GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 105731. Application No. 105731, dated 15th June 1966. Complete Specification left on 10th April 1967. (Application accepted 15th November 1967.)

Index at acceptance :—70CH[LVIII(5)].

IMPROVEMENTS IN OR RELATING TO THE DEPOSITION OF LEAD DIOXIDE FOR USE AS ELECTRODES.

PROVISIONAL 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).

The following specification describes the nature of this invention.

This is an invention by Srinivasa Sampath, Ramaswamy Thangappan Nadar and Subramaniam Nachappan, all of Central Electrochemical Research Institute, India, Karaikudi-3.

This invention relates to improvements in or relating to the deposition of lead dioxide on graphite, carbon, titanium or other substrates.

Hitherto it has been proposed to use stationary or flowing electrolyte with or without addition agent and keeping the anode stationary or rotating.

This is open to the objection that satisfactory adhesion of the lead dioxide to the substrate is not obtained and the thickness of the deposit is not uniform throughout the surface.

The object of this invention is to obviate these disadvantages by employing fluidised-bed technique wherein the object on which lead dioxide is to be deposited is surrounded by a bed of inert particles fluidized by flowing electrolyte.

To these ends, the invention broadly consists in the deposition of lead dioxide from an aqueous bath of lead nitrate and copper nitrate onto graphite, carbon, titanium or other rods and plates of various sizes in the presence of a fluidized-bed of inert silica sand, quartz or glass granules of suitable particle size. The above said process of deposition is carried out in a vertical cylindrical fluidizing column-*cum*- electrolyzer wherein a hollow cylindrical or rectangular copper cathode and the anode substrate are arranged coaxially, the anode being placed at the centre of the column with the cathode surrounding it.

The anode current density is maintained between 1 and 6 A/dm^2. The temperature and pH of the electrolyte are maintained at desired values between 30° and 60°C and between 1·0 and 5·0 respectively.

The following typical examples are given to illustrate the invention ;

Example 1

	(a)	(b)
Details of the fluidizing column-*cum*-electrolyser	All glass column (5·5 cm ø × 40 cm. long)	All PVC column (15 cm ø × 70 cm. long).
Details of the anode substract	Cylindrical carbon rod (1 cm ø × 14 cm long)	Cylindrical graphite rod (5·15 cm ø × 32 cm. long).
Fluidized material and the average particle diameter.	Silica sand 0·202 mm.	Silica sand 0·165 mm.
Electrolyte	Aqueous solution of lead nitrate (350-375 g/l) & copper nitrate (20-25 g/l).	Aqueous solution of lead nitrate (350-375 g/l) and copper nitrate (20-25 g/l)
Superficial velocity of electrolyte based on empty cross section of the column.	0·44 cm/sec.	0·32 cm/sec.
Electrolyte temperature	55±1°C	30±1°C.
pH	1·0-5·0	1·0-5·0.
Anode current density	4·55 A/dm. sq.	5·45 A/dm. sq.
Cell voltage	1·7-1·8 volts	3·0-3·2 volts.
Duration of electrolysis	6 Hours	5 Hours.
Weight of lead dioxide deposited	54 grams	556 grams.
% current efficiency	100	100.
Thickness of deposit	1·45 mm	1·45 mm.
Nature of deposit	Smooth, hard and uniform deposit free from pin holes and pittings. The deposit is very adherent to the surface of the substrate.	Smooth, hard and uniform deposit free from pin holes and pittings. The deposit is very adherent to the surface of the substrate.

Example 2

	(a)	(b)
Details of the fluidizing column *cum* electrolyser	All glass column (5·5 cm ø × 40 cm. long)	All PVC column (15 cm ø × 70 cm. long).
Details of the anode substract	Titanium sheet (2·6 cm × 15·5 cm)	Rectangular graphite plate (3·1 cm × 7·8 cm × 30 cm).
Fluidized material and the average particle diameter.	Qurtz—0·215 mm	Silica sand 0·165 mm.

Example 2—contd.

	(a)	(b)
Electrolyte	Aqueous solution of lead nitrate (350-375 g/l) and copper nitrate (20-25 g/l).	Aqueous solution of lead nitrate 350-375 g/l) and copper nitrate (20-25 g/l).
Superficial velocity of electrolyte based on empty eross section of the column.	0·45 cm/sec	0·35 cm/sec.
Electrolyte temperature	30±1°C	30±1°C.
pH	1·0-5·0	1·0-5·0.
Anode current density	3·7 A/dm. sq.	4·36 A/dm. sq.
Cell voltage	1·9-2 volts	2·9-3 volts.
Weight of lead dioxide deposited	53·3 gram	553 gram.
Percentage of current efficiency	100	99·2.
Thickness of deposit	0·80 mm	1·1 mm.
Nature of deposit	Smooth, hard and uniform deposit free from pin holes and pittings. The deposit is very adherent to the surface of the substracte.	Smooth, hard and uniform deposit free from pin holes and pittings. The deposit is very adherent to the surface of the substract.

The following are among the main advantages of the invention :

(1) The deposit of lead dioxide obtained by the abovesaid method is smooth, hard, uniform and free from pinholes and is very adherent to the surface of the substrate material.

(2) The conditions to obtain deposits as said in (1) could be accomplished easily within the aforesaid limits of operating conditions. Such deposited electrodes can be used as anodes for the production of chlorate, perchlorate, hypochlorite, chlorine and other products.

R. BHASKAR PAI,

Patents Officer.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

Dated this 7th day of June, 1966.

COMPLETE SPECIFICATION.

COUNCIL OF SCIENTIFIC AND 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 particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This is an invention by Srinvasa Sampath, Ramaswamy Thangappan Nadar and Subramaniam Nachiappan, all of the Central Electrochemical Research Institute, Karaikudi-3, India, all Indian citizens.

This invention relates to improvements in or relating to the deposition of lead dioxide on graphite, carbon, titanium or other substrates for use as substitutes for graphite and/or platinum electrodes in the production of chlorate, perchlorate, alkali-chlorine, hypochlorite and like chemicals.

Hitherto it has been the practice to use stationary or flowing electrolyte, with or without addition agent, the anode being stationary or rotating for the electrodeposition from an aqueous bath of lead nitrate and copper nitrate, of lead dioxide on graphite, carbon, titanium or other substrates of different shapes and sizes.

The currently followed procedures suffer from certain drawbacks. Satisfactory adhesion of the lead dioxide to the substrate is not secured and the thickness of the deposit is not uniform throughout the surface of the electrode. The concentration of any addition agent, when used, has to be closely controlled.

The main object of this invention is to get a very adherent and uniform deposit of lead dioxide on graphite, carbon, titanium and other substrates. Such deposited lead dioxide is suitable for use as anode in the production of chlorates, perchlorates, alkali-chlorine, hypochlorite and like chemicals.

The new principle underlying the invention is the employment of fluidized bed technique wherein the object on which lead dioxide is to be deposited is surrounded by a bed of inert particles fluidized by flowing electrolyte.

The lead dioxide deposited as described above was very adherent and did not peel off even after storing for a period of fourteen months. The maximum variation in thickness of deposit (which was of the order of 1-2 mm) all over the surface of the substrate was within five percent. These electrodes were successfully used as anodes in cells for making chlorates, perchlorates, alkali-chlorine, hypochlorite and such chemicals and were found to be suitable substitutes for the conventional graphite and platinum electrodes. Such a uniformity of deposition arises out of the intense agitation at the electrode-electrolyte inter faces and the uniform current distribution made possible by the application of fluidized bed technique.

The present invention constitutes an improvement in the process of deposition of lead dioxide from an aqueous bath of lead nitrate and copper nitrate onto graphite, carbon, titanium or other substrates in the form of rods and plates of various sizes in the presence, of a fluidized bed of inert material like silica sand quartz or glass granules of suitable particle size. The aforesaid process of deposition is carried out in a vertical cylindrical fluidizing column-*cum*-electrolyzer wherein a hollow cylindrical or rectangular copper cathode and the anode substrate are arranged coaxially

the anode being placed at the centre of the column with the cathode surrounding it. The anode current density is maintained between 1 and 10 A/dm². The temperature and pH of the electrolyte are maintained at desired values between 30 and 60°C and between 1·0 and 5·0 respectively. The deposit of lead dioxide under these operating conditions is uniform, smooth, hard and free from pinholes and is very adherent to the substrate material.

Thus the central theme or novel feature of the present invention is the use of the fluidized bed of inert particles while depositing lead dioxide. This new step in combination with other known steps yields a deposit with desirable characteristics.

The flow sheet of the process is given in Fig. 1 of the accompanying drawings. It consists of a fluidizing column-cum-electrolyser (1) with the anode (2) and cathode (3) surrounded by the fluidized bed The electrolyte is continuously fed from the constant level tank (8). The depleted electrolyte leaving the fluidizing column is neutralized with fresh addition of a mixture of copper carbonate and lead monoxide in the neutralizing tank (5) from where it flows into the electrolyte storage tank (6). The circulation pump (7) serves to transfer the electrolyte from the electrolyte storage tank to the constant level tank.

Example I

	(a)	(b)
Details of the fluidizing column-*cum* electrolyzer	All glass column (5·5 cm dia. × 40 cm long) .	All PVC column (15 cm dia. × 70 cm long).
Details of the anode substrate	Cylindrical carbon rod (1 cm dia. × 14 cm long).	Cylindrical graphite rod (5·15 cm dia. × 32 cm long).
Fluidized material and the average particle diameter.	Silica sand 0·202 mm	Silica sand 0·165 mm.
Electrolyte	Aqueous solution of lead nitrate (350-375 g/l) and copper nitrate (20-25 g/l).	Aqueous solution of lead nitrate (350-375g/l) and copper nitrate (20-25 g/l)
Superficial velocity of electrolyte based on empty cross section of the column.	0·44 cm/sec.	0·32 cm/sec.
Electrolyte temperature	55°±1°C	30°±1°C.
pH	1·0-5·0	1·0-5·0.
Anode current density	4·55 A/dm²	5·45 A/dm².
Cell voltage . . .	1·7-1·8 volts.	3.0-3·2 volts.
Duration of electrolysis	6 hours	5 hours.
Weight of lead dioxide deposited . . .	54 g.	556 g.
Percentage current efficiency	100	100.
Thickness of deposit	1·45 mm	1·45 mm.
Nature of deposit	Smooth, hard and uniform deposit free from pinholes and pittings. The deposit is very adherent to the surface of the substrate.	Smooth, hard and uniform deposit free from pinholes and pittings. The deposit is very adherent to the surface of the substrate.

Example II

Details of the fluidizing column-*cum*-electrolyser	All glass column (5·5 cm dia. × 40 cm long) .	All PVC column (15 cm dia. × 70 cm long)
Details of the anode substrate	Titanium sheet (2·6 cm × 15·5 cm) . .	Rectangular graphite plate (3·1 cm × 7·8cm × 30 cm.).
Fluidized material and the average particle diameter.	Quartz 0·215 mm	Silica sand 0·165 mm.
Electrolyte	Aqueous solution of lead nitrate (350-375 g/l) and copper nitrate (20-25 g/l).	Aqueous solution of lead nitrate (350-375 g/l) and copper nitrate (20—25 g/l).
Superficial velocity of electrolyte based on empty cross section of the column.	0·46 cm/sec	0·36 cm/sec.
Electrolyte temp.	30±1°C	32±1°C.
pH	1·0-5·0	1·0-5·0.
Anode current density	3·7 A/dm²	4·36 A/dm².
Cell voltage	1·9 to 2 volts	2·9-3 volts.
Duration of elocrolysig	4 hours	5 hours.

Example II—contd.

	(a)	(b)
Weight of lead dioxide deposited	53·3 gm	553 g.
Percentage current efficiency	100	99·2.
Thickness of deposit	0·80 mm	1·1 mm.
Nature of deposit	Smooth, hard and uniform deposit free from pinholes and pittings. The deposit is very adherent to the surface of the substrate.	Smooth, hard and uniform deposit free from pinholes and pittings. The depisit is very adherent to the surface of the substrate.

The advantages of the invention are :

(1) The deposit of lead dioxide obtained by the above said method is smooth, hard, uniform and free from pinholes and is very adherent to the surface of the substrate material.

(2) The deposition of lead dioxide, as said in (1) on substrates of any shape such as rods, sheets, plates, etc., could be done in the same unit obviating the requirement of different equipment for substrates of different type and shape.

(3) Such deposited lead dioxide electrodes can be used as anodes for the production of chloratees, perchlorates, hypochlorites, chlorine, caustic soda and such materials.

Summarising, the present invention affords a convenient method for obtaining a smooth, hard, adherent deposit of lead dioxide on graphite and other substrate. This does not involve the use of addition agents or mechanical means for moving the electrode. The present invention yields a deposit of uniform thickness over the entire surface of the electrode due to the intense turbulence and interfacial agitation created by the fluidized bed.

We claim :

(1) A process for the deposition of lead dioxide for use as electrodes which consists in the electrodeposition of a smooth, uniform and adherent deposit of lead dioxide on substrates like graphite, carbon, titanium and other materials of different shapes and sizes from an electrolyte containing lead nitrate (350-375 g/l) and copper nitrate (20-25 g/l) in the presence of a fluidized bed of inert particles like silica sand, quartz or glass granules fluidized by the flowing electrolyte with the substrate material as anode and copper as cathode, the anodic current density being maintained at a value of 1 to 10 amp/dm², the temperature of the electrolyte being 30°C-60°C and pH of the electrolyte being maintained between 1·0 and 5·0.

(2) A process as claimed in Claim (1) wherein the electrodeposition of lead dioxide is carried out in the presence of a fluidized bed of inert particles like silica sand, quartz or glass granules fluidized by the flowing electrolyte.

(3) A process as claimed in the preceding claims wherein the electrolyte contains 350-375 g/l lead nitrate and 20-25 g/l copper nitrate.

(4) A process as claimed in the preceding claims wherein the anodic current density for electrodeposition is maintained between 1 and 10 amp/dm².

(5) A process as claimed in the preceding claims wherein the temperature of the electrolyte is maintained between 30 and 60°C.

(6) A process as claimed in the preceding claims wherein the pH of the electrolyte is adjusted to remain at a value between 1·0 and 5·0.

R. BHASKAR PAI,

Patents Officer,

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

Dated this 5th day of April 1967.

MGIP Sant.—SL—10 Patent/69—6-3-73—100.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

NO. OF SHEETS: 1
SHEET No: 1

No. 105731.

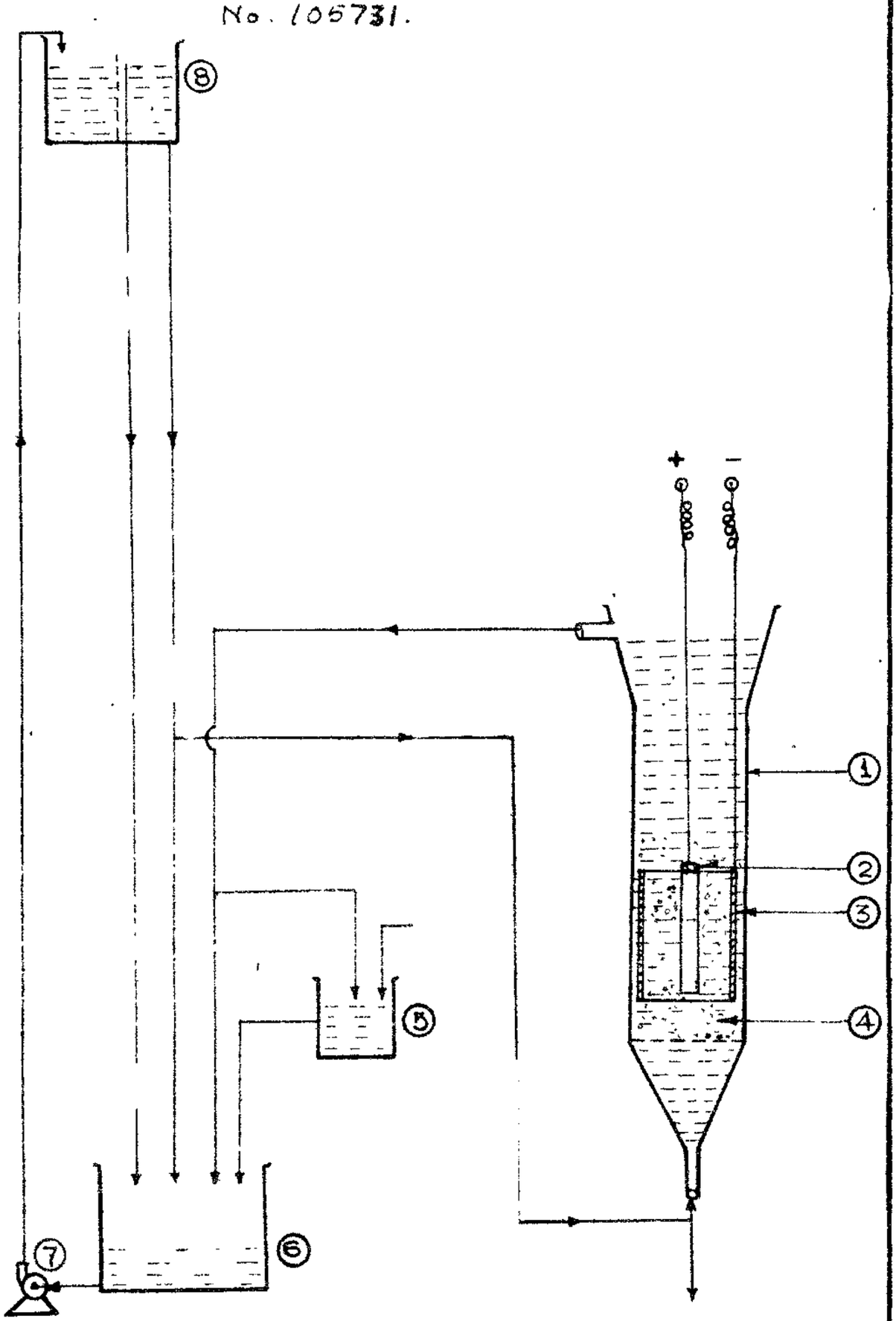

FIG. 1

R B Pai

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