This is an invention by HANANDY UENDATAKRISHNA UDUPA, GOBICHETTIPALAYAM SRINIVASAN SUBRAMANIAN and PAYYALUR NARAYANAN ANANTHARAMAN, all of the Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India, all Indian citizens.

This invention relates to the improvements in or relating to the electrolytic reduction of nitrobenzene to aniline.

The electrochemical methods so far employed use only stationary cathodes operating at low current densities and high anode area cells require larger flow space and considerable time was taken for completing the reduction.

The object of this investigation is to obviate these disadvantages by reducing nitrobenzene electrochemically using the rotating cathode technique and some suitable addition agents. By this technique, the design of high anode area cell is made easier. The reduction proceeds smoothly even at high current density ranges employed.

To these ends, the invention broadly consists in reducing a suspension of nitrobenzene in a catholyte of sulphuric acid or sodium sulphate but preferably the former up to a concentration of 10% with 0.1% copper sulphate using a rotating cathode of copper or zinc or tin but preferably copper in a divided cell. The reduction is further carried out at temperatures up to 70°C but preferably between 50-55°C using a range of current density up to 40 amp/dm² but preferably at 20 amp/dm². The electrolyte is dilute sulphuric acid up to 30% strength but preferably 20%. A ceramic porous pot is used as a diaphragm material and lead is the anode. Addition agents like ferrous sulphate, EDTA, titanic chloride or titanic sulphate are added but preferably titanic sulphate of concentration up to 5 per cent based on the volume of the catholyte but preferably one per cent is added to the catholyte. After the reduction is over, the catholyte is steam distilled to recover any unreacted nitrocompound and then neutralised with alkali such as ammonia, caustic soda or sodium carbonate or ammonium bicarbonate or ammonium carbonate up to pH=7, when the aniline separates out as an oil. It is again steam distilled and recovered as free oil. The distillate is further extracted with a suitable solvent preferably benzene to make a complete recovery of the product.
The following typical examples are given to illustrate the invention:

**EXAMPLE 1**

- Catholyte: 500 c.c. of 10% sulphuric acid
- Cathode: Rotating cylindrical type copper area = 0.8 dm²
- Nitrocompound taken: 120 gms.
- Temperature: 70-75°C
- Anolyte: 150 c.c. of 10% sulphuric acid
- Anode: Perforated lead
- Diaphragm: Ceramic porous pot
- Current: 20 amp.
- Cathode current density: 23 amp./dm²
- Cell voltage: 5.5-6.5 V
- Duration: 8 hours
- Wt. of titania sulphated added to catholyte: 4.2 gms. (as TiO₂)
- Wt. of CuSO₄·H₂O added to catholyte: 0.5 gms. (0.1%) 
- Nitrocompound recovered: Nil
- Aniline recovered: 75.8 gms.
- % Assay yield: 87.8%
- Total aniline estimated: 81.3 gms.
- % Yield: 89.5%
- Unaccounted nitrobenzene: 12.6 gms.
- % Nitrobenzene unaccounted: 10%
- Energy consumption: 9 Kwh/kg.

**EXAMPLE II**

- Conditions: Same as Example I
- Aniline recovered: 78.7 gms.
- % Assay yield: 86.7%
- Total aniline estimated: 80.0 gms.
- % Yield: 88.1%
- Unaccounted nitrobenzene: 14.3 gms.
- % nitrobenzene unaccounted: 11.2%

The following are the main advantages of the invention:

1. The use of rotating cathode enables employment of high current densities which increases the cell capacity.
2. The use of titania sulphate in the electrolyte increases the reduction efficiency.

_Dated this 4th day of September, 1970._

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1. The invention relates to the improvements in/or relating to the electrolytic reduction of nitrobenzene to aniline which will be useful in the dyestuff and pharmaceutical industries.

2. Hitherto it has been proposed to reduce nitrobenzene by chemical methods using iron and hydrochloric acid or by vapour phase reduction using a suitable catalyst or electrochemically using stationary-cathodes operating at low current densities.

3. These are open to objection in that by the chemical methods using iron and hydrochloric acid, considerable amount of sludge is obtained when aniline is being recovered by neutralisation and the disposal of the sludge will be a difficult problem. Moreover, more than three times the stoichiometric quantity of iron and a large excess of acid are required. Being a chemical reaction, it is not amenable to control and the cost of cooling the reaction is prohibitive. In the vapour phase reduction, high pressure autoclaves are necessary involving sophisticated equipments and a supply of pure hydrogen gas at high pressures. The life of catalyst is unpredictable and even traces of impurities lower the catalyst activity. Yield of aniline is affected by the formation of cyclohexylamine the formation of which is difficult to be avoided.

The electrolytic methods using stationary electrodes invariably employ low current densities and the design of high anode gap cells are rather difficult since they require larger floor space and higher investment costs.

4. The main object of the invention is to overcome these difficulties by reducing a suspension of nitrobenzene in a supporting electrolyte of sulphuric acid and suitable addition agents, using the rotating cathode technique. By this technique, it is possible to employ large current densities which has simplified the design of high anode gap cells and scale-up to any desired capacity.

5. It is found that by this technique it is possible to reduce a suspension of nitrobenzene in a supporting electrolyte of preferably sulphuric acid (upto 25% concentration v/v) using rotating cathode of copper. The catholyte contains a hydrogen carrier in the form of tannic sulphate which is added up to a concentration of 50 gms/litre calculated as titanium dioxide. The reduction is carried out at temperatures less than 40°C using a current density range up to 15 amp/dm². The reduction proceeds almost quantitatively and the yields of aniline up to 90% are obtained. The formation of p-aminophenol under these conditions was low (upto 5%).

6. As a result of the invention, it is possible to reduce a suspension of nitrobenzene in a supporting electrolyte of sulphuric acid using a rotating electrode of copper with high efficiencies. The reduction can be carried out in an aqueous medium at room temperature and at atmospheric pressure. No complicated equipments are needed and the processes of isolation is equally simple. The yield of aniline is high and very little formation of p-cyclohexylamine was observed.

7. The use of rotating cathode technique simplifies the scale up of cells to any desired capacity. The reduction efficiency is increased by addition of 0.1% copper sulphate to the catholyte and the use of tannic sulphate as hydrogen carrier.

8. The invention relates to the improvements in/or relating to the electrolytic reduction of nitrobenzene to aniline in a supporting electrolyte of a mineral acid preferably sulphuric acid up to a concentration of 25% (by volume) using rotating electrodes of copper and employing tannic sulphate as addition agent preferably up to a concentration of 50 calculated as TiO₂/litre.

9. The reduction is carried out in a divided cell at current densities up to 20 amp/dm² and preferably at 10 amp/dm² and at temperatures less than 40°C but preferably between 20 and 30°C.

10. To these ends, the invention broadly consists in reducing a suspension of nitrobenzene in a catholyte, a mineral acid, preferably sulphuric acid up to a concentration of 25% by volume containing tannic sulphate preferably up to a concentration of 5% gms. of titanium dioxide per 100 cc. of catholyte. The catholyte also contains 0.1% copper sulphate in order to give a spotty deposit of copper on the cathode. The reduction is carried out with a rotating cathode of copper, zinc or tin or lead but preferably copper. The reduction is carried out at a current density up to 40 amp/dm² but preferably 10 amp/dm² and at temperatures 40°C but preferably between 20-25°C. The catholyte is a dilute mineral acid but preferably sulphuric acid up to a concentration of 30% v/v but preferably 20% v/v. Theoretical quantity of current was passed (215-4 amp, hrs. for 100 gms. and 312.7 amp, hrs. for 240 gms.) after which the catholyte is stunned distilled to recover any unreacted nitrobenzene and further neutralised with an alkali preferably ammonia and the aniline is recovered by steam distillation followed by salting out the distillate and/or solvent extraction preferably with benzene.
11. The following examples are given to illustrate the invention.

**EXAMPLE I**

<table>
<thead>
<tr>
<th>Volume of catholyte</th>
<th>900 ml of 25% sulphuric acid (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of nitrobenzene taken</td>
<td>150 c.c.</td>
</tr>
<tr>
<td>Area of copper cathode (rotating disc type)</td>
<td>1.8 dm²</td>
</tr>
<tr>
<td>Current density</td>
<td>10 amp/dm²</td>
</tr>
<tr>
<td>Current passed</td>
<td>18 amp</td>
</tr>
<tr>
<td>Volume of titaniu-sulphate added</td>
<td>100 ml containing 15% titanius sulphate in 23% sulphuric acid</td>
</tr>
<tr>
<td>Cell voltage</td>
<td>5 volts</td>
</tr>
<tr>
<td>Temperature</td>
<td>25-30°C</td>
</tr>
<tr>
<td>Anolyte</td>
<td>25% sulphuric acid (v/v) 100 ml.</td>
</tr>
<tr>
<td>Anode</td>
<td>Lead</td>
</tr>
<tr>
<td>Weight of copper sulphate added to catholyte</td>
<td>1 gm.</td>
</tr>
<tr>
<td>Weight of nitrobenzene un-reduced</td>
<td>Nil</td>
</tr>
<tr>
<td>Weight of aniline recovered as free oil</td>
<td>122.4 gms.</td>
</tr>
<tr>
<td>Weight of total aniline as estimated</td>
<td>129.6 gms.</td>
</tr>
<tr>
<td>Current efficiency based on total aniline estimated</td>
<td>95.2%</td>
</tr>
<tr>
<td>Assay yield</td>
<td>90%</td>
</tr>
<tr>
<td>Energy consumption</td>
<td>7.8 Kwh/kg. of nitrobenzene</td>
</tr>
</tbody>
</table>

**CONDITIONS** same as Example I

| Weight of nitrobenzene taken | 240 gms. |
| Weight of nitrobenzene un-reduced | Nil |
| Weight of aniline recovered as free oil | 163.2 gms. |
| Weight of aniline estimated | 169.8 gms. |
| Current efficiency based on the total aniline estimated | 93.6% |
| Assay yield | 88.7% |
| Energy consumption | 8.5 Kwh/kg. of nitrobenzene |

12. The following are the main advantages of the invention:

(a) The reduction of nitrobenzene to aniline is smoothly carried out in an aqueous medium at room temperature and at atmospheric pressures and high yields of aniline are obtained without any bye products or sludge formation.

(b) No complicated equipments are needed such as high pressure autoclave, hydrogen generator, compressors as in the case of vapour phase reduction.

(c) The use of rotating cathode simplifies the design of high anapcege cells and scale up of cells to any desired capacity involving cells having lower floor space is possible on account of the higher current that could be passed on a smaller area of the cathode surface.

13. The invention consists in reducing a suspension of nitrobenzene in a supporting electrolyte of dilute sulphuric acid preferably 25% concentration (v/v) in the presence of titanium sulphate using a rotating cathode of copper. The temperature is kept between 20-30°C and the reduction is carried at current densities up to 10 amp/dm². By this technique high yields of aniline are obtained and practically no other bye products. The product isolation is simple and the process does not require any complicated equipment.
We Claim:

1. A process for the electrolytic reduction of nitrobenzene to aniline which consists in electrically reducing a suspension of nitrobenzene in a supporting electrolyte of sulphuric acid containing titanous sulphate using copper cathode at current densities upto 20 amp/dm² and temperatures of 20-30°C, the solution is then neutralised with alkali and aniline is recovered by steam distillation.

2. A process as claimed in claim 1 wherein electrolytic reduction is carried out involving the use of titanous sulphate and rotating cathodes.

3. A process as claimed in claim 1 for the electrolytic reduction of nitrobenzene to aniline which comprises in electrolytically reducing a suspension of nitrobenzene to aniline in a supporting electrolyte of a mineral acid preferably sulphuric acid up to a concentration of 25% v/v using rotating cathode of copper and anode of lead and employing titanous sulphate as addition agent preferably upto a concentration of 50 gms calculated as titanumoxide per litre of catholyte using current densities upto 20 amp/dm² but preferably 10 amp/dm² and temperatures less than 40°C, but preferably between 20-30°C.

4. A process as claimed in any of the preceding claims in which 0.1% of copper sulphate is added to the catholyte.

Dated this 5th day of June, 1971.

Sd.
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