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**."AN ELECTROLYTIC PROCESS FOR THE PRODUCTION
OF P-AMINOPHENOL FROM P-NITROSO PHENOL".**

**COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
Rafi Marg, New Delhi - 110001, 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.

PRICE : TWO RUPEES

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This is an invention by NANDADY VENKATAKRISHNA UDUPA, POYYALUR KARAYANAN ANANTHARAMAN and MICHAEL NOEL, Scientists all of Central Electrochemical Research Institute, Karaikudi-623006, all Indian citizens.

This invention relates to an electrolytic process for the production of p-aminophenol from phenol through the intermediate p-nitroso phenol.

Hitherto it has been proposed to produce p-aminophenol from phenol by nitrosation of phenol to obtain p-nitro phenol and chemically reducing the p-nitroso phenol obtained using sodium polysulfide in alkaline media.

This method is open to the following objections.

In the polysulfide reduction process many side reactions occur due to the instability of the p-nitroso phenol as well as the product p-aminophenol in alkaline media. Hence recovery of the pure p-aminophenol in alkaline media from the reduced black reaction mixture is a difficult task in this process. In addition, the yield reported (around 60.0% based on p-nitroso phenol) is also very low.

The object of the present invention is to obviate these disadvantages by electrolytically reducing the intermediate p-nitroso phenol using some addition agents which enables the reduction at a cathode current density in the range of $1-5 \text{ A/dm}^2$ with 75-85% yield with 54-62% current efficiency. The electrolysis is carried out in sulphuric acid medium and sufficient quantity of p-nitroso phenol is reduced to separate the p-aminophenol formed as its solid sulphate. The p-aminophenol is isolated from the sulphate by neutralising the salt with sodium bicarbonate.

The other main objectives of the processes are to achieve

- 1) a clean and simpler reduction when compared to the chemically method. The electrochemical process proceeds

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without any side reactions in the catholyte process medium employed. The product p-aminophenol is fixed as its sulphate salt as soon as it is formed and hence it is also quite stable in the medium employed;

2) the recovery of p-aminophenol formed as its solid sulphate from the catholyte medium, thus enabling the reuse of catholyte many times to reduce further nitroso compounds.

The main advantage of the process are as follows:-

- 1) The use of electrochemical reduction produces higher yield with very simple and clear unit operations when compared to the chemical method.
- 2) The recovery of p-aminophenol as its solid sulphate enables the reuse of catholyte many times for reducing nitroso compound.
- 3) The side reactions of p-nitroso phenol and p-aminophenol are avoided thus enabling the production of pure product.
- 4) The copper cathode employed may itself be used as the cell container.

Accordingly this invention provides an improved electrolytic process for the production of p-aminophenol from phenol by preparing p-nitroso phenol from phenol by nitrosation and electrochemically reducing the p-nitroso phenol in an electrolyte containing 8-10% titanio sulphate and 0.05-0.2% hydrated copper sulphate as additives, cooling and isolating the product as p-aminophenol sulphate formed and reusing the electrolyte for further reduction.

To these ends the invention broadly consists in preparing p-nitroso phenol chemically by the conventional method and electrochemically reducing it to p-aminophenol.

The p-nitroso phenol is prepared from phenol by dissolving the requisite quantity of phenol in alkaline media, adding

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Requisite amount of sodium nitrate, cooling the whole contents to a temperature range of 5-10°C, adding requisite amount of sodium-nitrate 30-40% sulphuric acid solution of the same temperature range slowly while mechanically stirring the solution and isolating the product p-nitroso phenol formed by filtering through a centrifuge. The resulting cake may be as such used in the electrochemical reduction or may be dried in vacuum and then used. The product obtained by this method is 98 ± 1% pure based on estimation using titanous sulphate method. The yield of p-nitroso phenol in such preparations vary from 75 to 80%. The method of preparation of p-nitroso phenol from phenol is further illustrated in Example 1.

The electrochemical reduction of p-nitroso phenol is carried out in an electrochemical cell with copper cathode, lead or lead-silver alloy anode which are separated by a ceramic porous pot diaphragm. The cell is covered with a wooden cover with provisions for a stirrer. The catholyte consists of a 15-40% sulphuric acid containing 8-10% titanous sulphate acid-solution and 0.05-0.2% hydrated copper sulphate and a 15-40% sulphuric acid solution is used as the anolyte. The electrolysis is carried out at 1-5A/dm² cathode current density and 10-20 A/dm² anode current density at a temperature within the range of 40-50°C. The nitroso phenol is added in small instalments into the catholyte such that titanous sulphate is always in excess. After reducing 20-30 gms of p-nitroso phenol per 100 ml of catholyte in this manner, the catholyte is cooled to 20-30°C and the p-aminophenol sulphate that precipitates out is filtered at the pump. The catholyte may again be reused for reducing further quantities of p-nitroso phenol.

The p-aminophenol sulphate obtained by the above method is dissolved in water and neutralised with ammonium bicarbonate to pH 7-8 and cooled to isolate the p-aminophenol. The yield of p-aminophenol from p-nitroso phenol by the above

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method ranges between 75-85%. The product was found to be 98 ± 1% pure after recrystallisation. The process for the production of p-aminophenol from p-nitroso phenol is further illustrated by Examples 2 and 3.

EXAMPLE 1

Preparation of p-nitroso phenol from phenol

90 g of sodium hydroxide was dissolved in 5 kg of ice water. 200 g of phenol was dissolved in this solution and 180 g of sodium nitrate was then added. The solution was cooled to a temperature range of 5-10°C. 270 ml of 96% sulphuric acid dissolved in 1350 ml of water. Water was then added during a period of two hours always maintaining the reactor temperature between 5 and 10°C. The mixture was allowed to settle for two hours and the solid p-nitroso phenol formed was filtered at a centrifuge. The precipitate was washed with cold dilute sulphuric acid and the wet cake obtained was employed in the electro-reduction. The estimation of a sample by titanous sulphate method indicated that 195 g of p-nitroso phenol was obtained which corresponds to over 75% yield.

EXAMPLE -2

Electrolytic reduction of p-nitroso phenol to p-aminophenol

Cell	:	.. 2000 ml Pyrex Glass beaker
Cathode	:	.. Semicircular copper electrode = 2.25 dm ²
Anode	:	.. Lead-silver alloy, 0.5 dm ²
Diaphragm	:	.. 4000 mg Ceramic porous pot
Catholyte	:	.. 1000 ml of 36.0% sulphuric acid containing 9.6% titanous sulphate and 0.1% hydrated copper sulphate.
Anolyte	:	.. 200 ml of 36% sulphuric acid

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Current : .. 5 A
Cathode current density: .. 2.66 A/dm²
Temperature : .. 40-45°C
Average cell voltage : .. 2.4 - 2.8V
Total amount of p-nitroso
phenol reduced : .. 190 g
Total amount of current
passed : .. 249 A-hrs
Total wt. of p-amino-
phenol obtained : .. 137.0 g
. . Yield : .. 81.4%
Current efficiency: .. 51.4%
Energy consumption: .. 4.1 Kwh/kg

Overall

Amt. of p-aminophenol
obtained from catholyte .. 74.8 g
. . Total amount of
p-aminophenol obtained .. 188.4 g
. . Yield .. 77.4%
Current efficiency .. 61.9%
Energy consumption .. 5.4 Kwh/kg

Dated this 17th day of November 1981.

I. M. S. MAMAK

(I. M. S. MAMAK)
SCIENTIST (PATENTS)
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COMPLETE SPECIFICATION

(Section—10)

"AN ELECTROLYTIC PROCESS FOR THE PRODUCTION OF
P-AMINOPHENOL FROM P-NITROSO PHENOL".

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH Rafi Marg,
New Delhi-110001, India, an Indian registered body incorporated
under the Registration of Societies Act (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 :—

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This is an invention by Handady Venkatakrishna Udupa, Polyvalur Narayanan Anantharaman and Michael Noel, scientists of Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India and all Indian citizens.

This invention relates to an improved electrolytic process for the production of p-aminophenol from p-nitroso phenol.

Hitherto it has been proposed to produce p-aminophenol from phenol by nitrosation of phenol to obtain p-nitroso phenol and chemically reducing the p-nitrosophenol obtained using sodium polysulfide in alkaline media.

This method is open to the following objections. In the polysulfide reduction process many side reactions occur due to the instability of the p-nitroso phenol as well as the product p-aminophenol in alkaline media. Hence recovery of the pure p-aminophenol from the reduced black reaction mixture is a difficult task in this process. In addition, the yield reported (around 60.0% based on p-nitroso phenol) is also very low.

The object of the present invention is to obviate these disadvantages by electrolytically reducing the p-nitroso phenol using a redox system and other addition agents which enables the reduction at 1-5 A/dm² cathode current density with 75-85% yield with 54-62% current efficiency. The electrolysis is carried out in sulphuric acid medium and sufficient quantity of p-nitroso phenol is reduced to separate the p-aminophenol formed as its solid sulphate. The p-aminophenol is isolated from the sulphate by neutralizing the salt with ammonium bicarbonate.

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The other main objectives of the process are to achieve :

(1) a clean and simpler reduction when compared to the chemical method. The electrochemical process proceeds without any side reactions in the catholyte medium employed. The product p-aminophenol is fixed as its sulphate salt as soon as it is formed and hence it is also quite stable in the medium employed;

(2) the recovery of p-aminophenol formed as its solid sulphate from the catholyte medium, thus enabling the reuse of catholyte many times to reduce further nitroso compounds.

The main advantages of the process are as follows:

(1) the use of electrochemical reduction produces higher yield with very simple and clean unit operations when compared to the chemical method.

(2) the recovery of p-aminophenol as its solid sulphate enables the reuse of catholyte many times for reducing nitroso compound.

(3) the side reactions of p-nitroso phenol and p-aminophenol are avoided thus enabling the production of pure product.

(4) the copper cathode employed may itself be used as the cell container.

Accordingly, this invention provides an improved electrolytic process for the production of p-aminophenol from p-nitroso phenol which comprises electrochemically reducing the p-nitroso phenol in a reusable electrolyte consisting of titanate sulphate and

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hydrate copper sulphate, dissolving the p-aminophenol sulphate formed in hot water, neutralising it with ~~sodium~~^{ammonium} bicarbonate at pH 7-8 and cooling to obtain p-amino phenol.

According to a feature of the invention the electrochemical reduction is carried out in an electrolytic cell containing a copper cathode and lead or lead-silver alloy anode separated by a ceramic porous pot diaphragm.

According to another feature of the invention catholyte used consists of 15-40% w/w sulphuric acid, 8 to 10% titanate sulphate and 0.05-0.2% of hydrated copper sulphate and anolyte consists 15-40% w/v of sulphuric acid.

According to a still another feature of the invention the electrolysis is carried out at 1-5 A/dm² of cathode current density of 10-20 A/dm² anode current density at a temperature range of 30° to 50°C.

The p-amino phenol sulphate obtained is ~~described~~^{dissolved} in hot water and the insoluble impurities are filtered. The clear filtrate is treated with ~~sodium~~^{ammonium} bicarbonate to a pH value of 7-8 and cooled wherein p-amino phenol separates out. This is filtered and dried. The cooling temperature may be 10-15°C.

To these ends, the invention broadly consists in preparing p-nitroso phenol chemically by conventional method and electrochemically reducing it to p-aminophenol. P-aminophenol is mainly used as a photographic developer and as an intermediate in dye manufacture.

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The p-nitrosophenol is prepared from phenol by dissolving the requisite quantity of phenol in alkaline media, adding requisite amount of sodium nitrite, cooling the whole contents to a temperature range of 5-10°C, adding requisite amount of 30-40% sulphuric acid solution of the same temperature range slowly while mechanically stirring the solution and isolating the product p-nitroso phenol formed by filtering through a centrifuge. The resulting cake may as such be used in the electrochemical reduction or may be dried in vacuum and then used. The product obtained by this method is 98 ± 1% pure based on estimation using titanous sulphate method. The yield of p-nitrosophenol in such preparations vary from 75 to 80%. The method of preparation of p-nitrosophenol from phenol is further illustrated in Example 1.

The electrochemical reduction of p-nitroso phenol is carried out in an electrochemical cell with copper cathode, lead or lead-silver alloy anode which are separated by a ceramic porous pot diaphragm. The cell is covered with a wooden cover with provisions for a stirrer. The catholyte consists of a 15-40% sulphuric acid (w/v) containing 8-10% titanous sulphate and 0.05 - 0.2 % hydrated copper sulphate and a 15-40% sulphuric acid (w/v) solution is used as the anolyte. The electrolysis is carried out at 1-5 A/dm² cathode current density and 10-20 A/dm² anode current density at a temperature ranging between 30 and 50°C. The nitrosophenol is added in small instalments into the catholyte such that titanous sulphate is always in excess. After reducing 20-30 g of p-nitroso phenol per 100 ml of catholyte in

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this manner, the catholyte is cooled to 20-30°C and the p-aminophenol sulphate that precipitates out is filtered at the pump. The catholyte may again be reused for reducing further quantities of p-nitroso phenol, after making up the sulphuric acid loss. The same electrolyte may thus be reused 8-10 times.

The p-aminophenol sulphate obtained by the above method may be dissolved in water and neutralized to pH 7-8 and cooled to isolate the p-aminophenol. The yield of p-aminophenol from p-nitroso phenol by the above method ranges between 75-85%. The product was found to be 98 ±1% pure after recrystallization.

The production of p-aminophenol from phenol thus consists of two stages : preparation of p-nitroso phenol from phenol by chemical method and the subsequent reduction of p-nitrosophenol to p-amino phenol by an electrochemical method. The electrolytic reduction of p-nitroso phenol is carried out in a cell containing copper cathode, lead or lead-silver alloy anode, using preferably 15-40% sulphuric acid as anolyte and the same solution containing 8-10% titanate sulphate and 0.05 -0.2% hydrated copper sulphate as anolyte employing 1-5A/dm² cathode current density and 10-20 A /dm² anode current density at a temperature ranging between 30-50°C. A sufficient amount of p-nitroso phenol is reduced in the electrolyte and the product p-aminophenol is separated outside the cell by cooling the electrolyte and filtering out the solid p-aminophenol sulphate and reusing the filtrate for reducing further quantities of p-nitroso phenol. The copper container itself may be used as an electrode.

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The new result achieved due to the process of the invention is to avoid the use of polysulfide which results in pure product (98 ±1% purity) with higher yield (75-80% compared to 60%) and elimination of the formation of many side products (due to blackening polymerization etc in presence of polysulfide and alkali). Reuse of electrolyte many times results in a cost effective process which also reduces pollution.

The prepared process involves:

(i) the electrolytic reduction of p-nitroso phenol may be carried out in electrolytic cells with copper cathode, lead anode and ceramic porous pot diaphragm using 15-40% sulphuric acid (w/w) as anolyte and the same containing 2-10% titanate sulphate and 0.05-0.2 % hydrated copper sulphate as catholyte at a cathode current density of 1-5 A/dm² and the anode current density of 10-20 A/dm² between the temperature range of 30-50°C.

(ii) the electrolytic reduction of p-amino phenol of p-nitroso phenol may be carried out in the electrolytic cell mentioned above, the catholyte may be preferably be 30-40 % sulphuric acid (w/w) containing 8-10 % titanate sulphate and 0.1 - 2.0 % hydrated copper sulphate. The cathode current density range may be between 2-3 A/dm² and the temperature range between 40-50°C.

The process for the production of p-aminophenol from p-nitroso phenol is further illustrated by Examples 2 and 3.

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EXAMPLE -1

Preparation of p-nitroso phenol from phenol-Hitherto known process

90 g of sodium hydroxide was dissolved in 5 kg of ice water 200 g of phenol was dissolved in this solution and 180 g of sodium nitrite was then added. The solution was cooled to a temperature range of 5-10° C. 270 ml of 96% sulphuric acid dissolved in 1350 ml of water was added during a period of two hours always maintaining the reactor temperature between 5-10°C. The mixture was allowed to settle for two hours and the solid p-nitroso phenol formed was filtered at a centrifuge. The precipitate was washed with cold dilute sulphuric acid and the wet cake obtained was employed in the electro-reduction. The estimation of a sample by titanous sulphate method indicated that 195 g of p-nitrosophenol was obtained which corresponds to over 75% yield.

EXAMPLE -2

Electrolytic reduction of p-nitroso phenol to p-aminophenol

Cell	: 2000 ml Pyrex glass beaker
Cathode	: Semicircular copper electrode, 2.25 sq dm
Anode	: Lead-silver alloy, 0.5 dm ²
Diaphragm	: Ceramic porous pot
Catholyte	: 1000 ml of 36.0% sulphuric acid (w/w) containing 9.6% titanous sulphate and 0.1 % hydrated copper sulphate

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Anolyte : 200 ml of 36% sulphuric acid (w/w)
Current : 6 A
Cathode current density : 2.66 A/dm²
Temperature : 40-50°C
Average cell voltage : 2.4 - 2.8 V

Total amount of p-nitroso phenol reduced : 190 g

Total amount of current passed : 249 Ah

Total weight of p-aminophenol obtained : 137.0 g

Yield : 81.4%

Current efficiency : 51.4%

Energy consumption : 4.1 kwh/kg

EXAMPLE -3

Electrolytic reduction of p-nitroso phenol with the reuse of catholyte

Cells, cathode, anode, diaphragm, current density : As in Example 2

Catholyte : 1000 ml 18% sulphuric acid (w/w) containing 10.3% titanous sulphate

Anolyte : 200 ml 18% sulphuric acid (w/w)

Temperature : 45-50°C

Average cell voltage : 3.4 V

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First batch

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Total weight of p-nitrosophenol reduced : 147.5 g

Total amount of current passed : 166.5 Ah

Catholyte cooling temperature : 10°C

The amount of solid sulphate isolated : 43.0 g

Amount of p-aminophenol obtained : 29.6 g

First reuse

Total weight of p-nitrosophenol added : 106.0 g

Total amount of current passed : 133.5 Ah

Temperature to which the catholyte was cooled : 10°C

Total amount of amine sulphate isolated : 154 g

Amount of p-aminophenol obtained : 84.0 g

Overall

Amount of p-aminophenol obtained from catholyte : 74.8 g

Total amount of p-aminophenol obtained : 188.4 g

Yield : 77.4%

Current efficiency : 61.9%

Energy consumption : 5.4 kWh/kg

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EXAMPLE -4

Cell, cathode, anode, and diaphragm : As stated in Example 2

Catholyte : 1000 ml 9% sulphuric acid (w/w) containing 2.4% titanic sulphate and 0.15 % hydrated copper sulphate

Anolyte : 200 ml 9% sulphuric acid (w/w)

Current : 9 A

Cathode current density : 4 A /dm²

Temperature : 50-55°C

Average cell voltage : 3.8 V

Total amount of p-nitrosophenol reduced : 40.0 g

Total amount of current passed : 39.0 Ah

Total amount of p-aminophenol obtained : 16.3 g

Yield : 40.7 %

Current efficiency : 38.8 %

Energy consumption : 9.1 kwh/kg

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We claim:

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1. An improved electrolytic process for the production of p-aminophenol from p-nitrosophenol comprising electrochemically reducing p-nitrosophenol in reusable electrolyte consisting of titanic sulphate and hydrated copper sulphate, dissolving the p-aminophenol sulphate formed in hot water neutralising it with ~~sodium~~ ^{ammonium} carbonate at pH 7-8 and cooling to obtain p-aminophenol.
2. Process ^{as} claimed in claim 1 wherein the electrochemical reduction is carried out in an electrolytic cell containing a copper cathode and lead or lead-silver alloy anode separated by a ceramic porous pot diaphragm.
3. Process as claimed in claims 1 or 2 wherein catholyte used consists of 15-40% w/w sulphuric acid, 8 to 10% titanic sulphate and 0.05-0.2 % of hydrated copper sulphate and anolyte consists 15-40% w/v of sulphuric acid.
4. Process as claimed in any of the preceding claims wherein the electrolysis is carried out at 1-5 A/dm² of cathode current density of 10-20 A/dm² of anode current density at a temperature range of 30° to 50°C.
5. An improved electrolytic process for the production of p-aminophenol from p-nitrosophenol substantially as described and illustrated herein *in Examples 2 to 4.*

Dated this *19th* day of *February* 1983.

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