TIN-ZINC ALLOY PLATING:
A NON-CYANIDE ALKALINE DEPOSITION PROCESS

by

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ABSTRACT

A new non-cyanide alkaline stannate/zincate electrolyte has been developed. This bath, called Stanzec, is a stable solution containing a complexing/stabilizing agent and is capable of electrodepositing tin-zinc alloys over the full range of compositions. The bath also contains an addition agent which considerably improves the coating properties, compared to the old cyanide tin-zinc bath, and produces a compact, non-porous semi-bright deposit. The 75-80% tin (balance zinc) alloy offers excellent corrosion protection with minimum formation of white corrosion product.

INTRODUCTION

Tin-zinc alloy electrodeposits, containing 20-30% zinc, offer outstanding corrosion protection for steel and other substrates. They combine the barrier protection offered by tin, with the galvanic protection of zinc, without the bulky corrosion products associated with pure zinc or high percentage zinc deposits. Traditionally, tin-zinc alloys have been plated from cyanide solutions developed in the 1940's[1,2] and it is therefore not surprising that a number of applications for this alloy have been known for many years[3,4]. However, since the mid-1960's the use of tin-zinc has declined considerably, and the coating is now not used as widely as expected. This may be partly because of the unpopularity of cyanide plating solutions, but is more probably due to the fact that cyanide tin-zinc plating solutions are very difficult to operate and require constant monitoring and control.

The problems encountered in the prior art of tin-zinc plating, necessitated the development of a non-cyanide process. This was also very pertinent in view of the current thinking on the toxic hazards associated with the use of cadmium coatings, for which tin-zinc offers a possible alternative. Finally, the price of tin has fallen dramatically since 1985, and so the use of the alloy is now economically more attractive. It is therefore likely that the 1990's will see a revival of interest in the use of tin-zinc alloy coatings.

This paper describes an alkaline non-cyanide tin-zinc alloy plating system[5] which overcomes many of the problems previously encountered. The properties of the coating produced from this bath are also discussed.

The Plating Process

The electroplating solution may be considered to be a mixture of potassium stannate, potassium zincate, potassium hydroxide, a complexing/stabilizing agent and a grain refiner/brightener. Tables 1 and 2 give typical electrolyte compositions and operating parameters required to give a deposit containing 20-25% zinc.

The concentrations of tin and zinc in the solution have a direct effect on the composition of the deposit; an increase in either one being reflected by an increase in the percentage of that metal in the deposit.

The level of free potassium hydroxide should not fall below 35 g/L (4.67 oz./gal.), since at these levels the bath becomes unstable and precipitation occurs, resulting in a depletion of zinc. If the bath is operated with the free caustic within the prescribed limits of 40-50 g/L (5.34-6.68 oz./gal.) a satisfactory deposit with the correct composition will be obtained. If the caustic level becomes too high, it should be reduced by the addition of a proprietary /corrector acid.

The complexant/stabilizer is obviously required to achieve the simultaneous deposition of tin and zinc, and its concentration within the prescribed limits has no effect on deposit composition. However, if the level drops substantially, the electrolyte will become progressively less thermally stable and excessive temperatures, for example in the immediate vicinity of internal heating elements, will give rise to the precipitation of zinc stannate.

Temperature and current density do not have an effect on deposit composition if kept within the specified ranges. Similarly the level of the grain refiner/brightener has no effect, and is present in the solution simply to improve the coating quality.

It may be noted that a choice of anodes is given. If cast alloy anodes containing 75%tin/25%zinc are employed, they must be operated in the filmed condition, as in the case of the deposition of pure tin from the stannate tin bath[6]. The anode film is important to prevent tin dissolving into the solution in the stannous form, Sn(II), resulting in the deposition of a dark, coarse deposit. The recommended current density for these anodes is 0.7-1.5

Amps per sq. dm (6.5-13.9 A/ft.^{2}). At higher current densities the anode efficiency drops due to passivation and at lower values the film is unstable. A disadvantage of the use of these anodes is that ideally they should be removed from the solution when the current is switched off, to prevent the film from dissolving. If such anodes are used, the bath should periodically be dosed with hydrogen peroxide, to oxidize any trace amounts of Sn(II) ions into the stannic form, Sn(IV). The use of inert anodes, for example stainless steel grade 316, overcomes the problems encountered with tin-zinc anodes, but the metal ions in solution must be replenished now by other means. Obviously, the addition of potassium stannate and potassium zincate is a possibility, but this leads to a gradual buildup of potassium ion in the solution, until no further dissolution occurs. Fortunately, however, zinc may be replenished by dissolving the metal directly into the solution, and tin may be added from a commercially available tin oxide sol.

Barrel plating may be successfully performed using this process, but some modification of the electrolyte composition is necessary. In particular, a higher ratio of zinc to tin is required to obtain the correct deposit composition. In addition, so as to reduce drag out losses, the concentration of tin is approximately halved.

With regard to the day to day operation of the plating bath, all that is required, in addition to regular constituent replenishment due to plate-out and drag-out, is daily analysis of the zinc and free caustic concentrations and a weekly analysis of the tin concentration. Analytical procedures for these constituents are available.

Properties of the Coating

Tin-zinc deposits obtained from this process are compact, fine-grained and essentially pore-free. Figure 1 compares the microstructure of 80%tin/20%zinc coatings obtained from a traditional cyanide-bath to that from the new process. As a result of the reduction in grain size, the coating from the new bath has a semi-bright sheen.

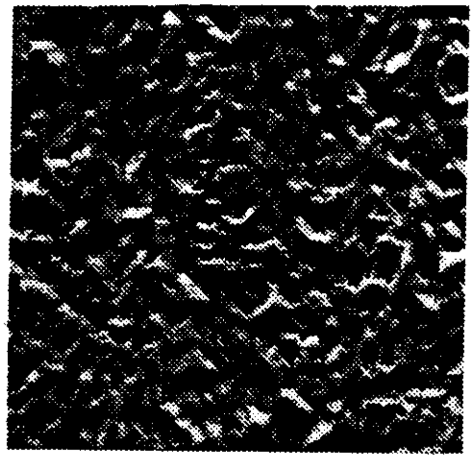

Figure 1a. Scanning electron micrograph (x1000) of 80%tin/20%zinc coating produced from cyanide electrolyte.

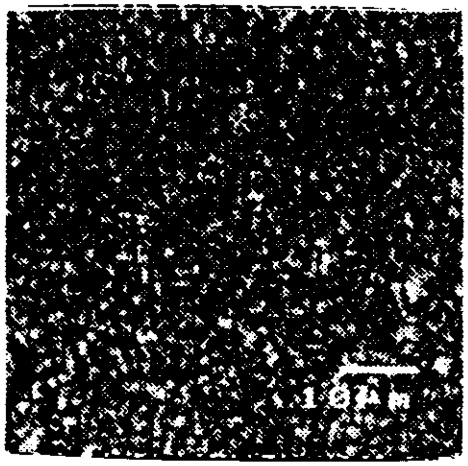

Figure 1b. Scanning electron micrograph (x1000) of 80%tin/20%zinc coating produced from the Stanzec process.

Salt-spray corrosion tests (ASTM B117) have been performed on unpassivated samples of80%tin/20%zinc and the results are given in Table 3. Similar tests were carried outon various alternative coatings which were also unpassivated and as can be seen in Figure 2, the results obtained from tin-zinc were either superior or roughly equivalent.

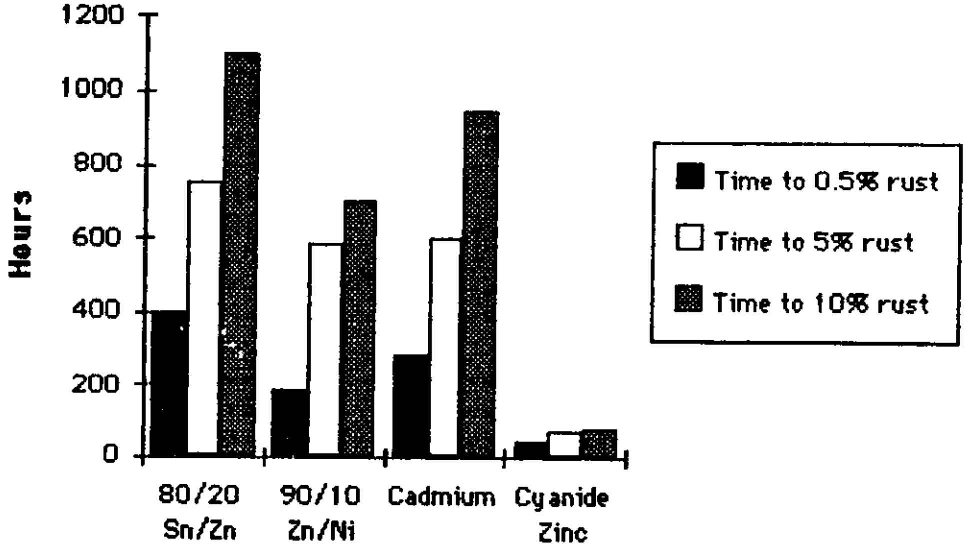

Figure 2. Salt-spray test results (ASTM B117) for unpassivated corrosion protective coatings

The appearance of a 'white' corrosion product has not been discussed because tin-zinc forms only minimal 'white-rust'. This manifests itself as surface staining, rather than as the unsightly, voluminous corrosion product associated with pure or high percentage zinc coatings. Therefore, tin-zinc could be used in many areas of application without chromate passivation. If, however, passivation is required, perhaps only for aesthetic reasons, it has been shown that a yellow passivate can be applied with the benefit of increased corrosion protection (Table 3).

With regard to other properties, the hardness of tin-zinc lies between that of tin and zinc, approximately 37 HV, but nevertheless it has good frictional properties, and good wear resistance, especially when lubricated. The coating is very ductile, and plated articles can be subjected to considerable deformation without impairment of the properties of the coating. It is solderable and has been found to be superior to pure tin for the resistance welding of coated mild steel sheet[6].

Conclusion

It is envisaged that the 1990's will see a revival in the usage of tin-zinc coatings. As a result of the properties of the coating, potential applications may arise in:

a) the automotive industry; for plating fasteners and components, such as on the fuel and brake lines.

b) the aerospace industry; where the absence of corrosion is of paramount importance, and where tin-zinc could be used as a replacement for cadmium.

c) the construction industry; for coating not just fasteners and general equipment, but also steel panels, as was recently used for the refurbishment of the Philadelphia City Hall[7].

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References

1. Miller, P. J., and Cuthbertson, J. W., *Metal Finishing*, 47, No. 44 (1949)
2. Lowenheim, F. A., and MacIntosh, R. M., *J. Electrodep. Tech. Soc.* 27, No. 115 (1991)
3. Angles, R. M., *J. Electrodep. Tech. Soc.*, 21, No. 45, (1946)
4. Cuthbertson, J. W. and Angles, R. M., *J Electrochem Soc.*, 94, No.73 (1948)
5. British Patent Applic. Nos. 9018984.6, 1990, and 9112289.5, 1990, International Patent Applic. No. PCT/GB1/1473 PCT/GB91/1473. S. J. Blunden and O. A. Ashiru, inventors; filed under B. T. K. Barry and R. R. Dean
6. Price, J. W., *Tin and Tin Alloy Plating* , Electrochemical Publications, Ayr, Scotland (1983)
7. Mason, B. J., Mazia, J. and Mooney, T., *Plating and Surface Finishing*, July, 20 (1989)

Table 1. Electrolyte composition.

	RACK PLATING		BARREL PLATING	
	g/L	(oz./gal.)	g/L	(oz./gal.)
TIN (ADDED AS POTASSIUM STANNATE)	80-100	(10.7-13.4)	45-55	(6.0-7.3)
ZINC (ADDED AS POTASSIUM ZINCATE)	2.5-3.0	(0.33-0.4)	2.5-3.0	(0.33-0.4)
FREE KOH	40-50	(5.3-6.7)	40-50	(5.3-6.7)
COMPLEXANT STABILIZER	190-210	(25.4-28.0)	90-110	(12.0-14.7)
GRAIN REFINER/BRIGHTENER	16-20	(2.1-2.7)	8-12	(1.1-1.6)

Table 2. Operating parameters

	RACK PLATING	BARREL PLATING
TEMPERATURE	60-70° C	60-70° C
CATHODE C. D.	0.5-2.0 A/dm^2 (4.6-18.6 A/ft^2)	0.5-1.5 A/dm^2 (4.6-13.9 A/ft^2)
CATHODE EFFICIENCY	90-95%	80-85%
ANODES	TIN-ZINC OR INERT	TIN-ZINC OR INERT

Table 3. Salt-spray corrosion data (ASTM B117) for 8μm 80%tin/20%zinc coatings on mild steel (15 X 10 cm)

NO. OF SAMPLES	% RED RUST	HOURS TO RED RUST	
		AVERAGE	ST. DEV.
19[a]	0.5	389	108
19[a]	5	771	127
16[a,b]	10	1181	198
6[c]	0.5	>1500	-

a. Unpassivated samples

b. Three of the samples had not reached 10% red by the termination of the test at 1500 hours.They are therefore not included in the calculation of the average and standard deviation times.

c. Passivated samples