

Government of India: The Patent Office: 214, Lower Circular Road,
Calcutta-17: Specification No. 127289: Application No. 127289 dated
27th June, 1970: Complete specification left on 17th March, 1971:
Application accepted 17th December, 1971.

Incl. of Acceptance-70 C4

INDIAN PATENTS AND DESIGNS ACT, 1911

PROVISIONAL SPECIFICATION

Section 4

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

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 Handady Venkatakrishna Udupa,
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Shunmugham Arumugasamy Gnanasekaran, Senior Scientific Assistant,
all of Central Electrochemical Research Institute, Karaikudi,
Tamil Nadu, and Srinivasa Sampath, Western India Match Co.,
Ambernath, Maharashtra State, all Indian citizens.

This invention relates to improvements in or relating to
the electrolytic preparation of lead dioxide powder from lead
monoxide, red lead and lead hydroxide.

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 the lead monoxide
by fusion with alkali chlorate or nitrate, (iii) by precipita-
ting 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/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.

The objection to the current practices are as follows:
The procedure 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. However, in all these
cases, the reaction is either time consuming or does not go
to completion.

Whereas method (vii) involves an elaborate grinding and sieving arrangement, no data pertaining to the conditions of electrolysis are available for the method (viii). Hence it is not possible to give any objections to the method (viii).

The object of this invention is to obviate these disadvantages by working out the following modified procedure. A solution of sodium chloride of 0.5 - 2 M concentration is electrolyzed in a divided cell, using graphite or lead dioxide coated graphite anode and mild steel or graphite cathode.

Lead monoxide or lead hydroxide or red lead (particle size 30 to 59 microns) is suspended in a solution of sodium chloride of 0.5 - 2 M concentration and electrolysed in a divided cell having cloth or microporous rubber diaphragm and using graphite or lead dioxide coated graphite anode and mild steel or graphite cathode. An anode current density of 2-10 amp/dm², a temperature of 25 to 65°C and pH of 2 - 3 or 8-10 have been employed. An yield efficiency of 60 - 70% is obtained.

It has also been found possible to carry out the reaction by fluidizing the suspended lead monoxide or hydroxide or red lead by electrolyte flowing upward in the column, and employing the conditions as described above.

After the electrolysis, agitation of the slurry is continued for about 30 minutes and the solid filtered off. The solid product is treated with dilute nitric acid (1:5) and again filtered off. It is again washed with dilute ammonium acetate solution and finally with hot water to get a product having lead dioxide content 88 - 92%.

To these ends, the invention broadly consists in electrolyzing a solution of sodium chloride of 0.5 to 2 concentration in a divided cell using graphite or lead dioxide coated graphite anode and mild steel or graphite cathode and suspending in the anolyte 5 to 30 g/l lead monoxide or lead hydroxide or red lead in the solution, the particle size being 30 to 50 microns. An yield efficiency of 60 - 70% is obtained when the electrolysis is carried out at an anode current density of 2 to 10 amp/dm², temperature of 25 to 65°C and a pH of 2 to 3 or 8 to 10. The product is given suitable treatment and washing so as to obtain lead dioxide content of 88 to 92%.

The following typical examples are given to illustrate the invention.

Conditions	Example I	Example II	Example III	Example IV Fluidized Bed Tech- nique.
Concentration of Sodium Chloride (M)	0.5	1.0	1.0	1.0
Substance added	Lead monoxide	Lead monoxide	Red Lead	Lead monoxide
Weight added (g)	25	25	25	25
Anode	Graphite	Graphite	Graphite	Lead dioxide coated Grap
Cathode	Graphite	Mild steel	Graphite	Mild steel
Quantity of Electricity passed (amp.hrs)	6	6	3.9	6
Anode current density (amp/dm ²)	5	10	5	5
Temperature (°C)	30-35	60 - 65	30 - 35	30 - 35
Bath voltage (v)	4.1	3.5	3.8	10
Weight of Lead dioxide obtained (g)	15.2	18.4	18.3	21
Yield efficiency (%)	57	69	69	73
Energy consumption (kwh/kg of PbO ₂)	1.62	1.14	0.81	2.9

Following are the main advantages of this invention:

1. Lead dioxide powder of varying bulk densities (1.7 - 2.0) can be prepared by suspending lead monoxide, lead hydroxide or red lead in sodium chloride solution and electrolyzing in a divided cell.
2. Sodium chloride solution of 0.5 - 2 M can be employed.
3. Anode current density range of 2 - 10 amp/dm² can be employed.
4. A wide temperature of 25 to 65°C can be employed.
5. Cloth or microporous rubber diaphragm can be employed.
6. It is also possible to carry out the reaction by fluidizing the suspended material, viz. lead monoxide, lead hydroxide or red lead by the electrolyte flowing upward in the column.

Dated this 24th day of June, 1970.

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INDIAN PATENTS AND DESIGNS ACT, 1911.

COMPLETE SPECIFICATION.

Section 4.

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

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 HANDADY VENKATAKRISHNA UDUPA,
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all of the Central Electrochemical Research Institute, Karaikudi,
Tamil Nadu and Srinivasa Sampath, Western India Match Co.,
Ambernath, Maharashtra, all Indian citizens.

This invention relates to improvements in or relating to the electrolytic preparation of lead dioxide powder from lead monoxide, red lead or lead hydroxide.

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 the 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/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.

The objection to the current practice 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. However, in all these cases, the reaction is not only time consuming but also the efficiency of these methods is lower.

Whereas method (vii) involves an elaborate grinding and sieving arrangement, no data pertaining to the conditions of electrolysis are available for the method (viii). Hence it is not possible to give any objection to the method (viii).

The object of this invention is to obviate these disadvantages and to establish the optimum conditions for preparing lead dioxide powder from lead monoxide/red lead/lead hydroxide.

Lead monoxide/lead hydroxide/or red lead, suspended in the anolyte solution of sodium chloride of 0.5 - 2M concentration is electrolysed in a divided cell or in a fluidized column, using graphite or graphite substrate lead dioxide anode and mild steel or graphite cathode.

Lead monoxide or lead hydroxide or red lead (5-30 g/s) (particle 30-50 microns) is suspended in a solution of sodium chloride of 0.5M - 2M concentration and electrolyzed in a divided cell having cloth or microporous rubber diaphragm, and using graphite or graphite substrate lead dioxide anode and mild steel or graphite cathode. Agitation of electrolyte by air or mechanical stirrer is employed, to keep the solid in suspension. The suspension is present only in the anolyte. An anode current density of 2-10 amp/dm², a temperature of 25-65°C and an initial pH of 6.5 to 7.5 have been employed. A yield efficiency of 60-70% is obtained. It has also been found possible to carry out the reaction by fluidizing the suspended lead monoxide or hydroxide or red lead in the anode compartment by electrolyte flowing upward in the column and employing the conditions as described above.

After the electrolysis agitation of the slurry is continued for about 30 minutes and the solid filtered off. It is washed with dilute ammonium acetate solution and finally with hot water to get a product having lead dioxide of purity of 88-92%.

The bulk density of the lead dioxide varies with the conditions of electrolysis. The product obtained at low current density and high temperature had a bulk density of 2 against 1.5 to 1.9 under other conditions.

The present invention consists of a process for the electrolytic preparation of lead dioxide powder which comprises in suspending 5-30 g/l of lead monoxide/red lead/lead hydroxide in the anolyte solution of sodium chloride of 0.5 - 2M concentration wherein the electrolysis is carried out in a divided cell or in a fluidized column, using graphite or graphite substrate lead dioxide anode and mild steel or graphite cathode and employing an anode current density of 2 - 10 amp/dm² temperature of 25-65°C and an initial pH of 6.5 to 7.5.

The bulk density of the lead dioxide powder is varied between 1.5 to 2.0 by carefully controlling the operating conditions of the cell. The product, after suitable treatment and washing contains lead dioxide content of 88-92%.

The cell assembly, for fluidizing column is shown in Fig. 1 of the accompanying drawings. An all glass apparatus with three glass limbs is employed. The middle compartment in which the suspended lead monoxide/red lead/lead hydroxide is kept in a fluidized state, acted as the anode compartment and the other two limbs separated from the middle compartment by sintered discs (3 in Fig. 1) acted as cathode compartments. The anode (1 in Fig. 1) is graphite or graphite substrate lead dioxide and the cathode (2 in Fig. 1) is mild steel or graphite. A perforated disc (4 in Fig. 1) is kept at the bottom of the anode compartment to prevent the suspended particles from falling when the circulation is stopped.

A flow diagram of the process is shown in Fig. 2. of an accompanying drawings _____

EXAMPLES:

<u>Conditions</u>	<u>Example I</u>	<u>Example II</u>	<u>Example III</u>	<u>Example IV</u> (Fluidized bed technique)	<u>Example V</u>
Conc. of sodium chloride (M)	0.5	1.0	1.0	1.0	1.0
Substance added	Lead monoxide	Lead monoxide	Red lead	Lead monoxide	Lead monoxide
Weight added (g)	25	25	25	25	30
Anode	Graphite	Graphite	Graphite	PbO ₂ coated graphite	Graphite
Cathode	Graphite	Mild steel	Graphite	Mild steel	Mild steel
Qty. of electricity passed (amp-hrs)	6	6	3.9	6	7.1
Anode current density (amp/dm ²)	5	10	5	5	3
Temperature (°C)	30-35	60-65	30-35	30-35	62-65
Bath voltage (V)	4.1	3.5	3.8	10	3.3
Weight of lead dioxide obtained (g)	15.2	18.4	18.3	21	25.2
Yield efficiency (g)	57	69	69	73	69
Energy consumption (kwh/kg of PbO ₂)	1.62	1.14	0.81	2.9	1.14
Bulk density	1.5	1.8	2.0

Following are the main advantages of this invention:

- i) Lead dioxide powder of varying bulk densities (1.5-2.0) can be prepared by suspending lead monoxide, lead hydroxide or red lead in sodium chloride solution (anolyte) and electrolyzing in a divided cell.
- ii) Sodium chloride solution of 0.5 - 2M can be employed as anolyte.
- iii) Anode current density range of 2-10 amp/dm² can be employed.
- iv) A wide temperature of 25 to 65°C can be employed.
- v) Cloth or microporous rubber diaphragm can be employed.
- vi) It is also possible to carry out the reaction by fluidizing the suspended material viz., lead monoxide, lead hydroxide or red lead in the anode compartment by the electrolyte flowing upward in the column.

A process for the electrolyte preparation of lead dioxide powder consists in suspending 5-30 g/l of lead monoxide/lead hydroxide/red lead in the anolyte solution of sodium chloride of 0.5 to 2M concentration and electrolyzing in a divided cell wherein the electrolyte is agitated or in a fluidized column using graphite or graphite substrate lead dioxide anode and mild steel or graphite cathode, at an anode current density of 2-10 amp/dm² at a temperature of 25 - 65°C and at an initial pH of 6.5 to 7.5. The product after suitable treatment and washing contains lead dioxide of purity of 88-92% having a bulk density of 1.5 to 2.0.

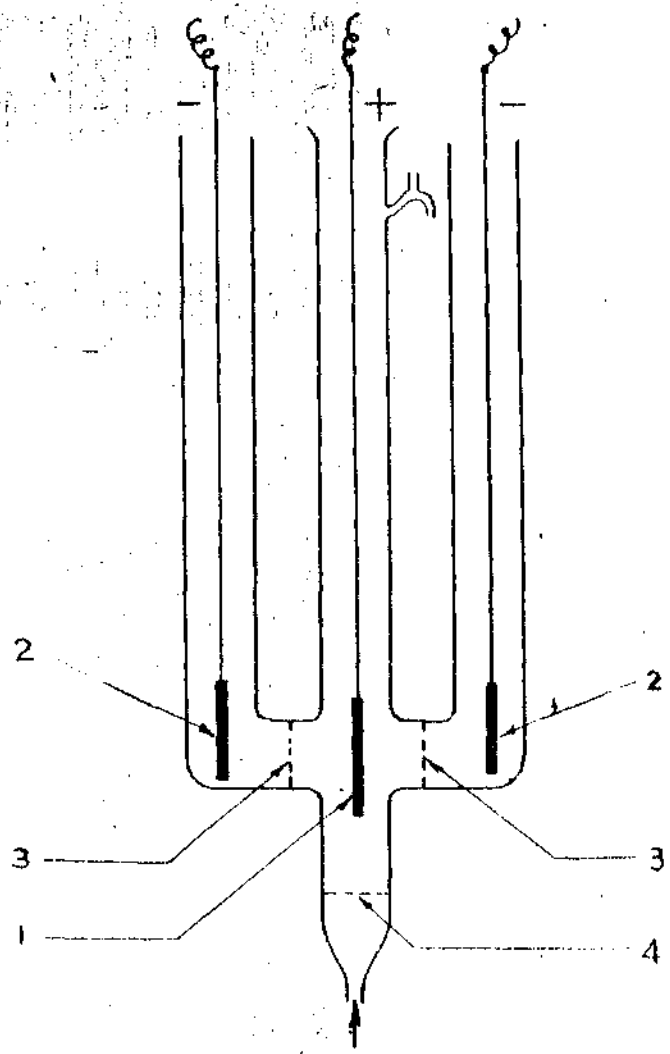
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1. A process for the electrolytic preparation of lead dioxide powder comprises in suspending 5-30 g/l of lead dioxide or red lead or lead hydroxide in the anolyte solution of sodium chloride of 0.5 to 2M concentration wherein the electrolysis is carried out in a divided cell or in a fluidized column using graphite or graphite substrate lead dioxide anode and mild steel or graphite cathode and employing an anode current density of 2-10 amp/dm², temperature of 25-65°C and an initial pH of 6.5 to 7.5.
2. A process as claimed in claim (1) in which 0.5 to 2M concentration of sodium chloride solution containing a suspension of lead monoxide/red lead/lead hydroxide is electrolyzed in a divided cell.
3. A process as claimed in claims (1) and (2) wherein a cloth or microporous rubber is used as a diaphragm material.
4. A process as claimed in claims (1) and (2) wherein the electrolysis is carried out in a fluidized column.
5. A process as claimed in claim (1) as substantially hereinbefore described.

Dated this 15th day of February, 1971.

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Council of Scientific and Industrial Research.

No. 127289.



DUPLICATE
17 MAR 1971

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(R. B. PAI)
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Complete specification

