted as cathode chamber. The pot was kept inside a beaker which served as anode chamber with a cylindrical lead anode. 40 per cent. sulphuric acid was the anolyte and 50 per cent. sulphuric acid catholyte. 1 per cent. copper sulphate was taken in the catholyte. Cathode current density was 30 amp/dm.<sup>2</sup>. Temperature was 100°C. Depolarizer ratio (weight/vol. of catholyte) was 1:18. 100 cc. catholyte was taken and 5.6 g. m-dinitrobenzene added. 2:4-diaminophenol sulphate was isolated as reported above. In the first run the yield was 38 per cent. The yields in the second and third runs were 52.3 per cent. and 55.3 per cent. respectively, giving an overall yield of 48.5 per cent. for the three trials using the same acid.

#### EXAMPLE II.

The cylindrical copper cathode used had the same dimensions as above. The copper was amalgamated by dipping it into acidic mercuric sulphate solution. 1 per cent. mercuric sulphate was also taken in the catholyte and the reduction carried out as above. The yields obtained in 3 experiments on successive use of the same catholyte were 42 per cent., 54.6 per cent. and 51.7 per cent. respectively, thereby giving an overall yield of 50 per cent. 2:4-diaminophenol.

#### EXAMPLE III.

Rotating monel cylindrical cathode was employed, other conditions being the same as in Example I. The yields obtained in 3 successive experiments were 52.3 per cent., 58.4 per cent. and 59.8 per cent. thereby giving an overall yield of 56.8 per cent.

#### Large laboratory scale preparation of 2:4-diaminophenol.

The cell set up is represented in Figure 1 of the accompanying drawings. A is a ceramic vessel (glazed) 11" inside diameter, 12" outer diameter and 5 $\frac{1}{2}$ " deep, having a capacity of 5 litres. It contains a lead-lined wooden cover E, 12 $\frac{1}{2}$ " outer diameter and  $\frac{1}{2}$ " thick covered with 1/8" thick lead sheet. There is a groove on the wooden cover which fits tightly on the cell and 1/16" thick klingeite gasket is introduced between the cell and the cover. Two porous pots B, B, (unglazed) serve as anode chambers. The anodes are perforated lead sheets (1/8" x 1 $\frac{1}{2}$ " x 10"). The cathode is amalgamated monel disc type (C). Amalgamation is done by dipping in 10 per cent. mercuric sulphate solution prepared by dissolving 100 g. of mercuric sulphate in concentrated sulphuric acid and making up to one litre. Temperature is read from the thermometer T.

The cell is assembled as shown in the figure. 4-4 $\frac{1}{2}$  litres of 50 per cent. H<sub>2</sub>SO<sub>4</sub> (strength measured by titration against standard alkali as well as by specific gravity) is taken into the cell. It is heated to 100° C. by means of an immersion heater (H), 750 watts capacity with 30 gauge nichrome wire and 3 $\frac{1}{2}$ " immersion depth. As soon as the temperature is reached, 220-250 g. of dinitrobenzene (1 g. for every 18 cc. of acid) is melted separately and taken into the cell. The catholyte also contained an addition of 1 per cent. mercuric sulphate. The amalgamated cathode is rotated at 2000 r.p.m. by means of a fractional horse power motor adjusted through a variac. Anolyte consists of 40 per cent.

generator of capacity 300 amp. at 6 volts. A current of 60 amps. is passed for the theoretical time. The voltage across the cell varied between 3.8-4.2. The temperature was almost remaining steady, a slight decrease can be raised by the immersion heater. When the reduction is over, the electrolyte is cooled, the cathodes and anodes are dismantled. It is found that no dinitrobenzene is generally left un-reduced. The catholyte is then vacuum concentrated till more than 1/3 of the volume is reduced. The electrolyte is then cooled in ice and salt mixture, the separated solid is then filtered and pressed

lized from minimum quantity of water after treatment with animal charcoal. White crystalline needle like sulphate is obtained which is estimated as oxalate by the method suggested by Dey *et al.* The filtrate is then made up to a strength of 50 per cent. free acid by estimating against standard alkali and re-used for the 2nd and 3rd times. After the third run, it is found that the yield decreases and as such the acid may be discarded.

The yield obtained in one complete run with the present set up are:

1st run :

Acid taken . . . . .	4500 cc.
m-dinitrobenzene taken . . . . .	250 g.
yield of crude sulphate . . . . .	= 284.2 g.
1.3547 g. of sulphate gave . . . . .	= 0.7789 of oxalate
Total oxalate from the crude sulphate . . . . .	= 163.2 g.
Theoretical yield of oxalate . . . . .	= 318.2 g.
	163.2
Therefore yield . . . . .	= $\frac{\quad}{318.2} \times 100$
	= 51.3%

2nd run :

Acid taken . . . . .	4500 cc.
m-dinitrobenzene taken . . . . .	250 g.
yield of crude sulphate obtained . . . . .	296.8 g.
1.8948 g. of sulphate gave . . . . .	= 1.1188 g. of oxalate
296.8 g. of sulphate should give . . . . .	= 175.4 g.
Theoretical yield . . . . .	= 318.2 g.
Therefore yield . . . . .	= 55.1%

3rd run :

Acid taken . . . . .	4500 cc.
m-dinitrobenzene taken . . . . .	250 g.
yield of crude sulphate obtained . . . . .	318.2 g.
Now 1.5364 g. of crude sulphate gave . . . . .	= 0.9160 g. of oxalate
Total oxalate obtained . . . . .	= 189.8 g.
Theoretical yield . . . . .	= 318.2 g.
Therefore yield . . . . .	= 59.6%
Average yield of 3 51.3, 55.1, 166.05	
59.6 experiment. . . . .	= $\frac{\quad}{3}$
	= 55.3%

The yield under these conditions were confirmed independently from a smaller cell of 3 litres capacity. Acid taken was 1800 cc. and m-dinitrobenzene 100 g., the other conditions being same. The yield obtained are:

1st run	=51.7%
2nd run	=55.3%
3rd run	=57.3%
<hr/>	
164.3	
<hr/>	=54.8%
3	
<hr/>	

The yield decreases after this and hence not reported.

We claim:

1. A process for the preparation of 2:4-diaminophenol which consists in the electrolytic reduction of m-dinitrobenzene using 30 to 60 per cent. sulphuric acid as catholyte but preferably sulphuric acid of 50 per cent. strength, and wherein a rotating cathode is employed.

2. A process as claimed in Claim 1 wherein a rotat-

copper plated-lead acts as the effective cathode.

3. A process as claimed in Claim 1, wherein a rotating amalgamated copper or mercuric cathode is used.

4. A process as claimed in any of the preceding claims wherein the electrolyte is heated to a temperature above the melting point of m-dinitrobenzene and preferably to 100° C.

5. A process as claimed in any of the preceding claims wherein a wide range of cathode current density is employed but preferably 30 amp/dm.<sup>2</sup>.

6. A process as claimed in any of the preceding claims wherein the 2:4-diaminophenol is recovered as sulphate by concentrating the catholyte under reduced pressure and cooling.

7. A process as claimed in Claim 6, wherein the spent electrolyte is made up to 50 per cent. sulphuric acid and reused so as to economise the use of acid and to increase the overall yield of 2:4-diaminophenol.

8. A process as claimed in any of the preceding claims wherein 20 to 40 per cent. sulphuric acid is used as anolyte but preferably 40 per cent. sulphuric acid.

R. BHASKAR PAI.

Patent Officer,

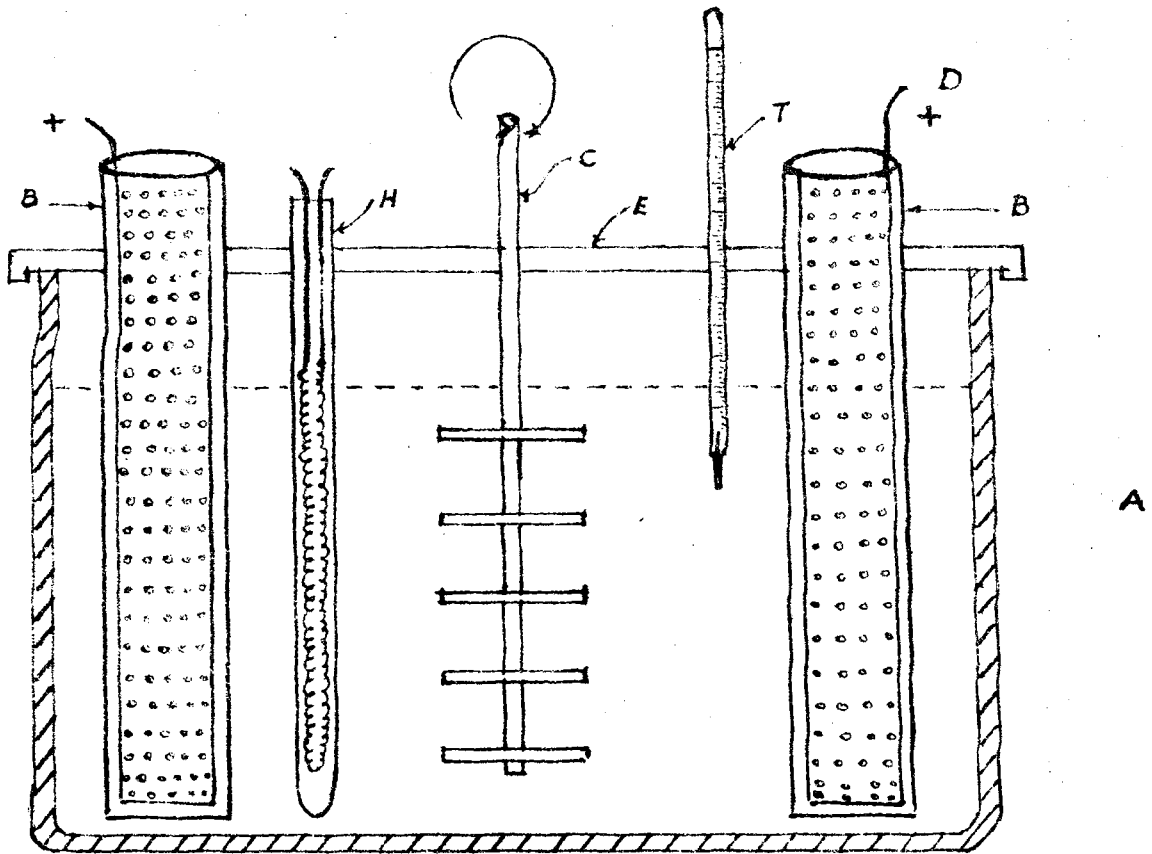


Fig. 1.

