Durability of Powder-Coated Hot-Dip Galvanized Steel

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In this study, the quality and durability of powder-coated hot-dip galvanized products have been investigated. Standard steel coupons hot-dip galvanized in conventional and delta (i.e., high temperature) conditions were coated with powder paint systems or a high quality solvent-based system and then subjected to a wide range of test methods representing mild or highly aggressive exposure conditions. Additional variables in the project were the silicon content of the steel and the treatment prior to painting. The use of delta-galvanized steel as a base for painting offers a number of advantages such as much greater hardness and improved paint adhesion. Maximum corrosion protection is observed if the galvanized base is treated with chromate and sequentially powder coated with an epoxy primer followed by a polyester topcoat.

INTRODUCTION

Steel is one of the most important building and construction materials in today's technology. In comparison with other materials, such as concrete, stone, wood, etc., steel has a number of both technical and economic advantages. It is relatively lightweight per unit of volume of construction, easy to repair, has easy formability, and has a wide range of available parts and forms. Next to these advantages steel has only one very important disadvantage, namely it will rust when exposed to the elements.

Duplex systems on steel materials are generally defined as a combination of a metallic coating followed by an organic paint or powder coating. The metallic coating is applied by either conventional hot-dip galvanizing at 450°C or by delta galvanizing at 550°C, whereas the following organic coating can be applied by spraying, brushing, roller coating, etc. The combination metallic coating followed by an organic coating has been proven to offer an optimal protection against rust during exposure to the elements.[1-4]

The advantages of delta galvanizing, in comparison with conventional hot-dip galvanizing, are a much greater hardness of the zinc alloy layer, improved paint adhesion due to the microporous alloy surface, and the negligible influence of the silicon concentration of steel particles on the thickness of the metallic coating.[5,6]

Numerous articles have been published in recent literature that provide useful information on test methods to measure the durability of different duplex systems (= galvanized steel with an organic coating).[7-22] But none of these previous research studies used such a comprehensive set of test methods.

The major goal of the project was to measure the corrosion protection performance of various duplex systems using different test methods. A systematic study of the various parameters was conducted using a wide range of analytical and electrochemical tools, such as salt spray test, UV/condensation test, and electrochemical impedance spectroscopy (EIS). EIS has been known for many years as a powerful tool in corrosion research of metals coated with organic paint systems. Mansfeld et al. and others have developed this technique to study the degradation process in coated metal panels and the properties of the coating-metal interface.[7,8,10,16-21]

Other objectives were to determine whether the high temperature galvanizing process offers advantages over conventional galvanizing and whether the currently used chromate pretreatment prior to painting equals or outperforms other pretreatments, e.g., grit blasting.

EXPERIMENTAL

Materials

A large number of steel panels (150 × 100 × 3 mm) were hot-dip galvanized and coated with a paint system. For

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Table 1—Steel Composition

Component	Steel 1 w/w%	Steel 2 w/w%
C	0.08	0.173
Si	0.01	0.308
Mn	0.42	1.450
P	0.014	0.016
Al	0.035	0.046
S	0.012	0.009

Table 2—Zinc Bath Composition

Component	Convenitonal Galvanizing	Delta Galvanizing
Pb	0.06%	0.07%
Fe	0.0247%	0.0764%
Al	0.0016%	0.0014%
Ni	0.001%	< 0.001%

the duplex systems, four different parameters were taken into account: the steel base, the galvanizing process, the pretreatment prior to coating, and the paint system.

Table 1 shows the steel composition used for the test panels. Cleaning and fluxing were carried out using standard industrial protocols for acid degreasing, pickling, fluxing, and drying. Galvanizing conditions were imposed for five minutes at 450°C and five minutes at 550°C for high temperature conditions, followed by ambient air-cooling. The zinc bath composition is shown in *Table* 2.

The pretreatments prior to painting the galvanized panels were:

(1) Yellow chromating (Granodine 108B from Mavom B.V., The Netherlands)—All panels were degreased for three minutes with alkaline cleaner Ridoline 1089 (pH 10.0) at 65°C followed by a water rinse. The next step consisted of two minutes of etching with Dioxidizer 395H at ambient temperature also followed by a water rinse step. The panels were sprayed with the chromate solution for three minutes under ambient temperature. The last three steps were a water rinse step, followed by a DI rinse step, and a drying step at 100°C in air. The chemicals used for degreasing, etching, and chromating were all from Mavom B.V. in The Netherlands.

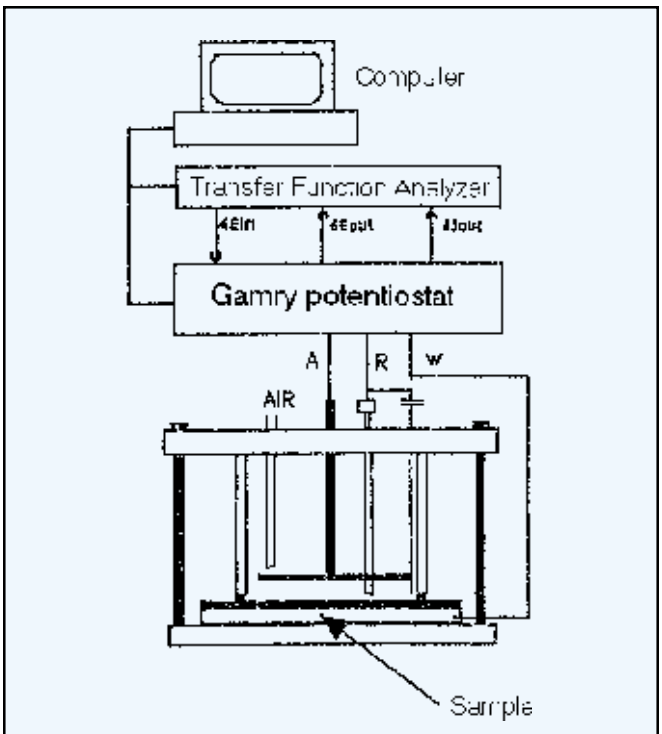


Figure 1—Electrochemical cell.

(2) Grit blasting (Eurogrit A2, 0.2-1 mm, The Netherlands)—All panels were manually grit blasted for several minutes with a pressure of about 1.5 bar.

(3) Silane treatment with an experimental product [mixture of vinyl silane (VS) and bistriethoxysilyl ethane (BTSE), both from Witco, Greenwich, CT] developed at the University of Cincinnati.[23-24] Hydrolyzing of BTSE was done in a solution of 0.5 ml acetic acid, 5 ml water, and 89.5 ml ethanol. VS was hydrolyzed in a solution of 5 ml water and 90 ml methanol. The hydrolyzing time for both silanes was two days. Both solutions were mixed with a 4:1 ratio and the final solution was immediately used for pretreating the panels. For this pretreatment all panels were degreased with alkaline degreaser AC1055 from Brent at 65°C for about seven minutes followed by a water rinse step. The panels were dipped for 100 sec in the silane mixture and dried with compressed air for 30 sec.

The coating systems used were:

(1) Polyester powder (Polydrox 36NF85, Akzo Nobel, The Netherlands), cured at 180°C for six minutes.

(2) Epoxy powder (Syntha Pulvin 11NT, Akzo Nobel, The Netherlands) initial cure for four minutes at 200°C, final cure as for polyester.

(3) Solvent-based systems from Zandleven Coatings BV, The Netherlands, consisting of epoxy primer (Monopox SF-HB), epoxy intermediate coat (Monopox HB), and an aliphatic polyurethane topcoat (Polyfinish MU-DL). All three solvent-based coats were cured at ambient conditions for 24 hr. Coatings were applied manually by spraying.

In total, a set of 720 panels was prepared and tested.

Overview of Test Methods

Direct Current (DC) electrochemical tests were used to determine the corrosion rate of the zinc surface of a galvanized steel panel in a salt solution.

Electrochemical impedance spectroscopy (EIS) was used to evaluate the performance of the organic coatings during exposure to a salt solution.

SEM/EDX analyses were used for investigating the metals' surface appearance, metallic and paint thickness, and alloy composition of the hot-dip galvanized panels.

Hardness test methods (Vickers) were used to determine the hardness of the outer alloy layer.

N-methyl pyrrolidone retention time (NMPRT) test was used to test paint adhesion on the substrate.[25]

Salt spray testing was used to evaluate the performance of the duplex systems (ASTM B-117). This is controversial

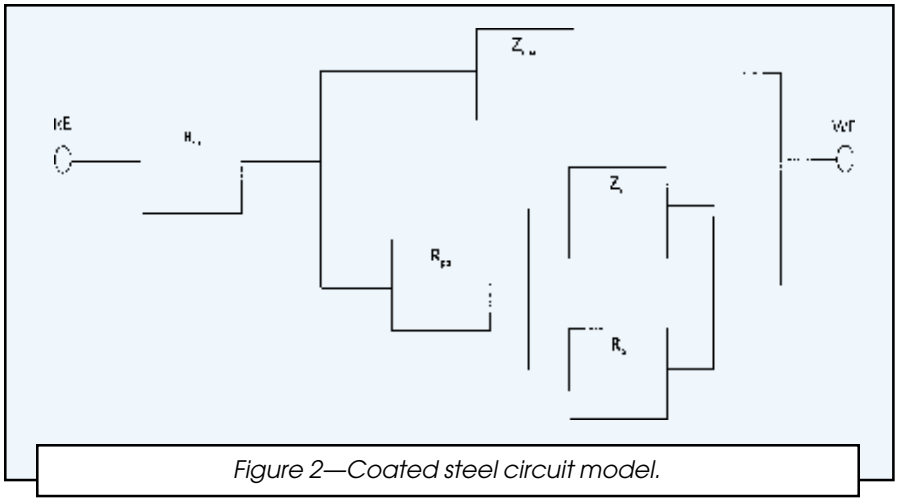


Figure 2—Coated steel circuit model.

for testing painted galvanized steel, but widely used for testing the resistance of a scribed painted panel to an environment of 100% wetness and high salt concentration. A very aggressive test, salt spray testing, is used to visualize the differences between the duplex systems.

The Machu test was used to evaluate the performance of the duplex systems by exposing panels to a solution containing salt and peroxide. This test is quite aggressive as it directly attacks the paint-metal interface by greatly accelerating the cathodic reaction in the scribe by providing excess oxidizer. This test does not simulate a particular outdoor environment and it is claimed to correlate with the salt spray test after 500 hr.[12-14] A major advantage of the Machu test is that test results are obtained in only two days while the salt spray test takes about 1.5 month.

UV/condensation testing was used to evaluate the performance of the duplex systems by alternating exposed panels to salt solution and UV light (ASTM D-5894). This is a relatively new test for painted metals, which employs lower salt concentrations, alternating dry and wet periods and UV/condensation periods. Many consider this the best test for painted hot-dip galvanized steel. It is much less aggressive than the salt spray test and includes the factor of UV radiation. It is slow, i.e., requires at least 12 weeks.

This comprehensive set of testing methods gives an indication of the overall performance of the tested systems.

TEST ROUTINES

Electrochemical Testing

The electrochemical cell used in the DC experiments is schematically shown in *Figure* 1. The area of the working electrode was 0.78 cm^2. The counter electrode was a platinum mesh, and the reference electrode was a saturated calomel electrode (SCE) connected to a salt bridge. DC measurements in the potential range of –0.02 to 0.02 V vs E_{oc}* (linear polarization) and –0.2 to 0.2 V vs E_{oc} (Tafel analysis) were carried out with a Gamry CMS 300 potentiostat. The test samples were 10 × 15 cm^2 delta galvanized or hot-dip galvanized panels, which were wiped clean prior to the test. These samples were exposed under free corroding conditions in 0.3 wt% or 3 wt% NaCl solutions with pH 3, 7, or 10. DC measurements were conducted after five minutes of exposure.

The resulting curve is a plot of the applied potential versus the logarithm of the measured current. To determine the corrosion current a straight line was superimposed along the linear portion of the anodic and the cathodic curve. The intersection of these two lines should intersect at E_{corr} and i_{corr}.

Once i_{corr} is determined, the corrosion rate (cm/yr) can be calculated from the following equation:

$$MPY = i_{corr} \frac{\Lambda \varepsilon}{\rho} 2.54 \times 10^{-4} \quad [cm/yr] \qquad (1)$$

where MPY is the corrosion rate in cm/year, i_{corr} is the current at open corrosion potential in A/cm^2, Λ is a combination of different conversion terms (=1.2866 × 10^5 eq.sec.mils/C.cm.yr), ε is the equivalent weight of the substrate in g/eq, and ρ is the density of the substrate in g/cm^3.

The slope of the straight line fit to the Tafel data is called a Tafel Constant (β). The anodic Tafel Constant (β_a) is determined from a fit of the anodic linear region and a cathodic Tafel Constant (β_c) from a fit of the cathodic linear region. Using the i_{corr}, β_c, and β_a values the polar-

*E_{oc} is the open corrosion potential of the zinc surface.

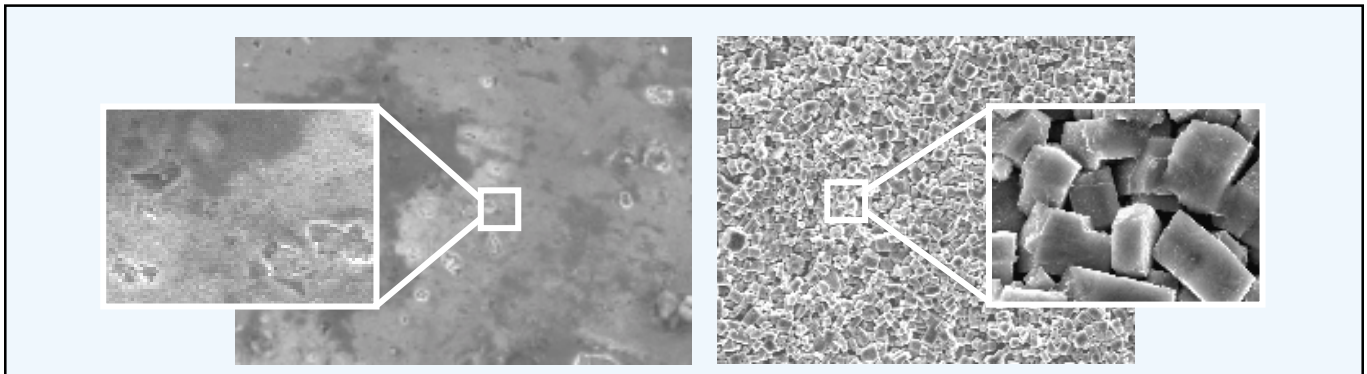


Figure 3—Top view SEM pictures of galvanized steel panels: (a) hot-dip galvanized (1,000x and 4,000x) and (b) delta galvanized (1,000x and 4,000x).

Table 3—Composition of the Zinc Alloy Layers Using EDX and Vickers Hardness of Top Layer

Steel Type and Galvanizing Method	Measuring Point	%Fe	%Zn	Structure	Alloy	Vickers
Steel 1, hot-dip galvanized	1	0	100	Zn	η	50
	2	7	93	$Zn_{12}Fe$	ζ	
	3	11	89	Zn_8Fe	δ	
	4	31	69	$Zn_{2,2}Fe$	γ	
Steel 2, hot-dip galvanized	1	6	94	$Zn_{14,5}Fe$	ζ	83
	2	7	93	$Zn_{14}Fe$	ζ	
	3	7	93	$Zn_{13,5}Fe$	ζ	
	4	7	93	$Zn_{14}Fe$	z	
	5	13	87	Zn_7Fe	δ	
Steel 1, delta galvanized	1	9	91	$Zn_{10}Fe$	ζ	173
	2	10	90	Zn_9Fe	δ	
	3	16	84	Zn_5Fe	δ	
Steel 2, delta galvanized	1	7	93	$Zn_{13}Fe$	ζ	210
	2	10	90	Zn_9Fe	δ	
	3	50	50	ZnFe	?	

Measuring points

Low silicon steel and hot dip galvanized

Coating
○1
○2
○3
○4
Steel

High silicon steel and hot-dip galvanized

Coating
○1
○2
○3
○4
○5
Steel

High and low silicon steel and delta galvanized

Coating
○1
○2
○3
Steel

ization resistance can be determined with the following equation:

$$R_p = \frac{1}{2.303\, i_{corr}} \frac{\beta_a \cdot \beta_c}{\beta_a + \beta_c} \quad [\text{ohms.cm}^2] \qquad (2)$$

The electrochemical cell used in the EIS experiments is schematically shown in *Figure* 1. The area of the working electrode (coated sample) exposed to the electrolyte was 78.54 cm^2. The counter electrode was a carbon rod, and the reference electrode was a saturated calomel electrode (SCE). All electrochemical impedance experiments in the frequency range 0.01 Hz to 100 kHz were carried out at open circuit potential using the Gamry potentiostat. The alternating current amplitude was set at 200 mV.

EIS measurements were carried out under potentiostatic control as a function of the exposure time to a salt solution over a period of 35 days. The test samples were 10×15 cm^2 galvanized and coated panels, which were wiped clean with water prior to the test. These samples were exposed to 3 wt% NaCl solution with neutral pH open to air.

Each impedance spectrum was displayed as a Bode plot (log Z vs frequency (f), and phase angle vs frequency (f)) and analyzed according to an equivalent circuit as shown in *Figure* 2.[11] The nonconducting organic coating is represented as a frequency-dependent element (CPE)

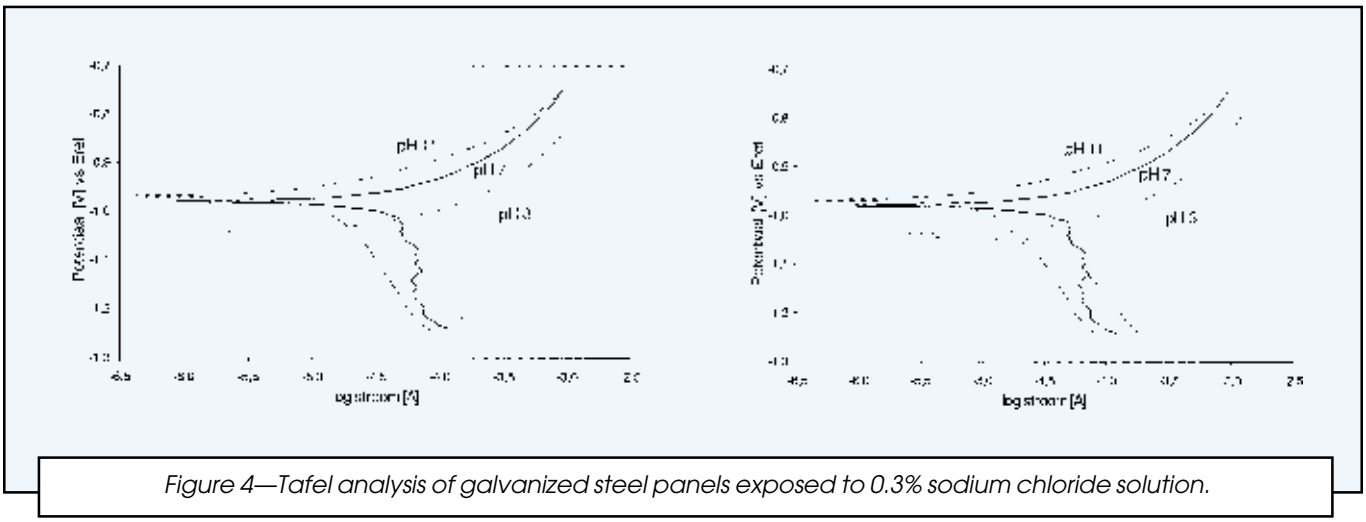


Figure 4—Tafel analysis of galvanized steel panels exposed to 0.3% sodium chloride solution.

Table 4—Open Corrosion Potentials (V) of Galvanized Steel as Function of Salt Concentration, pH in Galvanizing Method

		Open Corrosion Potential (OCP) (V)			
	pH	HD[a]	HN	LD	LN
0.3 w/w% NaCl	3	–0.9691	–1.0764	–0.9628	–1.0526
	7	–0.8932	–1.0121	–0.9018	–0.9737
	11	–0.7953	–0.9727	–0.8639	–0.9402
3 w/w% NaCl	3	–1.0954	–1.0895	–1.0332	–1.0906
	7	–0.9609	–1.0663	–0.9421	–1.0273
	11	–0.9569	–1.0635	–0.9513	–1.0422

(a) Legend: HD = steel 2, delta galvanized; HN = steel 2, hot-dip galvanized; LD = steel 1, delta galvanized; LN = steel 1, hot-dip galvanized.

Table 5—Corrosion Current (i_{corr}) in Polarization Resistance (Ω) as Function of Salt Concentration, pH in Galvanizing Method

		HD[a]		HN		LD		LN	
	pH	i_{corr} x 10^{-5} (A)	R_p (ohm)	i_{corr} x 10^{-5} (A)	R_p (ohm)	i_{corr} x 10^{-5} (A)	R_p (ohm)	i_{corr} x 10^{-5} (A)	R_p (ohm)
0.3 w/w% NaCl	3	164	249	27	337	59	283	3	1215
	7	5	1227	4	1229	5	1206	3	1376
	11	3	3121	4	1520	3	2223	1	2374
3.0 w/w% NaCl	3	74	123	18	273	71	124	5	497
	7	18	335	7	502	5	949	7	387
	11	12	503	10	434	5	872	8	607

(a) Legend: HD = steel 2, delta galvanized; HN = steel 2, hot-dip galvanized; LD = steel 1, delta galvanized; LN = steel 1, hot-dip galvanized; R_p = polarization resistance or corrosion resistance; i_{corr} = de corrosion current at OCP.

Z_{coat}. Ionically conducting paths, due to the presence of defects or pores, produce a finite resistive element or pore resistance, R_{po}. In series with this element is a parallel resistance, R_p, and a frequency-depending element Z_{dl} representing the impedance of the electrolyte-saturated coating/metal surface. The polarization resistance, R_p, relates inversely to the corrosion rate for the sample.

A CPE takes the mathematical form[11]:

$$Z(\text{CPE}) = \frac{(j\omega)^{-n}}{Y_o} \quad [\text{ohm}] \tag{3}$$

where Z is the impedance of the CPE in ohms, Y_0 is a constant, $j^2 = -1$, ω is the angular frequency (equal to 2πf) in rad s^{-1}, and n is a constant ranging between 0 and 1; n is the deviation from ideal behavior. In the case where n=1, the CPE is identical to a capacitor and Y_0 is then equal to C. When n=0, the CPE becomes a pure resistor with R=1/Y_0. The capacitance can be calculated from the experimentally found CPE parameter n and Y_0 by the equation,[11]

$$C = \frac{Y_o \omega^{n-1}}{\sin(n\frac{\pi}{2})} \quad [\text{farads}] \tag{4}$$

Finally, in series where the entire network representing the coated surface is R_{so}, the resistance due to the ohmic drops within the electrolyte. Values of all the parameters in the equivalent circuit were determined by fitting the EIS data using a complex, nonlinear, least square software package developed by Gamry.

SEM/EDX Analysis

Sections of galvanized steel (1 × 3 cm^2) with and without an organic coating were all hot molded, polished, and gold coated for SEM. For EDX analyses, the samples were etched using Timofeef's reagent to which a drop of a mixture of 100 ml nitric acid and 6 g chromic acid was added. All SEM/EDX analyses were carried out using a Cambridge Instruments Stereoscan 90. An accelerating voltage of 20kV was used for both SEM and EDX analysis.

Hardness Analysis

The surface hardness (Vickers hardness) was tested with an LECO M-400-H1 hardness testing machine. Two parameters are important for the hardness of the outer layer. The first one is the steel type of the test panels and the other parameter is the galvanizing temperature. It is well known that both these parameters have a strong effect on the alloy formation of the zinc coating.[5,6]

N-methyl Pyrrolidone Retention Time (NMPRT)[25]

N-methyl pyrrolidone is a swelling agent, which is used to test the type of bonding at the paint-metal interface by subjecting it to strong shear forces due to swelling in

Table 6—Thickness (μm) of the Organic Coating on the Galvanized Test Panels, Measured with SEM

	Coating Thickness (μm)				Corner Coverage (μm)			
Coating	1st	2nd	3rd	Total	1st	2nd	3rd	Total
One-layer powder coating	110	—	—	110	≈ 5	—	—	≈ 5
Two-layer powder coating	110	70	—	180	7	50	—	57
Three-layer solvent-based coating	130	110	50	290	37	51	69	157

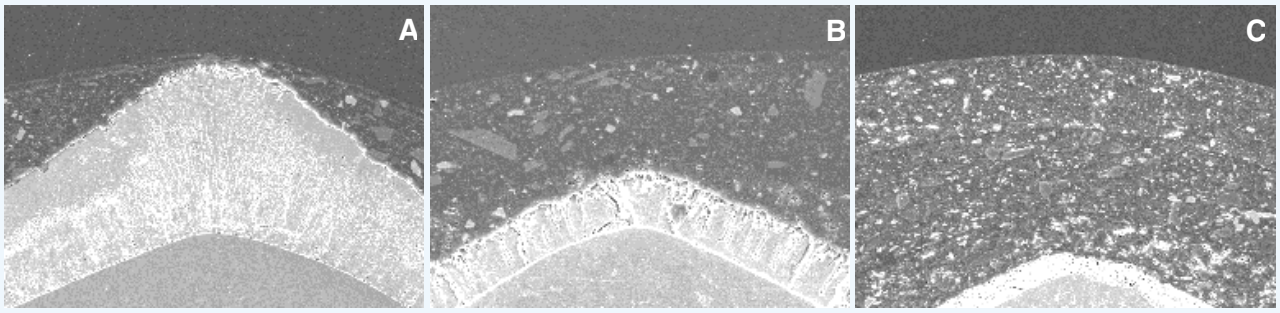


Figure 5—Corner coverage of the three coat systems (a) one-layer powder coating (400x), (b) two-layer powder coating (600x), and (c) three-layer solvent-based coating (300x).

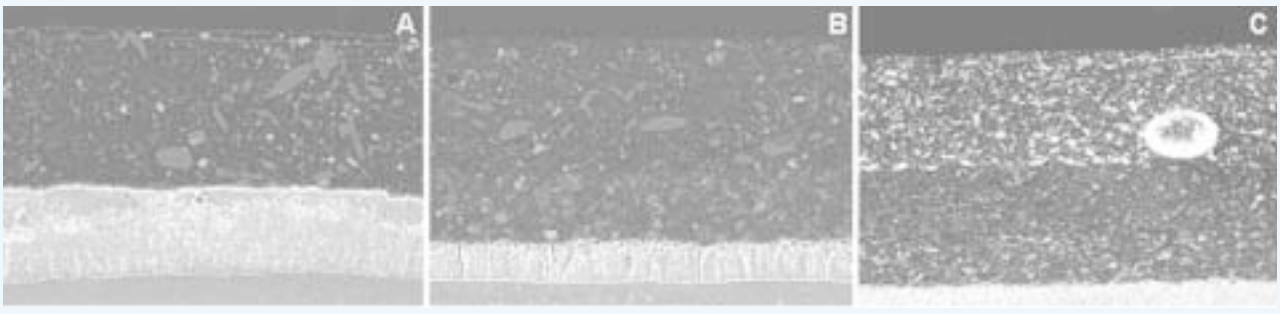
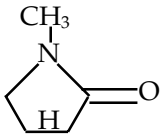


Figure 6—Coverage of the three coat systems (a) one-layer powder coating (400x), (b) two-layer powder coating (350x), and (c) three-layer solvent-based coating (200x).

the solvent N-methyl pyrrolidone. NMP (C_5H_9NO) is a colorless solvent (bp 203°C) with the molecular structure:



N-methyl pyrrolidone

From different panels, which were galvanized and coated, small square samples were cut (1.4×1.4 cm^2) and immersed in NMP at 60°C. The time it took for the coating to delaminate from the substrate was recorded and called NMPRT. A higher NMPRT value indicates a better adhesion between the substrate and coating.

Corrosion Testing

The salt spray test, according to ASTM B117, was done at Brent America Inc. (Lake Bluff, IL). This test was done with galvanized panels with an organic coating.

The UV/condensation test (ASTM D 5894) was done by Corrosion Control Consultants (Kentwood, MI). This test was done on galvanized panels ($150 \times 100 \times 3$ mm) with an organic coating.

The Machu test[12-14] is a standard test at the Weert Groep to test the coating adhesion on metal substrates. After applying a scribe, the panels were immersed in a solution of 5 wt% NaCl containing also 0.6 wt% H_2O_2 at 37°C. After 48 hr the delamination of the paint was determined with a Stanley knife and measured on one side of the scribe.

RESULTS AND DISCUSSION

Characterization of the Zinc/Iron Alloy Layers

In the first phase of this study the galvanized steel panels were characterized and the influence of steel composition and galvanizing temperature on the formation of the different alloy layers was determined.

Galvanized panels were cross-sectioned and studied with SEM/EDX. The thickness of the alloy layer and the corner coverage was investigated. The alloy structure was determined after etching the samples with Timofeef's reagent and gold sputtering. Typical top views of the different panels are shown in *Figure* 3 and EDX results are given in *Table* 3.

The steel test coupons produced a coating of 110 µm thickness for low-Si steel and about 190 µm for high-Si steel when galvanized in standard conditions. Corner coverage was good, but there was a strong growth of the ζ-alloy at the corners of the low-Si material with a disappearance of both η and δ. The alloy structure was γ, δ, ζ, η for the low-Si material and ζ, δ for the high-Si material with a strong outgrowth of ζ.

Table 7—Results of the Corrosion Tests on Galvanized Steel Panels with an Organic Coating

Coating System	EIS : Overall Resistance (Ω) at 10^{-3} Hz		NMPRT (min)		Machu	Salt Spray	QUV Test
	$R_1 \times 10^9$	$R_2 \times 10^9$	1st Coat Layer	2nd Coat Layer	Delamination (μm)		
NCP	1.7×10^{-2}	4.6×10^{-3}	30		0	1.5	0
NCE	10	11	10	35	0	0.9	0
NCL	2.1	2.8	> 3 hours		0	2.8	0
NAP	3.7×10^{-3}	0.5	8		>3	>3	0.8
NAE	11	43	10	16	>3	>3	0.2
NAL	3.4	2.6	26		>3	>3	0.2
NSP	1.1×10^{-2}	3.7×10^{-3}	> 3 hours		0	2.2	1.1
NSE	12	16	14	> 3 hours	0	1.1	1.2
NSL	3.5	3.9	18		0.9	1.8	>3
DCP	0.2	1.9×10^{-2}	26		2.8	0.7	0.1
DCE	50	4.7	9	38	0.3	0.5	0.3
DCL	2.2	2.1	> 3 hours		1.6	0.5	0.1
DAP	5.8	4.6×10^{-3}	5		>3	>3	0.3
DAE	24	6.7	13	18	>3	>3	1.3
DAL	2.5	1.5	25		>3	>3	0
DSP	3.7×10^{-4}	1.2×10^{-6}	> 3 hours		2.6	>3	0.3
DSE	7.5	6.7	17	88	>3	0.8	0.7
DSL	3.9		23		1.0	>3	>3

N = hot-dip galvanized steel
D = delta galvanized steel

A = grit blasting
C = chromate
S = silane

P = one-layer powder coating
E = two-layer powder coating
L = three-layer solvent-based coating

The delta-galvanized steel coupons formed coatings of 30 µm thickness for both low and high-Si steels, i.e., this process is largely insensitive to the Si content (Sandelin effect). The alloy structure was γ, δ for both. Corner and edge coverage was excellent and did not show any outgrowth phenomena. No cracking was observed anywhere in these inherently harder coatings.

The surface of the conventional material was smooth with an occasional ζ crystal visible in the high-Si material. The surface of the delta-galvanized material showed an open, microrough surface for both types of steel. Visible were the ζ crystals embedded in the δ layer. This surface topology is ideal for paint anchoring and confirmed previous studies of this material.[5,6]

The Vickers hardness of the delta coating was two and one-half times that of the conventional coating (δ vs the ζ hardness). Both processes produced greater hardness coatings with the high-Si steel (>200 for delta of high-Si steel) than with the low-Si steel.

Corrosion Behavior of Galvanized Steel

The corrosion rate of the alloy coatings was determined using direct current electrochemical testing methods named Tafel analysis and Linear Polarization analysis. A few examples of the obtained Tafel plots are shown in *Figure* 4. Using the fitting program of Gamry Systems the open corrosion potential (OCP), polarization resistance (R_p), and corrosion current (I_{corr}) could be determined.

In acidified solutions, the conventional coatings were slightly more resistant. In neutral and alkaline solutions, the delta coatings had a greater resistance against corrosion than the conventional ones. These results should be interpreted with care, as they cannot reliably predict a lifetime in service conditions, where the coating will normally become passivated. Also, the large difference in surface area due to the micro roughness of the delta coatings plays a role.

Of more importance than these corrosion rates data are the open circuit corrosion potentials. These determine

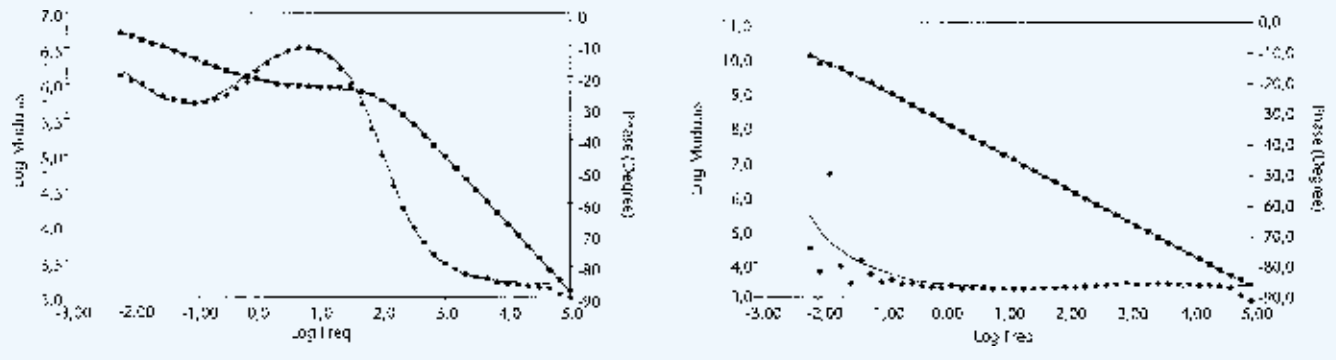


Figure 7—Typical Bode plot for (a) a one-layer powder coat system after 14 days' exposure to 3% sodium chloride and (b) a two-layer powder coat system after 35 days' exposure to 3% sodium chloride solution.

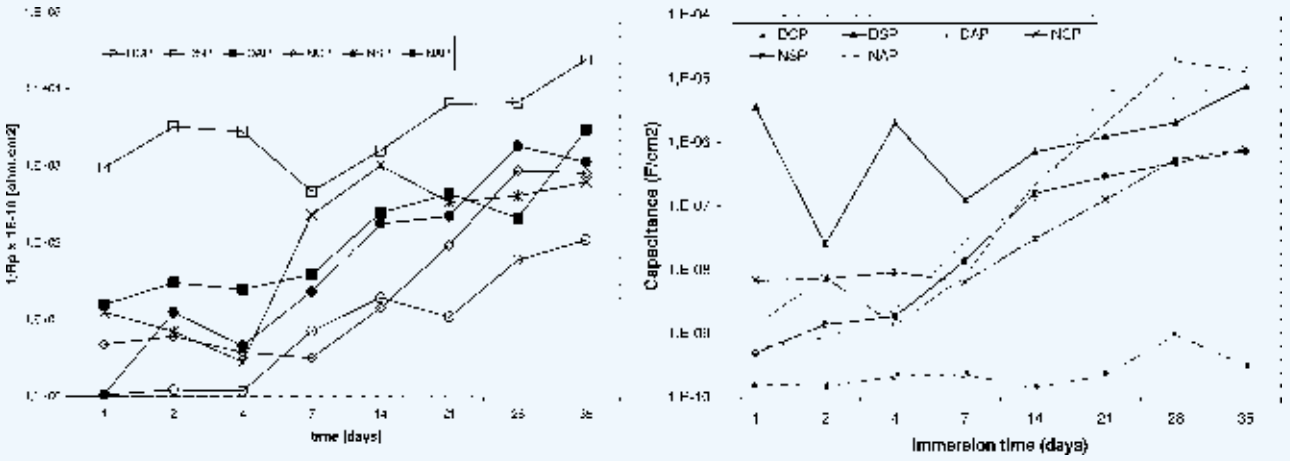


Figure 8—EIS analysis (a) polarization resistance, 1/Rp and (b) double layer capacitance, C_{dl} vs immersion time.

how actively the metal will dissolve when it is actively protecting the steel in cathodic protection situations. The open corrosion potential of the delta coatings was 50-100 mV higher than for the conventional coatings. This implies that at scribes, edges, and cuts the delta coatings will protect steel by cathodic protection, but the coating dissolution rate can be a factor of up to 10 lower, or in other words this factor more than compensates for the lower zinc alloy coating thickness. An overview of the results is shown in *Tables* 4 and 5.

Tests by Linear Polarization analysis were used to verify the results obtained with Tafel analysis. All the open corrosion potentials and corrosion resistance values were comparable with the Tafel plot results and are, therefore, not shown.

Properties of the Paint Coating

The thickness of the paint coatings was determined with SEM analysis. An overview of the results is shown in *Table* 6. An important property of the coating is the coverage of sharp corners because corrosion will start at the least protected areas. This coverage, as shown in *Figure* 5, was poor for the systems with one polyester powder coat (*Figure* 5a), but was much improved for the dual layer powder system (*Figure* 5b). The solvent-based system has the best corner coverage of the three paints (*Figure* 5c).

The wettability of the metal surface by the paint was equal for all systems (cross-sectional analysis) but the solvent-based system contained a large number of voids formed by solvent bubbles (*Figure* 6c). The powder paint systems did not contain any bubbles or voids and showed a very good pigment and filler dispersion (*Figures* 6a and 6b). Such voids can be weak spots in the coating where corrosion can initiate because they can fill with water and electrolyte.

NMPRT test showed (*Table* 7) that there was little difference between the conventional and the delta substrates. When the three metal pretreatments were compared, it was observed that the silane treatment had the best adhe-

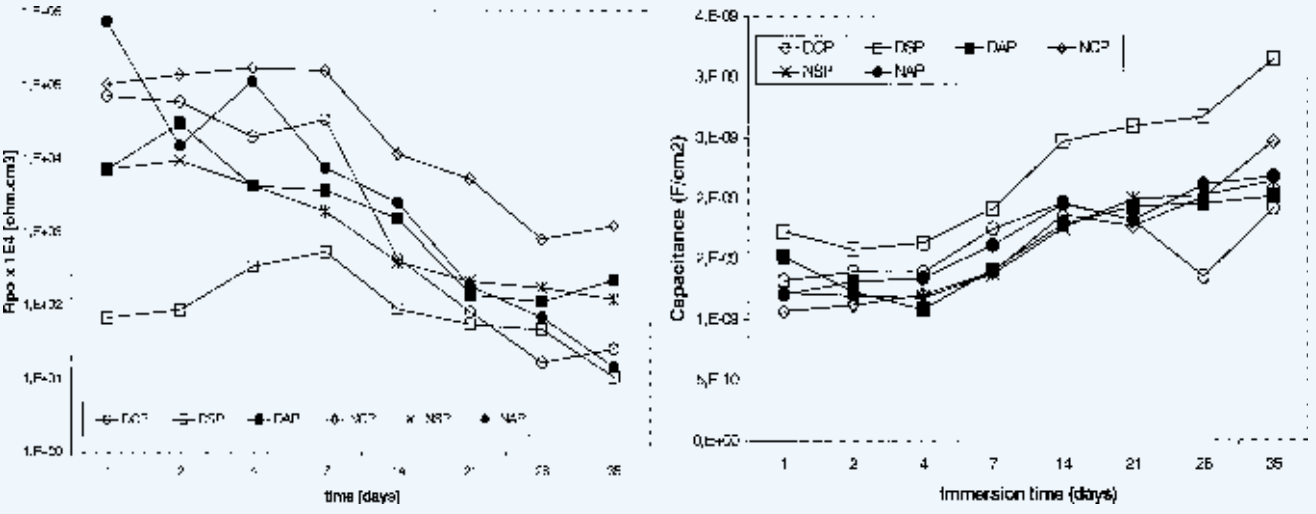


Figure 9—EIS analysis (a) coating resistance, R_{po} and (b) coating capacitance, C_{coat} vs immersion time.

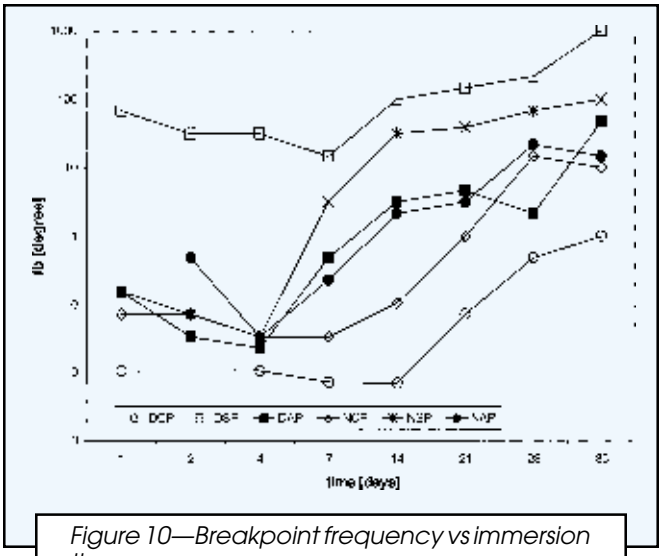


Figure 10—Breakpoint frequency vs immersion time.

sion (or least swellable interface) for the powder paints but not with the solvent-based systems. The standard chromate process gave outstanding adhesion to the solvent-based system, but was slightly poorer for the powder paint systems. Blasting gave the poorest adhesion to all paint systems.

Corrosion Measurements on Duplex Systems

Electrochemical Impedance Spectroscopy: *Figure* 7 shows typical Bode plots for a one-layer powder-coat system and a two-layer powder-coat system. The Bode plots from the solvent-based coat system, not shown, were comparable with the plots from the two-layer powder-coat system. There was little change after 35 days of exposure for the two-layer powder-coat systems and three-layer solvent-based systems, demonstrating that the water uptake into the coating was minimal. For this reason these systems were only taken into account for the overall resistance measurements and were excluded from the specific EIS analysis.

Overall Resistance, $R_s + R_{po} + R_p$: One of the parameters that was easily determined was the overall resistance of the different coat systems at the lowest frequency (10^{-3} Hz) after 35 days of exposure to 3% sodium chloride. This value is a combination of the solvent resistance (R_s), the polarization resistance (R_p), and the coating resistance (R_{po}). A higher value of the overall resistance indicated a better resistance of the system against corrosion. An overview of the overall resistance is shown in *Table* 7. The values R_1 and R_2 are the results of the EIS experiments on two different panels. Comparing these values indicates that this experiment is reproducible.

Clearly visible is the relation between the overall resistance and coating system. The lowest values are obtained with the one-layer powder-coat systems, followed by the three-layer solvent-based coating. The highest values are obtained from the two-layer powder-coat system, which indicates the best protection of the substrate against corrosion. The two-layer powder coat outperforms the three-layer solvent-based system despite the fact that the latter is 100 µm thicker. It is believed that the reasons for this observation are the specific coating properties like coating hardness and density.

Due to the thickness of the organic coating and the minimal water uptake into the coating, the influence of the pretreatment or substrate was not evident in the test results.

Thus, based on the overall resistance of EIS results, the corrosion resistance of coatings is in the following order:

two-layer powder coat > three-layer solvent-based paint > one-layer powder coat

Polarization Resistance, R_p, and Double Layer Capacitance, C_{dl}, vs Immersion Time: The polarization resistance, R_p, is related to corrosion as shown by the equation[11] :

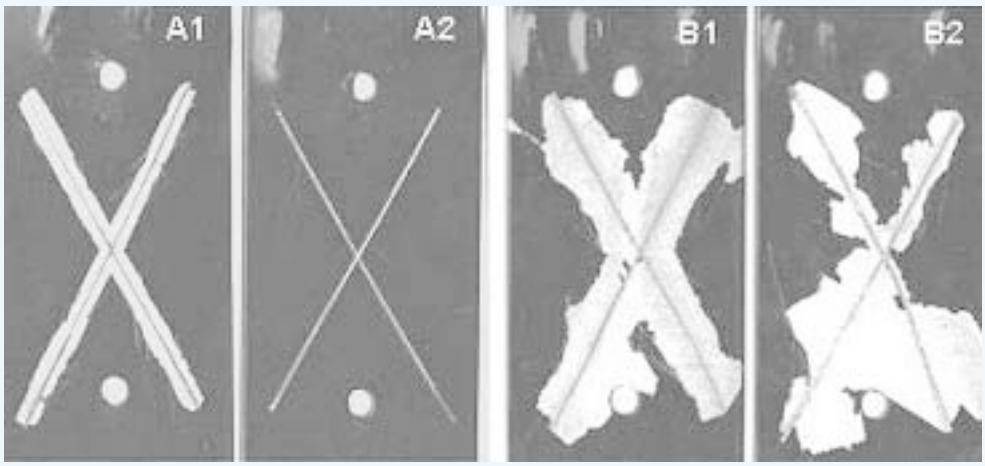


Figure 11—Machu results of (a) delta galvanized panels with chromate pretreatment and one-layer powder coat (a1) or two-layer powder coat (a2) and (b) delta galvanized panels with grit blasting pretreatment and one-layer powder coat (b1) or two-layer powder coat (b2).

$$\text{Corrosion rate} = \frac{\beta_a \cdot \beta_c}{2.303(\beta_a + \beta_c)} \cdot \left(\frac{1}{R_p}\right) = K \cdot \left(\frac{1}{R_p}\right) \quad [\text{cm/yr}] \quad (5)$$

Here, K is a system constant which is related to the anodic and cathodic Tafel constants β_a and β_c, respectively. The higher the polarization resistance, the lower is the corrosion rate. Plots of $1/R_p$ of all the one-layer coat systems versus time are shown in *Figure* 8a. The polarization resistance for all the tested coatings decreases ($1/R_p$ increases) gradually in time and with comparable speed. The highest polarization resistance was obtained with the delta + chromate system, which indicates the highest corrosion resistance. The system delta + silane gave the lowest polarization resistance. Based on these results, the corrosion resistance of coatings is in the following order:

DCP > NCP, NAP, DAP, NSP > DSP
(see *Table 7* for legend)

A plot of double layer capacitance for all the one-layer systems vs time is shown in *Figure* 8b. For each coating, the double layer capacitance increases with immersion time. A higher C_{dl} in time is usually attributed to an increase in corrosion area underneath the organic coating since the capacitance of a coating can be defined as,[9]

$$C = \varepsilon_0 \varepsilon \frac{A}{d} \quad [\text{farads}] \quad (6)$$

where A is the surface area in cm^2, d is the thickness in cm, ε_0 is a constant ($=8.87 \times 10^{-14}$ farads/cm), and ε is the dielectric constant of the coating medium in farads/cm.

An increase in corrosion area results in lower polarization resistance and higher corrosion rates. After 35 days of immersion the system delta + chromate gave the lowest double layer capacitance and the other systems gave C_{dl} values which were all a factor 10^4 times higher. Based on these results, the corrosion resistance of coatings is in the following order:

DCP > NCP, NSP > DAP, NAP, DSP
(see *Table 7)*

Pore Resistance, R_{po}, and Coating Capacitance C_{coat} vs Immersion Time: Plots of R_{po} and C_{coat} of all the one-layer coat systems versus time are shown in *Figure* 9. As expected, R_{po} decreases in time and C_{coat} increases slowly in time. Since both parameters are coating dependent, and only one coating is evaluated, the differences between the panels are little. The variation in coating thickness can especially cause these differences.

Breakpoint Frequency, f_B, vs Immersion Time: The breakpoint frequency is the frequency where the phase shift is 45°. It has been suggested that the breakpoint frequency is related to the delamination of the organic coating.[5] A higher breakpoint frequency is usually attributed to an increase in the corroding area underneath the organic coating. A plot of f_b versus time is shown in *Figure* 9. The lowest values of f_b, which means best adhesion and corrosion protection, are obtained with delta-galvanized panels with a chromate pretreatment. Based on the results, the corrosion resistance of coatings is in the following order:

DCP > NCP, NAP, DAP, NSP > DSP
(see *Table* 7)

Corrosion Measurements of the Complete Systems

Machu Test: Very little difference was observed among the three coating systems when a chromate or silane pretreatment was used. Some examples are shown in *Figure* 11. Combining the three-layer solvent-based coating with grit blasting as pretreatment gave poor results. In terms of the metal pretreatment, the blasted panels were all much worse than the silane or chromate treatments; the conventional galvanized substrate was slightly better than the delta-galvanized system. No differences were observed between the two steel types.

Salt Spray Test: A comparison between the different pretreatment methods showed that chromate was the best pretreatment in most systems; only for low-Si steel and conventional hot-dip galvanizing was chromate second to the silane treatment. Blasting was by far the worst

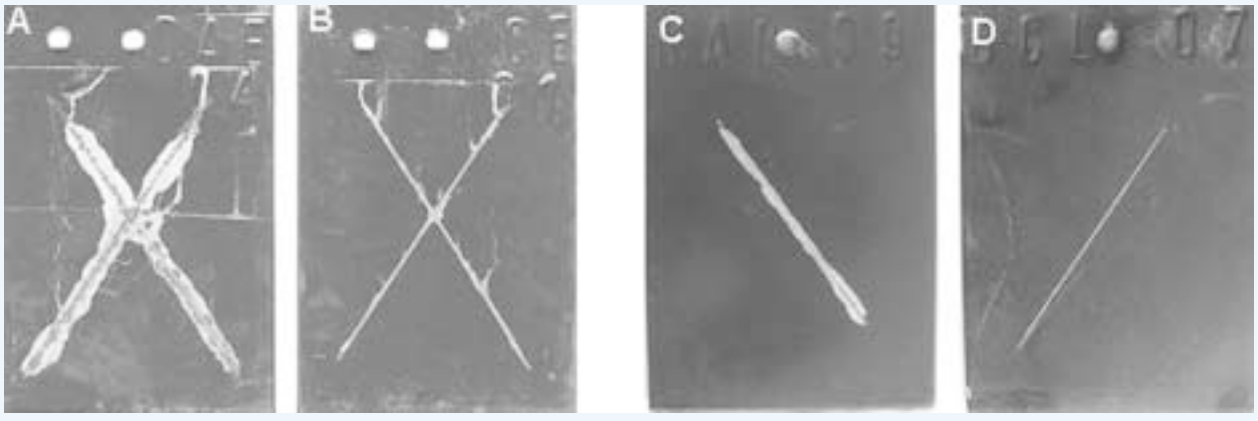


Figure 12—Test results after salt spray test (a, b) and ASTM 5894 test (c, d): (a) delta galvanized panel with grit blasting pretreatment and two-layer powder coat, (b) hot-dip galvanized panel with chromate pretreatment and double layer powder coat, (c) hot-dip galvanized panel with grit blasting pretreatment and one-layer powder coat, and (d) delta galvanized panel with chromate pretreatment and three-layer solvent-based coat.

treatment in all systems. Of the three coat systems the two-coat powder system was clearly the best of the three coat systems; the other two showed comparable performance. However, the solvent-based system lost 30% of its gloss in this test, the polyester lost only 10%. A comparison between galvanizing processes indicated that for high-Si steel the hot-dip process gave a marginal better result, for standard Si content the delta process performed marginally better. However, these marginal differences were not completely reproducible. Some examples are shown in *Figures* 12a and 12b.

THE UV/CONDENSATION TEST: The delamination area here was much less than in the salt spray test. However, the UV radiation caused a loss of gloss that varied between 11 and 77% for the polyester paint and 15-45% for the solvent-based paints. Thus, essentially they behave the same, which is quite remarkable as the solvent-based system has a polyurethane topcoat which is, in general, very resistant to UV. A comparison of the galvanizing process showed that the differences here are marginal and not reproducible. Comparison of the metal pretreatment shows that the chromate process was here, again, superior to the others. However, due to the lower wet time, the blasted panels did not perform as poorly as in the salt spray test. Since this test is less aggressive and has been shown to discriminate better between coated metals, we can actually conclude that most systems performed very well in this test. If we look at those that performed rather poorly, they were all combinations of the applied silanes with this specific solvent-based coating. Apparently, these two factors are incompatible. Some examples are shown in *Figures* 12c and 12d.

CONCLUSIONS

This study has resulted in a large amount of data from which we can confidently draw the following conclusions. Since there are so many factors involved (steel quality, galvanizing process, pretreatment, type of paint, etc.) we cannot rely on just one test to determine the quality of painted galvanized steel. Each test emphasizes different properties and factors and accelerates certain reactions in a different way. Therefore, it is absolutely essential that we compare these systems in a gamut of different test conditions. The best system will then be the system that shows the best overall performance. The weight factors of the different test results were all equal.

Blasting of hot-dip galvanized steel can be rated as a poor pretreatment prior to coating. Our results indicate that its performance becomes worse as the wetness and salt concentration of the environment increase. The silane pretreatment shows some promise as a replacement for chromate but requires further optimization for each specific system. More work is recommended here. The delta galvanizing process has the advantage over conventional galvanizing in that it is much less sensitive to the silicon content of the steel. Thus, it can be used for more steel qualities than the conventional process. Another important advantage is that it has a much greater hardness than that of conventional hot-dip galvanized steel. Its lower coating thickness of 30 µm is more than compensated for by the fact that when cathodic protection is called for, i.e., in cracks and knicks, its dissolution rate is considerably lower than that of the η alloy. Furthermore, this type of galvanized steel is always painted. As a result of the high quality of the pretreatment and the paint systems, the rate of corrosion of the zinc underneath the paint is essentially zero. The polyester powder paint system has an outstanding hot water and UV resistance. The former is better than that of high-quality polyurethane solvent-based paint systems, the latter is equivalent to solvent-based systems.

Of all the systems tested here, the system consisting of delta-galvanized steel, chromate pretreatment, and a two-layer coat powder paint system has the best overall performance characteristics. It performs best in almost all tests that were considered in this project. The corrosion rate of the metal underneath the paint, i.e., in the absence of defects, is approximately zero. The adhesion of the paint, measured by several test protocols, is excellent. The corner coverage is more than adequate. The paint system does not contain solvent bubbles and the adhesion between the two powder paint layers is also good. The excellent results obtained with this system are remarkable in view of its total thickness, which is at least 100 µm less than the high-quality solvent-based system tested here. The system consisting of normal galvanized steel, chromate treatment, and the two-layer powder coating also performs well. However, it does not offer the high hardness and it is more sensitive to variations in the steel quality. The system consisting of delta-galvanized steel, chromating, and one coat of powder paint (polyester) will be an excellent choice for all but the most highly corrosive environments. In that case the dual layer system is recommended.

ACKNOWLEDGMENT

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APPENDIX

Parameters and Scenarios Tested

- Silicon concentration in the steel test panels
  - —high silicon steel (0.31%)
  - —low silicon steel (0.01%)
- Hot-dip galvanizing process
  - —conventional hot-dip galvanizing at 450°C
  - —delta galvanizing at 550°C
- The pretreatment after galvanizing and before coating
  - —shot blasting
  - —chromate pretreatment
  - —silane pretreatment
- The organic coating
  - —one-layer powder coating
  - —two-layer powder coating
  - —three-layer solvent-based paint

Combining these parameters gives 36 different duplex systems which were all taken into account.

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