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Elucidation of corrosion failure mechanisms of coated phosphated steel substrates

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Abstract Coatings are commonly believed to protect metal surfaces from corrosion based on some combination of their barrier properties and electrochemical properties. Various physical and electrochemical tests were performed on seven different coatings (latex, alkyd, 2-PK epoxy, and electrocoat) to determine which properties were the main determinants of corrosion resistance in continuous and cyclic corrosion tests. Physical property tests and AC electrochemical tests were all related to barrier behavior, while DC electrochemical tests were related to electrochemical behavior. DC electrochemical properties are commonly associated with inhibitor chemistry, but can be broadly related to all components of the paint. These test results were compared with corrosion test results from both continuous (B-117) and cyclic (GM9540) accelerated tests. The best correlation was seen with a model emphasizing barrier behavior with a secondary component relating to electrochemical protection.

Keywords Corrosion, Failure mechanisms, Film barrier behavior, Electrochemical properties, Phosphated steel, AC impedance measurements, DC potentiodynamic scans, Passivation index,

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Continuous salt spray, Cyclic salt spray, Cathodic delamination, Oxygen permeability, Water vapor transmission, Water vapor permeance, Waterborne paints, Solventborne paints

Introduction

There is abundant literature describing the collective beliefs of the coatings industry regarding the mechanisms by which coatings protect (or fail to protect) metals from corrosion during subsequent exposure to corrosive conditions. A good summary can be found in the volume by Dickie and Floyd.¹ Such mechanisms can be grouped into two categories: film barrier behavior, and electrochemical interruption properties.

Film barrier behavior refers to the physical barrier created by the coating that prevents corroding species from contacting the steel in any way that would cause corrosion. Such barrier behaviors include permeability to water, ions, and oxygen. Barrier behavior also includes adhesion under adverse conditions (commonly wet), and film resistance to hydrolysis, since they relate to blistering and cathodic delamination, respectively, both of which detract from barrier protection.

Electrochemical properties relate not to physical barriers, but to electrochemical interruptions of at least one of the half-cell reactions in the corrosion circuit. Electrochemical properties are commonly associated with inhibitor chemistry only, but should more broadly be considered as related to all components of the paint.²

It is sometimes asserted that several mechanisms typically operate in concert to determine the corrosion resistance of any given coating system.³ Although substrate certainly plays a major role,⁴ the present mechanism work focuses on coatings-related mechanisms. We have employed zinc phosphated cold-rolled

steel in our mechanism studies, because most earlier studies utilized bare cold rolled steel. We wanted to see if the phosphating process materially changed the protection picture.

We have expanded our repertoire of monitoring techniques to include resistance to cathodic delamination, and permeability to both water and oxygen. We also monitored the adhesion of the coatings as a function of soak time, to determine the extent of their protection under adverse conditions. In this way, we seek to illuminate the prevailing mechanism by which a given coating fails in corrosion testing, and whether that prevailing mechanism varies by coating type.

There is precedent in the literature for believing that different coatings chemistries function by different protective mechanisms, that a multiparameter model is likely required to explain widely varying compositions, and that some coatings types can actually change the underlying corrosion process that occurs on protected metals³⁻⁵ (see Appendix I for example). We included seven paints in our study out of which five are water-based paints and two are solvent-based paints.

Experimental

Materials

Seven paints were used in this study having a range of barrier properties. The paint codes used in this study and their descriptions are given below in Table 1. Paints “B” and “E” are lab prepared paints.

Methods

Water vapor transmission rate and permeance of pigmented coatings

As per ASTM method D 1653-93 the wet cup method was used to determine the water vapor transmission and permeance of pigmented coatings. This test method determines the rate at which water vapor passes through free films of pigmented coatings. Small Gardco perm cups of 10 cm² were used as standard

apparatus to carry out the experiments. The test specimens were free films of 3.0–4.0 mils dry film thicknesses. These films were sealed to the open mouth of these cups containing water, and then the whole assembly was placed in desiccators containing desiccants. Three replicates of each coating were made and tested. Paint “I” was not tested because it was not possible to produce a free film. The tests were run for three continuous weeks noting down the changes in weight, humidity and temperature. When the tests were completed the water vapor transmission (WVT) and water vapor permeance (WVP) were calculated according to ASTM D 1653-93 and then the average values based on three replicates were obtained.

Cathodic delamination

The apparatus for cathodic delamination⁶ consists of a round bottom flat glass jar, graphite rods, metal rods, electrical wires, alligator clips, a direct voltage supplier and 5% NaCl solution. The apparatus is shown in Fig. 1.

A constant voltage of –1.5 V was applied to the panels and the current was measured throughout the experiment. This causes the coated panels to remain at a cathodic potential during the experiment. The cathodic delamination experiment was run for 1000 h with two replicates of each and during that period of time the voltage was kept constant at 1.5 V and the current was between 170 and 175 mA. The 5% NaCl solution was changed at 15 days cycle so that the impurities and the rust from the screws which are used to mount the panels (see Fig. 1) deposited in the solution are removed and replaced with a fresh solution of 5% NaCl. The dry film thicknesses of the coatings on the panels were between 3 and 4 mils. A 2 in. straight scribe was made at the center of the panel which is shown in Fig. 2.

Table 1: Paint code descriptions

Code	Description
B	Lab prepared latex DTM paint based on Haloflex latex
C	Commercial solventborne alkyd paint
E	Lab prepared acrylic latex DTM paint
F	Commercial acrylic latex DTM paint
G	Commercial fail control latex house paint
H	Commercial 2 pack solvent-based epoxy paint
I	Cathodic electrodeposition paint

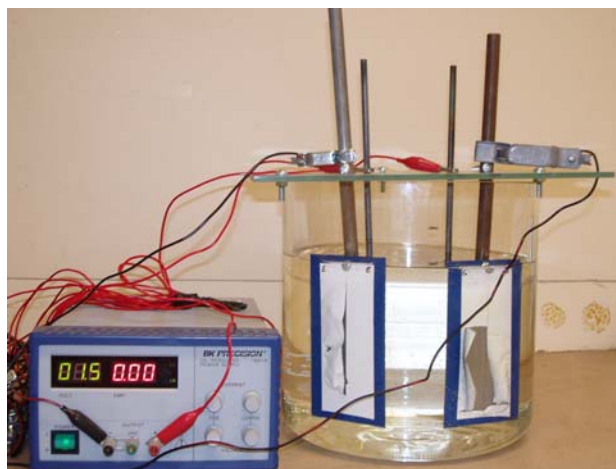


Fig. 1: Cathodic delamination apparatus



Fig. 2: Scribed panel for cathodic delamination experiment

Oxygen (O_2) permeability

Free films of Paints “B”, “E” and “H” were prepared at two thicknesses: 3–4 and 6–8 mils dry film thickness on Teflon coated release paper. These films were air dried for 7 days at ambient conditions and then sent to Prof. Eric Baer, Macromolecular Science Department, Case Western Reserve University who kindly agreed to test for the oxygen permeability. The oxygen permeability was measured with a Mocon Ox-Tran 2/20 instrument.

Accelerated exposure testing

For the accelerated exposure testing in both continuous salt fog and cyclic salt fog testing, six replicate panels of each paint were made with 3.0–4.0 mils dry film thickness. The Q-Fog Corrosion Tester CCT1100 was used to do both the continuous corrosion testing as per ASTM method B-117 and cyclic corrosion testing as per GM9540 method. The panels were scribed straight 2 in. at the bottom right hand side of the panel (see exposed panel in Fig. 3).

The B-117 testing was conducted to 1200 h and the GM9540 testing was conducted to 50 cycles (1 cycle is completed in 24 h). The panels were evaluated every 240 h for B-117 and 10 cycles for GM9540 testing. Blister ratings in the field were evaluated as per ASTM method D 714-87. Scribe creep ratings were evaluated as per ASTM method D 1654-92. Field corrosion ratings were evaluated as per ASTM D 610-95. Real world field testing was not done due to limitations of resources and time. Also it is worth noting that there is no agreement on how to do field testing. Our focus was on correlating material tests with corrosion tests (B-117 and GM9540).



Fig. 3: Scribed panel after subjected to B-117 accelerated exposure test

Wet adhesion

The wet adhesion of “B”, “C”, “H”, and “I” were checked as soon as the panels were removed from the B-117 at regular intervals of 240, 480, 720, 960, and 1200 h and for GM9540 testing at 10, 20, 30, 40, and 50 cycles. For paints “E”, “F”, and “G” in B-117 the panels were checked at 1, 4, 8, 24, 48, 72, 96, 120, 144, 192, and 216 h intervals. The panels were washed with tap water and the surfaces of the panels were blotted surface dry with paper towel before checking the wet adhesion. The tape used for the wet adhesion testing was a 3 M Scotch Premium Cellophane tape 610. Wet adhesion values are reported in Table 12.

DC electrochemical measurements

DC measurements were done with the Gamry (Warminster, PA) PC14/300 Potentiostat/Galvanostat/ZRA. We utilized two instruments each with two potentiostats (multiplexed) for all DC measurements. CorrView Electrochemical Analysis software (Scribner Associates, Inc., Southern Pines, NC) was used to interpret and illustrate all DC data.

DC POTENTIODYNAMIC CATHODIC SCANS: According to the Zurilla⁷ technique, the cathodic polarization scans were conducted on the phosphated panels, with the sodium hydroxide solution of pH 12. The purpose of running the cathodic scan was to select the best lot of phosphated panels from two lots. The scans were conducted between 0.5 and –4 V. Values of the current at –2 V were used to assess the variability in the phosphated panels.

DC POTENTIODYNAMIC ANODIC SCANS: The passivation index (PI), for systems that passivate², is defined as the difference (in millivolts) between the open circuit potential and the breakdown potential, without regard to minor features that may occur in between.

WATERBORNE PAINTS: For DC potentiodynamic anodic scans the waterborne paint samples from different manufacturers were diluted to 5% by weight with DI water, mixed thoroughly, centrifuged and the supernatant was analyzed by the potentiodynamic anodic scan technique.

SOLVENTBORNE PAINTS: For paint “H” which is a solventborne epoxy paint 50 g of the paint sample and 50 g of toluene were taken in a 1 L conical flask and stirred for 5 min. Then 450 g of acetone was added to the flask followed by 450 g of deionized water. Then the mixture was stirred for 24 h. After that the toluene was removed by centrifugation and the acetone was removed under vacuum using rotavapor. The remaining phase after acetone is removed is used as the electrolyte for the DC potentiodynamic anodic scans. The same type of procedure is used for paint “C” with 50 g of acetone and 450 g of isopropyl alcohol used for the extraction. All the potentiodynamic anodic scans were done on bare phosphated panels.

AC electrochemical measurements

The EIS (Electrochemical Impedance Spectroscopy) instrumentation used in our studies is a Gamry (Warminster, PA) MultEchem 4 Electrochemistry System consisting of 4 FAS2 Femtostats for EIS measurements in a parallel multiplexing mode with EIS300 Electrochemical Impedance Spectroscopy Software. ZView Electrochemical Analysis software (Scribner Associates, Inc., Southern Pines, NC) was used to analyze and illustrate the AC data. Following is a brief summary of the essential elements in the testing protocols, as provided by Gamry:

- Measure E_{oc} (open circuit potential) and allow it to stabilize.
- Apply a DC voltage equal to the measured value of E_{oc} .
- In addition to the DC voltage, apply a small sinusoidal voltage (10 mV) perturbation of fixed frequency and measure the current response.
- Calculate the impedance and the phase shift.
- Repeat the measurement at a wide range of frequencies (1 mHz to 100 kHz).
- Model the electrochemical process with a two-time-constant equivalent circuit model as shown in Fig. 4. The values of the circuit elements are adjusted to fit the EIS data to the model.

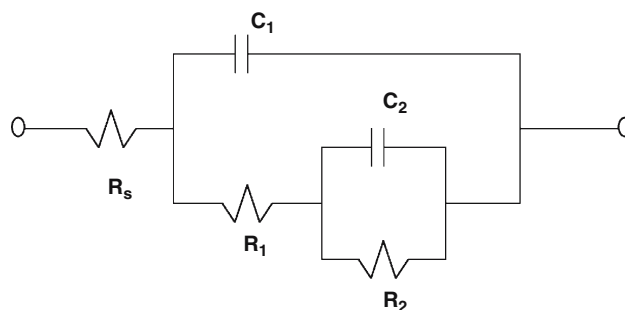


Fig. 4: Two time constant equivalent circuit model. Note: R_s = solution resistance (aka uncompensated resistance R_u), R_1 = coating resistance (aka blister resistance R_b , pore resistance R_p), R_2 = interfacial resistance (aka charge transfer resistance R_{ct} , corrosion resistance R_{cor} , polarization resistance R_p), C_1 = coating capacitance (aka C_c), and C_2 = double-layer capacitance (aka C_{dl})

- Record the data in a spreadsheet, and convert to \log_{10} transform for subsequent statistical analysis.

We obtained AC impedance data on unexposed paints on phosphated panels immersed in B-117 and GM9540 electrolytes for time periods 0, 1, 2, 4, 8, and 24 h.

Results

Water vapor transmission rate and permeance of pigmented coatings

As can be seen in Table 2, the coatings are separated in 3 permeability groupings: extremely low (H), moderate (B, C, E, F), and quite high (G). While the solventborne 2-PK epoxy primer (H) sample's very low reading and the housepaint's (G) very high reading were expected, the closeness of the latex and alkyd samples was a bit surprising.

Cathodic delamination

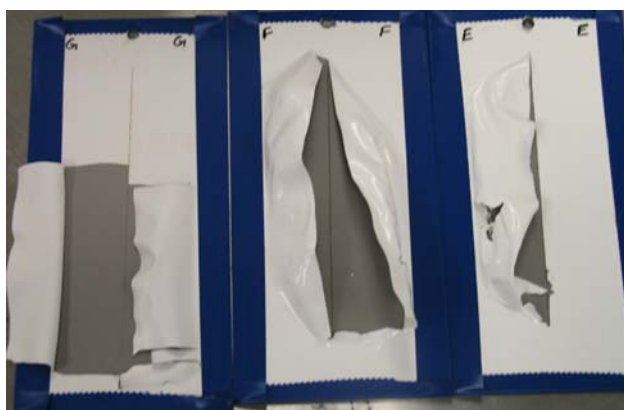
After 4 h of testing it was found that paints “E”, “F”, and “G”, delaminated fully from the panels as shown in Fig. 5, while paints “B”, “C”, “H”, and “I” did not delaminate at the scribe at all on the panel even after 1000 h of testing. Also, there were no blisters or corrosion on the scribe and on the field as shown in Fig. 6. Both the replicates showed the same kind of behavior.

Oxygen permeability

Because of cost and time constraints, we selected three of the samples for oxygen permeability measurements: B (Haloflex-based), E (housepaint), and H

Table 2: WVT and WVP results

Paint code	WVT		WVT		WVP		WVP		Average	
	grains/sq.ft/h/in.Hg	Std. deviation	g/sq.m/24 h/mm.Hg	Std. deviation	grains/sq.ft/h/in.Hg	Std. deviation	g/sq.m/24 h/mm.Hg	Std. deviation	Humidity (RH) at vapor source	Temperature (°C) in dessicator
B	4.00	0.22	67.40	3.60	7.99	0.43	5.27	0.28	40.31	23.3
C	3.00	0.77	49.90	12.89	5.91	1.53	3.90	1.01	40.31	23.3
E	3.80	0.22	63.20	3.61	7.49	0.43	4.94	0.28	40.31	23.3
F	3.40	0.27	56.10	4.52	6.65	0.54	4.38	0.35	40.31	23.3
G	12.50	0.50	209.60	8.29	24.83	0.98	16.37	0.65	40.31	23.3
H	0.20	0.03	4.00	0.43	0.47	0.05	0.31	0.03	40.31	23.3

**Fig. 5: Panels showing cathodic delamination of paints E, F, and G after 4 h of testing**

(solventborne 2-PK epoxy primer). Table 3 shows the oxygen permeability data for these paints at two different dry film thicknesses. As can be seen, the housepaint had quite high permeability, while the latex (Haloflex) and solventborne 2-PK epoxy primer paints had very low permeabilities to oxygen. The oxygen permeability increases as the dry film thickness of the

Table 3: Oxygen permeability results

Paints	Dry film thickness (mils)	Average flux [cc(STP)/m ² day]	Average permeability [cc(STP) cm/(m ² day atm.)]
B	3–4	8.305	0.102
	6–8	5.245	0.109
E	3–4	39.25	19.4
	6–8	31.55	26
H	3–4	38.25	0.321
	6–8	26.4	0.486

coating increases for the housepaint and solventborne 2-PK epoxy primer paint, but not for Paint “B”.

Accelerated exposure testing

The accelerated exposure test results for B-117 and GM9540 are shown in Table 4. For paint G there were

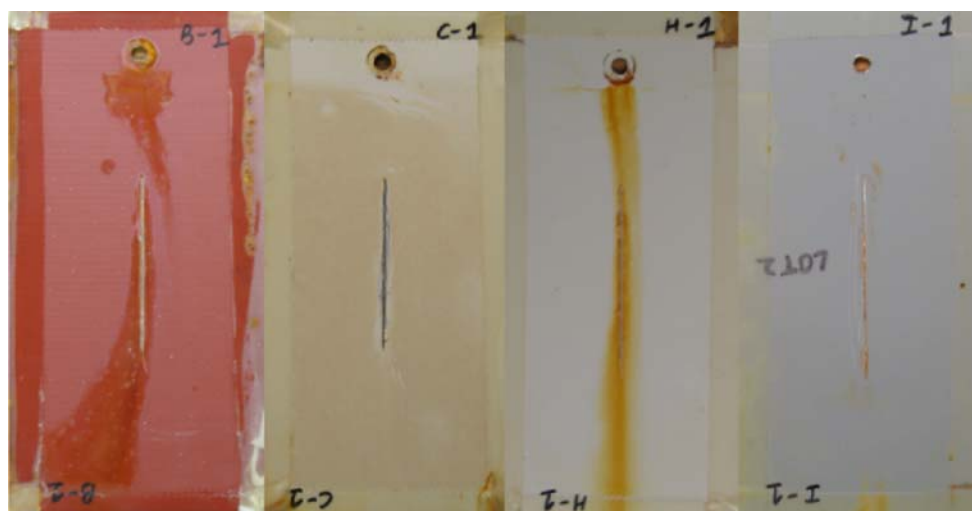
**Fig. 6: Cathodic delamination of paints B, C, H, and I after 1000 h of testing**

Table 4: B-117 and GM9540 ratings

B-117						GM9540					
Panel	240 h	480 h	720 h	960 h	1200 h	Panel	240 h	480 h	720 h	960 h	1200 h
B1	9BIF10	8BIF6	8BIF4	8BIF2	8BIF0	B1					
B2	9BIF10	7BIF7	7BIF6	6BIF2	6BIF0	B2					
B3	9BIF10	8BIF7	8BIF5	8BIF3	8BIF0	B3					
B4	9BIF10	8BIF8	8BIF4	8BIF2	8BIF0	B4					
B5	9BIF10	9BIF8	9BIF6	8BIF3	8BIF1	B5					
B6	8BIF10	7BIF8	7BIF5	7BIF2	7BIF0	B6					
C1	9BIF7	8BIF4	8BIF4	8BIF4	8BIF2	C1	10BIF10	10BIF10	10BIF9	10BIF9	10BIF8
C2	9BIF10	9BIF4	9BIF4	8BIF4	8BIF2	C2	10BIF10	10BIF10	10BIF9	10BIF9	10BIF8
C3	8BIF10	8BIF3	8BIF3	8BIF3	8BIF2	C3	10BIF10	10BIF10	10BIF9	10BIF9	10BIF8
C4	9BIF5	8BIF3	8BIF3	7BIF3	7BIF2	C4	10BIF10	10BIF10	10BIF9	10BIF9	10BIF8
C5	9BIF8	9BIF4	8BIF4	8BIF4	8BIF2	C5	10BIF10	10BIF10	10BIF9	10BIF9	10BIF8
C6	9BIF6	9BIF4	9BIF4	8BIF4	8BIF2	C6	10BIF10	10BIF10	10BIF9	10BIF9	10BIF8
E1	2BIF8	0BIF4				E1	8BIF7	8BIF4	8BIF3	8BIF2	8BIF0
E2	2BIF7	0BIF5				E2	8BIF7	8BIF4	8BIF3	8BIF2	8BIF0
E3	2BIF8	0BIF8				E3	8BIF7	8BIF4	8BIF3	8BIF2	8BIF0
E4	2BIF8	0BIF5				E4	8BIF7	8BIF4	8BIF3	8BIF2	8BIF0
E5	2BIF8	0BIF5				E5	8BIF7	8BIF4	8BIF3	8BIF2	8BIF0
E6	1BIF6	0BIF4				E6	8BIF7	8BIF4	8BIF3	8BIF2	8BIF0
F1	4BIF6	2BIF4	1BIF3			F1	10BIF9	10BIF6	10BIF5	10BIF5	10BIF4
F2	4BIF6	2BIF4	0BIF2			F2	10BIF9	10BIF6	10BIF5	10BIF5	10BIF4
F3	3BIF6	2BIF4	0BIF2			F3	10BIF9	10BIF6	10BIF5	10BIF5	10BIF4
F4	3BIF7	1BIF4	0BIF1			F4	10BIF9	10BIF6	10BIF5	10BIF5	10BIF4
F5	3BIF7	2BIF5	0BIF3			F5	10BIF9	10BIF6	10BIF5	10BIF5	10BIF4
F6	4BIF8	3BIF5	2BIF4			F6	10BIF9	10BIF6	10BIF5	10BIF5	10BIF4
G1	0BIF0					G1	8BIF8	8BIF1	0BIF0		
G2	0BIF0					G2	8BIF8	8BIF1	0BIF0		
G3	0BIF0					G3	8BIF8	8BIF1	0BIF0		
G4	0BIF0					G4	8BIF8	8BIF1	0BIF0		
G5	0BIF0					G5	8BIF8	8BIF1	0BIF0		
G6	0BIF0					G6	8BIF8	8BIF1	0BIF0		
H1	8BIF10	8BIF10	7BIF10	7BIF10	7BIF10	H1	10BIF7	10BIF5	10BIF5	10BIF5	10BIF4
H2	7BIF10	7BIF10	7BIF10	7BIF10	6BIF10	H2	10BIF7	10BIF5	10BIF5	10BIF5	10BIF4
H3	8BIF10	7BIF10	7BIF10	7BIF10	6BIF10	H3	10BIF7	10BIF5	10BIF5	10BIF5	10BIF4
H4	7BIF10	7BIF10	7BIF10	7BIF10	6BIF10	H4	10BIF7	10BIF5	10BIF5	10BIF5	10BIF4
H5	7BIF10	7BIF10	7BIF10	7BIF10	6BIF10	H5	10BIF7	10BIF5	10BIF5	10BIF5	10BIF4
H6	8BIF9	8BIF9	7BIF9	6BIF9	6BIF9	H6	10BIF7	10BIF5	10BIF5	10BIF5	10BIF4
I1	8BIF10	7BIF10	7BIF10	7BIF10	6BIF10	I1	10BIF10	10BIF8	10BIF8	10BIF7	10BIF7
I2	7BIF10	7BIF10	7BIF10	6BIF10	6BIF9	I2	10BIF10	10BIF8	10BIF8	10BIF7	10BIF7
I3	8BIF10	7BIF10	7BIF10	7BIF10	7BIF10	I3	10BIF10	10BIF8	10BIF8	10BIF7	10BIF7
I4	8BIF10	7BIF10	6BIF10	6BIF10	6BIF10	I4	10BIF10	10BIF8	10BIF8	10BIF7	10BIF7
I5	7BIF10	7BIF10	7BIF10	6BIF9	6BIF9	I5	10BIF10	10BIF8	10BIF8	10BIF7	10BIF7
I6	8BIF10	7BIF10	6BIF10	5BIF10	5BIF10	I6	10BIF10	10BIF8	10BIF8	10BIF7	10BIF7

Note: The first number in the above ratings is for corrosion creep from scribe. A second number indicates that there is failure in the unscribed portion of the panel (BIF = blisters in field). The blank region without any ratings indicates that the panels were removed from the testing because they got fully corroded. For paint “H” in GM9540, the testing was not done

no blisters on the panel but there was field corrosion all over the panels. These ratings are converted to a numerical summation of all replicates for all 5-time intervals (6 readings per coating). Thus, higher numbers represent better corrosion results. The error for the summed readings is ± 1 unit (based on replicate panels). The numerical summation ratings are shown in Table 12.

Variability between lots of phosphated steel

Cathodic scans were conducted on four different spots on each of four different panels from each of two lots of phosphated steel. The relative quality of the phosphate treatment (Zurilla⁷ technique) is reported as the current flow at -2 V. Comparatively the Lot 2 panels have less variability than the Lot 1 panels.

Table 5: Log current values at -2 V

Panel No.	Mean (mA)	Std. deviation (mA)	Range (mA)
<i>Lot 1</i>			
1	6.004	0.808	1.55
2	5.166	0.406	0.76
3	5.045	0.588	1.269
4	5.726	0.504	1.199
Averages	5.485	0.576	1.1945
<i>Lot 2</i>			
1	6.246	0.469	1.045
2	5.778	0.378	0.842
3	6.060	0.106	0.225
4	5.847	0.070	0.17
Averages	5.983	0.256	0.571

Table 5 shows that Lot 2 had less variability than Lot 1 in terms of both standard deviation and the range.

Therefore, Lot 2 was selected as the Lot of phosphated panels used in this study.

Passivation index

The DC anodic potentiodynamic scans showed a wide variation in the degree of passivation from strong passivator to nonpassivator for the paints used in this study. As observed from the potentiodynamic scans, paint sample H (solventborne 2-PK epoxy), paint sample E and paint sample C (SB alkyd) showed strong passivation. The paint sample H (solventborne 2-PK epoxy) had a lower standard deviation value compared to paint E and the paint C. The other paint samples demonstrated freely corroding behavior.

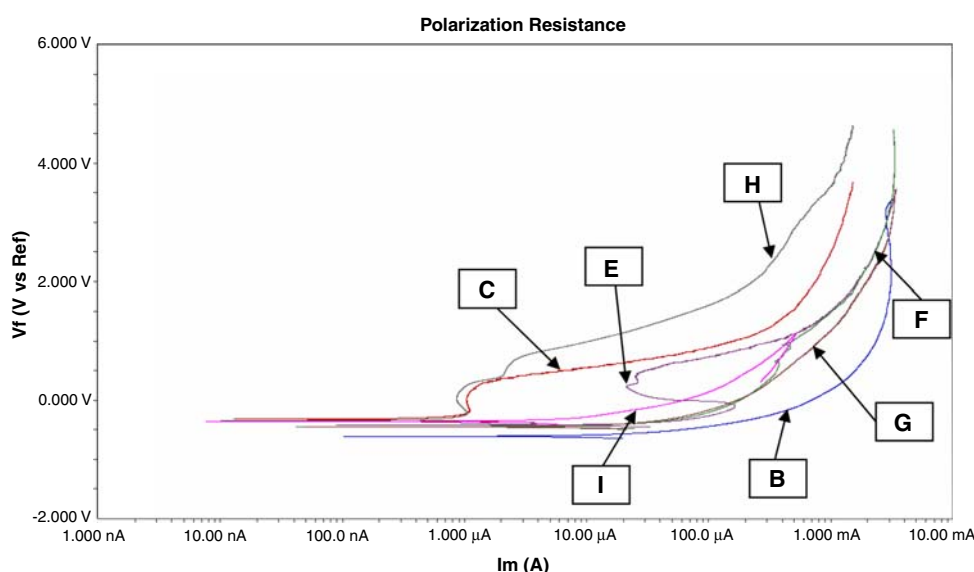
Surprisingly, paint sample B (based on Haloflex resin) exhibited freely corroding behavior. On the basis of the manufacturer's technical literature Haloflex has very good corrosion control behavior. Clearly, this is not due to any initial passivation mechanism.

In paint sample F (Acrylic DTM) only one of the three replicates showed a slight passivation behavior, so paint F was considered to be freely corroding. Paint sample G (commercial fail control housepaint) also exhibited freely corroding behavior as expected. The only exception was in the case of Paint I (cathodic electrodeposition), where the polarization curves exhibited unusual features at very high voltage. No passivation behavior was observed, and an unexplained drop in current and voltage was observed at high voltages. This could conceivably be due to unintended deposition processes occurring (Fig. 7).

Table 6 summarizes the passivation index behavior for the coatings utilized in this study.

Table 6: Passivation index value for coatings on phosphated panels

Paint descriptions	Summary		
	Mean (delta mv)	Std. deviation (delta mv)	Range (delta mv)
<i>Liquid paints</i>			
Paint B	0	0	0
Paint C	566	219	436
Paint E	919	218	435
Paint F	0	0	0
Paint G	0	0	0
Paint H	1048	52	103
Paint I	0	0	0

**Fig. 7: Coplots of DC anodic potentiodynamic scans of paint samples B, C, E, F, G, H, and I**

AC electrochemical measurements on unexposed coated panels

The equivalent circuit analysis of the AC impedance data on immersed unexposed paint samples in B-117 and GM9540 electrolytes yielded values of R_s , R_1 , R_2 , C_1 , and C_2 as a function of immersion time. The initial (0 h of immersion) and equilibrium values (24 h of immersion) of these parameters are shown as \log_{10} values in Tables 7 and 8.

Discussion

Cross correlations among factors

Before considering any correlations, one must first examine the results to determine whether the various factors measured are truly independent of one another. For any cases where they are not independent, then they become essentially duplicates of one another, and invalidate any attempt to construct multiple correlations. Table 9 shows the cross correlations among supposed independent variables.

Physical properties

In the present case, high correlations are seen in three areas:

- (1) water permeability and wet adhesion in GM9540 cyclic test;

- (2) oxygen permeability and cathodic delamination and wet adhesion in B-117 continuous test; and
- (3) cathodic delamination and wet adhesion in B-117.

In case 1, the high correlation between water permeability and wet adhesion in GM9540 is not at all surprising, since diffusion of the water through the film is a necessary precursor to the loss of adhesion under wet conditions. The lack of correlation with B-117 wet adhesion is surprising.

In case 2, a correlation between oxygen permeability and cathodic delamination is expected, since oxygen reduction at the advancing cathode front is the controlling step in delamination. The correlation between oxygen permeability and wet adhesion in B-117 is a bit surprising. The lack of correlation between oxygen permeability and wet adhesion in GM9540 is a mathematical artifact which defines a zero slope as being an indeterminate correlation.

In case 3, the correlation between cathodic delamination and B-117 adhesion is not surprising, since the tests would be expected to detect similar behavior (loss of adhesion).

In any event, one should not employ the above pairs in attempts to develop multiple correlations with corrosion test results.

Equivalent circuit elements

In Table 10, the cross correlations that are significant at the 5% (2-sided) level are shown in bold, to make them easy to find. As can be seen, there are about 20

Table 7: EIS equivalent circuit components at time zero

Paint code	Description	AC impedance, unexposed, B-117									
		Initial					Equilibrium				
		Log R_s	Log R_1	Log R_2	Log C_1	Log C_2	Log R_s	Log R_1	Log R_2	Log C_1	Log C_2
B	Waterborne lab prepared paint based on Haloflex latex	4.76	5.20	10.60	(8.84)	(2.72)	1.51	1.96	19.53	(4.50)	(2.64)
C	Commercial solventborne alkyd paint	2.89	5.53	8.62	(8.54)	(8.51)	2.80	5.87	7.29	(8.44)	(7.73)
E	Lab prepared DTM paint	2.93	5.74	7.45	(8.27)	(8.36)	2.20	5.30	7.38	(8.17)	(7.86)
F	Commercial acrylic DTM paint	3.32	3.65	8.03	(8.44)	(8.33)	2.89	3.20	6.50	(9.88)	(7.03)
G	Commercial fail control house paint	2.46	5.54	19.56	(7.62)	(4.34)	1.14	0.92	3.51	(4.62)	(3.27)
H	Commercial 2 pack solvent based epoxy paint	1.57	4.79	10.39	(8.62)	(8.85)	4.18	8.44	17.70	(8.72)	(8.37)
I	Cathodic electrodeposition paint	1.50	1.81	18.95	(9.29)	(8.39)	1.42	1.80	15.93	(12.25)	(8.36)
Mean:		2.77					2.31				
Std. dev.:		1.11					1.07				
Pct. std. dev.:		40%					46%				
Regression correlation vs B-117:		(0.26)	(0.42)	0.02	(0.84)	(0.21)	0.33	0.35	0.83	(0.39)	(0.35)
Regression correlation vs GM9540:											
		Correlation between initial and equilibrium values:					(0.28)	0.30	0.01	0.60	0.98

Table 8: EIS equivalent circuit elements at equilibrium time

Paint code	Description	AC impedance, unexposed, GM9540									
		Initial					Equilibrium				
		Log R_s	Log R_1	Log R_2	Log C_1	Log C_2	Log R_s	Log R_1	Log R_2	Log C_1	Log C_2
B	Waterborne lab prepared paint based on Haloflex latex	1.29	3.02	6.79	(9.83)	(7.62)	1.89	3.29	19.96	(4.36)	(3.29)
C	Commercial solventborne alkyd paint	3.35	3.83	8.82	(10.63)	(8.65)	3.02	3.44	7.12	(10.34)	(8.02)
E	Lab prepared DTM paint	3.05	3.38	7.50	(10.77)	(8.20)	1.19	3.14	6.76	(7.94)	(7.34)
F	Commercial acrylic DTM paint	3.05	3.52	7.75	(10.91)	(8.15)	2.55	2.73	5.53	(9.13)	(6.42)
G	Commercial fail control house paint	1.01	3.42	12.46	(7.35)	(4.60)	1.42	2.61	3.68	(4.70)	(3.69)
H	Commercial 2 pack solvent-based epoxy paint	4.61	4.98	11.29	(9.00)	(9.24)	1.41	5.06	7.85	(8.73)	(8.21)
I	Cathodic electrodeposition paint	1.48	1.33	17.11	(9.91)	(8.36)	1.56	2.85	13.26	(9.19)	(8.30)
Mean:		2.55					1.86				
Std. dev.:		1.32					0.68				
Pct. std. dev.:		52%					36%				
Regression correlation vs B-117:											
Regression correlation vs GM9540:		0.46	(0.13)	0.04	(0.70)	(0.85)	0.58	0.28	0.64	(0.98)	(0.86)
							0.18	0.68	(0.03)	0.60	0.76

Table 9: Cross correlations of physical properties

	PI	H ₂ O	O ₂	Cath Del	WA B-117	WA GM9540
Passivation Index	1.00					
H ₂ O permeability	(0.58)	1.00				
O ₂ permeability	0.41	0.44	1.00			
Cathodic delamination	0.11	(0.54)	(1.00)	1.00		
Wet adhesion B-117	0.18	(0.56)	(1.00)	0.99	1.00	
Wet adhesion GM9540	0.42	(0.95)	Low ^a	0.45	0.48	1.00

^a Slope of zero makes correlation indeterminant (very low)

pairs that are cross-correlated, and which should therefore not be used in constructing multiple correlation models.

It is interesting to note that there are five cases where R_s correlates with other factors. As mentioned earlier, since R_s is supposed to be invariant, and independent of all other factors and conditions, its actual variation can be used as an estimate of total experimental error. Therefore, any cross correlations seen with R_s are purely by chance, even though we are operating at a level of 5% chance of such fortuitous occurrences. This is a good reminder to the reader that while infrequent, such chance correlations do occur, and this possibility needs to be considered as one interprets other data.

The notable correlations (ignoring those involving R_s) are given in Table 11.

It is notable that most of the capacitance readings are cross-correlated with one another. In the case of correlations between initial and equilibrium times, this implies that whatever water is absorbed initially is sufficient to establish and maintain the ranking

observed at equilibrium times. [Recall that initial times are not true zero, but represent the shortest time interval possible experimentally. In addition, it takes about an hour to run the EIS scans for a given sample.]

In the case of correlations between electrolytes, this suggests that the two electrolytes affect the paint films similarly, even though they are quite different chemically.

In any event, to be valid, any multiple correlations must contain only one element on any given line in Table 10.

Single correlations

Single correlations were calculated via regression analysis and Pearson rank order analysis. Multiple correlations were calculated via SPSS software. Following Occam's Razor,⁸ the simplest 2-factor models were extracted for further analysis and discussion.

Table 10: Cross correlations of EIS equivalent circuit elements

Cross correlations																					
	BRsI	BR1I	BR2I	BC1I	BC2I	BRsE	BR1E	BR2E	BC1E	BC2E	GRsI	GR1I	GR2I	GC1I	GC2I	GRsE	GR1E	GR2E	GC1E	GC2E	
BRsI	Pearson correlation	1	0.418	-0.447	0.078	0.638	-0.278	-0.313	0.034	0.597	0.650	-0.306	0.010	-0.795	-0.300	0.144	0.338	-0.303	0.451	0.493	0.670
	Sig. (2-tailed)		0.351	0.314	0.868	0.123	0.547	0.494	0.943	0.157	0.114	0.505	0.983	0.033	0.513	0.759	0.458	0.509	0.310	0.261	0.099
BR1I	Pearson correlation	0.418	1	-0.412	0.682	0.327	0.112	0.297	-0.326	0.770	0.383	0.178	0.660	-0.672	0.178	0.271	0.004	0.201	-0.242	0.372	0.374
	Sig. (2-tailed)	0.351		0.359	0.091	0.474	0.811	0.518	0.476	0.043	0.397	0.703	0.106	0.098	0.703	0.556	0.993	0.666	0.600	0.411	0.409
BR2I	Pearson correlation	-0.447	-0.412	1	0.038	0.316	-0.618	-0.623	0.009	0.023	0.285	-0.678	-0.540	0.839	0.726	0.612	-0.400	-0.336	0.036	0.350	0.238
	Sig. (2-tailed)	0.314	0.359		0.936	0.491	0.139	0.135	0.985	0.961	0.535	0.094	0.211	0.018	0.065	0.144	0.374	0.461	0.938	0.442	0.607
BC1I	Pearson correlation	0.078	0.682	0.038	1	0.243	-0.088	-0.073	-0.769	0.596	0.386	-0.052	0.470	-0.282	0.486	0.704	-0.123	-0.207	-0.710	0.383	0.436
	Sig. (2-tailed)	0.868	0.091	0.936		0.599	0.851	0.876	0.043	0.158	0.392	0.913	0.288	0.540	0.269	0.077	0.792	0.656	0.074	0.397	0.328
BC2I	Pearson correlation	0.638	0.327	0.316	0.243	1	-0.639	-0.640	0.146	0.843	0.981	-0.734	-0.151	-0.205	0.488	0.671	-0.154	-0.303	0.476	0.941	0.955
	Sig. (2-tailed)	0.123	0.474	0.491	0.599		0.123	0.122	0.755	0.017	0.000	0.061	0.747	0.659	0.266	0.099	0.741	0.508	0.281	0.002	0.001
BRsE	Pearson correlation	-0.278	0.112	-0.618	-0.088	-0.639	1	0.908	0.149	-0.317	-0.603	0.970	0.764	-0.246	-0.271	-0.687	0.219	0.797	-0.309	-0.595	-0.587
	Sig. (2-tailed)	0.547	0.811	0.139	0.851	0.123		0.005	0.750	0.488	0.152	0.000	0.045	0.594	0.557	0.088	0.637	0.032	0.500	0.159	0.166
BR1E	Pearson correlation	-0.313	0.297	-0.623	-0.073	0.123	0.908	1	0.160	-0.244	-0.646	0.957	0.732	-0.242	-0.272	-0.702	0.063	0.848	-0.265	-0.569	-0.657
	Sig. (2-tailed)	0.494	0.518	0.135	0.876	0.122	0.005		0.733	0.598	0.117	0.001	0.061	0.601	0.555	0.079	0.893	0.016	0.566	0.183	0.109
BR2E	Pearson correlation	0.094	-0.326	0.009	-0.769	0.146	0.149	0.160	1	-0.099	-0.012	0.047	-0.120	0.151	-0.046	-0.495	0.542	0.825	0.022	0.100	-0.070
	Sig. (2-tailed)	0.943	0.476	0.985	0.043	0.755	0.750	0.733		0.832	0.979	0.920	0.797	0.747	0.922	0.258	0.619	0.209	0.022	0.831	0.882
GC1E	Pearson correlation	0.597	0.770	0.023	0.596	0.843	-0.317	-0.244	-0.099	1	0.873	-0.362	0.329	-0.472	0.511	0.637	-0.130	-0.049	0.117	0.847	0.854
	Sig. (2-tailed)	0.157	0.043	0.961	0.158	0.017	0.488	0.598	0.832		0.010	0.425	0.471	0.285	0.241	0.124	0.781	0.918	0.016	0.014	
GC2E	Pearson correlation	0.650	0.383	0.285	0.386	0.981	-0.603	-0.646	-0.012	0.873	1	-0.703	-0.067	-0.262	0.508	0.747	-0.079	-0.358	0.322	0.926	0.988
	Sig. (2-tailed)	0.114	0.397	0.535	0.392	0.000	0.152	0.117	0.979	0.010		0.078	0.887	0.570	0.244	0.054	0.867	0.431	0.003	0.000	
GRsI	Pearson correlation	-0.306	0.178	-0.678	-0.052	-0.734	0.970	0.957	-0.362	-0.703	-0.703	1	0.730	-0.274	-0.367	-0.717	0.179	0.747	-0.379	-0.667	-0.683
	Sig. (2-tailed)	0.505	0.703	0.094	0.913	0.061	0.000	0.001	0.920	0.425	0.078		0.062	0.552	0.418	0.070	0.701	0.054	0.402	0.102	0.091
GR1I	Pearson correlation	0.010	0.660	-0.540	0.470	-0.151	0.764	0.732	-0.120	0.329	-0.067	0.730	1	-0.502	0.133	-0.155	0.110	0.681	-0.438	-0.072	-0.054
	Sig. (2-tailed)	0.983	0.106	0.211	0.288	0.747	0.045	0.061	0.797	0.471	0.887	0.062		0.251	0.776	0.740	0.814	0.092	0.325	0.879	0.908
GR2I	Pearson correlation	-0.795	-0.672	0.839	-0.282	-0.205	-0.246	-0.242	0.151	-0.472	-0.262	-0.274	-0.502	1	0.442	0.129	-0.345	-0.058	-0.033	-0.159	-0.313
	Sig. (2-tailed)	0.033	0.098	0.018	0.540	0.659	0.594	0.601	0.747	0.285	0.570	0.552	0.251		0.321	0.783	0.449	0.902	0.944	0.734	0.494
GC1I	Pearson correlation	-0.300	0.178	0.726	0.486	0.488	-0.271	-0.272	-0.046	0.511	0.508	-0.367	0.133	0.442	1	0.722	-0.485	0.073	-0.171	0.604	0.470
	Sig. (2-tailed)	0.513	0.703	0.065	0.269	0.266	0.557	0.555	0.922	0.241	0.244	0.418	0.776	0.321		0.067	0.270	0.876	0.715	0.151	0.287
GC2I	Pearson correlation	0.144	0.271	0.612	0.704	0.671	-0.687	-0.702	-0.495	0.637	0.747	-0.717	-0.155	0.129	0.722	1	-0.250	-0.238	0.729	0.758	
	Sig. (2-tailed)	0.759	0.556	0.144	0.077	0.099	0.088	0.079	0.258	0.124	0.054	0.070	0.740	0.783	0.067		0.589	0.176	0.607	0.063	
GRsE	Pearson correlation	0.338	0.004	-0.400	-0.123	-0.154	0.219	0.063	-0.230	-0.130	-0.079	0.179	0.110	-0.345	-0.485	-0.250	1	-0.143	-0.053	-0.444	-0.112
	Sig. (2-tailed)	0.458	0.993	0.374	0.792	0.741	0.637	0.893	0.619	0.781	0.867	0.701	0.814	0.449	0.270	0.589		0.759	0.910	0.319	0.812
GR1E	Pearson correlation	-0.303	0.201	-0.336	-0.207	-0.303	0.797	0.848	0.542	-0.049	-0.358	0.747	0.681	-0.058	0.073	-0.576	-0.143	1	0.060	-0.237	-0.402
	Sig. (2-tailed)	0.509	0.666	0.461	0.656	0.508	0.032	0.016	0.209	0.918	0.431	0.054	0.092	0.902	0.876	0.176	0.759		0.898	0.609	0.372
GR2E	Pearson correlation	0.451	-0.242	0.036	-0.710	0.476	-0.309	-0.265	0.825	0.117	0.322	-0.379	-0.438	-0.033	-0.171	-0.238	-0.053	0.060	1	0.333	0.264
	Sig. (2-tailed)	0.310	0.600	0.938	0.074	0.281	0.500	0.566	0.022	0.803	0.481	0.402	0.325	0.944	0.715	0.607	0.910	0.898		0.466	0.568
GC1E	Pearson correlation	0.493	0.372	0.350	0.383	0.941	-0.595	-0.569	0.100	0.847	0.926	-0.667	-0.072	-0.159	0.604	0.729	-0.444	-0.237	0.333	1	0.929
	Sig. (2-tailed)	0.261	0.411	0.442	0.397	0.002	0.159	0.183	0.831	0.016	0.003	0.102	0.879	0.734	0.151	0.063	0.319	0.609	0.466		0.002
GC2E	Pearson correlation	0.670	0.374	0.238	0.436	0.955	-0.587	-0.657	-0.070	0.854	0.988	-0.683	-0.054	-0.313	0.470	0.758	-0.112	-0.402	0.264	0.929	1
	Sig. (2-tailed)	0.099	0.409	0.607	0.328	0.001	0.166	0.109	0.882	0.014	0.000	0.091	0.908	0.494	0.287	0.048	0.812	0.372	0.568		0.002

Heading codes: B: B1I7; G: GM9540; R_s: solution resistance; R₁: coatings resistance; R₂: interface resistance; C₁: coatings capacitance; C₂: interface capacitance; I: initial soak time; E: equilibrium soak time

Tables 7, 8, and 12 contain all the physical property and electrochemical data for this study, plus the single factor correlations as calculated by MS Excel. The

correlations that were considered significant by the authors are shown in bold italics for ease of identification. We only considered correlations with coefficients greater than 0.7 (+ or -) based on collective experience.

Some correlations are shown in bold type: they are considered as having too little data to justify a strong claim of correlation, despite their numerical results. For example, cathodic delamination data was of a bi-variant type, which has the effect of connecting a straight line between two points or clusters of data. In the case of oxygen permeability, there are only 3 data points, which yield a low significance to its correlations; and in the case of comparison with cyclic corrosion testing, there are only two common data points between them. This does not mean that the correlations are incorrect, but only that they should be viewed with some caution since they are based on limited data sets.

The single-factor correlations are summarized in Table 13 for the reader's convenience.

Table 11: Cross correlations among circuit elements

Factors in each row are correlated, and not Independent

B R1 I	B C1 E			
B R2 I	G R2 I			
B C1 I	B R2 E			
B C2 I	B C1 E	B C2 E	G C1 E	G C2 E
B R1 E	G R1 E			
B R2 E	G R2 E			
B C1 E	B C2 E	G C1 E	G C2 E	
B C2 E	G C1 E	G C2 E		
G C2 I	G C2 E			
G C1 E	G C2 E			

B, G: electrolyte; R1, R2, C1, C2: circuit element; I, E: soak time (initial, equilibrium)

Table 12: Physical Properties of Test Paints on Phosphated Steel

Paint code	Description	Corrosion results		Passivation index ^a (delta mv)	Permeability		Cathodic delamination (hours-to-failure)	Wet adhesion during corrosion testing	
		B-117 Sum of all ratings (1200 h)	GM9540 Sum of all ratings (50 cycles)		H ₂ O g/m ² / 24 h/ mmHg	O ₂ cc(STP) cm/ (m ² day atm.)		B-117 (hours-to-failure)	GM9540 (cycles-to-failure)
B	Waterborne lab prepared paint based on Haloflex latex	386	n.r.	0	5.27	0.102	1000	1200	n.r.
C	Commercial solventborne alkyd paint	372	576	566	3.90	n.r.	1000	1200	50
E	Lab prepared DTM paint	75	336	919	4.94	19.4	4	216	50
F	Commercial acrylic DTM paint	117	476	0	4.38	n.r.	4	4	50
G	Commercial fail control house paint	0	150	0	16.38	n.r.	4	48	1
H	Commercial 2 pack solvent-based epoxy paint	504	458	1048	0.31	0.321	1000	1200	50
I	Cathodic electrodeposition paint	498	540	0	n.r.	n.r.	1000	1200	50
Mean:									
Std. Dev.:									
Pct. Std. Dev.:									
Regression correlations vs B-117:			0.76	0.17	(0.72)	(0.96)	0.96	0.95	0.57
Regression correlations vs GM9540:		0.76		0.12	(0.84)	(1.00)	0.71	0.70	0.85

^a Passivation index for solventborne (SB) paints determined for water extract of that paint

Table 13: Single factor correlations with corrosion results

Factors	B-117	GM9540
Passivation index	0.17	0.12
Water permeability	(0.72)	(0.84)
Oxygen permeability	(0.96)	(1.00)
Cathodic delamination	0.96	0.71
Wet adhesion	0.95	0.85

B-117 correlations

Strong single-factor correlations with B-117 continuous corrosion results were seen with water permeability (negative) and wet adhesion (positive). This is consistent with a barrier model, where higher water permeability would be expected to yield poorer corrosion results, and where better wet adhesion would be expected to yield better corrosion results.

The negative 0.96 correlation seen with oxygen permeability is very interesting, and probably suggestive of something significant. However, it is based on only 3 data pairs, and must therefore be considered inconclusive for the present study. It does however suggest that oxygen permeability can be significant in determining corrosion resistance, in contrast to several previous workers' opinions and findings.^{9–13}

The positive 0.96 correlation with cathodic delamination results is also encouraging, but represents bi-variant data, which has the effect of drawing a straight line through two clusters of data, which is not a very believable relationship. We say encouraging, because the automotive industry relies heavily on cathodic delamination resistance in the design of effective coatings.

The reader should recall that oxygen permeability and cathodic delamination are themselves highly cross-correlated, so the above correlations may be considered surrogates of one another.

The positive 0.95 correlation with wet adhesion is consistent with a barrier model of protection, and is more convincing than the cathodic delamination data, because it contains a more continuous set of results.

Single factor correlations were seen with equivalent circuit elements C_1 (initial) and R_2 (equilibrium). Thus, the initial capacitance of the paint film and the equilibrium resistance of the interface are detecting behavior that correlates with subsequent corrosion testing in B-117. *The correlation with C_1 is probably just fortuitous, since all values are within the error of the test.* It is much easier to visualize the correlation between equilibrium film resistance and corrosion results, since that is a pure play on a barrier theme. In addition, the variation among samples is outside the error of the test.

GM9540 correlations

The only credible single-factor correlation with GM9540 cyclic corrosion results was with water

permeability (negative). The correlation seen with oxygen permeability represents only two common data points, and is therefore not considered compelling. The correlation with cathodic delamination is encouraging, but is based on bi-variant data which makes any strong correlation suspect. Likewise, the correlation with wet adhesion represents bi-variant data and is similarly suspect.

EIS testing produced strong negative correlations with C_1 and C_2 , both initially and at equilibrium. The initial results may be considered fortuitous, since most data are within the error of the test. However, the equilibrium correlation is quite believable, being well outside the error limit of the test. The equilibrium capacitance correlations with corrosion test results strongly support a barrier model for protection, and suggest that both film and interface properties are important.

Effect of estimates of paint B results in GM9540 testing

Since we could not fill in the missing information for paint B in GM9540 testing, we decided to assign a range of possible outcomes, and measure the resulting effect on the correlations of physical properties with GM9540 corrosion results. The results can be seen in Table 14.

First one should note that all but one of the paints showed higher ratings in cyclic testing than continuous testing. This suggests that performance in B-117 (386) could be considered a lower boundary. Second, the correlations that do exist decline monotonically from assumed performance levels of 600 to about 400, after which two of the three fall sharply. Over the range of 400–600, the correlations change in magnitude, but not in significance. We therefore conclude that the omission of a value for performance in GM9540 cyclic test did not materially compromise the correlations in this study.

Multiple correlations

In something as complex as protection of a metal substrate from corrosion, it is probably unrealistic to expect any single factor to account for *all* the observed results, particularly when the coatings options differ greatly as in the present study. Other workers in the field have expressed a similar view.^{3,10}

It was therefore not surprising that significant two-factor correlations with corrosion results were obtained with passivation index and several other factors (Table 15).

This model means that there are strong electrochemical (passivation index) and barrier (cathodic delamination, wet adhesion, and water permeability) effects at play in the present range of coatings tested.

Table 14: Effect of Estimate of Paint B Results in GM9540 on Single Correlations between Cyclic Corrosion and Paint Physical Properties

Resulting correlations of GM9540 with physical properties	Assumed B perf in GM9540						
	100	200	300	400	500	600	Omitted
Passivation index	0.30	0.26	0.21	0.13	0.04	(0.04)	0.12
Water permeability	(0.61)	(0.71)	(0.80)	(0.84)	(0.82)	(0.76)	(0.84)
Oxygen permeability	0.19	0.04	(0.29)	(0.88)	(0.97)	(0.85)	(1.00)
Cathodic delamination	0.28	0.40	0.52	0.64	0.72	0.75	0.71

Note: Since there was no wet adhesion value for paint B in GM9540, correlations are not affected by varying the corrosion result of paint B

Table 15: Two-factor correlation coefficients between corrosion results and physical properties

Factor 1	Factor 2	B-117			GM9540			Comments
		Corr.	Coef. 1	Coef. 2	Corr.	Coef. 1	Coef. 2	
O ₂	H ₂ O	1.000	(16.00)	(25.00)				Factors are correlated
O ₂	PI	1.000	(22.00)	0.12				
WA	H ₂ O	0.975	0.27	(10.00)	0.858	4.12	(8.45)	For GM, factors are correlated
PI	CD	0.960	0.03	0.38				
H ₂ O	PI	0.720	(28.00)	(0.02)	0.904	(31.00)	(0.15)	
CD	H ₂ O				0.867	0.08	(19.00)	

Factor codes: O₂: oxygen permeability; WA: wet adhesion; PI: passivation index; H₂O: water permeability; CD: cathodic delamination

Numbers in bold italics are significant; individual factors are *not* correlated

This is certainly the belief of the formulators of those coatings.

Some significant two-factor correlations with corrosion resistance were also obtained with some of the equivalent circuit elements calculated from EIS measurements (Table 16).

It is interesting that significant correlations were seen with B-117 corrosion results, but not with GM9540 cyclic test results. Only those correlations rising above 0.7 (+ or –) were included in Table 16. None of these correlations had problems with cross correlation of factors.

For initial times, the high correlations for the capacitance pair and the film pair suggest that water has not yet penetrated to the interface with the substrate.

Table 16: Two-factor correlation coefficients between corrosion results and equivalent circuit elements

Factors	B-117	GM9540
C ₂ init, C ₁ init	0.838	None
C ₁ init, R ₁ init	0.862	Were
R ₂ equil, R ₁ equil	0.862	Significant
C ₂ equil, R ₂ equil	0.899	

For equilibrium times, the high correlations for the resistance pair and the interface pair suggest a barrier theme, with resistance and interface properties controlling corrosion results, at least in continuous testing. The absence of a corresponding correlation with cyclic testing suggests that the cyclic test produces results unrelated to the barrier properties of the film or interface.

Conclusions

Even though we had seven different paints with widely varying chemistries and film properties, it appears that we had an insufficient number in each subset to draw absolute conclusions regarding the mechanism by which paints protect the metal substrate.

Nevertheless, the data are certainly suggestive of a primary barrier model with a secondary electrochemical model as the means by which coatings protect a metal substrate from corrosion. This view is primarily derived from two-factor correlations which consistently show this behavior for both continuous and cyclic testing.

The electrochemical component is independent of the barrier component in these models.

EIS testing supports the barrier component view, but is incapable of measuring the electrochemical component. DC testing supports the electrochemical component view, but is incapable of measuring the barrier component.

It was shown that water extracts can be utilized to measure the passivation index of solventborne paints, analogous to the water extracts of reactive pigments reported previously. This makes it possible for the first time to assess the electrochemical contribution of a nonaqueous coating (or component) to the corrosion protection of metal substrates.

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Appendix I

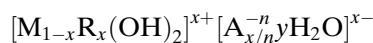
An example of reversal of half-cell reactions with coatings having ultra low O₂ permeability

Previous work^{3,5} has shown that (1) it is possible to develop organic polymers that form films having ultra-low oxygen permeability, and that (2) when applied as coatings to steel substrates, such coatings provide exceptional corrosion resistance. These materials are copolymers of vinyl chloride and vinylidene chloride, and can be thought of as similar to Saran[®] wrap films, which are well known for their low oxygen permeability. However, unlike more conventional materials, the steel substrate gradually turns dark under this coating, in direct relation to the corrosiveness of the environment to which it is exposed. Conventionally, the coatings and steel protection industries have been accustomed to looking for bright metal under coatings

that are protective. The appearance of this dark layer was disconcerting, in spite of the exceptional corrosion resistance that resulted.

Composition

Considerable work by Moreland and Padgett⁵ have shown that this dark layer is a member of the mineralogical group known as pyroaurite. They form hexagonal plate crystals which tend to lay down as layered barrier films. The composition accommodates all of the common corrosive influences for steel (plus its common alloying elements), and provides buffering capacity via the large number of hydroxyl groups.¹⁴ This buffering property could also change the common localized corrosion attack to a more uniform lateral process. Precedent for this thinking comes from known similar hydrotalcite films that form on aluminum in sea water.¹⁵



where M = divalent cation (Fe, Mg, Zn, Co, Ni), R = trivalent cation (Fe, Al, Mn, Co, Ni), A = anion (CO₃²⁻, OH⁻, Cl⁻, SO₄²⁻).

Key attributes of dark layer

It is strongly passivating,⁵ and increases in thickness during exposure to corrosive environments in direct relation to the degree of corrosivity of the environment. The layer is also cathodic to steel, which means that the normal half-cell arrangement on steel is reversed: a damage site becomes the cathode, while the spreading dark interlayer becomes the anode.^{3,5} This means that this process becomes a form of in situ cathodic protection for the underlying steel, which would give it virtually unlimited life in a corrosive environment. Experiments to date show *no* failure in B-117 salt spray exposure even after 10,000 h⁵ (exposure stopped arbitrarily, so true duration of lifetime is unknown).

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