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PROVISIONAL SPECIFICATION.

IMPROVEMENTS IN/OR RELATING TO THE ELECTROLYTIC REDUCTION NITROBENZENE TO p-AMINOPHENOL.

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).

The following specification describes the nature of this invention.

This is an invention by Handady Venkatakrishna Udupa, Gobichettipalayam Srinivasan Subramanian, Kodethoor Shrivara Udupa and Tirunelveli Duraiswamy Balakrishnan, all of the Central Electrochemical Research Institute, Karaikudi 3, Madras State, India, all Indian citizens.

This invention relates to improvements in/or relating to the electrolytic reduction of nitrobenzene to p-aminophenol

Hitherto it has been proposed to reduce nitrobenzene to p-aminophenol by rotating/or stationary amalgamated cathodes of copper, lead or monel in a glass/or glass lined or porcelain cell using ceramic porous pot as diaphragm.

This is open to objection that by such a method the investment cost are higher by the use of glass-lined cells and the fragile nature of the glass or porcelain cells make them unsitable for commercial exploitation The ceramic porous pots of suitable dimensions required for the large scals cells are difficult to be prepared and have poor mechanical strength and are fragile.

The object of this invention is to obviate these disadvantages by modifying the cell container by teakwood and using blue asbestos cloth as diaphragm. By this modification, the design of high amperage cells are simplified and ceil and diaphragm of any desired shape can be fabricated.

To these ends, the invention broadly consists in reducing a suspension of nitrobenzene in a supporting electrolyte of a mineral acid preferably sulphuric acid in a wooden cell having a wooden cover with necessary openings for the electrodes, diaphragm, cooling coils and condenser. The diaphragm is blue asbestos cloth supported in a wooden frame or on a suitable anode preferably lead or lead alloy. A rotating or stationary amalgamated cathode of copper, brass, lead, zinc or monel is used. The catholyte is a mineral acid preferably sulphuric acid upto a strength of 30% but preferably 20% and the same acid is used as anolyte also. A quantity of nitrobenzene preferably¹ part by volume to 5 parts (by volume) of catholyte is added either in one lot or in instalments and the reduction is carried out at a current density upto 40 amp/ dm^2. The temperature is kept upto 100°C but preferably between 90-95°C. The escape of nitrobenzene as vapour is minimised by maintaining a slight suction at the top of the condensor and further trapped in a chilled trap. The reduction is carried to theoretical time corresponding to 4 F/mole of nitrobenzene taken. After electrolysis the catholyte is steam-distilled to remove any unreduced nitrobenzene and then neutralised with a suitable alkali preferably either $(NH_4)_2$ CO_3 or NH_4HCO_3 or NH_3 gas to pH 6-7. The separated aniline is recovered by steam distillation and the solution is filtered hot after treatment with decolorising charcoal and chilled and the p-aminophenol base is filtered washed with benzene and then with a stabilizer solution containing 1% gelatine and sulphur dioxide or sodium bisulphite. The material is then quickly dried under vacuum.

The following typical examples are given to illustrate the invention :

EXAMPLE I

Catholyte : 1200 ml 30% H_2So_4

Anolyte : 120 ml 30% H_2SO_4

Cathode : Rotating cylindrical amalgamated monel cathode (area 0.75 sq.dm)

Anode : Perforated cylindrical lead

Current : 15 amps ; Cell voltage : 4.5 to 5.5 volts

Temp. 90-95°C

Diaphragm : Blue asbestos diaphragm wound over lead

Nitrobenzene taken : 300 gms (of 95% pure)

P-Aminophenol base isolated = 140 gms

% isolated yield =55.8%

Aniline obtained = 31.5 gms

% aniline = 11%.

EXAMPLE II

Conditions same as Example I, except that the same surface was used without reamalgamation.

P-Aminophenol base isolated = 150 gms

% isolated yield = 59.5%

Aniline obtained = 35.0 gms

% aniline = 15.5%

Price : RUPEES TWO.

EXAMPLE III

Conditions same as Example I except that the same surface was used without reamalgamation.

P-Aminophenol base isolated = 145 gms

% isolated yield = 57.6%

Aniline obtained = 12.0 gms

% aniline = 13.7%

EXAMPLE IV

Conditions same as Example 1 except a cylindrical ceramic porous pot is used as a diaphragm.

P-Aminophenol isolated = 155 gms

% isolated yield = 58.5%

Aniline obtained = 26 gms

% yield of aniline = 11.5%

The following are among the main advantages of the invention :

(a) The use of wood has simplified the material of construction for the cells for the preparation of P-aminophenol and with such a material of construction, it is possible to fabricate large scale commercial cells to any desired size and capacity,

(b) the use of wooden cell container permits use of not only blue asbestos cloth as a diaphragm material giving the advantage of ease of fabrication and good mechanical strength but also enables use of ceramic diaphragms also.

(c) such diaphragms are more durable and stronger than ceramic pots.

Sd/- Illegible

PATENTS OFFICER,

Council of Scientific and Industrial Research.

Dated this 13th day of May, 1970.

COMPLETE SPECIFICATION

IMPROVEMENTS IN/OR RELATING TO THE ELECTROLYTIC REDUCTION OF NITROBENZENE TO p-AMINOPHENOL.

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).

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, Cobichettipalavam Srinivasan Subramanian, Kodethoor Shrivara Udupa and Tirunelveli Duraiswamy Balakrishnan, all of the Central Electrochemical Research Institute, Karaikudi-3, Madras State, India, all Indian citizens.

The invention relates to the improvements in/or relating to the elctrolytic reduction of nitrobenzene to p-aminophenol, the latter being useful as an intermediate in the synthesis of metol and for the preparation of certain drugs like p-acetamol in the Drug and Pharmaceutical industry.

Hitherto it has been proposed to reduce nitrobenzene to p-aminophenol by rotation/or stationary amalgamated cathods of copper, lead or monel in a glass/or glass lined/or porcela in cell using ceramic porous pot as diaphragm.

The objection to the hitherto known process is that by such a method the investment costs are higher by the use of glass lined cells and the fragile nature of the glass or porcelain cells make them unsuitable for commercial exploitation. The ceramic porous pots of suitable dimensions required for the large scale cells are difficult to be prepared and have poor mechanical strength.

The main object of this invention is to obviate these disadvantages by modifying the cell container by teak-wood and using blue asbestos cloth as diaphragm. By this modification, the design of high amperage cells is simplified and cell and diaphragm of any desired shape can be fabricated.

According to the present invention, there is provided a process for the electrolytic reduction of nitrobenzene to p-aminophenol by reducing a suspension of nitrobenzene in a supporting electrolyte of a mineral acid preferably sulphuric acid using a rotating/stationary amalgamated cathode of copper/monel characterised in that the reduction is carried out in a wooden cell having blue asbestos cloth as diaphragm.

As a result of the invention, it is now possible to operate high amperage cells with less of capital investment and such a thing was not possible in the earlier methods since use of glass lined vessels increased the capital cost of cells and the ceramic pots of large size was difficult to be procured/made.

On account of the use of blue asbestos cloth diaphragm, it is possible to operate the cell at lower voltage with the consequent reduction in power consumption.

The diaphragm is blue asbestos cloth supported on a wooden frame or on a suitable anode preferably lead or lead alloy. The cell is made of teak wood and is provided with a teak wood lid having the necessary openings for introducing the cathode, anode chamber, condenser and thermometer. The catholyte is a mineral acid preferably sulphuric acid upto a strength of 30% but preferably 20% and the same acid is used as anolyte also. A quantity of nitrobenzene preferably

ne to five parts by volume of the catholyte is added either in one lot or in instalments and the reduction is carried out at a current density upto 40 amp/dm² but preferably at 20 amp/dm². The temperature is kept upto 100°C but preferably between 90-95°C. The escape of nitrobenzene as vapour is minimised by maintaining a slight suction at the top of the condenser and further trapped in a chilled trap. The reduction is carried to theoretical time corresponding to 4F/mol of nitrobenzene taken. After electrolysis, the catholyte is steam distilled to remove any unreduced nitrobenzene and then neutralised with a suitable alkali preferably either ammonium carbonate or ammonium bicarbonate or ammonia gas to pH 6-7. The separated aniline is recovered by steam distillation and the solution is filtered hot after treatment with decolorising charcoal and chilled. The p-aminophenol base is filtered, washed with benzene and then with a stabilizer solution containing 1% gelatine and sulphur dioxide or sodium bisulphite. The material is then quickly dried under vacuum.

The cells can be operated at a lower voltage than possible when ceramic porous pots are used as diaphragm material.

The flow sheet for the "process" is given in Fig. 1 of the accompanying drawings. The cell is charged with the supporting electrolyte of sulphuric acid upto 30% but preferably 20% and a quantity of nitrobenzene corresponding to 1 part (by volume) to 5 part (by volume) of catholyte is taken either in one lot/or in instalments. The reduction is carried to theoretical time corresponding to 4 F/mol of nitrobenzene taken. After electrolysis, the catholyte is steam distilled to remove any unreduced nitrobenzene and then neutralised in a neutraliser with a suitable alkali like ammonium carbonate/ammonium bicarbonate/ammonia gas to pH 6-7. The separated aniline is then removed by steam distillation and the solution is filtered hot after treatment with decolorising charcoal and chilled. The liberated p-aminophenol base is filtered washed with benzene and then stabilised. The material is quickly dried under vacuum and then packed.

The following typical examples are given to illustrate the invention :

EXAMPLE I

Catholyte	...	1200 ml 30% H_2SO_4
Anolyte	...	120 ml —do—
Cathode	...	Rotating cylindrical amalgamated monel cathode (area 0.75 sq.dm
Anode	...	Perforated cylindrical lead
Current	...	15 amp.
Cell voltage	...	4.5-5.0 Volts
Temperature	...	90-95°C
Diaphragm	...	Blue asbestos cloth wound over lead
Nitrobenzene taken	...	300 gms (95% pure)
Unreduced nitrobenzene recoverd	...	10 gms
Aniline obtained	...	12.5 ml (13.5 gm)
Aniline in solution	...	18.5 gms
Total aniline	...	32 gms
Therefore yield of aniline	...	13.7%
Weight of p-aminophenol obtained	...	145 gms
% isolated yield	...	56.5%

EXAMPLE II

Conditions same as above		
Nitrobenzene (unreduced)	...	Nil
Aniline obtained	...	15 ml (16.5 gms)
Aniline in solution	...	15 gms
Total aniline	...	31.5 gms
% yield of aniline	...	13%
Weight of p-aminophenol obtained	...	140 gms
Isolated yield of p-aminophenol	...	53%

The main advantages of the invention are the following :

i. The use of wood has simplified the material of construction for the preparation of p-aminophenol and with such a material of construction it is possible to fabricate large scale commercial cells to any desired size and capacity.

ii. The use of blue asbestos cloth as a diaphragm material makes the operation of high amperage cells easier and diaphragms can be made to any desired shape and size.

iii. such diaphragms are mechanically strong and durable.

The electrolytic reduction of a suspension of nitrobenzene in a supporting electrolyte of dilute sulphuric acid using a rotating amalgamated electrode of monel/copper is carried out in a wooden cell using blue asbestos cloth as a diaphragm material. By such a method, the fabrication of large scale cells is simplified and it is possible to design and operate cells of any capacity. The use of wood as a cell material and blue asbestos cloth as diaphragm for this reduction are the novel features of the invention since hitherto it was the practice to use glass lined cell/porcelain vessels along with ceramic porous pots which limited the size of cells. In the hitherto known techniqne, it would be difficult to design and operate large scale cells which otherwise require heavy investment cost.

We claim

1. A process for the electrolytic reduction of nitrobenzene to p-aminophenol by reducing a suspension of nitrobenzene in a supporting electrolyte of a mineral acid preferably sulphuric acid using a rotating/stationary amalgamated cathode of copper/monel characterised in that the reduction is carried out in a woden cell having blue asbestos cloth as diaphragm.

2. A process as claimed in Claim 1 wherein the reduction is carried at a current density upto 40 amp/dm^2 but preferably at 20 amp/dm^2 and at temperatures upto 100°C but preferably at 90-95°C.

3. A process for the electrolytic reduction of nitrobenzene to p-aminophenol substantially as hereinbefore described.

Sd/- Illigible

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COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

No. 126677

COMPLETE.

No. OF SHEETS:- 1

SHEET No. . . . :-1

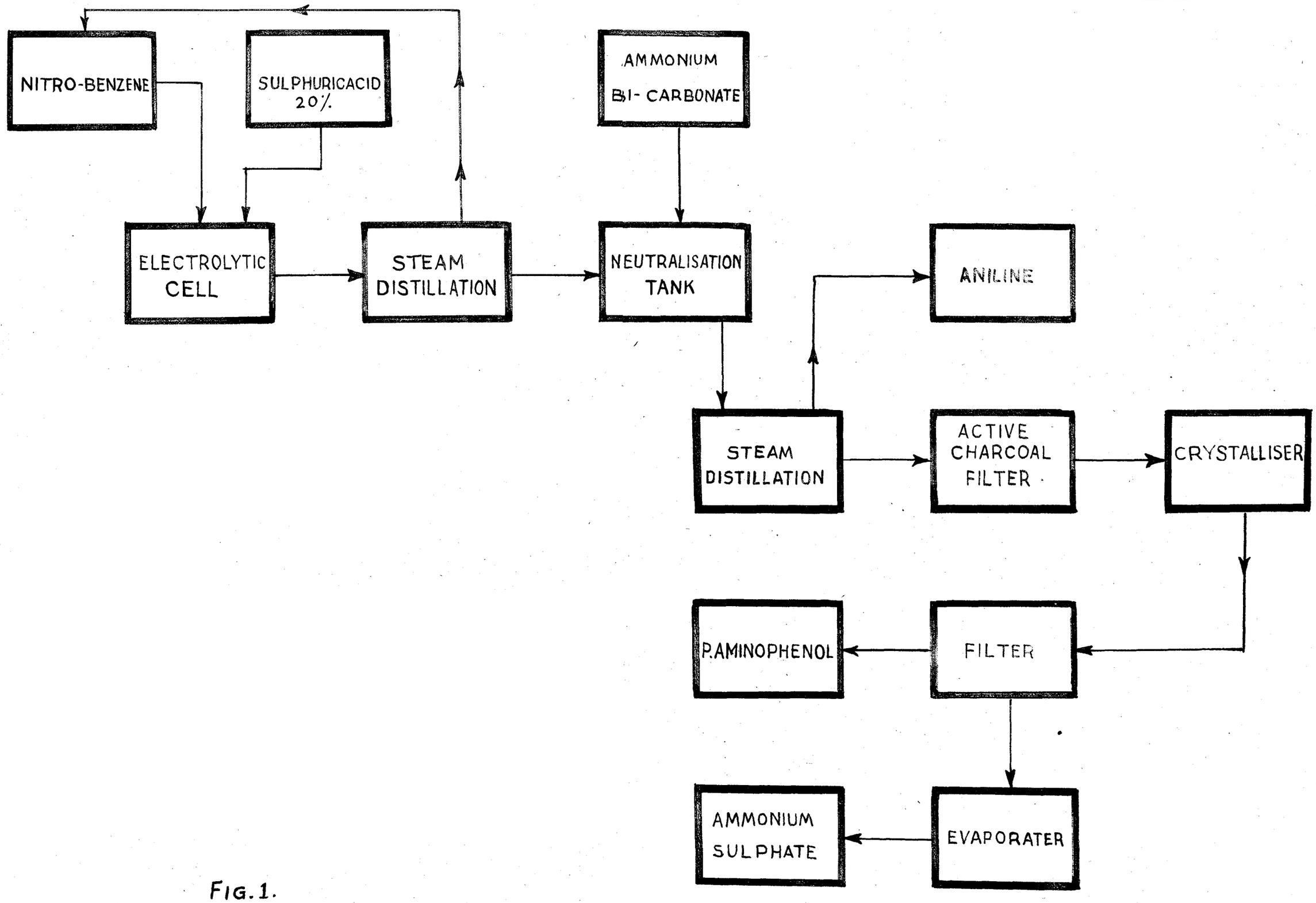

FIG. 1.

QUALITATIVE BLOCK TYPE FLOW-SHEET

FOR P. AMINOPHENOL

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