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PROVISIONAL SPECIFICATION

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

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJ MARG, 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 this invention:—

This is an invention by HANDADY VENKATAKRISHNA UDUPA, Director GOBICHETTIPALAYAM SRINIVASAN SUBRAMANIAN, Scientist, PAYYALLUR NARAYANA ANANTHARAMAN, Scientist, ANNAMALAI POURASSAMY, Senior Laboratory Assistant, All Indians working at Central Electrochemical Research Institute, Karaikudi-3.

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

Hitherto it has been proposed to reduce nitrobenzene to aniline using stationary cathode using alcohol, sulphuric acid and nitrobenzene at a temperature of 40° to 60° at a zinc or lead cathode with a current density of 10-15 amps per dm². The yield obtained was 80-90% (Els & Silbermann: Z. Elektrochem 7,589, (1901). Later the use of solvent like alcohol was avoided by developing a new addition agent Ti⁺⁺⁺ ion which by virtue of its two valency states act as an intermediary ion in reducing nitrobenzene whose solubility is very poor in aqueous medium. It was thought that titanous ion in combination with a rotating cathode can work well and results were encouraging in that line. Accordingly a patent was filed (Patent No. 128412).

But later experiments proved that even a stationary cathode can work with same current efficiency and yield for the same current density used for a rotating cathode. This is because of the fact that the main reduction of nitrobenzene to aniline occurs at the bulk of the electrolyte and not at the double layer adjoining the cathode surface. Hence the reduction is independent of the double layer thickness. Much reduction depends on the availability of titanous ions. The more the presence of titanous ions the more efficient is the reduction. Since Ti⁺⁺⁺⁺ ion can reach the cathode surface by virtue of its charged nature it can reach the surface even when the cathode is stationary and can get reduced to Ti⁺⁺⁺

Although rotating cathode satisfies the above requirements major advantages of stationary cathode over rotating cathode can be summarised as follows:—

- (i) Its ease of construction.
- (ii) Its ease of maintenance.
- (iii) Since the container itself acts as a cathode for container can be solved for the above conditions.
- (iv) Since the cell must be provided with cooling coils copper cooling coils can be used which itself will act as cathode and give better heat conductance.

To obviate these disadvantages a process which would yield high current efficiency by using suitable hydrogen carrier and a stationary cathode has been developed.

By this technique, the design of high amperage cell is made easier. The reduction proceeds smoothly even at high current density ranges employed. Same electrolyte is used any number of times but not less than four times to make it more economical.

To these ends, the invention broadly consists in reducing a suspension of nitrobenzene in a catholyte of sulphuric acid upto a concentration of 25% (v/v) with about 0.1% copper sulphate using a stationary cathode of copper or zinc or tin

but preferably between 50-60°C using a range of current density upto 40 amp/dm² but preferably at 20 amp². The anolyte is sulphuric acid solution upto 30% strength but preferably 25% (v/v). As diaphragm ceramic or blue asbestos but preferably ceramic is used. Lead is used as anode material. Addition agents like titanous or titanous sulphate of concentration upto 10 gms TiO₂ in one litre is added to the catholyte.

It is already known that a rotating cathode will bring shear over the layer adjoining the cathode surface. This is necessary for compounds which are not ionic in nature. They will move towards the double layer from the bulk of the solution by this movement of cathode and get reduced. Similarly those which have been reduced will be removed from that layer by same mechanism. The bulk of the solution is relatively static to the layer adjoining the cathode surface. If the solution is stirred by keeping the cathode stationary the mechanism is reversed. The layer adjoining the cathode is static relative to the bulk of the solution where it is stirred. Due to the simplicity of the stationary cathode it is preferred to the rotating cathode. Moreover, Ti⁺⁺⁺ ion acts as intermediary ion in reducing nitrobenzene to aniline and Ti⁺⁺⁺ can get reduced to Ti⁺⁺⁺ even at a stationary cathode by virtue of its ionic nature.

After the reduction, the solution is cooled to remove aniline sulphate and the solution is used again for the next charge. After removal of each crop of aniline sulphate, the solution is replenished with sufficient sulphuric acid, water and titanous or titanic sulphate before running the next reduction. Sulphuric acid must be added in the molar ratio of 1 : 1 to the aniline formed, titanous or titanic sulphate upto 1% of the initial charge and water to the required volume if necessary. After four reductions total aniline sulphate along with the final liquor after fourth reduction is treated with soda ash, calcium carbonate or ammonia but preferably soda ash until the pH is above 7. Aniline thus liberated is steam distilled and recovered. Water containing aniline sulphate is saturated with sodium chloride and solvent extraction of aniline is done with solvents like benzene. The solvent is recovered by fractional distillation and used for further extraction. Moisture from aniline is removed by shaking with sodium chloride when water separates out along with sodium chloride. Aniline is made colourless by distilling with zinc dust.

The following typical examples are given to illustrate the invention:—

EXAMPLE-I

Catholyte	..	900 ml of 25% sulphuric acid (v/v)
Cathode	..	Stationary copper cathode of area 1.8 dm ²
Nitro compound taken	..	1020 g (360+240+120+240)
Temperature	..	50-60°C
Anolyte	..	180 ml 25% sulphuric acid (v/v)

Anode	..	Lead of area 0.5 dm ²
Diaphragm	..	Ceramic porous pot
Current	..	36 amp.
Current density (cathode)	..	20 amp/dm ²
Cell Voltage	..	5 to 6 V
Weight of titanous or titanous sulphate added to catholyte	..	13 g
Weight of copper sulphate added to catholyte	..	1g
Nitro compound recovered	..	Nil
Aniline recovered	..	668 g
p-Aminophenol recovered.	..	6 g
Current efficiency	..	86.6%
Assay yield	..	87.3%
Energy consumption	..	12 kWh/kg of aniline

EXAMPLE-II

Conditions same as Example I

Nitrocompound taken	..	710.6 g (360 + 120 + 120 + 110.6)
Nitrocompound recovered	..	Nil
Aniline recovered	..	437.5 g
p-Aminophenol recovered	..	4 g
Current efficiency	..	81.4%
Assay yield	..	82%
Energy consumption	..	12.8 kWh/kg of aniline

The following are the main advantages of the invention:

1. The use of titanous sulphate in the electrolyte increases the reduction efficiency.
2. The use of stationary cathode enables design of high amperage cells easier as the container itself acts as the cathode.
3. The use of solvent has been avoided with same current efficiency as was obtained by earlier workers.

Dated this 11th day of August, 1972.

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THE PATENT ACT OF 1970 COMPLETE SPECIFICATION

(See Sect on 10)

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

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJ MARG, NEW DELHI-110001, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1960)

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, DIRECTOR, GOBICHETTIPALAYAM SRINIVASAN SUBRAMANIAN, SCIENTIST, PAYYALLUR NARAYANAN ANANTHARAMAN, SCIENTIST AND ANNAMALAI POURASSAMY SENIOR LABORATORY ASSISTANT, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAİKUDI-6, INDIA—ALL INDIAN CITIZENS.**

This invention relates to a process for the electrolytic reduction of nitrobenzene to aniline sulphate. This invention relates more particularly to an improvement in or modification of the invention of our prior patent No. 128412/70 which claims a process comprising 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 electrode of copper and employing titanous sulphate as addition agent preferably upto a concentration of 50g titanium sulphate per litre of catholyte and using current densities upto 20A/dm² but preferably 10A/dm² and temperatures upto 50 deg. centigrade but preferably between 20 and 30 deg. cent. The patent also discloses the use of stationary cathodes. Addition of 0.1% copper sulphate to the catholyte has been recommended. The base aniline was recovered by neutralising and steam distillation.

This is open to the objection that the process involves recovery of aniline which makes the electrolyte unfit for reuse.

We have now found: (i) that if the electrolyte is cooled after reduction of aniline sulphate the salt can be recovered by filtration;

(ii) if aniline sulphate is recovered, the steps of neutralising and steam distillation to obtain the base aniline are avoided;

(iii) the salt aniline sulphate can be used directly for the manufacture of sulphanilic acid by known methods whereas an additional step viz. production of aniline sulphate from

aniline by sulphuric acid treatment would be involved for conversion of aniline to sulphanilic acid.

According to the present invention, there is provided a process for electrolytically reducing a suspension of nitrobenzene to aniline sulphate which consists, in reducing a suspension of nitrobenzene as claimed in the claims of Indian Patent No 128412/70 in a supporting electrolyte of mineral acid preferably sulphuric acid upto a concentration of 25% V/V using stationary/rotating electrode of copper and employing titanous sulphate as addition agent preferably upto a concentration of 10g titanium dioxide per litre of catholyte and using current densities upto 25A/dm² and temperatures upto 60 deg. cent. characterized in that, after the reduction the catholyte is cooled to room temperature (30-35 deg. cent.) and filtered to recover aniline sulphate. It will be noted that according to prior patent No. 128412/70, the catholyte was neutralised and steam distilled to recover aniline base. According to the present modification the catholyte is cooled to room temperature (30-35 deg. cent) and filtered to obtain the salt aniline sulphate. The merit of the present invention is that we are directly getting aniline sulphate without vacuum concentrating the catholyte.

Titanous sulphate may be added up to a concentration of 10 gms calculated as TiO₂, per litre of catholyte. The preferred temperature is between 50 and 55 deg. cent. 0.1% of copper sulphate may be added to the catholyte. After passing the theoretical quantity of electricity and if no more nitrobenzene is left behind, the solution is cooled and solid aniline sulphate is separated and the electrolyte is used again for another charge by adjusting the acid strength to 25% by adding fresh acid. The electrolyte may be used not less than four times before it is neutralized to recover the aniline left after fourth use.

No complicated equipments are needed and the processes of isolation of aniline sulphate is equally simple. The yield of aniline sulphate is high and very little formation of p-aminophenol and practically no cyclohexylamine was observed.

As described in our prior Indian Patent No. 128412/70, a suspension of nitrobenzene is reduced in a catholyte, a mineral acid, preferably sulphuric acid upto a concentration of 25% by volume containing titanous sulphate preferably upto a concentration of 1 g TiO_2 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 at a current density upto 20 A/dm² but preferably 10 A/dm² and at temperatures upto 60 deg. cent. but preferably between 50—55 deg. cent. The anolyte is a dilute mineral acid but preferably sulphuric acid upto a concentration of 30% but preferably 25% V/V. Theoretical quantity of electricity was passed (viz 6 Faradays per gram mole of nitrobenzene) after which the catholyte is steam distilled to recover any unreduced nitrobenzene. In the modification according to the present improvement, the catholyte is then cooled to recover aniline sulphate, which can be used for the manufacture of sulfanilic acid by known methods. The sulphate is worked up by washing the acid by recrystallisation in water and adding the water used for recrystallisation to the mother liquor itself. Mother liquor is again used for further electrolysis by adding nitrobenzene and required amount of acid. Nitrobenzene added was equal to the aniline sulphate separated out. Thus the same electrolyte was used not less than 4 times and each time the aniline sulphate recovered was recrystallised and dried in an oven. The temperature of the oven was adjusted to 80 deg. to 100 deg. cent.

The following examples are given to illustrate the invention:

EXAMPLE-I

Catholyte	..	5 l of 25% H_2SO_4 (V/V)
Anolyte	..	2 l do
Volume of nitrobenzene taken	..	1.25 l (purity 99.0%)
Current	..	150 amps
Area of cathode (stationary)	..	20 dm ²
Current density	..	7.5 amps/dm ²
Titanous sulphate	..	625 ml solution containing 50 gm TiO_2
Duration	..	14 Hours
No. of amp hours passed	..	2100
No. of amp hours theoretical	..	1961
Cell voltage	..	5-7 V
Temperature	..	45-50 deg. cent.
Anode	..	Lead
Diaphragm	..	Ceramic porous pot
Anode area	..	7.5 dm ²
Wt. of copper sulphate added to catholyte	..	5g

Wt of nitrobenzene unreduced	..	Nil
Wt. of p-aminophenol estimated	..	Nil
Wt. of aniline sulphate recovered	..	1570 gm
Energy consumption	..	12.3 kwh/kg of aniline sulphate

EXAMPLE-II

Catholyte	..	1 l of 25% H_2SO_4 (V/V)
Anolyte	..	200 ml do
Wt of nitrobenzene taken	..	(480+228+270+360) gm
Current	..	30 amp
Area of the cathode (Stationary)	..	1.5 dm ²
Current density	..	20 amps/dm ²
Titanous sulphate	..	150 ml solution containing 10 gm TiO_2
Duration	..	64 hours (4 batches)
No. of amp hours passed	..	1920 "
No. of amp hours theoretical	..	1750 "
Cell voltage	..	4.5-6.5 V
Temperature	..	50-55 deg. cent.
Anode	..	Lead
Diaphragm	..	Ceramic porous pot
Anode area	..	1 dm ²
Wt of copper sulphate added to catholyte	..	1 gm
Wt. of nitrobenzene recovered	..	Nil
Wt. of p-aminophenol estimated	..	Nil
Wt. of aniline sulphate	..	531+253+305+399 gm

We Claim:

A process for electrolytically reducing a suspension of nitrobenzene to aniline sulphate which consists in reducing a suspension of nitrobenzene as claimed in the claims of Indian patent No. 128412/70 in a supporting electrolyte of mineral acid preferably sulphuric acid upto a concentration of 25% V/V using stationary/rotating electrode of copper and employing titanous sulphate as addition agent preferably upto a concentration of 10 gm titanium dioxide per litre of catholyte and using current densities upto 25A/dm² and temperatures upto 50 deg. cent. characterised in that, after the reduction the catholyte is cooled to room temperature (30—35 deg. cent) and filtered to recover aniline sulphate.

Dated this 4th day of September, 1973.

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