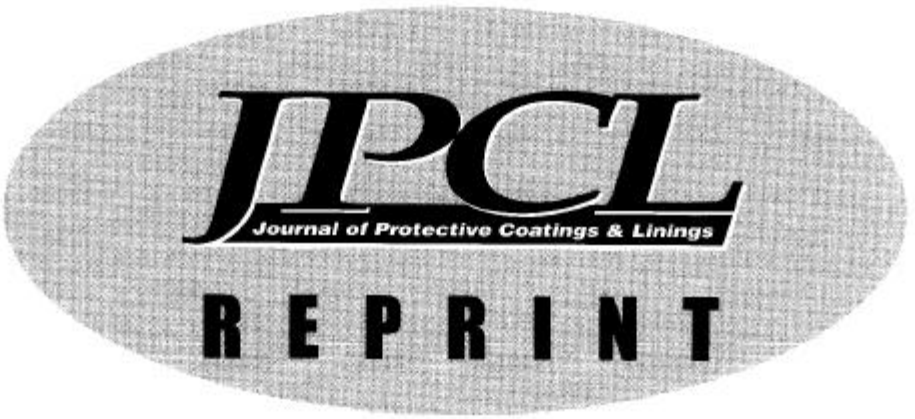

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Zinc Loadings, Cathodic Protection, and Post-Cathodic Protective Mechanisms in Organic Zinc-Rich Metal Primers

By Clive H. Hare, Coating System Design, Inc.; and Matthew Steele and Steven P. Collins, Z.R.C. Worldwide

2002 SSPC Outstanding Publication Award

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RESEARCH

The initial mechanism by which zinc-rich primers protect steel and deteriorated zinc-galvanized surfaces is ascribed to cathodic protection. An electrically continuous and, therefore, conductive zinc film is in contact with a contiguous steel or degraded galvanized substrate. Under corrosive conditions (i.e., in the presence of a continuous electrolyte), the zinc film acts as the anode of an induced corrosion cell, and the steel becomes the cathode. As long as the conductivity of the cell is preserved and sufficient zinc remains to act as an anode, the steel will be protected galvanically.

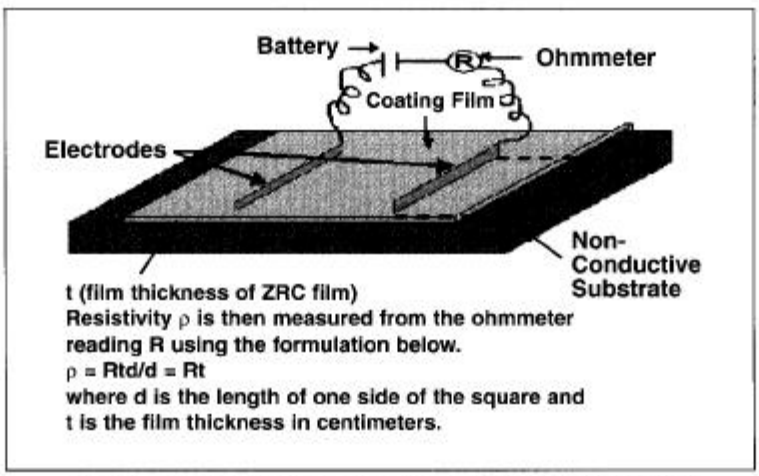

Fig. 1: Apparatus for measuring electrical resistivity of zinc-rich coating film. (Figure and photos courtesy of the authors)

The cathodic protection phase of zinc-rich protection is finite. After the zinc has corroded for some period (which appears to vary with primer type and composition), electrical conductivity diminishes enough for the current flow from the steel to the zinc to cease. The progressive loss of current flow is accompanied by a gradual build-up of zinc corrosion product on the surface of the zinc film, which polarizes the zinc.

In spite of the loss of galvanic activity, the zinc primer still protects the covered steel. However, if the film is damaged after the corrosion product has formed across the anode's surface, the protection of the exposed steel is much more limited. Protection of the covered steel by the primer during this "second phase" protection is unlikely to be galvanic in origin because of the insulative effect of the polarizing corrosion product and the lack of current flow.

Several mechanisms may underlie this second phase protection. These include inhibition of the cathode reaction by basic zinc corrosion products (Schuster[1] and Ross and Wolstenholme[2]), a locally elevated pH (Lindquist et al.[3]), and inhibition of oxygen reduction at the cathode and absorption of oxygen by the zinc (Romagnoli and Vetere[4]). More generally and in spite of the findings of Lindquist, who used electrochemical potential time and polarization techniques, corrosion control during the post-cathodic phase has been ascribed to enhanced barrier properties of the coatings.[5,6,7]

Zinc loading is critical in the initial galvanic phase of protection, and, to a lesser extent, in the secondary phase. In organic zinc-rich films, loading is entirely dependent upon the pigment volume concentration/critical pigment volume concentration (PVC/CPVC) ratio of the film, which is conventionally placed at, or near, unity. Several authors[8,9] have discussed the importance of the spatial orientation of zinc within the film to cathodic protection with organic zinc-rich films. Zinc packing geometries have been shown to significantly affect the PVC/CPVC ratio and the zinc loadings necessary for cathodic protection. Zinc loadings have been attained by controlling the weight of zinc in the dry film. Levels of zinc between 87% and 94% (depending on system and formulation) have been described as the minimum loading criteria for viable zinc-rich protection. Some zinc loading variations are possible. As the CPVC is manipulated downward by the use of small amounts of more

Table 1:
Epoxy/Polyamide Zinc-Rich Primer

	24274A	24274B	24274C	24274D	24274E	24274F	24274G	24274H	24274I
Low molecular wt. DGEBA	187.10	187.10	187.10	187.10	187.10	187.10	187.10	187.10	187.10
Wetting agent	5.90	5.90	5.90	5.90	5.90	5.90	5.90	5.90	5.90
Fumed silica	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Urea formaldehyde resin	24.60	24.60	24.60	24.60	24.60	24.60	24.60	24.60	24.60
Solvent (parachlorobenzotrifluoride)	148.00	135.90	123.70	111.60	99.50	87.40	75.20	63.10	51.00
Aromatic 100	177.00	161.50	146.00	130.50	115.00	99.40	84.00	68.50	53.00
Sub total	552.60	525.00	497.30	469.70	442.10	414.40	386.80	359.20	331.60
Polyamide resin	123.40	123.40	123.40	123.40	123.40	123.40	123.40	123.40	123.40
Fumed silica	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
n-Butanol	98.00	90.00	82.00	74.00	66.00	58.00	50.00	42.00	34.00
Aromatic 100	18.00	17.50	17.00	16.50	16.00	15.50	15.00	14.50	14.00
Sub total	241.40	232.90	224.40	215.90	207.40	198.90	190.40	181.90	173.40
Pigmentary anode (zinc dust)	5400.00	4804.00	4209.00	3613.00	3017.00	2152.00	1826.00	1230.00	635.00
Total	6194.00	5561.90	4930.70	4298.60	3666.50	2765.30	2403.20	1771.10	1140.00
Volume solids	69.70	69.70	69.70	69.70	69.70	69.70	69.70	69.70	69.70
% zinc by wt. of dry film	94.10	90.50	87.10	83.50	80.00	76.20	72.40	68.60	65.10
PVC/CPVC ratio	1.12	1.03	0.94	0.86	0.77	0.67	0.58	0.50	0.42

Table 2:
Moisture-Curing Urethane Zinc-Rich Primer

	22361A	22361B	22361C	22361D	22361E	22361F	22361G	22361H	22361I
Moisture-curing urethane	243.00	243.00	243.00	243.00	243.00	243.00	243.00	243.00	243.00
Thixotrope	30.00	30.00	30.00	30.00	30.00	30.00	30.00	30.00	30.00
Super HiFlash naptha	100.00	89.75	79.50	69.25	59.00	48.75	38.50	28.25	18.00
Moisture scavenger (pTSMI)	15.90	15.90	15.90	15.90	15.90	15.90	15.90	15.90	15.90
Pigmentary anode	4100.00	3648.12	3196.25	2744.37	2292.50	1840.62	1388.75	936.87	485.00
Fumed silica	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Moisture scavenger (additive OF)	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Solvent (parachlorobenzotrifluoride)	100.00	89.90	79.75	69.62	59.50	49.37	39.25	29.12	19.00
Catalyst	1.70	1.70	1.70	1.70	1.70	1.70	1.70	1.70	1.70
Total	4630.60	4158.37	3688.10	3213.84	2741.60	2269.34	1797.10	1324.84	852.60
Volume solids	67.80	67.80	67.80	67.80	67.80	67.80	67.80	67.80	67.80
% zinc by wt. of dry film	94.10	90.50	87.10	83.50	80.00	76.40	72.40	68.90	65.00
PVC/CPVC ratio	1.16	1.08	1.00	0.92	0.84	0.76	0.68	0.60	0.53

comparatively oil-absorbent ancillary pigments (e.g., inhibitors, extenders, thixotropes, and even colored prime pigments), the resultant reductions possible in PVC allow for reduced zinc loadings.

Also, lower levels of zinc have been used in certain zinc dust/zinc oxide formulations designed to maximize the adhesion of oleoresinous-based coatings to galvanized steel. These films provide no cathodic protection, and their use on old, disrupted, or corroding galvanizing offers only weak barrier protection. These types of coatings are not discussed here.

This article reports on a study that sought to establish the PVC/CPVC ratio or zinc content necessary to secure the required conductivity and, therefore, cathodic protection in three alternative zinc-rich (zinc only) systems. Loading was correlated with resistance to salt spray and

Table 3:
High-Solids, Highly Monodispersed Epoxy Ester-Based Zinc-Rich Primer

	22764A	22764B	22764C	22764D	22764E	22764F	22764G	22764H	22764I
High solids (80%) epoxy ester resin	222.20	222.20	222.20	222.20	222.20	222.20	222.20	222.20	222.20
Thixotrope	17.00	17.00	17.00	17.00	17.00	17.00	17.00	17.00	17.00
Mix to homogeneity									
Pigmentary anode (zinc dust)	3350.00	2980.30	2610.70	2241.10	1871.50	1501.80	1132.20	762.60	393.00
Aromatic 100	164.00	151.25	138.50	125.75	113.00	100.25	87.50	74.75	62.00
Moisture scavenging pigment	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
Anti-oxidant (butyraldoxime)	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Drier mix	18.00	17.80	17.62	17.43	18.00	18.00	17.99	17.99	18.00
Mineral spirits	95.00	83.12	71.25	59.37	47.50	35.62	23.75	11.87	0.00
Total	3881.20	3486.67	3092.27	2697.85	2304.20	1909.87	1515.64	1121.41	727.20
Non. vol. by volume	64.00	64.00	63.90	63.90	63.90	63.90	63.80	63.80	63.80
% zinc in dry film	94.10	90.50	87.10	83.50	80.00	76.20	72.40	68.30	65.00
PVC/CPVC ratio	1.09	1.01	0.92	0.83	0.74	0.66	0.57	0.48	0.39

humidity, electrical resistivity, and film adhesion/cohesion.

PROCEDURES

Formulations

Three PVC/CPVC ladder experiments were performed on a stoichiometrically balanced epoxy/polyamide, a moisture-curing toluene diisocyanate-based polyurethane, and a high-solids, highly monodispersed epoxy ester. All primers were stripped of ancillary pigmentation, except for small amounts of a pigmentary thixotrope. This precluded many of the effects of high oil absorption extenders on the CPVC, as well as the effects of spacers that would interfere with establishing tangential contact between the particles of zinc pigment.

Two master primers based on each resin were prepared, one at excessive zinc loading and one at a very low loading. In each case, the PVC/CPVC levels approximated a zinc loading of about 94% zinc on the dry film weight for the higher loaded system and about 65% zinc for the lower loaded system. In the epoxy/polyamide, the zinc was mixed into the high- and low-loaded systems immediately before application and just after the epoxy and polyamide components were combined. In the moisture-curing polyurethane and the epoxy ester, the zinc was dispersed into the formulations as they were compounded. The polyurethanes were formulated at 67% volume solids; the epoxies at 70%; and the epoxy esters at 64%. In each of the three systems, the two master paints (high and low PVC) were mixed in appropriate amounts to produce a series of nine paints with the levels of zinc shown in Tables 1, 2, and 3.

Panel Preparation and Evaluation Techniques

The paints were applied to ground steel test panels in triplicate. Each paint was also applied in duplicate to glass plates for electrical resistivity testing. Film thicknesses on steel were measured with an electronic film thickness gauge and were averaged over six points on each panel. The numbers were averaged to give a single value for each panel. Film thicknesses on glass were measured with a thickness gauge near the actual test location (but after electrical measurements were taken).

One set of panels of each series of paints was exposed to 5% salt spray. This set was selected from panels that were closely grouped in film thicknesses. Environments such as that of ASTM B117 (Standard Procedure for Operating Salt Spray [Fog] Apparatus), 5% salt spray, are more aggressive than actual field conditions compared to cyclic test conditions such as those found in ASTM D5894 (Standard Practice for Cyclic Salt Fog/UV Exposure of Painted Metal). B117 conditions are also less representative of actual field conditions compared to those found in D5894. It is, however, the very aggressive nature of the salt spray environment that is valuable in this study.

Only such an aggressive environment will accelerate

Table 4:
5% Salt Spray Response of Zinc-Rich Primers

Primer	PVC/ CPVC	% Zinc by Wt. on Dry Film	Zinc Corrosion	General Panel Steel Corrosion	Panel Scribe Corrosion	Blister Degree	Blister Size	Bare General Corrosion	Bare Scribe Corrosion	Overall Rating	Exposure Duration (Hours)
Epoxy/Polyamide-Based											
24274A	1.12	94.10	Heavy	10.00	10.00	10.00	10.00	8.50	10.00	9.75	1,220
24274B	1.03	90.50	Heavy	10.00	10.00	10.00	10.00	8.00	10.00	9.67	1,200
24274C	0.94	87.10	Mod.-heavy	10.00	9.50	1.00	1.00	4.00	8.00	5.58	1,200
24274D	0.86	83.50	Light	10.00	9.00	2.00	3.00	4.00	6.00	5.67	1,200
24274E	0.77	80.00	Light	10.00	9.00	3.00	5.00	4.00	6.00	6.17	1,200
24274F	0.67	76.20	Light	10.00	9.00	8.00	5.00	4.00	4.00	6.67	1,200
24274G	0.58	72.40	Light	10.00	7.00	10.00	10.00	7.00	4.00	8.00	1,200
24274H	0.50	68.60	Very light	10.00	8.00	10.00	10.00	10.00	5.00	8.83	1,200
24274I	0.42	65.10	None	10.00	7.00	10.00	10.00	10.00	7.00	9.00	1,200
Moisture-Curing Polyurethane-Based											
22361A	1.16	94.10	Moderate	10.00	10.00	9.00	5.00	9.00	10.00	8.83	670
22361B	1.08	90.50	Moderate	10.00	10.00	3.00	5.00	1.00	10.00	6.50	670
22361C	1.00	87.10	Light-mod.	9.50	6.00	3.00	7.00	1.00	5.50	5.33	670
22361D	0.92	83.50	Light-mod.	10.00	8.00	3.00	6.00	1.00	6.00	5.67	670
22361E	0.84	80.00	Light	10.00	6.00	5.00	5.00	1.00	6.00	5.50	670
22361F	0.76	76.20	Light	9.50	7.00	6.00	6.00	1.00	7.00	6.08	670
22361G	0.68	72.40	Light	9.00	6.00	4.00	5.00	2.00	7.00	5.50	670
22361H	0.60	68.90	Light	4.00	5.50	4.00	2.00	4.00	4.00	3.92	670
22361I	0.53	65.00	Light	9.00	5.00	6.00	7.00	4.00	6.50	6.25	670
Epoxy Ester-Based											
22764A	1.09	94.10	Heavy	10.00	10.00	6.00	8.00	9.00	10.00	8.83	670
22764B	1.01	90.50	Mod.-heavy	10.00	7.00	6.00	8.00	8.00	7.00	7.67	670
22764C	0.92	87.10	Moderate	10.00	8.00	9.00	8.00	5.00	8.50	8.08	670
22764D	0.83	83.50	Light	10.00	8.00	5.00	6.00	7.00	7.00	7.17	670
22764E	0.74	80.00	Light	9.00	8.00	5.00	8.00	8.00	7.00	7.50	670
22764F	0.66	76.20	Very light	9.00	7.00	6.00	8.00	8.00	6.00	7.33	670
22764G	0.57	72.40	None	9.00	8.00	9.00	7.00	9.00	7.50	8.25	670
22764H	0.48	68.30	None	9.50	7.00	6.00	8.00	7.00	8.00	7.58	670
22764I	0.39	65.00	None	10.00	6.00	10.00	10.00	9.50	8.00	8.92	670

the conversion of zinc metal to its corrosion salt and shorten, therefore, the duration of the necessary exposure. Before salt spray exposure, a very thin scribe was cut into the film down the centerline of each panel with a sharp razor blade.

A second set of panels (also grouped closely in film thicknesses) was exposed to continuous condensing humidity at 50 C (122 F). These films were not scribed.

Before exposure, both sets of panels were backed and edged with adhesive vinyl tape. In the case of the epoxies, the salt spray panels were exposed for 1,220 hours; in the case of the other two series, exposure durations were 670 hours. Humidity exposure lasted for 1,104 hours (312 hours for the epoxy/polyamide coatings).

At the end of the exposure, the panels were evaluated for zinc corrosion (qualitatively) and for steel corrosion across the general panel and along the immediate scribe area using the rating scales of ASTM D610 (Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surfaces) and D1654 (Standard Test Method for Evalua-

Table 5:
Continuous Humidity Response of Zinc-Rich Primers

Primer	PVC/ CPVC	% Zinc by Wt. on Dry Film	Zinc Corrosion	General Panel Steel Corrosion	Blister Degree	Blister Size	Bare Corrosion	Overall Rating	Exposure Duration (hours)
Epoxy/Polyamide-Based									
24274A	1.12	94.10	Heavy	10.00	10.00	10.00	9.00	9.75	312
24274B	1.03	90.40	Heavy	10.00	9.00	2.00	9.00	7.50	312
24274C	0.94	87.10	Moderate	10.00	8.00	6.00	10.00	8.50	312
24274D	0.86	83.50	Light	10.00	3.00	6.00	10.00	7.25	312
24274E	0.77	80.00	None	10.00	4.00	6.00	10.00	7.50	312
24274F	0.67	76.20	None	10.00	4.00	6.00	10.00	7.50	312
24274G	0.58	72.40	None	10.00	4.00	7.00	10.00	7.75	312
24274H	0.50	68.60	None	10.00	3.00	6.00	10.00	7.25	312
24274I	0.42	65.10	None	10.00	3.00	6.00	10.00	7.25	312
Moisture-Curing Polyurethane-Based									
22361A	1.16	94.10	Moderate	10.00	10.00	10.00	8.00	9.50	1,104
22361B	1.08	90.50	Mod.-heavy	10.00	10.00	10.00	9.00	9.75	1,104
22361C	1.00	87.10	Light	10.00	1.00	1.00	3.00	3.75	1,104
22361D	0.92	83.50	None	10.00	2.00	1.00	2.00	3.75	1,104
22361E	0.84	80.00	None	10.00	2.00	1.00	1.00	3.50	1,104
22361F	0.76	76.20	None	10.00	2.00	2.00	1.00	3.75	1,104
22361G	0.68	72.40	None	10.00	1.00	2.00	1.00	3.50	1,104
22361H	0.60	68.90	None	10.00	2.00	2.00	1.00	3.75	1,104
22361I	0.53	65.00	None	10.00	1.00	2.00	1.00	3.50	1,104
Epoxy Ester-Based									
22764A	1.09	94.10	Heavy	10.00	10.00	10.00	9.50	9.88	1,104
22764B	1.01	90.50	Light-Mod.	10.00	9.00	9.00	8.00	9.00	1,104
22764C	0.92	87.10	None	10.00	2.00	5.00	1.00	4.50	1,104
22764D	0.83	83.50	None	10.00	1.00	4.00	1.00	4.00	1,104
22764E	0.74	80.00	None	10.00	1.00	3.00	1.00	3.75	1,104
22764F	0.66	76.20	None	10.00	1.00	2.00	1.00	3.50	1,104
22764G	0.57	72.40	None	10.00	1.00	2.00	1.00	3.50	1,104
22764H	0.48	68.30	None	10.00	1.00	3.00	1.00	3.75	1,104
22764I	0.39	65.00	None	10.00	1.00	4.00	1.00	4.00	1,104

tion of Painted or Coated Specimens Subjected to Corrosive Environments). The blistering of the film was also evaluated using the numerical rating scale noted in Federal Standard Test Method TT-P-141a, Method 6461 (Blistering of Paints, Degree of). This scale gives numerical values to blistering degree as well as blister size. (The 10–0 rating measures increasing blistering degree as well as increasing blister size.) Being numerical, these ratings are more adaptable to computer averaging of data than are the descriptive blistering resistance scales used in ASTM D714, Standard Test Method for Evaluating Degree of Blistering of Paints.

After evaluation, the steel panels were stripped of coating on the lower half of each panel using a neutral pH-based methylene chloride/methanol paint remover and a razor blade. (Careful note was taken of the relative ease of coating film removal.) After removal of this film, the underfilm metal was evaluated for corrosion on both the general exposed field of the panel and on the bared metal around the cut scribe.

Data from all six evaluation points in the salt spray evaluations (coated and bare panel, general and scribe corrosion, as well as blistering degree and blister size) were then averaged to give one overall rating for the performance of each primer (Table 4). Humidity panel ratings were averaged using four data points only: rusted steel, bare steel, blistering degree, and blister size (Table 5).

To assess adhesion, pull-off tests were performed on the remaining coated areas of each of the panels that had been exposed to salt spray (ASTM D4541, Standard Test Method for Pull-off Strength of Coatings Using Portable Adhesion Testers). Excessively blistered films were not tested for adhesion. Adhesion tests were also prepared on the third set of the panels, which were unexposed coated steel. In this way, it was possible to compare the relative adhesive strengths of each film before and after exposure.

Before affixing the dolly to the coated panel, both the under-surface of the dolly and the upper face of the coated panel were lightly scuffed with a 20-grit emery cloth. Scuffing roughened the surface to improve adhesion and removed contamination from the surface of the exposed film after coating. Abraded surfaces were afterwards washed with VM&P naphtha. Data from the pull-off adhesion tests, along with qualitative evaluations of the response of the various films to paint remover, may be reviewed in Table 6.

Using the unexposed films applied on glass and a commercial ohmmeter, the electrical resistivity over 1.5 sq in. (10 sq cm) of film was measured by means of a pair of 1.5-inch (3.75-centimeter) razor edges (placed 1.5 in. [3.75 cm] apart), which cut into each film through to the glass. Resistance measurements were taken of the dry films and of the same films wetted with fresh distilled wa-

ter and alternatively with salt water. For the wet electrical resistance tests, water was poured onto a saturated paper towel in contact with the film and allowed to maintain contact for five minutes. At the end of this time, the towel was removed and all standing water on the film was wiped away with a dry, absorbent cloth. The razor edges were then cut through the film to the glass substrate, and the resistance values were immediately taken. Salt water and fresh water tests were performed on different panels. Resistivity (ρ) was calculated from the resistance, R, and film thickness data, t, in cm by $\rho = Rtd/d = Rt$ and expressed as ohms/cm, where d is the length of one side of the 1.5-inch (3.75-centimeter) square (Fig. 1).

Fig. 2: Panel of 24272A half-stripped with paint remover after 1,220 hours in 5% salt spray.

DATA

Five Percent Salt Spray Data

The most immediate observation from all of these data was the heavy build-up of zinc corrosion product on the high zinc-loaded films compared to primers with zinc loadings of 83% and below. Also evident was the uniform excellence of the uncorroded scribe of the salt spray panels bearing 94% zinc. In some series (the epoxy/ polyamides and, to a lesser extent, the polyurethanes), scribe corrosion was also minimized at slightly lower zinc loadings. Only the epoxies retained good scribe corrosion resistance at a PVC/CPVC ratio slightly below unity. In this latter case (24274C), the film blistered very badly. In all cases, the elimination of scribe corrosion was found to coincide with a PVC/CPVC ratio slightly over unity (but not as low as unity). In most cases, blistering and bare panel corrosion were also minimized as loadings achieved that same very high PVC/CPVC ratio.

Patterns of film response at lower PVC/CPVC ratios were also similar in all three series and show that as this ratio dropped below unity, overall performance dropped off rapidly. Performance was generally depressed throughout the mid-range of the ladder between ratios of about 0.6 and 0.9.

At the lowest end of each ladder (PVC/CPVC ratios below 0.6), there was a definite re-establishment of overall performance, although not of corrosion resistance at the scribe. This upgrade was based on improved general panel corrosion resistance and blistering resistance. In this low PVC range, the films were much darker in color and glossier than they were at high PVC (a phenomenon probably associated with the elimination of voids).

Continuous Humidity Data

Data patterns in continuous humidity mirrored the patterns in salt spray (Table 5). All of the highest PVC primers showed moderate to heavy zinc corrosion product on the surface of the film but only minimal corrosion of the steel beneath the films. The extent of the white discoloration of these films lessened as PVCs (zinc loadings) were reduced. Little whitening was apparent at PVC/CPVC ratios below unity (more considerably below unity in the epoxy/polyamides). Where blistering was apparent, the panels all assumed a typical gray color. The relationship among PVC/CPVC ratio, blistering tendency, and the formation of zinc corrosion product was apparent. Also noted was the relationship between the PVC/CPVC ratio and the amount of underfilm corrosion, especially in the urethane and epoxy ester series, where severe underfilm corrosion was noted as PVC/CPVC ratios dropped below unity. Films of all three series exhibited severe blistering in the mid- and low-range PVCs. In this environment, little improvement in blistering resistance or underfilm corrosion was noted at the lowest zinc loadings. The onset of blistering appeared to coincide with decreased zinc corrosion on the exposed film and, in the case of the polyurethane epoxy esters, increased underfilm corrosion. The lack of underfilm corrosion on the epoxy polyamide series at PVC/CPVC ratios below unity may be solely a reflection of the short exposure of this series compared to the other two series.

Film Removal with Paint Remover

Films exposed to salt spray and continuous humidity showed marked variations in the relative resistance to paint removers and stripping. This was especially true for the epoxy/ polyamide primers in salt spray and the urethane and epoxy ester primers in continuous humidity (Table 6). Removal of most of the lower loaded films of all three series was very easy. Some of the mechanically stronger films (24272H and 24278I, bound with epoxy/polyamide) were lifted spontaneously during removal of backing tape before

Table 6:
Pull-Off Adhesion Response and Response of Zinc-Rich Primers to Paint Remover

Primer	PVC/ CPVC	% Zinc by Wt. on Dry Film	Response to Paint Remover after Salt Spray Exposure	Response to Paint Remover after Continuous Humidity Exposure	Adhesive/Cohesive Loss of Unexposed Film (psi)	Adhesive/Cohesive Loss of Film Exposed to Salt Spray (psi)
Epoxy/Polyamide-Based						
24274A	1.12	94.10	Impermeable: required repeated applications and mechanical chipping	Required application of paint remover	80 (Cohesive within film)	40 (Adhesive at substrate)
24274B	1.03	90.40	Impermeable: required repeated applications and mechanical chipping; Easier than 24274A	Required application of paint remover	90 (Cohesive within film)	80 (Adhesive at substrate)
24274C	0.94	87.10	Impermeable: required repeated applications	Required application of paint remover	110 (Cohesive within film)	*
24274D	0.86	83.50	Only single application of paint remover necessary	Could be removed by scraping only	300 (Mixed failure/all elements)	*
24274E	0.77	80.00	Only single application of paint remover necessary	Could be removed by scraping only	420 (Mixed failure/all elements)	*
24274F	0.67	76.20	Rapid lifting	Could be removed by scraping only	>250 (Cohesive within glue)	30 (Adhesive at substrate)
24274G	0.58	72.40	Rapid lifting	Could be removed by scraping only	>360 (Cohesive within glue)	20 (Adhesive at substrate)
24274H	0.50	68.60	Rapid lifting	Could be removed by scraping only	>410 (Cohesive within glue)	40 (Adhesive at substrate)
24274I	0.42	65.10	Spontaneous de-adhesion; paint remover not applied	Could be removed by scraping only	>180 (Cohesive within glue)	40 (Adhesive at substrate)
Moisture-Curing Polyurethane-Based						
22361A	1.16	94.10	Two applications of remover required	Impermeable: required repeated application of paint remover	90 (Cohesive in film, near substrate)	60 (Cohesive within film)
22361B	1.08	90.50	Rapid lifting	Impermeable: required repeated application of paint remover	180 (Cohesive within film)	*
22361C	1.00	87.10	Rapid lifting	Impermeable: required repeated application of paint remover	330 (Cohesive in film and glue)	*
22361D	0.92	83.50	Rapid lifting	Required one application of paint remover	380 (Cohesive in film and glue)	*
22361E	0.84	80.00	Rapid lifting	Required one application of paint remover	400 (Cohesive in film and glue)	*
22361F	0.76	76.20	Rapid lifting	Required one application of paint remover	490 (Mixed failure/all elements)	*
22361G	0.68	72.40	Rapid lifting	Scraped off without application of paint remover	500 (Mixed failure/all elements)	*
22361H	0.60	68.90	Rapid lifting	Scraped off without application of paint remover	480 (Mixed failure/all elements)	130 (Adhesive at iron corrosion product)
22361I	0.53	65.00	Rapid lifting	Scraped off without application of paint remover	490 (Mixed failure/all elements)	*
Epoxy Ester-Based						
22764A	1.09	94.10	Two applications of remover required	Impermeable: required repeated application of paint remover	60 (Cohesive within film)	70 (Adhesive at substrate)
22764B	1.01	90.50	Two applications of remover required	Impermeable: required repeated application of paint remover	110 (Cohesive within film)	60 (Adhesive at substrate)
22764C	0.92	87.10	Rapid lifting	Impermeable: required repeated application of paint remover	100 (Cohesive within film)	90 (Adhesive at substrate)
22764D	0.83	83.50	Rapid lifting	Required one application of paint remover	120 (Cohesive within zinc near substrate)	90 (Cohesive in zinc near substrate)
22764E	0.74	80.00	Rapid lifting	Required one application of paint remover	150 (Cohesive within zinc near substrate)	*
22764F	0.66	76.20	Rapid lifting	Required one application of paint remover	180 (Cohesive within zinc near substrate)	*
22764G	0.57	72.40	Rapid lifting	Scraped off without application of paint remover	160 (Cohesive within zinc near substrate)	*
22764H	0.48	68.30	Rapid lifting	Scraped off without application of paint remover	160 (Cohesive within zinc near substrate)	120 (Cohesive in zinc near substrate)
22764I	0.39	65.00	Rapid lifting	Scraped off without application of paint remover	No panel available (lost)	180 (Mixed failure/all elements)

*Adhesion pull test taken on exposed film because of heavy blistering across panel after exposure

any paint remover was applied.

In both test environments, removal became progressively more difficult with increasing PVC/CPVC ratio. Removal was especially difficult in the case of the high-loaded primers. Although 24274C in salt spray had blistered badly after exposure, the film displayed areas that were still adherent and quite difficult to remove with the paint remover. Panel 24274B, requiring several applications of the paint remover, was even more resistant to lifting. Panel 24274A was absolutely resistant to the remover. In spite of multiple applications, the primer film on 24274A finally had to be chipped and scraped from the surface with a razor blade. The result of this scraping is clearly evident in Fig. 2 (bottom of panel).

The A paints of the other two series were also more difficult to strip than were their lower loaded offsets, although films could be stripped from the steel with a razor blade after a second application of paint remover.

Similarly, in continuous humidity, films of 24272A and B, 22361A and B, and 22764A and B were all very difficult to remove with a paint remover. Other films of primers having PVC/ CPVC ratios below unity (most of which had blistered) were far more readily removed.

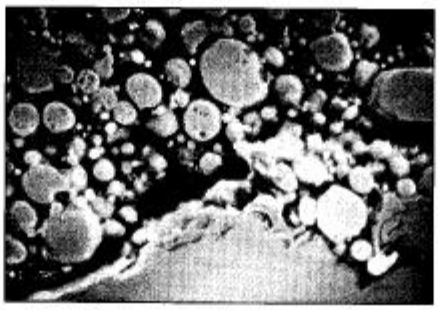

Fig. 3: Photomicrograph of unexposed film of 22764A. Note the crowding of the zinc dust particles within the resinous matrix.

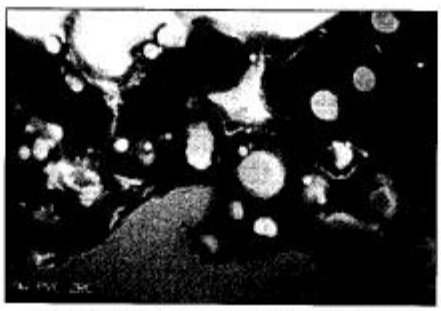

Fig. 4: Photomicrograph of unexposed film of 22764I. Note the presence of isolated zinc particles in electrically insulative resinous matrix.

Pull-Off Adhesion Tests

When the pull-off adhesion of salt spray-exposed and non-exposed films were examined (Table 6), it was shown that there was no actual increase in adhesion of the film after exposure. Films of very low PVC/CPVC ratio showed significant reductions in adhesion after exposure. This is typical of a barrier coating with insufficient impermeability. Films of high PVC/CPVC ratio showed less reduction in adhesive strength with exposure, although there was no actual improvement with exposure. The levels of adhesion of these high PVC/CPVC systems were invariably lower (both before and after exposure) than had been the adhesion of the low PVC/CPVC films before exposure. The plane of failure seems to shift on exposure from a cohesive failure in the body of the primer to an adhesive failure at the interface of the film and the substrate. Presumably, this changing site of failure reflects cohesive strength (relative to a constant or decreasing adhesive strength) that increases as the film is reinforced with zinc corrosion product.

Electrical Resistivity Data

Resistivity values of the dry films of all three systems are very high, and they decrease significantly when the wet film is measured (especially when the film is wet with salt water). In all cases, brine-wet films are conductive only when PVC/CPVC ratios are at least 0.94 and above. Fresh water-wet films are conductive only when formulated at PVC/CPVC ratios above 1.03. Dry films may remain (depending on the binder) virtually non-conductive even at PVC/CPVC ratios of 1:1.12. (The air in the interstitial areas of the dry film is a poorer electrical conductor than is pure water when the film is wet.)

After exposure and conversion of the zinc film to one in which the zinc is at least partially bound with zinc corrosion product, it is to be expected that the electrically insulative layer of zinc corrosion product will decrease the electrical conductivity of even highly pigmented films. This type of measurement was not, however, made.

Discussion

Most of these performance data are not surprising, considering the need for zinc particle to zinc particle contact with each other and with the steel substrate, if steel protection is to be afforded galvanically by anodic (zinc) dissolution. This condition is well illustrated in the scanning electron photomicrograph of the cross-section of the film at high PVC (Fig. 3), and may be compared to the cross-sectional photomicrograph of the low PVC film (Fig. 4), which shows the greater encapsulation of the zinc pigment spheres. The increasing zinc corrosion apparent at high PVC/CPVC ratios and its correlation with reduced (or eliminated) scribe corrosion is expected and is the sole consequence of cathodic protection. The decreased overall performance in the mid-range PVC/ CPVC areas is similarly explained, for at ratios much below unity, cathodic protection must be precluded because of increased

Table 7:
Resistivity of Zinc-Rich Primers on Glass

Primer	Dry Film Thickness Mils	Electrical Resistivity (ohm cm)		
		Dry Film	Fresh Water-Wet	5% Brine-Wet
24274A	4.5	∞	1,800,000	56,250
24274B	3.5	∞	446,250	78,750
24274C	3.5	∞	∞	∞
24274D	3.2	∞	∞	∞
24274E	3.5	∞	∞	∞
24274F	3.4	∞	∞	∞
24274G	3.2	∞	∞	∞
24274H	3.2	∞	∞	∞
24274I	3.2	∞	∞	∞
22361A	3.5	3,500,000	262,500	24.5
22361B	3.5	2,843,750	65,625	1,050,000
22361C	3.5	8,750,000	70,000	7,000,000
22361D	3.5	∞	∞	∞
22361E	3.4	∞	∞	∞
22361F	3.4	∞	∞	∞
22361G	3.2	∞	∞	∞
22361H	3.3	∞	∞	∞
22361I	3.3	∞	∞	∞
22764A	3.5	253,750	350,000	1,050
22764B	3.5	2,843,750	65,625	52,000
22764C	3.2	∞	1,120,000	32,000,000
22764D	3.2	∞	∞	80,000,000
22764E	3.2	∞	∞	∞
22764F	3.4	∞	∞	∞
22764G	3.3	∞	∞	∞
22764H	3.1	∞	∞	∞
22764I	3.5	∞	∞	∞

binder insulation. Barrier protection probably accounts for the slow upturn in performance (especially general panel corrosion resistance) at the lower PVC/CPVC end of the epoxy/polyamide series (< 0.5 PVC/ CPVC ratio or approximately < 70% zinc). These barrier effects are probably not substantial enough in the mid-range PVCs, so that above 0.5 PVC/ CPVC ratio and below 1.0 PVC/CPVC ratio, the film is less protective in terms of both cathodic and barrier protection. No such upturn in performance was noted with the urethane and epoxy ester continuous humidity panels at low PVC. This may be related to the greater permeability of these coatings.

The surprisingly high "adhesion" of the salt-sprayed 24274A primer (1.12 PVC/CPVC ratio) as well as the 24274B and high-loaded primers of the other two series needs to be interpreted. Presumably at so high a zinc loading, the film would be quite open and readily permeated by salt water. Under such conditions, it is likely that the interior of the film as well as its surface would be open and, therefore, more liable to zinc corrosion and to interstitial packing with zinc corrosion product than films with lower PVC/CPVC ratios. In this case, the zinc corrosion product may act in a manner similar to that which occurs in inorganic zinc-rich systems, so that the binding by the organic polymer may be buttressed by the binding power of the zinc corrosion product. While this would explain the cohesive integrity of the film above the CPVC, it does not necessarily explain the tenacious adhesion.

Lack of response to paint remover does not, however, necessarily equate with enhanced adhesion. If the film becomes impermeable to the paint remover solvents, it will not swell. Therefore, the film's adhesion to steel will not be subjected to the same shearing stresses that oppose adhesion and that are caused by expansion of the film by solvent imbibition and film swelling. Thus, the improved adhesion is, in fact, caused by a reduction in the stress opposing the adhesive force, rather than any actual increase in the adhesive force itself.

The adhesion data are also reasonably predictable and give further credence to the conclusion that the apparent increase in adhesion of the high PVC/CPVC films after exposure is an illusion. It is, in fact, more likely to be a result of diminished stress on the adhesive bond and is caused by the reduced swelling of the film by the paint remover. In turn, this is caused by increased inorganic bonding and reinforcement of the organic film with corrosion product. The corroding pigment supplies the film with additional pigmentary crosslinking centers. Presumably, this reinforcement occurs in spite of the presence of the monomolecular sheath of binder that should not be depleted until the film is formulated at a PVC so high that it becomes totally devoid of interstitial binder.

Our understanding of the observed phenomena is further buttressed by the electrical resistivity data on glass (Table 7). From these data it would appear that cathodic protection is significantly hindered in films of PVC/CPVC ratio below 0.94, or where zinc content of the dry film is below 87%. Dependable cathodic protection is only fully realized at PVC/CPVC levels well above unity (94% zinc on the dry film). These findings are mirrored in the visual extent of zinc corrosion on the painted panels after exposure.

Conclusion

In conclusion, the data bears out the concept that in organic zinc-rich primers formulated at high PVC/CPVC ratios (well above 1:1), excessive film porosity deprives the interstitial areas of binder, replacing this volume with air. Under corrosive conditions, these voids allow the ingress of electrolyte into the film, so that zinc corrosion may more freely occur. This, in turn, fills the inter-pigmentary interstices with zinc corrosion product (much the same as it occurs with the still more porous inorganic zincs). The corrosion product adds to the cohesive strength of the film by forming inorganic cross-linking centers across the interstitial voids. These centers reinforce film strength with an inorganic matrix that is more resistant to swelling by solvents than the original binder and, therefore, is less susceptible to the paint remover action.

The higher the PVC/CPVC ratio, the more the organic film acts like an inorganic film in the post-galvanic protection mode, and the more film properties depart from those of a classical organic zinc-rich. The prerequisite for such a condition is that the film (after application) is exposed to a corrosive environment. Such over-pigmented films, when not exposed (and, therefore, not inorganically reinforced), will probably remain mechanically weak and much more vulnerable to both chemical (solvent) attack and physical stress than a composition formulated at a low PVC/CPVC ratio.

This concept of film condition after exposure is something of a departure from the traditional view of organic zinc above a PVC/CPVC of unity. The traditional view considers it to be weak and ignores the strengthening effects of the zinc corrosion product. While the foregoing work does not definitively prove that after the establishment of the post-galvanic phase, the film is any more of a barrier to water, oxygen, or corrosive ions than before, the increased resistance to paint remover attack would strongly imply such increased impermeability.

Still broader interpretation of these findings would lead to postulations that the formulation of organic zinc-rich primers bearing minimal organic binder would produce viable coatings if introduced into a corrosive environment before undergoing other forms of stress. The deliberate post-treatment of these films in a manner similar to the post-curing of sodium silicate-based inorganic zinc primers may produce a more substantial second phase protection in the primer solely from the inorganic corrosion product created during post-curing.

The data reveals no evidence of cathodic protection below a PVC/CPVC ratio of about 1:1. This is equivalent to a zinc weight loading (dependent on system and other aspects of the pigmentation) between 87 and 90%. It must be assumed that any value derived from coatings pigmented with lower loadings of zinc comes from mechanisms other than cathodic protection. Optimized performance and the film strengthening effects noted above do not occur until loadings are nearer 1.1:1 or 94% on the dry film.

While zinc coatings formulated with zinc loadings less than unity may technically serve as primers on steel (or spent or abraded galvanizing), little true protection can be afforded to these substrates by such films at abraded or (on galvanizing) re-abraded areas. Below a PVC/CPVC ratio of about 0.5 or 0.6, these same films begin to act as rather poor barrier primers. In a PVC/CPVC range between about 0.5 or 0.6 and about 0.95, the films are of little use as either zinc-rich primers or barrier primers.

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