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## RAPID ZINC DEPOSITING BATH

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This invention relates to the electrodeposition of zinc from acid baths, and has for its object to rapidly deposit zinc in a fine-grained smooth structure at a high cathode efficiency and with good adherence and deformability so that the resulting plated basis metal may be mechanically worked without cracking or peeling of the deposit.

In making up the bath, I employ an aqueous electrolyte of zinc chloride and zinc acetate in such proportions and concentrations that the composite bath no longer possesses the faults of either a straight zinc-chloride bath or a straight zinc-acetate bath, but has certain properties peculiar to the use of these salts in association with each other. For example, the solution pressure of zinc in zinc chloride containing free hydrochloric acid is so high that it is difficult to secure any satisfactory deposit of zinc, and at the same time excessive chemical solution of the anode occurs when a soluble anode such as pure zinc or one of the usual zinc-alloy anodes is employed. On the other hand, the electrical resistance of a straight zinc-acetate bath is such that high current densities cannot be maintained without unpractical voltages and excessive development of heat in the electrochemical process. I have found that these disadvantages are eliminated by the conjoint use of zinc chloride and zinc acetate as substantially the entire electrolyte in such quantities and proportions that the total metal is within the range of 2 to 60 oz./gal., at least 4% of which is furnished by zinc acetate, and the remainder, not less than 4%, is furnished by zinc chloride. The optimum total metal lies within the range of 10 to 30 oz./gal., and the optimum ratio of metal from the respective salts is in the neighborhood of 80% from chloride to 20% from acetate.

Another important effect of the conjoint use of zinc chloride and zinc acetate in producing the aqueous electrolyte is with relation to the pH value at which the bath is most advantageously operated. For example, in a bath containing 60 ounces of zinc per gallon as total metal content, the pH value of the bath will be about 2.8 at 95% zinc from chloride and 5% zinc from acetate, whereas in a bath containing 2 ounces of zinc per gallon as total metal content at the same ratio of zinc from chloride to zinc from acetate, the pH value will be at about 5.6, with no free hydrochloric acid added in either case. With baths of the same total metal content, the pH value increases as the ratio of metal from acetate to metal from chloride is increased. A

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particularly favorable pH range is from 3.8 to 4.2 in a bath containing from 10 to 30 ounces of total metal per gallon when operated at a temperature of 120° F. and a current density of 15 to 450 amps./sq. ft. at the cathode. Under these conditions, employing a cold rolled steel cathode and a zinc-aluminum-alloy anode, as described for example in U. S. patent to Graham, No. 1,888,202, dated November 15, 1932, the specific resistivity of the bath is in the neighborhood of 8.5 ohms/c. c., and the anode and cathode efficiencies are both in the neighborhood of 99%. The deposit from such a solution is fine grained, very adherent and capable of being bent into any shape desired, so that a steel sheet or strip containing the electrodeposit may be rolled, drawn or otherwise mechanically worked without separation of the deposit from the basis metal or cracking of the deposit. Practical examples of zinc plating solutions within this preferred range are made up as follows:

| Total Metal Content | 10 oz./gal. | 30 oz./gal. |
|---|---|---|
| | *Oz./gal.* | *Oz./gal.* |
| Zinc Chloride | 16.8 | 50.4 |
| Zinc Acetate | 5.6 | 16.8 |

In addition to adjusting the pH value of the bath to the point desired, by the total metal content and the ratio of zinc from chloride to zinc from acetate, the conductivity of the bath is also affected by the total metal content and the metal ratio from the respective salts. Thus, as the ratio of zinc from chloride to zinc from acetate is increased from a low value to approximately 85% of the total metal, the specific resistivity of the bath at 120° F. steadily decreases. Beyond this ratio, further additions of zinc chloride produce only relatively small decreases in specific resistivity, and little is to be gained in this respect by increasing the zinc-chloride concentration beyond this point. In an engineering sense, the avoidance of further decrease of pH value may become more important than the slight further reduction of the specific resistivity.

In baths of relatively high zinc-acetate content, the pH value may be above the preferred operating range. In such case, hydrochloric acid may be employed to lower the pH value to, for example, 4.2 or 4.0, and such a bath, with its pH value thus adjusted, will give a fine-grained deposit of good mechanical properties. However, the presence of the hydrochloric acid will accelerate the chemical attack upon a pure zinc anode or a zinc-aluminum-mercury anode, and produce an objectionable coating on the anode or sludge in the bath. It is found that in such cases particularly, a zinc-aluminum-alloy anode of the type hereinbefore mentioned is much to be preferred, as it will suffer only very slight or insignificant chemical decomposition and operate satisfactorily under the conditions mentioned. In general, for all types of solutions within the principles of this invention, such a zinc-aluminum-alloy anode is most satisfactory, as it remains clean and does not develop the dark, high resistance coating on the surface or introduce objectionable quantities of suspended matter into the bath to adversely affect the cathode deposit. Since the bath is in most cases subjected to periodic or constant filtration and circulation, the aluminum does not build up to objectionable proportions in the bath.

The maximum of the temperature range is particularly important because at 130 to 140° F. decomposition of the zinc acetate sets in. For this reason, the temperature range is best limited to from room temperature to 125° F., with the optimum temperature at about 120° F. In this connection, it is important to bear in mind that the baths described present such a low degree of resistivity that the upper temperature limits are not automatically obtained by the plating current even at 450 amps./sq. ft. In most cases, artificial heating is resorted to in order to maintain the optimum temperature of 120° F. The reference to current densities in the neighborhood of 450 amps./sq. ft. applies, for example, to plate, sheet and strip stock of cold rolled steel in widths as great as thirty-six inches, continuously moved through the electrolyte at a distance of two inches from the anode surface. Obviously, on round wire much higher current densities are perfectly feasible, with satisfactory cathode contact distribution, so that artificial heating may become unnecessary and artificial cooling be required to maintain the proper temperature.

I claim:

1. An aqueous bath for the electrodeposition of zinc, comprising zinc chloride and zinc acetate as substantially the entire electrolyte, the total zinc being within the range of 10 to 30 oz./gal. with about 80% supplied from zinc chloride and about 20% from zinc acetate.

2. An aqueous bath for the electrodeposition of zinc, comprising zinc chloride and zinc acetate as substantially the entire electrolyte, the total zinc being within the range of 2.0 to 60.0 oz./gal., the zinc acetate and zinc chloride each furnishing at least 4% of the total zinc.

3. An aqueous bath for the electrodeposition of zinc, comprising zinc chloride and zinc acetate as substantially the entire electrolyte, the total zinc being within the range of 10.0 to 30.0 oz./gal., the zinc acetate furnishing from at least 4% to about 20% of the total zinc.

4. An aqueous bath for the electrodeposition of zinc, comprising zinc chloride and zinc acetate as substantially the entire electrolyte, the total zinc being within the range of 25.0 to 30.0 oz./gal., the zinc acetate furnishing from at least 4% to about 20% of the total zinc.

5. An aqueous bath for the electrodeposition of zinc, comprising zinc chloride and zinc acetate as substantially the entire electrolyte, the total zinc being within the range of 10.0 to 30.0 oz./gal., the zinc acetate furnishing from a least 4% to about 20% of the total zinc; the particular quantity within this range being that which with the zinc chloride provides a pH value between about 4.2 and 3.8 without the addition of free acid.

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