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ELECTROLYTIC REFINING OF LEAD

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The present invention relates to electrolytic refining of lead and more particularly it relates to a new and improved method using an aqueous electrolyte that is comprised of lead fluosilicate, fluosilicic acid, the electrolyte-soluble and water-soluble portions of goulac, and the electrolyte-soluble and water-soluble portions of chestnut extract.

The practice of utilizing addition agents in the electrolyte solutions in the refining of metals has long been recognized as essential in order to improve the structure of the cathode when more or less pure metal is deposited in the electrolytic process. In the electrolytic refining of lead, the ideal cathode, long sought after, is one that is smooth surfaced, dense and uniform in purity of deposited metal. However, in many instances the cathodes produced by the electrodeposition process have fallen short of the ideal in that they have often had irregular or porous surfaces and have possessed protuberances in the form of trees, lumps or feathers. The pores in the surface of the cathode tends to collect and retain impurities from the electrolyte bath. These impurities consist of valuable amounts of gold, silver and bismuth which can be recovered from the slimes if not entrapped within the surface of the cathode. The protuberances are particularly objectionable in that they grow to such an extent that they cause short-circuits in the bath.

There have been a great number of materials used as addition agents, in different electrolyte baths, for the refining of different metals, to attempt to overcome these difficulties and to produce, as nearly as possible, the ideal cathode. While experiments have been conducted on a wide range of different materials, in varying types of baths, as yet there is no theory or satisfactory explanation that would predict how a material successfully utilized in one electrolytic system will affect another system. In the refinement of lead by electrodeposition, the most commonly satisfactory addition agents have been glue and goulac in an aqueous electrolyte that is comprised of lead fluosilicate and fluosilicic acid (H_2SiF_6). After long experimentation it was found that a mixture of aloes or aloin residue with goulac gives more satisfactory results (Mathers and Lantz Patent No. 2,664,393). An objection to the use of aloes or aloin residue has been its high cost.

Another serious objection to known addition agents has been their tendency to form gummy residues which plug the electrolyte circulation system. The plugging of the electrolyte circulation system results in poor distribution of the electrolyte. Some cells receive too much, causing them to overflow, while others receive too little, causing stratification of ions in the cells. In such an instance lead ions, being the heavier, tend to settle causing their concentration to be lowest in the upper part and highest in the lower part of the bath and the distribution of other ions and of undissociated electrolytes becomes unbalanced. This results in higher cell voltage, poor cathode deposits, uneven corrosion of the anode and increased percentages of impurities in the cathode,

all of which cause poor current efficiency and result in increased power and operating costs.

It is the principal object of the present invention to provide baths for electrolytic refining and electrodeposition of lead which are less expensive than those heretofore used, and further to provide a bath which is substantially free of gummy and resinous materials.

With this object in view, with others that will hereinafter appear, the present invention comprises the use of a mixture of the water-soluble or electrolyte-soluble portions of goulac and chestnut extract as an addition agent in a lead fluosilicate electrolyte.

The terms water-soluble portions and electrolyte-soluble extract portions include respectively all water-soluble material and electrolyte-soluble materials present in the chestnut extract and the goulac. Inasmuch as we have not been able to identify all the materials present in such extracts and solutions and inasmuch as all such extracts and solutions may be used in the electrolytic bath of this invention, these terms are believed to be properly descriptive of the chestnut extract we have found useful.

Chestnut extract may be made from the dried ground leaves (*Castanea dentata*) of the chestnut tree called Castanea of the family Fagaceae. These leaves contain 95% to 99.5% water-soluble material. The extract is obtained by percolation with a suitable menstruum. The liquid so obtained is evaporated and the solid extract remains after evaporation is complete. The chestnut extract so manufactured is practically 100% soluble in water and dissolves readily with very little agitation so that special equipment is not required for its percolation.

Goulac, also used in the electrolytic bath of this invention, is a by-product of the sulfite paper process obtained from the waste sulfite liquor. It consists essentially of lignin sulfates and sulfonates. It is also known as sulfite lignose.

The electrolytic bath used in the present invention consists of an aqueous solution of lead fluosilicate and fluosilicic acid preferably containing from 4.0 percent to 9.5 percent lead as lead fluosilicate and from 4.0 percent to 9.5 percent fluosilicic acid. Since both of these compounds partially dissociate in water into their constituent ions, the electrolytic bath contains lead ions, fluosilicate ions, and hydrogen ions as well as undissociated electrolytes. In accordance with this invention there is then added to this electrolyte, for each ton of lead deposited on the cathodes, from 0.1 to 5.0 pounds of goulac and from 3.0 to 0.1 pounds of chestnut extract. The amounts of goulac and chestnut extract are complementary, in that the use of an increased amount of one calls for the use of a decreased amount of the other.

Although the goulac and chestnut extract addition agents may be varied within the relatively wide ranges indicated above, under normal conditions the best results are obtained within the somewhat narrower ranges of 1.0 to 2.0 lbs. of goulac and 0.9 to 0.3 lb. of chestnut extract. However, exceptional conditions due to a number of causes such as a change in current density, a shortage or change in the cost of one of the addition agents and numerous other conditions can make it necessary to change the rate of addition of goulac or chestnut extract toward or to one or the other of the extreme limits heretofore stated. It will be understood that the rule of complementary amounts, which has been previously mentioned, is not a rigid one inasmuch as operating conditions have an effect on the amounts of addition agents that must be used.

A suitable composition of the electrolytic bath for best economy of operation and production of satisfactory cathodes comprises an aqueous solution containing: lead (as lead fluosilicate) 85 grams per liter, fluosilicic acid 85 grams per liter. To this is added for each ton of lead

deposited: chestnut extract (99% water-soluble) 0.5 pound, goulac 1.5 pounds. Under these conditions a current density of 14 amperes per square foot of anode surface and an electrolyte temperature of approximately 115° F. is satisfactory.

In summary, it may be noted that one of the principal advantages of the invention lies in the solubility of chestnut extract. It may be added to the electrolyte as a solution or directly in the form of lumps or powder. (The weights given are for the extract in solid form.) The cathodes are equal or superior in quality to those obtained with the hitherto preferred aloes-goulac agent.

Having thus described the invention, we claim:

1. In the electrolytic process of depositing lead in an aqueous electrolyte containing lead fluosilicate, the step which comprises the addition to the electrolyte for each ton of lead deposited of from 0.1 to 5.0 pounds of goulac and from 3.0 to 0.1 pound of material selected from the group consisting of water-soluble portions of chestnut extract and electrolyte-soluble portions of chestnut extract.

2. In the electrolytic process of depositing lead in an aqueous electrolyte containing lead fluosilicate, the step which comprises the addition to the electrolyte for each ton of lead deposited of from 1.0 to 2.0 pounds of goulac and from 0.9 to 0.3 pound of material selected from the group consisting of water-soluble portions of chestnut extract and electrolyte-soluble portions of chestnut extract.

3. An electrolyte for depositing lead electrolytically comprising an aqueous solution of lead fluosilicate and fluosilicic acid and containing for each ton of lead to be deposited from 0.1 to 5.0 pounds of goulac and from 3.0 to 0.1 pounds of material selected from the group consisting of water-soluble portions of chestnut extract and electrolyte-soluble portions of chestnut extract.

4. An electrolyte for depositing lead electrolytically comprising an aqueous solution of lead fluosilicate and fluosilicic acid and containing for each ton of lead to be deposited from 1.0 to 2.0 pounds of goulac and from 0.9 to 0.3 pound of material selected from the group consisting of water-soluble portions of chestnut extract and electrolyte-soluble portions of chestnut extract.

5. An electrolyte for depositing lead electrolytically comprising an aqueous solution of lead fluosilicate and fluosilicic acid and containing for each ton of lead to be deposited approximately 1.5 pounds goulac and 0.5 pound of material selected from the group consisting of water-soluble portions of chestnut extract and electrolyte-soluble portions of chestnut extract.

6. An electrolyte for depositing lead electrolytically comprising an aqueous solution of from 4.0% to 9.5% lead as lead fluosilicate, from 4.0% to 9.5% fluosilicic acid and containing, for each ton of lead to be deposited from 0.1 to 5.0 pounds of goulac and from 3.0 to 0.1 pounds of material selected from the group consisting of water-soluble portions of chestnut extract and electrolyte-soluble portions of chestnut extract.

7. An electrolyte for depositiing lead electrolytically comprising an aqueous solution of from 4.0% to 9.5% lead as lead fluosilicate, from 4.0% to 9.5% fluosilicic acid and containing, for each ton of lead to be deposited from 1.0 to 2.0 pounds of goulac and from 0.9 to 0.3 pound of material selected from the group consisting of water-soluble portions of chestnut extract and electrolyte-soluble portions of chestnut extract.

8. An electrolyte for depositing lead electrolytically comprising an aqueous solution of from 4.0% to 9.5% lead as lead fluosilicate, from 4.0% to 9.5% fluosilicic acid and containing, for each ton of lead to be deposited approximately 1.5 pounds goulac and 0.5 pound of material selected from the group consisting of water-soluble portions of chestnut extract and electrolyte-soluble portions of chestnut extract.

References Cited in the file of this patent

UNITED STATES PATENTS

2,664,393 Mathers ---------- Dec. 29, 1953

OTHER REFERENCES

Transactions of the Electrochemical Society, vol. 26 (1914), pp. 99–116 by Mathers.