

ABSTRACT**“RECLAIMING OF LEAD IN FORM OF HIGH PURITY LEAD COMPOUND FROM RECOVERED ELECTRODE PASTE SLIME OF DISMISSED LEAD BATTERIES AND/OR OF LEAD MINERALS”**

An all-wet process for reclaiming the lead content of impure electrode paste or slime from discarded lead batteries and/or lead minerals, in form of high purity lead compound, comprises a) suspending the impure lead containing material in a lead sulphate dissolving aqueous solution of a salt belonging to the group composed of the acetates of sodium, potassium and ammonium; b) adding to the suspension sulphuric acid in an amount sufficient to convert all lead oxides to lead sulphate soluble in the acetate salt solution and slowly adding to the suspension either hydrogen peroxide or a sulphite or bubbling sulphurous anhydride through it, in a measure adapted to reduce any lead dioxide to lead oxide converted eventually to soluble lead sulphate by the sulphuric acid; c) separating a limpid acetate salt solution containing dissolved lead sulphate from a solid phase residue including all undissolved compounds and impurities; d) adding to the separated solution of lead sulphate either carbonate or hydroxide of the same cation of the acetate salt of the lead sulphate dissolving solution for precipitating highly pure lead carbonate/oxy carbonate or lead oxide or hydroxide, respectively, while forming sulphate of the cation, soluble in the acetate salt solution; and e) separating the precipitated high purity lead compound from the acetate salt solution now containing also sulphate of the same cation of the acetate salt. The acetate salt solution containing also sulphate of the same cation of the acetate salt separated from the precipitated compound of lead is re-cycled to step a) and the content of sulphate of the same cation in the solution is maintained below saturation limit by continuously or periodically cooling at least a portion of the solution separated from the precipitated lead compound to cause selective crystallization of sulphate salt of the same cation of the acetate salt and removing it as a by-product. Optionally, the separated solid phase comprising insoluble compounds of lead and/or undissolved concretions of lead compounds is treated in hot concentrated hydroxide of the same cation of the selected acetate salt and converting these compounds of lead and/or undissolved concretions of lead compounds to soluble plumbites, and the separated lead containing alkaline liquor may be added to the limpid acetate solution for precipitating all reclaimable lead in form of high purity lead oxide or hydroxide.

Refer to Figure 2

CLAIMS

1. A process for reclaiming the lead content of impure electrode paste or slime from discarded lead batteries and/or lead minerals, in form of high purity lead compound, comprising the steps of

- a) suspending the impure lead containing material in a lead sulphate dissolving aqueous solution of a salt belonging to the group composed of the acetates of sodium, potassium and ammonium;
- b) adding to the suspension sulphuric acid in an amount sufficient to convert all lead oxides to lead sulphate soluble in the acetate salt solution and slowly adding to the suspension either hydrogen peroxide or a sulphite or bubbling sulphurous anhydride through it, in a measure adapted to reduce any lead dioxide to lead oxide converted eventually to soluble lead sulphate by the sulphuric acid;
- c) separating a limpid acetate salt solution containing dissolved lead sulphate from a solid phase residue including all undissolved compounds and impurities;
- d) adding to the separated solution of lead sulphate either carbonate or hydroxide of the same cation of the acetate salt of the lead sulphate dissolving solution for precipitating highly pure lead carbonate/oxy carbonate or lead oxide or hydroxide, respectively, while forming sulphate of the cation, soluble in the acetate salt solution;
- e) separating the precipitated high purity lead compound from the acetate salt solution now containing also sulphate of the same cation of the acetate salt.

2. The process of claim 1, wherein said acetate salt solution containing also sulphate of the same cation of the acetate salt separated from the precipitated compound of lead is re-cycled to step a) and the increasing content of sulphate of the same cation in the solution is maintained below saturation limit by continuously or periodically cooling at least a portion of the solution separated

from the precipitated lead compound to cause selective crystallization of sulphate salt of the same cation of the acetate salt and removing it as a by-product.

3. The process of claim 2, wherein prior to cooling for selectively precipitating sulphate salt of the same cation of the acetate salt, the solution is contacted with a chelating resin adapted to sequester any residual lead ions from the solution for selectively precipitating substantially lead-free sulphate salt of the same cation of the acetate salt, upon cooling.

4. The process of claim 1, wherein the selective dissolution of the lead sulphate is carried out by suspending the impure material in an aqueous solution of sodium acetate having a concentration comprised between 10g and 120g of salt in 100g of water at a temperature comprised between 20°C and boiling point, for a stirring time comprised between 5 and 180 minutes.

5. The process of claim 1, wherein selective dissolution of the lead sulphate is carried out by suspending the impure material in an aqueous solution of ammonium acetate having a concentration comprised between 20g and 120g of salt in 100g of water at a temperature comprised between 20°C and boiling point, for a stirring time comprised between 5 and 180 minutes.

6. The process of claim 1, wherein selective dissolution of the lead sulphate is carried out by suspending the impure material in an aqueous solution of potassium acetate having a concentration comprised between 20 g and 120 g of salt in 100g of water at a temperature comprised between 20 °C and boiling point, for a stirring time comprised between 5 and 180 minutes.

7. The process of claim 1, further comprising suspending said separated solid phase residue including all undissolved compounds and impurities in hot concentrated hydroxide of the same cation of the selected acetate salt for converting and dissolve compounds of lead or concretions thereof that could not be dissolved in the acetate salt solution in form of plumbite salt of the hydroxide cation, separating a lead plumbite containing alkaline liquor from a solid phase of

impurities contained in the starting material and adding the separated lead containing liquor to the separated acetate solution for precipitating all reclaimable lead as highly pure lead oxide or hydroxide.

8. A plant for reclaiming the lead content of impure electrode paste or slime from discarded lead batteries and/or lead minerals, in form of high purity lead compound, comprising:

- a) a first reactor (RAC (1)) having stirring and heating means for suspending the impure material in a lead sulphate dissolving aqueous solution of a salt belonging to the group composed of the acetates of sodium, potassium and ammonium, means for controlled addition of sulphuric acid and means for controlled addition of a reagent belonging to the group composed of hydrogen peroxide, sodium sulphite and sulphurous anhydride;
- b) a first solid-liquid separator (F1) for separating a solid phase constituted by insoluble compounds of lead and/or undissolved concretions of lead compounds and impurities from a limpid acetate salt and lead sulphate solution;
- c) a second reactor (RAC (2), RAC (3), RAC (4)) adapted to hold the limpid aqueous solution of acetate salt and lead sulphate solution, having stirring and heating means and means for adding to the solution either a carbonate or a hydroxide of the same cation of said acetate salt, for precipitating insoluble carbonate/oxycarbonate of lead or lead oxide or hydroxide, respectively, and forming sulphate of the same cation of the acetate salt, soluble in the aqueous solution;
- d) a second solid-liquid separator (F(2), F(3), F(4)) for separating the solid phase constituted by said precipitated compound of lead from an aqueous solution of acetate salt now containing also sulphate of the same cation of the acetate salt;
- e) means for re-cycling the separated solution to said first reactor (RAC (1));

- f) a third reactor (RAC (5)) having stirring means and means for controlled cooling and/or heating of a continuously or periodically treated portion of said recycling solution for selectively crystallizing sulphate of the same cation of the acetate salt contained in the solution;
- g) a third solid-liquid separator (F(5)) for separating said crystallized sulphate of the same cation of the acetate salt of said treated portion of recycling solution that is then recycled to said first reactor (RAC (1)).

9. The plant of claim 8, further comprising a column filled with chelating resin, through which said continuously or periodically treated portion of recycling solution is passed for sequestering residual lead ions from the solution, before introducing it in said fourth reactor (RAC (5)) for selectively crystallizing sulphate of the same cation of the acetate salt contained in the solution.

10. The plant of claim 9, further comprising means for periodically stripping sequestered lead ions from said chelating resin by circulating acetic acid through the column and means for introducing the circulated amount of acetic acid to said first reactor (RAC (1)).

11. The plant of claim 8, further comprising a fourth reactor (RAC (2bis)) having stirring and heating means for suspending said separated solid phase comprising insoluble compounds of lead and/or undissolved concretions of lead compounds in hot concentrated hydroxide of the same cation of the selected acetate salt and converting said compounds of lead and/or undissolved concretions of lead compounds to soluble plumbites; a fourth solid-liquid separator (F (2bis)) for separating lead containing alkaline liquor from a solid phase of impurities; and means for introducing the lead containing alkaline liquor into said second reactor (RAC (2), RAC (3)) for precipitating all reclaimable lead in form of high purity lead oxide or hydroxide.

12. The plant of claim 8, further comprising an oven in which the separated lead compound, if in form of lead carbonate and/or oxycarbonate or hydroxide, is decomposed to lead oxide and carbon dioxide or water, respectively.

Dated this 27th day of February 2012



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Steps		←inlet substances →outlet substances
(1)	Reducing, sulfatation and solubilization	← raw electrode slime ← make up sodium acetate ← sulphuric acid ← hydrogen peroxide ← acetate leach solution recycling
(2)	Filtration	→ insoluble compounds and solid impurities
(3)	Oxide formation > 72-73°C	← sodium hydroxide
	Hydroxide formation < 72-73°C	← sodium hydroxide
	Carbonate formation	← sodium carbonate
(4)	Filtration	→ lead oxide or → lead hydroxide or → lead carbonate
(5)	Solution depuration	→ lead acetate to (1) ← acetic acid
(6)	Crystallization	
(7)	Filtration	→ sodium sulphate
(8)	Solubilising salt solution recycling to (1)	

Steps		←inlet substances →outlet substances
(2 Bis)	Insoluble compounds and solid impurities from step (2)	← sodium hydroxide
(2 Bis)	Filtration	→ insoluble compounds → soluble lead plumbite to step (3)

Fig. 1

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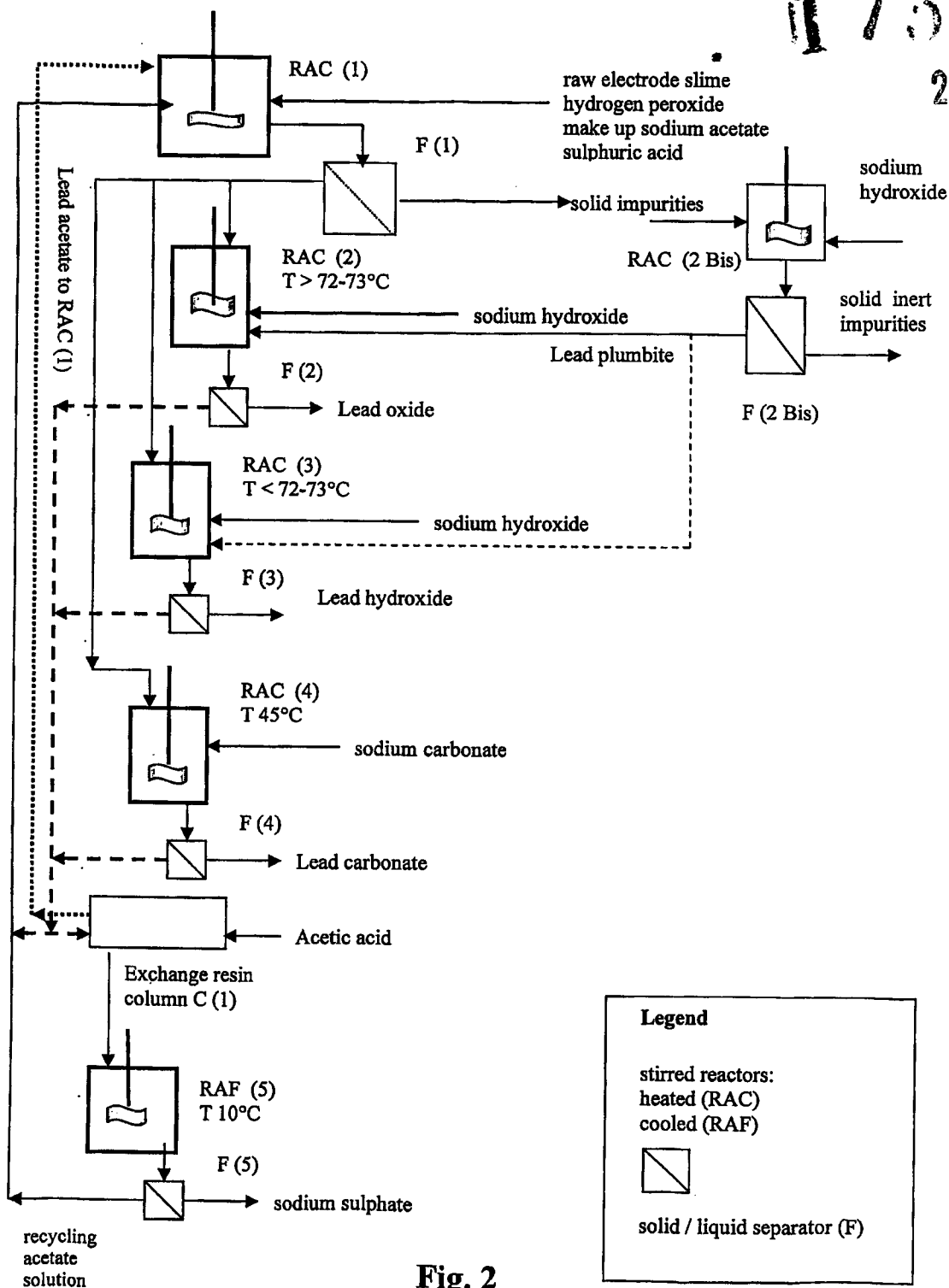


Fig. 2

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"RECLAIMING OF LEAD IN FORM OF HIGH PURITY LEAD COMPOUND FROM RECOVERED ELECTRODE PASTE SLIME OF DISMISSED LEAD BATTERIES AND/OR OF LEAD MINERALS"

FIELD OF THE INVENTION

This disclosure relates to techniques for reclaiming high purity lead compound from impure mixtures, like recovered electrode paste slime of dismissed batteries or lead minerals.

BACKGROUND OF THE INVENTION

Departing from the long established processes for reclaiming valuable lead content from recovered electrode paste of dismissed lead batteries or lead minerals based on calcination, prior PCT patent application No. PCT/IT2008/000022, in the name of the present applicant, the content of which is herein incorporated by express reference, disclosed a novel process almost completely based on wet treatment of the recovered electrode paste or lead minerals capable of producing highly purified lead carbonate at high yield with much reduced burden of disposing of noxious residues and efficient use of reagents. Nevertheless, in order to use the reclaimed lead for making new battery paste, the lead carbonate has to be decomposed to lead oxide by heating the carbonate to about 400-450°C. This is expensive in terms of energy required.

According to the process disclosed in the above-mentioned prior PCT patent application, the starting material in the form of electrode paste slime or finely ground and eventually pre-treated lead mineral, is leached using an acid different from sulphuric, adding hydrogen peroxide or other reducing agent or lead dioxide that may be present in the starting material and sulphuric acid for converting all lead compounds to insoluble lead sulphate which is separated together with other insoluble substances and is thereafter selectively dissolved in an aqueous solution of a solubilizing compound. To the separated clear solution of lead sulphate is

added a carbonate salt for precipitating carbonate/oxycarbonate of lead.

Besides the energy required for eventually converting the carbonate to lead oxide, the acid leaching step of the impure starting material implies certain costs and treatment plant complexities.

OBJECTIVES AND SUMMARY OF THE INVENTION

With the aim of reducing the lead reclaiming cost in terms of plant inventory of treatment vessels and related agitators, heaters and/or coolers, filters, overall treatment plant complexity, pumping and energy requirements, the applicant has found that an outstandingly effective simplification of the all wet lead reclaiming process flow is not only viable but even more efficient.

The novel approach, unexpectedly found outstandingly efficient consists in directly suspending the impure starting material in a lead sulphate dissolving aqueous solution of an acetate salt and adding thereto either hydrogen peroxide or a sulphite or alternatively bubbling sulphurous anhydride through it, in a measure adapted to reduce any lead dioxide expected to be present in the impure starting material to lead oxide, and sulphuric acid in a measure adapted to convert all lead oxide to lead sulphate that remains dissolved in the selected dissolving salt solution.

A clear solution containing the dissolved lead sulphate may then be separated from a solid phase residue that includes all undissolved impurities contained in the impure starting material.

Together with the solid phase of all insoluble substances, separated from the lead sulphate dissolving acetate salt solution, depending on the origin of the impure starting material to be processed, there may be present certain compounds of lead such as oxysulphates or other oxides that could not be dissolved in the acetate salt solution. Even the lead of these compounds undissolved by the acetate salt solution can eventually be reclaimed if considered economically or for other

reason desirable to do so. This can be carried out by suspending the separated solid phase consisting of impurities and insoluble compounds of lead in a concentrated solution of hydroxide of the same cation of the acetate salt for decomposing and convert these compounds to soluble plumbites, that dissolve in the hot hydroxide solution which may then be separated from the remaining insoluble impurities. The hydroxide solution now containing the residual lead stripped from the previously separated solid phase of impurities may be introduced in the liquid acetate solution containing the lead sulphate in the vessel in which hydroxide of the same cation of the acetate salt is introduced for precipitating the lead contained as lead sulphate in the liquid acetate solution in form of lead oxide or hydroxide.

Precipitation of high purity lead compound from the clear lead sulphate solution may then be effected either by adding to the solution carbonate of the same cation of the acetate salt used for selectively dissolved lead sulphate for precipitating insoluble carbonate/oxycarbonate of lead, as contemplated in the process disclosed in said prior PCT patent application No. PCT/IT2008/000022, or, more preferably, according to an alternative embodiment, instead of a carbonate salt, to the clear solution of lead sulphate is added hydroxide of the same cation of the acetate salt used for selectively dissolved lead sulphate for causing precipitation of either oxide or hydroxide of lead, depending from the temperature of the precipitation bath, thus eliminating even the burden of eventually having to convert the reclaimed lead carbonate to lead oxide by heating the carbonate in an oven.

The applicant has found that whether a carbonate salt or a hydroxide is used for causing it, precipitation of all lead in the solution as highly pure lead compound is practically complete. Therefore, separation of a solid phase of the highly pure lead compound from the acetate solution is carried out from the same acetate solution in which the impure starting material had been suspended.

Though the clear solution of acetate salt becomes progressively enriched of

sulphate of the same cation of the acetate salt used for selectively dissolving lead sulphate, it may be recycled to the suspension step of the impure starting material for as long as the sodium sulphate concentration remains below saturation. When the sulphate concentration in the clear acetate salt solution approaches saturation, the solution may be cooled to about 10°C for selectively crystallizing and precipitating solid phase constituted by sulphate of the cation of the acetate salt used, which is recovered by filtering. The clear acetate salt solution freed of the sulphate salt may then be recycled to the suspension bath of the impure starting material.

Preferably, before cooling it for selectively crystallizing and precipitating solid phase constituted by sulphate of the cation of the acetate salt used, the acetate solution is percolated through a column filled with chelating resin for sequestering any residual lead ions in the solution, before cooling the solution in order to produce lead-free sulphate salt, as a by-product, of broader market acceptance.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow sheet of the main steps of the process of this disclosure for reclaiming high purity lead oxide from dismissed battery electrode slime or lead minerals, alternatively for producing pure lead carbonate/oxy carbonate or pure lead oxide/hydroxide.

Figure 2 is a simplified diagram of a plant for reclaiming highly pure lead compound from dismissed battery electrode slime or lead minerals, alternatively as pure lead carbonate/oxy carbonate or pure lead oxide/hydroxide, according to the alternative process flows of Figure 1.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

Referring to the flow sheet of **FIG. 1**, according to a first embodiment of the process of this invention, particularly suited for treating raw electrode paste slime recovered from crushed dismissed batteries, but usable, with eventual trivial adaptations, also with finely ground lead minerals, for example galena commonly

roasted for converting lead sulphite to lead sulphate, anglesite and lesser common minerals, the impure starting solid material is suspended in an aqueous solution of a salt capable of dissolving lead sulphate, such as for example an acetate salt of sodium, ammonium, potassium, urea, mono-, di- or tri-ethanolamine.

To this suspension, sulphuric acid in an amount necessary to convert all oxides present in the starting material to sulphate, and a reducing agent chosen among hydrogen peroxide, a sulphite salt and sulphurous anhydride, is gradually added or bubbled through the suspension bath in an amount necessary to reduce any lead dioxide that may be contained in the starting material (as would be the case with slime from discarded lead batteries) to lead oxide.

Therefore, in this first **Step (1)** of the process flow sheet of **FIG. 1**, in the suspension bath of the starting material take place the chemical reactions that are formally described herein below in view of the fact that they take place simultaneously, causing the conversion of all lead compounds to sulphate that dissolves in the aqueous solution containing the specific dissolving salt mentioned above.

The below described reactions make clearly recognizable the existence of a synergical action that results in a sensible increment of the speed of the chemical conversion process, in view of the fact that dissolution of lead sulphate frees the lead oxide to which (for the case of dismissed battery electrode paste slime) it was originally intimately tied in the electrode paste, to form compounds of the type 3PbOPbSO_4 and 4PbOPbSO_4 , in consequence of which the oxide quickly reacts, transforming itself to sulphate, which in turn dissolves in the acetate salt solution that, in the considered embodiment, is sodium acetate, while the lead dioxide physically embedded in concretions of the above-identified oxysulphates, become more easily reached by the reacting species and therefore is more quickly reduced to lead oxide.

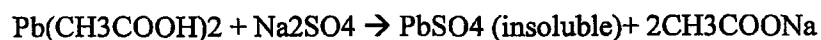
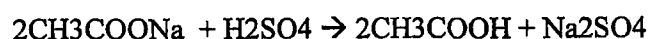
The following reactions relate to an exemplary embodiment of reclaiming high purity lead compound from electrode paste slime of dismissed batteries in which

lead sulphate is present as measure component (close to about 60% by weight) in the impure starting material and dissolved in the aqueous solution of sodium acetate.

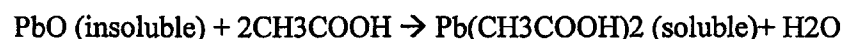
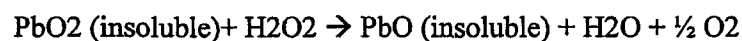
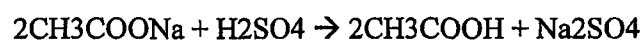
Reaction 1: dissolution of lead sulphate



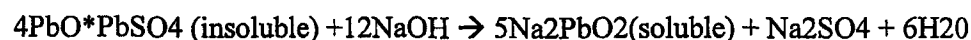
Reaction 2: dissolution of lead oxide



Reaction 3: reduction of lead dioxide and dissolution



(Optional) Reaction 4: solubilization of insoluble lead compounds possibly present in the impure starting material separated together with impurities for reclaiming of such a minor amount of lead



By way of example, in order to process electrode paste slime recovered from crushed discarded lead batteries, an aqueous solution of tri-hydrated sodium

acetate dissolved in water in a concentration comprised between 37,5 and 54,5% by weight can be satisfactorily used. Sulphuric acid is added in an amount corresponding to or just exceeding the stoichiometric requirement for converting all lead oxides to lead sulphate as pre-evaluated for the impure starting material to be processed. Preferably, after having added the required amount sulphuric acid, to the suspension bath is added hydrogen peroxide the amount of which may also be pre-calculated in terms of the stoichiometric requirement for reducing the lead dioxide contained in the starting material.

The amount of electrode paste that can be treated in a certain volume of solution, depends on the solubilizing capacity of the lead sulphate in the solution of the selected acetate salt and of the added amount of sulphuric acid. The ability of dissolve lead sulphate of the acetate salt solution depends from its salt concentration. By way of example, one liter of aqueous solution with a concentration of 37,5% by weight of sodium acetate is able to dissolve 100 g of lead sulphate. By increasing the concentration of the acetate salt, the amount of lead sulphate that can be dissolved increases proportionally. The temperature at which the above described reactions can be carried out in the suspension bath may be comprised between about 10°C up to boiling point. The suspension may be stirred with a pails or turbine mixer in order to favor breaking down of lead compound aggregates.

The combination of the chosen operating conditions (type and fineness of the starting solid material, type and concentration of the lead sulphate dissolving salt solution, eventual lead dioxide reducing agent addition, temperature, stirring mode) will influence the time needed for completing this first step (1) of the all-wet reclaiming process. The sulphuric acid used for the sulphation of all the lead oxide in the solution should preferably have a high concentration in order not to excessively dilute the lead sulphate dissolving solution.

Once the reaction time that, depending on the combination of the numerous parameters may generally range between 6 and 15 minutes, a limpid acetate

solution containing lead sulphate may be separated from the solid phase residues, for example by filtration. All insoluble impurities and substances are therefore separated from the solution (**Step 2** of the flow sheet of **FIG. 1**).

The subsequent reaction conducted in the limpid acetate solution containing substantially all the lead content of the starting material in form of lead sulphate by adding to the solution a hydroxide of the same cation of the selected acetate salt (i.e. either sodium, potassium or ammonium), according to the preferred alternative contemplated for the **Step 3** of the flow sheet of **FIG. 1**, at a temperature sufficiently high to ensure precipitation of all the lead in solution in form of PbO (of yellow aspect) instead of in form of lead hydroxide (of white aspect) produces a selective precipitation of lead oxide because of its much lower solubility than that of lead sulphate. Generally, the critical temperature is in the vicinity of 70°C, therefore the precipitation may be carried out at about 72-73°C (unless for some reason one should prefer to recover a highly purified lead hydroxide, thermally convertible to lead oxide eventually).

The other alternative contemplated for the **Step 3** of the flow chart of **FIG. 1**, consists in adding to the liquid acetate solution containing substantially all the lead content of the starting material in the form of lead sulphate, instead of a hydroxide, a carbonate of the same cation of the selected acetate salt (i.e. either sodium, potassium or ammonium), which produces a selective precipitation of lead carbonate or a mixture of lead carbonate and oxycarbonate, because of their much lower solubility than that of lead sulphate. In this alternative embodiment, precipitation may be conducted at any temperature comprised between ambient temperature up to boiling point.

Once the reaction of **Step 3** is complete, the precipitated lead oxide or hydroxide or carbonate/oxycarbonate is separated by filtration (**Step 4** of the flow chart of **FIG. 1**) from the solution while sulphate of the cation of the hydroxide or carbonate used for precipitating the lead as insoluble oxide (or hydroxide) or carbonate (and/or oxycarbonate) remains in the solution.

The limpid acetate solution, now containing also the sulphate of the same cation of the acetate salt, can be integrally recycled to the suspension bath of selective dissolution of the lead sulphate (**Step 1**) of the process, for as long as the content of sulphate remains below saturation (this limit depends primarily on the type of dissolving salt solution of the lead sulphate and processing conditions).

Of course, precipitation of excess sulphate salt together with the lead oxide or hydroxide or carbonate/oxycarbonate must be prevented. Therefore, excess sulphate salt must be eventually eliminated from the solution, well before approaching the saturation limit (**Step 8** of the flow sheet of **FIG. 1**). This may be easily done by exploiting the different solubilities at different temperatures of the sulphate salt (i.e. of sodium, potassium or ammonium sulphate) from that of the corresponding acetate salt for selectively crystallizing the sulphate and separating it from the acetate solution.

The concentration of the aqueous solubilizing salt solution and the temperature at which lead sulphate dissolution in it is carried out are not essential parameters because they simply influence the time necessary for completing the reactions discussed above and the quantity of lead sulphate that may be dissolved in the solution. In practice, if the solubilizing solution, after precipitation of the dissolved lead as oxide or hydroxide or carbonate/oxycarbonate, is recycled back and therefore one's operates with a recycled solution, more and more recycles may be necessary to complete dissolution of a given quantity of lead sulphate.

The novel approach of this disclosure has proved itself outstandingly suitable to process electrode paste slimes where the amounts of the three main lead compounds, namely lead sulphate, lead oxide and lead dioxide, oscillate in the vicinity of a mean value by a range of variability of about 2% by weight and this may in practice impede to calculate exactly the quantity of sulphuric acid solution for converting to sulphate all lead oxides present in the impure starting material.

Nevertheless, if in conducting the novel process of this disclosure sulphuric acid happens to be added in excess of the stoichiometrically necessary amount, after

having precipitated the pure lead compound by adding a hydroxide or a carbonate of the same cation of the selected acetate salt, an excess of sulphate of the cation of the added compound forms compared to the amount strictly relative to the precipitation of lead sulphate, because of the presence in the solution of free sulphuric acid. Vice versa, if sulphuric acid happens to be added in defect of the stoichiometrically necessary amount, incomplete conversion of oxides to sulphate occurs, thus a residual amount of oxide remains undissolved in the acetate solution when separating the solid impurities. Should this accidentally occur, the separated solid phase may be simply reintroduced in the suspension bath to be eventually converted by introducing an excess of sulphuric acid.

Continuously or intermittently, whenever the sulphate concentration in the clear acetate salt solution approaches saturation, the solution is preferably percolated through a column filled with chelating resin for sequestering any residual lead ions in the solution (Step 5 of the flow sheet of FIG. 1), before cooling the solution to about 10°C for precipitating a crystalline solid phase (Step 6 of the flow sheet of FIG. 1), constituted by sulphate of the cation of the acetate salt used, which is recovered by filtering (Step 7 of the flow sheet of FIG. 1). The clear acetate salt solution freed of the sulphate salt may then be recycled to the suspension bath of the impure starting material while the lead-free sulphate salt constitutes a marketable by-product.

Herein below several examples are reported solely for illustrating different possible embodiments of the process of this invention without in any manner meaning to exclude other possible embodiments.

Example 1

80 g of recovered dried electrode paste having a lead content, expressed as metal equivalent, of 72% was treated under stirring with 1000 ml aqueous solution of tri-hydrated sodium acetate at 37,5 % by weight, with the addition of g 12,2 of concentrated sulphuric acid at 94-96% by weight, at the temperature of 83°C. Successively, hydrogen peroxide at 32% by weight was slowly added to the

suspension (dropwise for about 10 minutes) until no further clarification of the suspension was observed.

The hot suspension was then filtered and the separated solid phase was constituted by insoluble lead compounds and lead compound concretions, electrode grid fragments and various additives used for making the electrode paste such as carbon black, barium sulphate, fibers, etc. and impurities such as sand, plastic materials, etc.. The amount of this dark grey solid phase was about 4-12 % by weight of the solid mass of the dry electrode paste.

The filtered limpid solution containing lead sulphate was stirred at 83 °C adding thereto sodium hydroxide until reaching a practically complete precipitation of the lead in the form of lead oxide. The suspension was thereafter filtered separating the precipitate from the solubilizing solution of sodium acetate now enriched of sodium sulphate that was recycled to the stirred lead sulphate dissolution vessel for as long as the content of sodium sulphate in the solution remained below saturation.

When the content of sodium sulphate in the sodium acetate solution became close to the saturation limit, the solution was percolated through a column filled with chelating resins, for example of the commercial type denominated Chelex-100 or Dowex A-1, though any other equivalent resin may be used. The resin filler sequestered almost completely the surprisingly small quantity of lead ions residually present in the sulphate solution.

Subsequently the purified sulphate solution (practically lead-free) was slowly cooled to 10°C, under slow stirring, for precipitating a crystalline solid phase constituted by sodium sulphate that was then recovered by filtering the suspension, while the clear solution was recycled to the dissolution vessel of the lead sulphate.

The filtered lead oxide accurately rinsed with de-ionized water was dried at 160°C for as long as reaching constancy of weight.

The separated dark grey solid phase was suspended in sodium hydroxide at 40% by weight, at 50°C for 15 minutes. The separated limpid liquid phase was introduced into the limpid acetate solution containing also the lead sulphate, as part of the required amount of sodium hydroxide for precipitating all lead in solution as lead oxide or hydroxide (according to a preferred embodiment) in consideration of the fact that also the lead present in the solution as sodium plumbite converts itself to lead oxide (or hydroxide).

At the end of the tests, the following mass balance was recorded.

In 80 g amount of recovered electrode paste used in an experiment, there were 4 g of insoluble substances of dark grey color containing metallic lead and extraneous substances such as sand, carbon black, barium sulphate and other substances in minor amounts.

The calculated maximum quantity of recoverable lead oxide was of 62,05 g while the quantity of lead oxide effectively recovered was of 62,03 g for a recovery yield of 99,96%.

Chemical analysis of the recovered solid product confirmed that it was constituted exclusively by PbO at 99.99% purity, while the sodium sulphate that was eventually recovered had a purity of about 99.90%.

The following table summarizes relevant conditions, peculiarities and results of other four exemplary embodiments of the process of Example 1, described in detail above, but with the indicated alternative conditions and the results that were obtained, always using as starting material electrode paste of the same lot recovered from crushed dismissed batteries.

n.	Lead sulphate dissolving solution	Reaction time and temperature	Precipitating compound	Obtained purified lead compound	Yield %
2	1000ml Sodium acetate, @37.5%	10 minutes 65 °C	NaOH	Pb(OH) ₂	99.94
3	1000ml Sodium acetate, @40.0%	8 minutes 90 °C	NaOH	PbO	99.95
4	1000ml Sodium acetate, @42.5%	12 minutes 45 °C	Na ₂ CO ₃	PbCO ₃	99.91

The lead oxide (whether directly produced by the all-wet process or obtained by heating lead carbonate/oxy carbonate produced by the all-wet process) is perfectly suitable for preparing electrode pastes for new batteries.

The practice of the process of this invention using as starting material a mineral or a mixture of minerals of lead may be substantially similar to the above described embodiments, an essential pre-step being that of converting as much as possible any different salt of lead present in the mineral to either lead sulphate or to lead oxide. For example, in case of galena, the most common lead mineral, the mineral should be heated in air, according to common roasting techniques, until oxidizing the lead sulphite to sulphate. The other common mineral anglesite does not need any prior treatment being itself already constituted by lead sulphate. Of course the mineral(s) should be finely ground for facilitating their processing.

FIG.2 is a schematic diagram of possible embodiments for an industrial plant for reclaiming variable lead in form of high purity compounds from recovered electrode paste of dismissed lead batteries and/or finally ground lead minerals, eventually pretreated for converting as much of the lead compounds to lead sulphate.

The scheme of **FIG. 2** provides a multi-embodiment illustration of the discussed processing alternatives (though sodium is indicated as the exemplary selected cation of both the acetate salt and of the alternatively added compounds for precipitating the desired pure compound of lead, according to the various alternatives).

In practice, the plant requires essentially three stirred and temperature-controlled reactors. To a first reactor RAC (1) in which the impure material is suspended in an aqueous acetate salt solution, is associated a first solid-liquid separator F(1) for separating the lead sulphate containing solution from the solid phase constituted by insoluble impurities of the impure starting material.

To a second reactor for precipitating the desired lead compound of high purity, that in the multiple alternative scheme of **FIG. 2** is anyone of the reactors RAC (2), RAC (3) and RAC (4), is associated a second solid-liquid separator, that is the related one F(2), F(3) and F(4).

The third and last reactor RAC (5) and associated third and last solid-liquid separator F(5) are required for at least periodically (or more preferably continuously) treating the recycling acetate salt solution and to recycle it to the first sulphate dissolving reactor RAC (1). The treatment consists of selectively crystallizing by virtue of the significantly different solubilities of the acetate salt and of the sulphate of the same cation of the acetate salt, introduced in the second reactor for precipitating the desired lead compound, and removing it from the system. This step must be performed (continuously or intermittently) in order to prevent saturating the recycling acetate salt solution with the sulphate of the same cation, which if let to occur would cause co-precipitation of this salt together with the lead sulphate (making vain the purification process).

According to the preferred embodiment, in order to ensure that the "by-product" sulphate salt (e.g. sodium sulphate) be substantially lead-free and thus economically marketable, the plant may include an exchange resin column C(1) filled with an appropriate chelating resin, through which the solution, when

directed to the selective sulphate crystallization reactor RAC (5) (whether continuously or periodically) passes, for sequestering residual lead ions that may be present in the solution.

Of course, the chelating resin filler will gradually lose its activity and periodically a stripping of sequestered lead ions must be carried out by circulating through the column (C1) acetic acid for a certain period of time. The lead laden stripping solution of acetic acid used for this periodical re-activation of the exchange resin, now containing lead acetate, may be "disposed of" by simply introducing it into the first reactor RAC (1), as shown by the relative line.

The multi-embodiment plant diagram of FIG. 2, illustrates also the optional reactor RAC (2bis) in which, if desirable, in consideration of the composition of the impure starting material to be processed, residual amount of lead that may remain associated with the separated solid phase of impurities, in form of compounds or concretions that could not be dissolved during the treatment of the impure material in the first reactor RAC (1). The separated solid phase is suspended in hot concentrated solution of hydroxide of the same cation of the selected acetate salt for dissolving also these compounds of lead or concretions thereof. The associated liquid-solid separator F (2bis) permits to separate all non-lead impurities from a liquor of hydroxide containing sodium plumbite dissolved in it which may be conveniently used as part of hydroxide addition in a second reactor RAC (2) or RAC (3) that may be used for precipitating all the lead in the solution as lead oxide or lead hydroxide, according to a preferred embodiment.