GOVERNMENT OF INDIA, THE PATENT OFFICE
214, ACHARYA JAGADISH BOSE ROAD
CALCUTTA-700017.

Complete Specification No. 150086 dated 9th October, 1979
Application and Provisional Specification No. 745/ Del/78 dated 9th October, 1978
Acceptance of the complete specification advertised on 17th July, 1982

Index at acceptance— $32F_{2(b)}$ [IX (1)]

International Classification— C 07 d 55/ 00

" IMPROVED TWO - STAGE PROCESS FOR THE PREPARATION OF 4-4' DIAMINOSTILBENE 2-2' DISULPHONIC ACID ".

COUNCIL OF SCIENTIFIC & 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.

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This is an invention by Handady Venkatakrishna Udupa, Director, Payyallur Narayanan Anantharaman, Scientist and Michael Noel, Junior Scientific Assistant, all of Central Electrochemical Research Institute, Karaikudi-623006, India - all Indian citizens.

This invention relates to the improvements in or relating to the electrolytic reduction of 4-4' dinitro stilbene 2-2' disulphonic acid to 4-4' diaminostilbene 2-2' disulphonic acid.

Hitherto 4-4' diamino stilbene 2-2' disulphonic acid has been synthesised by chemical reduction of 4-4' dinitro stilbene disulphonic acid with iron powder and acetic acid or hydrochloric acid. Electrochemical reduction of 4-4' dinitro stilbene 2-2' disulphonic acid has been reported and the yield is 57%.

This is open to the objection that the yield reported is very low in chemical as well as electrochemical methods and purity is also very low.

The object of the invention is to obviate these disadvantages by a method of reducing the 4-4' dinitro stilbene 2-2' disulphonic acid using titanous sulphate which can be regenerated electrochemically was developed with a current efficiency of 85-91% and the yield is between 85-97%. The 4-4' diamino stilbene 2-2' disulphonic acid obtained by this method gave 98% assay.

The invention broadly consists in reducing the titanic sulphate electrochemically and utilising the titanous sulphate solution thus produced to chemically reduce the 4-4' dinitro stilbene 2-2' disulphonic acid. During the chemical reduction, the titanous sulphate solution is converted to titanic sulphate solution which is recycled again to obtain titanous sulphate electrochemically. Thus the electrochemical reduction is carried out indirectly in two stages through the intermediate titanous/titanic redox system.

The electrochemical reduction of titanic sulphate solution is carried out by using a catholyte containing 25-50 gms/litre of TiO_2 as titanic or titanyl sulphate and 200-250 gms/litre of sulphuric acid, with a stationary or rotating copper cathode. The sulphuric acid solution containing 200-250 gms/litre was used as the anolyte and a lead in the pure form or lead alloys like lead-silver, lead antimony are used as anodes.

The electrolysis was carried out between 30-90°C but preferably between 40-50°C. When a stationary cathode is used, a glass stirrer is used to improve mass-transfer. Cathode current density ranging from 3A/dm^2 to 10 A/dm^2 but preferably in the range of 3-6 A/dm^2 depending on the TiO_2 content of the catholyte was applied. Anode current density upto 10 A/dm^2 may be applied. Ceramic diaphragm was used.

The second stage of the present investigation, the chemical reduction of 4-4' dinitro stilbene 2-2' disulphonic acid to 4-4' diamino stilbene 2-2' disulphonic acid is carried out as outlined below. 90% to 100% of the theoretical quantity of 4-4' dinitro stilbene 2-2' disulphonic acid required to oxidise the titanous sulphate solution completely is mixed with the catholyte taken in a beaker. It is kept between 40-90°C but preferably between 40-50°C for about 1 hour. It is then filtered. The filtrate containing titanic sulphate solution is used for recycling. The precipitate contains the product 4-4' diamino stilbene 2-2' disulphonic acid with a small quantity of hydrolysed titanium compound.

This sample is purified as follows: The sample is treated with water. This mixture is treated with soda ash till the solution is completely alkaline. The red coloured solution containing the sodium salt of 4-4' diamino stilbene 2-2' disulphonic acid is filtered off from the hydrolysed titanium compound which separates out as a yellow gel. This gel is dissolved in sulphuric acid and recycled with the titanic sulphate solution for electro reduction.

The red coloured filtrate obtained above is made acidic to congo red. The 4-4' diamino stilbene 2-2' disulphonic acid separates out. It is allowed to stand for 5-10 hours and then filtered and dried in open air or in an oven at 60-70°C. The yield obtained ranges between 85-97%. Examples I-8 and II-8 describe the exact conditions of the chemical reduction of 4-4' dinitro stilbene 2-2' disulphonic acid to 4-4' diamino stilbene 2-2' disulphonic acid.

The titanic sulphate solution may be reused many times. In the present investigation this solution was used 4 times.

Chemical reduction of 4-4' dinitro stilbene 2-2' disulponic acid with the recycled titanous sulphate solutions was also carried out 4 times. Analysis of the product by ISI method indicates that the sample produced by this method is 99 ± 0.5%.

The following are the main advantages of the invention:

1) The use of large quantity of iron filings and acetic acid is avoided and electricity is the only raw material consumed in the reduction.

2) The problem of handling excess sludge is avoided by this method. The solution from the purification stage is the only wastage one encounters in this process

3) The electrolyte is reused many times without any heavy loss during reuse.

4) The yield obtained in this method is 85-97% and the current efficiency is 85-91%

5) The purity of the product is 99 ± 0.5%

6) Since no solid material is introduced into or formed in the electrochemical cell the cell operations are made simpler and cell life will also be longer.

7) Since the organic compound is not introduced into the cell the cell voltage is kept at minimum and this results in energy saving.

EXAMPLE I-A

Conditions:

Catholyte	:	1000 ml solution containing 245 g of sulphuric acid and 28.2 g of TiO_2 as titanic sulphate
Analyte	:	100 ml solution containing 245 g of sulphuric acid
Cathode	:	Stationary copper cathode of area 1 dm^2
Anode	:	Lead
Diaphragm	:	Ceramic porous pot
Temperature	:	40-45°C
Voltage	:	3.2 - 3.4V

Current	:	3A
Cathode current density	:	3 A/dm^2
Quantity of current	:	9 A hrs
TiO_2 equivalent of titanous sulphate obtained	:	23.1 g
Current efficiency	:	86.0%
Energy consumption	:	1.29 kwh/kg TiO_2 reduced

EXAMPLE I-B

Volume of titanous sulphate solution taken	:	960 ml
Total TiO_2 equivalent of titanous sulphate	:	23.1 g
Weight of 4-4' dinitrostilbene 2-2' disulphonic acid taken	:	18.5 g
Maximum temperature to which the solution was heated	:	80°C
Weight of 4-4' diaminostilbene 2-2' disulphonic acid obtained	:	8.3 g
Yield	:	91.9%

EXAMPLE II-A

Catholyte	:	350 ml solution containing 196 g/lit of sulphuric acid and 46.2 g/litre of TiO_2 as titanyl sulphate
Anolyte	:	50 ml solution containing 196 g/litre of sulphuric acid
Catholyte	:	Stationary copper cathode of area 0.8 dm^2
Anode	:	Lead
Diaphragm	:	Ceramic porous pot
Temperature	:	40-45°C
Voltage	:	3.0 - 3.2V
Current	:	2 A
Cathode current density	:	4 A/dm^2
Total quantity of current passed	:	5 A hrs
TiO_2 equivalent of titanous sulphate obtained	:	13.72 g
Current efficiency	:	91.3%
Energy consumption	:	1.13 kwh/kg TiO_2 reduced

EXAMPLE II-B

Volume of titanous sulphate solution taken	350 ml
Total TiO_2 equivalent of titanous sulphate	13.72 g
Weight of 4-4' dinitrostilbene 2-2' disulphonic acid taken	6.3 g
Maximum temperature to which the solution was heated	50°C
Dry weight of 4-4' diaminostilbene 2-2' disulphonic acid obtained	5.2 g
Yield	95.9 %

TABLE 1 : REUSE OF CATHOLYTE FOR THE REGENERATION OF TITANOUS SULPHATE UNDER CONDITIONS SIMILAR TO EXAMPLE I-A

Reuse Number	Current efficiency
1	86.0 %
2	88.9 %
3	84.9 %
4	83.4 %

TABLE 2 : REDUCTION OF 4-4' DINITRO STILBENE 2-2' DISULPHONIC ACID UNDER CONDITIONS SIMILAR TO EXAMPLE I-B USING REGENERATED TITANOUS SULPHATE SOLUTION

Recycle Number	Yield
1	91.9 %
2	86.7 %
3	90.3 %
4	97.4 %

Dated this 4th day of October, 1978.

Sd/-

Asstt. Patents Officer,
Council of Scientific & Industrial Research.

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THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10)

" IMPROVED TWO - STAGE PROCESS FOR THE PREPARATION OF 4-4' DIAMINOSTILBENE 2-2' DISULPHONIC ACID ".

COUNCIL OF SCIENTIFIC & 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 :—

This is an invention by Handady Venkatakrishna Udupa, Director, Payyallur Narayanan Anantharaman, Scientist and Michael Noel, Junior Scientific assistant, all of Central Electrochemical Research Institute, Karaikudi-623006, India - all Indian citizens.

This invention relates to an improved process for the preparation of 4-4' diamino stilbene 2-2' disulphonic acid. The product of this process has wide application for use as an optical whitener in the dye industry.

Hitherto 4-4' diamino stilbene 2-2' disulphonic acid has been synthesised by chemical reduction of 4-4' dinitro stilbene 2-2' disulphonic acid with iron powder and acetic acid or hydrochloric acid. The chemical yield reported is 70%. Electrochemical reduction of the dinitro compound is also known but the yield of the diamino compound obtained is 57%.

These processes are open to the objection that the yield by the known process is very low in chemical as well as electrochemical methods and purity of the product obtained is also very low: In the chemical method, large quqntity of pure iron powder is to be used and the removal of iron sludge also poses a problem. Separation of the pure product is also tedious.

The object of this invention is to provide an improved process to obviate these disadvantages by reducing the dinitro compound using titanous sulphate which can be regenerated electrochemically with a current efficiency of 60-90% and the yield is between 89-97%. The dinitro compound obtained by this method gave a purity index of 99.0 + 0.5% assay.

The other objectives of the invention are to:

1) avoid use of large quantity of iron filings and acetic acid.
2) avoid problem of handling excess sludge.
3) provide for the reuse of electrolyte many times without any heavy loss during reuse, and
4) to provide that the product obtained is highly pure and the yield obtained is also maximum.

The process consists in reducing the titanic sulphate electrochemically and utilising the titanous sulphate solution to reduce the dinitro compound chemically. During the chemical reduction, the titanous sulphate solution is converted to titanic sulphate solution which is recycled again to obtain titanous sulphate electrochemically. Thus the electrochemical reduction is carried out indirectly in two stages.

The step of electrochemical reduction of titanic sulphate solution is carried out using a catholyte containing 25-50 gms/litre of TiO_2 as titanic or titanyl sulphate and 200-400 gms/litre of sulphuric acid, with a stationary or rotating copper or lead cathode. The sulphuric acid solution containing 200-400 gms/litre was used as the anolyte where porous pot is used as the diaphragm and lead in the pure form or lead alloys like lead-silver, lead antimony are used as anodes. The electrolysis was carried out between 35-65°C. When a stationary cathode was used a glass stirrer was used to improve mass transfer. Cathode current density ranging from 2A/dm^2 to 10 A/dm^2 depending on the TiO_2 content of the catholyte was applied. Anode current density upto 10 A/dm^2 was applifed. The ceramic porous pot or blue asbestos fibre wound around the lead anode was used as the diaphragm. In the latter case no separate anode compartment and anolyte are required.

Thus, the invention provides an improved two stage process for the preparation of 4-4' diamino-stilbene 2,2'-disulphonic acid which comprises treating titanic sulphate to electrochemical reduction to form titanous sulphate and further treating the reaction product with 4-4' dinitro--stilbene 2-2'-disulphonic acid.

According to feature of the invention the electrochemical reduction of titanic sulphate is carried out by subjecting a titanic sulphate solution as a catholyte consisting of 25-30 gms/litre of TiO_2 as titanic sulphate or titanyl sulphate and 200-400 gms/litre of sulphonic acid to electrolysis with a copper or lead cathode and 200-400 gms/litre of sulphonic acid solution as anolyte in a porous diaphragm cell with lead or a lead alloy as anode.

According to another feature of the invention the electrolysis is carried out at 35° - 65°C and a cathode current density with a stationary cathode in the range of from 2A/dm^2 to 10 A/dm^2.

According to a further feature of the invention the 4-4' dinitro stilbene 2-2' disulphonic acid is reacted with titanous sulphate at 40°- 90°C for upto 1 hour.

According to a stil further feature of the invention the titanic sulphate obtained as filtrate on the separation of 4-4-diamino stilbene 2-2' -disulphonic acid by the electrochemical reduction to form titanous sulphate for reuse.

The reduction of 4-4' dinitrostilbene 2-2' disulphonic acid to 4-4' diamino stilbene 2-2' disulphonic acid in the second step of the process comprises treating the 4-4' dinitrostilbene 2-2' disulphonic acid with titanous sulphate solution obtained by electrochemical reduction of titanic sulphate.

Further the chemical reduction of the dinitro compound to the diamino compound is carried out as outlined below. 90% to 100% of the theoretical quantity of the dintro compound required to oxidise the titanous sulphate solution completely is mixed with the catholyte taken in a beaker. It is kept between 40-90°C for about 1 hour. It is then filtered. The filtrate containing titanic sulphate solution is used for recycling after adjusting the H_2SO_4 content. The precipitate contains the product diamino compound with a small quantity of hydrolysed titanium compound.

This sample is purified as follows. The sample is treated with water. This mixture is treated with soda ash till the solution is completely alkaline. The red coloured solution containing the sodium salt of the diamino compound is filtered off from the hydrolysed titanium compound which separates out as a yellow gel. This gel is dissolved in sulphuric acid and recycled with the titanic sulphate solution for electro-reduction.

The red coloured filtrate obtained above is made acidic to congo red. The diamino compound separates out. It is allowed to stand for 5-10 hours and then filtered and dried in open air or in an oven at 60-70°C. The yield obtained ranges between 85-97%. The two stages of the process of the invention are illustrated in the following examples:

Stage I	Example I
Conditions:	
Catholyte :	: 1000 ml solution containing 245 g of sulphuric acid and 28.2 g of TiO_2 as titanic sulphate.
Anolyte	: 100 ml solution containing 245 g of sulphuric acid.
Cathode	: Stationary copper cathode of area 1 dm
Anode	: Lead
Diaphragm	: Ceramic porous pot
Temperature	:40°- 45°C
Voltage	: 3.2 - 3.4 V
Current	: 3 A
Cathode current density	: 3 A/dm^2
Quantity of electricity passed	: 9 A hrs
TiO_2 equivalent of titanous sulphate obtained.	: 23.1 g
Current efficiency	: 86.0%
Energy consumption	: 1.29 Kwh/Kg of TiO_2 reduced

EXAMPLE II

Catholyte	:	350 ml solution containing 196 g/l of sulphuric acid and 40.3 g/l of TiO_2 as titanic sulphate.
Anolyte	:	50 ml solution containing 196, g/l of sulphuric acid.
Catholyte	:	Stationary copper cathode of area 0.5 dm^2
Anode	:	Lead silver alloy
Diaphragm	:	Ceramic porous pot
Temperature	:	3.0 - 3.2 V
Current	:	2 A
Cathode current density	:	4 A/dm^2
Total quantity of electricity passed	:	5 A hrs
TiO_2 equivalent to titanous sulphate obtained.	:	13.72 g
Current efficiency	:	91.3%
Energy consumption	:	1.13 Kwh/Kg TiO_2 reduced

STAGE II EXAMPLE III

Volume of titanous sulphate solution taken	:	950 ml
Total TiO_2 equivalent of titanous sulphate	:	23.1 g
Weight of the dinitro compound taken	:	10.5 g
Maximum temperature to which the solution was heated	:	80°C
Weight of the diamino compound obtained	:	8.3 g
Yield	:	91.9%

EXAMPLE IV

Volume of titanous sulphate solution taken	:	350 ml
Total TiO_2 equivalent of titanous sulphate	:	13.72 g
Weight of the dinitro compound taken	:	6.3 g
Maximum temperature to which the solution was heated	:	50°C
Weight of the diamino compound obtained	:	5.2 g
Yield	:	95.9%

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The details of the preparation of the diamino compound using asbestos fibre diaphragm is reported in Example IV.

EXAMPLE IV

Cell	: Rectangular glass cell (30x15x 15cm) with PVC cover having provisions to insert electrodes
Electrodes	: Rectangular lead electrodes
Electrode area	: 4 dm^2 (active area)
Cell arrangement	: 3 cathodes with 2 asbestos wound anodes in between
Inter electrode distance	: 1.5 cm
Electrolyte	: 1500 ml aq. solution containing 545 gms of H_2SO_4 and 129.3 gm of $Ti(SO_4)_2$.
Cell current	: 8A
Current density	: 2A/dm^2
Cell voltage	: 2.4V
Temperature	: 38° - 40°C
No. of times the electrolysis carried out	: 4 times
Total quantity of current passed	: 60A hrs
Average current efficiency for titanic sulphate reduction	: 62.6% (average)
Total quantity of dinitro compound taken	: 45 gms (12 + 12 + 11 + 10)
Total quantity of diamino compound obtained	: 33.7 gms (total of 4 cycles)
Yield efficiency of the diamino compound	: 88.44% (average)
Energy consumption	: 4.274 Kwh/kg diamino compound produced.

The titanic sulphate solution may be reused many times. In the present investigation this solution was used 4 times.

Chemical reduction of the dinitro compound with the recycled titanous sulphate solutions was also carried out 4 times. Analysis of the product by ISI method indicates that the sample produced by this method is 99.0 + 0.5% purity.

WE CLAIM:

1. An improved two-stage process for the preparation of 4-4'-diamino-stilbene 2,2'-disulphonic acid comprising treating titanic sulphate to electrochemical reduction to form titanous sulphate and further treating the reaction product with 4-4'-dinitrostilbene 2-2' disulphonic acid.

2. Process as claimed in claim 1 wherein the electrochemical reduction of titanic sulphate is carried out by subjecting a titanic sulphate solution as a catholyte consisting of 25-30 gms/litre of TiO_2 as titanic sulphate or titanyl sulphate and 200-400 gms/litre of sulphuric acid to electrolysis with a copper or lead cathode and 200-400 gms/litre of sulphuric acid solution as anolyte in a porous diaphragm cell with lead or a lead alloy anode.

3. Process as claimed in claim 2 wherein the electrolysis is carried out at 35°-65°C and a cathode current density with a stationary cathode in the range of 2A/dm^2 to 10A/dm^2.

4. Process as claimed in any of the preceding claims wherein the 4-4'-dinitro-stilbene 2-2' disulphonic acid is reacted with titanous sulphate at 40°-90°C for upto 1 hour.

5. Process as claimed in any of the preceding claims wherein the titanic sulphate obtained as filtrate on the separation of 4-4'-diamino stilbene 2-2'-disulphonic acid by the electrochemical reduction to form titanous sulphate for reuse.

6. An improved two stage process for the preparation of 4-4', diamino-stilbene, 2-2', disulphonic acid substantially as herein described and illustrated in the examples.

Dated this 4th day of October, 1979.

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