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PROCESS FOR THE ELECTROLYTIC REFINING OF LEAD

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This invention relates to an improvement in the electrolytic refining of lead by the Betts process. The invention is particularly directed to providing a new and useful addition agent to improve the quality and the physical characteristics of the cathode deposit.

The Betts process for refining lead is well known and has been in commercial use for many years. For the Betts process, impure lead is cast in the form of slabs which form the anodes in an electrolytic cell. Refined lead cathode starting sheets are interspaced with the anodes in the cell. The electrolyte is an aqueous solution which contains from about 4 to 10 percent lead as lead fluosilicate and from about 5 to 12 percent free hydrofluosilicic acid. The current density employed is usually within the range of from about 12 to about 22 amperes per square foot of anode area.

The residence of the electrodes in the cell may vary over a relatively wide range depending on the nature and the amounts of the impurities present in the impure lead and on operating factors such as the composition of the electrolyte, current density and the operation temperature of electrolyte. A typical practice at one refinery has been to employ a three day cycle for the cathodes and a six day cycle for the anodes. Thus, two sets of cathodes are obtained from each set of anodes. The anodes are then removed, new electrodes are set and the cycle is repeated.

A problem associated with the electrolytic refining of lead is that of establishing and maintaining a dense, smooth cathode deposit. It is known that the lead tends to deposit on the cathode in a rough, irregular pattern with the formation of growths, known as "peanuts" and "trees." As deposition continues, these growths extend to and contact the anodes, cause short circuits, and reduce the efficiency of the cell. Also, the rough surfaces of the cathodes tend to collect and retain small particles of impurities which are suspended in the electrolyte.

This problem is well known and many addition agents have been suggested and used in an effort to overcome it. For example, small amounts of glue and mixtures of glue and goulac, a calcium lignin sulphonate, have been employed to improve the cathode deposit and overcome the problem of irregular growths. These known addition agents have improved the character of the cathode deposit to a certain limited extent but the problem has not been completely overcome.

I have discovered that the addition to the cell electrolyte of a finite amount of an extract prepared from the wood of western red cedar, either alone or in combination with a small amount of goulac, improves the quality and the structure of the cathode deposit.

The preparation of the addition agent of this invention is very simple. Western red cedar in the form of shavings, or chips, or sawdust, or in more finely divided form, is leached with hot water, for example, at 90° C. for 3 hours, to extract water soluble constituents. Wood

cellulose and lignin normally are not soluble in hot water; other constituents are at least partially soluble. At the end of the leaching period, the solids are separated from the solution, for example, by filtration. This filtrate may be evaporated to dryness and the residue redissolved in water as required, or the filtrate may be subjected to partial evaporation, if desired, to give a solution of convenient strength to be added to the electrolyte.

The cedar extract can be used as an addition agent alone or it can be used in combination with other known addition agents such as goulac. Preferably, the extract is added to the electrolyte as an aqueous solution of known strength.

Western red cedar, according to "Canadian Woods," 1951, published by the Forestry Branch, Forest Products Laboratories Division, Department of Resources and Development, Ottawa, Canada, is comprised of cellulose, 48 percent, lignin 31.8 percent, pentosans 9.0 percent, and is 11 percent soluble in hot water. The water soluble constituents provide the improved results in the quality and physical characteristics of the lead cathodes obtained in the operation of the present invention.

I have found, in the extensive investigations to which this addition agent has been subjected, that the improvement is noticeable in the use of small amounts of extract, of the order of about 0.1 gram per litre of electrolyte, calculated on a dry basis, and the optimum results appear to be obtained within the range of from about 0.5 to about 2.0 grams per litre when the addition agent is employed alone, or from about 0.1 to about 2.0 grams per litre when it is used in combination with goulac. The goulac when used is added in amounts greater than 1 gram per litre and less than 7 grams per litre of electrolyte.

The investigations have also shown that the regular addition of 0.5 pound of extract together with 1.0 pound of goulac per ton of lead deposited gave very good results in a continuous process using a lead fluosilicate electrolyte containing from 0.1 to 2.0 grams per litre of cedar extract and from 1.0 to 7.0 grams per litre of goulac.

These regular additions of cedar extract and goulac may vary between 0.1 and 1.5 pounds of extract and 0.5 and 3.0 pounds of goulac per ton of lead to be deposited.

The improvement described herein has been shown by actual investigations of the problem and is of course independent of theoretical considerations. The smoothness of the deposit and the reduction of coarse edges appear to be related to cathode polarization. It appears that goulac is responsible for grain refinement at the surface of the cathode and that the red cedar extract provides a useful degree of cathode polarization. Polarization tests indicate that the optimum range of concentrations of cedar extract is within the range set out above.

In a series of tests, it was found that an excellent lead cathode deposit was obtained by an initial addition to the electrolyte of about 0.5 gram of red cedar extract and 2.0 grams of goulac per litre of electrolyte followed by a daily addition of 0.05 gram of extract and 0.1 gram of goulac per litre, the daily addition being equivalent to 0.5 pound of extract and 1 pound of goulac per ton of cathode lead deposited. The cathode deposit was smooth and dense.

The electrolyte used for these tests contained 8.0% lead as lead fluosilicate and 8.5% and 9.0% free hydrofluosilicic acid. The current density was 22 amperes per square foot of anode surface and the electrolyte temperature was maintained at 45° C. The experimental

cells contained one anode and one cathode. The residence time for anodes and cathodes was three days.

The following series of examples further illustrates the improved results obtained in the use of the addition agent of the present invention. The electrolyte, in each instance, contained 8.0% lead and 10% free hydrofluosilicic acid. The cells were operated at room temperature with a current density of 20 amperes per square foot. In each instance, the stated amount of addition agent or agents was added at the start of each test and no further additions were made. The residence time of the cathodes was 48 hours.

Example No.	Cedar Extract (g. p. l.)	Goulac (g. p. l.)	48 hour Deposit, 20 amps. per sq. ft. Room Temp. (20° C.)	Deposit Rating
1	0	0	Rough, wires, not adherent	Poor.
2	0.1	0	Hard, rough, long needles, no shorting.	Do.
3	0.5	0	Hard, rough, coarse crystals, good edges.	Good.
4	2.0	0	Hard, smooth, few bumps, good edges.	Do.
5	5.0	0	Hard, smooth, very bumpy, wires on edges.	Poor.
6	0.0	1	Hard, rough, small bumps, poor edges.	Fair.
7	0.1	1	Hard, smooth, few bumps, fair edges.	Do.
8	0.5	1	Hard, smooth, very bumpy, good edges.	Do.
9	2.0	1	Hard, smooth, few bumps, some wire, good edges.	Do.
10	5.0	1	Hard, smooth, bumps and wire, badly warped.	Poor.
11	0.0	4	Hard, smooth, fair edges	Fair.
12	0.1	4	Hard, smooth, fair to good edges.	Good.
13	0.5	4	Hard, smooth, few bumps, good edges.	Do.
14	2.0	4	Hard, smooth, few bumps, very good edges.	Do.
15	5.0	4	Hard, smooth, bumps and wires, badly warped.	Poor.
16	0.0	7	Hard, smooth, poor edges	Fair.
17	0.1	7	Hard, smooth, fair to good edges.	Good.
18	0.5	7	Hard, smooth, few bumps, good edges.	Do.
19	2.0	7	Hard, smooth, bumpy, good edges.	Do.
20	5.0	7	Hard, rough, bumpy, badly warped.	Poor.

Example 1 illustrates the type of deposit obtained without the use of an addition agent. Examples 3 and 4 illustrate that a good deposit is obtained by the addition of 0.5 and 2.0 grams of cedar extract without goulac. The remainder of the examples illustrate the results obtained using varying amounts of red cedar extract and goulac. In the operation of the process it is preferred to use a combination of red cedar extract and goulac.

The improved addition agent of the present invention possesses a number of important advantages. It is readily available and relatively inexpensive to produce. In use, it facilitates the electrodeposition of a smooth and dense cathode deposit.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. In the electrolytic refining of lead by the electrodeposition of lead from an aqueous, lead fluosilicate-hydrofluosilicic acid electrolyte, the improvement which comprises the addition to the electrolyte of the water soluble extract obtained by hot water leaching of the wood of western red cedar, the extract being added to provide from 0.1 to about 2 grams of extract, calculated on a dry basis, per litre of electrolyte.

2. The process according to claim 1 in which the electrolyte contains from about 1 to about 7 grams of goulac per litre of electrolyte.

3. In the electrolytic refining of lead by the electrodeposition of lead from an aqueous, lead fluosilicate-hydrofluosilicic acid electrolyte, the improvement which comprises providing in the electrolyte, per ton of lead electrodeposited therefrom, from about 0.5 to about 3 pounds of goulac and from about 0.1 to about 1.5 pounds, calculated on a dry basis, of the water soluble extract obtained by hot water leaching of the wood of western red cedar.

4. In the electrolytic refining of lead by the electrodeposition of lead from an aqueous, lead fluosilicate-hydrofluosilicic acid electrolyte, the improvement which comprises providing in the electrolyte, per ton of lead electrodeposited therefrom, from about 0.5 to about 3 pounds of goulac and from about 0.1 to about 1.5 pounds, calculated on a dry basis, of the water soluble extract obtained by hot water leaching of the wood of western red cedar, said electrolyte containing initially from 1 to 7 grams of goulac and from 0.1 to 2 grams of said water soluble extract per litre of electrolyte.

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