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

Complete specification left on 9th July, 1970. (Application accepted—12th April, 1971)
Index at acceptance—70B-1-C6[1L VIII(5)]

PROVISIONAL SPECIFICATION

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

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAY 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 HANANDY VENKATKRISHNIA UDUPA, DIRECTOR, KAPISHEMAL CHETTU NARASIMHAM, SCIENTIST AND KALIPPAI SHUROUGHAM ARAHMUGAM GNASCHEKAN, SENIOR SCIENTIFIC ASSISTANT, ALL OF CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAKURUM, TANGI NASU, 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 particularly 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 setup 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/triethyl tetra decyl ammonium bromide/dodecyl trimethyl ammonium bromide, all belonging to quaternary ammonium carboxylic surface active agents are added.

Graphite rods, which have been thoroughly cleaned by making them anodes in alkaline and electrolyzing for 3-5 minutes at a current density of 10 amp/dm² 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/dm² 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 neutralized by adding lead carbonate or lead monoxide 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 chlorine to chlorate, chlorate to perchlorate, chlorine to perchlorate, boron to bromate, iodide to iodate to periodate, chloroformic 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 substantially described in Patent No. 66, 195 is carried out under stationary conditions using addition agents like cetyl trimethyl ammonium bromide/triethyl tetra decyl ammonium bromide/dodecyl trimethyl ammonium bromide, all belong to quaternary ammonium cationic 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/dm².

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

Price: TWO RUPEES
<table>
<thead>
<tr>
<th>Example I</th>
<th>Example II</th>
<th>Example III</th>
<th>Example IV</th>
<th>Example V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead nitrate (g/l)</td>
<td>350</td>
<td>340</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Copper nitrate (g/l)</td>
<td>25</td>
<td>24</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Cetyl trimethyl ammonium bromide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quantity added (g/l)</td>
<td>0.2</td>
<td>0.25</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Substrate (Anode, stationary)</td>
<td>Graphite</td>
<td>Graphite</td>
<td>Graphite</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Cathode</td>
<td>Copper</td>
<td>Stainless steel</td>
<td>Stainless steel</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Current (amperes)</td>
<td>4.9</td>
<td>3.3</td>
<td>3.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Anode current density (amp/dm²)</td>
<td>15</td>
<td>10</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>58±2</td>
<td>60±2</td>
<td>59±2</td>
<td>31±2</td>
</tr>
<tr>
<td>pH Initial</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Cell voltage (volts)</td>
<td>3.2</td>
<td>3.3</td>
<td>3.4</td>
<td>2.8</td>
</tr>
<tr>
<td>Energy consumption (kwh/kg of lead dioxide)</td>
<td>0.67</td>
<td>0.73</td>
<td>0.73</td>
<td>0.65</td>
</tr>
<tr>
<td>Nature of deposit: Adherent, smooth, free from pinholes</td>
<td>Adherent, smooth, free from pinholes</td>
<td>Adherent, smooth, free from pinholes</td>
<td>Adherent, smooth, free from pinholes</td>
<td>Adherent, smooth, free from pinholes</td>
</tr>
</tbody>
</table>

Indicates, 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.

Dated this 13th day of November, 1969.

COMPLETE SPECIFICATION

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAJ 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 Harishkumar Shankarrao Umbe, Director, Centre for Scientific and Industrial Research, Council of Scientific and Industrial Research, Karol Bagh, New Delhi, India.

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 moist 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:

1. Depositing lead dioxide in a massive form and then shaping it suitably as anodes for electrolysis;
2. 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 solidified bed technique as described in Indian Patent No. 105731.

The main drawbacks to the current practices are as follows:

1. They are not energy efficient.
2. They require expensive equipment.
3. They are not environmentally friendly.

Therefore, it is desirable to develop a new method for the preparation of lead dioxide electrodes that addresses these drawbacks.
In the case of massive form of lead dioxide, the heavi-
ness and the brittle nature of the deposit requires care-
ful 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 ela-
borate 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 dis-
advantages 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 di-
oxide electrodes for electrolysis which comprises de-
positing lead dioxide on graphite or other metallic subs-
trates from lead nitrate-copper nitrate bath containing
0.1—2 gpl of cationic surfactants like cetyl trimethyl
ammonium bromide/dodecyl trimethyl ammonium bromide
lending to quaternary ammonium type at anode current
densities of 1—30 amp/dm² 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 quaternary 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/dimethyl
hexadecyl ammonium bromide/dodecyl trimethyl ammno-
ium 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 electrolyzing for 3 to 5
minutes at a current density of 10 amp/dm² 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/dm² and
at a temperature of 25—60°C. The pH of the bath is
maintained between 1 and 5. The nitric acid produced
during the electrolysis is neutralized by adding lead car-
bonate 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 precipi-
ting the same from copper nitrate. The current effi-
ciency 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, chlorite to perchlorate,
bromide to bromate, iodide to iodate, iodate to periodate,
other inorganic and organic compounds and in chlor-
alkali cells.

<table>
<thead>
<tr>
<th>Example I</th>
<th>Example I</th>
<th>Example III</th>
<th>Example IV</th>
<th>Example V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Concentration of electrolyte lead nitrate (gpl)</td>
<td>Copper nitrate (gpl)</td>
<td>350</td>
<td>340</td>
<td>350</td>
</tr>
<tr>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>2. (a) addition agent</td>
<td>Cetyl trimethyl ammonium bromide</td>
<td>Trimethyl tetradecyl ammonium bromide</td>
<td>Dodecyl trimethyl ammonium bromide</td>
<td>0.2</td>
</tr>
<tr>
<td>(b) quantity added (gpl)</td>
<td>Graphite</td>
<td>Graphite</td>
<td>Graphite</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>Stainless steel</td>
<td>Stainless steel</td>
<td></td>
</tr>
<tr>
<td>5. Current (amperes)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Temperature (°C)</td>
<td>56±2°C</td>
<td>60±2°C</td>
<td>59±2°C</td>
<td>31±2°C</td>
</tr>
<tr>
<td>8. pH—initial</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Final</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>10. Energy consumption (kwh/kg of lead dioxide)</td>
<td>0.67</td>
<td>0.73</td>
<td>0.73</td>
<td>0.65</td>
</tr>
<tr>
<td>11. Nature of deposit</td>
<td>Adherent, smooth free from pin holes</td>
<td>Adherent, smooth free from pin holes</td>
<td>Adherent, smooth free from pin holes</td>
<td>Adherent, smooth free from pin holes</td>
</tr>
</tbody>
</table>
The present invention consists of a process for the electrolytic preparation of lead dioxide electrodes which comprises in depositing lead dioxide on graphite substrate from a lead nitrate-copper nitrate bath, wherein 0.1 to 2 g p.l. of surface active agents like cetyl trimethyl ammonium bromide/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/dm² 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 tetradecyl 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/dm².

(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 cataionic quaternary ammonium type surfactant at an anode current density of 1—30 amp/dm² 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 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/dm² and at temperature 25 to 60°C, when copper or stainless steel is used as cathode.

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

(iii) A process as claimed in claim (i) 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/dm².

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

(vi) A process as claimed in claim (i) 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, chloride, 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.

Sd. Eligible
PATENTS OFFICER
Council of Scientific and Industrial Research

Dated this 6th day of July, 1970.

Prabhat Prasad, Meenut/Patent/73—150.
Fig. 1