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" AN ELECTROCHEMICAL PROCESS FOR THE PRODUCTION OF PARA TOLUIDINE FROM PARA NITROTOLUENE".

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(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 :-

PRICE : TWO RUPEES

This invention relates to an electrochemical process for the production of P-toluidine from P-nitro toluene which relates to the field of organic chemical industry with special reference to intermediate for dyestuff industries.

Hitherto it has been proposed to produce para toluidine chemically by employing generally zinc or iron powder for the reduction of p-nitrotoluene. It has been mentioned that p-toluidine can be prepared electrochemically employing stationary copper cathodes for the reduction of p-nitrotoluene.

The process hitherto reported in literature suffers from the following drawbacks: (1) It is rather tedious and laborious to separate the product from the reactants while employing chemical reducing agents; (2) The electrolytic method reported so far gives low amine content of the products and aminophenols are also obtained as byproducts which are to be separated.

The main object of the invention is to obviate the drawbacks by adopting an improved electrochemical reduction technique.

According to the present invention chemical reducing agents are avoided by using either stationary or rotating copper cathode for the electrolytic reduction of p-nitrotoluene to produce p-toluidine.

The present process is superior to the chemical processes, hitherto described in literature, since it not only eliminates the tedious and laborious process of separating the product from the reactants, but also gives a very pure product. This process is also superior to the electrochemical methods, hitherto described in literature, since high yield of amine is obtained and aminocresols are not formed, thus eliminating problems concerned with their separation. Additional advantages established by us are (a) the product is separated as amino-sulphate and that can be separately neutralised to get the amine. Thus isolation of the product is simplified and the cost of neutralisation is reduced; (b) the electrolyte can be reused at least a minimum of three times, after making up the acid concentration without affecting the efficiency of the process; (c) the employment of a copper container

as the cell which itself will act as cathode would help in the design of high amperage cells in order to adopt the process for large scale preparations.

Accordingly the process for the electrochemical preparation of p-toluidine from para nitrotoluene which consists in the electrolytic reduction of p-nitrotoluene using a copper cathode, either stationary or rotating and a lead ~~and~~ or lead alloy anode separated from the catholyte by means of a porous diaphragm characterised in that the electrolysis carried out using 27 to 54% (W/V) of sulphuric acid containing 0.5 to 1.5% of TiO_2 as catalyst present in the form of titanic sulphate as catholyte and 35 to 54% (W/V) of sulphuric acid as anolyte.

The present invention consists in the electrolytic reduction of p-nitrotoluene to give p-toluidine in an electrolytic cell fitted with either stationary or rotating copper cathode or in an electrolytic cell made of copper which acts also as the cathode. The catholyte was separated from the anolyte by means of a ceramic porous diaphragm. The catholyte employed a was dilute sulphuric acid the concentration of which could vary from 27 to 54% (W/V) containing titanic sulphate solution as catalyst. Sulphuric acid of concentration which could vary from 35 to 54% (W/V) was used as anolyte and the anode was lead or an alloy of lead and silver with 0.5 to 1% silver. A current density of 5 to 20 A/dm^2 in the case of stationary cathode and 10 to 30 A/dm^2 with rotating cathode could be employed. The temperature of catholyte could vary from 50 to 65°C. The depolariser concentration was kept between 15 and 25%. Since aminocresols are not formed, the product is free from impurities and separation is easier. A current efficiency of 75 to 85% and an yield of 85 to 95% could be obtained.

Example 1: Electrolytic preparation of p-toluidine from p-nitrotoluene

~~xxx~~ 1.5 litres of 45% (W/V) sulphuric acid containing titanic sulphate solution as catalyst was taken in cylindrical copper vessel of 2.5 litres capacity which acted also as the cathode. A ceramic porous pot was employed as the diaphragm in which 175 ml of 45% (W/V) of sulphuric acid was taken as the anolyte. A lead strip was used as anode. The solution was stirred vigorously by means of a mechanical stirrer. A cathode current density of 5 A/dm^2 was employed. 300 g

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of p-nitrotoluene was reduced. Temperature was maintained between 55 and 60°C. Voltage of the cell was 3 to 4 V. After passing 415 amp hrs the catholyte was cooled to 5°C and the amine sulphate was separated by

filtration. The solid amine salt was dissolved in water and neutralised with soda ash to pH 7. The separated amine was filtered washed with ice cold water and dried. Amine obtained was 216 g with an yield of 92% and a current efficiency of 78%. Purity 97%.

Example 2 : Electrolytic preparation of p-toluidine from p-nitrotoluene - reuse of the catholyte from example 1

Experimental set up and conditions are the same as that given in example 1; catholyte after separation of amine sulphate in example 1 was reused in which 75 ml conc. sulphuric acid was added. 320 g of p-nitrotoluene was reduced. 412 amp hrs was employed. Voltage of the cell was 3 to 4 volts. The amine sulphate was separated after cooling the catholyte and then it was neutralised to get the free base. 228 g of p-toluidine was obtained with an yield of 91.2% and current efficiency of 83.2%. Purity 98%

Example 3 : Electrolytic preparation of p-toluidine from p-nitrotoluene using a rotating copper cathode

1.5 litres of 36% (W/V) of sulphuric acid containing titanic sulphate to the equivalent of 1% TiO_2 was taken in a 3 litre pyrex beaker. A rotating disc type copper cathode was employed. The r.p.m. was kept between 1000 to 1500. A ceramic porous diaphragm was used to separate the catholyte from the anolyte. A lead silver alloy strip was used as the anode. 200 ml of 45% (W/V) sulphuric acid was taken in the diaphragm as the anolyte. 300 g of p-nitrotoluene was reduced. The temperature of the catholyte was kept between 50 and 55°C. A cathode current density of 20 A/dm^2 was employed. Voltage of the cell was 3 to 4 V. After passing 400 A hrs, the catholyte was cooled to 5°C. The solid amine sulphate was separated by filtration and then neutralised seperately to get the free base. 190 g of p-toluidine was isolated with an isolated yield of 85.4% and current efficiency of 77%. Purity of p-toluidine isulated was 98%.

A process has been invented for the electrolytic production of p-toluidine from p-nitrotoluene. This process eliminates the difficulties of conventional methods which involve tedious and laborious methods of separation and purification of the product. The employment

of copper container which itself acts as cathode would help in the design of high amperage cells in order to adopt the process for large scale operation. The possibility of reusing the electrolyte constitutes to economy in the process.

WE CLAIM:

1) A process for the electrochemical preparation of p-toluidine from para nitrotoluene which consists in the electrolytic reduction of p-nitrotoluene using a copper cathode, either stationary or rotating and a lead ~~and~~ or lead alloy anode separated from the catholyte by ~~means~~ means of a porous diaphragm characterised in that the electrolysis is carried out using 27 to 54% (W/V) of sulphuric acid containing 0.5 to 1.5% of TiO_2 as catalyst present in the form of titanic sulphate as catholyte and 35 to 54% (W/V) of sulphuric acid as anolyte.

2) A process as claimed in claim (1) wherein a lead or lead silver alloy with 0.5 to 1% silver is used as anode.

3) A process as claimed in (1) wherein a cathode current density of 5 to 20 A/dm^2 in the case of stationary cathode, ~~but preferably~~ and 10 A/dm^2 ~~and~~ to 30 to 30 A/dm^2 in the case of rotating cathode, ~~but~~ preferably 20 A/dm^2 is used.

4) A process as claimed in (1) wherein the temperature range of the catholyte used is 50 to 65°C but preferably 55 to 60°C.

5) A process as claimed in (1) wherein copper cathode is stationary and an auxillary stirrer is employed or copper container is ~~used~~ used acting both as the cell and cathode.

6) A process for the electrochemical preparation of p-toluidene from para nitrotoluene substantialy as herein described.

Dated this 3rd day of December, 1976.

(I.M.S. MAMAK)
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