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ELECTROLYTIC REFINING OF LEAD

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This invention relates to the electrolytic refining of lead and in particular it consists of a new and improved method using an aqueous electrolyte comprising lead fluosilicate, hydrofluosilicic acid, the electrolyte-soluble portion of goulac, and certain water-soluble and electrolyte-soluble portions of aloes.

It has long been the practice to add certain materials to the electrolyte used in the electrolytic refining of metals in order to improve the structure of the cathode of the more or less pure metal which is deposited during the refining process. Ideally the cathode should be dense and smooth surfaced, but in actual practice it tends to form as a porous mass having a surface which is irregular and often possessed of protuberances in the form of trees, lumps or feathers of the metal. Such deposits are undesirable for impurities become entrapped in the metal and the protuberances often bridge the gap between the anode and cathode and cause short circuits. There have been found a great number of materials which can be incorporated in the electrolyte to decrease this tendency and thus to improve the density and smoothness of the cathode. Many of these materials improve the cathode in relatively few specific electrolytic systems rather than generally. Some materials cause improved results only with certain metals; others require a specific salt of the metal or the presence of certain ions.

Several theories have been advanced to explain the results experienced when addition agents are present in the electrolyte, but no theory or explanation has ever made it possible to predict with certainty how a material which can be successfully incorporated in one electrolytic system will affect another system. Aloes derivatives have long been proposed as an additive; the results experienced demonstrate their unpredictability. Whereas aloes extract in an electrolyte containing 10 per cent lead acetate and 4 per cent ammonium perchlorate gave excellent deposits, the same material in an aqueous electrolyte containing lead perchlorate gave rough deposits having needle-like projections from the surface. Aloin alone when added to an aqueous electrolyte of stannous fluosilicate is reported to have given good results, but aloin alone added to an aqueous electrolyte of lead fluosilicate produced poor deposits. Thus it will be seen that no general statement can be made regarding the effect of aloes derivatives in electrolytes. The results range from good to poor, depending on the cation, the anion and presence of other additives.

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In the electro-deposition of lead including electrolytic refining with an aqueous electrolyte comprising lead fluosilicate and hydrofluosilicic acid the most common addition agents are glue, and goulac. Mixtures of these two addition agents give fair results. However, it has not heretofore been possible to eliminate the formation of protuberances on the cathodes, and it is still the practice to utilize manual labor regularly to break off these growths to stop active short circuits and to adjust the cathodes in order to prevent as far as possible the formation of new ones. Surface irregularities are objectionable in that they collect and retain slimes which interfere with the free flow of ions to the cathodes. These slimes which contain important values in the form of silver, gold and bismuth are entrapped in the irregularities of the surfaces. Even though the cathodes are washed after removal from the cells, some slimes are retained on the uneven surfaces and in this manner the values they contain are lost as impurities in the refined lead.

The objects of this invention are to provide baths for the electrolytic refining and the electrodeposition of lead from which lead cathodes can be formed that are more dense and have smoother surfaces than cathodes which have heretofore been produced, and to provide an electrolytic bath for the refining and the electro-deposition of lead which is less expensive than the best solutions heretofore used. The utilization of the electrolyte of this invention introduces important economies into the lead refining process. The smooth surfaced cathodes which are formed have very few protuberances and these rarely cause short circuits. This and other favorable conditions have made possible the elimination of the greater part of the manual labor that was formerly necessary for the inspection of cathodes and the prevention and correction of short circuits. Another economy is introduced by the longer periods during which the cathodes can be formed before they must be removed and replaced. Whereas it was formerly necessary to change cathodes every three to five days, depending on the character of the deposit, we find that this time can be increased to ten days by using the electrolytic baths of this invention. Furthermore a smaller amount of slimes are collected on the surfaces and purer and denser cathodes are formed.

After extensive investigation we have discovered that markedly improved results can be achieved when a combination of the electrolyte-soluble portion of goulac and the water-soluble

or electrolyte-soluble portion of aloes are incorporated in a lead fluosilicate electrolyte.

The expression "electrolyte-soluble" is used above and hereafter to mean that material which is soluble in the aqueous electrolytes, containing lead fluosilicate and hydrofluosilicic acid, that are used in the electrolytic refining and electrodeposition of lead.

Aloes is the dried juice of the aloe plant and contains from about 50 to 75 per cent water-soluble material, including from about 3 to 25 per cent aloin. Aloin is prepared commercially by extracting it from the aloes with water, acidifying the extract to cause the precipitation of resinous impurities, separating the aloin solution from the aloes residue and precipitated matter, and crystallizing the aloin from its solution. The aloes residue, which is the solid material remaining after the acidified solution has been separated, is generally spoken of as aloin residue rather than aloes residue. It consists of from about 16 to 54 per cent water-soluble material. We may use, in the electrolytic bath of this invention, aloes, aloin residue or aloin in the form of lumps or powder, or we may use water extracts of aloes, aloin residue or aloin, or combinations of the foregoing. We may use Curacao, Barbadoes, Socotrine, Cape, Uganda, Tafferabad, Zanzibar, or other aloes, in solid form or in a solution of water or of electrolyte. When added in the solid form, part of the aloes gradually dissolves in the electrolyte and the final result is essentially the same as when a previously made aqueous extract is added.

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

The electrolyte bath of this invention consists of an aqueous solution of lead fluosilicate and hydrofluosilicic acid preferably containing from 3.0 to 9.5 per cent lead as lead fluosilicate and from 3.0 to 9.5 per cent hydrofluosilicic 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 added to the electrolyte, for each ton of lead deposited on the cathodes, from 0.5 to 5.0 pounds of goulac and from 0.6 to 0.06 pound of water-soluble or electrolyte-soluble portions of aloes. The goulac and the aloes derivative may be varied within the range indicated above. For example, if the water-soluble or electrolyte-soluble portion of aloes is reduced to 0.06 pound the goulac should be increased to about 5.0 pounds or if the aloes portion is increased to 0.6 pound the goulac should be reduced to 0.5 pound. This illustrates the fact that complementary amounts of aloes and goulac should be used since a smaller amount of the latter will be combined with a larger amount of the former and vice versa.

When the water-soluble or electrolyte-soluble portion is obtained from aloin residue containing 30 per cent water-soluble material, from 0.2 to 2.0 pounds of aloin residue per ton of lead deposited will be used in conjunction with goulac, since the 0.06 to 0.6 range set forth above represents the amount of water- or electrolyte-soluble material.

A suitable composition of the electrolytic bath and satisfactory amounts of aloes or aloin residue that can be used are as follows:

An aqueous solution is prepared containing:

Lead (as lead fluosilicate)	per cent	6.5
Hydrofluosilicic acid	do	8.5

To this is added for each ton of lead deposited:

Aloes (60% water soluble)	pound	0.5
Goulac	pounds	1.5

It will be understood that the above example calls for the addition of about 0.3 pound of the water-soluble portion of aloes per ton of lead deposited and alternatively this may be supplied by adding 1.0 pound of an aloin residue containing 30 per cent water-soluble material or 0.6 pound of aloin residue containing 50 per cent water-soluble material. Under these conditions a current density of 14 amperes per square foot of anode surface and an electrolyte temperature of about 115 degrees F. are satisfactory.

If extremely smooth cathodes are desired or considerably higher current densities are to be used, the composition of the bath should be changed by increasing the addition of aloes (60 per cent water-soluble) to 1.0 pound or aloin residue (30 per cent water-soluble) to 2.0 pounds and goulac to 2.0 pounds for each ton of lead deposited.

Aloes or aloin residue are conveniently added to the electrolyte as solutions, extracts, or directly in the form of lumps or powder. Goulac is added as an extract prepared by dissolving the soluble portion in a solution from the electrolytic bath.

As will be evident to those skilled in the art, our invention permits of various modifications without departing from the spirit thereof or the scope of the appended claims.

As aloin residue may contain from 16 to 54 per cent water-soluble material the amount to be used to give a specified amount of aloes derivative will accordingly vary. The terms water-soluble aloes portions and electrolyte-soluble aloes portions include respectively all water-soluble material and electrolyte-soluble material present in crude aloes, including extracts of crude aloes, solutions of aloin and extracts of aloin residue. 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 aloes derivative we have found useful.

The lead cathodes that are formed according to the present invention are markedly improved over cathodes deposited from the heretofore preferred electrolyte in which glue and goulac were used as addition agents. The surface is much smoother. Whereas formerly cathodes were characterized by the presence of nodular protuberances, frequently as large as ¼ inch in diameter and sometimes larger, the cathodes made by the present invention exhibit only small protuberances, usually less than $\frac{1}{16}$ inch in diameter. These protuberances become less pronounced with the use of somewhat larger amounts of aloes derivative.

The greater smoothness and greater freedom from protuberances that results from the use of this invention makes it possible to form cathodes much thicker than have heretofore been considered possible and it has been found that a 100 per cent increase in thickness brings about no difficulties due to roughness of the surfaces. A further advantage arises from the economy of the aloes-goulac combination, which is substantially cheaper than prior addition agents.

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 0.5 to 5.0 lbs. of goulac and from 0.6 to 0.06 lb. of material selected from the group consisting of water-soluble portions of aloes and electrolyte-soluble portions of aloes.

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 1.5 lbs. of goulac and 0.3 lb. of material selected from the group consisting of water-soluble portions of aloes and electrolyte-soluble portions of aloes.

3. An electrolyte for depositing lead electrolytically comprising an aqueous solution of lead fluosilicate, hydrofluosilicic acid and containing for each ton of lead to be deposited from 0.5 to 5.0 lbs. of goulac and from 0.6 to 0.06 lb. of material selected from the group consisting of water-soluble portions of aloes and electrolyte-soluble portions of aloes.

4. An electrolyte for depositing lead electrolytically comprising an aqueous solution of from 3 to 9.5 per cent lead, as lead fluosilicate, from 3 to 9.5 per cent hydrofluosilicic acid and also containing for each ton of lead to be deposited from 0.5 to 5.0 lbs. of goulac and from 0.6 to 0.06 lb. of material selected from the group consisting of water-soluble portions of aloes and electrolyte-soluble portions of aloes.

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