Laboratory Evaluation of Waterborne Coatings on Steel

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Foreword

This report presents findings from the results of a Federal Highway Administration in-house study investigating the performance of the current waterborne acrylic, epoxy, and polyurethane coatings on new steel surfaces. Both the cyclic laboratory tests and the outdoor marine exposure were used to evaluate the performance of different commercial waterborne products that were then compared with that of zinc-rich coatings. This report also presents the effect of chemical properties of primers on coating performance.

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NOTICE

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16. Abstract
Ten commercial waterborne coatings formulated for protecting new steel (SSPC-SP 10) from corrosion were evaluated; they included five acrylic coatings, four epoxy coatings, and one polyurethane coating. The volatile organic compound content of all these waterborne coating materials was below 300 grams per liter. Several key chemical and physical properties were determined to investigate their effect on coating performance. In general, the binder-to-pigment weight ratio stayed above 1.0 for acrylic primers but remained below 1.0 for epoxy primers. A rapid infrared spectroscopic technique was developed in this study to distinguish styrene-modified acrylics from unmodified acrylics (vinyl acrylics). It was found that unmodified acrylics performed better than styrene-modified acrylics in terms of corrosion resistance at scribe. Most of the acrylic primers contained zinc phosphate that was otherwise not present in the epoxy primers. Virtually all the waterborne coatings showed adhesion strengths greater than 14 mega pascals. Both laboratory and outdoor tests were conducted for the performance evaluation. Two 3,000-h cyclic laboratory tests consisted of freeze, UV/condensation, salt-fog/dry-air cycles but 2 different salt solutions were used to generate salt fog-0.35 percent ammonium sulfate plus 0.05 percent sodium chloride (test A) and 5 percent sodium chloride (test B). Another set of test panels was exposed at Sea Isle City, NJ for 2 years for comparison purposes. Topcoat gloss and topcoat color all changed significantly after the tests. In general, little coating surface failures were observed, but all the coating systems developed creepage at an intentional scribe. The scribe creepage was used as the main parameter to compare coating performance; it was found to grow linearly with test time after the first detection time in all cases. The test results showed that the waterborne coating systems performed poorer than the zinc-rich systems. For the waterborne coatings, the performance ranked in the order of acrylics > epoxy > polyurethane. The performance of the currently used waterborne acrylic formulations has been significantly improved and the results are competitive with the best performing solvent-borne acrylic and epoxy barrier coatings. Furthermore, it is encouraging that properly formulated two-coat acrylic and epoxy systems can perform as well as generically-similar three-coat coating systems with different formulations. The analysis of the test results showed strong discrimination against zinc-rich

systems by test A but not by test B. The cyclic freeze/UV-condensation/salt fog-dry air test that used 5 pecent sodium chloride solution to generate salt fog was found to produce coating performance similar to that in salt-rich environment including zinc-rich and waterborne coatings.

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SI* (Modern Metric) Conversion Factors

Approximate Conversions to SI Units

Symbol	When You Know	Multiply By	To Find	Symbol
Length				
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
Area				
in²	square inches	645.2	square millimeters	mm²
ft²	square feet	0.093	square meters	m²
yd²	square yard	0.836	square meters	m²
ac	acres	0.405	hectares	ha
mi²	square miles	2.59	square kilometers	km²
Volume				
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft³	cubic feet	0.028	cubic meters	m³
yd³	cubic yards	0.765	cubic meters	m³
NOTE: volumes greater than 1000 L shall be shown in m³				

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Mass				
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
Temperature (exact degrees)				
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
Illumination				
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
Force and Pressure or Stress				
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

Approximate Conversions from SI Units

Symbol	When You Know	Multiply By	To Find	Symbol
Length				
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
Area				
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
Volume				
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.314	cubic feet	ft^3

m^3	cubic meters	1.307	cubic yards	yd^3
Mass				
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
Temperature (exact degrees)				
°C	Celsius	1.8C+32	Fahrenheit	°F
Illumination				
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
Force and Pressure or Stress				
N	newtons	02.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

* SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380. (Revised March 2003)

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INTRODUCTION

As the U.S. Environmental Protection Agency (EPA) continues reducing the allowable volatile organic compound (VOC) content for all types of coatings, more research needs to be conducted to identify low-VOC durable coatings to meet future regulation requirements. Currently the national VOC emission limit for architectural and industrial maintenance coatings that became effective on September 11, 1998, is 450 grams per liter (g/L). However, many States are considering in reducing the VOC levels below these limits. For instance, the California Air Management district (South Coast) has proposed even tighter restrictions for VOC content (150 g/L) by 2004, Delaware has set 340 g/L for architectural and industrial maintenance coatings, and Northeastern States also are considering VOC limit reductions.

Waterborne coatings are currently used by some States to meet the increasingly strict EPA regulations. Although users claim a good overall experience with waterborne coatings, the general view has been that waterborne coatings do not perform nearly as well as their solvent-containing alternatives. However, the interest and focus continues to be on waterborne coatings, because these coatings have advantages of lower flammability, reduced fire hazards, lower odor, reduced toxicity, easier cleanup, minimal disposal problems, and most importantly, low VOC content. However, waterborne coatings have some disadvantages such as low evaporation rate of water and difficulty in wetting substrates.

The Louisiana Department of Transportation and Development (LA DOTD) conducted a field evaluation using California Department of Transportation (CALTRANS) four-coat acrylic coating systems in 1982.[1] The system used styrene acrylic emulsions for the primers and solvent-resistant acrylic resins for the topcoats. At the same time, laboratory tests of various waterborne acrylic coating systems continued in the test program even after its unsuccessful results in 1980, and most of these systems blistered after the salt-fog test and chalked after the UV exposure. A two-coat vinyl with hard modified acrylic resin as topcoat was found to be the best performer in the test and was then adopted in the LA DOTD specifications.

In recent years, more waterborne formulations have been developed, but only limited performance data for these new generation coating systems are available. Furthermore, their performances relative to those of the generally proved durable zinc-rich coating systems are not known. The present study was designed to investigate the performance of some current representative types of waterborne bridge coatings including acrylic, epoxy, and polyurethane coatings; all the coating materials had VOC contents of less than 280 g/L. Four zinc-rich coating systems were used as controls. The laboratory test method chosen was the Federal Highway Administration (FHWA) cyclic freeze/ultraviolet light-condensation (QUV)/salt fog-dry air method using two different salt solutions in the third test cycle, this method was modified after the American Society of Testing and Materials (ASTM) D5894 Methods. An outdoor exposure in a salt-rich environment was also conducted as a comparison.

EXPERIMENTAL PROCEDURES

Several zinc-rich and waterborne coating systems were sprayed on new steel (SSPC-SP 10) surfaces. The size of all the test panels was 10 centimeters (cm) x 15 cm x 0.48 cm. A 5.0 cm scribe was made diagonally on all the coated panels prior to testing. Two separate sets of panels

with primers and topcoats were also prepared independently for the chemical and physical tests of the coating materials.

The pigment fractions were obtained by burning out organics (binders) at 450 ± 25 ºCelsius (ºC) for one hour in accordance with ASTM Method D3723. Fourier-Transform Infrared Spectrometry (FTIR) spectra were obtained using a FTIR spectrometer; a diffuse reflectance accessory with silicon carbide paper was used and the spectra were obtained at 4 wavenumbers resolution with 100 signal average scans. The elemental compositions of the isolated pigment fractions were semiquantitatively determined by a combined scanning electron microscopy/energy dispersive X-ray spectrometry technique (SEM/EDS) in which the pigment samples were pressed into a 10-millimeter (mm) diameter pellet using a manual FTIR pellet presser. The 60º gloss was measured following ASTM Method D523. The total color difference (E) was obtained from ASTM Method D2244. The adhesion strengths were measured by a pneumatic pull-off adhesion tester using ASTM Method D4541.

Both accelerated laboratory and natural outdoor tests were used to evaluate the coating performance in this study. Two cyclic laboratory tests (test A and test B) using freeze/QUV/salt fog-dry air test were conducted for a total period of 3,000 hours; table 1 gives the test conditions. Test A was a modification of ASTM Method D5894[2], a Harrison mixture [0.35 percent $(NH_4)_2SO_4$ plus 0.05 percent NaCl] was used in the alternating 1-hour (h) ambient salt-fog and 1-h hot air cycle. Test B used the same freeze and QUV cycles but with a different salt solution (5 percent NaCl solution) in the salt fog-dry air cycles; this was a modification of ASTM B117 with alternating 1-h of hot salt-fog and 1-h of ambient air. All the panels were examined for any surface failures such as blistering and rusting, and were measured for scribe creepages at 500-h test intervals. The rust creepage developed at the scribe was measured visually in a consistent manner.[2] On each side of the scribe line, a maximum scribe creepage was taken within each 1.0-cm interval along the scribe line. A total of ten readings were recorded from both sides of the scribe line and were averaged to obtain a creepage value for each test panel.[*] The value presented in this report is an average of four replicated test panels.

Another set of coated panels was exposed at Sea Isle City, NJ for 2 years. All these test panels were placed at a 45-degree angle on wooden racks, facing directly south and were sprayed with natural seawater daily to accelerate corrosion. After exposure, these outdoor panels were examined in a manner similar to those evaluated in the laboratory tests. The performance of the waterborne coatings from the laboratory tests and the outdoor exposure are presented and compared later in this report.

Table 1. Laboratory conditions of test A and test B for every 500-h test cycle.

Test cycle	Test A	Test B
Freeze: 68 hours Temperature: -23 °C	X	X
UV-condensation: 216 hours Test cycle: 4-h UV/4-h condensation UV lamp: UVA-340 UV temperature: 60 °C Condensation temperature: 40 °C Condensation humidity: 100 % RH	X	X
Salt fog-dry air: 216 hours Test cycle: 1-h wet/1-h dry air Wet cycle: 0.35 wt% $(NH_4)_2SO_4$ + 0.05 wt% NaCl at ambient temperature Dry air cycle: at 35 °C	X	
Salt fog-dry air: 216 hours Test cycle: 1-h wet/1-h dry air Wet cycle: 5 wt% NaCl at 35 °C Dry air cycle: at ambient temperature		X

RESULTS AND DISCUSSION

All the coating systems for this study are described in table 2. Various waterborne coating systems were evaluated in this study: five acrylic systems (systems 3-7), four epoxy systems (systems 8, 9, 10, and 13), and one polyurethane system (system 12). Four controls were employed as a baseline for comparison purposes, they were organic zinc-rich epoxy/epoxy/polyurethane (system 1), zinc-rich moisture-cured urethane (MCU)/MCU/MCU (system 2), inorganic zinc potassium silicate/polysiloxane (system 11), and inorganic zinc alkyl silicate/epoxy/fluorourethane (system 14).

Table 2. Description of coating systems.

System No.	Coating Description	Nominal Dry Film Thickness, micrometer (mil)	VOC Content[a], g/L
1	Zinc-rich epoxy/epoxy/polyurethane[b]	10/125/50 (4/5/2)	325/180/260
2	Zinc-rich moisture-cured urethane (MCU)/MCU/MCU[b]	75/75/75 (3/3/3)	340/340/420
3	Acrylic/acrylic/acrylic	75/75/75 (3/3/3)	131/129/129
4	Acrylic/acrylic/acrylic	50/50/50 (2/2/2)	67/67/56
5	Vinyl acrylic/acrylic	75/50 (3/2)	64/130
6	Vinylidene acrylic/vinyl acrylic/Al-filled acrylic (2)	50/50/50/50 (2/2/2/2)	35/35/237/237
7	Acrylic/acrylic	150/150 (6/6)	0.01/0.01
8	Epoxy/epoxy/polyurethane	50/50/50 (2/2/2)	180/180/276
9	Epoxy/epoxy/polyurethane	75/75/75 (3/3/3)	72/143/66
10	Epoxy/polyurethane	75/50 (3/2)	193/31
11	Inorganic zinc potassium silicate/polysiloxane[b]	75/125 (3/5)	0/120
12	Polyurethane, 3 coats	50/50/50 (2/2/2)	192/192/250
13	Epoxy/epoxy/acrylic epoxy	125/100/50 (5/4/2)	83/83/274
14	Inorganic zinc alkyl silicate/epoxy/fluorourethane[b]	75/75/75 (3/3/3)	288/195/532

a: Labeled by suppliers.
b: Control coatings.
Note: All systems were waterborne except for controls.

Chemical Properties

The pigment weights of all the primers were obtained by the isolation method (ASTM D3723) and the weights of binders were then calculated by difference. For comparison purposes, the binder/pigment (B/P) ratios by weight for each coating type are shown in table 3. The B/P ratios by weight of all the acrylic primers were found to be above 1, while those of the epoxy primers were below 1. The polyurethane primer also gave a high value (1.95) for B/P ratio. The equivalent ratio values exhibit special characteristics for each coating type. Furthermore, the results lead to a reasonable assumption that the binder density decreases in the order of polyurethane > acrylics > epoxy. In other words, more polyurethane and acrylic binders by weight than epoxy are needed to achieve the required volume to fill a similar amount of voids that are created by close pigment packing in the coating formulations.

Table 3. Binder-to-pigment ratio by weight for different waterborne primer types.

Coating Type	System No.	Binder/Pigment Ratio by Weight
Acrylics	3	1.10
	4	1.40
	5	1.60
	6	1.20
	7	1.70
Epoxy	8	0.71
	9	0.51
	10	0.59
	13	0.85
Polyurethane	12	1.95

The elemental compositions of pigment fractions were estimated using semi-quantitative SEM/EDS analysis; major elemental contents from these analyses are shown in table 4. These values, semi-quantitative values, should be considered "order-of-magnitude values." All the acrylic and epoxy primers consist of a certain amount of iron, mainly due to iron oxide that provides red color for primer. However, primer 12 with lemon green color did not contain any iron. Interestingly, all the acrylic primers except primer 6 contained a significant amount of zinc

and some phosphorus. On the other hand, no zinc was found in most of the epoxy primers (8, 9, 10) except primer 13 with 17 weight-percent of zinc in the pigment. This composition analysis indicated the difference in pigment composition between the acrylic primers and the epoxy primers. It suggests more need for zinc phosphate, a highly effective inhibitive pigment, for acrylic primers than for epoxy primers that generally exhibit excellent adhesion to metal. Polyurethane primer 12 also contained a large amount of zinc. In addition, significant amounts of calcium, silicon, aluminum, and barium were present as part of extenders or additives.

Table 4. Major elemental content in primer pigments determined by SEM/EDS analysis.

Coating Type	System No.	Zinc	Calcium	Iron	Phosphorus	Silicon	Aluminum	Barium
					Weight-Percent of Pigment			
Acrylics	3	25	14	9	3	9	0	0
	4	43	10	3	6	1	5	2
	5	34	0	7	4	1	1	24
	6	0	9	8	6	24	1	0
	7	43	9	14	3	2	3	3
Epoxy	8	0	24	12	0	23	1	0
	9	0	22	20	6	2	3	11
	10	0	6	17	0	13	7	13
	13	17	7	9	8	12	9	6
Polyurethane	12	33	0	0	1	9	1	17

Most of the primers and topcoats were characterized for their resin type by FTIR analyses. Their chemical nature of aromatic (AR) to aliphatic (AL) ratio, so called "aromaticity," was calculated from the ratio of reflectance peak areas at wavenumber of 3000-3100 cm^{-1} to that at wavenumber of 2800-3000 cm^{-1}. The measurement of this ratio is a fairly sensitive technique for estimating aromaticity of organic materials. The aromatic content seen in these acrylic samples is attributed to styrene modification of the acrylic. The typical FTIR spectra of styrene modified acrylics and unmodified acrylics are shown in figures 1a and 1b respectively; several distinct FTIR reflectance peaks were observed for styrene at the wavenumber between 3000 and 3100 cm^{-1}. The AR/AL ratios of the primers and topcoats are shown in table 5. The AR/AL ratio in primers 3, 4, and 7 were relatively high; they were calculated to be 6, 4, and 5, respectively, showing more aromatic character, i.e., higher styrene acrylics content. On the other hand, the ratio of AR/AL was found to be zero for systems 5 and 6, revealing their saturated structure of unmodified acrylics. All the epoxy primers 8, 9, 10, and 13 were found to be highly aromatic; the

AR/AL ratios were determined to be 5, 5, 6, and 6, respectively. The acrylic topcoats did not show significant difference in their aromaticity (5 to 9); the comparable values of aromaticity suggest that roughly a similar amount of styrene acrylic was used in all the topcoat formulations. However, the aromaticity of the polyurethane topcoats used for epoxy systems 8, 9, and 10 varied widely (0 to 7), suggesting that different manufacturers formulated different types of polyurethane, comprising compositions both high and low in aromatic content. In contrast, topcoat 13 was acrylic epoxy with a high aromaticity value of 12. This high aromaticity is not surprising, because aromatic epoxy is one component of the acrylic epoxy copolymer. Both primer and topcoat of system 12 showed zero or low aromaticity.

Table 5. Infrared aromatics/aliphatics intensity ratio of primers and topcoats.

Coating System	System No.	Primer	Topcoat
		Aromatics/Aliphatics Ratio	
Acrylic	3	6	7
	4	4	7
	5	0	6
	6	0	5
	7	5	9
Epoxy	8	5	7[a]
	9	5	0[a]
	10	6	2[a]
	13	6	12
Polyurethane	12	0	1

a: Polyurethane used as topcoat.

Physical Properties

The pencil hardness of all the topcoats was found to be similar (HB or 2B), with the exception of system 7. This system contained a fairly soft polymer with a hardness of only 6B. The hardness measurements are presented in table 6. The adhesion strengths of each whole-coating system and each primer before weathering tests were measured, and the values are illustrated in figures 2 and 3, respectively. There are no significant differences between the adhesion strength of the whole-coating systems and their primers. Nevertheless, primer 6 showed more than twice the adhesion strength of the entire system 6, which displayed weak topcoat cohesive strength in the pull-off test. For comparison, the adhesion strengths of acrylic and epoxy systems were all high (above 14 mega pascal (MPa)) except systems 6 and 7, which had lower adhesion strength. In the case

of zinc-rich primers, researchers found a relatively low cohesive strength (less than 7 MPa). The failures of all the unexposed coating systems during the pull-off test were either cohesive failures of primer or topcoat. No adhesive failure between steel substrate and primer was observed.

Table 6. Pencil hardness of various waterborne topcoats.

System No.	3	4	5	6	7	8	9	10	12	13
Pencil Hardness	2B	2B	2B	2B	6B	2B	2B	HB	2B	HB

Laboratory and Outdoor Tests

Test A, using the Harrison mixture in the salt-fog cycle, has been shown to be a more realistic laboratory test to predict field performance for bridge coatings; however, it induces unexpected rust creepage formation at scribe for zinc-rich coating systems. Therefore, another test (test B) using only NaCl in the cyclic salt-fog test was conducted to investigate its general coating evaluation feasibility. It should be noted here that test B included an alternating 1-h salt-fog/1-h dry-air test cycle, not a salt-fog test alone. The salt-fog test alone generated unrealistic performance results when compared to natural outdoor exposure results, especially for waterborne coatings that develop early blistering.[4,5]

The coating performance, including film thickness change, gloss reduction, color change, surface failures, and rust creepage at the scribe after two accelerated laboratory tests and an outdoor exposure, are illustrated and compared below.

Film thickness change—The coating film thickness of majority of the coating systems remained fairly constant through all the test periods, demonstrating the integrity of these coating films. The percent of the film thickness changes are shown in table 7. These results indicates that the waterborne polyurethane topcoats (systems 8, 9, 10, and 12) cannot maintain as much film thickness as the acrylics and zinc-rich control systems in the test environments.

Table 7. Coating film thickness change after three tests.

System	System No.	3,000-h Test A	3,000-h Test B	2-y Outdoor
		Film thickness change, %		
Zinc-rich	1	-3.1	0.0	-1.9
	2	-1.0	0.0	-2.9
	11	0.0	-1.2	-2.3
	14	-2.4	-1.7	0.8
Acrylic	3	0.9	0.0	0.0
	4	5.7	2.2	0.0
	5	-2.8	-1.2	-2.9
	6	-1.0	8.1	-2.1
	7	2.0	17.0	4.1
Epoxy	8	-13.7	-8.7	-10.0
	9	-7.8	-4.9	-5.8
	10	-6.8	-6.3	-5.1
	13	-5.3	-5.5	-2.3
Polyurethane	12	-10.0	-8.4	-5.6

Gloss reduction—After two laboratory tests and the outdoor test, the topcoat gloss of all the coating systems decreased. This is because certain chemical bonds in coating polymers are susceptible to UV light attack, especially UV light with short wavelengths. Free radicals are first produced after UV light absorption, i.e., bond cleavages in coating polymers. Thereafter, free radicals undergo oxidation so that crosslinking density decreases; this chemical composition change is the initiation process for topcoat gloss reduction. All the gloss reduction data are listed in table 8. To compare each coating type, the percent of mean gloss reduction of waterborne acrylics (systems 3-7) and polyurethanes (systems 8-10) after the three tests are plotted in figure 4. In this study, since both tests A and B used UVA-340 lamps at 60 ºC for 4 hours in each QUV cycle, the extent of the gloss reduction caused by UV light should be the same. However, two methods used different salt solutions that could induce different degree of coating failures. Test A results also suggested that the polyurethanes (systems 8-10) were more resistant to acidic

Harrison solution than acrylics (systems 3-7). Esters can be hydrolyzed when heated with catalytic amounts of acid in aqueous solution.[6] However, acrylic coatings in test B using NaCl solution lost much less gloss than those in test A, with the remaining results fairly similar to those from test A. After the natural marine exposure, the majority of the coating systems lost extensive gloss reflecting the severity of UV light present at the Sea Isle site. As in previous studies,[7] gloss reduction is attributed to UV radiation. In this study, three topcoats performed poorly in gloss retention. Topcoat 6 (acrylic), topcoat 12 (polyurethane), and topcoat 13 (acrylic epoxy) lost a substantial amount of gloss after all the three tests; therefore their gloss retention property needs to be improved. Surprisingly, topcoat 2 (moisture-cured urethane) lost 92 percent gloss after the 2-year (y) outdoor exposure. This gloss loss was much higher than 50.9 percent gloss loss of two-component solvent-based polyurethane (topcoat 1). These results suggest that two-component polyurethane has better UV resistance than does one-component polyurethane. Nevertheless, no clear trend can be seen for UV susceptibility of each topcoat type.

Color change—All the topcoats changed color after the tests, as shown in table 9. The color changes for acrylics and polyurethanes in test A also seem to be affected by acidic salt-fog; topcoat 6 demonstrated the most color change (E = 34.2). Among all the topcoats, topcoats 6 and 12 retained the least amount of color in all the tests. On the other hand, topcoat 7 has the highest resistance to color change and topcoat 5 is the second best performer; both these topcoats are acrylic topcoats. Figure 5 illustrates the mean topcoat color changes (E) of waterborne acrylics (systems 3-7) and polyurethanes (systems 8-10) after the 3,000-h laboratory tests and the 2-y outdoor exposure. In general, the outdoor exposure caused less color change for the topcoats than did tests A and B. This is attributed to the lower daily average of moisture content in the outdoor test period as opposed to the laboratory tests; these results support previous work demonstrating that moisture tended to induce color changes.[7]

Adhesion change—The adhesion strength of most coating systems either remained unchanged or was reduced after the tests. The worst case was system 12, which lost as much as 68 percent of adhesion strength after 2-y outdoor exposure; obvious adhesive failure between the primer and steel substrate was found during pull-off test after the exposure. This failure mode suggests that the polyurethane film porosity must be high enough for moisture to penetrate to the steel surface after 2 years. However, some systems became stronger, probably due to better curing of coated materials in the test environments that involved high temperatures. It was noted that some coatings do not cure very well at ambient conditions; maximum curing and crosslinking require high temperatures.[8] The changes in adhesion strength after the tests are listed in table 10.

Table 8. Topcoat gloss reduction after three tests.

System	System No.	3,000-h Test A	3,000-h Test B	2-y Outdoor
		Gloss reduction, %		
Zinc-rich	1	19.0	11.4	50.9
	2	59.0	33.1	92.1
	11	5.9	5.1	46.8
	14	10.3	0.6	29.3
Acrylics	3	46.6	22.8	46.0
	4	59.5	31.9	46.0
	5	70.5	17.8	56.1
	6	92.2	43.3	87.1
	7	51.7	56.3	76.9
Epoxy	8	8.7	2.6	77.5
	9	0.1	9.5	59.4
	10	30.7	43.3	87.6
	13	79.4	49.5	88.4
Polyurethane	12	81.7	68.1	94.7

Table 9. Topcoat color change after three tests.

System	System No.	3,000-h Test A	3,000-h Test B	2-y Outdoor
		Color change, E		
Zinc-rich	1	1.0	0.6	3.1
	2	6.4	5.1	9.5
	11	9.8	2.6	3.3
	14	5.0	2.5	1.3
Acrylics	3	18.3	18.2	2.9
	4	16.2	9.4	3.9
	5	8.0	6.2	0.9
	6	34.2	11.6	26.2
	7	1.8	2.1	4.1
Epoxy	8	15.1	12.6	1.0
	9	10.6	12.1	5.2
	10	18.4	7.6	4.0
	13	18.6	9.8	9.8
Polyurethane	12	22.6	22.3	29.9

Table 10. Adhesion strength changes after three tests.

System	System No.	3,000-h Test A	3,000-h Test B	2-y Outdoor
		Change in Adhesion Strength, %		
Zinc-rich	1	-13.6	-10.9	-7.0
	2	1.0	-10.3	-16.3
	11	-0.4	-23.4	-10.9
	14	25.2	0.7	-7.2
Acrylics	3	22.4	5.5	-11.3
	4	44.4	22.3	0.0
	5	0.8	-23.6	-35.4
	6	73.1	31.3	9.8
	7	1.0	-2.5	1.5
Epoxy	8	12.6	31.0	-16.1
	9	-9.3	-16.1	-28.1
	10	17.6	8.0	-34.5
	13	-17.6	-10.1	-22.5
Polyurethane	12	3.1	-5.9	-67.8

Surface failures—Virtually all the coating systems showed no visible surface failures. This demonstrated good barrier coating characteristics of these waterborne coating systems. An exception, system 6, exhibited extensive blistering with dense size 8 blisters (ASTM D714)that covered the entire surface after 3,000 h of both tests A and B. This behavior shows that topcoat 6 is susceptible to water permeation under the test conditions; the failure mode apparently resulted from the weak topcoat cohesive strength of topcoat 6, as observed during the pull-off adhesion test. No such failure was observed up to 2 years in the outdoor exposure. System 7 experienced a different surface problem—the softness of this acrylic material allowed foreign matters or particulates to easily be adsorbed on the coating surface. These particles could not be rinsed off by either water or rain. For aesthetic purposes, a topcoat with improved formulation is recommended for System 7.

Rust creepage at scribe—It has been shown that scribe creepage is a sensitive and useful parameter in determining coating durability; in particular, the plot of scribe creepage against

weathering time was found to be fairly linear.[5] Coating corrosion rate is proportional to the slope of plotted line but inversely proportional to incubation time after that creepage becomes visible. Researchers also used this evaluation technique to compare coating performance at scribe in this study. The creepage measurement results on laboratory and outdoor exposure specimens of all the waterborne coatings and zinc-rich controls are presented in table 11. Zinc-rich coating systems performed at scribe much better than did all the waterborne coatings. In general, waterborne acrylic and epoxy coatings showed slightly better performance than the waterborne polyurethane coating. However, the unmodified acrylic coatings (systems 5 and 6) outperformed the styrene acrylic coatings (systems 3, 4, and 7). The performance of different coating types at the scribe, including zinc-rich, acrylics, and epoxy systems, is detailed as follows.

- Zinc-rich systems—Organic zinc-rich system 1 and inorganic zinc-rich system 11 developed measurable creepages in the 3,000-h test A, creepages did not occur in the 2-y outdoor exposure test. The rust creepages generated in test A are believed to result from zinc sulfate formation, which is caused by the reaction of zinc dust and ammonium sulfate. On the other hand, zinc-rich systems 1 and 11 developed a lesser amount of scribe creepage after 3,000-h test B when compared with 3,000-h test A. Among all the zinc-rich coating systems, system 14 performed best and showed no creepage after all three tests. The moisture-cured zinc-rich coating system (system 2) did not perform as well at the scribe as either the epoxy zinc-rich system (system 1) or the inorganic zinc-rich systems (systems 11 and 14); it developed about 2-mm rust creepage in all the tests. The coating conditions of the moisture-cured urethane system after two 3,000-h laboratory tests and 2-y outdoor exposure are shown in figure 6. The performance of the one-component moisture-cured zinc-rich urethane system at the scribe is obviously poorer than the two-component zinc-rich systems; as an example the coating conditions of system 1 (also organic zinc-rich) after the tests are shown in figure 7. It seems that zinc-rich MCU primer (primer 2) is less effective in protecting steel from corrosion than zinc-rich primers in systems 1, 11, and 14. The reason for this difference is unclear. However, one-component zinc-rich MCU primer was also found to perform poorer than two-component zinc-rich epoxy primer by Kalendova.[9] The creepage growth for all the zinc-rich coating systems as a function of test time after the laboratory tests and the outdoor exposure are plotted in figures 8, 9, and 10; all the scribe creepage increased linearly with test time. The incubation times for creepage formation are longer for test B than for test A, indicating that zinc-rich systems perform better in a salt-rich environment than in an acidic salt environment.

- Waterborne acrylic systems—Acrylic systems 3-7 developed much larger creepage at the scribe than did zinc-rich systems. The creepage growth of the acrylic systems with test time is plotted in figures 11, 12, and 13. Styrene modified acrylics and unmodified acrylics (such as vinyl acrylics) displayed two levels of performance, the coating resistance of styrene modified acrylics (systems 3 and 4) at scribe are lower than that provided by unmodified (vinyl) acrylics (systems 5 and 6). The different coating conditions of typical styrene acrylics (system 3) and vinyl acrylics (system 5) after three tests are shown in figures 14 and 15. However, system 7 did not fit either of these two groups exactly. Its performance is similar to vinyl acrylics in test A while it is close to the performance of styrene modified acrylics in test B. It is of interest that system 7's performance fell between two acrylic types in the outdoor exposure. As a result, this soft

acrylic material showed high resistance to the acidic salt-fog as present in test A; but illustrated low resistance to the neutral salt-fog in test B. That system 7's outdoor performance fell between two tests of acrylics may be due to acid rain (pH = 4.2) at the outdoor exposure site. Overall, the two-coat vinyl acrylic system (system 5) performed the best; it has the lowest film thickness but exhibited the highest resistance at scribe, demonstrating the strong economic benefit of using this acrylic system. LA DOTD uses this acrylic system.

Table 11. Creepage developed for waterborne coatings by three test methods.

Coating Type	System No.	3,000-h Test A	3,000-h Test B	2-y Outdoor
Zinc-rich	1	3.2	1.2	0.0
	2	2.3	2.5	1.9
	11	1.3	0.0	0.0
	14	0.0	0.0	0.0
Acrylic	3	4.5	5.3	5.2
	4	4.6	5.2	6.9
	5	3.1	2.1	2.2
	6	2.6	3.7	3.0
	7	2.8	6.3	4.0
Epoxy	8	2.6	4.5	3.2
	9	3.9	6.7	10.0
	10	2.6	3.3	3.0
	13	6.4	9.2	11.8
Polyurethane	12	5.6	7.0	6.0

- Waterborne epoxy systems—Systems 8-10 and 13 developed even larger creepage at the scribe than did acrylic systems; four systems displayed a wide range of performance. The 3-coat system 8 and the 2-coat system 10 showed comparable performance (figures 16 and 17). Like the acrylic coating tests, these results also suggest that a properly formulated 2-coat epoxy systems can protect steel as well as a 3-coat system without sacrificing much anti-corrosive effectiveness. Most importantly, the use of 2-coat epoxy and acrylic systems would reduce labor costs and decrease traffic congestion. For

comparison, the creepage growth for all the epoxy systems versus test time are plotted in figures 18, 19, and 20. In all the tests, systems 8 and 10 performed better at the scribe than system 9, and even better than system 13. A substantial amount of scribe creepage developed by system 13 after three tests is demonstrated in figure 21. Figure (a) shows the exposed rust surface after the developed creepage area was scraped off by a knife after 3,000-h test A; the distance of undercutting was found to be exactly same as that of visible creepage on the coating surface that was measured prior to coating removal. The low corrosion resistance of system 13 at the scribe may be attributed to the presence of zinc phosphate in primer 13 or poor coating formulation. Using zinc phosphate may not be necessary for the formulation, because epoxy adheres to steel strongly itself; zinc phosphate, in contrast may interfere with epoxy's adhesion to steel.

- Waterborne polyurethane system—Only one waterborne polyurethane system was included in this study, so the test results may not be very representative for this class of coating. System 12 performed more poorly than acrylic and epoxy systems, as shown in figures 22, 23, and 24 after the tests. The scribe creepage developed on this coating system was found to be 5.6 and 7.0 mm after 3,000-h test A and 3,000-h test B respectively; the linearity of their developed scribe creepage with test time was excellent. However, the plot of scribe creepage developed by System 12 versus the outdoor exposure time did not show as good linearity as those obtained by the rest of coating systems.

•To compare the creepage results of different waterborne coating type generated by three test methods, the mean creepage of zinc-rich (systems 1, 2, 11, and 14), acrylic (systems 3-7), and epoxy (systems 8-10, 13) formulations are plotted in figure 25. The scribe creepage that different primers developed increased in the order of zinc rich< acrylic < epoxy. In the case of 2-y outdoor marine exposure, the mean creepage was 4.3 mm at scribe developed for waterborne acrylic coatings. This compares favorably to the results of similar testing performed several years ago, which showed scribe of 6.8 mm for a separate group of generically similar waterborne acrylic formulations.[4, 10] This latter mean value for 2-y exposure was calculated using a linear extrapolation of the reported values in References 4 and 10. Although these coatings did not outperform the zinc-rich control coatings, the performance improvement is significant because the waterborne results are competitive with those of the best performing solvent-borne barrier coating systems (e.g., epoxy and polyurethane) that FHWA has tested over the past several years. As a group, the waterborne epoxy coatings did not perform as well as the waterborne acrylics. These coatings featured an average creepage of 7.0 mm after the outdoor exposure. However, the performance of epoxy systems 8 and 10 at scribe are in line with that of acrylic systems 5 and 6. As mentioned earlier, the waterborne polyurethane coating (system 12) also failed to meet the average performance of the acrylics.

•*Test correlation*—The correlations between the laboratory tests and the outdoor exposure are summarized in table 12. The correlation coefficients (R value) for all the creepage results (14 coating systems) of tests A and B to the outdoor exposure were calculated to be 0.82 and 0.92, respectively. The waterborne coatings showed comparable performance in test A and test B after 3,000 hours. However, test A strongly discriminated against the zinc-rich coatings, and a different trend was found for test B. The similarities and differences between tests A and B can be seen by the R value of 0.79 and 0.86 for the waterborne coatings (systems 3-10, 12, 13), respectively, and 0.29 and 0.88 for the zinc-rich coatings (systems 1, 2, 11, 14), respectively.

These results indicate that test B is a more reasonable laboratory test to predict the performance of both zinc-rich and waterborne bridge coatings in a salt-rich environment. Therefore, a laboratory test method must be designed to simulate outdoor condition as close as possible.

Table 12. Correlation coefficient for developed scribe creepage between 3,000-h laboratory tests and 2-y outdoor marine exposure.

	Correlation Coefficient, R	
	Laboratory Test A	**Laboratory Test B**
For whole 14 systems	0.82	0.92
For 4 zinc-rich systems	0.29	0.88
For 10 waterborne systems	0.79	0.86

SUMMARY AND CONCLUSIONS

The binder-to-pigment weight ratio varied with different coating type; this ratio was found to be above 1.0 for waterborne acrylic primers and below 1.0 for waterborne epoxy primers. Zinc phosphate seems a more essential ingredient in waterborne acrylic primers than epoxy primers. Virtually all waterborne primers formulated for new steel have extremely high adhesion strength.

The waterborne coating systems showed essentially no surface failures, but they all developed creepage at scribe after the 3,000-h laboratory tests and the 2-y outdoor exposure at Sea Isle City, New Jersey. The scribe creepage grew linearly with test time beyond the first detection time; this feature allows some extrapolations to longer test times. None of the waterborne coating systems performed as well as the zinc-rich systems. However, the performance of the current waterborne acrylic coatings at scribe has been improved significantly after 2-y outdoor exposure—the mean creepage was 4.3 mm. It compares favorably to the test results of similar formulations several years ago, which showed creepage of 6.8 mm. The results are competitive with the best performing solvent-borne barrier coatings.

In comparing all the tested waterborne coating systems, the acrylic and the epoxy coating systems showed slightly better performance than the polyurethane coating system. For acrylic coating systems, unmodified (vinyl) acrylic primers outperformed styrene-modified acrylic primers; researchers discovered that these two different types of primers could be distinguished rapidly by a FTIR analysis. Properly formulated two-coat acrylic and epoxy systems can perform as well as generically-similar three-coat coating systems with different formulations.

All the coating systems retained their film thickness fairly well throughout the test periods, but most of their adhesion strengths were reduced. The gloss and the color of the topcoats all changed substantially after the tests; these changes were attributed to UV light and moisture attack, respectively.

The laboratory test results showed that test A using 0.35 percent $(NH_4)_2SO_4$ plus 0.05 percent NaCl solution to generate salt-fog, induced less failures on waterborne coatings than did test B, which used 5 percent NaCl solution, while the zinc-rich coating systems exhibited fewer failures in test B. The coating performance of both zinc-rich and waterborne coatings in test B correlated better with the outdoor exposure results than performance in test A.

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[*] A more accurate method for quantifying the amount of scribe creepage, an imaging technique has been recently developed by FHWA.[3] In this improved method, the total creepage area is traced on a piece of plastic sheet by a black marker with fine tip, the trace is imaged by a scanner, and then integrated by computer software.

(a)

(b)
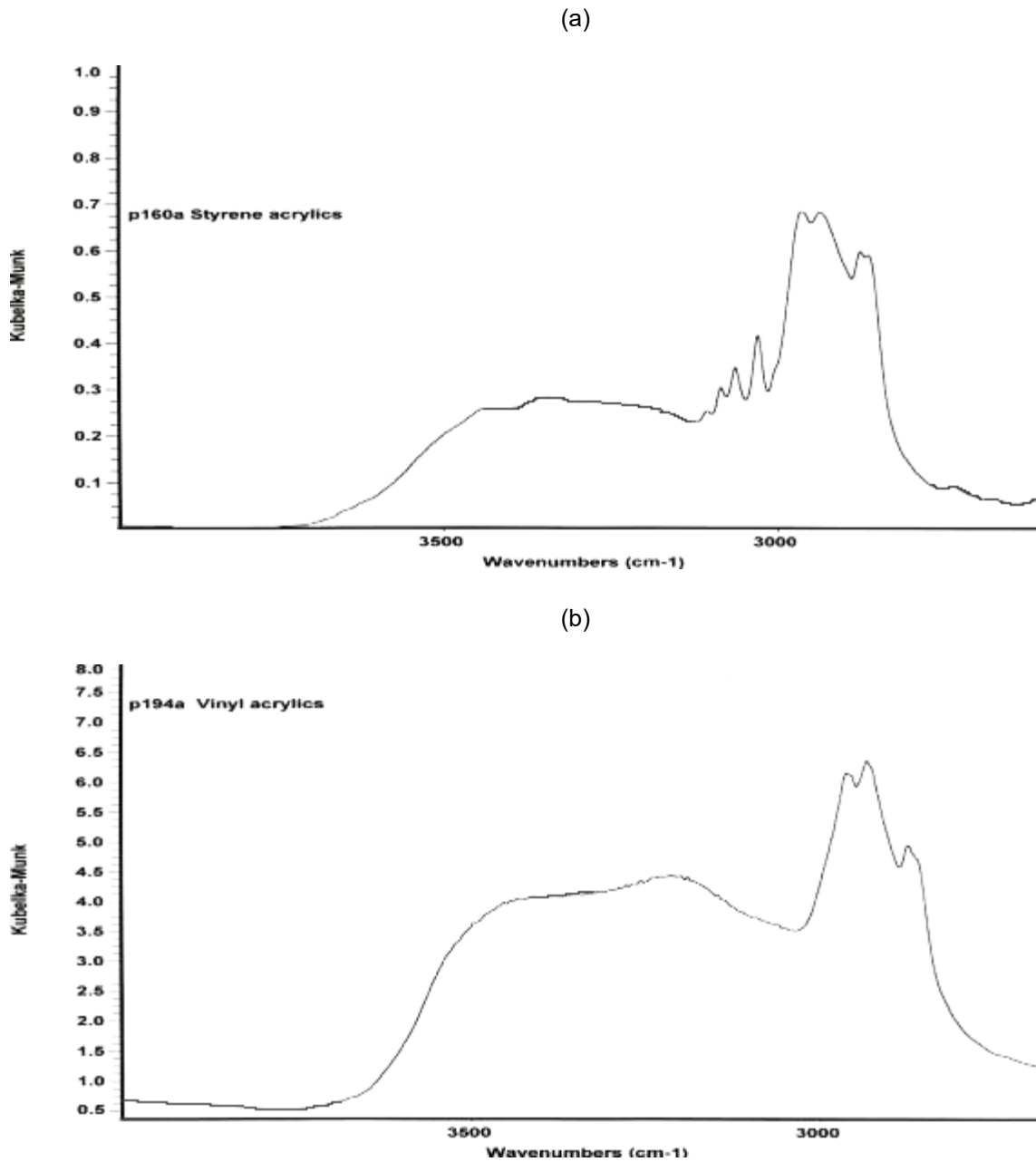
Figure 1. FTIR spectrum of (a) styrene modified acrylics, (b) unmodified (vinyl) acrylics using diffuse reflectance sample accessory.
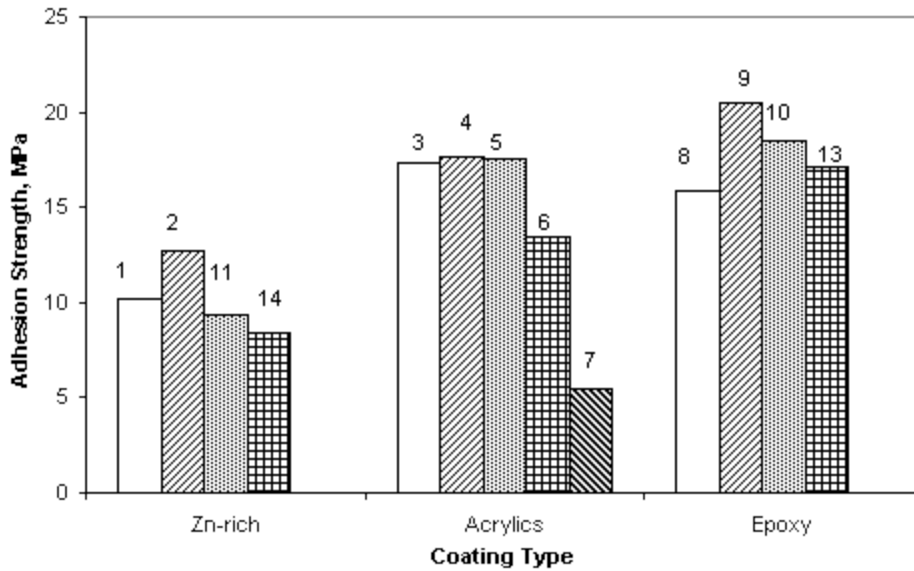
Figure 2. Adhesion strength of waterborne primers before test.

Conversion factor: 1 MPa = 145 psi
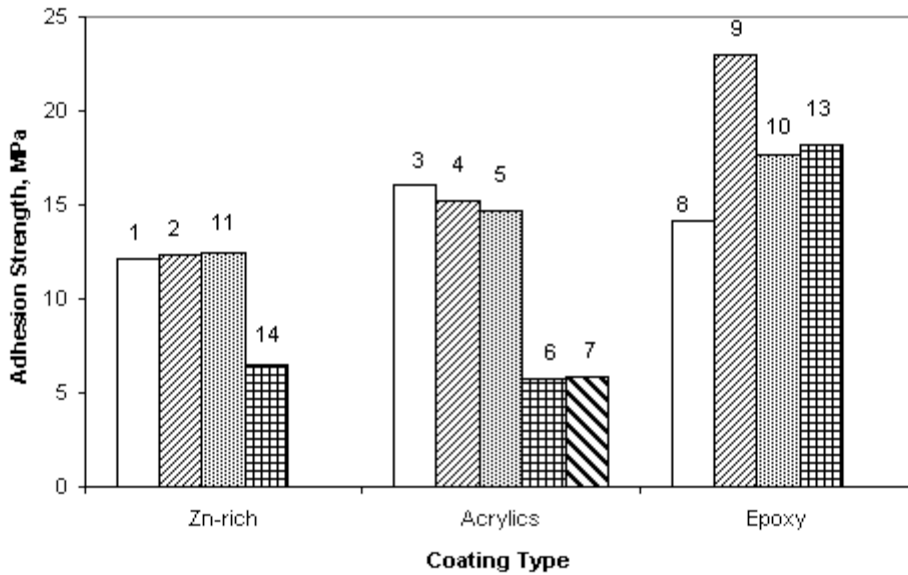
Figure 3. Adhesion strength of waterborne coating systems before test.

Conversion factor: 1 MPa = 145 psi
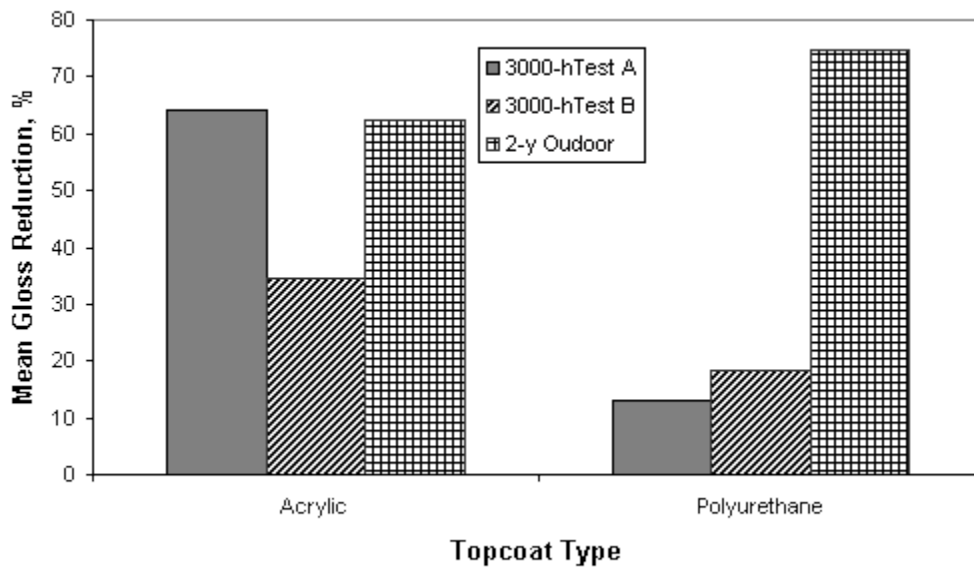
Figure 4. Comparison of topcoat gloss reduction by three test methods.
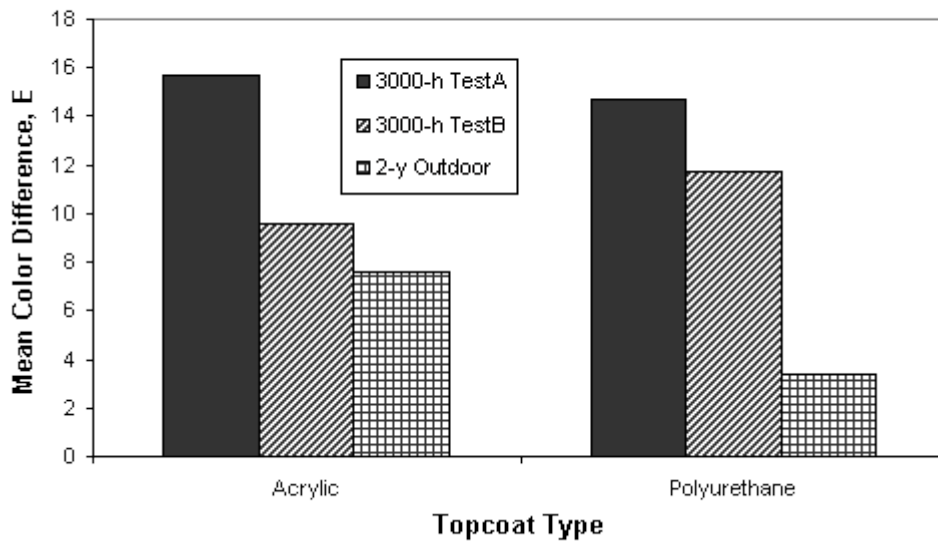
Figure 5. Comparison of topcoat color change by three test methods.
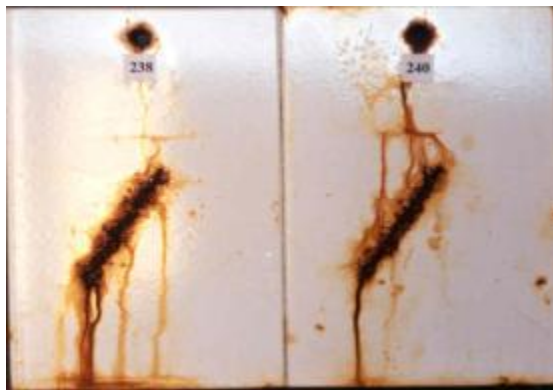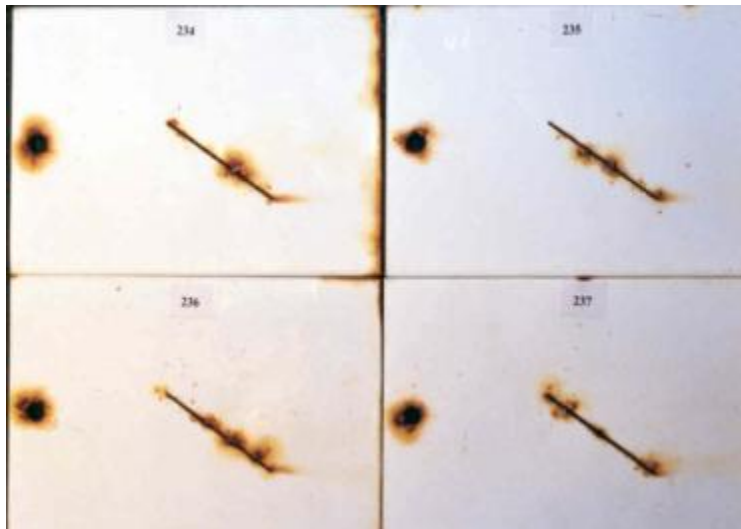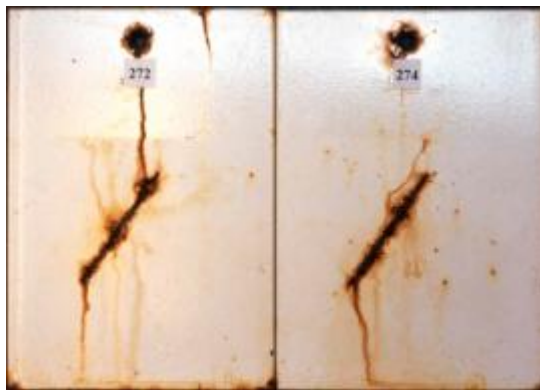
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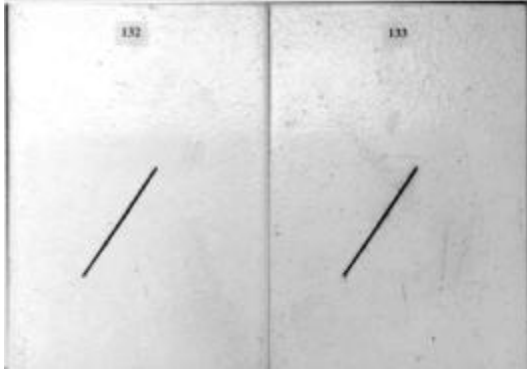
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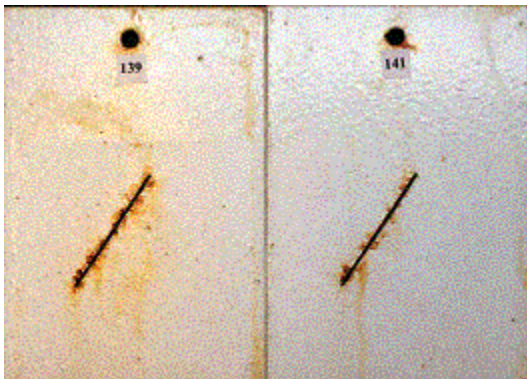
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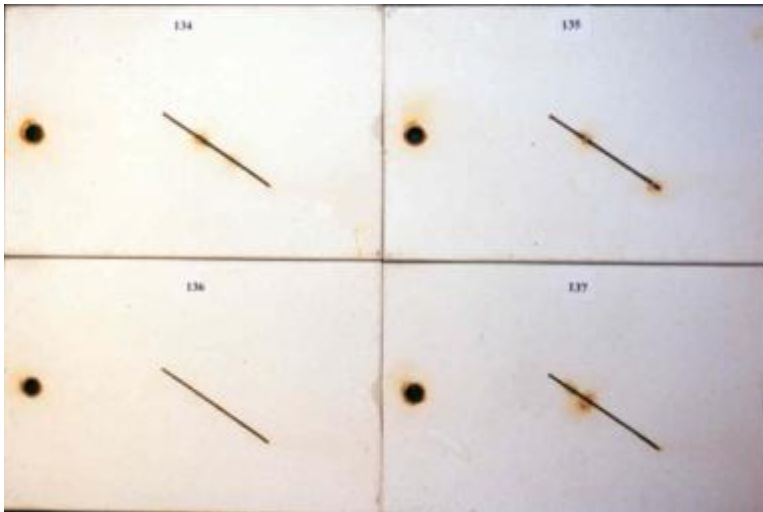
Figure 6. Coating conditions of system 2 after exposures.
a. 3,000-h test A   b. 3,000-h test B   c. 2-y outdoor exposure
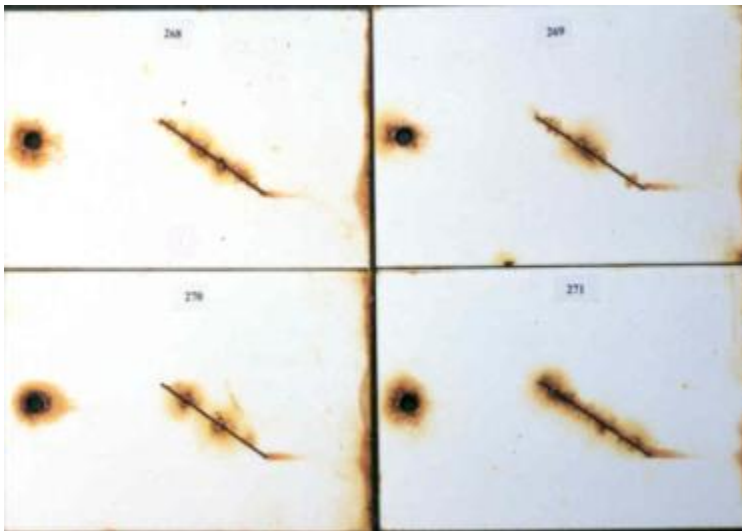
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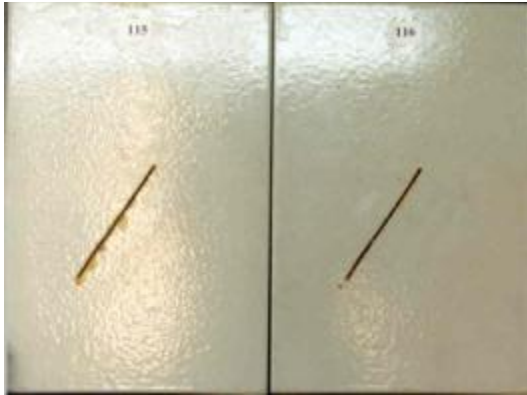
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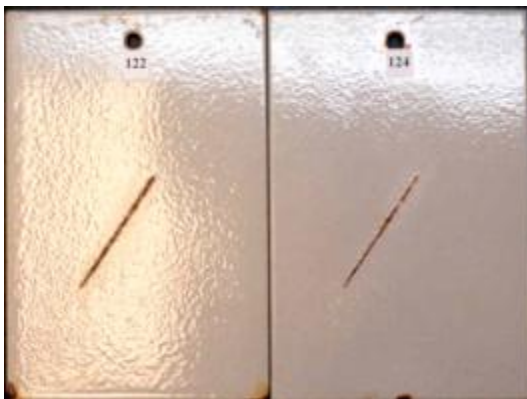
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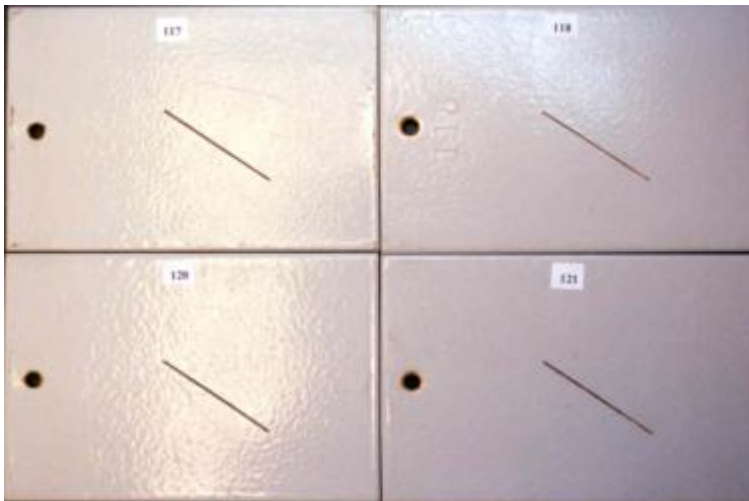
Figure 7. Coating conditions of system 1 after exposures.
a. 3,000-h test A   b. 3,000-h test B   c. 2-y outdoor exposure
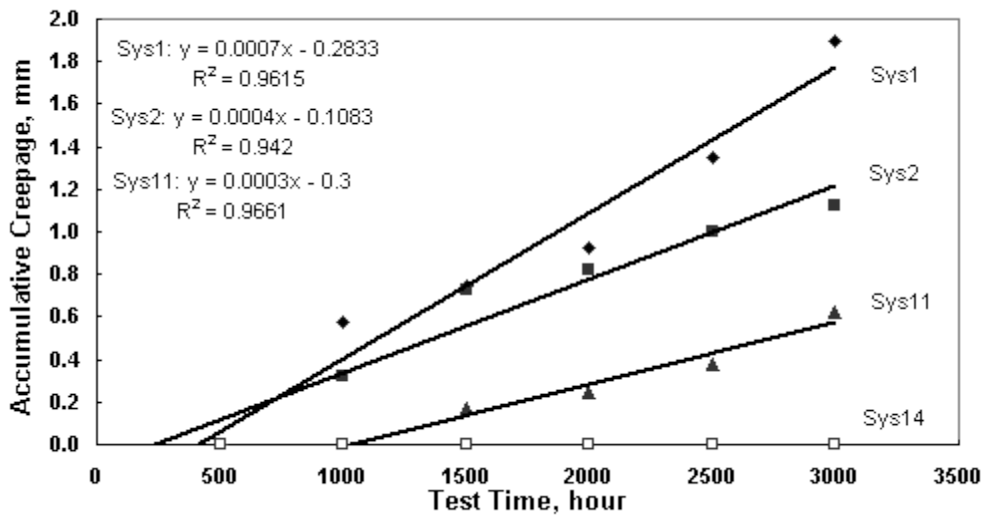
Figure 8. Plot of scribe creepage of zinc-rich coating systems over SP 10 surfaces versus laboratory test time after test A.
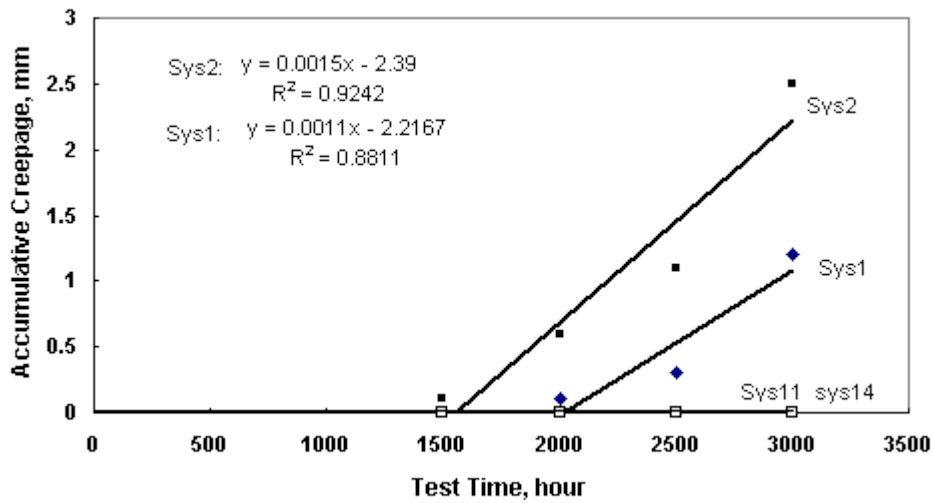
Figure 9. Plot of scribe creepage of zinc-rich coating systems over SP 10 surfaces versus laboratory test time after test B.
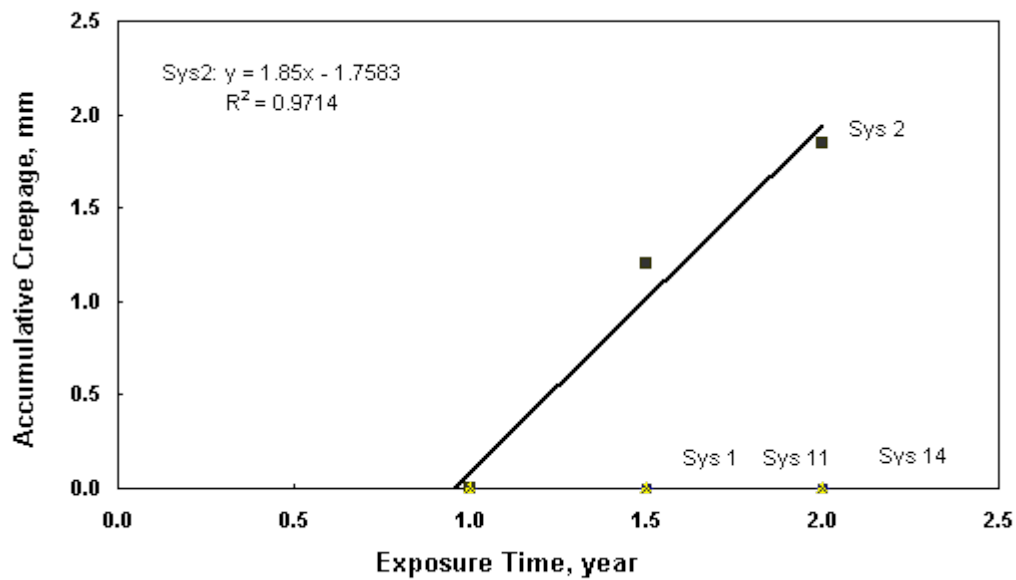
Figure 10. Plot of scribe creepage of zinc-rich coating systems over SP 10 surfaces versus outdoor exposure time.
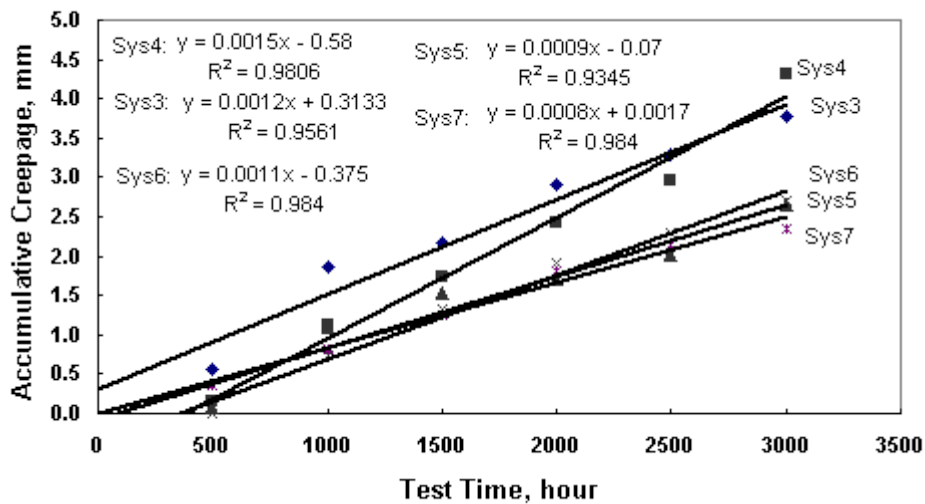
Figure 11. Plot of scribe creepage of acrylic coating systems over SP 10 surfaces versus laboratory test time after test A.

U.S. Department of Transportation
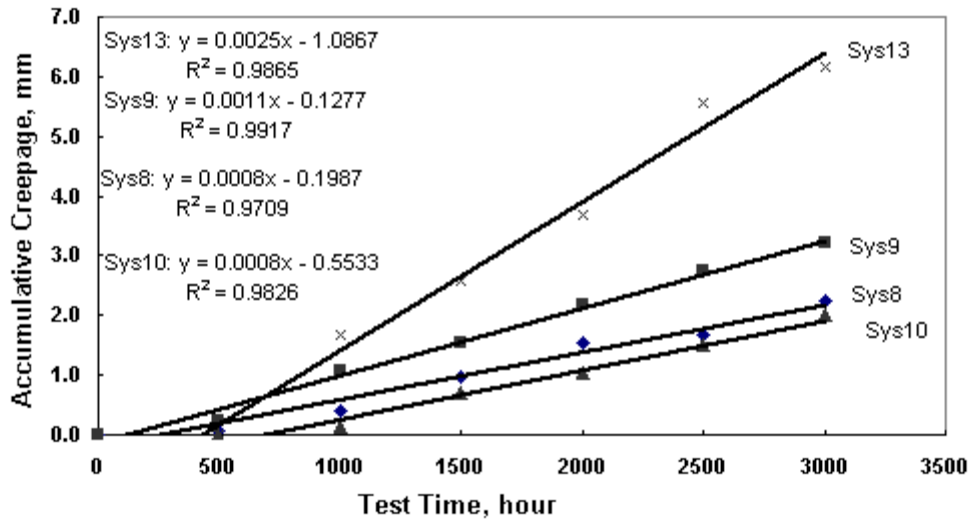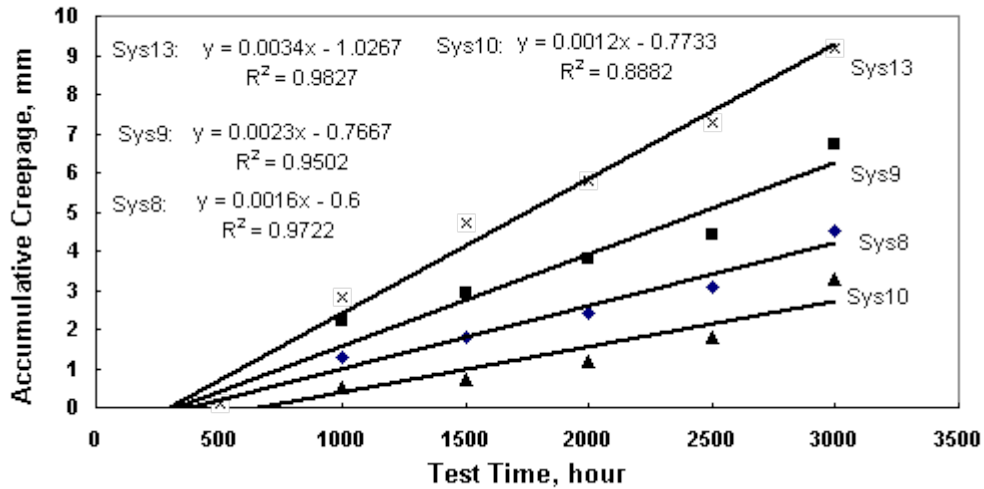Federal Highway Administration
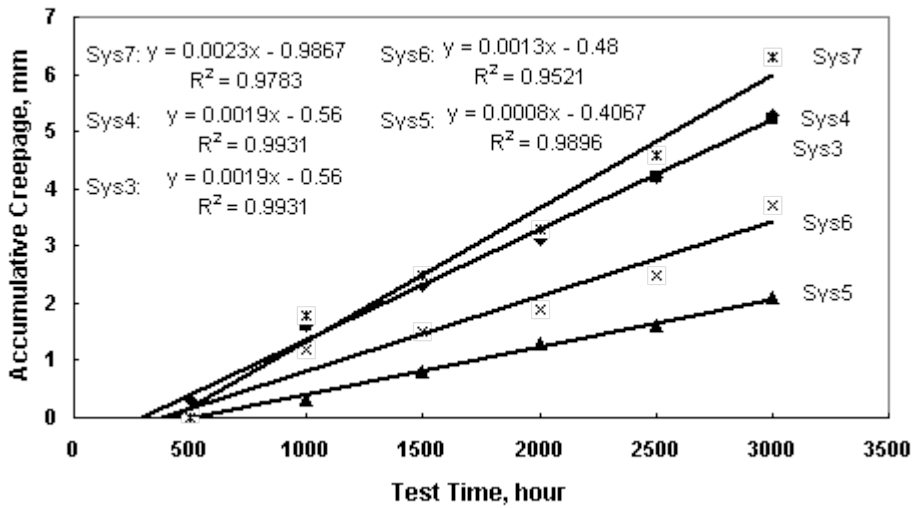
Figure 12. Plot of scribe creepage of acrylic coating systems over SP 10 surfaces versus laboratory test time after test B.
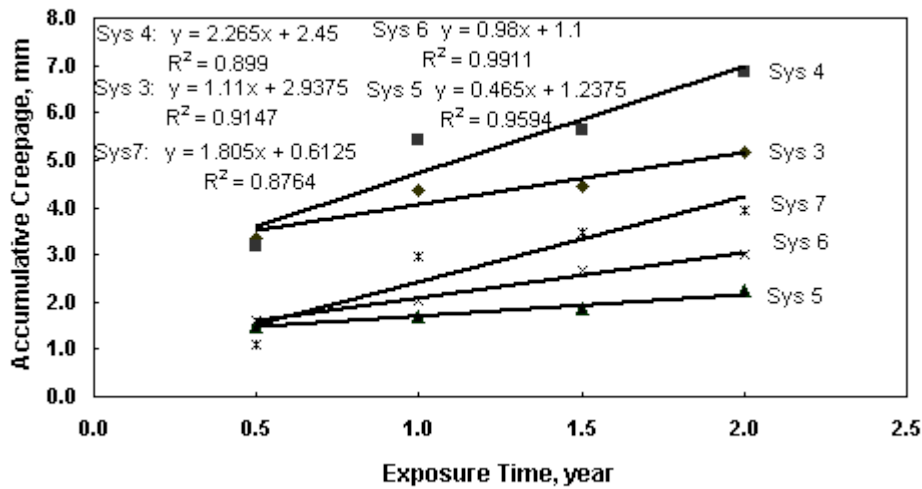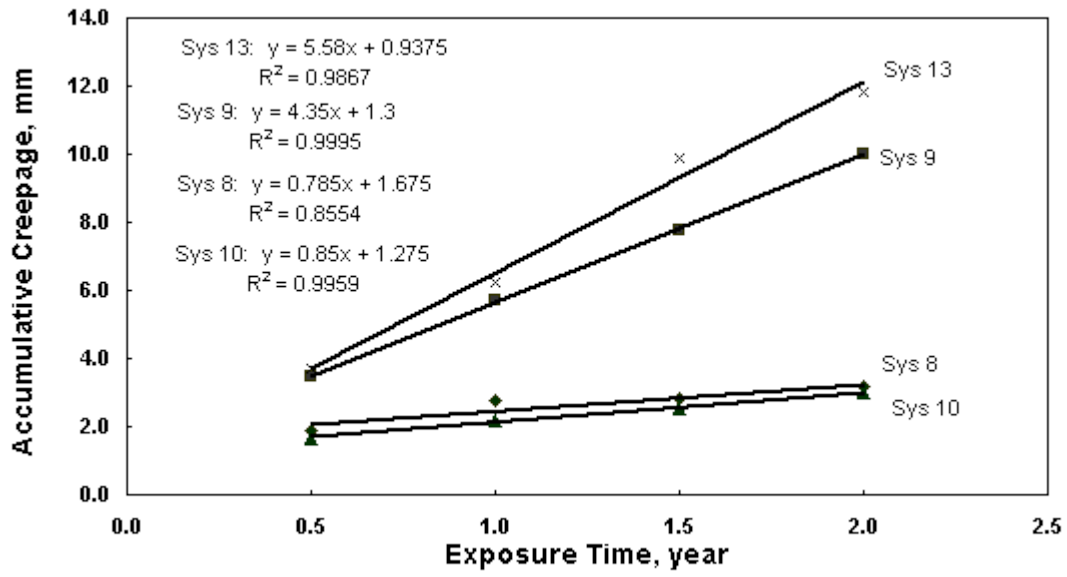

Figure 13. Plot of scribe creepage of acrylic coating systems over SP 10 surfaces versus outdoor exposure time.

a.
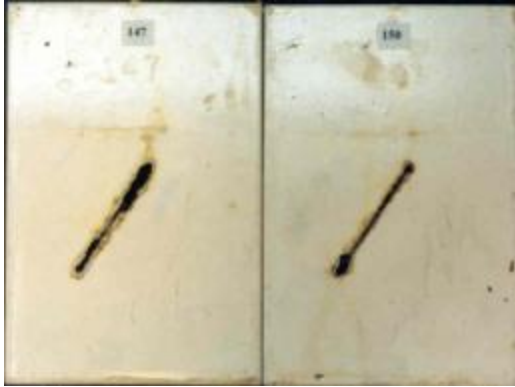
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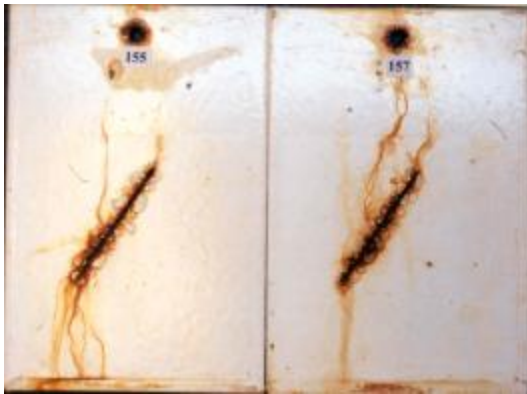
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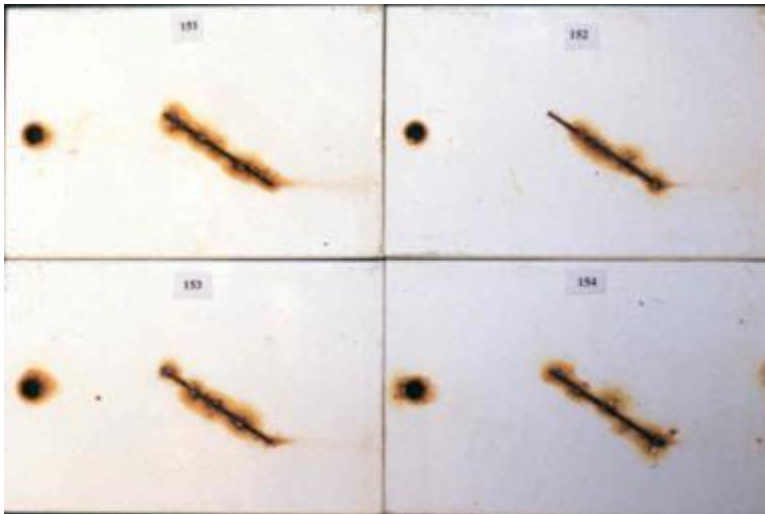
Figure 14. Coating conditions of system 3 after exposures.
a. 3,000-h test A   b. 3,000-h test B   c. 2-y outdoor exposure

a.
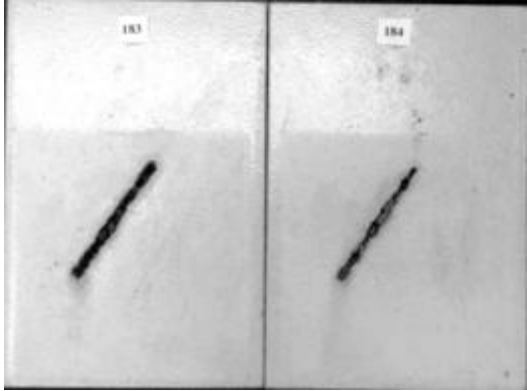
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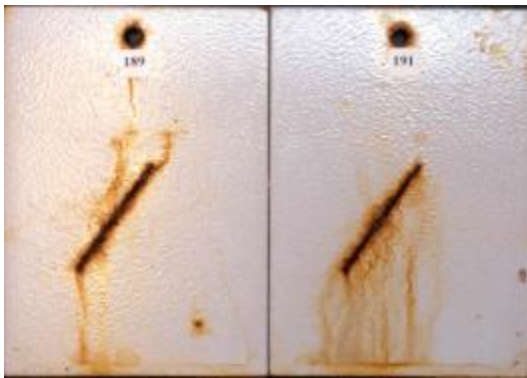
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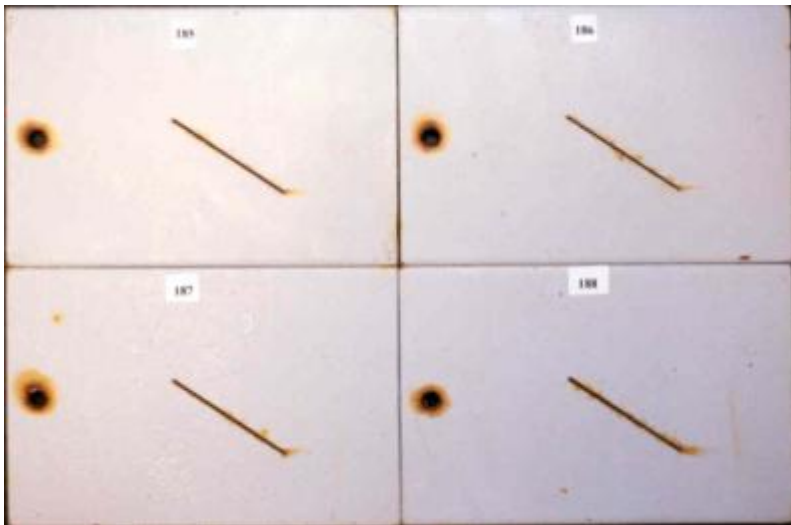
Figure 15. Coating conditions of system 5 after exposures.
a. 3,000-h test A   b. 3,000-h test B   c. 2-y outdoor exposure

a.
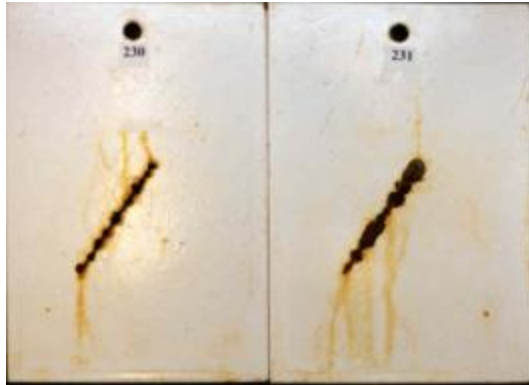
b.

c.

Figure 16. Coating conditions of system 8 after exposures.
a. 3,000-h test A   b. 3,000-h test B   c. 2-y outdoor exposure
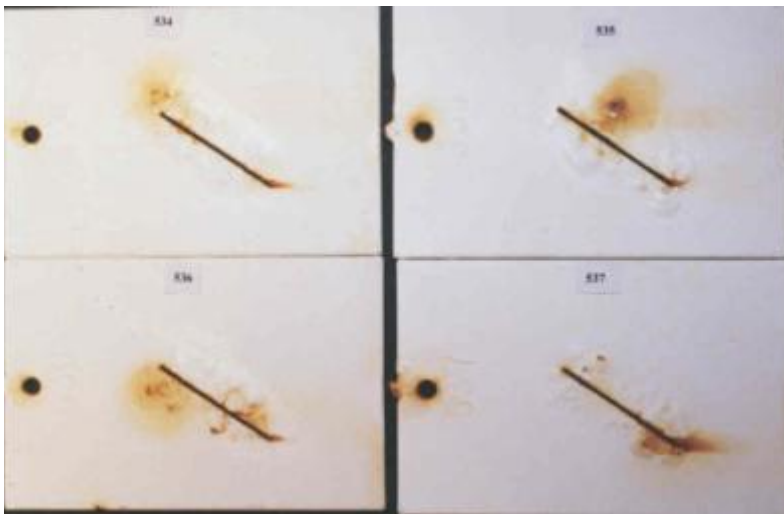
a.

b.

c.

Figure 17. Coating conditions of system 10 after exposures.
a.   3,000-h test A   b. 3,000-h test B   c. 2-y outdoor exposure

Figure 18. Plot of scribe creepage of epoxy coating systems over SP 10 surfaces versus laboratory test time after test A.

Figure 19. Plot of scribe creepage of epoxy coating systems over SP 10 surfaces versus laboratory test time after test B.

Figure 20. Plot of scribe creepage of epoxy coating systems over SP 10 surfaces versus outdoor exposure time.

a.

b.

.

c.

Figure 21. Coating conditions of system 13 after exposures.
a. 3,000-h test A   b. 3,000-h test B   c. 2-y outdoor exposure
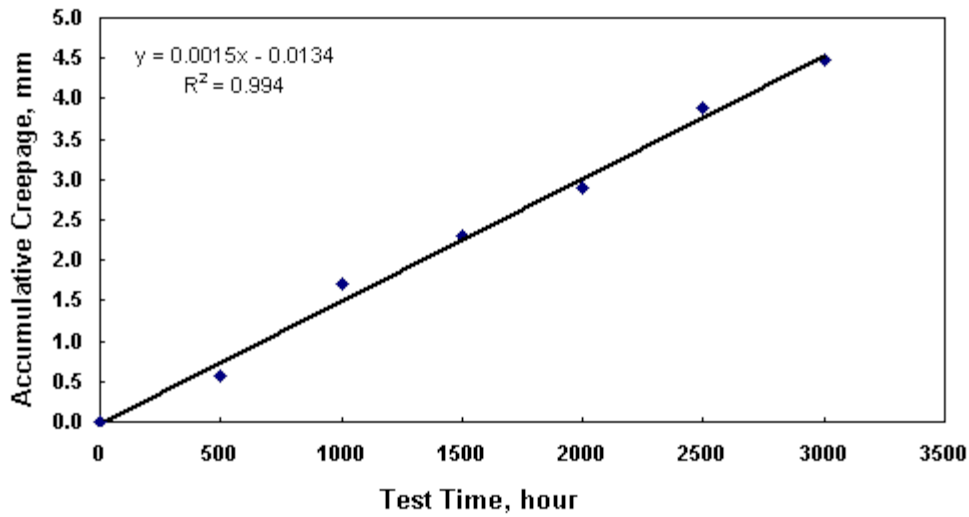
$y = 0.0015x - 0.0134$

$R^2 = 0.994$

Figure 22. Plot of scribe creepage of polyurethane coating system (system 12) over SP 10 surfaces versus laboratory test time after test A.
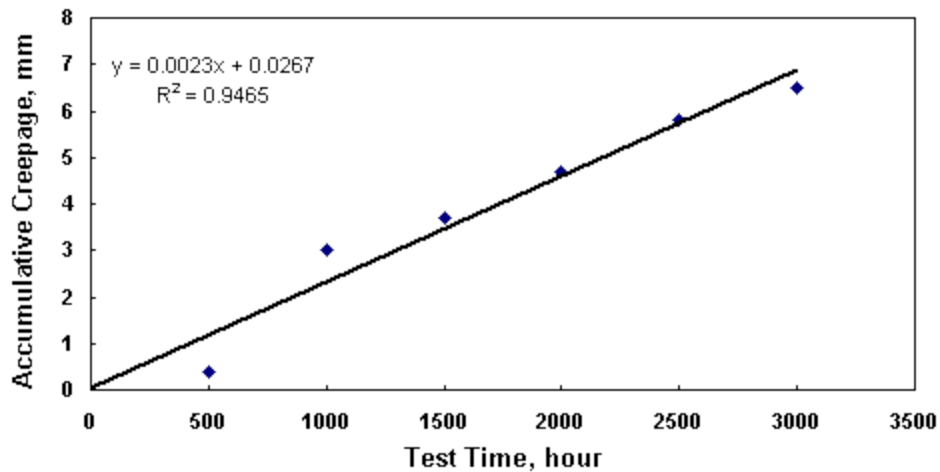

$y = 0.0023x + 0.0267$

$R^2 = 0.9465$

Figure 23. Plot of scribe creepage of polyurethane coating system (system 12) over SP 10 surfaces versus laboratory test time after test B.
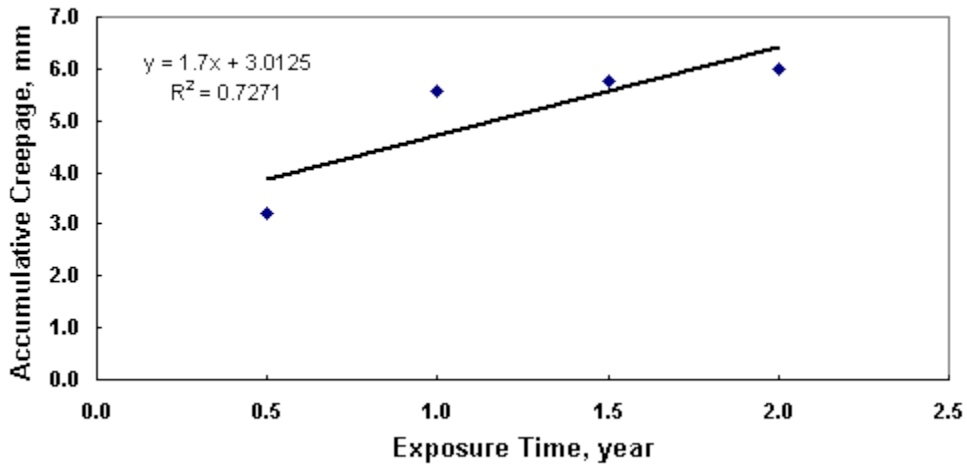
Figure 24. Plot of scribe creepage of polyurethane coating system (system 12) over SP 10 surfaces versus outdoor exposure time.
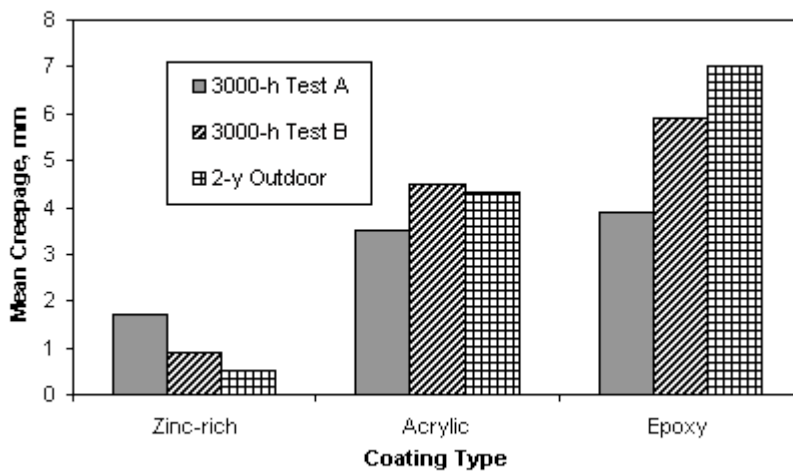

Figure 25. Comparison of mean scribe creepage developed by different coating types in three test methods.