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IMPROVEMENTS IN OR RELATING TO PRODUCTION OF LEAD POWDER BY DIRECT REDUCTION OF LEAD COMPOUNDS AND/OR OF ACTIVE METERIAL OBTAINED FROM DISCARDED OR SPENT LEAD ACID BATTERY PLATES.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH,

RAFI MARG, NEW DELHI-1, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXIOF 1860).

The following specification describes the nature of this invention :—

This is an invention by HANDADY VENKATAKRISHNN UDUPA, Director, PENNAGARAM VYASA RAO VASUDEVA RAO, Scientist and RENGASAMY VIJAYAWALLI, Scientist, all of the Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India, all Indian citizens.

This invention relates to improvements in or relating to production of lead powder by direct reduction of lead compounds and/or of active material obtained from discarded or spent lead acid battery plates.

Hitherto it has been proposed to produce lead powder by electrolytic deposition from sodium plumbate solutions or from acid solutions of lead compounds which produce lead in the form of spongy deposit. This cannot be either ground or disintegrated into powdery form. Lead in the form of powder could be obtained only from electrolysis of molten lead salts which is a cumbersome operation.

Fine lead powder (of any desired particle size) is obtained by the direct electrolytic reduction of lead compounds or waste active material from lead acid storage battery plates, the reduction being carried out in the soltd phase in an electrolyte of an alkali hydroxide. The material is kept as a sediment immersed in the alkaline electrolyte at the bottom of a suitable conducting container and an insoluble anode kept above the sediment, but immersed in the electrolyte. The container itself is used as the cathode and this process of direct reduction offers certain advantages viz., (a) this eliminates the intermediate steps of bringing the lead compounds into solution and electrolysing subsequently, (b) avoids handling of large volumes of solutions, (c) the process is simple to operate without involving control of different parameters, (d) the particle size of the end product may be controlled by the particle size of the starting material.

According to the present invention there is provided a process for the electrochemical production of lead powder from lead compounds and/or active material from discarded or spent lead acid battery wastes, which comprises of the direct electrochemical reduction of the compounds kept as a sediment on a lead, mild steel, nickel, nickel plated mild steel, stainless steel or lead lined container, preferably lead or lead lined container as cathode with an alkali hydroxide of sodium, potassium or lithium as electrolyte and using an anode of perforated sheet or wire mesh of lead, mild steel, nickel, nickel plated mild steel or stainless steel immersed in the electrolyte but above the bed of the sediment.

The object of this invention is to obviate these disadvantages by reducing lead compounds and/or waste active material from lead acid storage battery plates by a direct reduction of the same in the solid state so that lead is obtained in the form of powder which requires only a washing treatment and drying bofore it can be mildly crushed to separate the agglomerates and classified into the powder of desired mesh size.

To these ends the invention broadly consists in direct electrolytic reduction of lead compounds or waste storage battery active material in solid form in an alkaline electrolyte. The meterial is powdered to a mesh size of at least — 150 and kept as a sediment at the bottom of a container which itself is used as the cathode. An anode of metallic wire mesh or perforated sheet or grid which is not attacked by the alkaline electrolyte is disposed over the bed of lead compounds but not touching the same. 10-45% of aqueous solution of alkaline electrolyte like hydroxides of potassium, sodium or lithium is used as electrolyte. A current density of 5 to 20 amp/dm^2 based on the apparent cathode surface area is apdlied. The current efficiency for the reduction has been found to be over 95%. After the reduction is over, the alkaline electrolyte is drained off and stored or re-use. The reduced powder is washed thoroughly and finally kept soaked in 5N hydrochloric or sulphuric aeid for 10 minutes to two hours. Then the mass is washed thoroughly till the pH reaches 7. On drying at about 100°C, the mass can be easily powdered to any desired mesh size. The purity of such a powder has been found to be 95-98% metallic. The following typical examples are given to illustrate the invention :

	Example I	*Example II*
Wt. of active material	600 g.	14 kg.
Current passed	4 amp.	40 amp.
Current density	7.3 amp/dm^2	7 amp/dm^2
Cell voltage	2.8 V	2.2 V
Wt. of lead obtained	480 g.	25 lbs.
Conversion efficiency	100%	99%
Electrolyte	Aqueous solution of sodium hydroxide 20%	Aqueous solution of sodium hydroxide 20%

	Example III
Wt. of lead monoxide	5 g.
Current passed ;	10 amp.
Current density	50 amp/dm^2
Cell voltage	2.7 V
Wt. of lead obtained	4.3 g.
Conversion efficiency :	100%
Current efficiency :	98%
Electrolyte :	Aqueous solution of sodium hydroxide 40%

Price : TWO RUPEES

The following are among the main advantages.

(1) Very fine lead powder can be directly prepared from lead compounds such as lead monoxide, lead dioxide or a mixture of lead compounds and also from battery waste active material by direct electrolytic reduction of the same in the solid phase.

(2) There is no necessity of making an aqueous solution of the lead salts since the lead compounds are directly reduced in the solid state.

(3) The process of obtaining lead powder is simple and does not require specialised technical knowledge.

(4) Large amperage cells can ba easily operated which are not normally known for production of metal powders.

R. Bhaskar Pai

PATENTS OFFICER,

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(*See* Section 10)

IMPROVEMENTS IN OR RELATING TO PRODUCTION OF LEAD POWDER BY DIRECT REDUCTION OF LEAD COMPOUNDS AND/OR OF ACTIVE MATERIAL OBTAINED FROM DISCARDED OR SPENT LEAD ACID BATTERY PLATES.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

RAFI MRG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BOBY 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, Director, PENNAGARAM VYASARAO VASUDEVA RAO, Scientist and RENGASAMY VIJAYAWALLI, Scientist, all of the Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India, all Indian citizens.

This invention relates to improvements in or relating to production of lead powder by direct reduction of lead compounds and/or of active material obtained from discarded or spent lead acid battery plates.

Hitherto it has been proposed to produce lead powder by electrolytic deposition from sodium plumbite solutions or from acid solutions of lead compounds which produce lead in the form of spongy deposit. Lead in the form of powder could be obtained only from electrolysis of molten lead salts which is a cumbersome operation. Thermal methods have been used to recover lead from active material from discarded or spent lead acid batteries.

In the hitherto known processes lead was obtained by electrolytic deposition in the form of a spongy deposit which could neither be ground nor disintegrated into powder form. Further very fine powder could be obtained only by electrolysis of molten salts. These drawbacks are obviated by the present process of direct reduction in which the lead compounds are directly reduced in the solid state on a cathode substrate.

The object of the invention is to obviate these disadvantages by reducing lead compounds and/or waste active meterial from lead acid storage battery plates by a direct reduction of the same in the solid state so that lead is obtained in the form of powder which reqires only a washing treatment and drying before it can be mildly crushed to separate the agglomerates and classified into the powder of desired mesh size.

Thus, lead powder is produced from lead compounds or waste storage battery active material by the direct reduction of the lead compounds and waste storage battery active material kept as a sediment on a cathode wherein the lead powder can be directly produced without bringing the lead compounds into solution and subsequent electrolysis for the same. The conversion efficiency is 100% and current efficiency is over 95%.

In this process lead powder is produced by direct reduction of lead compounds and waste storage battery active material in a suitable cell arrangement using an alkaline electrolyte. The cell is made up of lead, mild steel, stainless steel, nickel or nickel plated mild steel container or lead lined vessel on the bottom of which the lead compounds and waste storage battery active material in a powder form of at least—150 mesh size or of any suitable mesh size is kept as a uniform bed.

Preparation of the bed of lead compounds for reduction : The nature of reduction depends to a great extent on the method of packing of the material to be reduced as well as the extent of reaction between lead compound and the electrolyte. In the case of waste active meterial, which is mainly composed of lead sulphate, metallic lead and mixture of oxides of lead, the uniformly powdered mass is spread on the cathode surface to form a uniform layer and when alkali is added the material gets easily wetted with alkali. Whereas in the case of pure oxide of lead such as battery grade red lead or litharge first a uniform bed of the oxide is made and alkali is added in small portions first to wet the oxide bed thoroughly and uniformly well. Once the bed is thoroughly wet with alkali the rest of the electrolyte is added without disturbing the sediment of oxide. Special care is taken to avoid lump formation, which may cause reduction in current efficiency.

Electrolytic reduction : The container is connected as the cathode. The anode assembly consists of a metallic wire mesh or perforated sheet or grid of mild steel, nickel, nickel plated mild steel or stainless steel suitably disposed over the bed of oxide and mounted in such a way that, while immersed in the electrolyte over the bed of the lead compounds it will facilitate uniform current distribution on the cathode surface 10-45% of aqueous solution of sodium, potassium or lithium hydroxide is used as electrolyte. A current density of 5 to 50 amp/dm^2 based on the apparent area of cathode substrate is applied. The current efficiency for the reduction has been found to be over 95%. After the reduction is over, the electrolyte is drained off and stored for reuse. The reduced metal is washed thoroughly and processed as follows :

Processing of the metal powder : The reduced metal, namely lead, is in the form of spongy agglomerates. To break the agglomerates the reduced metal is kept soaked in dilute hydrochloric acid or sulphuric acid of strength 2-20% (w/v) for 5 minutes to 2 hours. Then the acid is decanted off and the mass is washed well with distilled water till the pH reaches 7. The whole mass is then ground lightly to uniform powder. The powder is further treated with dilute solution of potassium chromate or liquid soap (1% solution) for 15 minutes to ½ hr centrifuged and dried. The treatment with sulphuric acid is adequate to produce lead powder of good keeping quality. On drying at about 100°C the mass can be easily powdered to any desired mesh size. The purity of such a powder has been found to be 95-98% metallic. The following typical examples are given in to illustrate the invention.

EXAMPLE I

Wt. of active material	600 g
Current passed	4.0 amps
Current density	7.3 amp/dm^2
Cell voltage	2.8 V
Wt of lead powder obtained	480 g
Conversion efficiency	100%
Electrolyte	20%NaOH
Duration of reduction	74 hrs.

EXAMPLE II

Wt. of active material	14 kgs
Current passed	40 amps
Current density	7 amp/dm²
Cell voltage	2.2 V
Wt. of lead powder obtained	12.1 kg
Conversion efficiency	99%
Electrolyte	20% NaOH
Duration of reduction	173 hrs.

EXAMPLE III

Wt. of lead monoxide	5 g
Current passed	5 amps
Current density	50 amp/dm²
Cell voltage	2.7V
Weight of lead obtained	4.3 g
Current efficiency	98%
Conversion efficiency	100%
Electrolyte	40% NaOH
Duration of reduction	15 minutes.

The following are the main advantages :

(1) Very fine lead powder can be directly prepared from lead compounds such as lead monoxide, lead dioxide, or a mixture of lead compounds and also from battery waste active material by direct electrolytic reduction of the same in the solid phase.

(2) There is no necessity of making an aqueus solution of the lead salts since the lead compounds are directly reduced in the solid state.

(3) The proeess of obtaining lead powder is simple and does not require specialised technical knowledge.

(4) Large amperage cells can be easily operated which are not normally known for production of metal powders.

(5) Apart from the production of lead powder, the process can be used for the recovery of lead from waste active material from discarded or spent batteries and by adopting this process loss of valuable antimony in thermal process can be avoided.

(6) The electrolyte can be reused a number of times with only a loss due to handling. Since some cumbersome unit process are not involved, the process cost is more economical than the conventional electrolytic process.

Summary : This invention relates to the production of lead powder by direct reduction of lead compounds and waste active material from discarded or spent batteries. Reducing the lead compounds by simple electrochemical reduction in alkaline medium eliminates the intermediate steps of dissolving the lead compound followed by electrolysis of the resulting solution. Lead, mild steel, nickel or nickel plated mild steel or lead lined container is used as the cell and the lead compounds or waste active material in a powder form is kept as a sediment at the bottom of the cell. The cell is made as the cathode and a mild steel, nickel, nickel plated mild steel or stainless steel mesh or perforated sheet mounted on an insulating frame suitably disposed over the bed of the powder so as to facilitate uniform current distribution serves as the anode. At the end of the reduction, the lead powder is taken out of the cell, washed thoroughly and finally kept soaked in dilute hydrochloric acid or sulphuric acid of strength 2-20% (w/v) for 5 minutes to 2 hrs. Then the mass is washed well till the pH reaches 7 and stabilised. On drying at about 100°C the mass can be easily powdered to any desired mesh size. The conversion efficiency is 100% and current efficiency is 95-98%.

WE CLAIM :

(1) A process for the electrochemical production of lead powder from lead compounds and/or active material from discarded or spent lead acid battery wastes, which comprises of the direct electrochemical reduction of the compounds kept as a sediment on a lead, mild steel, nickel, nickel plated mild steel, stainless steel or lead lined container, preferably lead or lead lined container as cathode with an alkali hydroxide of sodium, potassium or lithium as electrolyte and using an anode of perforated sheet or wire mesh of lead, mild steel, nickel, nickel plated mild steel or stainless steel immersed in the electrolyte but above the bed of the sediment.

(2) A process as claimed in Claim (1) wherein lead compounds and/or active material from discarded or spent lead acid battery wastes are reduced in an electrolyte of sodium hydroxide of 10-45%, preferably 20% solution at a current density of 5 to 50 amp/dm², preferably 10 amp/dm².

(3) A process as claimed in Claims (1) and (2) wherein the particle size of the lead powder obtained is controlled by suitably choosing the appropriate particle size of the solid lead compound or the battery waste active material.

(4) A process as claimed in Claims (1) to (4) wherein the alkaline electrolyte recovered from the cell is used again by making good the loss due to drag out and handling.

(5) A process for production of lead powder from lead compounds and/or active material from discarded or spent lead acid battery wastes as substantially hereinbefore described.

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Dated this 20th day of May 1971.

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