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COMPARATIVE CORROSION RESISTANCE OF
ZINC COATINGS PREPARED FROM
MINES BRANCH AND COMMERCIAL
CYANIDE PLATING BATHS

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Comparative Corrosion Resistance of Zinc Coatings
Prepared from Mines Branch and Commercial
Cyanide Plating Baths

by

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ABSTRACT

The corrosion resistance of zinc coatings deposited on mild steel from one Mines Branch and three commercial cyanide plating baths were compared by the following three testing methods: (a) neutral salt spray, (b) humidified SO_2-air, and (c) combined humidified SO_2-air and environmental chamber. No significant difference in corrosion rate was found when coatings of equal thickness prepared from the four different baths were tested under identical conditions. The corrosion resistance of the zinc coatings at various thickness levels indicated that the service lives of the coatings depended on the thickness of zinc applied and not on the type of bath from which the zinc was deposited.

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La Résistance comparative à la corrosion
des dépôts de zinc dans des bains de
placage de cyanure de zinc

par

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Résumé

Les auteurs ont comparé la résistance à la corrosion
du zinc déposé sur l'acier doux de quatre bains de placage de
cyanure de zinc, un de la Direction des Mines et les trois
autres de l'industrie, en suivant trois méthodes d'essais:
(a) le brouillard salin (neutre), (b) l'air-SO_2 humidifié,
(c) la combinaison de deux méthodes: l'air-SO_2 humidifié et la
chambre pour contrôler les conditions de l'environment. Ils
n'ont pas trouvé de différence significative dans la vitesse
de corrosion quand les couches de la même épaisseur préparées
de quatre bains différents ont été mises à l'essai sous des
conditions identiques. La résistance à la corrosion des dépôts
à épaisseur variée a indiqué que les durées de service des
couches dépendent de l'épaisseur du zinc appliqué et non pas
du type de bain dans lequel le zinc était déposé.

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INTRODUCTION

In previous Mines Branch investigations, Dingley and Bednar[1,2] improved the cyanide zinc plating bath and the plating process. The more important improvements of the Mines Branch bath as compared to the conventional ones were greater stability of plating solution, higher cathodic current efficiency, and less hydrogen embrittlement of steel.

In the course of their study, they also found that zinc coatings deposited from a commercial cyanide bath contaminated with iron, nickel, copper, and chromium gave spots of dark corrosion products after immersion in distilled water exposed to the air at 70°F. However, in similar experiments using plating baths made from pure chemicals, the zinc coating did not give dark spots. Accordingly, they purified the contaminated bath by means of zinc-dust electrolysis and performed the same exposure experiment with the coatings obtained, and no dark spots were observed. They further developed a hydrochloric acid test to compare the dissolution rates of the zinc coatings, based on the principle that pure zinc is attacked comparatively slowly by dilute acids and that small proportions of other materials in the zinc increases its rate of dissolution. In the test, they measured the dissolution rates of the zinc coatings in a 10 % HCl solution in terms of hydrogen evolved, and found that the rate was higher when the coating was deposited from an unpurified bath than when it was deposited from a purified bath. They concluded that the poor

resistance to corrosion of zinc coatings from unpurified baths was due to the presence of the contaminents, Fe, Ni, Cu, and Cr.

However, they did not compare the corrosion resistance of zinc coatings obtained from the Mines Branch bath and those from purified commercial baths. The purpose of this study was to investigate the Mines Branch zinc coatings to find out whether their resistance to corrosion was also significantly improved.

EXPERIMENTAL

Preparation of Zinc Coatings

Four types of cyanide plating baths (Mines Branch bath and conventional baths of both high and low contents of cyanide were used to electrodeposit zinc on mild steel panels. The compositions of the bath are shown in Table 1. The experimental set up consisted of a cylindrical cell containing $6\frac{1}{2}$ litres of plating solution into which the 3 x 5-inch mild-steel cathode and the zinc anode were suspended. Procedures for surface preparation of cathodes were essentially those of Dingley and Bednar[1,2]. They consisted of trichlorethylene vapor degreasing followed by HCl (18%) pickling under the influence of ultrasonic vibrations. The area ratio of anode to cathode was 2 to 1. The cathodic current density was maintained at 25 or 30 A/ft^2 by an Anotrol Potentiostat. The plating temperature was 30°C.

TABLE 1

Composition of Plating Baths (g/1)

	ZnO	NaCN	NaOH
Mines Branch Bath	49.5	87.5	118.6
Conventional Bath A	45.0	75.0	15.0
Conventional Bath B	44.0	90.0	75.0
Conventional Bath C	5.7.0	132.0	56.0

To secure uniform thickness of coatings, edges of steel panels were protected from excess current by means of a plastic shield. Coating thicknesses were measured by an Accuderm thickness gauge at 10 different locations on the panel. These readings were, in most cases, within 10 % of the nominal coating thickness on the panel.

Corrosion Testing Techniques

The techniques used to compare the corrosion resistance of the zinc coatings consisted of neutral salt spray, humidified SO_2-air and combined humidified SO_2-air, and environmental chamber testing methods.

In the neutral salt spray test, sample panels in triplicate were tested in the salt spray cabinet according to an ASTM standard[3]. The composition of the salt fog was maintained

constant and uniform by means of a "uni-fog" dispersion tower, a salt solution level control and a humidifying tower water level control (manufactured by the G.S. Equipment Company, Cleveland, U.S.A.). The cabinet was opened once every 24 hours and the panels were examined for signs of corrosion of the base metal. The protective value, as "time elapsed before the first sign of rust", was recorded and the panels were returned to the cabinet. After 75 % of the surface area was covered with rust, the panel was removed from the cabinet and the corrosion products were removed from the panel by cathodic treatment in a 5 % disodium phosphate solution at a c.d. of 5 A/ft^2. The corrosion rate of the coating was then evaluated.

In the humidified SO_2-air test, sample panels in duplicate were exposed to SO_2-air mixture in an air-tight perspex chamber, which was a modification of the unit used by Edwards[4]. The concentration of the gas mixture (1% SO_2) was controlled by gas flowmeters and Orsat analysis, and maintained uniform by a continuous inflow of fresh gas mixture and outflow of used gases. The testing conditions of the chamber were 95 to 99 % R.H. and a dry bulb temperature of 80 to 85°F. During the course of the experiment, water condensed on the panel surface to form sulfurous acid, and the entire surface was covered with white corrosion products consisting mainly of zinc sulfate. Corrosion products of steel were not obtained and "time to first sign of rust" could not be used

to report the testing results. The corrosion rate was therefore evaluated on the basis of 14 days exposure in the perspex chamber.

In the combined humidified SO_2-air and environmental chamber test, sample panels in duplicate were exposed in the SO_2 cabinet with conditions described above for 24 hours, and then in the environmental chamber (Model 1247LP, manufactured by Hotpack Company, Waterloo, Ontario) for a predetermined duration of time to form a testing cycle. The testing cycle was repeated until 75 % of each panel surface was covered with rust. Two cycles were used in this test. One cycle consisted of a 24-hour SO_2-air exposure followed by a 24-hour exposure in the environmental chamber; the second cycle consisted of one day of SO-air exposure followed by a 6-day exposure in the environmental chamber. Rusting of base metal was developed after the panels were in the environmental chamber and the first sign of rust was recorded. In the environmental chamber, the dry bulb temperature was kept constant at 50°C while the relative humidity varied uniformly between 50 % and 95 % over a period of 6 hours.

RESULTS AND DISCUSSION

Table 2 summarizes the results of corrosion testing by the neutral salt spray method. The corrosion rates (mdd) of four different types of zinc coatings were of similar magnitude. There was no trend that one rate was consistently lower than the other. The protective values given by "time to first sign of rust" showed wider variation among thinner coatings (0.5 mil), but, for
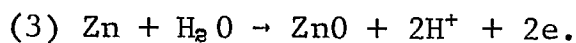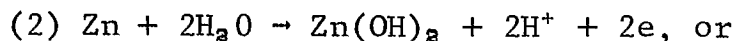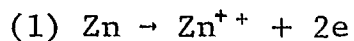
TABLE 2

Results of Neutral Salt Spray Test

Zn Coating	Coating Thickness (mil)	Time to First Sign of Rust (hr)	Corrosion Rate[*] (mdd)
Mines Branch	0.5	168	62.0
		168	55.0
		168	58.0
	1.0	408	55.2
		384	58.8
		408	52.4
	1.5	792	46.2
		984	46.2
		960	45.0
Commercial A	0.5	144	58.0
		168	59.0
		168	58.0
	1.0	360	60.0
		384	60.8
		360	61.6
	1.5	912	50.0
		936	49.2
		792	43.2
Commercial B	0.5	144	54.0
		120	56.0
		120	61.0
	1.0	384	59.2
		384	59.2
		384	60.8
	1.5	888	45.2
		864	44.5
		936	46.2
Commercial C	0.5	120	59.0
		120	53.0
		120	58.0
	1.0	384	52.8
		336	57.6
		408	50.4
	1.5	984	46.0
		816	47.0
		936	44.2

[*]Based on 75 % of surface corroded.

the thicker coatings (1.5 mil), the Mines Branch coatings and
commercial bath C coatings on the average offered approximately
4 % longer service life than the coatings from the commercial
baths A and B. Though thin coatings are not generally used in
practice[5], the figure, 4 % for thicker coatings was not signi-
ficant enough to consider that the coatings from Mines Branch and
from the commercial bath C were more resistant to corrosion.

Results from the humidified SO_2-air test (Table 3) and
the combined humidified SO_2-air and environmental chamber test
(Table 4) were in line with the above findings that no significant
difference in corrosion resistance was observed among zinc coat-
ings of equal thickness.

In protecting steel from corrosion, the role played by
zinc can be expressed in terms of barrier protection and galvanic
protection. While zinc is in contact with pure water containing
oxygen, corrosion of the metal occurs[6]. On cathodic sites,
oxygen is reduced as represented by the equation, $O_2 + 2H^+ + 4e$
$\rightarrow 2 (OH)^-$. On anodic sites, metal is oxidized according to the
following equations:

(1) $Zn \rightarrow Zn^{++} + 2e$

(2) $Zn + 2H_2O \rightarrow Zn(OH)_2 + 2H^+ + 2e$, or

(3) $Zn + H_2O \rightarrow ZnO + 2H^+ + 2e$.

Thus Zn ions either may pass into solution or they may pass into the
water layer displacing 2 hydrogen ions to form hydroxide or oxide.

TABLE 3

Results of Humidified SO_2-Air Test

Zn Coating	Coating Thickness (mil)	Corrosion Rate* (mdd)
Mines Branch	0.5	88.5
		83.0
	1.0	88.5
		90.0
	1.5	94.0
		102.0
Commercial A	0.5	89.0
		86.0
	1.0	88.0
		100.6
	1.5	102.0
		107.0
Commercial B	0.5	84.0
		95.0
	1.0	91.5
		93.5
	1.5	94.0
		107.0
Commercial C	0.5	86.0
		95.0
	1.0	90.2
		89.1
	1.5	94.0
		107.0

*Based on 14 days exposure.

TABLE 4

Results of Combined Humidified SO_2-Air and

Environmental Chamber Test

Zn Coating	Coating Thickness (mil)	Time to First Sign of Rust (days)	Corrosion Rate[*] (mdd)
Test Cycle A:	24 hr of SO_2 test followed by 144 hr of cyclic humidity test		
Mines Branch	0.5	14	14.2
		18	14.8
Commercial A	0.5	14	17.3
		14	15.1
Commercial B	0.5	14	14.8
		18	14.1
Commercial C	0.5	14	14.2
		18	19.0
Test Cycle B:	24 hr of SO_2 test followed by 24 hr of cyclic humidity test		
Mines Branch	0.5	4	90.0
		4	90.0
	1.0	16	86.0
		16	86.0
Commercial A	0.5	6	89.0
		6	88.5
	1.0	14	84.0
		18	88.5
Commercial B	0.5	4	120.0
		4	84.0
	1.0	14	76.5
		16	76.5
Commercial C	0.5	6	98.0
		4	82.0
	1.0	16	76.0
		14	76.0

[*]Based on 75 % of surface corroded.

A progressive build-up of the thickness of zinc oxide or hydroxide reduces the corrosion rate of zinc. In the presence of fine salt spray, zinc chloride formed at the anodic areas reacts with sodium hydroxide formed at the cathodic areas to form an adherent layer of hydroxide[7]. Under normal atmospheric conditions, formation of corrosion products leads to protection because the inner layer of the oxide film formed is hard and dense, and restricts the diffusion of oxygen into the metal substrate[8]. In the presence of SO_2 and moisture, sulfurous acid is formed on the metal surface, and the attack on zinc is more severe[9,10].

In the electromotive series, the standard oxidation potential of zinc is - 0.76 V (SHE) and that of iron is - 0.44 V (SHE); in the galvanic series in sea water, the position of zinc is active to that of iron or steel[11]. When there are holidays in the zinc coating, the bare steel remains protected due to cathodic protection conferred by the surrounding zinc.

In the corrosion testing of zinc coatings, Sample and his co-workers[12] found that, in sodium chloride spray, cyclic humidity, and actual field exposure, the length of time a given coating thickness of electrodeposited zinc provided protection to steel was dependent upon the environment to which the coating was exposed; if the testing environments were identical, the protective value of the coatings depended on the thickness of zinc applied. Evans'[13] and Hudson's[14] work on corrosion testing

of zinc coatings obtained from various methods of preparation also showed that the service life of zinc coatings of uniform thickness depended chiefly on their thickness and weight and that the method of preparation was not important.

In this study, the protective values of all types of zinc coatings expressed as "time to first sign of rust" increased as the coating thickness increased. This result agrees with the above investigators' finding that the service life of zinc coatings of uniform thickness depend on the thickness of zinc applied and not on the baths from which the metal was deposited.

SUMMARY

1. Mild steel panels were effectively protected from corrosion by all four types of zinc coatings deposited from cyanide plating baths (Mines Branch bath and 3 conventional baths), when tested under neutral salt spray, humidified SO_2-air and combined humidified SO_2-air and environmental chamber tests.

2. No significant difference in corrosion rates (mdd) was observed among the four types of zinc coatings when they were tested under identical conditions.

3. Protective values for all four types of zinc coatings, expressed as "time to first sign of rust", indicated that the service life of the coatings depended on the thickness of zinc applied and not on the type of cyanide bath from which the zinc was deposited.

ACKNOWLEDGEMENTS

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