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IMPROVEMENTS IN OR RELATING TO THE ELECTRO-CHEMICAL
PREPARATION OF O-TOLUIDINE SULPHATE FROM O-NITROTOLUENE

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg,
New Delhi 1, India, an Indian registered body incorporated
under the Registration of Societies Act (Act XIX of 1960).

The following specification describes the nature of this
invention:

This is an invention by Handady Venkatakrishna Vempu,
Scientist, Mysore Seshaiyer Venkatachalapathy, Scientist,
Sankaranarayana Iyer Chidambaran, Scientist and Karaidudi
Sankaranarayana Sastrigal Lalitha, Junior Scientific
Assistant, all of Central Electro-chemical Research
Institute, Tamil Nadu, India, all Indians.

PRICE: TWO RUPEES

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This invention relates to the improvements in or relating to the electrochemical preparation of ortho-toluidine sulphate.

Hitherto it has been proposed to reduce o-nitrotoluene by chemical reducing agents like iron powder and zinc and electrolytically by employing stationary cathodes for the preparation of o-toluidine sulphate from o-nitrotoluene.

This is open to the objection that the processes reported in literature suffer from the following drawbacks.

i) Number of steps are involved to separate the product from the reactants while employing chemical reducing agents.

ii) The product is contaminated with aminocresols in earlier electrolytic processes.

iii) Information available on the cathodic preparation of o-toluidine sulphate free from aminocresols is not adequate enough for setting up a practical scale unit.

The object of this invention is to obviate these disadvantages by the improvements now effected in the process by us.

According to the present invention, chemical reducing agents are avoided by using either a rotating or a stationary cathode for the reduction of o-nitrotoluene to produce o-toluidine sulphate. The present process is superior to the chemical processes hitherto described in literature since it not only eliminates the number of steps in the process of separating the product from the reactants but also gives a very pure product and thereby renders the process more easy to operate. Additional advantage in the process now established by us is that by using a rotating cathode, high current density could be employed without adversely affecting the energy economics of the process.

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To these ends, the invention broadly consists in reducing cathodically o-nitrotoluene to give o-toluidine sulphate in an electrolytic cell, made of copper which itself acts as cathode when stationary cathode is employed. The catholyte was separated from anolyte by means of a porous diaphragm. A 25% solution of sulphuric acid was used as anolyte and the anode was made of lead or lead-antimony alloy. The catholyte employed was 25% sulphuric acid containing titanium sulphate solution. A current density of upto 16 A/dm² in the case of stationary cathode and 10-25 A/dm² with a rotating cathode could be employed. The rpm of the cathode was kept between 1000 and 1500. The temperature of the catholyte could vary from 40-50°C but a temperature of 45-50°C was employed for most of the experiments. A current efficiency of 78% and an yield of 90% was obtained.

The following typical examples are given to illustrate the invention:

Example 1

ELECTROLYTIC REDUCTION OF o-nitrotoluene using a stationary copper cathode

225 ml of o-nitrotoluene was taken in 1.5 litres of 25% sulphuric acid containing 1% titanium oxide^{iron} solution. A copper vessel of ~~2.5~~ 2.5 litres capacity was employed as cathode. A 25% aqueous solution of sulphuric acid was employed as anolyte and lead was used as anode. The catholyte was separated from anolyte by means of a ceramic diaphragm. During the electrolysis, the temperature of the catholyte was kept between 40-45°C by means of a water bath. A current density of 5 A/dm² was employed. After passing 350 A.hrs. 268 g of o-toluidine sulphate was obtained with a current efficiency of 78% and an isolated yield of 85-90%. The energy consumption comes to 5.5 kWh/kg. The cell voltage was 4-4.5V.

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Example 2

Electrolytic preparation of o-toluidine sulphate using a rotating copper cathode

300 cc of O-nitrotoluene was taken in 1.5 litres of 25% sulphuric acid containing 1% titanium oxide in solution. A rotating disc copper was employed as cathode. The r.p.m. was kept between 1000 and 1500. The average cell voltage was 4-4.5 V. During the electrolysis, the temperature of the catholyte was kept between 40 and 45°C. A current density of 20 A/dm² was employed and after passing 450 A.hrs. 341 g of o-toluidine sulphate was obtained. No unreduced nitrocompound could be detected after electrolysis. A current efficiency of 78% and an isolated yield of 86% was obtained. The anode employed was the same as that given in Example 1. The energy consumption comes to 5.6 kWh/kg.

The following are among the main advantages of the invention:

1. The process does not involve the use of any chemical reagent as a reductant and as such its removal does not arise.
2. Isolation of the product is simplified, thereby also giving a product of 99% purity.
3. The employment of a copper container which itself acts as a cathode would help in the design of high amperage cells in order to adopt the process for large scale preparation.
4. The addition of 1% titanium ^{o sulphate solution} oxide in catholyte solution avoids the formation of aminocresols, thereby increasing the amine content.

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Dated this 25th day of July, 1975.

Sd/-
(S. KUMAR)
ASST. PATENT'S OFFICER,
Council of Scientific & Industrial Research.

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COMPLETE SPECIFICATION

(Section 10)

**IMPROVEMENTS IN OR RELATING TO THE ELECTRO-CHEMICAL
PREPARATION OF O-TOLUIDINE SULPHATE FROM O-NITROTOLUENE**

**COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg,
New Delhi 1, India, an Indian Registered body incorporated
under the Registration of Societies Act (Act XXX 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 Handady Venkatakrishna Udupa, Scientist,
Mysore Seshaiyer Venkatachalapathy, Scientist, Sankaranarayana
Iyer Chidanabaram, Scientist and Karaidudi Sankaranarayana
Sastrigal Lalitha, Junior Scientific Assistant, all of Central
Electro-chemical Research Institute, Tamil Nadu, India, all
Indians.**

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This invention relates to the field of organic chemical industry with special reference to intermediate for dyestuff industries.

Hitherto it has been proposed to reduce o-nitrotoluene by chemical reducing agents like iron powder and zinc and electrolytically by using hydrochloric acid as catholyte and tin and tin plated cathodes.

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) Further purification of the product is essential in a process employing chemical reducing agents
- 3) In an electrolytic method using hydrochloric acid as electrolyte, the problem of removal of chlorine gas from the anode chamber has to be encountered leading to pollution problems and corrosion of anode is considerable
- 4) The product is contaminated with aminocresols in earlier electrolytic processes
- 5) Reuse of electrolyte is not possible since electrolyte as such has to be neutralised after electrolysis to separate the product and thus cost of neutralisation is more

The main object of the invention is to obviate the drawbacks mentioned earlier by the modification and improvements effected by us employing an electrochemical reduction technique

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

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 more than 10% higher yields of amine are obtained and aminophenols

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are not formed thus eliminating problems concerned with their separation. Additional advantages established by us are (1) the electrolyte can be reused at least a minimum of five times after making up the acid concentration without affecting the efficiency of the process, (2) the employment of a copper container as the cell which itself acts as the cathode would help in the design of high amperage cells in order to adopt the process for large scale preparations, and (3) the amine sulphate separated can be neutralized to get *o*-toluidine. Thus the isolation of the amine is simplified and the cost of neutralization is reduced.

The present invention broadly consists in reducing cathodically *o*-nitrotoluene to give *o*-toluidine sulphate in an electrolytic cell fitted with either stationary or rotating copper cathode or in an electrolytic cell made of copper which acts as cathode. The catholyte was separated from the anolyte by means of a ceramic porous diaphragm. The catholyte employed was dilute sulphuric acid, the concentration of which would vary from 10 to 30% by volume. Titanic sulphat solution to the equivalent of 0.5 to 1.5% TiO_2 was added to the catholyte as catalyst. Sulphuric acid of the same concentration as that of catholyte was used as anolyte. The anode was lead or an alloy of lead and 0.5 to 1% silver. A current density of 5 to 20 A/eq.dm. in the case of stationary cathode and 10 to 30 A/eq.dm with a rotating cathode could be employed. The temperature of catholyte could vary from 40 to 60°C. A current efficiency of 75 to 85% and an yield of 85 to 95% could be obtained.

Example 1: Electrolytic reduction of *o*-nitro toluene

1.6 litres of 25% sulphuric acid containing 1% titanium oxide in solution was taken in a cylindrical vessel of 2.5 litres capacity which acts as cathode. A 25% aqueous solution of sulphuric acid was employed as anolyte and lead was used as anode. The catholyte was separated from anolyte by means of a ceramic porous diaphragm. The solution was stirred vigorously by means of a mechanical glass stirrer. 220 ml of *o*-nitro toluene was added. During the electrolysis, the temperature

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of the catholyte was kept between 40 and 45°C by means of a water bath. A current density of 5 A/sq.dm was employed. The cell voltage was 4 to 4.5V. After passing 350 A hrs the catholyte was cooled to 10°C. 268 g of o-toluidine sulphate was isolated by filtration with a current efficiency of 79% and an isolated yield of 92%. The energy consumption comes to 5.5 kWh/kg.

Example 2 : Electrolytic preparation of o-toluidine sulphate using a rotating copper cathode

1.5 litres of 25% sulphuric acid containing 1% titanium oxide in solution was taken in a 3 litre pyrex beaker. A rotating disc copper was employed as cathode. The rpm was kept between 1000 and 1500. A ceramic porous diaphragm was used and a lead silver alloy (1% silver) strip was used as anode. 175 ml of 25% sulphuric acid was taken in the diaphragm as anolyte. 300 ml of o-nitrotoluene was added. The cell voltage was 4 - 4.5V. During the electrolysis the temperature of the catholyte was kept between 40 and 45°C. A current density of 20 A/sq.dm was employed and after passing 450 A hrs the catholyte was cooled to 10°C. 341 g of o-toluidine sulphate was isolated. A current efficiency of 78% and an isolated yield of 86% was obtained.

Example 3: Electrolytic preparation of o-toluidine sulphate from o-nitrotoluene - Reuse of the catholyte from example 1

Experimental set up and condition are the same as given in example 1. The catholyte after separation of solid o-toluidine sulphate in example 1 was reused in which 30 ml of concentrated sulphuric acid was added to make up the acid concentration. 300 ml of o-nitrotoluene was reduced. After passing a current of 450 A hrs the catholyte was cooled to 10°C and 375 g of amine sulphate was isolated. An isolated yield of 94.6% and current efficiency of 86% was obtained. The catholyte is reused five times after the separation of the amine sulphate as in example (3). The isolated yield of amine sulphate varied from 95% to 85%. The yield obtained during the fifth reuse was 87% with a current efficiency of 76%. No aminocresol are obtained during the separation of amines. The purity of the recrystallised product was of the order 98 to 99% in all the examples.

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A process has been invented for the electrolytic production of *o*-toluidine sulphate/*o*-toluidine from *o*-nitrotoluene. This process eliminates the use of conventional methods which involve tedious and laborious methods of separation and purification of the product. The employment of a copper container which itself acts as cathode would help in the design of high amperage cells in order to adapt the process for large scale operation. The possibility of reusing the electrolyte makes the process economically viable.

We claim:

- 1) A process for the electrochemical preparation of *o*-toluidine sulphate/~~*o*-toluidine~~ ^{*from o-nitro*} using a copper cathode either stationary or rotating and having a lead or an alloy of lead and silver anode which has been separated from the catholyte by means of a porous diaphragm with 10 to 30% (V/V) of sulphuric acid containing 0.5 to 1% TiO₂ in the form of titanous sulphate solution as catalyst and 10 to 30% (V/V) sulphuric acid as anolyte.
- 2) A process as claimed in claim 1 wherein a lead or lead silver alloy is used as anode.
- 3) A process as claimed in claim 1 wherein the copper cathode is either stationary or rotating, while stationary an auxiliary stirrer being employed and a copper container is also used acting both as the cell and stationary cathode.
- 4) A process as claimed in claim 1 wherein 10 to 30% (V/V) sulphuric acid preferably 20% by volume containing 0.5 to 1% TiO₂ as titanous sulphate solution is used as catholyte.
- 5) A process as claimed in claim 1 wherein sulphuric acid of the same concentration as that of catholyte is used as anolyte.
- 6) A process as claimed in claim 1 wherein a cathodic current density of 5 to 20 A/sq.dm in the case of stationary preferably 10 A/sq.dm and 10 to 30 A/sq.dm in the case of rotation preferably 20 A/sq.dm is used.

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7. A process as claimed in claim 1 wherein the temperature range could be 40 to 60°C but preferably 45 to 50°C.

Dated this 18th day of October, 1976.

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PATENTS OFFICER,
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

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