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" AN IMPROVED PROCESS FOR THE ELECTROLYTIC
PRODUCTION OF GLYOXYLIC ACID FROM OXALIC
ACID "

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.

This is an invention by Handady Venkatakrishna Udupa,
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Subbiah, Krishnamoorthy Jayaraman and Pachamuthu Thirunavukkarasu,
all of Central Electrochemical Research Institute Tamil Nadu,
all Indian citizens.

Price. Rs. 2.00

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This invention relates to improvements in or relating to the electrolytic production of glyoxylic acid from oxalic acid.

Hitherto it has been proposed to produce glyoxylic acid by the reduction of oxalic acid in the presence of a mineral acid such as sulphuric acid as a supporting electrolyte at a rotating/stationary lead/amalgamated lead cathode (Indian Patent No. 132716).

This is open to objection that such a method involves difficulties in the isolation of the product in the presence of sulphuric acid in the catholyte.

The object of this invention is to obviate these disadvantages by reducing the oxalic acid without any supporting electrolyte at a rotating/stationary cathode of lead/amalgamated lead so that the isolation of the glyoxylic acid is made simpler.

To these ends, the invention broadly consists in reducing an aqueous solution of oxalic acid (40 to 80 g/l) on a lead/amalgamated lead cathode at a current density between 1 and 10 amp/dm² employing diaphragms like porous ceramic, micro porous PVC/cation exchange membrane. Dilute sulphuric acid upto a concentration of 20% (W/V) but preferably a concentration of 10% (W/V) is used as anolyte having lead/lead silver (1%) alloy anode. The temperature of catholyte is maintained between 10 and 25°C but preferably between 10 and 18°C by circulation cold brine through lead cooling coils. The reduction is carried out to theoretical time corresponding to 2F/mole of oxalic acid

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initially present in the catholyte. After the completion of the electrolysis glyoxylic acid and the unreduced oxalic acid content of the catholyte are estimated. The catholyte is then vacuum concentrated to 50% (W/W) of glyoxylic acid and cooled to 0 to 10°C. Unreduced oxalic acid crystallises out and is removed by filtration. Final glyoxylic acid content in the syrup is estimated.

The following typical examples are given to illustrate the invention:

EXAMPLE I

Catholyte:	..	45 litres of oxalic acid solution containing 3.6 kg of oxalic acid.
Anolyte:	..	12 litres of 10% (W/V) of H ₂ SO ₄
Cathode:	..	Stationary lead (area 40 dm ²)
Anode:	..	Lead-silver alloy (1%)
Diaphragm:	..	Ceramic porous pot
Current:	..	100 amps
Current density:	..	2.5 amp/dm ²
Temperature:	..	10 to 15°C
Cell voltage:	..	5.4 to 9.0V
Glyoxylic acid estimated:	..	1.570 kg
Unreduced oxalic acid:	..	0.371 kg
Assay yield:	..	72.2%
Current efficiency:	..	64.7%

EXAMPLE II

Catholyte:	..	45 litres of oxalic acid solution containing 3.6 kg of oxalic acid.
Anolyte:	..	12 litres of 10% (W/V) of H ₂ SO ₄
Cathode:	..	Stationary lead (area 40 dm ²)

Anode:	..	Lead silver (1%) alloy
Diaphragm:	..	Ceramic porous pot
Current:	..	120 amps
Current density:	..	3 amp/dm ²
Temperature:	..	10-15°C
Cell voltage:	..	5.6 to 9.0V
Glyoxylic acid estimated:	..	1.314 kg
Unreduced oxalic acid:	..	0.392 kg
Assay yield	..	71.65%
Current efficiency:	..	63.87%

EXAMPLE III

Catholyte:	..	45 litres of oxalic acid solution containing 1.8 kg of oxalic acid.
Anolyte:	..	12 litres of 10% (W/V) of H ₂ SO ₄
Cathode:	..	Stationary lead (area 40 dm ²)
Anode:	..	Lead-silver alloy (1%)
Diaphragm:	..	Ceramic porous pot
Current:	..	120 amp
Current density:	..	3 amp/dm ²
Temperature:	..	10 to 15°C
Cell voltage:	..	7.3 to 12.0V
Total oxalic acid reduced:	..	3.6 kg
Glyoxylic acid estimated:	..	1.355 kg
Unreduced oxalic acid:	..	0.367 kg
Assay yield:	..	70.09%
Current efficiency:	..	64.12%

EXAMPLE IV

Catholyte:	..	500 ml oxalic acid solution containing 40 g of oxalic acid
Anolyte:	..	150 ml of H_2SO_4 (10% w/v)
Cathode:	..	Rotating cylindrical lead
Anode:	..	Lead silver alloy (1%)
Diaphragm:	..	Ceramic porous pot
Current:	..	3.5 amp
Current density:	..	7 amp/dm ²
Temperature:	..	13 to 15°C
Cell voltage:	..	8.6 to 13.0V
Glyoxylic acid estimated:	..	15.96 g
Unreduced oxalic acid:	..	3.50 g
Assay yield:	..	74.46%
Current efficiency:	...	67.65%

The following are the main advantages of the invention:

a) Isolation of glyoxylic acid is made simple by avoiding a separate supporting electrolyte such as sulphuric acid.

b) Complete reduction of oxalic acid by passing excess current is not essential for the isolation of glyoxylic acid, since the glyoxylic acid can be isolated even in the presence of small quantities of unreduced oxalic acid.

c) The present method of isolation avoids neutralisation of H_2SO_4 with calcium carbonate thus economising the process.

Dated this 21st day of December, 1977

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COMPLETE SPECIFICATION

(Section--10)

**" AN IMPROVED PROCESS FOR THE ELECTROLYTIC
PRODUCTION OF GLYOXYLIC ACID FROM OXALIC
ACID "**

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH,
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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, Director; Kodethoor Shrivara Udupa, Scientist; Subbarayan Thangavelu, Scientist; Poominathan Subbiah, Scientist; Krishnamurthy Jayaraman, Senior Scientific Assistant, and Pachaimuthu Thirunavukkarasu, Senior Laboratory Assistant, all of Central Electrochemical Research, Institute, Karaikudi-623006, India, all Indian citizens.

An invention relates to an improved process for electrolytic production of glyoxylic acid from oxalic acid. Glyoxylic acid is used to synthesis perfumery chemicals like vanillin and pharmaceuticals like allantoin, vitamin C derivatives. The invention thus will be highly useful in the pharmaceutical and perfumery industries.

Hitherto it has been proposed to produce glyoxylic acid by electrolytic reduction of oxalic acid in the presence of a mineral acid such as sulphuric acid as supporting electrolyte at a rotating/stationary lead/amalgamated lead cathode.

The objection to the hitherto known process is that the method involves difficulties in the isolation of the product due to the presence of sulphuric acid in the catholyte.

The object of the invention is to obviate these disadvantages by reducing the oxalic acid without any supporting electrolyte at a rotating/stationary cathode of lead/amalgamated lead so that the isolation of the glyoxylic acid is made simpler.

The other main objectives of the inventions are

a) to make the isolation of glyoxylic acid ^{separate} simple by avoiding a/supporting electrolyte such as sulphuric acid;

b) to effect complete reduction of oxalic acid, the passing of excess current is not essential for isolation of glyoxylic acid, since the glyoxylic acid can be isolated even in the presence of small quantities of unreduced oxalic acid.

c) The present method avoids the neutralisation of oxalic acid and sulphuric acid with calcium carbonate thus economising the process.

The process broadly consists in reducing an aqueous solution of oxalic acid (40 to 80 g/l) on a lead/amalgamated lead cathode at a current density between 1 and 10 A/dm² employing diaphragms like porous ceramic, microporous PVC/cation exchange membrane. The catholyte temperature being maintained between 10 and 25°C but preferably between 10 and 18°C.

Accordingly the invention provides an improved process for the electrolytic production of glyoxylic acid from oxalic acid in an electrolytic diaphragm cell characterised in that an aqueous solution of oxalic acid is used as catholyte and dilute sulphuric acid as anolyte and separating the unreacted oxalic acid from the catholyte by crystallisation to obtain glyoxylic acid in the filtrate. The process is carried at a current density of 1 to 10 amp/dm² and at a ~~current-density-of~~ temperature maintained between 10 and 25°C of the catholyte and glyoxylic acid formed is separated therefrom.

As a result of the invention the isolation of glyoxylic acid is made simpler as it involves only the evaporation of the catholyte to the required concentration. Oxalic acid is recovered without neutralisation as it separates out during vacuum concentration. The process thus avoids the neutralisation step involving the neutralisation of sulphuric acid and oxalic acid as well as the oxalic acid recovery step involving the leaching of calcium oxalate with dilute sulphuric acid.

The present method does not involve the use of calcium carbonate for neutralisation and sulphuric acid for the leaching of calcium oxalate and for supporting electrolyte, thereby economising the process.

The present invention consists of a process for the electrolytic production of glyoxylic acid from oxalic acid which comprises of the reduction of an aqueous solution of oxalic acid (40 to 80 g/l) on a lead/amalgamated lead cathode at a current density between 1 and 10 amp/dm² employing diaphragms like porous ceramic, microporous PVC/cation exchange membrane. Dilute sulphuric acid upto a concentration of 20% (W/V) but preferably a concentration of 10% (W/V) is used as anolyte having lead/lead-silver (1%) alloy anode. The temperature of catholyte is maintained between 10 and 25°C but preferably between 10 and 18°C by circulating cold brine through lead cooling coils. The reduction is carried out to theoretical time corresponding to 2F/mole of oxalic acid initially between present in the catholyte. After the completion of electrolysis, glyoxylic acid and the unreduced oxalic acid content of the catholyte are estimated. The catholyte is then vacuum concentrated to 50% (W/W) of glyoxylic acid and cooled to 0 to 10°C. About 75% to 80% of unreduced oxalic acid crystallises out and is removed by filtration. The purity of recovered oxalic acid is 98%. Final glyoxylic acid content in the syrup is estimated.

The process consists in the electrolytic reduction of an aqueous solution of oxalic acid (40-80 g/l) on a rotating/stationary lead/amalgamated lead cathode using porous ceramic, micro porous PVC/cation exchange membrane as diaphragm. At the end of the theoretical time of electrolysis, the catholyte is vacuum evaporated to a glyoxylic acid concentration of 50% W/W. The concentrated syrup is filtered to remove the unreduced oxalic acid which separates out during vacuum concentration. The filtrate is estimated for its glyoxylic acid content and marketed.

The following typical examples illustrate the invention:

EXAMPLE 1

Catholyte:	.. 45 litres of oxalic acid solution containing 3.6 kg of oxalic acid.
Anolyte:	.. 12 litres of 10% (W/V) of sulphuric acid.
Cathode:	.. Stationary lead (area 40 dm ²)
Anode:	.. Lead-silver ₂ alloy (1% silver) (area 20 dm ²)
Diaphragm;	.. Ceramic porous pot.
Current density:	.. 2.5 amp/dm ²
Current	.. 100 amperes
Temperature:	.. 10 to 15°C

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Cell voltage: .. 5.4 to 9.0V
Glyoxylic acid estimated:.. 1.370 kg
Unreduced oxalic acid: .. 0.371 kg
Assay yield: .. 72.2%
Current efficiency: .. 64.7%

EXAMPLE 2

Catholyte: .. 45 litres of oxalic acid solution
containing 3.6 kg of oxalic acid.
Anolyte: .. 12 litres of 10% W/V of sulphuric
acid
Cathode: .. Stationary lead (area 40 dm²)
Anode: .. Lead-silver alloy (1%) (area 20 dm²)
Diaphragm: .. Ceramic porous pot
Current: .. 120 amperes
Current density: .. 3 amps/dm²
Temperature: .. 10 to 15°C
Cell voltage: .. 5.6 to 9.0V
Glyoxylic acid estimated:.. 1.314 kg
Unreduced oxalic acid: .. 0.392 kg
Assay yield: .. 71.68%
Current efficiency: .. 63.87%

EXAMPLE 3

Catholyte: .. 500 ml of oxalic acid solution
containing 40 g of oxalic acid.
Anolyte: .. 140 ml of 10% W/V sulphuric acid.
Cathode: .. Rotating amalgamated lead cylinder
(Area = 0.6 m²)

Anode: Lead (Area 0.33 dm^2)
Diaphragm: .. Ceramic porous pot
Current: .. 4 amps
Current density: .. 6.6 amp/dm^2
Temperature: .. $10-15^\circ\text{C}$
Cell voltage: .. 10 - 11V
Glyoxylic acid, estimated: .. 16.57 g.
Unreduced oxalic acid: .. 7.42 g
Assay yield: .. 86.62%
Current efficiency: .. 70.53%

EXAMPLE 4

Catholyte: .. 500 ml of oxalic acid solution containing 40 g of oxalic acid
Anolyte: .. 140 ml of 10% W/V sulphuric acid
Cathode: .. Stationary amalgamated lead (Area = 1.3 dm^2)
Anode: .. Lead (Area 0.33 dm^2)
Diaphragm: .. Ceramic porous pot
Current: .. 4 amps
Current density: .. 3.07 amp/dm^2
Temperature: .. $10-15^\circ\text{C}$
Cell voltage: .. 9 - 10V
Glyoxylic acid estimated: .. 19.3 g.
Unreduced oxalic acid .. 2.1 g

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Assay yield .. 86.74%
Current efficiency: .. 82.17%

EXAMPLE 5

The reduction was carried out with 40 g/l initial concentration and the concentration was maintained until another 1.8 kg of oxalic acid has been added in regular instalments.

Catholyte: . 45 litres of oxalic acid solution containing 1.8 kg of oxalic acid
Anolyte: .. 12 litres of 10% (W/V) sulphuric acid
Cathode: .. Lead (stationary) Area 40 dm²
Anode: .. Lead-silver alloy (1%) Area 20 dm²
Diaphragm: .. Ceramic porous pot
Current: .. 120 amps
Current density: .. 3 amp/dm²
Temperature: .. 10 - 15°C
Cell voltage: .. 9.3 - 12.0V
Total oxalic acid reduced.. 3.6 kg
Glyoxylic acid estimated .. 1.355 kg
Unreduced oxalic acid: .. 0.367 kg
Assay yield: .. 70.09%
Current efficiency: .. 64.12%

The electrolytic reduction of oxalic acid to glyoxylic acid is carried out using a rotating/stationary lead/amalgamated lead cathode at current densities ranging from

1-10 amp/dm² without the use of any supporting electrolyte such as sulphuric acid. By such a method, the processing operations for the isolation of glyoxylic acid are simplified. The process is also made economical due to the avoidance of calcium carbonate for neutralisation and sulphuric acid for the recovery of oxalic acid and as supporting electrolyte.

WE CLAIM:

1) An improved process for the electrolytic production of glyoxylic acid from oxalic acid in an electrolytic diaphragm cell characterised in that an aqueous solution of oxalic acid is used as catholyte and dilute sulphuric acid as anolyte and separating the unreacted oxalic acid from the catholyte by crystallisation to obtain glyoxylic acid in the filtrate.

2) Process as claimed in claim 1 wherein the electrolysis is carried out at a current density between 1 and 10 amp/dm² and a temperature of 10 to 25°C of the catholyte.

3) Process as claimed in claim 1 wherein oxalic acid is used in an aqueous solution of concentration of 40-80 g/l and reduction is carried out to 2F/mole of oxalic acid initially present in the catholyte.

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4) Process as claimed in claim 1 wherein the temperature of the catholyte is preferably maintained at 10-18°C.

5) Process as claimed in any of the preceding claims wherein the catholyte obtained is vacuum concentrated to 50% (W/W) of glyoxylic acid and cooled to 0-10°C to crystallise out unreduced oxalic acid and to obtain δ glyoxylic acid as a su syrup.

6) Improved process for the electrolytic production of glyoxylic acid from oxalic acid substantially as described and illustrated herein.

Dated this 14th day of December 1978

B. S. Manan

Patents Officer
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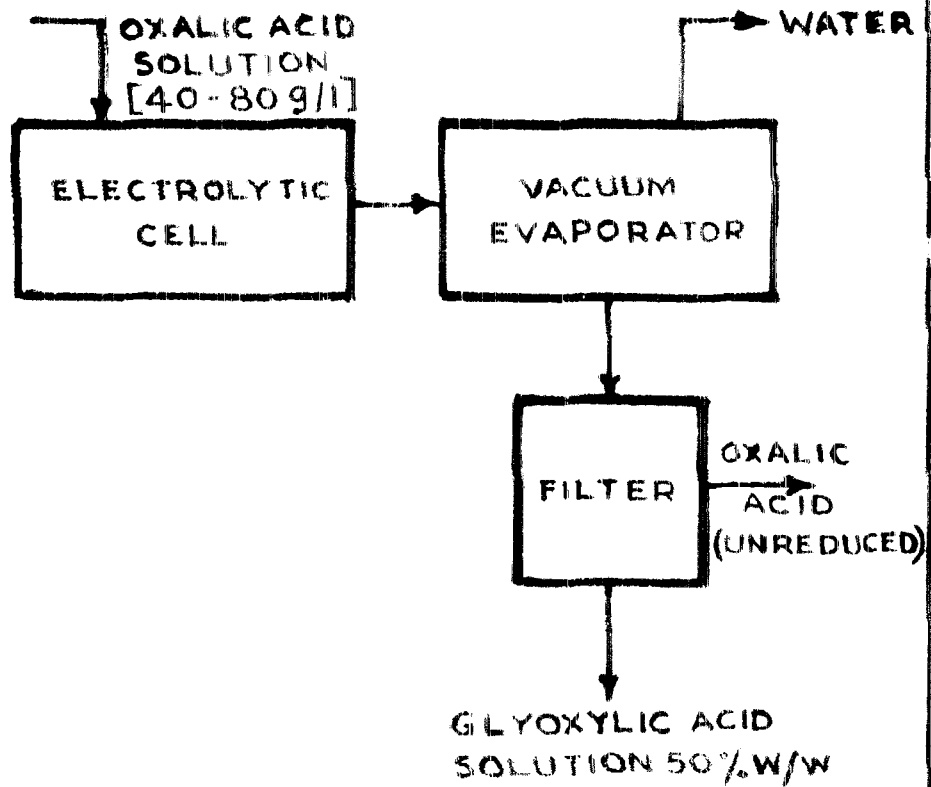


FIG. 1

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