

## UNITED STATES PATENT OFFICE

2,529,700

## METHOD OF ELECTROLYTICALLY PRODUCING ZINC OF HIGH PURITY

Sherwin Pope Lowe, George William Long, Kenneth William Downes, and George Henry Kent, Flin Flon, Manitoba, Canada, assignors to Hudson Bay Mining and Smelting Co. Limited, Winnipeg, Manitoba, Canada

No Drawing. Application August 1, 1946,  
Serial No. 687,707

9 Claims. (Cl. 204—119)

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This invention relates to a method of electrolytically refining zinc, particularly zinc produced by an electrolytic process, to obtain zinc of high purity.

Zinc of extremely high purity is of great importance in a number of fields and particularly in the production of die cast zinc articles. The purer is the zinc used, particularly as to the lead content, the better are the castings. As an example of the strict requirements as to zinc purity it may be mentioned that the British Ministry of Supply will not permit die casters supplying war equipment to use zinc of a lower quality than the following:

|                                         |                   |             |
|-----------------------------------------|-------------------|-------------|
| Zn                                      | -----percent min. | 99.99       |
| Pb                                      | -----percent max. | 0.003       |
| Cd                                      | -----do           | 0.003       |
| Total impurities including Pb and Cd    | -----do           | 0.01        |
| Impurities other than Pb, Cd, Fe and Cu | -----             | traces only |

When zinc is refined electrolytically, using zinc sulphate solution as the electrolyte and an anode of quite impure zinc, the refined zinc has a considerably lowered content of impurities, particularly of lead, but is still not of really high purity. The difficulty is that if an attempt is made further to refine this zinc electrolytically very little result is obtained because as the zinc in the anodes becomes purer the refining action decreases. It is thus impossible by methods now known to produce zinc of really high purity by electrolytic methods exclusively.

According to the present invention these disadvantages are overcome and zinc of an exceedingly high degree of purity may be produced by a method of which the essential feature consists in adding a stable aldehyde to a zinc sulphate electrolyte in a state of substantial equilibrium neutrality, while maintaining the electrolyte free from nitrogen containing compounds. An important object of the invention resides in the provision of such a method, and particularly such a method in which one of the following stable aldehydes is added: formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, and 2-ethylbutyraldehyde. Other objects reside in the addition of glucose and pine oil to the electrolyte in addition to such aldehydes.

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As used throughout this specification and claims, "a stable aldehyde" means an aldehyde which will not undergo conversion in the electrolyte to insoluble products which will precipitate out, and "a zinc sulphate solution in a state of equilibrium neutrality" means a zinc sulphate solution having the same hydrogen ion concentration as one which has been in contact with an excess of zinc oxide or roasted zinc ore until equilibrium is established. The pH of a zinc sulphate solution in a state of equilibrium neutrality depends on the temperature and concentration of the solution and also on the amounts and nature of addition agents which it contains. Over a range of concentrations of from 80 to 150 grams per litre of zinc in the solution, the pH value at equilibrium neutrality lies generally between 5.1 and 5.5 as determined by the glass electrode. The zinc sulphate electrolyte used need not be in a state of strict equilibrium neutrality but must be substantially in that state, i. e. its pH, as determined by the glass electrode, should not differ by more than .2 from its pH at equilibrium neutrality under the same conditions of temperature, concentration, etc. The more nearly it is in a state of strict equilibrium neutrality the better. In order to obtain a smooth, coherent plate the electrolyte should contain about 90 grams of zinc per litre.

Stable aldehydes which have been used with good results are, for example, formaldehyde, acetaldehyde, furfural, propionaldehyde, n-butyraldehyde, 2-ethylbutyraldehyde, n-hexaldehyde, chloral hydrate, acrolein, crotonaldehyde, heliotropin (piperonyl aldehyde) and vanillin (methyl protocatechuic aldehyde). An example of an unstable and thus unsuitable aldehyde is benzaldehyde, which oxidizes in the electrolytic solution to benzoic acid, an insoluble substance which precipitates out.

The aldehydes should be added as such rather than in chemical combinations from which they would be released in the electrolyte, because the other elements of the combinations may have a harmful effect on zinc purity. In any event, the electrolyte must be maintained substantially free from nitrogen containing compounds, as these have such a harmful effect.

The concentration of aldehyde in the electrolyte may vary within wide limits, depending in part

on the particular aldehyde used. In the case of formaldehyde, it should seldom be maintained at less than about 0.3 gram per litre. Taking all considerations into account the preferable concentration in the case of formaldehyde is from about 0.5 to about 1.0 gram of 100% HCHO per litre of electrolyte. If the concentration drops below 0.3 gram the purity of the zinc appears to suffer. Higher concentrations, e. g. of 2 or 3 grams, did not injure purity but appeared to lower current efficiency and needlessly increased expense. The above considerations and conditions, in general, apply to the other aldehydes mentioned above, such as acetaldehyde, propionaldehyde, n-butyraldehyde, and 2-ethylbutyraldehyde.

The purity of the zinc produced may be improved even beyond that obtained by the addition of a stable aldehyde alone by also adding to the electrolyte either cresylic acid or pine oil or both. Cresylic acid, if used, may be added in an amount of from about 2 to 10 lbs. per ton of zinc deposited, and pine oil in an amount of up to 5 lbs. per ton of zinc. Additions of 5.8 lbs. of cresylic acid and 2.6 lbs. of pine oil per ton of zinc deposited have been found very satisfactory.

It is desirable to add to the electrolyte agents for enhancing the smoothness of the plate, a well known example of such agents being glucose. Cresylic acid and pine oil both have this property, as well as that of increasing the purity of the deposit.

A typical analysis of the electrolyte, when using only a stable aldehyde addition is as follows:

|              |                      |       |
|--------------|----------------------|-------|
| Zinc         | grams per liter      | 91.5  |
| Formaldehyde | do                   | 1.08  |
| Cadmium      | milligrams per liter | 0.3   |
| Copper       | do                   | 0.4   |
| Arsenic      | do                   | 0.01  |
| Antimony     | do                   | 0.028 |
| Cobalt       | do                   | 1.0   |
| Iron         | do                   | 77.   |
| Manganese    | do                   | 36.1  |
| Chlorine     | do                   | 8.2   |
| Silica       | do                   | 95.   |

The method is preferably carried out with comparatively low current densities of not over about 25 amperes per square foot of cathode. While refining is being carried out, film or slime often forms on the anode and falls from the latter to the bottom of the cell. This slime should not be allowed to touch the cathode as it contains relatively high proportions of impurities from which the zinc is to be freed. The electrolyte is accordingly kept substantially quiescent, only sufficient circulation being allowed to ensure a proper mixture of all its constituents.

The results obtained by the method of the invention are indicated by the following typical analysis, in which the first column of figures relates to zinc before treatment by the method of the invention using formaldehyde and the second column to zinc after such treatment:

|         | Before treatment | After treatment |
|---------|------------------|-----------------|
|         | Per cent         | Per cent        |
| Lead    | 0.0021           | 0.0040          |
| Copper  | 0.0015           | 0.0025          |
| Cadmium | 0.0005           | 0.0011          |
| Iron    | 0.0002           | Trace           |

When glucose (which is commonly used as an

addition agent in zinc refining) and pine oil are used with aldehydes, the reduction in impurities is even more marked, as may be seen from the following table of results obtained from zinc anodes containing in each case about .0025% lead:

| Addition Agents                            | Lead in Cathode Zinc |
|--------------------------------------------|----------------------|
|                                            | Per cent             |
| Pine Oil, Glucose and Formaldehyde         | .00002               |
| Pine Oil, Glucose and Acetaldehyde         | .00002               |
| Pine Oil, Glucose and Propionaldehyde      | .00002               |
| Pine Oil, Glucose and n-butyraldehyde      | .00003               |
| Pine Oil, Glucose and 2-ethylbutyraldehyde | .00004               |

The relative effect of formaldehyde alone and with cresylic acid or pine oil or both is shown by the following table of results obtained in all cases from zinc having the same initial lead content:

| Addition Agents                             | Lead in Cathode Zinc |
|---------------------------------------------|----------------------|
|                                             | Per cent             |
| Formaldehyde                                | .002                 |
| Formaldehyde and pine oil                   | .00013               |
| Formaldehyde and cresylic acid              | .00003               |
| Formaldehyde and pine oil and cresylic acid | less than .00002     |

This application is a continuation-in-part of our prior application Serial No. 519,650, filed January 25, 1944 (now abandoned), which was itself a continuation-in-part application Serial No. 419,504, filed November 17, 1941 (now abandoned). Pine oil and cresylic acid are referred to in Patent 2,471,965.

What we claim as our invention is:

1. The method of electrolytically refining zinc to a high purity from a zinc sulphate electrolyte containing at least one of the impurities, lead, copper, cadmium and iron, to reduce at least the lead content of the zinc deposited, which comprises adjusting the pH of the electrolyte to a state of substantial equilibrium neutrality, said neutrality being a pH of about 5.1 to 5.5, adding to the electrolyte a stable aldehyde selected from the group consisting of formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, and 2-ethylbutyraldehyde, in an amount sufficient to reduce the amounts of said impurities in the zinc which is deposited by an amount greater than the reduction in such impurities incident to electrolysis in the absence of such aldehyde, meanwhile maintaining said electrolyte substantially free of nitrogen containing compounds, and passing electric current from an impure zinc anode containing at least one of said impurities to a cathode through said electrolyte containing said aldehyde, to deposit zinc of high purity.

2. The method according to claim 1, including the addition of glucose and pine oil to said electrolyte in addition to said aldehyde.

3. The method according to claim 1, in which said aldehyde is formaldehyde.

4. The method according to claim 1, in which said aldehyde is formaldehyde, and in which the concentration of formaldehyde in said electrolyte is maintained at at least 0.3 gram per liter of electrolyte.

5. The method according to claim 1, in which said aldehyde is formaldehyde, and in which the concentration of formaldehyde in said electrolyte is maintained at between 0.5 and 1.0 grams per liter of electrolyte.

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6. The method according to claim 1, in which said aldehyde is acetaldehyde.

7. The method according to claim 1, in which said aldehyde is propionaldehyde.

8. The method according to claim 1, in which said aldehyde is n-butyraldehyde.

9. The method according to claim 1, in which said aldehyde is 2-ethylbutyraldehyde.

SHERWIN POPE LOWE.

GEORGE WILLIAM LONG.

KENNETH WILLIAM DOWNES.

GEORGE HENRY KENT.

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