

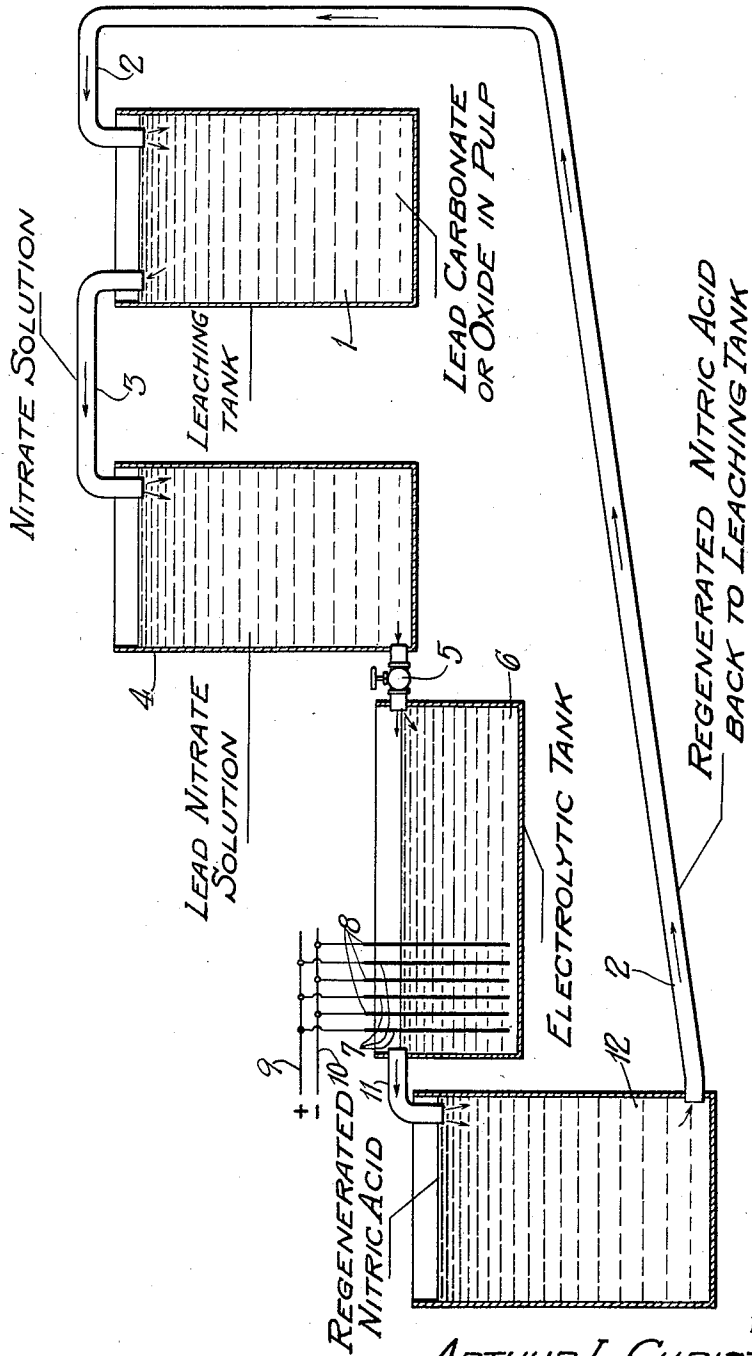
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LEAD OXIDE AND ELECTROLYTIC PROCESS OF FORMING THE SAME

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LEAD OXIDE AND ELECTROLYTIC PROCESS OF FORMING THE SAME

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5 My invention relates to the production of lead oxides, more particularly lead dioxide and litharge of special properties and characteristics, and to an electrolytic process for the recovery of lead in the form of oxides from ores, concentrates, or from secondary or other sources. Such secondaries, for example, may be the slimes resulting from the electrolytic treatment of secondary or scrap copper.

10 Such slimes or secondaries, and some ores or ore concentrates, frequently contain a number of various elements. For example, some slimes contain lead, copper, arsenic, iron, nickel, tin, sodium, calcium, antimony, zinc, magnesium and silver. Other sources may contain some or all of the above metals and others in addition. The separation of the various metals, or mixtures of them, presents a number of difficulties.

20 My invention avoids these various difficulties and provides a process in which dense deposits of lead dioxide of high purity and capable of ready reduction to litharge are obtained by the electrolytic treatment of a nitric acid solution or leaching of the metal containing material.

25 In my invention a metal bearing material to be treated as, for example, a secondary or slime from the electrolytic treatment of scrap copper, and containing tin oxide, lead sulphate, metallic copper and the sulphates or other compounds of zinc, copper, arsenic, nickel, iron and other metals in small amounts, is first roasted to convert the metallic copper to an oxide. The roasted material or calcine is then leached with copper electrolyte to remove a large part of the copper. The roasted residues are washed with water. The removal of copper and of small amounts of zinc, arsenic, nickel and iron, however, is incomplete. The washed slime is then treated with sodium carbonate in a water solution to convert the lead sulphate to lead carbonate, and the resulting sodium sulphate is removed by washing. The lead carbonate is soluble in nitric acid and serves as the starting material for my electrolytic process. It is removed from the sulphate, free pulp or slime by treatment with dilute nitric acid or a solution containing a large proportion of free nitric acid. The lead nitrate solution resulting from this leaching also contains copper and other impurities in variable quantities, generally small in com-

parison with the lead content. A representative analysis is as follows:

	<i>Grams per liter</i>	
Free nitric acid.....	9.4	5
Lead.....	87.5	
Copper.....	6.7	
Arsenic.....	0.02	
Iron.....	0.10	
Nickel.....	0.51	10
Tin.....	0.01	
Sodium.....	4.20	
Calcium.....	0.74	
Antimony.....	0.003	
Zinc.....	2.36	15
Magnesium.....	0.03	
Silver.....	0.03	

The impure lead nitrate solution is then subjected to electrolysis whereby the lead is deposited on the anodes as lead dioxide, and the copper is deposited on the cathodes as a metallic sponge. Nitric acid is liberated at the anode proportionally to the deposition of copper at the cathode, and of lead dioxide at the anode, the formation of the lead dioxide at the anode being due to the oxidizing conditions at the anode. As a result of the electrolytic action, therefore, the electrolyte solution increases in nitric acid content and decreases in lead and copper, these two metals, however, being separately deposited. The nitric acid may, therefore, again be used to leach a fresh quantity of the treated secondaries or source material. The other impurities remain unchanged in the solution, being too small in quantity and so located in the electro-motive series as not to be deposited. If, on long continued use or circulation of the electrolyte solution they increase to a troublesome point, they may be removed by evaporation and crystallization.

40 In the continuous operation of my process, therefore, the electrolyte liquid, after being subjected to electrolysis sufficiently to decrease the lead and copper content and regenerate the nitric acid, is again passed through the leaching process, coming into contact with fresh quantities of the calcined material that has been treated with sodium carbonate. Having dissolved additional quantities of lead and copper, it then returns to the electrolytic bath for a new electrolysis. The 50

removal of the lead and copper and other impurities during the leaching process leaves an unleached residue in which the tin content has been greatly increased. A typical example of such a residue is one of the following composition:

	Per cent
Lead	2.0
Tin	65.0
Copper	0.2
Antimony	3.0

In carrying on the electrolysis the best results are obtained when the free nitric acid content is between 30 and 60 grams per liter, the lead content between 35 and 50 grams per liter, and the copper content between 2 and 15 grams per liter. In operating the process continuously leach liquor is supplied continuously to the electrolytic tanks at such a rate as to equal the rate at which the lead and copper are electrolytically deposited, and at such a rate as to maintain the concentration of free nitric acid, lead and copper within the limits set forth above.

For example, the fresh leach liquor supplied to the electrolytic bath in a typical example contains the following quantities of lead, copper and free nitric acid:

	Grams per liter
Lead	87.5
Copper	6.7
Free nitric acid	9.4

Inasmuch as this liquor is admixed with liquor undergoing electrolysis, the concentrations of lead and copper drop and the percentage of free nitric acid increases. Analysis of a typical electrolytic bath solution shows the following content:

	Grams per liter
Lead	50.0
Copper	2.5
Free nitric acid	31.0

The overflow liquor is weaker in lead and copper and stronger in free nitric acid than the solution in the bath. A typical analysis shows the following content:

	Grams per liter
Lead	40.2
Copper	2.1
Free nitric acid	41.9
Ammonia	0.59

It will be understood, therefore, that the fresh leach liquor may contain larger quantities of lead and smaller quantities of nitric acid than those best suited for the electrolysis inasmuch as they will be immediately mixed with electrolytic liquors of such concentration as to bring them within the desired limits.

During electrolysis the electrolyte liquor is agitated, either mechanically or by air, to prevent stratification and to obtain uniform deposition of lead dioxide.

In the operation of the electrolytic bath the maximum current density is desirable for the purpose of obtaining as high a production or capacity as possible. Current densities up to 40 amperes per square foot may be employed without obtaining too rough a deposition of lead dioxide or of bulky nodules. These current densities also permit a good retention of the copper sponge at the cathode.

The deposition of lead dioxide is also most successfully attained when an anode containing silicon is employed. An iron silicon alloy is especially useful as an anode material. Duriron,

which is an alloy of iron and silicon with other elements in lesser amounts, forms an excellent anode material. Chiles, having the following percentage composition—

	Per cent
Copper	60
Silicon	23
Iron	10
Tin	3
Lead	2
Manganese	2

also is a desirable anode material. In general, however, any silicon alloy having sufficient electrical conductivity may be used as an anode material.

In order to enable the lead dioxide deposit to be readily stripped from the anode, the surface of the latter may be finished to facilitate stripping. A surface prepared by sand blasting is particularly suited for this purpose. Such a surface is not altered by continued use. In case a deposit of a minute film of lead dioxide a few thousandths of an inch thick may remain on the anode and cause a poor retention of the new deposit if immediately used, this residual film of lead dioxide may be easily removed by placing the anodes and cathodes in the electrolytic cell in their normal operating positions and short circuiting the cell. The cell then acts as a battery, causing the resolution of the lead dioxide from the anode and a re-solution of some copper from the cathode. After a period of time, 24 hours for example, the anodes are entirely clean of lead dioxide and the electrolytic operation may be resumed by connecting the cell back into its regular circuit.

Any suitable shape and arrangement of anodes may be employed. A convenient shape is one in which the anode is long and narrow as, for example, 5 inches wide and 1 inch thick, so that it may be hung from one end. Four or five such anode bars may be suspended on a single rod and closely spaced so that about 100 may be placed in a single electrolytic cell. This makes a cell of convenient size.

Any suitable material may be used for the cathode as, for example, copper, stainless steels or other metals. These metals do not need to be resistant to nitric acid. The use of any particular metal does not have any influence on the cathode deposit.

It is desirable to have as large a cathode area as is practically possible because this gives an opportunity to lessen the current density on the cathode, resulting in a better retention of the deposited copper and permitting the use of a higher concentration of copper in the electrolyte which results in less cathodic reduction of nitric acid.

Apparatus suitable for operating the process is shown diagrammatically in the accompanying drawing.

In this diagrammatic apparatus, a quantity of lead carbonate or oxide prepared as described above is placed into a leaching vat 1 into which a stream of regenerated nitric acid is circulated through a pipe 2. The nitric acid, after dissolving the lead and copper and smaller quantities of impurities, overflows from the leaching tank 1 through an overflow pipe 3 into a storage tank 4. From the storage tank 4 the solution passes through a control valve 5 into the electrolytic tanks 6 into which dip alternate anodes 7 and cathodes 8 connected, respectively, to a positive main 9 and a negative main 10. The liquor that has been impoverished in lead and copper, and

enriched in nitric acid in the electrolytic tank 6, then overflows through the pipe 11 into a regenerated nitric acid tank 12, from which it is pumped to the pipe 2 to return to the leaching tank 1.

5 In a typical installation a cell was arranged to take 1212 amperes with a current density of 13 amperes per square foot on the anode. The temperature of the cell was about 80° F., although it may vary from this temperature, and
10 the voltage was 2.2 volts. A current efficiency of 92.5% was reached. The electrolysis could be run somewhat over six days before it was necessary to strip the deposit. The rate of deposit
15 was 262 pounds. The deposit of lead dioxide was vitreous in character and could be easily removed from the anode and broken down to any desired size. It could be pulverized. An analysis of the typical deposit showed it to have the
20 following composition:

	Percent
Total lead.....	85.6
Lead dioxide.....	96.2
Copper.....	0.005
25 Silver.....	None
Bismuth.....	0.00005
Insoluble.....	0.06
Water soluble.....	0.10
Nitric acid.....	0.008
30 Moisture.....	0.10

It was easily reduced with coke, coal or charcoal, producing a lead having the following impurities:

	Percent
35 Copper.....	0.006
Iron.....	0.0004
Bismuth.....	0.00005
Silver.....	None

40 The lead dioxide can be easily converted to litharge by direct roasting. An acid soluble lead compound is thus obtained of such high purity that it can be used for the preparation of any lead compound without further purification.

45 The lead dioxide produced by my process is denser and more resistant to deterioration in storage than lead dioxide heretofore known. It converts into a litharge having a coarser crystalline structure and weighing more per unit of volume, and freer from dust, than litharge made
50 from lead sulphide. Whereas litharge made from lead sulphide was cast into blocks and ground, the litharge of my process may be made by mere roasting, whereupon the lead dioxide disintegrates upon forming the litharge. The litharge
55 obtained by my process is of great purity owing to the purity of the lead dioxide from which it is made.

What I claim is:

1. A process for the electrolytic production of

lead dioxide, which comprises subjecting to electrolysis an aqueous solution containing between 35 and 50 grams per liter of lead and maintaining between about 9 and 42 grams of free nitric acid per liter.

2. A process for preparing lead dioxide electrolytically, which comprises electrolyzing an aqueous solution containing between 35 and 50 grams per liter of lead, and maintaining between 30 and 60 grams per liter of nitric acid in said solution during electrolysis.

3. A process for preparing lead dioxide electrolytically, which comprises electrolyzing an aqueous solution containing between 35 and 50 grams per liter of lead, and maintaining between 30 and 60 grams per liter of free nitric acid, and between 2 and 15 grams per liter of copper in said solution during electrolysis.

4. The process of producing lead dioxide and copper from roasted materials containing lead and copper compounds soluble in nitric acid, which comprises leaching said roasted materials with nitric acid containing aqueous solution to obtain a leach liquor containing lead in excess of 35 grams per liter, copper in excess of 2 grams per liter, and free nitric acid, electrolyzing the solution containing lead, copper and free nitric acid to deposit lead dioxide at the anode and copper at the cathode, and passing the leach liquors into said electrolytic bath, overflowing the exhausted liquor from said electrolytic bath in such relation to the current consumption as to maintain a concentration of between 35 and 50 grams per liter of lead, between 30 and 60 grams per liter of free nitric acid, and between 2 and 15 grams per liter of copper in said bath, and leaching the roasted lead and copper containing materials with the overflow liquor from said electrolytic bath.

5. A process of preparing lead dioxide from materials containing lead and copper compounds soluble in nitric acid which comprises leaching such materials with an aqueous solution containing nitric acid to dissolve said lead and copper compounds to form nitrates while maintaining the nitric acid content above about 9 grams per liter, passing the resulting solution into an electrolytic bath and electrolytically depositing lead dioxide at the anode and copper at the cathode and regenerating the nitric acid from the nitrates of lead and copper and thereafter returning the solution from said electrolysis to said leaching of said material.

6. The process of claim 5 in which the lead is deposited on an anode surface containing silicon.

7. The process of claim 6 in which said oxide is deposited from electrolysis on an anode surface containing silicon.

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