

11

[FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL
SOCIETY, Volume XVII, 1910, being the Transactions of the Seventeenth
General Meeting, at Pittsburgh, Pa., May 4, 5, 6, 7, 1910.]

Electrodeposition of Lead from Perchlorate Baths

By

FRANK C. MATHERS

A paper presented by C. G. Schleuderberg at the Seventeenth General Meeting of the American Electrochemical Society, at Pittsburgh, Pa., May 7, 1910, President L. H. Baekeland in the Chair.

ELECTRODEPOSITION OF LEAD FROM PERCHLORATE BATHS.

By FRANK C. MATHERS.

General Statement.

The electrolysis of most solutions of lead salts gives a loose crystalline deposit upon the cathode, which is valueless for refining or plating purposes. Betts has patented¹ the use of a lead fluo-silicate bath containing free fluo-silicic acid and small amounts of gelatine or glue. This bath gives dense, non-crystalline deposits which are commercially valuable.² Without the glue or gelatine, loose crystals are formed, such as are characteristic of the nitrate or acetate baths. "Fluo-silicic acid has some specific property not possessed by the nitrate and acetate solutions, and the solid deposit is not the result of the gelatine alone."³ The addition of gelatine to acetate or nitrate baths does not give satisfactory deposits.⁴

The author⁵ has found that a solution of lead perchlorate containing some free perchloric acid and a small amount of an addition substance, such as glue, tannin, licorice, but preferably peptone, works very satisfactorily as an electrolyte for the plating or refining of lead. Cathode deposits may be obtained over an inch in thickness, very smooth and of a density 11.36.

Lead perchlorate, $Pb(ClO_4)_2 \cdot 3H_2O$, possesses many properties that are ideal for making electro-plating or refining baths. It is "extremely easily soluble in water—one part of salt dissolving in about one part of water."⁶ Its great solubility permits the making of solutions of any desired concentration without danger of the crystallization of salts. It is not decomposed by boiling,

¹ U. S. Patent, 713,278.

² Betts, *Electrochem. Met. Ind.*, 1, 407 (1903).
Ulke, *Eng. Min. J.*, Oct 11, 1902.

³ Senn, *Z. Electrochem.*, April 14, 1905.

⁴ Kern, *Trans. Am. Electrochem. Soc.*, 15, 454 (1909).

⁵ U. S. Patent, 931,944 (1909).

⁶ Comey, "Dictionary of Solubilities"

by alkalis, by acids or by electrolysis. It is unacted upon by the air, and cannot be reduced by nascent hydrogen—not even by the zinc-copper couple. It can only be decomposed by fusion with sodium carbonate or with sodium nitrate. It does not easily give basic salts. When electrolyzed, it gives dense, solid deposits upon the cathode. The efficiency of corrosion of the anode and of deposition on the cathode is near theoretical, so the composition of the bath remains approximately constant. It does not corrode glass or earthenware vessels, which is an advantage, at least in laboratory work. It conducts the electric current extremely well. Perchloric acid solution has a conductivity near that of hydrochloric acid and greater than sulphuric acid.

	Gram Equivalents per Liter	Percent Composition	Equivalent Conductivity at 18° in. C. G. S. units, $\times 10^3$
HCl ⁷	0.03	0.109	3581
HClO ₄ ⁷	0.0312	0.313	3840
H ₂ SO ₄ ⁷	0.03	0.147	2673
H ₂ SiF ₆			5 percent greater than H ₂ SO ₄ . ⁸

The specific conductivity of perchloric acid of about 35 percent strength is 0.8395⁹ (temp. 40°) compared with 0.8257¹⁰ (25°) for sulphuric acid of maximum conductivity (30 percent).

Preparation of Materials.

Sodium perchlorate was used as the starting material for the preparation¹¹ of the perchloric acid. The solid, dry sodium perchlorate was treated with an excess of concentrated hydrochloric acid. After thorough stirring to break up lumps, the mixture was filtered through asbestos and the residue of sodium chloride was washed with successive small portions of concentrated hydrochloric acid. The filtrate, consisting of a mixture of aqueous perchloric acid, hydrochloric acid and small amounts of sodium perchlorate, was heated on the hot plate until the temperature reached 135°. This completely volatilized the hydrochloric acid with only an insignificant loss of perchloric acid. This aqueous perchloric acid is stable, and is no more dangerous to handle

⁷Whetham, "Theory of Solution," 1902, pages 410, 436 and 437.

⁸ Betts, "Lead Refining by Electrolysis," page 21.

⁹ Unpublished work by A. F. O. Germann, in this laboratory.

¹⁰ Tower, "Conductivity of Liquids," page 35.

¹¹ Mathers, Jour. Amer. Chem. Soc., 32, 66 (1910).

than nitric acid. Impurities, such as sodium chloride and sodium chlorate in the commercial sodium perchlorate, are entirely eliminated by this method, and are only objectionable since they act as filling agents, reducing the quantity of perchloric acid that may be obtained. The lead perchlorate was made by neutralizing this aqueous perchloric acid with litharge. There is no need to use white lead for this reaction, except perhaps for the sake of speed in the neutralization of the last small amounts of the perchloric acid. In the preparation of lead fluo-silicate, the fluo-silicic acid must be neutralized with white lead, because litharge is strongly enough alkaline to decompose the fluo-silicic acid into silica and lead fluoride. Perchloric acid is a stable acid that is not decomposed by an alkali. Perchloric acid may also be made by treating barium perchlorate with sulphuric acid. It is necessary to heat the perchloric acid thus obtained until the temperature reaches 135° in order to volatilize the hydrochloric acid, since chlorides are generally present in the commercial material. It is best to use an excess of sulphuric acid, which is precipitated later by the addition of the litharge.

The free perchloric acid in the lead perchlorate baths was determined by direct titration with standard sodium hydroxide using methyl orange as an indicator. The results obtained by this method are approximately correct. The lead was then determined as lead peroxide by deposition from a nitric acid solution.

Beakers were used as electrolyzing vessels.

The lead anodes were cast in graphite molds. They were suspended in the bath by means of copper wires passing through holes. Two anodes were placed in each beaker. The cathode of copper foil was suspended between them. The volume of the bath was 400 c.c. in most of the experiments, although baths containing 2,000 c.c. were used in a few experiments. The solutions were stirred by a current of air during the day and by a current of hydrogen gas at night. The hydrogen generator was so connected that it automatically kept up the current of gas at those times when the laboratory air blast was not running. A very slow current of gas through the solutions seemed to be the best laboratory substitute for the circulation of the electrolyte from tank to tank which is practiced in commercial work. The worst objection to the use of the current of gas is that it stirs

up slime from the bottom of the vessel. Some of these impurities adhere to the cathode. This greatly lowers the purity of the deposited lead.

"Addition Substances."

The lead perchlorate bath does not give good deposits without the use of some "addition substance," except at very low current densities. Numerous experiments were tried, using high concentration of perchloric acid and of lead, but no satisfactory results were obtained.

The addition of small amounts of certain substances to plating and refining baths for the purpose of eliminating or restraining crystals and of improving the density, color and smoothness of the deposits has been a very common practice, or, at least, has been frequently described.¹²

Perhaps the best known example in commercial work is the use of glue in the lead fluo-silicate bath described by Betts. His patent calls¹³ for "reducing agents," and he finds that "gelatine, pyrogallol, resorcinol, saligenin, orthoamidophenol, hydroquinone and sulphurous acid" are available. He recommends gelatine because it is the cheapest and gives the best results.

In the course of this work many different addition substances were tried. Tannin, pyrogallol, resorcine, licorice and eucalyptus extract all helped to a considerable extent, but "trees" would form at the corners of the cathode whenever the deposit reached a certain thickness. Tannin might be successfully used if no better substance was available. A high-grade gelatine, which was purchased for use in bacteriology, gave poor results. A commercial grade of glue gave fair deposits. Ordinary commercial glue, which is used in the lead fluo-silicate baths instead of the more expensive gelatine, is a very impure product, containing many things, among which is found a variety of peptone. Analyses¹⁴ of some samples of glue and gelatine show:

	Percent of Gelatine
"Gelatine"	70.95
Superior glue	51.98
Common glue	23.71

¹² Kern, Trans. Amer. Electrochem. Soc., 15, 441 (1909).

Watts, "Electrometallurgy," 1895, pages 15, 46, 76.

McMillen, "A Treatise on Electrometallurgy," 1890, page 9.

¹³ Betts, U. S. Patent, 713,277 (1902).

¹⁴ Allen, "Commercial Organic Analysis," 4, 479 (1898).

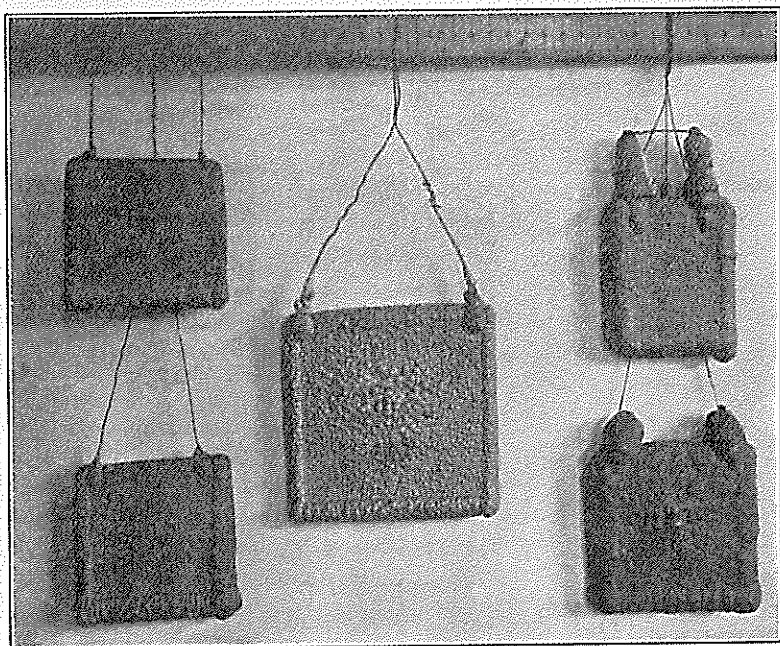
Any decomposition of gelatine or glue by ferments or acids forms gelatin-peptones or gelatones. From the fact that the purest gelatine for bacteriological use showed a less beneficial effect upon the lead deposits than a low grade commercial glue, the conclusion was drawn that some impurity in the glue was responsible for the good work. Glue which had been warmed for several hours with perchloric acid to form gelatin-peptone was tried. The results were uncertain—sometimes good, but more often bad. Acting along the line of this theory, meat peptones were tried. Two different brands of these meat peptones were used—Wittes', probably the purest to be obtained, and a commercial sample from Merck, which was five years old and badly decomposed. Both gave approximately the same results, consequently Wittes' peptone was used on account of its greater convenience and lack of foul odor. Experiments showed that about 0.03 to 0.05 grams of this peptone per 100 c.c. of solution was required. This quantity should be renewed after four or five days, in other words, after the passage of about 25 ampere-hours per 100 c.c. of solution. An excess of the peptone did not have any bad effect. The baths did not become ill-smelling even after long runs. There is some material present in or is formed from the peptone which separates as a pale yellow flocculent precipitate. This precipitate is not always formed, and the conditions for its production are not known. The presence of this precipitate does not interfere with the working of the bath in any way.

Experimental Data.

The current yields are near to the theoretical, as shown by the following table:

Grams of Cu in Coulometer	Amperes per Sq. Dm.	Volts	Cathode		Anode	
			Grams Lead Deposited	Yield Percent	Grams Lead Dissolved	Ampere Efficiency Percent
4.6475	2.8	0.2	15.1526	99.77	15.2111	100.15
1.2350	.	0.22	4.0277	99.8	4.0828	101.1
0.7290	1.2	.	2.3725	99.6	2.4124	101.3
1.4283	2	0.3	4.6580	99.8	4.7027	100.7
1.2054	1.4	0.2	3.7246	99.6	3.9656	100.7

The lead for the anodes had been once refined, but even then a small quantity of slime was formed. Betts has shown¹⁵ that anodes of triple refined lead, which dissolve in the lead fluo-silicate bath without the formation of slime, gave corrosion efficiencies greater than 100 percent. In some of his experiments, the anode corrosion efficiencies, in percent, were as follows: 101.4, 101.8, 101.3 and 101.8. This shows that the free fluo-silicic acid is



This photograph shows the general appearance of lead cathodes from lead perchlorate baths.

gradually changed to lead fluo-silicate. After a time the bath might even become alkaline. This extra loss from the anode is, no doubt, the result of chemical solution by the free acid in the bath. The perchloric acid in the perchlorate bath dissolves lead on open circuit, as shown by the following table. The bath contained 5 percent lead and 5 percent free perchloric acid.

Lead suspended by	Area of lead	Grams dissolved per sq. dm. per 24 hours.
Platinum wire	10.2	0.495
Cotton string	10.2	0.339; 0.414

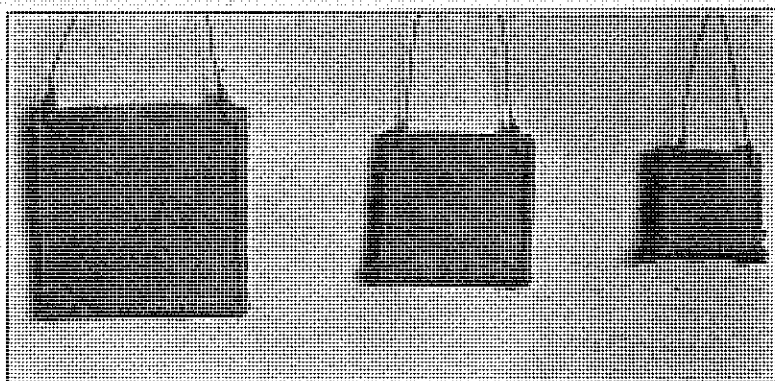
¹⁵ Betts, Trans. Amer. Electrochem. Soc., 6, 67 (1904).

Contact with the platinum wire increased the action, just as would be expected. The finely divided lead in the anode slime would be more rapidly attacked than the massive lead, due to the greater surface exposed and to contact with more positive metallic impurities. The above experiments were made with refined lead, which would dissolve more slowly than bullion. The free perchloric acid which is thus gradually neutralized must be restored. Two methods were tried: When electrolyzing with platinum anodes, the objection is that some lead peroxide is formed on the anode. Of course, the cost of platinum would present difficulties in commercial work. Graphite cannot be used, because it disintegrates during electrolysis. A simpler method is to add the required amount of sulphuric acid to a portion of the electrolyte. Lead sulphate is precipitated and perchloric acid remains in solution. The filtrate is returned to the bath. This diminution in acidity is not rapid. It is greater, of course, with baths containing large amounts of acid. This may be seen from the following table:

Percent of Acid in the Bath	Loss of HClO ₄ in Percent. Per Day
1.6	0.025
4.5	0.07
4.9	0.05

Current Density: Many things have an effect upon the practicable current density. A high current density is favored by concentrated solutions, high percent of free acid, large amounts of peptone, and good stirring. With 5 percent lead, 5 percent perchloric acid, 0.05 percent peptone and enough stirring or mixing of the solution to prevent large differences in concentration between the top and the bottom, a current density of from 2 to 3 amperes per sq. dm. (18 to 27 amperes per sq. ft.) gives good deposits, as shown by the accompanying photographs. With lower current densities, less care need be taken with stirring, proper spacing of the electrodes, acidity and quantity of peptone. For plating purposes, low current densities are recommended. With 0.4 amperes per sq. dec., fair deposits may be obtained from baths containing only 0.2 percent free perchloric acid. With higher current densities, these neutral baths give poor deposits, even when large amounts of peptone are used.

Voltage: The relation between concentration of the solution, current density and fall in potential or volts is shown in the following table. These measurements were made upon baths which had been running for several days and which were giving excellent deposits. The anodes were of ordinary commercial lead from a plumber's scrap pile. Two anodes were used—one on each side of the cathode. The anodes had been made purposely smaller than the cathodes to prevent, as much as possible, the thickening of the cathodes at the edges.



Showing the Effect of Current Density.
1 amp. per sq. dec.; 2 amp. per sq. dec.; 4 amp. per sq. dec.; 5.4 percent lead; 4.5 percent perchloric acid; 0.05 percent peptone.

Experiment 1.

Composition of the bath: 4.5 percent HClO_4 , 5.4 percent lead, and 0.05 percent peptone. The distance between anode and cathode was 2.2 cm. Volume of the solution was 400 c.c.

Amperes Per Anode	Sq. Dm. Cathode	Volts
3.2	1.6	0.21
4.0	2.0	0.27
5.6	2.8	0.38
8.0	4.0	0.55

Experiment 2.

Composition of bath: 6.1 percent HClO_4 , 7.13 percent lead, and 0.05 percent peptone. The distance between anode and cathode was 4 cm. Volume of solution was 800 c.c.

Amperes Per Anode	Sq. Dm. Cathode	Volts
1.0	0.21	0.08
2.2	0.45	0.15
2.6	0.55	0.18
3.8	0.8	0.25
4.2	0.9	0.26
5.0	1.6	0.30
6.2	2.	0.34

The results were the same with new anodes or with anodes that were covered lightly with slime containing enough mercury to give a bright color.

Purification Results.

The purity of the deposited lead which is obtained by the electrolysis of this bath is shown by the accompanying analyses of the different products.

	Cu. Percent	Sb. Percent	Pb. Percent	As. Percent	Ag. Percent	Bi. Percent
<i>Experiment (1)</i>						
Slime	1.89	37.56	6.49	.	6.29	30.83
Bullion	0.18	1.5	.	0.24	1.48	0.87
Refined Metal	0.005	0.004	99.984	none	0.003	0.004
<i>Experiment (2)</i>						
Slime	83.9	.	4.05	.	.	.
Bullion	0.45
Refined Metal	0.0007
<i>Experiment (3)</i>						
Slime	1.1	.	91.0	.
Bullion	1.84	.
Refined Metal	none	.

In these experiments, the copper, antimony, silver, arsenic and bismuth were added to the bullion in order to obtain a low-grade material. The anodes were suspended with platinum wires to avoid a slight contamination with copper which resulted when copper wires were used. The copper connecting wires, while not attacked very rapidly, nevertheless become appreciably smaller after being used for a long time in making connections to the anode. This might be avoided if the copper was cast into the anodes and not merely hooked through holes. The fact that these copper wires, in contact with the anodes, are only very

slightly attacked gives a striking visible proof that lead may be easily purified from copper.

The analyses show that the refined lead from very impure bullion contains only minute quantities of impurities. These impurities¹⁶ are, for the most part, due to the method of circulating the solution by a current of gas. This stirs up the slime from the bottom, some of which adheres to the cathode.

The slime contains only a small amount of lead. This is important, because it simplifies the subsequent treatment for the recovery of the valuable metals which are in the slime.

Loss of Perchloric Acid.

Some of the electrolyte is always mechanically trapped or held within the metal of the cathode. The loss of perchloric acid caused by this was determined by fusing portions of the cathodes with sodium nitrate. This treatment decomposes the perchlorate into chloride.¹⁷ The chlorine was determined by Volhard's method, and was calculated into perchloric acid. The results are:

	Gms. of Cathode Used	Gms. of Chlorine in terms of Perchloric Acid	Percent Loss of Perchloric Acid
Very smooth cathode . . .	25.	0.0041	0.018
Very rough cathode . . .	18.	0.0035	0.02

This represents a loss of about 0.4 pounds of perchloric acid per ton of lead deposited.

The perchlorate baths, which had been used for months, did not give any test for chlorides with silver nitrate. This shows that there is no loss of perchloric acid by slight reduction.

The slime, even after careful washing, contains some of the perchlorate of the bath. One sample of slime showed, 1.1 percent of perchloric acid. This result includes the chlorine from chlorides calculated to perchlorate. Some chlorine had come, perhaps, from the dust and fume of the laboratory. These chlorides, during electrolysis, would unite with the silver of the anode and thus remain in the slime. The total loss of perchloric acid in the slime represents a loss of 1.1 pounds per ton of lead refined if the bullion contained 5 percent of impurities.

¹⁶ Kern, *Trans. Amer. Electrochem. Soc.*, 6, 39 (1904).

¹⁷ Mathers, *Jour. Amer. Chem. Soc.*, 32, 66, (1910).

Thus the total loss of perchloric acid from unpreventable sources amounts to about 1.5 pounds per ton of lead refined. This does not include any loss from leaky tanks and pipes or careless handling.

Precautions.

Chloride and barium salts must be absent. A bath that has been giving good deposits will form very bad "trees" if a quantity of hydrochloric acid or some barium perchlorate is added to it. The injurious action of these substances was accidentally discovered from the fact that some baths, made from reagents containing these impurities, would not give good deposits. There are, perhaps, other salts that would act injuriously, but only those mentioned above have been tried.

SUMMARY.

This paper describes experiments with the lead perchlorate plating and refining bath. The properties of lead perchlorate, which are of special value in a plating or refining solution, are:

1. Great solubility.
2. Cathode deposits which are smooth, dense and free from "trees."
3. Approximately theoretical corrosion of the anode and deposition upon the cathode.
4. Absolute stability under all conditions to which it is subjected in a plating or refining bath.
5. No polarization from the formation of lead peroxide on the anode.
6. Very high electrical conductivity.

The bath should contain about 5 percent of lead, 2-5 percent of free perchloric acid, and 0.05 percent of peptone. A current density of from 2.3 amperes per sq. dm. (18-27 amp, per sq. ft.) may be used. The peptone is gradually used up, and after about four days a quantity equal to the original amount should be added. The free acid, which is very slowly neutralized by chemical solution of the lead, must be restored by the treatment of a suitable portion of the solution with the right amount of sulphuric acid.

This precipitates lead sulphate and leaves perchloric acid in solution. The filtrate is to be returned to the bath. The bath gives excellent purification, the cathode being about 99.98 percent pure. The deposit is smooth, coherent, and has a density of 11.36. As a plating bath, the lead perchlorate solution works exceptionally well on account of the absence of "trees" or loose crystals on the edges, even when the deposits reach a thickness of an inch. The bath shows no deterioration with use, and gives as good deposits after two months as at the beginning if the concentration, acidity and the required amount of peptone are maintained.

From the successful results obtained by the above method on a laboratory scale, I see no reason why it cannot be applied on a commercial scale especially for the plating of lead, since the deposits are of exceptional smoothness and are entirely free from "trees" or loose crystals on the edges or points.

University of Indiana.

April, 1910.

DISCUSSION.

MR. A. G. BETTS (*Communicated*): A correction should be made of the ratio of the conductivity of sulphuric and fluosilicic acids. If the reference is consulted the ratio will be seen to be 62:57, or a difference of about 9 percent.

Probably perchloric acid is not entirely stable in the presence of metal electrodes, and especially in that of metal sponge or anode slime. It would be interesting to know whether or not appreciable quantities of metallic impurities go into solution from chemical action of the acid on the anode slime.

The favorable result obtained when using perchloric acid as basis of the lead-depositing electrolyte should be ascribed to the fact that it is a strong, *i. e.*, strongly dissociating acid, and practically non-oxidizing, at least as far as the cathode surface is concerned. No good lead deposit has been obtained when the basis of the electrolyte is a weakly dissociating acid.

DR. J. W. RICHARDS: I regard this paper as a very important addition to our knowledge of the electrometallurgy of lead, and it

is particularly interesting as showing some more of the possibilities of addition agents. I am convinced that the possibilities of addition agents in various fields of electrolysis is by no means exhausted, in fact, have just begun to be investigated.

I was informed yesterday of an electroplating process being worked on a commercial scale in which the addition of a small amount of an organic addition agent, one entirely different from any that has so far been proposed, permitted the increase of the current density to three times its former strength and produced a plating of even better quality. The simple use and discovery of this addition agent increased the capacity of the plant 200 percent. I am not at liberty of giving further details of the method, but I state this to show some of the latent possibilities of addition agents and the value of research upon their applications.

MR. J. S. GOLDBAUM: A very recent German paper has advised the use of lead boro-fluoride as electrolyte, also with a recommendation of the use of gelatine or peptone. This is a very complete and interesting paper.

