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PLATING OF TIN-ZINC ALLOYS

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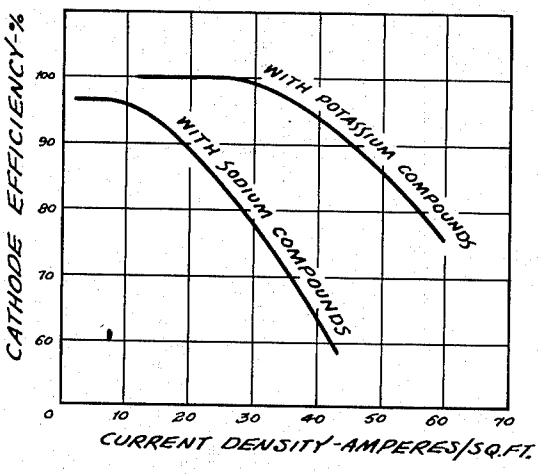
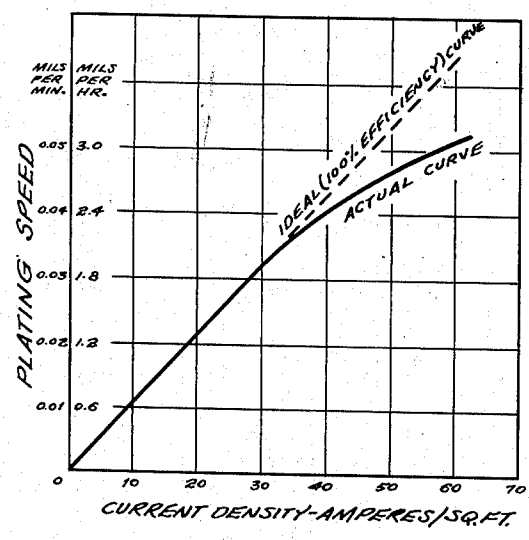


FIG. 1.

FIG. 2.



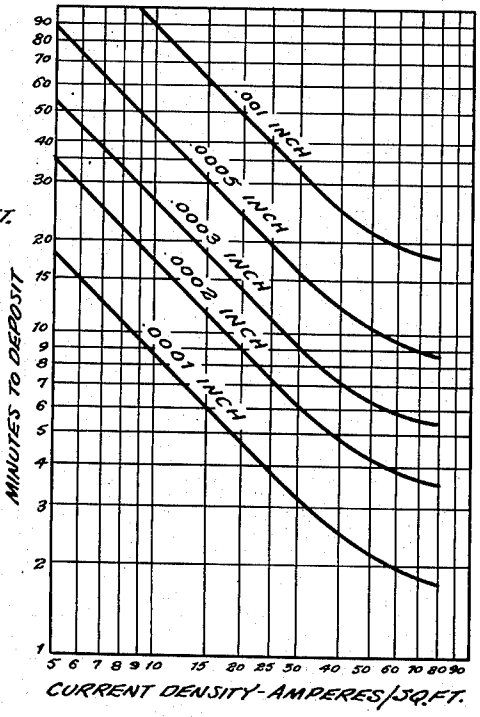


FIG. 3.

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PLATING OF TIN-ZINC ALLOYS

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1 Claim. (Cl. 204—43)

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The present invention relates to a process of electrodepositing alloys of tin and zinc.

It has been found that an alloy of tin and zinc, electrodeposited on metals such as steel, affords excellent protection against corrosion. Tin and zinc can be deposited in all proportions from electrolyte solution but a most serviceable composition from the viewpoint of the protection afforded to the steel is around 80% tin, 20% zinc with a tolerance of about 5% either way. The 80–20 tin-zinc alloy deposited has an appearance much like pure tin, that is a satiny white matte finish and has many other properties which make it a desirable replacement for cadmium. For example, (1) it has excellent corrosion resistance properties, (2) it is easily solderable even without flux, (3) the throwing and covering powers of the electrolyte bath are approximately equal to those of stannate tin, i. e. excellent, and therefore somewhat better than zinc or cadmium, and (4) it is economical to apply compared with cadmium.

Hitherto, the electrodeposition of the tin-zinc alloy has been accomplished from electrolytic solutions containing sodium stannate, sodium hydroxide, sodium zinc cyanide and free sodium cyanide. For replenishing the metal content of the electrolytic bath, alloy anodes of the same composition as the alloy to be deposited were employed.

With such a solution, the upper current density permitted with practicality is about 30 amperes per square foot. Attempts to increase this current density and therefore the rate of plating are nullified by a rapid falling off of cathode efficiency and a change in the proportions of tin and zinc in the deposit.

It has been found in accordance with the present invention that the use of potassium compounds instead of the sodium compounds in the electrolyte bath permits the electroplating operation to be performed at higher current densities up to 60 amperes per square foot and also makes the alloy deposition less dependent on the current densities. The deposition can thereby be controlled by the alloy anode and bath composition. The use of potassium compounds therefore permits the attainment of higher plating speeds and renders the process less critical in control.

The accompanying Figures 1–3 illustrate the advantages of the invention, wherein:

The curves of Figure 1 compare sodium and potassium compounds for current density versus cathode efficiency,

The curve of Figure 2 illustrates current density versus plating speed for potassium compounds, and

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The curve of Figure 3 illustrates current density versus minutes to deposit for potassium compounds.

The solutions used in accordance with the present invention comprises basically potassium stannate plus a small amount of zinc cyanide, larger quantities of potassium cyanide and a small amount of free potassium hydroxide. For a deposit of an alloy containing between 15 and 25% of zinc and between 75 and 85% of tin, the plating bath may comprise approximately between 32 and 45 grams per liter of tin, added as potassium stannate, between 3.5 and 9.0 grams per liter of zinc added as zinc cyanide, between 30 and 50 grams per liter of total potassium cyanide and between 5 and 11 grams per liter of free potassium hydroxide. A typical formulation is as follows:

Example I

	Make-up, grams/liter	Control Limits (by analysis), grams/liter
Potassium Stannate (corresponds to tin content)	120 45	37 –45
Zinc Cyanide (corresponds to zinc content)	9.0 5.0	3.5– 6.0
Potassium Cyanide	19.0	30 –45
Free Potassium Hydroxide	6.5	5.0– 8.0

It should be noted that potassium cyanide by analysis differs from potassium cyanide actually added due to cyanide added as zinc cyanide. Thus analysis determines the total cyanide, which is free potassium cyanide plus the cyanide in the complex $K_2Zn(CN)_4$ or $2KCN.Zn(CN)_2$.

It should also be noted that the wide control limits for the KCN are due partially to the permissible variation in zinc content because of the above relationship. The actual free cyanide should preferably vary only between 15 and 20 grams per liter.

The formulation in Example I is particularly useful for plating in still tanks. For barrel plating the following formulation may be employed:

Example II

	Make-up, grams/liter	Control Limits (by analysis), grams/liter
Potassium Stannate (corresponds to tin)	95 35	32-40
Zinc Cyanide (corresponds to zinc)	13.5 7.5	7- 9
Potassium Cyanide	15.0	38-50
Free Potassium Hydroxide	10.0	8-11

In both Examples I and II, the temperature of operation is 150° F., controlled to ±5°. Cathode current densities are in the range of 10–75 amperes per square foot and preferably in the range of 30–50 amperes per square foot, and anode current densities are about 15–25 amperes per square foot.

Anodes of the same composition as the deposit are employed, namely 80% tin and 20% zinc. The anodes must be filmed for satisfactory operation. In order to form the film, a current somewhat higher than the normal operating current is impressed upon the anodes for a short time (usually less than a minute is sufficient), and then the current is cut back to the proper operating value. Formation of the film can be noted by a rise in the voltage reading and/or a decrease in the ammeter reading. The anodes should gas slightly, an indication that oxygen is being evolved and that the film is present.

In the absence of the anode film, the tin dissolves as stannous tin which will cause rough and spongy deposits and will also throw the bath composition out of balance.

A typical operation with potassium compounds in accordance with the present invention gave the following results:

Current Density, Amps./Sq. ft.	Current, Amp.	Grams Deposit, theoretical, Wgt.	Grams Deposit, Actual, Wgt.	Percent Eff.	Percent Zinc deposited
30	120	2.230	2.267	102	21.5
30	60	1.115	1.154	104	20.9
45	120	2.230	2.094	93	22.4
45	240	4.460	4.003	90	22.0
60	120	2.230	1.770	79	23.0
60	240	4.460	3.460	77	22.7

A curve following substantially this characteristic is indicated in Fig. 1.

A typical operation, employing sodium compounds and in accordance with the prior art, gave the following results:

Current Density	Percent Eff.	Percent Zinc
5	96	13.6
10	98	19.9
15	93	22.7
20	91	24.2
30	76	21.2
40	67	17.8

A curve following substantially this characteristic is indicated in Fig. 1 for the purpose of comparison.

The important advantages which are gained by the use of potassium compounds instead of sodium compounds in the electrolytic bath are made evident by consideration of the curves in Fig. 1.

It is apparent from these curves that with sodium compounds, the practical upper limit of current density which can be used is about 30 amperes per square foot. Any current densities beyond this level causes sudden drop in cathode efficiency beyond the limits of practical operation. On the other hand, with potassium compounds, current densities up to 60 amperes per square foot can be employed at practically operable efficiencies.

With potassium compounds in the electrolytic bath, the composition of the alloy deposited is less dependent on current density, as indicated in the comparative test data set forth above. Also, with potassium compounds, the composition of the alloy deposited is less dependent on the proportion of ingredients of the electrolytic bath.

In Fig. 2, the curve indicates plating speed in a typical operation with potassium compounds in the electrolyte bath and in Fig. 3 the curves indicate different plating speeds for typical operations performed in the presence of potassium compounds in the electrolyte bath.

While the invention has been described with particular reference to specific embodiments, it is to be understood that it is not to be limited thereto but is to be construed broadly and restricted solely by the scope of the appended claim.

What is claimed is:

A process for the electrolytic deposition of tin-zinc alloy containing 15–25% zinc and 85–75% tin which comprises subjecting an article to be plated, as a cathode, to electrolysis in an aqueous plating bath containing 32 to 45 grams per liter of tin in the form of potassium stannate, 3.5 to 9.0 grams per liter of zinc in the form of zinc cyanide, 30 to 50 grams per liter of total potassium cyanide and 5 to 11 grams per liter of free potassium hydroxide, while maintaining a current density of between 30 and 50 amperes per square foot, and a bath temperature of between 145° F. and 155° F.

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