

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

Complete Specification No. 131959. Application and Provisional Specification
filed on 2nd July, 1971. Complete Specification filed on 23rd February, 1972.
Acceptance advertised on 23rd June, 1973.

Index at acceptance—70C4[LVIII(5)]

"IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC PREPARATION OF LEAD DIOXIDE POWDER".

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH RAFI MARG, NEW DELHI, AN INDIAN
REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT, ACT XXI OF 1860.

Provisional Specification

The following specification describes the nature of the invention.

This is an invention by Handady Venkatakrishna Udapa, Director, Kapistharam Chetlur Narasimham, Scientist and Srinivasaraghavan Vasundara, Senior Laboratory Assistant, all of Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India, all Indian citizens.

The invention relates to the improvements in or relating to the electrolytic preparation of lead dioxide powder from salts of lead.

Hitherto it has been the practice to prepare lead dioxide powder by the following methods : (i) treating red lead with concentrated nitric acid, (ii) by oxidising lead monoxide by fusion with alkali chlorate or nitrate (iii) by precipitating with bleaching powder or sodium hypochlorite solution from a solution of plumbite, (iv) by passing chlorine into a hot suspension of lead sulphate and magnesium hydroxide, (v) by the action of hypochlorous acid on a solution of lead acetate, (vi) by adding sodium hypochlorite or hypobromite to a solution of lead acetate, (vii) to deposit lead dioxide anodically and then pulverize it to the required sieve size, (viii) by electrolysis a solution of alkali chloride in which litharge was suspended.

The objection to the current practices are as follows :

The procedures described in methods (i) to (vi) are purely chemical even though in some cases one of the reactants may have to be prepared by an electrochemical method and no detailed data are available for the chemical reaction. Even though no data pertaining to the preparation of lead dioxide powder anodically are available, some methods are known already for getting flaky deposits at an anode, like method (vii) in which case elaborate grinding

and sieving are essential. The conditions of electrolysis for method (viii) has been covered by Indian Patent No. 127,289.

The object of this invention is to obviate these disadvantages by working out the following simple procedure.

Fine lead dioxide powder is obtained by electrolysis a solution of 50-100 g/l lead nitrate containing 0.5 to 2 g/l addition agents like sodium lauryl sulphate, cetyl trimethyl ammonium bromide, saccharin and p-toluene sulphonamide in a divided cell using graphite substrate lead dioxide or nickel anode and graphite or stainless steel cathode. An anode current density of 15-40 amp/dm², a temperature of 25-40°C and pH of 1 to 4 can be employed for obtaining the lead powder. An yield efficiency of 40 to 50% is obtained. The product is washed well with water so as to obtain lead dioxide powder of more than 95% purity.

Lead dioxide powder is also obtained from a solution of lead perchlorate (90-100 g/l) at anode current densities of 30-40 amp/dm² and temperature of 25-35°C. In this case the powder is coarser than that obtained from lead nitrate bath. Lead dioxide powder could not be obtained from lead acetate or lead sulphamate.

To these ends, the invention broadly consists in electrolysis a pure lead nitrate solution containing addition agents like sodium lauryl sulphate, cetyl trimethyl ammonium bromide, saccharin and p-toluene sulphonamide in a divided cell using graphite substrate lead dioxide anode and graphite or stainless steel cathode at anode current densities of 15 to 40 amp/dm² and temperature of 25 to 40°C.

The typical examples are given in the attached sheet, to illustrate the invention.

S. No.	Conditions	Example I Lead nitrate	Example II Lead Nitrate	Example III Lead Nitrate	Example IV Lead Nitrate	Example V Lead Nitrate	Example VI Lead perchlorate
1.	Conc. of lead salt (g/l)	100	50	75	75	75	92
2.	Addition agent (g/l)	0.5 CTAB	2 p-toluene sulphonamide	0.5 sodium lauryl sulphate	...
3.	Initial pH	~4.0	~4.0	~1.0	~1.4	~1.0	~1.0
4.	Anode	Nickel	PbO ₂ coated graphite substrate	PbO ₂ coated graphite substrate	PbO ₂ coated graphite substrate	PbO ₂ coated graphite substrate	PbO ₂ coated graphite substrate

PRICE : TWO RUPEES.

		Stainless Steel	Stainless Steel	Graphite	Graphite	Graphite	Graphite
5.	Cathode						
6.	Anode c.d. (amp/dm ²)	20	15	30	30	30	30
7.	Temperature (°C)	Room temp.	Room temp.	Room temp.	Room temp.	30-35°C	30-35°C
8.	Bath voltage (volts)	6.0	6.2	7.2	7.8	6.8	7.0
9.	Quantity of electricity passed (amp-hrs)	5.653	6.523	6.523	6.523	78.3	6.523
10.	Yield of PbO ₂ (g)	25.2	11.8	11.98	12.27	140.3	16.8
11.	Yield efficiency (%)	76.6	40.4	41.2	42.2	40.2	57.8
12.	Energy consumption Kwh/kg of PbO ₂	1.347	3.438	3.920	4.147	3.796	2.715

Following are the main advantages of this invention :

(1) Lead dioxide powder of -100 to -200 mesh (particle size) can be prepared from a lead nitrate solution, thereby avoiding the need for grinding the product.

(2) Since the electrolyte is based on lead nitrate solution, the contamination of the product by chloride and sulphate can be avoided.

(3) Lead dioxide powder, having lead dioxide content of more than 95% and bulk density of more than 2.0 can be prepared.

(4) Anode current density of 15-40 amp/dm² can be employed as against 2 to 10 amp/dm² employed in method (VIII) described earlier.

(5) The experiment can be conveniently carried out at room temperature (i.e. 30-35°C).

(6) Since the anode is graphite substrate lead dioxide, the product will not be contaminated with any foreign ions even if there is slight anodic dissolution.

Dated this 28th day of June, 1971.

Sd.

PATENTS OFFICER,
Council of Scientific and Industrial Research.

Complete Specification

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 HANDADY VENKATAKRISHNA UDUPA, Director, KAPISTHALAM CHETLUR NARASIMHAM, Scientist and SRINIVASARAGHAVAN VASUNDARA, Senior Laboratory Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India, all Indian Citizens.

1. This invention relates to the improvements in or relating to the electrolytic preparation of lead dioxide powder from salts of lead and which can be used as an oxidising agent in dyestuffs, explosives and pyrotechnic compositions.

2. Hitherto it has been the practice to prepare lead dioxide powder by the following methods: (i) treating red lead with concentrated nitric acid, (ii) by oxidising lead monoxide by fusion with alkali chlorate or nitrate, (iii) by precipitating with bleaching powder or sodium hypochlorite solution from a solution of plumbite, (iv) by passing chlorine into a hot suspension of lead sulphate and magnesium hydroxide, (v) by the action of hypochlorous acid on a solution of lead acetate, (vi) by adding sodium hypochlorite or hypobromite to a solution of lead acetate, (vii) to deposit lead dioxide anodically and then pulverize it to the required sieve size, and (viii) by electrolyzing a solution of alkali chloride in which litharge was suspended.

3. The objections to the current practices are as follows: The procedures described in methods (i) to (vi) are purely chemical even though in some cases one of the reactants may have to be prepared by an electrochemical method and no detailed data are available for the chemical reaction. Even though no data pertaining to the prepara-

tion of lead dioxide powder anodically are available, some methods are known already for getting flaky deposits at an anode like method (vii) in which case elaborate grinding and sieving are essential. The conditions of electrolysis for method (viii) has been covered by Indian Patent No. 127,289. In this process, the final product is always contaminated with the unconverted lead monoxide thereby involving an elaborate purification steps.

4. The object of this invention is to obviate these disadvantages and to standardise the optimum conditions for the electrolytic preparation of a fine powder of lead dioxide with maximum purity.

5. A solution of 50-100 g/l lead nitrate containing 0.5 to 2 g/l addition agents like sodium lauryl sulphate, cetyl trimethyl ammonium bromide, saccharin and p-toluene sulphonamide is electrolysed in a divided cell using graphite substrate lead dioxide or nickel anode and graphite or stainless steel cathode.

6. Lead nitrate (500-100 g/l) solution with 0.5-2 g/l of addition agents like sodium lauryl sulphate, cetyl trimethyl ammonium bromide, saccharin, p-toluene sulphonamide is electrolysed in a divided cell having the porous pot diaphragm, graphite substrate lead dioxide anode and graphite or stainless steel cathode (see Fig. 1 of accompanying drawings). An anode current density of 15-40 amp/dm², a temperature of 25-40°C and an initial pH of 1 to 4 have been employed. 10% nitric acid is used as catholyte. An yield efficiency of 40-50% is obtained. The product is washed well with water so as to obtain lead dioxide powder of more than 95% purity.

Lead dioxide powder is also obtained from a solution of lead perchlorate (90–100 g/l) at anode current densities of 30–40 amp/dm² and temperature of 25–35°C. In this case the powder is coarser than that obtained from lead nitrate bath.

S. No.	Conditions	Example I Lead Nitrate	Example II Lead Nitrate	Example III Lead Nitrate	Example IV Lead Nitrate	Example V Lead Nitrate	Example VI Lead perchlorate
1.	Conc. of lead salt (g/l)	100	50	75	75	75	92
2.	Addition agent (g/l)	0.5 CTAB	2 p-toluene sulphonamide	0.5 sodium lauryl sulphate	...
3.	Initial pH	~4.0	~4.0	~1.0	~1.0	~1.0	~1.0
4.	Anode	Nickel	PbO ₂ coated graphite substrate	PbO ₂ coated graphite substrate	PbO ₂ coated graphite substrate	PbO ₂ coated graphite substrate	PbO ₂ coated graphite substrate
5.	Cathode	Stainless steel	Stainless steel	Graphite	Graphite	Graphite	Graphite
6.	Anode current density (amp/dm ²)	20	15	30	30	30	30
7.	Temperature (°C)	Room temp.	Room temp.	Room temp.	Room temp.	30–35	30–35
8.	Bath voltage (volts)	6.0	6.2	7.2	7.8	6.8	7.0
9.	Quantity of electricity passed (amp-hrs.)	5.653	6.523	6.523	6.523	78.3	6.523
10.	Yield of PbO ₂ (g)	25.2	11.8	11.98	12.27	140.3	16.8
11.	Yield efficiency (%)	76.6	40.4	41.2	42.2	40.2	57.8
12.	Energy consumption (kwh/kg of PbO ₂)	1.347	3.438	3.920	4.147	3.796	2.715

7. The use of graphite substrate lead dioxide as anode for the preparation of lead dioxide powder avoids the contamination of any foreign ions.

8. The present invention consists of a process for the electrolytic preparation of lead dioxide powder which comprises in electrolyzing a solution of 50–100 g/l lead nitrate in a divided cell wherein 0.5–2 g/l of addition agents like sodium lauryl sulphate, cetyl trimethyl ammonium bromide, p-toluene sulphonamide or saccharin are added and a graphite substrate lead dioxide anode and stainless steel or graphite cathode are used and employing an anode current density of 15–40 amp/dm², a temperature of 25–40°C and an initial pH of ~ 1 to 4.

9. The use of graphite substrate lead dioxide as anode prevents the contamination of the product with any foreign ions even if there is anodic dissolution. Lead dioxide powder, having lead dioxide content of more than 95% and bulk density of more than 2.0 can be prepared.

10. The flow diagram of the process is shown in Fig. 1.

11. The following are the main advantages of the invention :

- (i) Lead dioxide powder of —100 to —200 mesh (particle size) can be prepared from a lead nitrate solution, thereby avoiding the need for grinding the product.

(ii) Since the electrolyte is lead nitrate solution, the contamination of the product by chloride and sulphate can be avoided.

(iii) Lead dioxide powder, having lead dioxide content of more than 95% and bulk density of more than 2.0 can be prepared.

(iv) Anode current density of 15–40 amp/dm² can be employed as against 2 to 10 amp/dm² employed in method (viii) describe earlier.

(v) The experiment can be conveniently carried out at room temperature itself (i.e. 30–35°C).

(vi) Since the anode is graphite substrate lead dioxide the product will not be contaminated with any foreign ions even if there is slight anodic dissolution.

12. Fine lead dioxide powder is obtained by electrolyzing a solution of 50–100 g/l lead nitrate containing 0.5 to 2.0 g/l addition agents like sodium lauryl sulphate, cetyl trimethyl ammonium bromide, saccharin and p-toluene sulphonamide in a divided cell using graphite substrate lead dioxide anode and graphite or stainless steel cathode at an anode current density of 15–40 amp/dm², a temperature of 25–40°C and pH of ~ 1 to 4. The product is washed well with water so as to obtain lead dioxide powder of more than 95% purity and having a bulk density of more than 2.

We Claim :

1. A process for the electrolytic preparation of lead dioxide powder which comprises electrolysing a solution of 50-100 g/l lead nitrate or 90/100 g/l lead perchlorate in a divided cell, wherein 0.5 to 2.0 g/l of addition agents like sodium lauryl sulphate, cetyl trimethyl ammonium bromide, p-toluene sulphonamide or saccharin are added and graphite substrate lead dioxide anode and stainless steel or graphite cathode are used and employing an anode current density of 15-40 amp/dm², a temperature of 25-40°C and an initial pH of 1 to 4.
2. A process as claimed in claim (1) wherein the lead nitrate solution of 50-100 g/l or lead perchlorate solution of 90 to 100 g/l can be electrolysed.
3. A process as claimed in claim (1) wherein 0.5 to 2.0 g/l of the addition agents like sodium lauryl sulphate, cetyl trimethyl ammonium bromide, p-toluene sulphonamide or saccharin can be employed for obtaining the fine lead dioxide powder.
4. A process as claimed in claim (1) wherein the electrolysis is carried out in a divided cell using the graphite substrate lead dioxide anode and stainless steel or graphite cathode.
5. A process as claimed in claims (1) and (4) wherein the porous pot is used as a diaphragm and 10% nitric acid as catholyte to prevent the deposition of lead at the cathode.
6. A process as claimed in claim (1) wherein anode current densities of 15-40 amp/dm² are employed.
7. A process as claimed in claim (1) wherein temperature range of 25-40°C is employed.
8. A process as claimed in claim (1) wherein pH range of 1 to 4 is employed.
9. A process as claimed in claim (1) wherein the lead dioxide powder having lead dioxide content of more than 95% purity and a bulk density of more than 2.0 can be prepared.
10. A process as claimed in claim (1) as substantially hereinbefore described.

Dated this 16th day of September, 1971.

Sd.
PATENTS OFFICER,
Council of Scientific & Industrial Research.

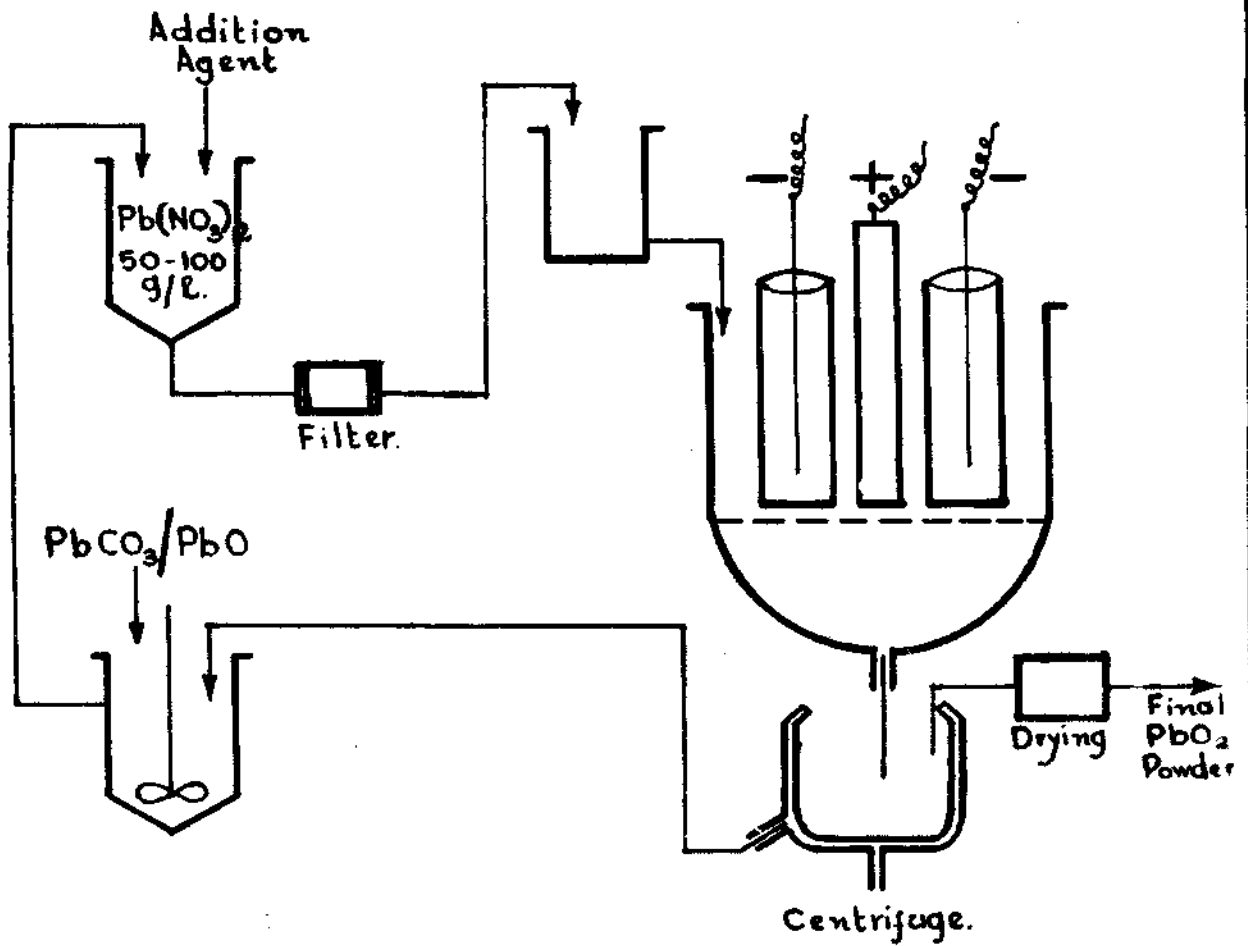


Fig. 1.

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