

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, ACHARYA JAGADISH BOSE ROAD, CALCUTTA-17.

Complete Specification No. 132716. Application and Provisional Specification filed on 31st August, 1971. Complete Specification filed on 1st July, 1972. Acceptance advertised on 13th April, 1974.

Index at acceptance—32F3b[IX(1)]

Provisional Specification

IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC PRODUCTION OF GLYOXYLIC ACID FROM OXALIC ACID

COUNCIL OF SCIENTIFIC AND 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 Udpa, Director, Gobichettipalayam Srinivasan Subramanian, Scientist, and Subbarayan Thangavelu, Senior Scientific Assistant, all Indians, all of Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu.

The invention relates to improvements in or relating to the electrolytic production of glyoxylic acid.

Hitherto it has been proposed to produce glyoxylic acid by (1) chemical method from different starting materials, and (2) electrochemical method wherein oxalic acid and its esters were electrolytically reduced.

These are open to objection that in the chemical method of reduction of oxalic acid the reducing agent used (Magnesium and sulphuric acid) was costly. In the electrochemical method, complete conversion of oxalic acid to glyoxylic acid was not achieved and the isolation of glyoxylic acid in presence of oxalic acid was difficult as reported in the literature. Due to the above difficulties, the reported isolated yield of glyoxylic acid was low.

The object of this invention is to obviate these disadvantages by making use of the rotating electrode technique and a cation exchange membrane as diaphragm. By this technique, it was possible to attain the complete reduction of oxalic acid to glyoxylic acid in a catholyte containing very low sulphuric acid concentration. Catholyte of very low acid concentration and complete conversion of oxalic acid into glyoxylic acid make the isolation of glyoxylic acid simple without involving the separation of oxalic acid and glyoxylic acid from the solution.

To these ends, the invention broadly consists in reducing oxalic acid in a divided cell having the cation exchange membrane separating the anode and cathode compartments. A rotating cathode of lead or amalgamated lead is used and catholyte of dilute sulphuric acid upto a concentration of 5% but preferably 0.1 to 2.5% is used keeping the anolyte concentration of 10% by weight sulphuric acid unaltered. The reduction is carried out upto a current density of 10 amp/dm² but preferably at 6—8 amp/dm². Anode material is lead. The temperature of the cell is maintained between 10 and 25°C but preferably between 10—18°C. After the electrolysis, both glyoxylic acid as well as the oxalic acid contents of the elec-

trolyte are estimated. In the case of the experiment in which 30% excess of theoretical current was passed, complete conversion of oxalic acid into glyoxylic acid is achieved. The product is isolated as free glyoxylic acid as syrupy liquid by vacuum concentrating the solution after removing the sulphuric acid present in the solution by adding calculated amount of calcium carbonate or by neutralising the solution completely with calcium carbonate, isolating the calcium glyoxylate along with calcium sulphate, then adding calculated amount of concentrated sulphuric acid to the above salt mixture, filtering and vacuum concentrating the filtrate.

The following typical examples are given to illustrate the invention.

Example I

Catholyte	W/v 500 ml of 0.7% H ₂ SO ₄ solution
Depolariser oxalic acid added	41 gm
Anolyte	10% by wt H ₂ SO ₄
Cathode	Amalgamated Lead
Anode	Lead
Diaphragm	Cation exchange membrane
Current	3 amperes
Current density	6 amp/dm ²
Temperature	10—18°C
Voltage	6.6 volts.
Total current passed	22.5 amp. hours (30% excess)
Glyoxylic acid formed	22.62 gms
Current efficiency	72.66%
Assay yield	94%

Example II]

Catholyte	500 ml of 0.7% H ₂ SO ₄ solution
Depolariser oxalic acid added	41 gm
Anolyte	10% by weight H ₂ SO ₄
Cathode	Amalgamated Lead
Anode	Lead

Price : TWO RUPEES.

Diaphragm	Cation exchange membrane	Voltage	5.5 volts
Current	4 amperes	Total current passed	23.8 amp. hours (40% excess)
Current density	8 amp/dm ²	Glyoxylic acid formed	22.43 gm
Temperature	10—18°C	Unreduced oxalic acid	Nil
Voltage	7.5 volts	Current efficiency	68.17%
Total current passed	22.5 amp. hours (30% excess)	Assay yield	95.5%
Glyoxylic acid formed	22.76 gm		
Oxalic acid left unreduced	Nil		
Current efficiency	73%		
Assay yield	94%		

Example III

Catholyte	500 ml of 2.5% by weight H ₂ SO ₄ solution
Depolariser oxalic acid added	40gm
Anolyte	10% by weight H ₂ SO ₄ solution
Cathode	Amalgamated Lead
Diaphragm	Cation exchange membrane
Current	3 amperes
Current density	6 amp/dm ²
Temperature	10—18°C

The following are the main advantages of the invention :

1. Isolation of glyoxylic acid is made simple by achieving complete reduction of oxalic acid.
2. This is the method by which half aldehydes can be prepared from oxalic acid without much difficulties.
3. The rotating electrode technique permits the use of high current densities and simplifies the design of high amperage cells.

Dated this 26th day of August, 1971.

Sd/-

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COMPLETE SPECIFICATION

IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC PRODUCTION OF GLYOXYLIC ACID FROM OXALIC ACID

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIS 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, Gobichettipalayam Srinivasan Subramanian, Scientist, and Subbarayan Thangavelu, Senior Scientific Assistant, all Indians, all of Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu.

The invention relates to improvements in or relating to the electrolytic production of glyoxylic acid.

Hitherto it has been proposed to produce glyoxylic acid by (1) Chemical method from different starting materials (2) Electrochemical method wherein oxalic acid and its esters are electrolytically reduced. These are open to objection that in the chemical method of reduction of oxalic acid, the reducing agent used (magnesium powder and sulphuric acid) is costly. In the electrochemical method, complete conversion of oxalic acid to glyoxylic acid is not achieved and the isolation of glyoxylic acid in presence of oxalic acid is difficult due to the temperature sensitiveness of glyoxylic acid which undergoes decomposition. Due to the above difficulties, the reported isolated yield of glyoxylic acid is low.

The object of this invention is to obviate these disadvantages by making use of the rotating electrode technique and a cation exchange membrane as diaphragm. By this technique it is found possible to attain the complete reduction of oxalic acid to glyoxylic acid in a catholyte containing very low sulphuric acid concentration. Catholyte of very low sulphuric acid concentration and complete conversion of oxalic acid into glyoxylic acid make the isolation of glyoxylic acid simple without involving the difficulties of separation of oxalic acid and glyoxylic acid from the solution.

According to the present invention, there is provided a process for the production of glyoxylic acid which consists in the electrolytic reduction of a solution of oxalic acid characterised in that the reduction of oxalic acid requiring a theoretical current equal to 2 F/gm mole of oxalic acid is made complete by passing 30% excess of theoretical current at a rotating lead/or amalgamated lead cathode using cation exchange membrane as diaphragm.

The reduction of oxalic acid is carried out in a divided cell having cation exchange membrane as diaphragm separating anolyte and catholyte

at a current density up to 10 A/dm² but preferably at 6-8 A/dm² in a catholyte of dilute sulphuric acid up to a concentration of 10% (w/v) but preferably 0.1 to 2.5% at a temperature between 10-25°C but preferably between 10-18°C having a lead anode in an anolyte of 10% (w/v) sulphuric acid.

After passing theoretical quantity of current equal to 2 F/gm. mole of oxalic acid, the glyoxylic acid and the unreduced oxalic acid content of the electrolyte are estimated. Complete conversion of oxalic acid to glyoxylic acid is achieved by using cation exchange membrane diaphragm and by passing 30% excess of theoretical current.

Complete conversion is not possible with ceramic porous pot diaphragm under the identical conditions. This product is isolated as free glyoxylic acid as a syrupy liquid by vacuum concentrating the solution after removing the sulphate content of the solution by adding calculated amount of calcium carbonate or by neutralising the solution completely with calcium carbonate, isolating the calcium glyoxylate along with calcium sulphate, then adding calculated amount of 70 to 80% sulphuric acid to the above salt mixture, filtering and vacuum concentrating the filtrate. Qualitative block type flow sheet for the process is given in Fig. 1 of the accompanying drawing.

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

Example -I (with cation exchange diaphragm)

Catholyte	W/v 500 ml of 0.7% H ₂ SO ₄ solution containing 40g of oxalic acid.
Anolyte	10% by wt. H ₂ SO ₄ solution
Cathode	Amalgamated lead
Anode	Lead
Diaphragm	Cation exchange membrane
Current	3 amperes
Current density	6 amp/dm ²
Temperature	10-18°C
Voltage	6.3 V
Total current passed	22.1 AH (30% excess)
Glyoxylic acid formed	23.25 g
Current efficiency	76%
Assay yield	98%
Oxalic acid left unreduced	Nil

Example-II (with cation exchange diaphragm)

Catholyte	500 ml of 0.6 to 0.7% by wt. H ₂ SO ₄ solution containing 40 g of oxalic acid
Anolyte	10% by wt. H ₂ SO ₄ solution
Cathode	Amalgamated lead
Anode	Lead
Diaphragm	Cation exchange membrane

Current	3 Amps
Current density	6 A/dm ²
Temperature	10-18°C
Total current passed	21.26 AH(25% excess)
Oxalic acid left unreduced	2.288 g
Current efficiency	69.70%

Example-III(with ceramic porous pot)

Catholyte	500 ml of 0.7 by wt. H ₂ SO ₄ solution containing 41 g of oxalic acid
Anolyte	10% by wt. H ₂ SO ₄ solution
Cathode	Amalgamated lead
Anode	Lead
Diaphragm	Ceramic porous pot
Current	3 amperes
Current density	6 A/dm ²
Temperature	10-18° C
Voltage	6 V
Total current passed	22.1 AH (30% excess)
Glyoxylic acid formed	16.55 g
Oxalic acid left unreduced	5.187 g
Oxalic acid unaccounted	7.64 g
Current efficiency	55.4%

Example-IV (Stationary electrode with stirring)

Catholyte	800 ml of 0.7% by wt. H ₂ SO ₄ solution containing 65 g of oxalic acid
Anolyte	10% by wt. H ₂ SO ₄ solution
Cathode	Stationary amalgamated lead electrode with stirring
Anode	Lead
Diaphragm	Cation exchange membrane
Current	3A
Current density	6 A/dm ²
Temperature	10-18°C
Total current passed	35.91 AH (30% excess)
Glyoxylic acid formed	25.11 g
Oxalic acid left unreduced	21.48 g
Current efficiency	50.62%

The following are the main advantages of the invention :

1. Isolation of glyoxylic acid is made simple by achieving complete reduction of oxalic acid using cation exchange membrane diaphragm

2. This is the method by which half aldehyde can be prepared from oxalic acid without much difficulties.

3. The rotating electrode technique permits the use of high current densities for the reduction and it simplifies the design of high amperage cells.

SUMMARY

The invention consists of a process for the production of glyoxylic acid by the electrolytic reduction of oxalic acid using the rotating electrode technique. The reduction is carried out using a nearly saturated solution of oxalic acid (80g/lit) containing about 6-7 g of concentrated sulphuric acid. A divided cell having a cation exchange membrane diaphragm is employed. As cathode material either lead or amalgamated lead is used. Complete conversion of oxalic acid to glyoxylic acid is achieved by passing 30% excess of theoretical current. Glyoxylic acid is isolated as syrupy liquid by completely neutralising the solution with calcium carbonate, isolating the calcium glyoxylate along with calcium sulphate, then adding calculated amount of concentrated sulphuric acid to the above salt mixture, filtering and vacuum concentrating the filtrate. Crystalline solid of glyoxylic acid can be obtained by allowing the syrupy liquid to crystallise under vacuum over concentrated H_2SO_4 or phosphorus pentoxide.

WE CLAIM :

1. A process for the production glyoxylic acid which consists in the electrolytic reduction of a solution of oxalic acid characterised in that the

reduction of oxalic acid requiring a theoretical current equal to 2 F/gm mole of oxalic acid is made complete by passing 30% excess of theoretical current at a rotating lead/or amalgamated lead cathode using cation exchange membrane as diaphragm.

2. A process as claimed in claim 1 wherein the reduction of oxalic acid is carried out in a divided cell having cation exchange membrane as diaphragm separating anolyte and catholyte at the rotating cathode of lead/or amalgamated lead at a current density up to 10 A/dm² but preferably at 6-8 A/dm² in a catholyte of dilute sulphuric acid up to a concentration of 10% (w/v) but preferably 0.1 to 2.5% at a temperature between 10-25°C but preferably between 10-18°C having a lead anode in an anolyte of 10% (w/v) sulphuric acid.

3. A process for the production of glyoxylic acid substantially as herein before described.

Dated this 27th day of June, 1972.

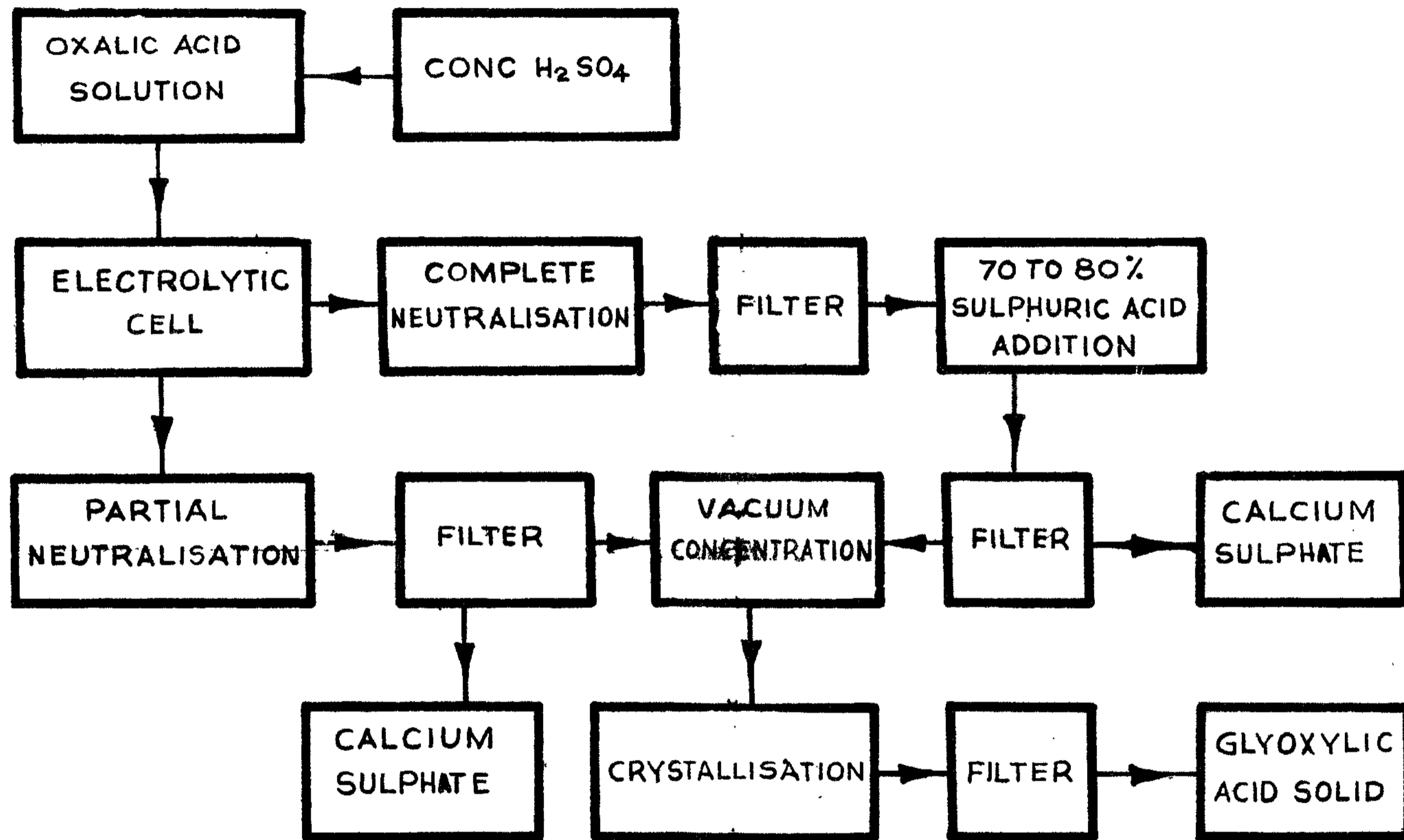
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No. 132716

SHEET NO:- 1



**QUALITATIVE BLOCK TYPE FLOW SHEET
FOR GLYOXYLIC ACID**

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