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Index at acceptance—70C7 [LVIII(5)]

PROVISIONAL SPECIFICATION

“IMPROVEMENTS IN/OR RELATING TO THE ELECTROLYTIC REDUCTION OF SALICYLIC
ACID TO SALICYLALDEHYDE”

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

This invention relates to improvements in/or relating to the electrolytic reduction of salicylic acid to salicylaldehyde.

Hitherto it has been proposed to reduce salicylic acid electrolytically by rotating/or stationary amalgamated cathodes of copper, lead or monel in a divided cell using a ceramic or microporous rubber diaphragm.

This is open to objection that by such a method it was fairly difficult to control the pH of the catholyte at the desired range (5.4-6) and the amalgam surface was becoming black or dull giving low reproducibility of results in a number of runs. The cell voltage was also higher (10-12 volts) for the range of current density employed (upto 15 amp/dm²). Moreover by such a technique it was difficult to scale up the cells to larger amperages due to unsuitability of such diaphragms under high hydraulic heads and or/fragile nature of the ceramic pots.

The object of this invention is to obviate these disadvantages and has been achieved by using blue asbestos cloth as a diaphragm by which it is possible to maintain the pH of the catholyte at the desired value and the operating voltage of the cell is lower (8 to 10V) for the same current density range (upto 15 amp/dm²) thereby lowering the cost of cooling and the power consumption for the process. There is no deposit of scale on the diaphragm surface which is observed at times on the ceramic pots/or microporous rubber diaphragm.

To these ends, the invention broadly consists in reducing salicylic acid in a divided cell having the blue asbestos cloth diaphragm separating the anode and cathode compartments. A rotating/or stationary amalgamated cathode of copper, brass, lead, zinc or monel is used or an agitated pool of mercury as cathode. Alkali metal sulphates preferably of sodium are used as catholyte and a strength upto 20% is used, but preferably 15%. The reduction is carried out in the presence of boric acid which is added to the catholyte upto a concentration of 5-15% but preferably 12% concentration. The reduction is carried at a current density range of 1-15 amp/dm² but preferably at 10 amp/dm². The pH of the catholyte is maintained between 5 and 6 but preferably at 5.4-5.7 by addition of dilute sulphuric acid if required. The anolyte is sulphuric acid of 5 to 30% strength but preferably 20% concentration. The anode material may be lead, lead dioxide over graphite. The temperature of the cell is maintained between 10 and 20°C but preferably between 15-18°C. The salicylaldehyde is fixed as it is formed as bisulphite addition compound by adding sodium bisulphite or by feeding the cell with a mixture of salicylic acid and sodium sulphite. The depolariser mixture is added preferably in instalments rather than in one whole lot. 2 Faradays are required for every

mole of salicylic acid reduced and preferably such quantities of depolariser mixture are taken so that the electrolysis is complete in 2 hours. The catholyte is subjected to steam distillation to recover the aldehyde. It is then treated with active charcoal and recycled again for further use, the recycling being done at least two times before the solutions are discarded after recovering the unreduced salicylic acid, boric acid and bisulphite from the solution.

The following typical examples are given to illustrate the invention :

EXAMPLE I

Catholyte :	390 ml of water containing 60 g. of sodium sulphate (anhydrous), 45 g. of boric acid. 14 g. of salicylic acid and 15 g. of sodium sulphate dissolved in 30 ml. water.	
Current :	6 amps	
Current density :	10 amp/dm ²	
Temperature :	15-16°C	
Cell voltage :	8-10V	
Duration of electrolysis :	1 hour	
Anolyte :	10 ml of 20% sulphuric acid	
Diaphragm :	Blue asbestos cloth	
Anode :	Lead	
Cathode material :	Salicylaldehyde obtained as free oil (cc)	Current efficiency (%)
1. Rotating amalgamated copper. Area 0.6 dm ²	3.0	30
2. Rotating amalgamated zinc. Area 0.6 dm ²	3.4	34
3. Rotating amalgamated model. Area 0.6 dm ²	3.2	32
4. Pool of mercury 0.75 dm ²	3.0	30

EXAMPLE II

Catholyte :	390 ml of water containing 60 g. of sodium sulphate (anhydrous) 45 g. of boric acid. 42 g. of salicylic acid and 45 g. of sodium sulphite dissolved in 90 ml. water.	
Temperature :	15-16°C	
Current density :	12 amp/dm ²	
Anode :	Lead	
Anolyte :	100 ml of 20% sulphuric acid	
Diaphragm :	Blue asbestos cloth	
Duration of electrolysis :	2 hours, 40 minutes	

Price : TWO RUPEES

Cathode material	Salicylaldehyde obtained as free oil (cc)	Current efficiency (%)	Depolariser :	14 g. of salicylic acid 15 g. of sodium sulphate	Dissolved in 30 ml water
1. Rotating amalgamated copper. Area 0.6 dm ²	9.6	32	Temperature ;	15-16°C	
2. Rotating amalgamated Zinc. Area, 0.6 dm ²	11.2	35.17	Cathode :	Stationary amalgamated copper	
			Current density :	3 amp/dm ²	
			Anode :	Lead	
			Anolyte :	100 ml 20% sulphuric acid	
			Diaphragm :	Blue asbestos cloth	
			Salicylaldehyde obtained as free oil :	2.1 cc	
Catholyte :	130 ml water containing 20 g. sodium sulphate (anhydrous), 15 g. borric acid.		Current efficiency :	21%	

EXAMPLE III

EXAMPLE IV

Effect of recycling of the electrolyte		Conditions same as in Example II for the fresh charge					
Cathod	Salicylic acid taken (g)	Salicylaldehyde obtained as free oil (cc)	Current efficiency (%)	Salicylic acid present in solution (g)	Acid corresponding to aldehyde obtained	Acid unaccounted	Remarks
Rotating amalgamated copper	28	10.0	50	10.85	13.12	4.0	Fresh amalgamation done
—do— —do—	17	7.0	35	17.76	9.2	0.8	—do— —do—
—do— —do—	15	6.8	34	Not estimated	—do— —do—
Rotating amalgamated Zinc	56	15	35	38.11	19.68	..	Fresh amalgamation
—do— —do—	18	7	20	40.7	9.3	6.0	No fresh amalgamation done, Same amalgam surface used.

The following are among the main advantages of the investigation :

(a) The use of blue asbestos cloth as a diaphragm material has the advantage of ease of operation of the cell in that the [catholyte pH] is easily maintained at the desired range (5.4-6) throughout the course of reduction.

(b) The cell voltage is lowered thereby lowering the power costs.

(c) The cost of cooling is also brought down due to the reduction in cell voltage.

(d) The diaphragm has the advantage that any desired shape and size can be fabricated and there will not be any

deformity of the diaphragm due to hydraulic head during the scale up of the cells.

(e) The mechanical strength of the diaphragms are better and are more durable than ceramic pots or microporous rubber diaphragm.

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Dated this 9th day of October 1969.

COMPLETE SPECIFICATION

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The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:—

This invention relates to improvements in/or relating to the electrolytic reduction of salicylic acid to salicylaldehyde. Salicylaldehyde is largely used for synthesis of coumarin which has a great demand in perfumery and flavouring essences, soap and cosmetic industry, food and beverage industry. To a limited extent, salicylaldehyde is useful as a dye intermediate and in certain pharmaceutical formulation as salicylaldoxime.

Hitherto it has been proposed to reduce salicylic acid electrolytically by rotating/stationary amalgamated cathodes of copper, lead or monel in a divided cell using a ceramic

or microporous rubber diaphragm.

This is open to the objection that by such a method, it was fairly difficult to control the pH of the catholyte at the desired range (5.4-6) and the amalgam surface was becoming black or dull giving low reproducibility of results in a number of reuses. The cell voltage was also higher (10-12 volts) for the range of current densities employed (upto 15 amp/dm²). Moreover by such technique it was difficult to scale up the cells to larger amperages due to unsuitability of such diaphragms under high hydraulic heads/ or fragile nature of the ceramic pots.

The object of this invention is to obviate these disadvantages. This has been achieved by using blue asbestos cloth as diaphragm by which it is possible to maintain the pH of the catholyte at the desired value, and the operating voltage of the cell is lower (8 to 10 v) for the same current density range (upto 15 amp/dm²) thereby lowering the cost of cooling and the power consumption for the process. There is no deposit of scale on the diaphragm surface which is observed at times on the ceramic pots/or microporous rubber diaphragm.

To these ends, the invention broadly consists in reducing salicylic acid to salicylaldehyde characterised in that use is made of a blue asbestos cloth diaphragm separating the anode and cathode compartments. A rotating/or stationary amalgamated electrode of copper, brass, lead, zinc or monel or an agitated pool of mercury is used as cathode. Alkali metal sulphates preferably of sodium are used as catholyte and a strength upto 20% is used but preferably 15%. The reduction is carried out in the presence of boric acid which is added to the catholyte upto a concentration of 5 moles/mole of salicylic acid taken but preferably 12% concentration. The reduction is carried at a current density upto 15 amp/dm² but preferably 10 amp/dm². The anolyte is sulphuric acid upto 30% strength but preferably 20% concentration. The anode material may be lead, lead dioxide or graphite as the case may be. The temperature of the cell is maintained upto 20°C but preferably below 18°C. The reduction is carried out to theoretical time 2F/mole of salicylic acid taken. The salicylaldehyde is fixed as it is formed as bisulphite addition compound by adding sodium bisulphite or by feeding the cell with a mixture of salicylic acid and sodium sulphite. The depolariser mixture is added preferably in instalments rather than in whole lot-2 Faradays are required for every mol of salicylic acid reduced and preferably such quantities of depolariser mixture are taken so that the electrolysis is complete in 2 hrs. The catholyte is subjected to steam distillation to recover the aldehyde. It is then heated with active charcoal and recycled again for further use, the recycling being done at least two times before the solutions are discarded after recovering the unreduced salicylic acid, boric acid and bisulphite from the solution.

As a result of the use of the new diaphragms the maintenance of the pH of the catholyte between 5 and 6 but preferably at 5.4-5.7 is made easier. The cell voltage is also lowered and the working voltage is between 8 to 10v. There was no scale formation or deposit on the diaphragm surface leading to increased cell resistance and decreasing the efficiency. On account of the lowering in cell voltage, the cooling requirements are also reduced for a given capacity.

The use of such diaphragm simplifies the design of high amperage cells of any capacity which was not possible with earlier diaphragm material like ceramic pots/or microporous rubber. The ceramic pots of large capacity are not easily available and are of fragile nature. Microporous rubber diaphragms are unsuitable due to their poor mechanical strength and failure against large hydraulic heads.

The electrolytic reduction of salicylic acid to salicylaldehyde is carried out with a device for the diaphragm material which comprises the use of blue asbestos cloth as the diaphragm separating the anode and the cathode material. The other conditions for carrying out the electrolytic reduction of salicylic acid to salicylaldehyde are common to the new as well as old processes/devices except for the fact that the new device is to employ a blue asbestos cloth as diaphragm material which has specific advantage in the operation of the cells.

There is no scale formation on the diaphragms, easy maintenance of the pH of the catholyte at the desired range and good mechanical strength of the diaphragm. By this device, it is possible to scale up to any desired capacity cell.

Detailed description with reference to the accompanying drawings :

The invention relates to the process for the electrolytic reduction of salicylic acid to salicylaldehyde and flow sheet for the same is included and the drawings of a typical diaphragm box is also attached.

A few typical examples to illustrate how the invention is carried out in practice :

The following examples are given to illustrate the invention :

EXAMPLE I

Catholyte : 40 lts. containing 6 kg. sodium sulphate (analysed) 4.5 kg boric acid.
 Anolyte : 10 lits of 20% sulphuric acid
 Depolariser mixture : 1.5 kg salicylic acid + 1.6 kg of sodium sulphate added
 0.5 kg for every 15 minutes.
 Current : 300 amp
 Cathodes : Rotating amalgamated copper 10 cm × 25 cm invention — 3 nos.
 Diaphragm : Blue asbestos cloth supported on a wooden frame — 4 nos.
 Diaphragm boxes : 10 cm × 10 cm × 30 cm — 2 nos
 5 cm + 10 cm × 30 cm — 2 nos.
 Anode : Perforated lead.
 Current density : 12 amp/dm²
 Temperature : Less than 18°C
 Cell voltage : 9 to 10 V
 Aldehyde obtained - 330 cc (383)
 Percentage of current efficiency : 30%

EXAMPLE II

Conditions same as above.
 Aldehyde obtained 330 cc.
 Percentage of current efficiency : 30%
 The main advantages of the invention are that by use of blue asbestos cloth diaphragm the cell voltage is lowered ; the cooling requirements are reduced ; the scale formation is avoided and the design of high amperage cells are made easier.

Summary and critical discussion :

In the electrolytic reduction of salicylic acid to salicylaldehyde, both ceramic pots and microporous rubber diaphragms are normally used. These have disadvantages especially when the problem of scale up of cells are considered. The cells with these diaphragm have higher operating voltages and scale formation on the diaphragm were normally observed. The ceramic pots are fragile in nature and are likely to be damaged. Microporous rubber diaphragms have poor mechanical strength especially at high hydraulic heads. To obviate these difficulties, the use of blue asbestos cloth as diaphragm has been described in this invention. Such diaphragms have good mechanical strength and have no scale formation. The maintenance of catholyte pH at the desired value is simpler and the working voltage of the cell is also low. The cooling requirements are also reduced. The scale up of high amperage cells is also made easier since diaphragm of any desired shape and size can be easily prepared.

Noteworthy features

(i) The process for the electrolytic reduction of salicylic acid to salicylaldehyde in a divided cell using blue asbestos cloth diaphragm lowers the operating voltage and the cooling requirements are reduced.

(ii) The maintenance of catholyte pH is easier,

(iii) The scale up to any desired capacity is made more simple.

We Claim :

1. A process for electrolytically reducing salicylic acid to salicylaldehyde characterised in that use is made of a blue asbestos cloth diaphragm separating the anode and cathode compartments.

2. A process for electrolytically reducing salicylic acid to salicylaldehyde by which the operating voltage is lowered, the colling requirements are reduced and the maintenance of

the pH in the cathode compartment is made easier substantially as herein before described.

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Dated this 3rd day of August, 1970.

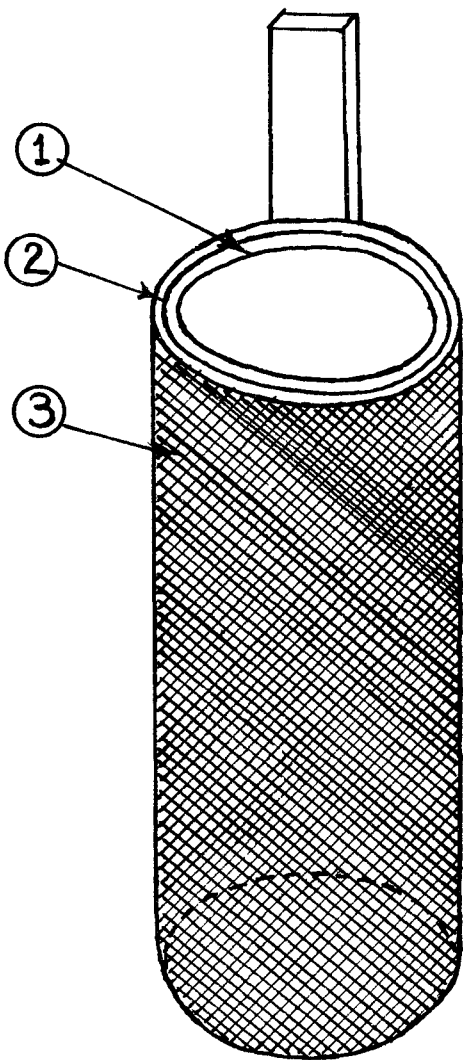


FIG. 1.

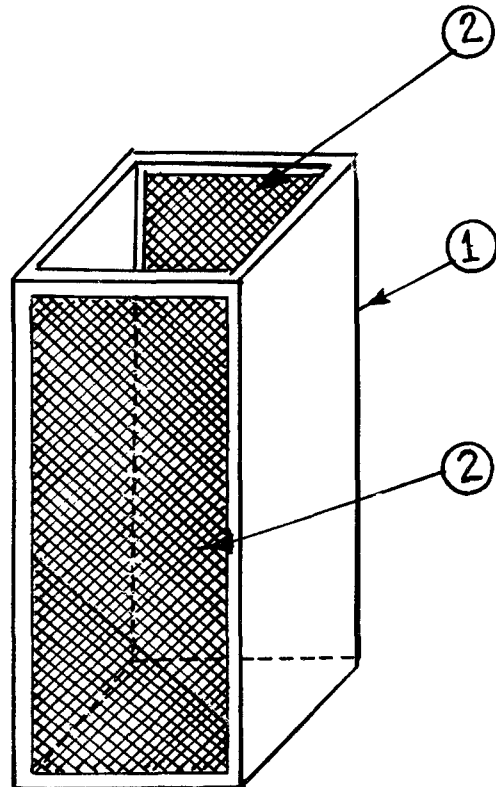


FIG. 2.

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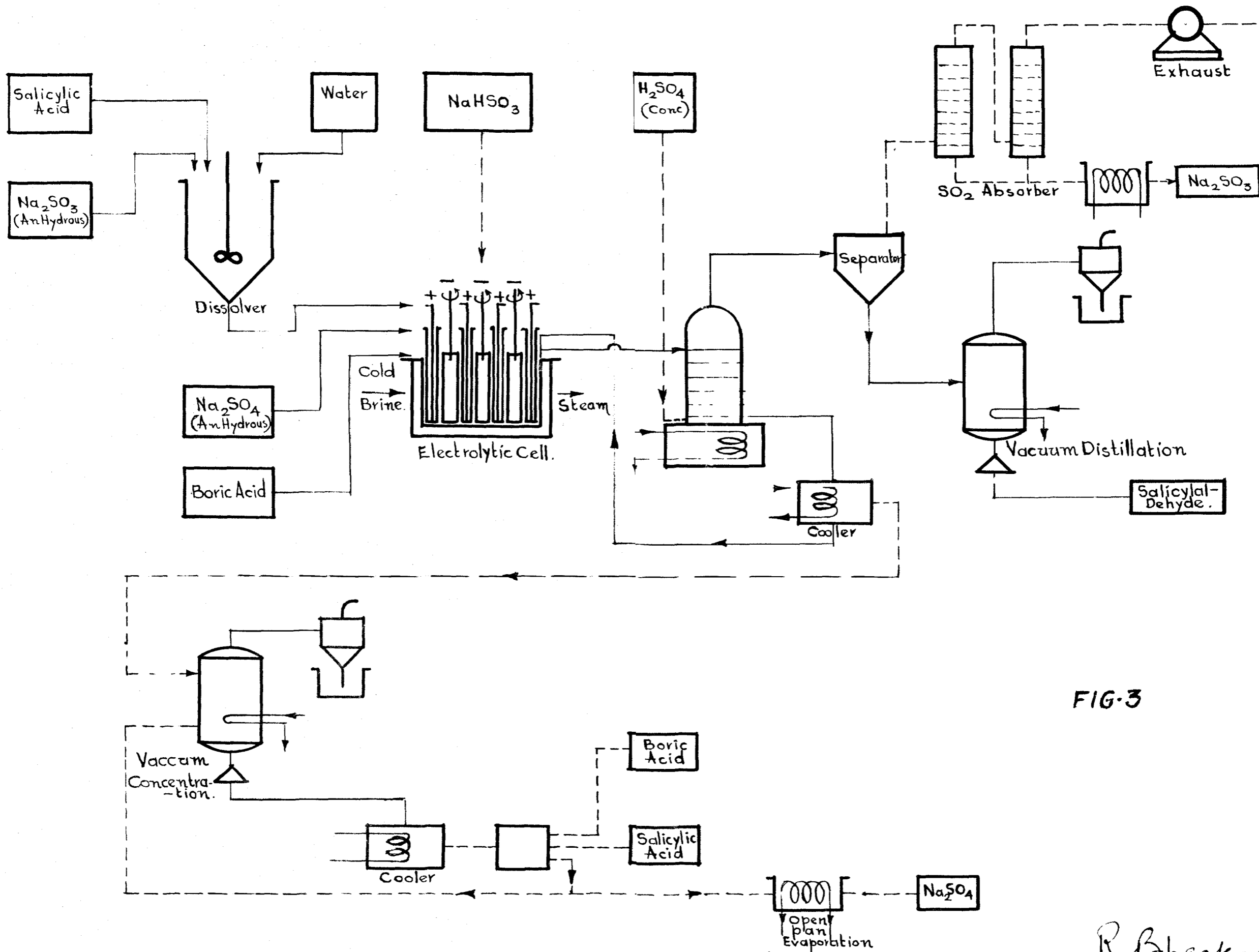


FIG-3

QUALITATIVE BLOCK TYPE FLOW-SHEET FOR THE ELECTROLYTIC REDUCTION OF SALICYLIC AND SALICYLALDEHYDE .

----- Dotted Lines show the course of the process after every 4th re-use of the Electrolyte.

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