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Index at acceptance—70B+C6[LVIII(5)]

PROVISIONAL SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO ELECTROLYTIC PREPARATION OF LEAD DIOXIDE ELECTRODES FOR ELECTROLYSIS"

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, KAPISTHALAM CHETLUR NARASIMHAM, SCIENTIST AND KALIAPPAN SHUNMUGHAM ARUMUGASAMY GNANASEKARAN, SENIOR SCIENTIFIC ASSISTANT, ALL OF CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, TAMIL NADU, INDIA, ALL INDIAN CITIZENS.

The following specification describes this nature of the invention :—

This invention relates to the improvements in or relating to the electrolytic preparation of lead dioxide electrodes for electrolysis mostly as anodes in electrolytic oxidations.

Hitherto it has been the practice to prepare lead dioxide electrodes by the following methods:

(i) Depositing lead dioxide in a massive form and then shaping it suitably as anodes for electrolysis; (ii) Depositing lead dioxide over various substrates particulary on graphite or carbon using a rotating technique for rods or a to-and-fro motion for plates, as described in Indian Patent No. 66,195 or a fluidized bed technique as described in Indian Patent No. 1, 05, 731.

The objections to the current practice are as follows:

In the case of massive form of lead dioxide, the heaviness and the brittle nature of the deposit requires careful handling and is normally expensive involving high energy consumption for its preparation. It is also difficult to give electrical contact on the lead dioxide by the usual methods. Cutting of this massive lead dioxide in suitable shapes pose a great problem as deposit is brittle and hard.

In the case of lead dioxide deposited over graphite or carbon the to-and-fro motion technique or rotation technique or fluidized bed technique involves not only an elaborate set up but also additional power to drive the motor used to keep the electrodes or fluidized bed in motion.

The object of this invention is to obviate these disadvantages by adopting the following improved method over the methods given in the earlier Indian patent. The electrolysis is carried out using a solution containing 300–500 g/l lead nitrate and 20–40 g/l of copper nitrate, preferably 340–350 g/l lead nitrate and 24–25 g/l of copper nitrate to which 0.1 to 2 g/l of surface active agents like cetyl trimethyl ammonium bromide/trimethyl tetra decyl ammonium bromide/dodecyl trimethyl ammonium bromide, all belonging to quaternary ammonium cationic surface active agents are added. Graphite rods, which have been thoroughly cleaned by making them anodes in alkali and electrolysing for 3–5 minutes at a current density of 10 amp/dm^2 and giving acid dip in 10% nitric acid and washed in distilled water, are used as anodes. Copper or stainless steel cathodes are used. The deposition is carried out on the stationary anode at an anode current density of 1–30 amp/dm^2 and at a temperature of 25-65°C. The ph of the bath is maintained between 1 and 5. The nitric acid produced during the electrolysis is neutralised by adding lead carbonate or lead monxide or lead hydroxide and suitable quantity of copper carbonate. Copper which is deposited on the cathode, could be redissolved in nitric acid after the electrolysis and reused either as copper nitrate or as copper carbonate by precipitating the same from copper nitrate. The current efficiency for the process is nearly quantitative on the basis that 2 Faradays of electricity is required to deposit a mole of lead dioxide.

The deposition has also been carried out from the above bath on other substrates like stainless steel, nickel and platinum after giving suitable pretreatment.

In all the cases the deposit is smooth, adherent and free from pinholes and suitable as an anode for electrolysis like chloride to chlorate, chlorate to perchlorate, chloride to perchlorate, boromide to bromate, iodide to iodate to periodate, chloralkali cells and other inorganic and organic oxidation reactions.

The following typical examples are given for illustration (sheet enclosed).

The following are the main advantages of the invention:

(1) The deposition of lead dioxide over graphite or carbon substrates as substanially described in Patent No. 66, 195 is carried out under stationary conditions using addition agents like cetyl trimethyl ammonium bromide/trimethyl tetra decyl ammonium bromide/dodeyl trimetheyl ammonium bromide, all belong to quaternary ammonium cationc surface active agents.

(2) The deposition of lead dioxide is carried out at a temperature of 25–65°C.

(3) The deposition of lead dioxide is carried out over other substrates like stainless steel, nickel and platinum.

(4) The deposition of lead dioxide is carried out at a much wider current density range from 1–30 amp/dm^2.

(5) The lead dioxide deposit obtained under these conditions is smooth, adherent and free from pinholes and can be suitably used as anodes for the electrolytic preparations of hypochlorites, chlorates, perchlorates, bromates,

		Example I	Example II	Example III	Example IV	Example V
(1)	Concentration of electrolyte:					
	Lead nitrate (g/l)	350	340	350	350	340
	Copper nitrate (g/l)	25	24	25	25	25
(2)	Addition agent:	Cetyl trimethyl ammonium bromide	Trimethyl tetra decyl ammonium bromide	Dodecyl trimethyl ammonium bromide	Cetyl trimethyl ammonium bromide	Cetyl trimethyl ammonium bromide
	Quantity added (g/l)	0.2	0.25	0.3	0.5	2.0
(3)	Substrate (Anode, stationary)	Graphite	Graphite	Graphite	Stainless steel	Graphite
(4)	Cathode	Copper	Stainless steel	Stainless steel	Stainless steel	Stainles steel
(5)	Current (amperes)	4.9	3.3	3.6	1.6	9
(6)	Anode current density (amp/dm^2)	15	10	10	5	27
(7)	Temperature (°C)	58±2	60±2	59±2	31±2	55±3
(8)	pH Initial:	4	4	4	4	4
	Final	1	1	1	1	1
(9)	Cell voltage (volts)	3.2	3.3	3.4	2.8	3.5
(10)	Energy consumption (kwh/kg of lead dioxide)	0.67	0.73	0.73	0.65	0.79
(11)	Nature of deposit:	Adherent, smooth, free from pinholes	Adherent, smooth, free from pinholes	Adherent, smooth, free from pinholes	Adherent, smooth, free from pinholes	Adherent, smooth, free from pinholes

iodates, periodates and as anodes in chloralkali cells and other inorganic and organic oxidation processes.

(6) The preparation of any size commercial electrode is made easy as a result of the choice of appropriate size graphite substrate itself, which is rather impractical from any of the other techniques known so far.

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

Dated this 15th day of November, 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, Kapisthalam Chetlur Narasimham, Scientist and Kaliappan Shunmugham Arumugasamy Gnanasekaran, Senior Scientific Assistant, all of Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India, All Indian citizens.

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 preparation of lead dioxide electrodes for electrolysis mostly as anodes in electrolytic oxidations of inorganic and organic products.

Hitherto it has been the practice to prepare lead dioxide electrodes by the following methods :

(i) depositing lead dioxide in a massive form and then shaping it suitably as anodes for electrolysis;

(ii) depositing lead dioxide over various substrates particularly on graphite or carbon using a rotating technique for rods or a to and from motion for plates, as described in Indian Patent No. 66195 or a fiuidized bed technique as described in Indian Patent No. 105731.

The main drawbacks to the current practices are as follows :

In the case of massive form of lead dioxide, the heaviness and the brittle nature of the deposite requires careful handling and is normally expensive involving high energy consumption for its preparation. It is also difficult to give electrical contact on the lead dioxide by usual methods. Cutting of this massive lead dioxide in suitable shape pose a great problem as the deposit is brittle and hard.

In the case of lead dioxide deposited over graphite or carbon, the to and fro motion technique for plates or rotation technique for rods involves not only an elaborate set up but also additional power to drive the motor used to keep the electrodes or fluidized bed in motion

The object of this invention is to obviate these disadvantages and to adopt an improved method over the methods given in the earlier Indian patents.

According to the present invention, there is provided a process relating to the electrolytic preparation of lead dioxide electrodes for electrolysis which comprises in depositing lead dioxide on graphite or other metallic substrates from lead nitrate-copper nitrate bath containing 0.1—2 gpl of cationic surfactants like cetyl trimethyl ammonium bromide/trimethyl tetradecyl ammonium bromide/dodecyl trimethyl ammonium bromide all belonging to quaternary ammonium type at anode current densities of 1—30 amp/dm^2 and at temperature 25 to 60°C, when copper or stainless steel is used as cathode.

The new process avoids the need for movement of the electrodes or fluidizing the column by incorporating a cationic surfactant of quarternary ammonium type in the bath for the electro-deposition of lead dioxide on suitable substrates. The electrolysis is carried out using a solution containing 300—500 gpl of lead nitrate and 20—40 gpl of copper nitrate to which 0.1 to 2 gpl of surface active agents like cetyl trimethyl ammonium bromide/trimethyl tetra decyl ammonium bromide/dodecyl trimethyl ammonium bromide all belonging to quaternary ammonium cationic surface active agents, are added. Graphite or carbon rods, which have been thoroughly cleaned by making them anodes in alkali and electrolysing for 3 to 5 minutes at a current density of 10 amp/dm^2 and giving acid dip in 10% nitric acid and washed in distilled water, are used as anodes. Copper or stainless steel cathodes are used. The deposition is carried out on the stationary anode at an anode current density of 1—30 amp/dm^2 and at a temperature of 25—65°C. The pH of the bath is maintained between 1 and 5. The nitric acid produced during the electrolysis is neutralised by adding lead carbonate or lead monoxide or lead hydroxide and suitable quantity of copper carbonate. Copper is deposited on the cathode and could be redissolved in nitric acid and used either as copper nitrate or as copper carbonate by precipitating the same from copper nitrate. The current efficiency for the process is nearly quantitative on the basis that 2 Faradays of electricity is required to deposit a mole of lead dioxide.

The deposition has also been carried out from the above bath on the other substrates like stainless steel, nickel and platinum after giving suitable pre-treatment.

In all the cases the deposit is smooth, adherent and free from pin holes and suitable as an anode for electrolytic oxidation of chloride to chlorate, chlorate to perchlorate, bromide to bromate, iodide to iodate, iodate to periodate, other inorganic and organic compounds and in chlor-alkali cells.

	Example I	Example I	Example III	Example IV	Example V
1. Concentration of electrolyte-lead nitrate (gpl)	350	340	350	350	340
Copper nitrate (gpl)	25	24	25	25	25
2. (a) addition agent	Cetyl trimethyl ammonium bromide	Trimethyl tetradecyl amonium bromide	Dodecyl trimethyl ammonium bromide	Cetyl trimethyl ammonium bromide	Cetyl trimethyl ammonium bromide
(b) quantity added (gpl)	0.2	0.25	0.3	0.5	2.0
3. Substrate (anode, stationary)	Graphite	Graphite	Graphite	Stainless steel	Graphite
4. Cathode	Copper	Stainless steel	Stainless steel	Stainless steel	Stainless steel
5. Current (amperes)	4.9	3.3	3.6	1.6	9
6. Anode current density (amp/dm^2)	15	10	10	5	27
7. Temperature (°C)	58±2°C	60±2°C	59±2°C	31±2°C	55±3°C
8. pH—initial	4	4	4	4	4
Final	1	1	1	1	1
9. Cell voltage (volts)	3.3	3.3	3.4	2.8	3.5
10. Energy consumption (kwh/kg of lead dioxide)	0.67	0.73	0.73	0.65	0.79
11. Nature of deposit	Adherent, smooth free from pin holes	Adherent smooth free from pin holes	Adherent, smooth free from pin holes	Adherent, smooth free from pin holes	Adherent, smooth free from pin holes

The present invention consists of a process for the electrolytic preparation of lead dioxide electrodes which comprises in depositing lead dioxide on graphite snbstrate from a lead nitrate-copper nitrate bath, wherein 0.1 to 2 g. p. l. of surface active agents like cetyl trimethyl ammonium bramide/trimethyl tetradecyl ammonium bromide/dodecyl trimethyl ammonium bromide, all belonging to the quaternary ammonium cationic surface active agents and an anode current density of 1 to 30 amp/dm^2 and a temperature of 25 to 65°C are employed.

The deposition of lead dioxide has been carried out from the above bath on other substrates like stainless steel, nickel and platinum after giving suitable pre-treatment.

Flow-diagram for the electrolytic preparation of lead dioxide electrodes for electrolysis is given in Fig. 1 of ten accompanying drawings.

A few typical examples are given for illustration in the attached statement.

The following are the main advantages of the invention :

(i) The deposition of lead dioxide over graphite or carbon substrates as substantially described in Patent No. 66195—is carried out, Under stationary conditions using addition agents like cetyl trimethyl ammonium bromide/trimethyl tetradecly ammonium bromide/dodecyl trimethyl ammonium bromide, all belonging to the class of quaternary ammonium cationic surface active agents.

(ii) The deposition is carried out at a temperature of 25—65°C.

(iii) The deposition of lead dioxide is carried out over substrates like stainless steel, nickel and platinum.

(iv) The deposition of lead dioxide is carried out at a much wider current density range from 1—30 amp/dm^2.

(v) The lead dioxide deposit obtained under these conditions is smooth, adherent and free from pin holes and can be suitably used as anodes for the electrolytic preparation of hypochlorites, chlorates, perchlorates, bromates, iodates, periodates and as anodes in chlor alkali cells and other inorganic and organic oxidation processes.

(vi) The preparation of any size of commercial electrode is made easy as a result of the choice of appropriate size of graphite substrate itself, which is rather impractical from any of the other technique known so far.

The present invention consists in electrodepositing lead dioxide on graphite and other metallic substrates from a lead nitrate-copper nitrate bath containing 0.1 to 2 gpl cationic quaternary ammonium type surfactant at an anode current density of 1–30 amp/dm^2 and temperature of 25 to 65°C:

We Claim

(i) A process relating to the electrolytic preparation of lead dioxide electrodes for electrolysis which comprises in depositing lead dioxide on graphite or other metallic substrates from lead nitrate-copper nitrate bath containing 0.1–2 gpl of cationic surfactants like cetyl trimetyl ammoniumbromide/trimethyl tetradecyl ammonium bromide/dodecyl trimethyl ammonium bromide all belonging to quaternary ammonium type at anode current densities of 1–30 amp/dm^2 and at temperature 25 to 60°C, when copper or stainless steel is used as cathode.

(ii) A process as claimed in claim (1) wherein lead dioxide is deposited over graphite or other metallic substrates like nickl/stainless steel/platinum, which are kept in station - ary conditions.

(iii) A process as claimed in claim (1) wherein lead dioxide is deposited from a lead nitrate-copper nitrate bath containing cationic surfactants like cetyl trimethyl ammonium bromide/dodecyl trimethyl ammonium bromide/trimethyl tetradecyl ammonium bromide all belonging to quaternary ammonium type.

(iv) A process as claimed in claim (i) wherein the lead dioxide deposition is carried out an anode current density range of 1–30 amp/dm^2.

(v) A process as claimed in claim (i) wherein copper or stainless steel is used as cathode.

(vi) A process as claimed in claim (1) wherein lead dioxide is deposited at a temperature range of 25 to 65°C.

(vii) A process as claimed in claim (i), wherein the preparation of any size of commercial electrode is made easy as a result of the choice of appropriate size of graphite substrate itself which is rather impractical in any of other techniques known so far.

(viii) A process as claimed in claim (i), wherein lead dioxide deposited can be suitably used as anodes for the electrolytic preparation of hypochlorite, chlorate, perchlorate, bromates, iodates and periodates and as anodes in chlor alkali industries and other inorganic and organic oxidation processes.

(ix) A process for the electrolytic preparation of lead dioxide electrodes, as substantially herein described.

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Dated this 6th day of July, 1970.

Prabhat Prass, Meerut/Patent/73—150.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

No. 124215

COMPLETE SPECIFICATION

Nº OF SHEETS :- 1
SHEET Nº :- 1

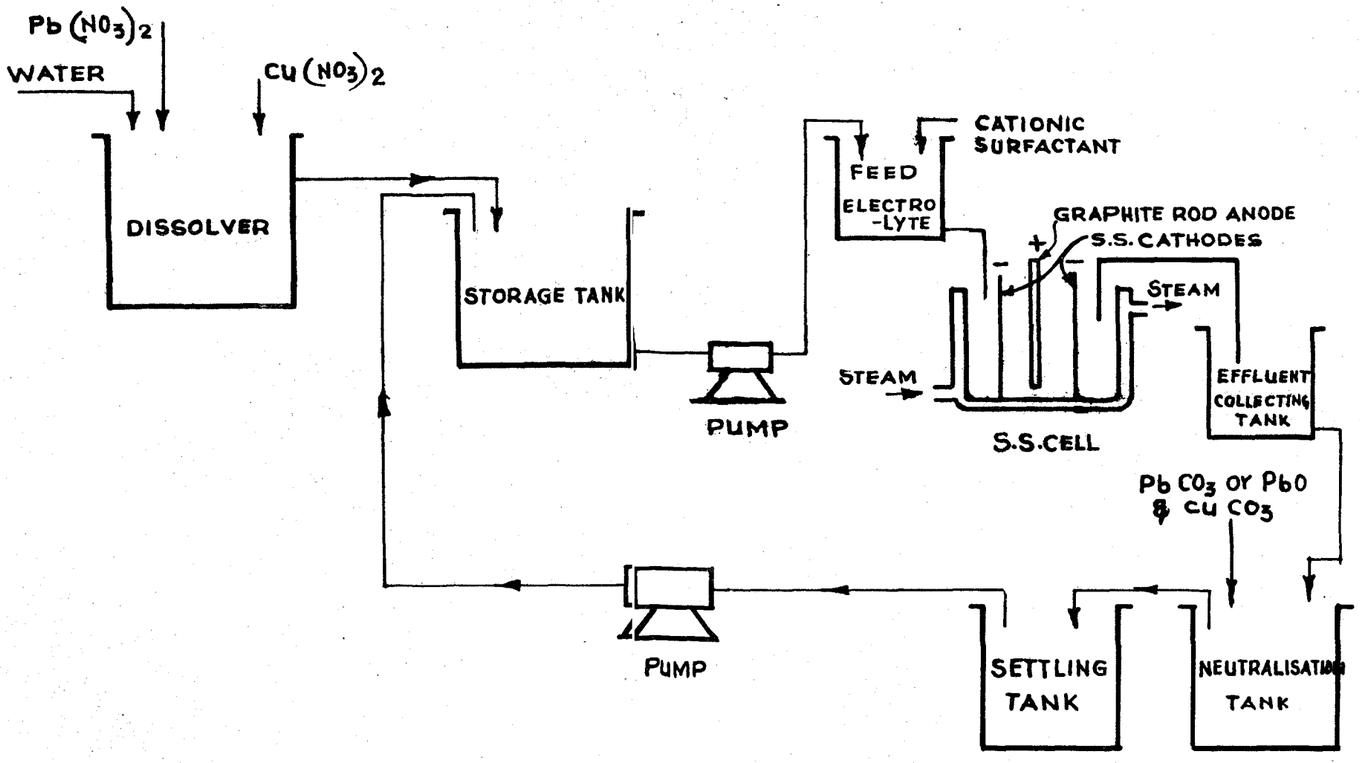

Fig. 1

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