Passivation and Corrosion Resistance Of Tin-Zinc Alloy Electrodeposits on Steel

By M.E. Warwick and P.E. Davis, CEF

The protection of steel by tin-zinc alloy electrodeposits may be increased significantly by passivation in solutions containing oxoanions of chromium, molybdenum, and tungsten. Treatment conditions affect the corrosion of both the basis metal and the coating. Although bichromate treatments gave the best results in accelerated and natural weathering tests, further development of processes based on molybdenum and tungstate oxoanions may prove advantageous.

Electroplated tin-zinc alloy coatings impart corrosion protection to steel and are reasonably solderable. in certain situations, the alloy deposit offers advantages compared with both zinc and cadmium, and serious consideration has been given to the substitution of tin-zinc for cadmium in a number of industrial laboratories.

The equilibrium diagram for tin-zinc shows a simple eutectic system with, low primary solid solutions. Plated alloys have been shown to be two-phase mixtures of pure tin and zinc.[1] The phases are so finely mixed that the coating appears to be single-phase in the as-deposited condition, and islands of zinc appear only after aging at 150° C for 1 hr.

The electrode potentials of tin and zinc are far apart, and it is not possible to codeposit them from simple acid solutions. The use of fluoborate and fluorosilicate electrolytes has been examined,[2] and a mildly acidic bath based on sodium gluconate, triethanolamine, and the sulfates of tin and zinc has been proposed.’ These solutions all require addition agents to achieve smooth deposits, however, and operating difficulties with each have prevented commercial exploitation.

In alkaline solutions of stannate and zincate, zinc is preferentially deposited; such deposition is inhibited by the addition of suitable complexants. The most effective complexant found so far is the cyanide ion. Cyanide-stannate electrolytes based on both sodium[4]’ [5] and potassium” salts are probably the only systems in commercial use.

Considerable work was carried out on baths in which cyanide was replaced by the N-hydroxyethyl-ethylenediamine triacetic acid trisodium salt.[7] The encouraging results suggest that further study is warranted, particularly in view of growing resistance to processes employing cyanide. An alkaline tin-zinc electrolyte using Sn^{2+} salts and pyrophosphate as the principal completing agent has also been described,[8,9] but this solution requires an addition agent and may not be capable of producing deposits over the entire tin-zinc composition range.

Tin-Zinc Alloys

Tin coatings on steel act as an inert barrier to protect the substrate from corrosion. Thus, porosity, and hence coating thickness, controls rusting. When a coated sample is placed in an aggressive environment, initial corrosion of the exposed substrate occurs very quickly. However, tin is attacked slowly in most environments and it has a high hydrogen overpotential. Consequently, the corrosion rate of the basis material after the first appearance of rust may be quite slow.

In contrast to tin, zinc galvanically protects steel in a number of environments, and in doing so produces a white corrosion product which itself can be a problem in some applications. The corrosion of zinc-plated steel is normally delayed by this galvanic action, but once the coating has been depleted, rusting can proceed rapidly.

Because tin-zinc electrodeposits area simple mixture of the component metals, their behavior in protecting steel substrates combines the benefits of both. Making comparisons between tin, zinc, and tin-zinc deposits, however, can be difficult. Tin and tin-rich deposits may show some early substrate corrosion and little coating corrosion, while zinc and zinc-rich finishes may themselves corrode while protecting the basis metal. As corrosion proceeds, the tin and tin-rich deposits may show little further degradation, while zinc and zinc-rich coatings may allow progressively further rusting of the steel.

Studies of the corrosion resistance of steel plated with tin-zinc alloys were recently reviewed, [1O] and, despite one report, [11] it is generally accepted that the best coatings contain about 25 percent Zn. Such coatings were superior to both zinc and cadmium in salt spray tests, while they were equal to cadmium and superior to zinc in humidity tests.[12] In outdoor tests, the order of merit for zinc, tin-zinc, and cadmium coatings was affected by the environment. The alloy coating was never the worst of the three and never much inferior to the best. Tin-zinc can thus be recommended as a good general-purpose finish.

Little attention has been paid to the possible advantages of applying a conversion coating to tin-zinc electrodeposits. However, it has been demonstrated that immersion in solutions based on Cr^{6+} oxoanions can produce transparent films that increase the resistance of the coating to finger-staining.[12] Accelerated corrosion tests of passivated samples seem to show increased corrosion resistance,[II] but there is some doubt as to whether the same occurs during natural weathering. “’” It was for that reason that this study was undertaken. Also, because of the growing resistance to the use of chromium-based treatments, other types of treatment solutions were tested.

Electrodeposition Procedures

As a rule, this project was carried out on cold-rolled mild steel plated with 10 ±1 µm of Sn/25-28 percent Zn alloy. The steel was the grade used as the basis material for electrolytic tinplate[15] and requires only limited preparation for plating. This was achieved by cathodic decreasing in 3 percent trisodium phosphate solution at 70° C for 20 sec. then anodically for 5 sec. After rinsing, the steel was pickled for 30 sec in 50 percent HCl, rinsed again, and immersed immediately in the plating solution. In a more limited series of experiments, low-alloy steel panels (SAE 4130) were cleaned by abrasive blasting with alumina and solvent degreased in 1,1,1-trichloroethane before receiving the same decreasing and pickling treatments as the mild steel samples.

A 12-L mild steel tank, heated from below by a gas burner, was used to contain the sodium stannate/zinc cyanide electrolyte. The bath was operated with tin-zinc anodes under the conditions summarized in Table 1.[16] Because the composition and thickness of the deposit could be expected to influence the corrosion test results, bath operating parameters were closely controlled. Destructive testing of plated panels was carried out twice daily, and, providing both tests met the composition and thickness requirements, the samples produced in the intervening period were also considered to be acceptable.

Plated samples were thoroughly rinsed in running water and most were given one of the passivation treatments to be described. However, some samples were left untreated, while others were left unpassivated for up to four weeks, at which time these were split into two groups. The first was passivated in the “aged” condition, while the second was immersed in dilute hydrochloric acid to remove surface oxides before rinsing and passivation.

Passivation Treatments

The simplest passivation treatments (A,B,C in Table 2) applied to the tin-zinc deposits on steel consisted of a 30-sec immersion in 0.1 M chromic acid at pH 0.2 to 0.4. The pH was controlled by adding sulfuric acid, and the solution temperature was maintained at 30, 50 or 60° C. Similar treatments had already been shown to confer improved fingerstain resistance on tin-zinc coatings.[12] Limited experiments were carried out with a 10-sec immersion in a treatment solution containing 180 g/L of sodium dichromate and 3 mL/L of sulfuric acid at room temperature (D). A similar process for zinc coatings has been patented. ”

Electrolytic treatments using Cr^{6+} oxoanions (E, F, G) were based on 0.1M sodium bichromate solution at room temperature and pH 4. A current density of 30 to 40 mA/cm^2 was employed either catholically (30 see) or in a cathodic/anodic sequence (60/15 sec or 20/5 see). A number of authors have examined the cathodic and anodic polarization of tin[18,20] and zinc[19,21] in this and similar solutions, indicating the possibility of passivation of both metals.

Similarly, polarization studies have shown that tin and zinc exhibit a tendency to become passivated in both molybdate and tungstate solutions.[18,20-23] A decision was therefore made to study the effect on corrosion performance of cathodic polarization of the coated samples in 0.1 M solutions of sodium molybdate (H) and sodium tungstate (J, K) at room temperature. The molybdate solution, made from the sodium salt, had a pH of 7, and a cathodic current of 10 to 15 mA/cm^2 was applied for 30 sec. The tungstate solution, which was also made from the sodium salt, was brought to pH 9 by adding sodium borate, and the test piece was polarized catholically at 5 mA/cm^2 for 60 sec. In addition, alternating anodic/cathodic polarization and current conditions were carried out through 10 cycles, holding each current reversal for 10 sec. This treatment has been shown to produce a conversion coating on tin-plated steel[24] and it conferred additional rust resistance to the substrate.

Table 1
Composition of Sn-Zn Alloy Plating Bath*

Constituent	Conc., g/L
Tin	30
Zinc	2.5
Free hydroxide	4-6
Free cyanide	28

*Temperature was 65 ±3° C and current density (anodic and cathodic) was 1.7 A/dm^2.

Corrosion Tests

In most cases, plated panels measuring 12.5 x 8 cm were used in the corrosion tests. Resistance to salt fog was estimated using 5 percent NaCl in the plastic chamber

Table 2
Passivation Treatments for Tin-Zinc Coatings

Treatment	Solution	Temp., °C	Procedure
A B C	0.1M CrO_3 to pH 0.2-0.4 with H_2SO_4	30 50 60	Immersion for 30 sec
D	0.6M $Na_2Cr_2O_7$ 3 mL/L H_2SO_4	20	Immersion for 10 sec
E	0.1M $Na_2Cr_2O_7$ pH 4	20	30-40 mA/cm^2 60 sec cathodic 15 sec anodic
F			30-40 mA/cm^2 20 sec cathodic 5 sec anodic
G			30-40 mA/cm^2 30 sec cathodic
H	0.1M Na_2MoO_4 pH 7	20	10-15 mA/cm^2 30 sec cathodic
J	0.1M Na_2WO_4 to pH 9 with $NaBO_3$	20	5 mA/cm^2 60 sec cathodic
K			5 mA/cm^2 10 sec cathodic 10 sec anodic for 10 cycles

conforming with British Standard 3900, Part 4, but operated at room temperature. The main program of study was carried out with all the test pieces exposed in the chamber at the same time. However, studies on the effects of pre-passivation aging and the type of steel used, along with the extended corrosion test of samples treated in chromium-based solutions, were carried out separately.

A humidity test was performed in a cabinet with a nominal relative humidity of 100 percent. It was operated according to British Standard 3900, Part F2, with a temperature cycle of 1 hr from 42 to 48° C and no dwell time.

Natural weathering was achieved by exposing test panels on the roof of the International Tin Research Institute's building west of London, England. Exposure was arranged according to British Standard 3900, Part F6, and was continued for two years. The local atmospheric conditions may be described as a mild urban environment with some light industry.

Test Data

The results of salt spray tests on steel plated with tin-zinc alloy are summarized in Table 3. Treatments based on chromic acid (A, B, C) stimulated corrosion of the substrate. The dip bichromate (D) and the molybdate and tungstate treatments (H, J, K) had some effect on the corrosion of the coating, although this requires some amplification. It was not always easy to decide when the molybdate and tungstate treatments had broken down and zinc corrosion had begun because the surface tended to darken during the course of all corrosion tests.

The tungstate treatments (J, K) did not delay the onset of substrate rusting, but the molybdate (H) had a significant effect. However, by far the best rust resistance was achieved with the treatments based on the bichromate anion. It was not possible to differentiate between these treatments (D, E, F); therefore, a longer salt spray test was conducted, using both mild steel and low-alloy steel substrates. Table 4 shows that with SAE 4130 steel, and possibly with mild steel, a simple immersion in bichromate solution (D) gave the best results. Aging tin-zinc electroplated panels before treatment in bichromate had no significant effect on the performance of the passivation films with respect to either zinc or iron corrosion. This was true whether the treatment was applied to the aged surface or to the aged coating that had been activated by immersion in dilute hydrochloric acid.

Available humidity test results are shown in Table 5. As with the salt spray test, the chromic acid treatments (B, C) produced the poorest performance, the tungstates (J, K) were better, and the molybdate (H) produced good substrate corrosion resistance. The bichromate treatments (F, G) showed the best results for both zinc and iron corrosion, and the appearance of rust at only the bottom edge of the test piece suggests the actual performance was even better than that shown in Table 5.

As might be expected, the results of the weathering tests were much more complex and difficult to summarize (Table 6). Choosing different criteria for failure (e.g., zinc corrosion, first appearance of rust, and time for 10 percent coverage by rust) could significantly affect the order of merit for each surface treatment. However, it is possible to make some general remarks that apply to all the finishes. Iron corrosion, which often occurred before zinc corrosion, typically appeared at the edges of the test pieces and moved progressively toward the center. In the accelerated

Table 3
Salt Spray Test Data for Passivated Tin-Zinc Coatings

Treatment	Time required for corrosion, days	
	Zinc	Iron
Unpassivated	<2	23
A	<2	2
B	<2	15
C	<2	5
D	5	>150
E	21	>150
F	25	>150
G	12	>150
H	5	50
J	5	18
K	5	27

Table 4
Steel Substrate Effects on Salt Spray Test Data For Sn-Zn Coatings Treated in Cr Oxoanion Solutions

Treatment	Time required for corrosion, days	
	Mild steel	SAE 4130
B	11	No test
D	>208	>208
E	>208	78
F	69	53

Table 5
Corrosion Data for Cyclic Temperature Humidity Test

Treatment	Time required for corrosion, days	
	Zinc	Iron
A	NT*	NT
B	<1	1
C	<1	1
D	NT	NT
E	NT	NT
F	154	223**
G	63	152**
H	19	165
J	12	50
K	18	50

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*Not tested

**Rust spots only at lower edge of sample. No rust elsewhere when test ended after 300 days.

tests, particularly salt spray, copious zinc corrosion products were formed and rust spots appeared randomly over the surfaces of the samples.

With the exception of chromic-acid-treated samples (A, B, C), which rusted too quickly for an effect to be noted, all the passivation films delayed the onset of zinc corrosion in the weathering tests. Samples given a molybdate or tungstate treatment (particularly K) showed early darkening of the surface, but this was not considered to be due to the formation of corrosion products. At the end of the test period, the samples given the electrolytic treatment in a tungstate solution showed no corrosion of the coating.

Although no passivation treatment extended the time before samples showed the first signs of substrate rust, treatments J and K improved resistance to outdoor corrosion. Rust appeared earlier on samples treated by methods A, B, C, E and H than on the unpassivated controls. Samples treated by methods F and G seemed initially to perform as well as unpassivated samples but eventually rusted more rapidly. Only the treatment based on low-frequency polarization in a tungstate solution showed improved performance over the entire duration of the weathering test.

Discussion

The only valid corrosion test result is that obtained under the same exposure conditions confronted in service. While accelerated tests can be useful, they can also lead to erroneous conclusions. The accelerated tests successfully predicted that treatment in acidic solutions of chromium trioxide would severely impair the capability of tin-zinc alloy coatings to protect a steel substrate. However, they underestimated the capability of unpassivated coatings to give long-term protection in outdoor environments. The tests also suggested that one of three bichromate treatments (E, F, G in Table 2) might significantly improve the performance of tin-zinc, and, although the coatings showed some merit, the best treatment (K) in the weathering tests did not fare well.

Table 6
Outdoor Weathering*

Treatment	Time required for corrosion, days		Rusted area, percent**	
	Zn	Fe	539 days	748 days
Unpassivated	120	437	2.5	45
A	None	24	100	100
B	None	24	100	100
C	None	39	100	100
D	NT***	NT	NT	NT
E	374	200	50	97
F	475	437	2.5	64
G	475	437	2	66
H	475	162	25	90
J	308	437	40	98
K	None	461	1.5	18

*Passivated tin/25 percent zinc coatings on mild steel were exposed outdoors in mild urban atmosphere. Data refer to fronts of test panels; corrosion on backs was generally same but appeared later.

**Average value for replicate panels.

***Not tested.

The difference in the mode of coating failure in the accelerated tests compared with that in the weathering tests probably explains the discrepancy in the results. Where agreement was seen (A, B, C), it is suggested that the treatment caused some dissolution of the coating, increasing porosity and thus reducing the galvanic protection afforded the substrate. In other cases, it seems probable that the passivation treatments reduced the capability of the zinc in the coating to offer sacrificial protection to any exposed steel.

During accelerated corrosion tests, the severity of the environment could have caused sufficient coating corrosion to retain a degree of substrate protection. However, in the weathering tests, the passivation films resisted attack by the mild environment and rusting was accelerated. The only clear exception to this was one of the tungstate-treated samples (K) in which both zinc and iron corrosion were inhibited. This may be explained either by assuming that coating corrosion occurred but failed to produce obvious corrosion products or that the tungstate treatment passivated both the coating and the exposed steel.

The second explanation would be consistent with the previously demonstrated effect of a tungstate treatment on tinned steel.[24] It would also explain why corrosion, which appeared at about the same time as on unpassivated samples, should progress at a slower rate thereafter on passivated than on unpassivated samples; this is in contrast with the rate of rusting on dichromated samples F and G.

Little work has been done to determine the best conditions for applying the tungstate treatment to the tin-zinc alloy coatings. The process successfully used in this study was based on the optimum one for pure tin coatings. There is therefore reason to believe that further study could improve the performance of the tungstate treatment. However, the results show that to achieve good performance under particular exposure conditions, a careful balance must be maintained between coating passivation and galvanic protection of the basis material.

Conclusions

The resistance of tin/25 percent zinc alloy coatings on steel to zinc corrosion products was enhanced by bichromate, molybdate or tungstate treatments. The resistance of the alloy-coated steel to corrosion in salt spray and humidity tests was also enhanced by such treatments. The corrosion resistance of the alloy-coated steel in an outdoor exposure test was improved by an electrolytic treatment in a solution of sodium tungstate.

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Warwick

Davis

About the Authors

Malcolm E. Warwick is head of the Metallurgy and Tinplate Division at the International Tin Research Institute (ITRI), Fraser Rd., Greenford, Middlesex, England UB6 7AQ. He received his BS degree from Nottingham University in 1669 and his PhD from London University in 1976. The division performs research on tin plating, soldering, general metallurgy, powder metallurgy, electrochemistry, and other applications of tin and its alloys.

Paul E. Davis, CEF, is manager of the Tin Research Institute, Inc., 2600 El Camino Real, Suite 224, Palo Alto, CA 94306. Mr. Davis received his BS degree in chemistry from the University of Michigan in 1950 and worked in a plating jobshop before joining TRI as a technical consultant. He spent 23 years at Its Columbus, OH, facility before establishing the Palo Alto office In 1973. Mr. Davis Is Involved with plating of tin and tin alloys and other uses of the metal relating to electronics manufacture. He is a member of AESF, ASTM, IPC, and the Electrochemical Society.