Corrosion Evaluation of CN & Non-CN Zinc Coatings Using Electrochemical Polarization

By S. Rajendran, S. Bharathi, C. Krishna & T. Vasudevan

Electrochemical techniques can rapidly evaluate the quality of electroplated finishes relatively faster than the conventional long-term neutral salt spray test. In addition to quantifying the corrosion, they also yield mechanistic information about the corrosion process. One such application of these techniques to evaluate the corrosion resistance of zinc coatings is discussed. Comparison of two zinc coatings shows that deposits from a non-cyanide zinc bath provide excellent corrosion resistance in contrast to those from a cyanide zinc bath. Of the three types of chromate coatings tested, the least protection is provided by the blue chromate; the most protection is from olive green chromate passivation.

Historically, corrosion protection of steel by electrodeposits from commercially available cyanide, acid chloride and alkaline cyanide-free baths has dominated the literature on zinc corrosion.[1-3] Evaluating the corrosion resistance of zinc coating on steel surfaces presents a difficult analytical problem. Techniques based on salt spray (fog) exposures are commonly used to evaluate the corrosion resistance of zinc coatings. Specifications such as ASTM A164-71[4] and ASTM B201-68[5] require use of the ASTM B117 method[6] and may entail salt spray exposure for as long as 500 hr. In addition to being time-consuming, the results of this procedure are mostly subjective and therefore relatively imprecise. Because of these problems, an alternate test is needed to evaluate the corrosion protective qualities of plated samples rapidly and accurately. Because corrosion resistance is the key evaluation criterion, it is logical to consider electrochemical polarization techniques as the basis for accelerated tests. It has been established beyond doubt that corrosion of metals in aqueous environments proceeds by electrochemical processes.[7] Electrochemical measurements can, therefore, be used to study and interpret corrosion phenomena and to measure corrosion rates. In this paper, we report the results of the investigations carried out on zinc deposits obtained from cyanide and non-cyanide baths. The results of the investigations are compared with the actual salt spray corrosion test conducted on the same specimen (after masking the electrochemically tested area).

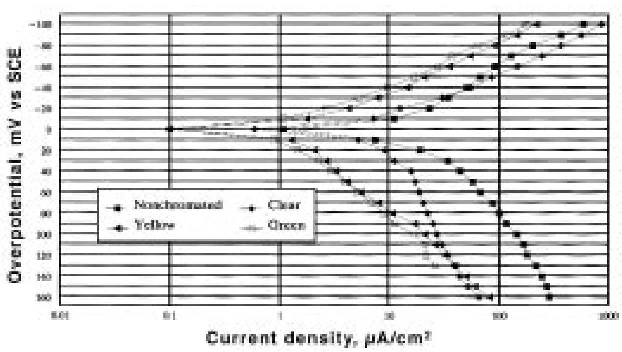

Fig. 1—Typical Tafel polarization curves for non-cyanide zinc deposits (7.5 µm) with different chromate conversion coatings.

Experimental Procedure

Conventional cyanide and non-cyanide alkaline zinc plating solutions were prepared per the supplier's recommendation. Similarly, the chromating solutions (clear blue, golden yellow and olive green) were also prepared, using the proprietary pre-mix solutions.

Mild steel specimens were plated at an optimum current density of 2 A/dm^2 after a sequence of pretreatments starting from degreasing, pickling, and electrocleaning, with in-between water rinses. Uniform electrodeposition of zinc was carried out with a proper assembly of two anodes and one cathode. Zinc coatings of various thicknesses were prepared by adjusting the Amp-hr so as to get uniform coatings of 1, 2, 4, 6.5, 7.5, 10, 12.5, 15.0, 17.5 and 20-µm thickness. The deposit thickness was measured by weight gain, coulometric, magnetic, eddy current and X-ray fluorescence methods.

Corrosion Tests

The electrochemical instrumentation consisted of a computer-controlled potentiostat/galvanostat[a] and an electrochemical corrosion cell consists of a three-electrode assembly (working electrode - plated specimen, counter electrode - graphite, and a saturated calomel electrode).

The electrochemical behavior of the samples was determined in a stagnant 5-percent analytical-reagent-grade sodium chloride solution at pH 7.0 ± 0.2. Tafel polarization was carried out on a given sample of 1 cm^2 by polarizing it to ±250 mV from the corrosion potential. The resulting current was plotted on a logarithmic scale and the corrosion current, i_{corr}, obtained by extrapolating the linear portion of the curve back to the corrosion potential.

Salt spray corrosion tests were also carried out, using a neutral 5-percent solution of NaCl. The specimens were arranged in a salt spray cabinet and exposed in accordance with ASTM B-117.[6]

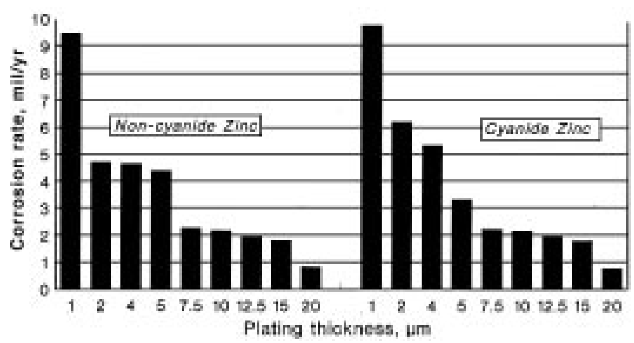

Fig. 2—Influence of plating thickness on corrosion rate of zinc deposits with golden yellow passivation.

Table 1
Tafel Polarization Results of Non-Cyanide Zinc Plating With Different Chromate Conversion Coatings (7.5 µm on mild steel)

Finish	E_{corr} V vs. SCE	βa mV/dec	βb mV/dec	i_{corr} µA/cm²	C.R. mil/yr
Mild steel	-0.6936	92.21	237.2	36.23	16.63
Pure zinc	-1.0320	83.79	119.0	38.13	18.76
Zinc plating					
Non-chromated	-1.0760	93.30	123.2	40.32	23.77
Clear blue	-1.0000	49.39	200.9	9.19	5.42
Golden yellow	-1.0270	58.85	101.4	3.87	2.28
Olive green	-1.0450	34.18	80.86	0.87	0.51

Table 2
Tafel Polarization Results of Cyanide Zinc (non-chromated finish on mild steel)

Thickness µm	E_{corr} V vs. SCE	βa mV/dec	βb mV/dec	i_{corr} µA/cm²	C.R. mil/yr
1.00	-1.168	87.20	206.90	73.23	43.17
2.00	-1.165	69.85	122.10	58.71	34.61
4.00	-1.172	148.20	178.10	47.28	27.88
5.00	-1.180	185.50	113.60	36.63	21.60
6.50	-1.158	107.60	175.00	31.44	18.54
7.50	-1.125	264.20	107.30	21.68	12.781
10.00	-1.143	192.20	118.40	18.16	10.710
12.50	-1.151	52.42	110.70	11.59	6.833
15.00	-1.151	118.60	283.60	11.01	6.486
17.50	-1.139	100.10	135.20	10.07	5.755
20.00	-1.150	69.39	200.90	9.19	5.420

Results and Discussion

Figure 1 shows the typical Tafel polarization curves for cyanide-free alkaline zinc plating (7.50 µm thickness) on steel with different chromate conversion coatings. The corrosion potential of mild steel in 5-percent NaCl solution normally occurs between -600 to -650 mV vs. SCE (Saturated Calomel Electrode), whereas zinc-plated steel shows the corrosion potential between -950 to -1150 mV. Table 1 shows Tafel extrapolation results of curves depicted in Fig. 1. The highest corrosion rate was obtained with the non-chromated zinc deposits, indicating least corrosion resistance.

With the application of other chromate conversion coatings, the corrosion rate is found to be reduced and the corrosion resistance increased. A non-chromated cyanide-free alkaline zinc deposit shows a corrosion rate of 20.66 mil/yr, a clear passivated ones show 5.419 mil/yr, golden yellow passivated ones show 2.283 mil/yr, whereas green passivated deposits show 0.513 mil/yr.

Tables 2-5 show the polarization potential, E_{corr}, Tafel constants $ß_a$ and $ß_b$, and the corrosion rate calculated from the Tafel polarization curves for cyanide zinc platings of various thicknesses ranging from 1 to 20 µm without chromate (Table 2), with clear blue passivation (Table 3), with golden yellow passivation (Table 4), and with olive green passivation (Table 5). Tables 6-9 show the Tafel polarization results for non-cyanide alkaline zinc deposits of various thicknesses, without chromate (Table 6), with clear blue passivation (Table 7), with golden yellow passivation (Table 8), and with olive green passivation (Table 9).

Influence of Plating Bath

Tables 2-5 show the Tafel polarization results of cyanide zinc plating of various thicknesses with different passivation. Tables 6-9 show the results for non-cyanide zinc deposits. In nearly all cases, comparatively lower corrosion rates are obtained from non-cyanide zinc deposits. Comparison of cyanide and non-cyanide alkaline zinc plating baths shows that the non-cyanide zinc deposits appeared to offer better corrosion resistance. The observed differences in corrosion resistance could result from the nature, structure and grain size difference in the deposit.[8] Structure and morphology of the zinc deposits vary with the type of plating baths and the additive systems used for the deposition.

Influence of Plating Thickness

Plating thickness is the prime factor in assessing the corrosion performance of zinc coatings. It is usually considered that the protective capability of a zinc deposit is determined by its thickness. The corrosion resistance of zinc-plated steel is directly proportional to zinc thickness. Of course, post-treatment, such as chromate coatings, further extends the resistance and, as expected, zinc thick-

Table 3
Tafel Polarization Results of Cyanide Zinc (clear blue chromate conversion coating)

Thickness µm	E_{corr} V vs. SCE	βa mV/dec	βb mV/dec	i_{corr} µA/cm²	C.R. mil/yr
1.00	-1.040	62.22	177.20	15.81	9.628
2.00	-1.002	41.23	140.60	13.60	8.021
4.00	-1.002	45.98	153.20	13.14	7.748
5.00	-1.004	47.55	135.40	12.42	7.424
6.50	-1.039	55.06	183.00	11.45	6.755
7.50	-1.020	60.42	148.50	7.724	4.379
10.00	-0.997	42.38	216.60	6.913	4.077
12.50	-1.073	50.05	124.10	4.297	2.534
15.00	-1.004	45.10	170.60	2.575	1.519
17.50	-1.038	36.46	196.50	2.159	1.273
20.00	-1.104	48.45	129.08	1.734	1.022

Table 4
Tafel Polarization Results of Cyanide Zinc (golden yellow chromate conversion coating)

Thickness µm	E_{corr} V vs. SCE	βa mV/dec	βb mV/dec	i_{corr} µA/cm²	C.R. mil/yr
1.00	-1.083	66.09	112.50	16.58	9.772
2.00	-1.090	69.88	109.10	10.57	6.230
4.00	-1.001	95.58	115.50	9.092	5.360
5.00	-1.005	49.72	102.90	6.282	3.345
6.50	-1.021	31.61	129.50	4.442	2.619
7.50	-1.046	48.77	109.90	3.820	2.252
10.00	-1.041	36.78	135.00	3.679	2.178
12.50	-1.007	61.62	101.98	3.348	1.974
15.00	-1.015	82.51	105.76	3.113	1.815
17.50	-1.070	50.28	102.69	2.752	1.625
20.00	-1.087	36.51	112.50	1.329	0.783

ness is a most significant factor. Figure 2 shows the influence of plating thickness on the corrosion rate of zinc deposits (with golden yellow passivation) obtained from both cyanide and non-cyanide baths. With the increase of thickness from 1 to 20 µm, both cyanide and non-cyanide zinc deposits show gradual increase of corrosion resistance.

Influence of Chromate Conversion Coatings

It is reported[1] that the corrosion resistance of a chromate film depends on composition of the chromating solutions, the nature of the zinc substrate, the thickness of the chromate conversion layer and the composition of the plating bath. The Tafel polarization test results, for both cyanide and non-cyanide alkaline zinc deposits with different chromate conversion coatings, are shown in Tables 2-9. Figure 3 shows the consolidated corrosion rate data obtained for zinc deposits (10 µm thickness) with different chromate conversion coatings. It is clear that corrosion rate is linearly dependent on chromate conversion coatings. Of the three types of chromate conversion coatings tested, the least protection is provided by the blue chromate, and the most is by olive green chromates via media of golden yellow passivation. Accordingly, chromate conversion coatings have a substantial inhibiting effect on the zinc coating.

Comparison with Salt Spray Corrosion Test

Figure 4 shows the salt spray corrosion test results of zinc deposit of various thickness ranging from 1 to 20 µm deposited from both cyanide and non-cyanide plating baths. Figure 5 shows the salt spray corrosion test results of zinc deposits (10 µm thickness) with different chromate conversion coatings. In nearly all cases, electrochemical corrosion results are closely correlated with the actual salt spray corrosion results.

Findings

Electrochemical polarization techniques based on Tafel extrapolation methods can be used successfully to evaluate the corrosion resistance of zinc coatings and, based on the results, it becomes possible to predict salt fog test results.

As can be seen from the results cited, corrosion resistance offered by non-cyanide alkaline zinc deposits is compara-

Table 5
Tafel Polarization Results of Cyanide Zinc
(olive green chromate conversion coating)

Thickness µm	E_{corr} V vs. SCE	βa mV/dec	βb mV/dec	i_{corr} µA/cm²	C.R. mil/yr
1.00	-1.028	99.94	136.90	6.770	5.792
2.00	-0.993	58.69	181.30	5.704	3.634
4.00	-1.008	107.70	164.10	4.216	2.487
5.00	-1.020	60.00	196.20	2.874	1.695
6.50	-1.001	56.77	170.80	2.041	1.204
7.50	-1.006	51.42	141.30	1.835	1.082
10.00	-1.006	58.48	148.35	0.897	0.554
12.50	-1.008	43.71	132.50	0.768	0.453
15.00	-1.009	58.51	174.89	0.421	0.285
17.50	-1.019	89.57	124.90	0.406	0.240
20.00	-1.029	107.70	164.10	0.341	0.201

Table 6
Tafel Polarization Results of Non-Cyanide Zinc
(non-chromated finish on mild steel)

Thickness µm	E_{corr} V vs. SCE	βa mV/dec	βb mV/dec	i_{corr} µA/cm²	C.R. mil/yr
1.00	-1.105	99.29	103.60	52.71	31.01
2.00	-1.084	45.85	132.90	40.32	23.77
4.00	-1.115	79.04	99.23	20.43	12.05
5.00	-1.064	58.90	96.13	19.36	11.41
6.50	-1.058	65.80	109.50	15.36	9.05
7.50	-1.112	64.75	75.04	14.61	8.62
10.00	-1.102	65.40	118.40	13.74	8.10
12.50	-1.105	52.42	110.70	11.59	7.85
15.00	-1.121	118.60	183.60	10.68	6.50
17.50	-1.045	52.42	110.90	9.77	5.75
20.00	-1.065	65.40	105.60	7.26	4.23

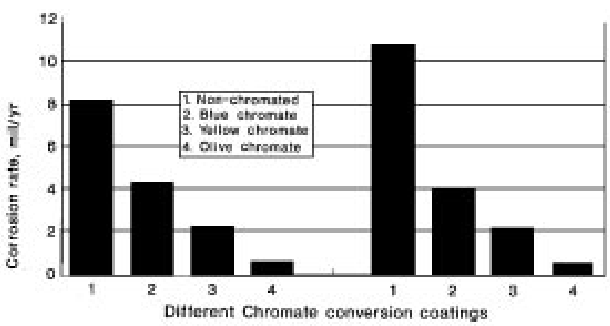

Fig. 3—Influence of chromate conversion coating on corrosion rate of 10-µm-thick zinc deposit.

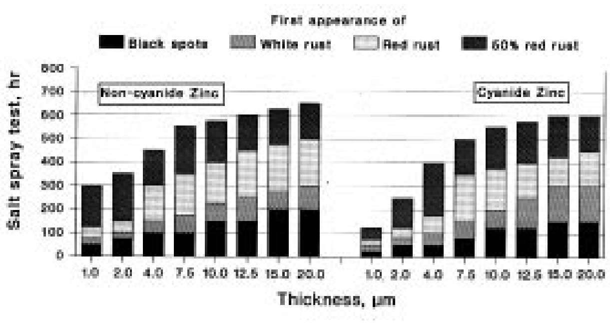

Fig. 4—Influence of plating thickness on salt spray corrosion resistance of zinc deposits with golden yellow passivation.

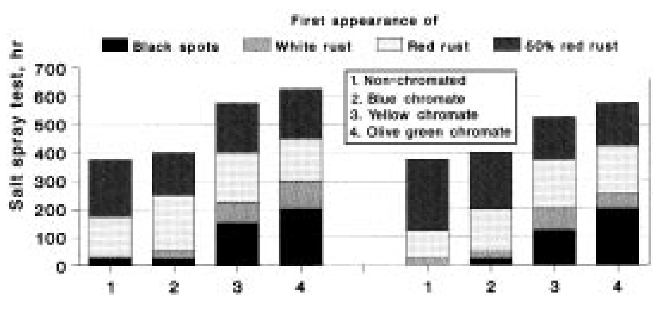

Fig. 5—Salt spray corrosion resistance of zinc deposits with different chromate conversion coatings.

Table 7
Tafel Polarization Results of Non-Cyanide Zinc (clear blue chromate conversion coating)

Thickness µm	E_{corr} V vs. SCE	βa mV/dec	βb mV/dec	i_{corr} µA/cm²	C.R. mil/yr
1.00	-1.008	58.90	95.21	14.61	8.614
2.00	-1.020	46.33	236.68	13.05	7.691
4.00	-1.012	52.46	133.20	11.89	6.996
5.00	-1.000	34.45	129.90	11.59	6.831
6.50	-1.012	65.63	190.50	9.04	5.321
7.50	-1.021	62.46	208.00	7.76	4.575
10.00	-1.007	64.83	106.50	7.26	4.279
12.50	-1.023	75.50	242.00	3.73	2.200
15.00	-1.014	38.25	117.30	2.25	1.331
17.50	-1.023	56.46	91.02	1.67	0.985
20.00	-1.014	68.50	88.96	0.87	0.513

Table 8
Tafel Polarization Results of Non-Cyanide Zinc (golden yellow chromate conversion coating)

Thickness µm	E_{corr} V vs. SCE	βa mV/dec	βb mV/dec	i_{corr} µA/cm²	C.R. mil/yr
1.00	-0.9591	44.79	144.30	16.07	9.474
2.00	-1.005	55.93	58.04	8.017	4.727
4.00	-1.001	65.58	115.50	7.920	4.651
5.00	-0.917	90.72	102.90	7.468	4.403
6.50	-1.021	61.61	112.50	4.221	2.375
7.50	-1.034	48.77	109.90	3.481	2.286
10.00	-1.041	36.78	135.00	3.679	2.178
12.50	-1.007	61.62	100.01	3.341	1.969
15.00	-1.015	82.51	105.76	3.113	1.815
17.50	-1.070	50.28	102.69	2.217	1.307
20.00	-1.083	59.06	100.00	1.270	0.849

Table 9
Tafel Polarization Results of Non-Cyanide Zinc (olive green chromate conversion coating)

Thickness µm	E_{corr} V vs. SCE	βa mV/dec	βb mV/dec	i_{corr} µA/cm²	C.R. mil/yr
1.00	-0.992	91.59	63.92	7.490	4.368
2.00	-0.993	45.69	81.30	6.430	3.795
4.00	-1.008	100.70	129.40	3.127	2.166
5.00	-1.015	48.92	134.80	2.282	1.346
6.50	-1.008	65.33	78.80	1.880	1.109
7.50	-1.008	53.42	61.86	1.600	0.943
10.00	-1.010	58.48	148.35	0.780	0.588
12.50	-1.024	43.71	132.50	0.768	0.453
15.00	-0.998	85.35	40.52	0.643	0.379
17.50	-1.071	89.57	120.40	0.351	0.207
20.00	-1.072	43.50	100.20	0.335	0.197

tively better than that obtained from cyanide baths. Application of chromate conversion coatings substantially reduces corrosion rates and provides an inhibiting effect for zinc against corrosion. Moreover, plating thickness plays an important role in determination of the corrosion resistance of zinc coatings.

[a] *Model-263, EG&G Princeton Applied Research Corp., Princeton, NJ*

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Session at SUR/FIN '97 "Corrosion in Electronics" Will Honor Dick Baker
The "Corrosion in Electronics" Session, scheduled for June 25 and organized/chaired by Dr. I-yuan Wei, AMP, Inc., Harrisburg, PA, will be dedicated to the honor of Richard E. Baker, CEF-SE, of Baker Consultants, Winter Springs, FL. Mr. Baker's career of more than 40 years in the telecommunications industry focused on the study of corrosion in electronics.
SUR/FIN '97 details to be announced soon