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METHOD OF ELECTROLYSIS

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This invention relates to improvements in the art of the electrodeposition of metals and particularly to the deposition of zinc from sulphate solutions.

In the electrolytic recovery of zinc from ores, the zinc is ordinarily brought into solution as a sulphate. On account of the fact that manganese is universally present in zinc ores, such solutions always contain manganese sulphate in addition to zinc sulphate.

When such a solution is electrolyzed, say between aluminum cathodes and lead anodes, as described in my prior Patent No. 1,247,179, issued November 20, 1917, zinc is deposited at the cathode and manganese dioxide is precipitated at the anode.

It is found that under the conditions above described, which are also the conditions almost universally employed in practice, the zinc deposited at the cathode always contains small but important amounts of lead which definitely reduce the purity of the deposited metal.

I have found that this impurity is not deposited with the zinc from solution, but is mechanically introduced in the following way: when ordinary lead anodes are used, some manganese is precipitated as the dioxide in the form of flakes or scales on the anode and this precipitated dioxide always contains substantial amounts of lead. As electrolysis is continued, small pieces of this scale become detached and are carried in suspension through the electrolyte and deposited on the cathode. Lead is thus mechanically occluded in the zinc deposit and lowers the purity of the metal.

I have found that the above effect may be minimized or entirely prevented in the following way: instead of using a pure lead for the anode, an alloy of lead with silver and preferably also another metal is used. The amount of silver required is comparatively small—less than one percent of the weight of the lead will give good results. The amount required, however, is greater than will be found in any ordinary commercial lead metal. Quantities in excess of one percent may, however, often be used with advantage.

In this invention, while the lead-silver anode may be used alone, there are often benefits to be gained from the addition of small amounts of other metals as well. Particularly well adapted for this purpose are arsenic and tin.

The use of this anode makes possible a number of improvements in present day electrolytic zinc practice. Not only is the purity of the zinc increased, but it also becomes possible to recover the manganese dioxide in a commercially valuable form. Ordinarily the manganese dioxide precipitate contains considerable quantities of lead which make it valueless for most commercial purposes; moreover, the deposit is largely in the form of flakes or scales which are undesirable for industrial uses. For these reasons the manganese dioxide produced at the zinc plants has little if any market value. Under the present invention, the manganese dioxide is precipitated in the form of a very finely divided powder, and contains so little lead that it may be employed directly for drycells, varnish making, ink manufacture and other industrial purposes.

Moreover, owing to the absence from the electrolyte of the flakes of manganese dioxide above mentioned, it is found that the deposited zinc is much smoother than normally, and the growth of nodules or "trees" on the deposit is prevented. This is of great importance because it permits the electrodes to be spaced nearer together without danger of shortcircuiting, and so reduces power consumption which is ordinarily the largest item in electrolytic zinc costs.

Yet another advantage is that the extraction of the zinc from the ore may be materially raised. In the ordinary process of zinc electrolysis, sulphuric acid is set free at the anode in amount exactly corresponding to the zinc deposited at the cathode and no more. In order to make the acid balance therefore in the leaching step, it is necessary to use nothing but zinc in the form of oxide to neutralize the acid. Towards the end of the neutralization as the acid becomes weaker, the extraction of zinc oxide from the roasted ore becomes quite inefficient. It would be of advantage at this stage to finish

the neutralization with another base, say ordinary lime, but it is not possible to do this without disturbing the acid balance, making it necessary to add acid from an outside source.

It has been proposed to add extra manganese sulphate to the circuit to precipitate manganese dioxide at the anode and set free more sulphuric acid. Hitherto, owing to the fact that the precipitated manganese dioxide had no commercial value, such a course was commercially impracticable as the cost of the manganese sulphate would exceed the benefit of increased zinc extraction which the extra acid allows. With the present invention, however, since the manganese, as dioxide, may be sold at a higher price than the manganese, as sulphate, will cost, there is a clear gain in increased acid regeneration and therefore in possible zinc recovery from the ore.

In carrying this invention into effect I prefer the following procedure. Anodes are made from lead to which has been added enough silver to bring the total silver content up to, say, two hundred and fifty ounces of silver per ton of alloy. Arsenic may also be added in amount, say, of one to five per cent according to the hardness of lead required. If a hard lead anode is not wanted, tin may be substituted for arsenic.

I prefer to make the anodes in the form of a flat sheet, perforated freely with holes. I recommend the use of two such sheets, about one inch apart, between each pair of cathodes. This permits a lower voltage and a better circulation of the electrolyte than when only one sheet is used. Both cathodes and anodes should be so placed in the cell that the faces are kept strictly parallel. This may be conveniently done by the use of grooved guides of wood, hard rubber, or other non-conducting substance fixed in the cell and holding the edges of the electrodes. Because of the smooth nature of the zinc and also the fact that the anodes so made stay flat and do not buckle, the faces of the electrodes may be as close as five-eights of an inch. When the zinc on the cathode becomes sufficiently thick, the cathode is withdrawn, the zinc stripped and the cathode placed back in the guides. The manganese dioxide falls to the bottom of the cell as a fine powder and may be sluiced out as occasion requires, filtered, washed, and sent to market.

On account of the expense of making the whole anode of lead silver alloy, it may be desirable to use the silver only at the working face of the anode. An anode sheet may, for example, be made by rolling a lead billet which has a core of arsenical lead with a layer of lead-silver on each side. When this is rolled into a sheet say one quarter inch in thickness, the lead-silver layer on each side may be only one thirty second inch thick with a three sixteenths layer of arsenical lead between.

Having thus described my invention, what I claim and desire to secure by Letters Patent is:—

1. An anode for use in the electrolysis of zinc and manganese salts, said anode consisting of an alloy containing lead and silver.

2. An anode for use in the electrolysis of zinc and manganese salts, said anode consisting mainly of lead but containing a substantial proportion of silver.

3. An anode for use in the electrolysis of zinc and manganese salts, said anode consisting mainly of lead but containing substantially one percent of silver.

4. An anode for use in the electrolysis of zinc and manganese salts, said anode consisting mainly of lead and containing substantial proportions of silver and arsenic.

5. An anode for use in the electrolysis of zinc and manganese salts, said anode consisting of a perforated plate consisting mainly of lead and containing a substantial proportion of silver.

6. In the electrolysis of zinc sulphate solutions an anode having an active surface composed of a lead silver alloy.

7. In the electrolysis of zinc sulphate solutions an anode having an active surface composed of an alloy consisting mainly of lead but containing a substantial proportion of silver.

8. In the electrolysis of zinc sulphate solutions an anode having an active surface composed of an alloy consisting mainly of lead but containing silver to the extent of one part per thousand or more of lead.

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