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"IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC REDUCTION OF NITROBENZENE TO ANILINE".

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).

PROVISIONAL SPECIFICATION
SECTION—4

The following specification describes the nature of this invention :—

This is an invention by HANDADY VENKATAKRISHNA 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 amperage 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 amperage 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 upto a consideration 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 upto 70°C but preferably between 50-55°C using a range of current density upto 40 amp/dm^2 but preferably at 20 amp/dm^2. The anolyte is dilute sulphuric acid upto 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, titanous chloride or titanous sulphate are added but preferably titanous 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 unreduced nitrocompound and then neutralised with alkali such as ammonia, caustic soda or sodium carbonate or ammonium bicarbonate or ammonium carbonate upto 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.

PRICE : TWO RUPEES

The following typical examples are given to illustrate the invention :

EXAMPLE I

Catholyte	:	500 c.c. of 10% sulphuric acid
Cathode	:	Rotating cylindrical type copper area=0.8 dm^2
Nitrocompound taken	:	120 gms.
Temperature	:	50-55°C
Anolyte	:	150 c.c. of 10% sulphuric acid
Anode	:	Perforated lead
Diaphragm	:	Ceramic porous pot
Current	:	20 amp.
Cathode current density	:	25 amp/dm^2
Cell voltage	:	5.5-6.5 V
Duration	:	8 hours
Wt. of titanous sulphated added to catholyte	:	4.3 gms. (as TiO_2)
Wt. of $CuSO_45H_2O$ added to catholyte	:	0.5 gm. (0.1%)
Nitrocompound recovered	:	Nil
Aniline recovered	:	79.8 gms.
% Assay yield	:	87.8%
Total aniline estimated	:	81.3 gms.
% Yield	:	89.5%
Unaccounted nitrobenzene	:	12.6 gms.
% Nitrobenzene unaccounted	:	10%
Energy consumption	:	8 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 titanous sulphate in the electrolyte increases the reduction efficiency.

Dated this 4th day of September, 1970.

Sd.
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COMPLETE SPECIFICATION

SECTION—4

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

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 metods using stationary electrodes invariably employ low current densities and the design of high amperage 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 amperage 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 titanous sulphate which is added up to a concentration of 50 gms/litre calculated as titanium dioxide. The reduction is carried at temperatures less than 40°C using a current density range upto 15 amp/sq.dm The reduction proceeds almost quantitatively and the yields of aniline upto 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-aminophenol and practically no formation of 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 titanous 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 upto a concentration of 25% (by volume) using rotating electrodes of copper and employing titanous sulphate as addition agent preferably up to a concentration of 50 calculated as TiO_2/litre.

9. The reduction is carried out in a divided cell at current densities upto 20 amp/dm^2 but preferably at 10 amp/dm^2 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 upto a concentration of 25% by volume containing titanous sulphate preferably upto a concentration of 5·0 gms. of titanium dioxide per 100 cc. of catholyte. The catholyte also contains 0·1% copper sulphate in order to give a spongy 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 upto 20 amp/dm^2 but preferably 10 amp/dm^2 and at temperaturec 40°C but preferably between 20–30°C. The anolyte is a dilute mineral acid but preferably sulphuric acid upto a concentration of 30% v/v but preferably 20% v/v. Theoretical quantity of current was passed (235·4 amp. hrs. for 180 gms. and 313·7 amp. hrs. for 240 gms.) after which the catholyte is steam distilled to recover any unreduced 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

Volume of catholyte	900 ml. of 25% sulphuric acid (v/v)
Volume of nitrobenzene taken	150 c.c.
Area of copper cathode (rotating disc type)	1.8 dm^2
Current density	10 amp/dm^2
Current passed	18 amp
Volume of titanous sulphate added	100 ml. containing 15% titanous sulphate in 23% sulphuric acid
Cell voltage	5 volts
Temperature	25-30°C
Anolyte	25% sulphuric acid (v/v) 100 ml.
Anode	Lead
Weight of copper sulphate added to catholyte	1 gm.
Weight of nitrobenzene unreduced	Nil
Weight of aniline recovered as free oil	122.4 gms.
Weight of total aniline as estimated	129·6 gms.
Current efficiency based on total aniline estimated	95.2%
Assay yield	90%
Energy consumption	7.8 Kwh/kg. of nitrobenzene

EXAMPLE II

CONDITIONS same as Example I	
Weight of nitrobenzene taken	240 gms.
Weight of nitrobenzene unreduced	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 autoclaves, hydrogen generator, compressors as in the case of vapour phase reduction.

(c) The use of rotating cathode simplifies the design of high amperage 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 titanous sulphate using a rotating cathode of copper. The temperature is kept between 20-30°C and the reduction is carried at current densities upto 10 amp/dm^2. 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/dm^2 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 upto 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 titaniumdioxide per litre of catholyte using current densities upto 20 amp/dm^2 but preferably 10 amp/dm^2 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.

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Adarsh Bharat Printers, Meerut.