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PROVISIONAL SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO THE LIFE OF THE LEAD DIOXIDE ANODES IN THE ELECTROLYTIC PRODUCTION OF PERCHLORATES"

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).

This is an invention by Handady Venkatakrishna Udupa, Scientist-in-charge, Central Electrochemical Research Institute, Srinivasa Sampath, Engineer, The Western India Match Co. (WIMCO) Ambernath, Bombay, Kapisthalam Chetlur Narasimham, Scientist, Muthiah Nagalingam, Senior Scientific Assistant, Narayanasamy Sarma Thiagarajan, Senior Scientific Assistant, Ganesa Ganapadigal Subramanian, Junior Scientific Assistant, Rasappa Gounder Palanisamy, Junior Scientific Assistant, Subramanian Pushpavanam, Senior Laboratory Assistant, Muthuramalingam Asari Sadagopalan, Senior Laboratory Assistant, all of Central Electrochemical Research Institute, Karaikudi,-3, all Indians.

The following specification describes this nature of the invention :—

This invention relates to the improvements in or relating to the life of graphite and/or carbon substrate lead dioxide anodes, for the electrolytic production of perchlorates.

Hitherto it has been the practice to use either platinum or massive lead dioxide or lead dioxide deposited over platinum-clad tantalum or a thin coating of leaddioxide deposited over carbon/graphite substarte.

The main objection to the use of platinum are its prohibitive cost and its corrosion during the electrolysis for the preparation of perchlorates. The objection to the use of massive lead-dioxide are its heaviness, fragile nature and the difficulty in giving electrical contact during electrolysis.

In the case of platinum clad tantalum, the high cost of both the metals warrants their replacement with a cheaper material.

The objection to the use of thin coating of lead dioxide

	Example 1	Example 2	Example 3
Concentration of feed (sodium chloride) (g/1)	650–700	650–700	600–700
Addition agent (g/1) (sodium fluoride)	2	2	2
Anode	Graphite substrate lead dioxide	Graphite substrate lead dioxide	Graphite substrate lead dioxide
Thickness of the deposit (mm)	2	5	10
Cathode	Stainless steel	Stainless steel	Stainless steel
Current (amps)	75	75	75
Current density (amp/dm^2)	18–22	15–20	15–20
Temperature (°C)	40–45	40–45	40–45
Current efficiency (%)	65–70	65–70	65–70
Cell voltage (volts)	4.5–4.8	4.5–4.8	4.6–4.8
Cell dimensions	An oval shaped porcelain tank of 15 litre capacity	An oval shaped porcelain tank of 15 litre capacity	An oval shaped porcelain tank of 15 litre capacity
Quantity of electricity passed through each anode (amp-hrs)	1,33,232	7,68,200	4,13,000
Energy consumption (kwh/kg of $NaClO_4$)	2.9–3.2	2.9–3.2	2.9–3–2

Price : TWO RUPEES

deposited over carbon/graphite substrate is that the anode does not withstand longer duration of electrolysis thereby necessitating the frequent replacement of the anodes.

The object of this invention is to obviate these difficulties by adopting the following method developed.

Lead dioxide is deposited over graphite substrate to a thickness of 2 to 10 mm using lead nitratecopper nitrate bath and employing the electrolytic conditions standardised earlier, as given in the Indian Patent No. 66, 195. Using such anodes, the electrolytic oxidation of a saturated solution of sodium chlorate is carried out by employing an anode current density of 15–25 amps/dm^2 and a temperature of 40–45°C. The pH of the electrolyte was maintained between 6 and 7 by the addition of hydrochloric acid during electrolysis. 2 g/l sodium fluroide is added initially to the electrolyte. Under these conditions, the lead dioxide coated graphite can be used for a minimum period of four months. A current efficiency of 70–75% is obtained. The cell liquor containing less then 5 g/l sodium chlorate is used for the production of potassium and ammonium perchlorates by double decomposing the sodium perchlorate liquor with either potassium chloride or ammonium chloride respectively.

The experiments carried out on laboratory scale showed that lead dioxide deposited over carbon can also be used in the electrolytic preparation of perchlorates.

The following typical examples illustrate the invention:

The following are the main advantages of the invention-

(1) Lead dioxide anode replaces costly platinum anode in the production of perchlorates, thereby effecting a saving in foreign exchange.

(2) The graphite or carbon substrate lead dioxide anode not only provides easy electrical contact to the anode but also increases the mechanical strength of the brittle lead dioxide.

(3) Lead dioxide deposited over graphite or carbon for thickness of 2 to 10 mm (preferably 5 mm) increases the life of the lead dioxide anode as compared to deposits of less than 2 mm thick when the cell is operated at anode current density ranging from 15–25 amp/dm^2 and at temperatures 40 to 45°C, containing sodium fluoride of 2 g/1 initially in the electrolyte.

(4) The current efficiency of the process is fairly high (65–70%) and the energy consumption is also comparable.

(5) The anode could for a minimum period of four months thereby showing that the cost of production of perchlorates could be comparable to that produced with platinum anodes.

(6) Graphite or carbon substrate lead dioxide anodes could be used for the electrolytic oxidation of sodium chlorate containing even sodium chloride (upto 10 g/1) whereas with platinum anode the corrosion of the metal is higher under such conditions.

(7) The potassium and ammonium perchlorates obtained by double decomposing the sodium perchlorate liquor got from the process, are found to conform to the required specifications.

Sd. Illegible
PATENTS OFFICER,
Council of Scientific and Industrial Research.

Dated this 17th day of September, 1969.

COMPLETE SPECIFICATION

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)

This is an invention by Handady Venkatakrishna Udupa, Director, Central Electrochemical Research Institute, Karaikudi-3; Srinivasa Sampath, Western India Match Company Ltd., Ambernath, Maharashtra State; Kapisthalam Chetlur Narasimham, Scientist, Central Electrochemical Research Institute, Karaikudi; 3: Muthiah Nagalingam, Senior Scientific Assistant, Central Electrochemical Research Institute, Karaikudi-3; Narayanasamy Sarma Thiagarajan, Senior Scientific Assistant, Central Electrochemical Research Institute, Karaikudi-3; Ganesa Ganapadigal Subramanian, Junior Scientific Assistant, Central Electrochemical Research institute, Karaikudi-3; Rasappa Gounder Palanisamy. Junior Scientific Assistant, Central Electrochemigal Research Institute, karaikudi-3; Subramanian Pushpavanrm, Junior Scientific Assistant, Central Electrochemical Research Institute, Karaikudi-3; Muthuramalingam Asari Sadagopalan, Junior Techanical Assistant, Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, and all Indians.

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 the improvements in or relating to the electrolytic production of sodium perchlorate.

Hitherto it has been the practice to use either platinum or massive lead dioxide or lead dioxide deposited over platinum-clad-tantalum or a thin coating of lead dioxide deposited over carbon/graphite substrate.

The main objections to the use of platinum are its prohibitive cost and its corrosion during electrolysis for the preparation of perchlorates. The objections to the use of massive lead dioxide are its heaviness, fragile nature and the difficulty ϕ in giving electrical contact during electrolysis. In the case of platinum clad tantalum, the high cost of both the metals warrants their replacement with a cheaper material. The objection to the use of thin coating of lead dioxide deposited over carbon/graphite substrate is that the anode does not withstand longer duration of electrolysis thereby necessitating the frequent replacement of the anodes.

The object of this invention is to obviate these difficulties by adopting the following method developed.

According to the present invention, there is provided a process for the electrolytic production of sodium perchlorate using saturated solution of sodium chlorate characterised in that lead dioxide anodes formed by electrodeposition of lead dioxide of 2 to 10 mm thick over graphite or carbon substrate from lead nitratecopper nitrate bath are used for the electrolytic oxidation of sodium chlorate to sodium perchlorate along with stainless steel cathode at an anode current density of 15–25 amp/dm^2 and a temperature of 40–45°C and 2 g/1 sodium fluoride as addition agent.

Lead dioxide is deposited over graphite to a thickness of 2 to 10 mm, using lead nitrate-copper nitrate bath and employing the electrolytic conditions standardised earlier, as given in the Indian Patent No. 66,195. Using such anodes, the electrolytic oxidation of a saturated solution of sodium chlorate is carried out by employing an anode current density of 15–25 amp/dm^2 and a temperature of 40—45°C. The pH of the electrolyte was maintained between 6 and 7 by the addition of hydrochloric acid during electrolysis. 2 g/1 sodium fluoride is added initially to the electrolyte. Under these conditions, the lead dioxide coated graphite can be used for a minimum period of four months. A current efficiency of 70–75% is obtained. The cell liquor

containing less than 5 g/l sodium chlorate is used for the production of potassium and ammonium perchlorates by double decomposing the sodium perchlorate liquor with either potassium chloride or ammonium chloride respectively.

The experiments carried out on laboratory scale showed that lead dioxide deposited over carbon can also be used in the electrolytic preparation of perchlorates.

The lead dioxide anode replaces costly platinum anode in the production of perchlorates, thereby effecting a saving in foreign exchange. Lead dioxide deposited over graphite or carbon for thickness of 2 to 10 mm. (preferably 5 mm) increases the life of the lead dioxide anode as compared to deposits of less than 2 mm thick. It also helps to operate the cell over a wide range of current density condition. The graphite or carbon substrate lead dioxide anode not only provides easy electrical contact to the anode but also increases the mechanical strength of the brittle lead dioxide.

The current efficiency of the process is fairly high (65—70%) with the addition of 2 g/l sodium fluoride and the energy consumption is also comparable. The potassium and ammonium perchlorates obtained by double decomposing the sodium perchlorate liquor got from the process, are found to conform to the required specifications.

Graphite or carbon substrate lead dioxide anodes can be used for the electrolytic oxidation of sodium chlorate containing even sodium chloride (10g/l) whereas with platinum anode the corrosion of the metal is higher under such conditions.

Flow sheet is attached (Fig. 1 of accompanying drawings). Typical Examples:

	Example I	Example II	Example III
Concentration of feed (sodium chlorate g/l)	650–700	650–700	600–700
Addition agent (sodium fluoride g/l)	2	2	2
Anode	Graphite substrate lead dioxide	Graphite substrate lead dioxide	Graphite substrate lead dioxide
Thickness of the deposite (mm)	2	5	10
Cathode	Stainless steel	Stainless steel	Stainless steel
Current (amps)	75	75	75
Current density (amp/sq. dm.)	18–22	15–20	15–20
Temperature (°C)	40–45	40–45	40–45
Current efficiency (@%)	65–70	65–70	65–70
Cell voltage (volts)	4.5–4.8	4.5–4.8	4.6–4.8
Cell dimensions	An oval shaped porcelain tank of 15 lit. capacity	An oval shaped porcelain tank of lit. eapacity	An oval shaped porcelain tank of lit. capacity
Quantity of electricity passed through each anode (amp-hrs)	1,33,232	7,68,200	4,13,000
Energy consumption (kwt/kg of $NaClO_4$)	2.9–3.2	2.9–3.2	2.9–3.2

The following are the main advantages of the invention : Lead dioxide anode replaces costly platinum anode in the production of perchlorates, thereby effecting a saving in foreign exchange. The graphite or carbon substrate lead dioxide anode not only provides easy electrical contact to the anode but also increases the mechanical strength of the brittle lead dioxide. Lead dioxide deposited over graphite or carbon for thickness of 2 to 10 mm (preferably 5 mm) increased the life of the lead dioxide anode as compared to deposits of less than 2 mm thick when the cell is operated at anode current density ranging from 15–25 amp/dm^2 and at temperatures 40 to 45°C, containing sodium fluoride of 2 g/l initially in the electrolyte. The current efficiency of the process is fairly high (65–70%) and the energy consumption (2.9 to 3.2 kwh/kg of sodium perchlorate) is low as compared to the process employing platinum anode where it is of the order of 3.2 to 3.5 kwh/kg of sodium perchlorate. The anode could be used for a minimum period of four months thereby showing that the cost of production of perchorates could be comparable to that produced with platinum anodes. Graphite or carbon substrate lead dioxide anodes can be used for the electrolytic oxidation of sodium chlorate containing even sodium chloride (upto 10 g/l) whereas with platinum anode the corrosion of the metal is higher under such conditions. The potassium and ammonium perchlorates obtained by double decomposing the sodium perchlorate liquor got from the process, are found to conform to the required specifications.

The present invention increases the life of graphite substrate lead dioxide anodes for the production of perchlorates by electrodepositing lead dioxide for thickness of 2 to 10 mm (preferably 5 mm) from a lead nitrate–copper nitrate bath. A saturated solution of sodium chlorate containing sodium fluoride as addition agent is electrolysed using the graphite substrate lead dioxide anode and stainless steel cathods. The anode could be used for a mininum period of four months.

We Claim :

1. A process for the electrolytic production of sodium perchlorate using saturated solution of sodium chlorate characterised in that lead dioxide anodes formed by electrodeposition of lead dioxide of 2 to 100 mm thick over graphite or carbon substrate lead nitrate–copper nitrate bath are used for the electrolytic oxidation of sodium

chlorate to sodium perchlorate along with stainless steel cathode at an anode current density of 15-25 amp/dm^2 and a temperature of 40-45°C and 2 g/l sodium fluoride as addition agent.

2. A process as claimed in claim (1) wherein lead dioxide 2 to 10 mm deposited over graphite or carbon substrate from lead nitrate-copper nitrate bath is used as anode for the production of perchlorates.

3. A process as claimed in claim (1) wherein the electrolytic cell can be operated using an anode current density range of 15 to 25 amp/dm^2.

4. A process as claimed in claim (1) wherein the electrolytic cell can be oparated at a temperature of 40–45°C.

5. A process as claimed in Claim (1) wherein an addition of 2 g/l sodium fluoride is made to the electrolyte at the beginning to increase the current efficiency.

6. A process as claimed in Claim (1) wherein stainless steel is used as cathode.

7. A process as claimed in claims (1) to (6) wherein graphite/carbon substrate lead dioxide anode is used for the oxidation of sodium chlorate containing even 10 g/l sodium chloride.

8. A process for the electrolytic production of sodium perchlorate as substantially hereinbefore described.

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Industrial Research

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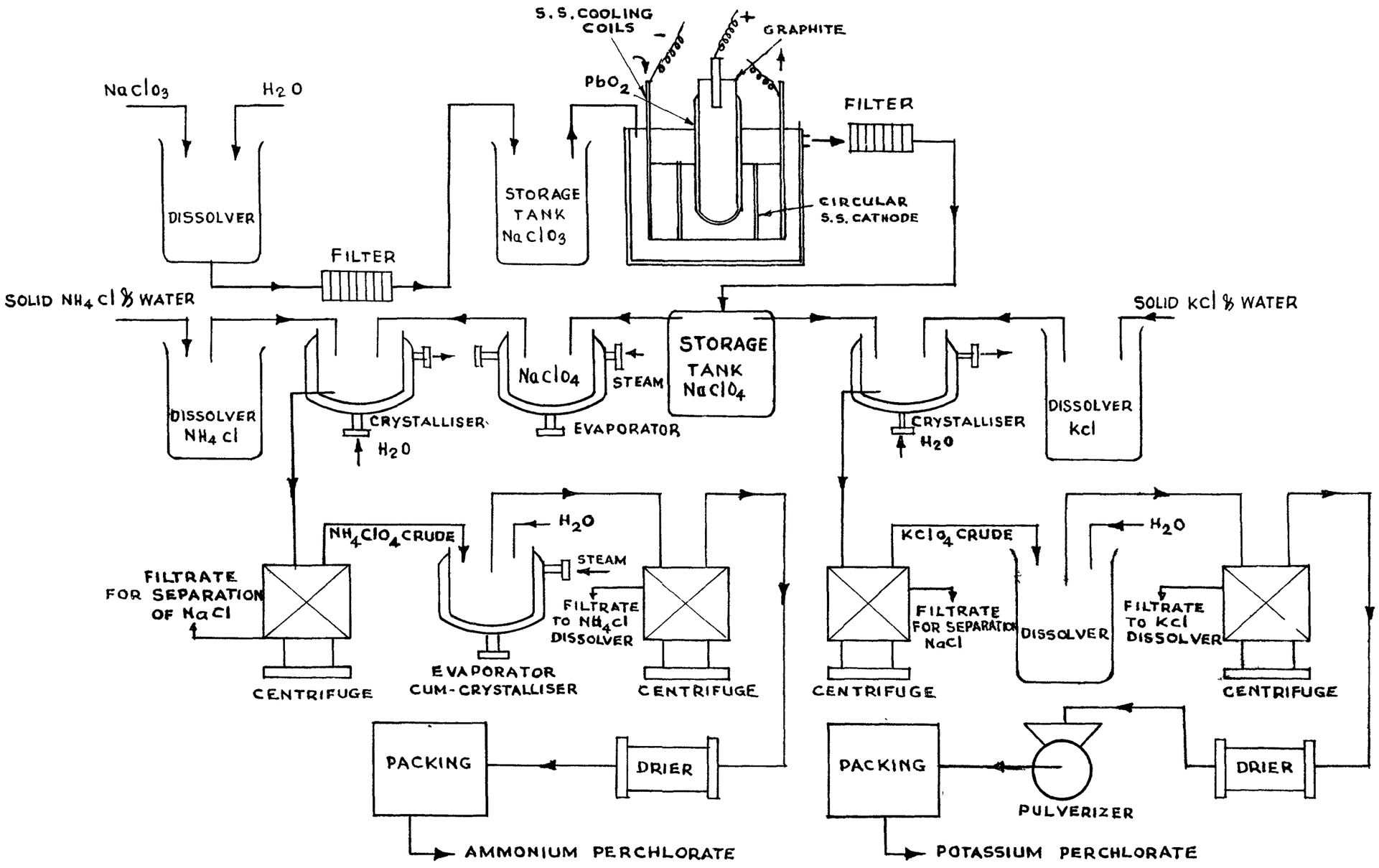

Fig. 1

R. B. Bhaskar Pai

R.B. PAI,
PATENTS OFFICER,
C.S.I.R.