Laboratory and Test-Site Testing of Moisture-Cured Urethances on Steel in Salt-Rich Environment

December 2000

FHWA-RD-00-156

US Department of Transportation

Federal Highway Administration

Research, Development, and Technology
Turner-Fairbank Highway Research Center
6300 Georgetown Pike
McLean, VA 22101-2296

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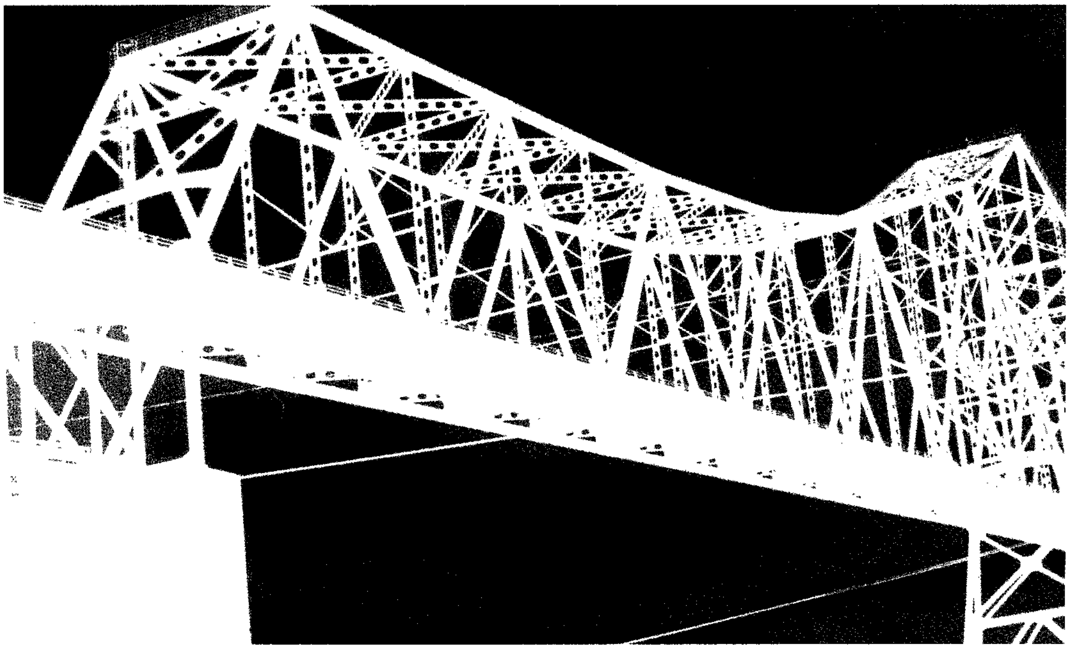

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FOREWORD

This report presents findings from the results of a Federal Highway Administration in-house study investigating the performance of three-coat moisture-cured urethanes on new steel and power tool-cleaned steel surfaces. This report presents the effects of substrate salt contamination, chemical properties of primers, pigment particle size distribution in primers, and application of sealer prior to primer for power tool-cleaned surfaces on coating performance. Both the cyclic laboratory test method and outdoor marine exposure were used to compare the performance of different commercial moisture-cured urethane products.

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Research, Development, and Technology

NOTICE

Technical Report Documentation Page

1. Report No.
FHWA-RD-00-156

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
LABORATORY AND TEST-SITE TESTING OF MOISTURE-CURED URETHANES ON STEEL IN SALT-RICH ENVIRONMENT

5. Report Date
December 2000

6. Performing Organization Code

7. Author(s)
Shuang-Ling Chong and Yuan Yao

8. Performing Organization Report No.

9. Performing Organization Name and Address

Office of Infrastructure RD & T
6300 Georgetown Pike
McLean, Virginia 22101

10. Work Unit No. (TRAIS)
2E4A

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
Office of Infrastructure RD & T
6300 Georgetown Pike
McLean, Virginia 22101

13. Type of Report and Period Covered

Final Report
October 1, 1996-September 30, 1998

14. Sponsoring Agency Code

15. Supplementary Notes
Ms. Yuan Yao is an employee of Soil and Land Use Technology, Inc. (SaLUT). Particle size distribution analysis was provided by Dr. Pedro Romero of SaLUT.

16. Abstract
Three 3-coat moisture-cured (MC) urethane commercial products formulated for protecting new steel (SSPC-SP 10) and power tool-cleaned steel (SSPC-SP 3) surfaces against corrosion were evaluated; the total coating film thickness was about 75 microns. Zinc-rich MC-urethane primers were used for SSPC-SP 10 steel surfaces whereas the primers for SSPC-SP 3 surfaces contained zero or a small amount of zinc; the same midcoats and topcoats were used for both steel surfaces. Sealers with film thickness of 25 microns were also studied for any potential effect on coating performance of the coating systems for power tool-cleaned surface. The volatile-organic-compound content of all the coating materials was below 340 g/L. The Federal Highway Administration (FHWA)-developed cyclic testing method was conducted to compare the performance of these coating systems. The test included freeze, ultra-violet light/condensation, and salt-fog/dry-air cycles. An aggressive outdoor marine exposure at Sea Isle City, New Jersey, was also performed for all the coating systems for comparison. A number of physical and chemical properties of the MC-urethanes were examined to study their effect on coating performance. All of the coating systems maintained their total film thickness, topcoat hardness, and adhesion strength throughout the 4,000-h test period. The three commercial products were found to contain different chemical compositions and performed differently. All the coating systems had an adhesion strength about 10.5 MPa. No surface failures were observed on any of the test panels after the 4,000-h laboratory test; however, all of them developed creepages at an intentional scribe (undercutting). The laboratory test results in conjunction with the chemical analysis results suggested that pigment particle size distribution in the primers played a more important role than other factors in the formation of creepage at the scribe. A proper pigment particle gradation improved the coating performance. A chloride concentration of 20 micrograms per square of centimeter on the steel surfaces was found to be significant to reduce the coating performance at the scribe of SSPC-SP 10 steel surfaces; however, the chloride effect was found to be minimal for SSPC-SP 3 steel surfaces. Interestingly, all the scribe creepages increased linearly with the laboratory test time up to 4,000 h. Furthermore, the addition of a sealer to the primer/midcoat/topcoat systems unexpectedly impaired the performance at the scribe on SSPC-SP 3 steel surfaces when compared with those systems without a sealer. On the other hand, a coating system with sealer/primer/topcoat without a midcoat developed severe underfilm corrosion probably due to insufficient film thickness.

17. Key Words
Paint, coatings, testing, performance, barrier pigments, urethanes, micaceous iron oxide, organic zinc, sealer, new steel, power tool-cleaned steel, corrosion, environmental compatibility, coating repair, accelerated test, outdoor exposure.

18. Distribution Statement
No restrictions. This document is available to the public through the National Technical Information Service, Springfield, VA 22161.

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	75	

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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		
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yards	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
NOTE: Volumes greater than 1000 l shall be shown in m^3.				
		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)		
°F	Fahrenheit temperature	5(F-32)/9 or (F-32)/1.8	Celcius temperature	°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	35.71	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)		
°C	Celcius temperature	1.8C + 32	Fahrenheit temperature	°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	0.225	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 September 1993)

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INTRODUCTION

Moisture-cured (MC) urethanes were designed for protecting steel bridges from corrosion in high humidity climates, especially in coastal areas. Urethane formulations originated in Germany and were brought to this country in the last decade. The special characteristics of the coating systems are reported to be attributed to the excellent resin properties of the urethanes and the inclusion of micaceous iron oxide (MIO) with a lamellar crystalline structure as shown in figure 1. This type of MIO structure enhances shielding of ultraviolet (UV) light, provides good abrasion resistance,[1] and retards the penetration of moisture, oxygen, and other corrosive substances to steel surfaces. Naturally mined MIO is quite expensive and exists in several countries, with the best quality believed to be from Austria. However, synthetic MIO with similar properties has been recently manufactured and can reduce the material cost substantially. These MC-urethane coating materials have been applied over many steel bridges in the United States either over blast-cleaned surface (Steel Structures Painting Council Surface Preparation Specification No. 10, i.e., SSPC- SP 10) or over power tool-cleaned steel surfaces (SSPC-SP 3) with good reported performance to date. The technical, practical, and economic aspects of this coating type were discussed by Schwindt.[2] The MC-urethane is a single-component coating material without use of a curing reagent; its binder is isocyanate that forms high-molecular-weight polyureas by reacting with the moisture in air. The MC-urethanes provide users with easy application properties such as single package, longer pot life, fast topcoating, low temperature and high humidity applications. Its tolerance to high humidity allows wider painting seasons at humid locations. However, because of the high reactivity of MC-urethane prepolymers (isocyanates) to moisture, special care should be taken to keep the spray lines absolutely dry during application and to keep paint cans tightly sealed when not in use. Careful handling and the use of proper protection equipment for workers against overexposure to isocyanates as well as solvents are also indispensable.

This report describes the performance of commercial MC-urethane products. Three coating systems formulated for SSPC-SP 10 and SSPC-SP 3 steel surfaces were evaluated in this study. The Federal Highway Highway Administration (FHWA)-developed cyclic accelerated testing method[3] was employed to compare the performance of these coating systems. The test included freeze, ultraviolet light (UV)/condensation, and salt-fog/dry-air (Prohesion) cycles. This laboratory test method has been shown to generate failure results that correlate much better with those developed in an outdoor aggressive environment than the salt-fog test alone.[4-7] An outdoor exposure was also conducted in this study for all the coating systems in an attempt to compare it with the laboratory test.

A number of physical and chemical properties of the MC-urethanes were examined to seek critical parameters affecting coating performance. Also, it was deemed desirable to investigate, in view of Appleman et al.'s findings[8] relevant to the detrimental effect of chloride (Cl^-) contamination, the effect of chloride contamination on coating life. Therefore, the performance of the MC-urethanes over chloride-doped steel surfaces was also evaluated.

EXPERIMENTAL METHODS

Various MC-urethane coating systems were sprayed on SSPC-SP 10 surfaces (figure 2) and SSPC-SP 3 surfaces (figure 3) in accordance with each manufacturer's specifications. All the test panels were 10 cm x 15 cm x 0.48 cm. The SSPC-SP 3 steel panels were prepared by rusting the SSPC-SP 5 (white metal) steel panels using the cyclic immersion method for 2 weeks and then power tool-cleaning by a rotary needle gun. Another set of coating systems was prepared on the corresponding steel surfaces doped with 20 μg/cm^2 chloride (Cl^-). The area doped was actually 8.9 cm x 14 cm or 125 cm^2. A 0.4-cc sample of the sodium chloride solution with a concentration of 6.3 mg/cc was placed in the center of the steel panel with a syringe and then spread uniformly over the test area with a plastic straight edge. A 5.1-cm (2-in) scribe was made diagonally on all the coated panels following the instructions specified in American Society for Testing Materials (ASTM) Method D1654. This scribe breeches the coating down to study the potential performance of the coating system at the site of any film defects in the coating, such as scratches, holidays, pinholes, etc.

The volatiles of all the paint materials were calculated from weight loss by evaporation determined in accordance with ASTM Method D2369. The pigment fractions were isolated using ASTM Method D2371 and their contents were determined; the amount of binder was calculated by difference. The metallic zinc as well as the total zinc present in the primer pigments was quantified by ASTM Method D521. Coating film thickness was measured with a magnetic thickness gauge. The 60° gloss was measured following ASTM Method D525. Three parameters of the topcoat colors (X, Y, Z) were measured by an incandescent light in a digital tristimulus colorimeter using amber, green, and blue filters, respectively, and a value of total color difference (E) was then calculated mathematically as E = square root of $[(\Delta X)^2 + (\Delta Y)^2 + (\Delta Z)^2]$. The adhesion strengths were measured by a pneumatic pull-off adhesion tester (ASTM D4541). This adhesion tester uses compressed inert gas to apply a continuous tensile load to a 1.3-cm (0.5-in) OD aluminum pull stub that is bonded to the test surface with an adhesive. Once the adhesive cures, the operator attaches a piston to the stub and a continuous load is applied perpendicular to the pull stub until failure occurs, and the adhesion value is obtained. The piston design ensures uniaxial alignment with the pull stub axis for "true tensile testing."

The coating films of all the primers, midcoats, and topcoats were individually prepared for Fourier-Transform infrared spectral (FTIR) analysis; a diffuse reflectance accessory with silicon carbide paper was used for all the FTIR analyses. The double-rub solvent test was performed using both methyl ethyl ketone (MEK) and Stoddard solvent for all the topcoats. The elemental contents of the pigment fractions were determined by a combined scanning electron microscopy/energy dispersive X-ray spectrometry technique (SEM/EDS) using a fixed size of sample pellets. The SEM/EDS instrument was calibrated by a pellet with a known concentration of metal oxides prior to sample analysis. The particle size distribution of each isolated pigment fraction was obtained by a particle size analyzer that measures light intensity reductions after passing a laser light through the particle-suspended solution.

Both the laboratory test and outdoor exposure were used to evaluate the coating performance in this study. Five replicate panels were used for each coating system in each test to ensure data reliability. A cyclic laboratory test method, freeze/UV-condensation/Prohesion test, was employed to evaluate the performance of the MC-urethane coating systems. This test method is a modification of ASTM D5894; table 1 gives the test conditions. All the tests were conducted for a total time period of 4,000 h. Two separate laboratory test runs were performed to obtain an average performance – one with two replicates and the other with three replicates. This test matrix took into account the condition variations of the testers in different test batches. The panels were examined for any surface failures such as blistering, rusting, etc., and were measured for scribe creepages at 500-h intervals. The creepage developed at the scribe was measured visually in a consistent manner. On each side of the 5.1-cm (2-in) scribe line, a maximum creepage reading was taken within every 1.3-cm (0.5-in) region along the scribe line. A total of eight readings was recorded from both sides of the scribe line, and a creepage value was obtained by averaging the eight readings for each test panel. The value presented in this report is an average of five test replicated panels, actually an average of 40 readings. A more accurate method for quantifying the amount of scribe creepage, an imaging technique, is currently being developed at FHWA.[9] In this improved method, the total creepage area is traced by a black marker with thin tip, photographed by a scanner, and then integrated by computer software.

Table 1. Laboratory test conditions.

Every 500-h cycle included the following tests:
1. Freeze: 68 h
    Temperature: -23°C (-10 °F)
2. UV-Condensation: 216 h (9 days)
    Test cycle: 4-h UV/4-h condensation cycle
    UV lamp: UVA-340
    UV temperature: 60 °C (140 °F)
    Condensation temperature: 40 °C (104 °F)
    Condensation humidity: 100% relative humidity
3. Prohesion (cyclic salt-fog, ASTM G85): 216 h (9 days)
    Test cycle: 1-h wet/1-h dry
    Wet cycle: A Harrison Mixture of 0.35 wt% ammonium sulfate and 0.05 wt% sodium chloride was used. Fog was introduced at ambient temperature.
    Dry cycle: Air was preheated to 35 °C (95 °F) and then was purged to the test chamber.

Another set of coated panels was exposed at Sea Isle, NJ, an aggressive marine exposure site. All the 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 similar manner as those panels used in the laboratory test. The Sea

Isle test site is an extremely harsh environment, with characteristics shown in table 2 that were described in a FHWA funded study.[10] The rainwater at this site has the highest salt content and conductivity among the seven studied exposure sites, including Arizona (New River), Florida (Miami), Indiana (near Michigan City), Louisiana (near Lafayette), Massachusetts (northernmost point of Cape Cod), and Oregon (outside of Eugene).

Table 2. Annual characteristics of Sea Isle exposure site.

Sunshine: 2,840 h
Relatively humidity: 70%
Time of wetness: 51%
Rainfall: 150 cm
    pH of rain water: 4.2
    Conductivity of rain water: 163 μS/cm*
    Composition of rain water: 27 ppm Cl^-, 25 ppm SO_4^{-2}
    Water temperature: 9.1 °C (48.4 °F)
Spray seawater:
    pH = 7.5
    Salt content: 2.7 wt%

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* Microsiemens per centimeter.

RESULTS AND DISCUSSION

This report is divided into two parts for clarity. Part I and Part II describe the performance of MC-urethane coating systems applied over SSPC-SP 10 steel surfaces and over SSPC-SP 3 steel surfaces, respectively.

PART I: Moisture-cured Urethane Coating Systems for Blast-Cleaned Steel Surfaces

Background

In a previous FHWA study, zinc-rich MC-urethane systems with topcoats of different volatile-organic-compound (VOC) contents were found to perform extremely well. They showed no failures or minute failures at the scribe on the SSPC-SP 10 steel surfaces after the 3,000-h cyclic laboratory test, and no failures after 28-month natural marine exposure.[6] This strong corrosion resistance is in line with the excellent performance of other zinc-rich bridge coating systems such as inorganic zinc silicates and zinc-rich epoxy coating systems.[11,12] In service, some MC-urethane coatings still remain in extremely good condition with less than 1 percent failure after 8 years of service in Oregon.[13] However, there have been different performances observed in the field for different manufacturers' products. In fact, some products failed due to poor materials within 1 year after application,[13] resulting in complicated court cases. To investigate the disparity in performance of MC-urethane formulations, it is necessary to systematically study the performance and composition difference in various products.

Three separate commercial products were evaluated. All the MC-urethane systems used for tests consisted of three coats with a total dry film thickness of 200 to 225 microns (8 to 9 mil) and VOC contents of all the coating materials equal to or less than 340 g/L (2.8 lb/gal) as shown in table 3. Virtually all the midcoats and the topcoats contained MIO, which is an excellent pigment for barrier coatings.

Chemical Properties – The chemical composition of these three MC-urethane primers was found to vary with their formulations. The volatile content, solid content, pigment content, and binder content are listed in table 4. The pigment contents did not differ significantly, but the difference in binder content was significant, ranging from 8.8 to 15.5 wt% of the wet paint film of the primers. System A contained the highest amount of binder (presumably polyurea) while System C had the lowest amount of binder. These data yield the ratio of pigment to binder of 4.8, 6.6, and 8.8 for Primer A, Primer B, and Primer C, respectively. The metallic zinc content and total zinc content in these primers were determined using oxidation followed by titration; the zinc values are listed in table 5. The experimentally determined total zinc values were similar to but slightly less than the manufacturers' reported data. The amounts of the total zinc used in these three primers for SP 10 surfaces were different and they ranged from 78.8 to 86.8 wt% of the dry paint film. The metallic zinc amounted to 5 to 6 wt% less than total zinc because zinc dust usually contains a small amount of zinc oxide.

Table 3. Description of zinc-rich moisture-cured urethane coating systems.

System	Coating System	VOC, g/L
A	Zinc-rich urethane/MIO[a]-filled urethane/urethane	314/315/314
B	Zinc-rich urethane/MIO-filled urethane/MIO-urethane	336/336/336
C	Zinc-rich urethane/MIO & Al[b]-filled urethane/MIO-filled urethane	337/340/336

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[a] Micaceous iron oxide.
[b] Aluminum.

Table 4. Chemical composition of zinc-rich MC-urethane primers.

Content	A	B	C
		wt% of wet paint	
Volatiles[a]	10.8	9.3	13.4
Solid[b]	89.2	90.7	86.6
Pigment[c]	73.7 (82.6)[e]	78.8 (86.9)	77.8 (89.8)
Binder[d]	15.5 (17.4)	11.9 (13.1)	8.8 (10.2)
Pigment/binder	4.8	6.6	8.8

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[a] ASTM D2369.
[b] 100 wt% - wt% volatiles.
[c] ASTM D2371.
[d] 100 wt% - wt% volatiles – wt% pigment.
[e] wt% of dry paint film.

Similarly, the chemical compositions of the midcoats and topcoats of the three systems were not the same. The content of binder and pigment are shown in table 6. Basically, pigments amounted to approximately twice the binder amount by weight except Topcoat A which had a higher amount of binder that provided the high gloss. The aluminum, iron, and zinc contents in the midcoats and the topcoats were identified and quantified by SEM/EDS technique; the key anti-corrosive elements such as aluminum (Al), iron (Fe), and zinc (Zn) are given in table 7. It is believed in large part that aluminum and zinc existed in their metal forms and iron was in the form of micaceous iron oxide. Midcoat C contained a higher amount of the three anti-corrosive elements than did Midcoat A and Midcoat B. On the other hand, Topcoat B and Topcoat C had similar amounts of these elements and were higher than those in Topcoat A. The main elements that imparted the protective properties of the midcoats and the topcoats were Al and Fe (micaceous iron oxide), but zinc dust was virtually not present in these coat materials except in Midcoat B.

Table 5. Zinc content of zinc-rich MC-urethane primers.

Zinc Type	A	B	C
	wt% of Dry Film		
Metallic zinc[a]	72.8	75.9	80.1
Total zinc[a]	78.8	80.4	86.8
Total zinc[b]	80	83	89

[a] ASTM D521.
[b] Value on manufacturer's product data sheet.

Table 6. Pigment and binder contents of MC-urethane midcoats and topcoats.

Weight Percent	A	B	C
Pigment			
Midcoat	53.3[a] (67.2)[b]	59.8 (70.9)	52.7 (67.4)
Topcoat	32.9 (44.9)	52.8 (66.2)	57.5 (70.4)
Binder[c]			
Midcoat	26.0 (32.8)	24.5 (29.1)	25.5 (32.6)
Topcoat	40.4 (55.1)	27.0 (33.8)	24.2 (29.6)

[a] wt% of wet paint.
[b] wt % of dry film.
[c] 100% - wt% volatiles – wt% pigment.

The three MC-urethane products consisted of binder with different degrees of aromaticity. This difference in binder type was detected by the FTIR analyses of these MC-urethanes materials. Since the MC-urethane coating films containing micaceous iron oxide are generally brittle and coarse, they will not only scratch an attenuated total reflection (ATR) crystal plate but also will not provide a good contact to the ATR plate. Therefore, an alternative method using a diffuse reflectance accessory (DRIFT) was adopted for the analysis. The relative amount of aromatics to aliphatics (AR/AL) of binder in table 8 was estimated from the ratio of intensity (peak area) at the wavenumber of 3100 cm^{-1} to that at the wavenumber of 3000 - 2800 cm^{-1} in the FTIR spectra of the coating materials. Using this ratio for comparison is known to be fairly quantitative, whereas measurement of individual FTIR peaks is only for qualitative purposes unless special sample preparation method and FTIR accessory are selected. The primer and the midcoat of System A are more aromatic in nature (AR/AL = 0.036, 0.042), whereas those of System C are more aliphatic (AR/AL = 0.015, 0.015). System B consists of a primer with a moderate AR/AL ratio (0.020) and a high aliphatic midcoat (AR/AL = 0.008). All the topcoats have either all aliphatic or highly aliphatic chemical structures. In general, aromatic compounds cure more rapidly and cost less than aliphatic compounds, but aliphatic compounds are less susceptible to oxidation and UV attack, thereby offering higher chemical resistance and mechanical strengths. It is one of the formulators' objectives to select the best combination of aliphatic and aromatic characters to achieve optimum coating performance results at a reasonable cost.

Table 7. Major anti-corrosive metal elements in MC-urethane midcoats and topcoats.

System		Al	Fe	Zn	Fe_2O_3[a]
			wt% of dry film		
Midcoat					
	A	1.0	6.3	0	8.6
	B	1.8	3.4	5.3	4.9
	C	7.6	6.6	0	9.4
Topcoat					
	A	1.3	0.1	0	0.1
	B	0.6	3.2	0	4.6
	C	1.2	2.5	0	3.6

[a] Calculated from the amount of Fe.

Table 8. FTIR aromatics/aliphatics peak ratio of MC-urethanes.

System	Primer	Midcoat	Topcoat
		AR/AL x 1000	
A	36	42	0
B	20	8	0
C	15	15	6

The chemical resistance of the topcoats was examined by solvent rub tests with MEK and Stoddard reagent. The test results are presented in table 9. Topcoat A, a glossy topcoat, exhibited the highest chemical resistance against MEK and Stoddard reagent by requiring more than 50 double rubs to induce coating failures, while flat Topcoat B and Topcoat C showed lower solvent resistance.

Table 9. Solvent rub test results of MC-urethane topcoats.

Topcoat	Times of Double Rubs to Fail	
	MEK	Stoddard Reagent
A	>50	>50
B	1	15
C	3	>50

Zinc was found to be the primary component in all the zinc-rich primers. The elemental analysis results of the isolated primer pigments obtained by the SEM/EDS method are displayed in figure 4. Other elements present included magnesium, aluminum, silicon, iron, and oxygen. The only significant difference among the three products is that Primer B contained a significant amount of silicon and oxygen, probably due to silicates known to be an extender pigment. All the pigments were preliminarily examined for their particle sizes by an SEM at the magnification of 500X; the spherical zinc particles showed different sizes in Primer A, B, and C (figure 5). To quantitatively determine the particle sizes, a particle size analyzer was utilized to investigate the details. The particle size distribution of pigments A, B, and C are plotted in figure 6. The particle sizes of pigments are in the order of Pigment B < Pigment A < Pigment C; they peaked at 3 µm, 5 µm, and 10 µm respectively. These results indicate that different grades of zinc particles were used in the three different primers, especially for Primer C. In principle, the more small pigment particles are used, the more air voids or interstitial areas between large zinc particles are filled by these particles and the tighter the packing of coating film becomes. This phenomenon has been demonstrated in dense-graded asphalt-aggregate mixture for asphalt pavement for which a specification was established for aggregate particle size distribution.[14,15] In other words, a proper gradation of pigment particles will result in a less porous film, thereby decreasing film permeability and enhancing barrier properties. Furthermore, the tight packing of zinc particles increases film conductivity, which in turn benefits their sacrificial properties for the protection of steel.[12]

It appears that isocyanate prepolymers cured very slowly. When the topcoats were analyzed by FTIR within 1 month of panel preparation, isocyanates were still present in most of the topcoats. However, all the isocyanates disappeared after the 4,000-h laboratory test, presumably forming more crosslinking polyurea. The ratio of FTIR peak area of isocyanate (2270 cm^{-1}) to that of the total organics (3100-2800 cm^{-1}) was calculated before and after the test, and the values are presented in table 10. The slowing curing of isocyanate has been previously illustrated by Ludwig and Urban[16] in their work, in which it took about 80 days for the eventual disappearance of isocyanate at 40% relative humidity and 25 °C. Based on these results, the MC-urethane topcoats, virtually all aliphatic, need at least 2 to 3 months for all isocyanates to cure completely.

Table 10. FTIR ratio of isocyanate peak to total organic peak of topcoats before and after 4,000-h laboratory test.

System	Before Test	After Test
	X 1000	
A	47	0
A (Cl^-)[a]	62	0
B	0	0
B (Cl^-)	0	0
C	21	0
C (Cl^-)	20	0

---

[a] Chloride-doped surface.

Physical Properties – In general, the total coating film thickness and the pencil hardness (2H) of the topcoats stayed fairly constant throughout the laboratory test period. The plot of thickness against test time is shown in figure 7; the nearly constant thickness showed no photolytic degradation from UV and no swelling from moisture.

As bridge aesthetics is an increasing concern to urban planning and local communities, the gloss and color of the topcoats before and after the test were measured in this study. The changes in 60° gloss of the topcoats with increasing test time is plotted in figure 8. The low gloss (flat) Topcoats B and C changed their gloss slightly but high-gloss Topcoat A lost about 50% of gloss after the 4,000-h test. This finding implied that the use of a high-gloss topcoat might not be cost-effective. In the case of color appearance, the total color difference (E) between unexposed panels and those after the 4,000-h laboratory test as well as those after the 2-yr outdoor exposure at Sea Isle site are both illustrated in figure 9. The total color change was found to be in the decreasing order of Topcoat C > Topcoat A > Topcoat B after the 4,000-h laboratory test. The color difference of Topcoat A and Topcoat B after the test were equal to or less than 2, which was superior in terms of color retention.

The adhesion strengths of MC-urethanes applied over both SP 10 and chloride-doped SP 10 steel surfaces were extremely high (around 10.4 MPa or 1,500 psi), and they essentially remained the same as the original strength after the laboratory test as shown in figure 10. In the pull-off adhesion test, all the coating failure modes were cohesive failure of either midcoats or topcoats; no cohesive failure of primers or adhesive failure between primer and steel substrate was observed. These failure modes demonstrated that the adhesion strength of all primers to the steel substrates were higher than the reported values in figure 10. The mechanical strength, i.e., cohesive strength, of all the primers were apparently strong but their difference cannot be estimated from these test results. The adhesion value for each coating system shown in figure 10 was an average of 15 measurements (3 tests for each test panel), which were highly reproducible; the overall relative standard deviation was ± 6.0 %.

Coating Failures – The laboratory test results and the outdoor exposure results are presented below. Coating failures discussed here include surface failures and visible surface rust creepage developed at the intentional scribe.

A. Laboratory Test

No surface failures were observed on all the SP 10 and the chloride-doped SP 10 test panels throughout the 4,000-h laboratory test period; this good performance demonstrated the excellent barrier properties of the test systems. The polyureas as well as presence of MIO in the midcoats and in the topcoats are believed to reduce permeability of corrosion-causing elements to steel; these elements are water, oxygen, and electrolytes.

However, all the coating systems started to develop rust creepages in the form of individual blisters directly adjacent to the scribe line at the test duration around 1,500 h. The rust creepage was generated through the steel dissolution process in the corrosive environment at the scribe area. After 4,000 h of the laboratory test, all the blisters coalesced to form a continuous bulk surface along the scribe. The coating conditions of the MC-urethanes over SP 10 and chloride-doped SP 10 surfaces for each coating system after the test are shown top-to-bottom for easy comparison in figures 11, 12, and 13. The pictures of the panels tested in two separate batches were taken immediately after each 4,000-h laboratory test. For simplicity, only three replicates in one batch are shown here, whereas the creepages presented in this report are the average values of the creepages generated in the five replicated test panels. The average creepage developed progressively with test time; a fairly linear relationship was observed up to 4,000 h (figure 14). This constant rate of growth may not continue beyond 4,000 h; however, no trend can be predicted between rust creepage and test time without further testing. The linearity has been observed and reported in the previous FHWA studies;[3, 6] it may indicate a pseudo zero-order reaction for rust creepage formation in the early test period. In this case, the rate of rust formation at the scribe can be written as:

$dx/dt = k$ where,

x = rust concentration at the scribe
t = test time
k = rate constant, i.e., slope of the plotted line
dx/dt = rate of rust creepage formation at the scribe

From the test results, a different k value was observed for a different primer. As a result, primer performance on steel can be distinguished by plotting rust creepage versus test time. It is believed that the nature of primers plays a key role in the rust creepage formation. In general, different primers have different adhesion strengths to steel, film porosity, and different rate of hydrolysis, all of which are important factors contributing to creepage formation. In other words, low adhesion, high film porosity, and high hydrolysis rate will facilitate the diffusion of water through the water-weak zone that is the polymer zone near the metal surface.[17] The diffusion rates of water through different polymers vary due to their different chemical and physical properties. Systems A, B, and C over SP 10 surfaces exhibited slightly different amounts of creepage ranging from 2 to 3 mm in the order of B < C < A after 4,000 h of the laboratory test (figure 14). It is difficult to conclude if these differences are significant because of higher error within this measurement range using a ruler. On the other hand, the amount of creepage developed by the three systems over the chloride-doped SP 10 surface were higher than those over the clean SP 10 surface, especially System C. Three systems over the chloride-doped SP 10 surface generated creepages from 3 to 5 mm and increased in the order of B< A< C as illustrated in figure 15. All the plots of scribe creepage versus test time were again found to be linear. The incubation time along the x-axis for scribe creepage to appear was found to be shorter for the systems over chloride-contaminated SSPC-SP 10 surfaces than the systems over chloride-free counterparts, whereas the slopes were steeper, indicating their faster corrosion rates. This linearity characteristic indeed provides a convenient and scientific way to compare the performance of each primer at the scribe of the steel surface. These plots suggest that the slopes characterize generic coating type and steel surface condition, while the incubation time determines the corrosion resistance at the scribe. Figure 16 gives a better picture of the effect of chloride contamination on the extent of scribe creepage developed after the laboratory test. These creepage results in combination with the data of blister size and density at the scribe (table 11) suggested the better performance of System B than Systems A and C under the environmental conditions employed in the test.

As rust creepage (i.e. undercutting in most cases) developed at the scribe reflects the corrosion resistance of a primer,[18] many properties of the primers were investigated. The rate of scribe creepage formations can be strongly influenced by coating composition, including resin type and ratio of pigment content to binder content in primers, etc. The weight ratios of pigment to binder were found to be 4.8, 6.6, and 8.8 for primers A, B, and C, respectively (table 4). With polyurea as the main binder and more than 80 wt% of zinc dust, the specific gravities of primers A, B, and C ought to be fairly similar. Hence, the volume ratios of binder to pigment are believed to be in the same order as the weight ratios. The zinc-rich primer in System C has the highest weight ratio of pigment content to binder content (i.e., high PVC) as well as the highest amount of zinc content. It is known that pigment volume concentration/critical pigment volume concentration (PVC/CPVC) value plays an important role in the coating film properties, and thereby to the coating performance. When the PVC/CPVC ratio is less than 1, film is glossy and impermeable; when the PVC/CPVC ratio is more than 1, film becomes porous with poor physical properties.[19] The high PVC/CPVC ratio in conjunction with the high concentration of large zinc particles in

Primer C are believed to produce a more permeable film for Primer C; the resulting faster water diffusion rate, faster osmosis, and loose film packing may be the main factors that yielded the poorest performance for System C among all three chloride-doped systems at the scribe. The failures of the chloride-doped System C included large rust-filled blisters (2VD, 4VD) and 5.1 mm of creepage, which is twice the amount (2.5 mm) generated on the chloride-free counterparts. In comparison, the effect of chloride on the performance of System A and System B are less severe than System C in terms of scribe creepage (see table 11 and figure 16). These creepage results suggest that System B may be the best formulation among the three systems over clean SP 10 surfaces, with System C rated the second best. Furthermore, the ratio of the rust creepage exhibited over SP 10 surfaces to that on chloride-doped SP 10 surfaces for Systems A, B, and C were 1.3, 1.5, and 2.0, respectively; the effect of chloride was more pronounced for System C than for System A and B. The performance of System C seemed to be impaired most by the chloride contamination on the steel surface. The best performer was found to be System B whose primer contained more small zinc particles, i.e., high-grade zinc dust. These results lead to the conclusion that it is essential to include a sufficient amount of small particle pigment in the coating to optimize performance.

Table 11. Failure results of MC-urethane systems over SP 10 and over chloride-doped SP 10 surfaces after 4,000-h laboratory test.

System	Blistering at Scribe[a]	Creepage, mm	Creepage Ratio, Cl^-/no Cl^-
A	6MD, 4MD	3.3	
A (Cl^-)[b]	4D	4.2	
			1.3
B	6F, 4F	1.9	
B (Cl^-)	6MD, 4MD	2.8	
			1.5
C	4M	2.5	
C (Cl^-)	4D, 2D	5.1	
			2.0

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[a] ASTM D714 where MD = medium dense, D = dense, F = few, M = medium.

[b] Chloride-doped surface.

It is clear that the chloride-doped test panels developed more severe blistering and larger scribe creepages than those for chloride-free test panels. The failure results suggest that chloride contamination as low as 20 μg/cm^2 level is significant enough to induce a detrimental effect on the coating performance. It was reported that epoxy zinc-rich (organic zinc-rich) coatings will tolerate up to 30 μg/cm^2 chloride contamination without showing significant difference in performance.[8] However, this work demonstrated that a 20 $\mu g/cm^2$ level of chloride contamination is sufficient to reduce the corrosion resistance at film defects in the MC-urethanes applied over new steel even though the primer films contain a substantial amount of zinc dust (79 to 89 wt%).

B. Outdoor Exposure

After 2 years of outdoor exposure of the test panels in the high salt marine environment, none of the coating systems has exhibited any surface failures or creepage other than rust at the scribe line. Therefore, no comparison can be made for the SP 10 MC-urethane failure results between the laboratory test and the outdoor exposure as of this date.

The gloss change of all the topcoats after 2-yr outdoor exposure is shown in figure 17. The trends are similar to those obtained from the laboratory test. The gloss of Topcoat A decreased drastically with exposure time, and the gloss of flat Topcoat B and Topcoat C stayed fairly constant throughout the exposure time. The color difference of three topcoats after 2 years of outdoor exposure are also shown in figure 9. Apparently there was no correlation between ranking of E in the 4,000-h laboratory test and ranking of E in the field test. Contrary to the laboratory test results, the field color change of 13 for Topcoat A, 10 for Topcoat B, and 6 for Topcoat C would be considered very poor after 2 years of exposure. Therefore, one-pack MC-urethane topcoat is not a proper choice in terms of the color retention in a humid and salt-rich environment. This phenomenon was observed in the study.[10] A better topcoat formulation, probably two-pack aliphatic polyurethane, is needed to improve the color appearance. The degree of color change of the MC-urethanes exposed at Sea Isle City, NJ, is in the decreasing order of A >B >C. The difference in order in the color change seen in the laboratory test and the outdoor exposure must be due to the different sensitivity of the topcoats to the environmental conditions in the laboratory test and those in the outdoor exposure.

Part II. Moisture-cured Urethane Coating Systems over Power Tool-Cleaned Steel Surfaces

Background

Moisture-cured urethanes have been increasingly used to overcoat or repair aged lead-based alkyd paint by various States. Their tolerance to power tool-cleaned steel surface (SSPC-SP 3) and compatibility to old alkyd paint provide a great deal of advantage over other coating systems for rehabilitation of steel bridges. Their adhesion to these surfaces is enhanced by scavenging moisture in rust or old paint during the curing process of MC-urethanes. The repair or overcoating procedure eliminates expensive costs such as containment, collection of dust, waste disposal, worker safety protections, and equipment associated with abrasive blasting methods. MC-urethanes are quick to dry and to cure with good adhesion after overcoating. However, two possible failure modes may occur after overcoating – delamination and rust- through. To investigate the performance of MC-urethanes applied over SSPC-SP 3 steel surface and to identify products that minimize these failures, several systems were tested for their durability in this study. **However, the test results obtained here should be referenced cautiously and should only be applied to repairing rust areas, not to aged coatings on steel bridges.**

Similarly, three different three-coat MC-urethane commercial products were evaluated in this study. In addition, a urethane sealer was used prior to primer application over SSPC-SP 3 steel surface in order to study the possible benefit of using an extra layer of sealer. Product C had two versions of sealer coating systems with different primers. Furthermore, a chloride concentration of 20 $\mu g/cm^2$ was also applied over the SP 3 surfaces to investigate the impact of this salt contamination. Both the laboratory test method and outdoor exposure were performed in order to compare the relative coating performance of three MC-urethanes in these two tests. Two sets of coating systems for SP 3 surfaces were studied. Table 12 presents the first set of three-coat MC-urethane systems (A1, B1, C1) with total coating film thickness of 225 to 250 microns (9 to 10 mil); each coat was about 75 microns (3 mil). The second set of test panel systems (A2, B2, C2) was prepared with an additional coat of urethane sealer (about 25-micron thickness) to the first set to form four-coat systems; however, System C2 used a different primer (Zn & Al-filled urethane) as recommended by Manufacturer C. In addition, System C3 was a three-coat system of sealer/primer/topcoat that eliminated the use of the midcoat. Again, the VOC content of all coating materials was equal to or less than 340 g/L (2.8 lb/gal). It should be noted here that sealer is usually recommended by manufacturers as the first coat to be applied over aged lead paint surfaces and irregular rusted and pitted surfaces to enhance bonding. It is generally a requirement to clean rust areas on aged lead coating or other coating surface by power tools prior to overcoating.

Table 12. Description of MC-urethane coating systems without sealers for SP 3 surfaces.

System Code	Coating System	VOL, g/L
A1	MIO[a] & Al[b] filled urethane/MIO-filled urethane/ urethane	315/315/314
B1	Zn[c] & MIO-filled urethane/MIO-filled urethane/ MIO-filled urethane	336/336/336
C1	MIO & Al-filled urethane/MIO & Al-filled Urethane/MIO-filled urethane	340/340/336

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[a] Micaceous iron oxide.
[b] Aluminum.
[c] Zinc.

The determination methods of all the chemical properties as well as physical properties, the conditions of the laboratory test, and the outdoor exposure were same as those used for the MC-urethanes with zinc-rich primers described in Part I.

Chemical Properties – The amount of the pigment and binder in the primers, midcoats, and topcoats of set one are presented in table 13. The composition data for the midcoats and the topcoats were already shown in table 6 since these same coating materials were applied for both SP 10 and SP 3 coating systems. Primer A1 contained 26.8 wt% binder, whereas Primer B1 and primer C1 contained lower amounts of binder (15.3 wt% and 19.5 wt%, respectively). It is obvious that much higher concentrations of binder were used in the SP 3 MC-urethane primers than those used in the SP 10 MC-urethane primers. It is essential to use more binder in barrier coatings for protecting SP 3 surfaces than those for SP 10 surfaces that are protected by a sacrificial primer, i.e., zinc dust that provides a cathodic protection.

Table 13. Chemical compositions of MC-urethane primers for SP 3 surfaces.

Fraction	A1	B1	C1
		Weight Percent	
Pigment	53.2[a] (66.5)[b]	68.6 (81.8)	63.4 (76.5)
Binder[c]	26.8 (33.5)	15.3 (18.2)	19.5 (23.5)

[a] wt% of wet paint.
[b] wt % of dry film.
[c] 100% - wt% volatiles – wt% pigment.

The MC-urethane coating materials were formulated for SP 3 surfaces to obtain excellent barrier properties that essentially mitigate the access of moisture, oxygen, and soluble electrolytes to steel. In principle, the coating layer in direct contact with steel substrate plays the most important role in corrosion resistance. Hence, the chemical composition of both the primers and the sealers were examined in more detail. The key anti-corrosive elements in the primer pigments and the sealer pigments identified by SEM/EDS technique are shown in table 14. On the weight basis of dry coating film, Primers A1, B1, and C1 contained 4.5 to 9.2% of Al, and iron varied from 4.2 to 9.3%. Primer B1 contained 3.5% Zn dust but Primer A1 and Primer C1 did not have any Zn at all. All three formulations used fairly equal amounts of Al and Fe with a ratio of 1. In fact, Primer A1 and Primer C1 had the identical amounts of Al, Fe, and Zn. The total amount of anti-corrosive elements in Primer B1 was lower than those in Primer A1 and Primer C1. The SEM/EDS analysis of the pigment revealed many extremely large platey pigment particles in Primer C1 (figure 18); the SEM micrographs of pigments of Primer A1 and Primer B1 are also shown in figure 18 for comparison. Obviously, the pigment particle sizes of Primer A1 and

Primer B1 were much smaller than those of Primer C1. A different primer (Primer C2) was used with sealer system C2, which is discussed later. Primer C2 contained 7.7% Al, 1.1% Fe, and 23.5% Zn. The SEM image of pigment C2 is shown in figure 19; again, large pigment particles were detected. The use of large size pigment appears to be a common formulation approach found both in the SP 3 formulation and in the SP 10 zinc-rich formulation of Product C. During the pigment packing process, large size pigments tend to form coating film with more unfavorable air voids that allow moisture, oxygen, and electrolytes to penetrate. Three sealers in Systems A2, B2, and C2 were found to contain less metal-containing pigments than did the corresponding primers. Sealer A2 contained essentially no pigments. Sealers B2 and C2 contained 18.3, and 1.3% Al, respectively. Sealer B2 contained only 0.4% Fe whereas Sealer C2 contained 10.1% Fe. These chemical analyses clearly showed large chemical variations in the primers and in the sealers. The same midcoats and topcoats were used in both System 1 (without sealer) and System 2 (with sealer) for SSPC-SP 3 steel surfaces; the chemical composition of all the midcoats and topcoats were shown in table 7 in Part I.

Table 14. Major anti-corrosive metal elements in dry paint film.

System		Al	Fe	Zn	Fe_2O_3[a]
		wt % of Dry Film			
Primer					
	A1	9.2	9.2	0	13.2
	B1	4.5	4.2	3.5	6.0
	C1	9.0	9.3	0	13.2
	C2[b]	7.7	1.1	23.5	1.6
Sealer	A2	0	0	0	0
	B2	18.3	0.4	0	0.6
	C2	1.3	10.1	0	14.4

[a] Calculated from the amount of Fe.
[b] This primer was used in sealer system C2.

Physical Properties – The film thickness, hardness (2H), and adhesion strength of the coating systems remained essentially unchanged after the 4,000-h laboratory test. Since the same topcoats were used for both the SP 10 and SP 3 steel surfaces, the hardness change, gloss change, and color change were identical to those reported in Part I. The adhesion strengths of all the coating systems without and with sealer were found to be about 10.5 MPa (1,500 psi) before and after the laboratory tests as shown in figure 20 and figure 21, respectively. For the majority of the coating systems, cohesive failures of either the midcoats or the topcoats were also observed during the pull-off adhesion tests. These failure modes suggest that the adhesion strengths between the MCU primers for SP 3 steel surfaces and the steel as well as between the sealers and the steel were above10.5 MPa.

Coating Failures – The laboratory test results and the outdoor exposure results are presented below.

A. Laboratory Test

No surface failures were visible on any the coated panels after the 4,000-h laboratory test. These results demonstrated the excellent barrier protection for SP 3 steel surfaces by the MC-urethanes. However, all systems developed some degree of rust creepage at the scribe.

Systems without sealer – Each of the three systems (A1, B1, C1) generated almost the same amount of creepage on either the SP 3 surfaces (figure 22) or the chloride-doped SP 3 surfaces (figure 23) after the 4,000-h laboratory test. Their coating conditions for A1, B1, and C1 are shown in figures 24, 25, and 26 for the SP 3 and chloride-doped SP 3 coating pairs, respectively. The less severe chloride effect on the coating performance than that of the MC-urethanes on SSPC-SP 10 surfaces may be due to the better adhesion between the primers and steel substrate; the higher amount of binders and sufficient amount of pigments in the SP 3 primers would enhance adhesion strength. Apparently, these systems over SP 3 surfaces are less sensitive to chloride contamination than Zn-rich systems over SP 10 surfaces. The undercutting resistance of System A1 and System B1 were found to be slightly higher than that of System C1. Both System A1 and System B1 developed 2-mm creepage, whereas System C1 developed 4-mm creepage at the scribe. Furthermore, a shorter incubation time was observed for System C1, indicating earlier failure at the scribe. The poor performance of Primer C1 again may be attributed to the use of extremely large pigment particles causing porous coating film. The overall failure results are summarized in table 15 and a performance comparison of SP 3 and chloride-doped SP 3 MC-urethanes can be observed clearly in figure 27a.

Systems with sealer – All three systems with sealers, A2, B2 and C2, developed significantly more rust creepage than their non-sealer counterparts. All three systems (A2, B2, C2) applied over the SP 3 surfaces and over the chloride-doped SP 3 surfaces developed as much as 4-mm to 6-mm creepage at the scribe after the 4,000-h laboratory test (figures 28 and 29). The coating conditions for Systems A2, B2, and C2 are shown in figures 30, 31, and 32, respectively. The overall failure results are shown in table 16 and the performance comparison of SP 3 and chloride-doped SP 3 MC-urethanes is shown in figure 27b. The addition of a sealer was unexpectedly found to impair the coating performance on the SP 3 surfaces at defects such as cuts, pinholes, and mechanical damages, etc. It is interesting that the creepage difference among the three sealer-containing products appeared to be minimal. The poor performance of the sealer systems is believed to be caused by the low PVC/CPVC ratio and their low amount of pigments.[20] Certain pigments, particularly plate-like or flake-like pigment, can increase adhesion over that of binder alone. It should be emphasized here that these results do not apply to the application of sealers over aged lead bridge coating surfaces.

Table 15. Failure results of MC-urethane systems without sealers over SP 3 and chloride-doped SP 3 surfaces after 4,000-h laboratory test.

System	Blistering at Scribe[a]	Creepage, mm
A1	6M	2.2
A1 (Cl$^-$)[b]	6M	2.0
B1	6MD	2.4
B1 (Cl$^-$)	4MD	2.6
C1	4D	4.2
C1 (Cl$^-$)	4D	4.4

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[a] ASTM D714 where M = medium, MD = medium dense, D = dense.

[b] Chloride-doped surface.

Table 16. Failure results of MC-urethane systems with sealers over SP 3 and chloride-doped SP 3 surfaces after 4,000-h laboratory test.

System	Blistering at Scribe[a]	Creepage, mm
A2	6M	4.5
A2 (Cl$^-$)[b]	6MD	6.0
B2	4M	4.5
B2 (Cl$^-$)	4MD	6.2
C2	4MD	5.6
C2 (Cl$^-$)	4MD	6.3

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[a] ASTM D714 where M = medium, MD = medium dense.

[b] Chloride-doped surface.

One additional coating system from manufacturer C was also investigated. It was a sealer/primer/topcoat system without a midcoat (System C3), the film thicknesses were 25 µm (1 mil), 75 µm (3 mil), and 75 µm (3 mil), respectively. In other words, System C3 was System C2 without the midcoat. The total film thickness of the whole coating system was 175 µm

(7 mil) instead of 250 µm (10 mil) for all the four-coat systems. This system has been recommended by some manufacturers for overcoating. Unfortunately, System C3 exhibited 100% surface failure with size 8 blisters, and severe underfilm corrosion was observed after the pull-off adhesion test as shown vividly in figure 33a after the 4,000-h laboratory test. This failure mode was not developed by either the sealer/primer/midcoat/topcoat systems with a total thickness of 250 µm or the primer/midcoat/topcoat systems with a total thickness of 225 µm; the formation of underfilm corrosion for System C3 was likely due to its insufficient film thickness. A similar phenomenon was found for System C3 over the chloride-doped SP 3 steel surface (figure 33b). It appears that the total thickness of MC-urethane system is very critical to its performance and it should not be much less than 225 µm. The rust creepages developed at scribes plotted against test time for System C3 over both SP 3 and chloride-doped SP 3 surfaces are shown in figure 34. Two lines almost superimposed each other with the same slope but different incubation time; therefore, the extent of the creepage developed at the scribe was not affected much by the chloride contamination in this case. Furthermore, System C3 generated a slightly higher amount of scribe creepage than did System C2 (figure 35); both systems used the same sealer as the first coat. These failure results agree with the theory that the coating directly adjacent to steel controls the degree of rust creepage at the scribe.

B. Outdoor Exposure

After 2 years of outdoor marine exposure, the three systems behaved similarly to the laboratory tests, i.e., they all developed a significant amount of scribe creepage without any surface failures.

Systems without sealer – All three systems, A1, B1, and C1, developed about 3-mm scribe creepage after 2-yr outdoor marine exposure (Figure 36a) over clean SP 3 surfaces; the coating conditions for the SP 3 and chloride-doped SP 3 MC-urethanes are shown in figures 37, 38, and 39. When the steel surface was contaminated with 20 $\mu g/cm^2$ chloride, the amount of creepage that developed for these three systems is shown in figure 36b. The overall failure results are shown in table 17, and the performance comparison of the SP 3 and chloride-doped SP 3 pairs is illustrated in figure 40a. The performance of System B1 was not affected by the chloride contamination, whereas System A1 and System C1 generated much larger creepage (~ 6 mm) on the chloride-doped surface. These results did not exactly agree with the laboratory test in which System A1 and System B1 provided the same degree of performance. The observed difference is again probably caused by different environmental conditions for laboratory tests and field exposures in which salt content is higher (~ 2.7 wt%) in the natural seawater used for spraying panels daily at the exposure site. The contribution of a high amount of rainfall, extensive time of wetness, and high salt concentration at this exposure site to the formation of scribe creepage was also noted in a FHWA contract study.[10]

Systems with sealer – When a sealer was painted over SP3 surfaces prior to primer application, a higher amount of scribe creepage developed, especially for System A2 (figure 41b) as compared with systems without sealers. The sealer effect was the least on System B2. The coating conditions for the SP 3 and chloride-doped SP 3 MC-urethanes after the exposure are shown in figures 42, 43, and 44. As mentioned previously, A2 sealer contained no pigment. Zero or low amount of pigment in the sealers, i.e., low PVC/CPVC, will suppress their corrosion resistance at the scribe. All of the systems with sealer performed worse than those without sealer. Basically, the rust creepage at any scratch is a measure of adhesion between steel and the coating directly in contact with the steel. The bonding of the coating to steel is partly mechanical interlocking to steel with an anchor pattern but the remainder has to do with compatibility and the ability of the coating to form chemical bonds with steel. Inorganic pigments are more compatible with steel in nature, and their polarity will help coating to bond to steel more strongly. Therefore, coatings with a proper amount of pigments will adhere to steel better than those with little pigments. Therefore, sealers containing extremely low amount of pigments caused more scribe creepages due to lower adhesion to steel, because oxygen, moisture, and electrolytes had more access to the steel-sealer interface.[20] The high concentration of pigments in the primers may have reduced the oxygen diffusion rate, similar to research results that the pigmented film of maleinized oil resin showed less failure than clear resin in the cathodic test.[18] Furthermore, it has been proved that coating film with either very low PVC or very high PVC decreases cohesive strength (tensile strength). This finding also explains the above phenomenon.[21]

Table 17. Failure results of MC-urethane systems without sealers over SP 3 and chloride-doped SP 3 surfaces after 2-yr outdoor exposure.

System	Blistering at Scribe[a]	Creepage, mm
A1	6F	3.3
A1 (Cl^-)[b]	6D	5.9
B1	6F	2.9
B1 (Cl^-)	6F	2.8
C1	4VF	3.3
C1 (Cl^-)	4F	5.5

[a] ASTM D714 where F = few, D = dense, VF = very few.
[b] Chloride-doped surface.

When the SP 3 surface is contaminated with chloride, the performance of System C2 was not affected as much as other two systems over SP 3 surfaces as illustrated in figures 41a and 41b. The relatively good corrosion resistance of Sealer C2 at the scribe to chloride was believed to be provided by the presence of micaceous iron oxide that reduced oxygen and water ingestion. This result suggested that micaceous iron oxide (14.4 wt% Fe_2O_3) in Sealer C2, compared to aluminum (18.3 wt% Al) in Sealer B2, was more effective in reducing ingestion of corrosion-initiating substances, and in preventing undercutting of the primer. The better corrosion resistance of MIO was expected because MIO is less susceptible to acid and alkali attacks than aluminum,[20] since the solution used in the Prohesion chamber had a pH of 5.0. The overall failure results are presented in table 18, and the performance comparison for the SP 3 and chloride-doped pairs appear in figure 40.

Table 18. Failure results of MC-urethane systems with sealers over SP 3 and chloride-doped SP 3 surfaces after 2-yr outdoor exposure.

System	Blistering at Scribe[a]	Creepage, mm
A2	2VD	13.2
A2 (Cl^-)[b]	2VD	15.6
B2	4MD	5.3
B2 (Cl^-)	2VD	10.2
C2	4MD	6.7
C2 (Cl^-)	2D	6.6

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[a] ASTM D714 where VD = very dense, MD = medium dense, D = dense.

[b] Chloride-doped surface.

After 2-yr outdoor exposure, the coating conditions of System C3 over SP 3 surfaces and chloride-doped SP 3 surfaces are shown in figure 45. Blisters of size 8 also developed all over the surfaces (100%) and underfilm corrosion was observed. The scribe creepage that developed for System C3 over SP 3 and chloride-doped SP 3 surfaces after 2-y outdoor exposure is compared in figure 46; the resulting creepage showed little effect from chloride.

C. Comparison between Laboratory Test and Outdoor Exposure

After 2 years of the outdoor marine exposure, the three SP 3 MC-urethane systems behaved similarly to the laboratory tests, i.e., they all developed a significant amount of scribe creepage without any surface failures. The SP 3 MC-urethane systems with sealer performed worse than those without sealer in both the laboratory test and the outdoor exposure, as shown in figures 47 and 48, respectively. Therefore, the performance trend was the same in these two tests at least for the SP 3 MC-urethanes. However, no comparison can be made for SP 10 MC-urethanes because no failures have occurred even after 2 years of outdoor exposure.

SUMMARY AND CONCLUSIONS

- The MC-urethane coating systems formulated for both SSPC-SP 10 and SSPC-SP 3 steel surfaces exhibited strong mechanical properties, including topcoat hardness and adhesion strength of the whole coating systems. The chemical composition of the three manufacturers' products varied in amount of both isocyanates and pigments, isocyanate type (aromaticity), and pigment composition – demonstrating variations in their formulations.

- In general, no surface failures were observed on all the three-coat systems for SSPC-SP 10 surfaces and the three-coat and the sealer plus three-coat systems for SSPC-SP 3 surfaces after the 4,000-h cyclic laboratory test. This phenomenon illustrates that these MC-urethane systems are excellent barrier coatings for steel. However, all the MC-urethane products applied over SSPC-SP 10 and SSPC-SP 3 steel surfaces developed different degrees of creepage at an intentional scribe after the test. The systems applied over the 20-$\mu g/cm^2$ chloride-doped SSPC-SP 10 steel surfaces developed larger creepages at the scribe than the systems over the chloride-free steel surfaces. However, the chloride effect was not found to be significant for the coating systems applied over SSPC-SP 3 steel surfaces.

- It is interesting to see that all the creepages at the scribe grew linearly with the test time, indicating a pseudo zero-order reaction in the complicated process of rust formation at the scribe. For every primer, there is a constant rate for rust creepage formation within the test period. Using the test method and the data plot technique used in this study, it is very easy to differentiate the performance of each primer at the scribe from the slope of the plotted line. The incubation time measures corrosion resistance of primer, and the slope distinguishes generic primer type and steel surface conditions. Due to this linearity, it is not necessary to conduct a long test; a test time of 2,000 to 3,000 hours should be long enough for coating evaluation.

- The observed small amount of failure at the scribe suggests that the zinc-rich MC-urethane systems used in this study are excellent anti-corrosive coatings but do not provide as high a degree of cathodic protection to steel as do inorganic zinc silicate systems.

- No scribe failures have been observed for zinc-rich MC-urethane systems applied over SSPC-SP 10 surfaces after a 2-yr outdoor marine exposure; therefore, no correlation between laboratory test and outdoor exposure can be made at this time. The difference in the performance of zinc-rich MC-urethanes must be caused by different weathering variables in these two test environments.

- The accelerated test results in conjunction with chemical analysis results suggested that zinc particle size distribution in the zinc-rich primers played a more important role in primer performance on SSPC-SP 10 surfaces than did the amount of zinc. Too much large pigment particles reduced the coating performance of the MC-urethanes over both SSPC-SP 10 and SSPC-SP 3 steel surfaces. It seems critical to have a proper size gradation for pigment particles with a sufficient amount of high-grade small particles in order to achieve good coating performance. A minimum amount of small particles should be included in the formulation and is recommended as a key element in the coating specifications.

- The coating performance of the MC-urethane coating systems on steel was also believed to be affected by different chemical compositions. These variables included the ratio of the aromatic content to the aliphatic content of MC-urethanes, the ratio of the pigment content to the binder content, and the elemental content of the pigment and other factors. As a result, material testing and product quality control practices are necessary prior to material delivery acceptance and coating applications.

- The total film thickness of the MC-urethanes stayed constant throughout the test time. The high-gloss topcoat decreased its gloss rapidly with test time but flat topcoats maintained their gloss almost the same after the test; the high-gloss topcoats, however, retained some luster over the flat formulations.

- This study showed that the addition of a sealer did not produce visual changes in the surface performance of MC-urethane systems applied over SSPC-SP 3 steel surfaces within the test periods conducted in this study. Whether the extra layer of a sealer can improve the surface performance in the long term cannot be concluded at this time. Nevertheless, the test results showed that a sealer addition surprisingly reduced the performance of the MC-urethane coating systems at the scribe instead of improving the performance. The failure results seen in this study suggest that the use of a sealer prior to primer application at areas prone to damage is not recommended for protecting power tool-cleaned steel surfaces, mainly because sealer not only increases material cost but also impairs the coating performance of MC-urethanes at the scribe. Furthermore, the coating systems with sealer, primer, and topcoat are not recommended for coating repair over SSPC-SP 3 steel surfaces because of the development of severe underfilm corrosion after the test; insufficient total film thickness without a midcoat may be the key cause for the corrosion mode. It should be noted here that the benefit of using a sealer as the first coat for overcoating lead-based alkyd paint cannot be predicted from the test results obtained in this study.

- The MC-urethanes with sealer developed larger scribe creepage than did those without sealer over SSPC-SP 3 surfaces; the same performance trend was observed for the 4,000-h laboratory test and the 2-yr outdoor marine exposure.

REFERENCES

1. S. Fannin, "Specification of Coatings Containing Micaceous Iron Oxide Pigments," *JPCL*, Vol. 16, No. 7, p. 22, July 1999.

2. J. Schwindt, "Moisture-Cured, Polyurethane-Based, Surface Tolerant Coatings: An Economical Alternative for Corrosion Control," *Material Performance*, p. 25, December 1996.

3. S-L. Chong, M. Jacoby, J. Boone, and H. Lum, *Comparison of Laboratory Testing Methods for Bridge Coatings*, FHWA Publication No. FHWA-RD-94-112, 67 pp., June 1995.

4. C. H. Simpson, C. J. Ray, and B. S. Skerry, "Accelerated Corrosion Testing of Industrial maintenance Paints Using a Cyclic Corrosion Weathering Method," *JPCL*, Vol. 8, No. 5, p. 28, May 1991.

5. S. K. Boocock, "A Report on SSPC Programs to Research Performance Evaluation Methods," *JPCL*, Vol. 11, No. 10, p. 51, October 1994.

6. S-L. Chong, "A Comparison of Accelerated Tests for Steel Bridge Coatings in Marine Environment," *JPCL*, Vol. 14, No. 3, p. 20, March 1997.

7. G. Gardner "ASTM's New Coating Test Method Addresses Interactive Effects of Weathering and Corrosion," *JPCL*, Vol. 15, No. 9, p. 60, September 1998.

8. B. Appleman, S. Boocock, R. Weaver, and G. Soltz, *Effect of Surface Contaminants on Coating Life*, FHWA Publication No. FHWA-RD-91-011, 242 pp., November 1991.

9. Y. Yao, S-L Chong, and N. Shashidhar, "Using Imaging Analysis Technique to Measure Rust Creepage at Scribe of Coated Panels after Exposures," Presented at the *1999 WPTG Meeting*, Washington, DC, April 13-14, 1999.

10. J. Ault, J, Ellor, J. Repp, and B. Shaw, *Characterization of the Environment*, FHWA Publication No. FHWA-RD-00-30, August 2000.

11. C. Hare, "Zinc-rich Primers I: Design Principles," *JPCL*, Vol. 15, No. 7, p.17, July 1998.

12. S-L. Chong and J. Peart, *Evaluation of Volatile Organic Compound (VOC)-Compatible High Solids Coating Systems for Steel Bridges*, FHWA Publication No. FHWA-RD-91-054, 34 pp., August 1991.

13. Personal communication with Mr. Douglas Eakins, Oregon State bridge engineer, June 1997.

14. R. B. McGennis, R. M. Anderson, T. W. Kennedy, and M. Solaimanian, *Background of Superpave Asphalt Mixture Design and Analysis*, FHWA Publication No. FHWA-SA-95-003, 160 pp., February 1995.

15. AASHTO Designation MP-2-00 Standard Specification for Superpave Volumetric Mix Design, *AASHTO Provisional Standards*, April 2000.

16. B. W. Ludwig and M. W. Urban, "A Quantitative Determination of Isocyanate Concentration in Crosslinked Polyurethane Coatings, *J. of Coating Technology*, Vol. 68, No. 857, p. 93, June 1996.

17. W. Brockman, "Durability of Metal Polymer Bonds" in *Adhesion Aspects of Polymeric Coatings* edited by K. L. Mittal, Proceedings of the Symposium on Adhesion Aspects of Polymeric Coatings, Minneapolis, Minnesota, May 10-15, 1981.

18. A. Smith and R. Dickie, "Adhesion Failure Mechanism of Primers," *Ind. Eng. Chem. Prod. Res. Dev.*, Vol. 17, No. 1, p. 42, 1978.

19. C. Hare, *Protective Coatings - Fundamentals of Chemistry and Composition*, SSPC 94-17, 514 pp., 1994.

20. C. G. Munger, *Corrosion Prevention by Protective Coatings*, NACE Publication, 512 pp., 1986.

21. T. C. Patton, *Paint Flow and Pigment Dispersion: a rheological approach to coating and ink technology*, 2nd edition, Wiley-Interscience, New York, 656 pp., 1979.

Figure 1. SEM micrograph of natural micaceous iron oxide.

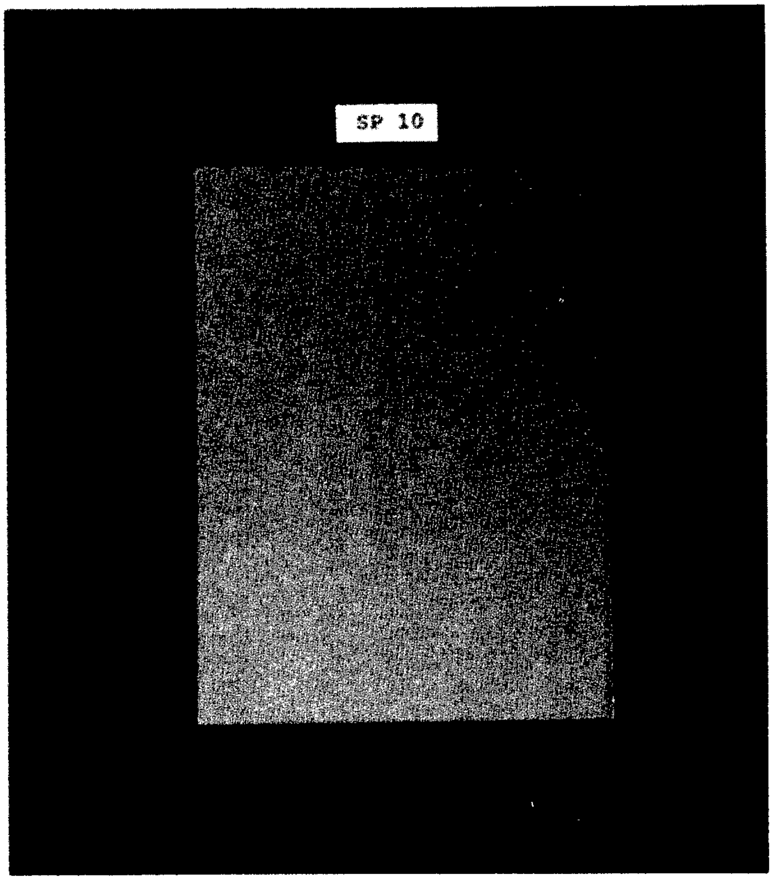


Figure 2. SSPC-SP 10 steel surface.

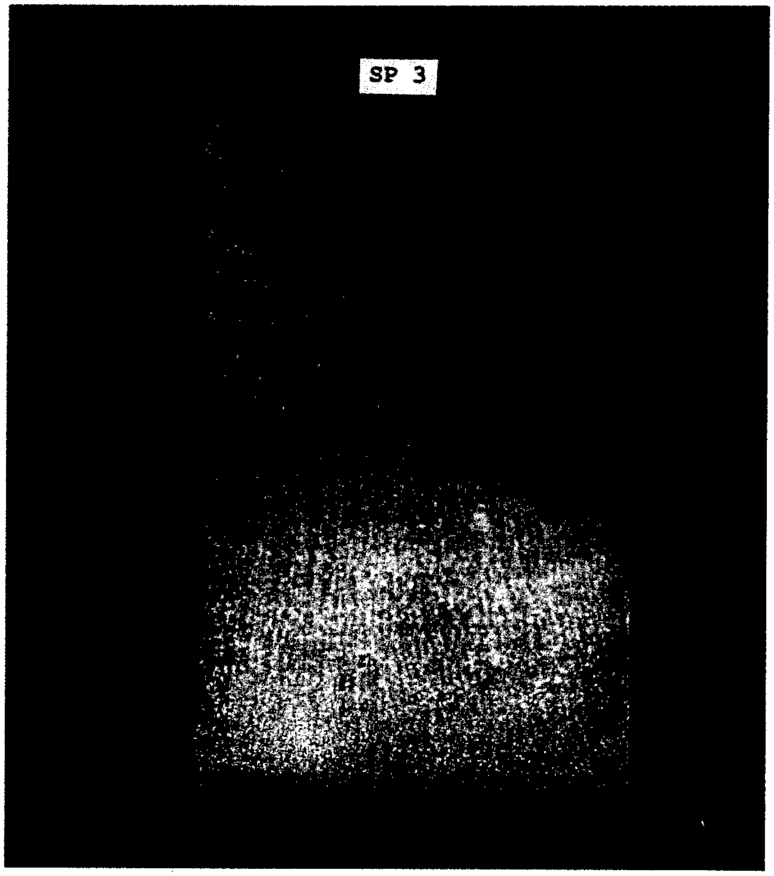


Figure 3. SSPC-SP 3 steel surface.

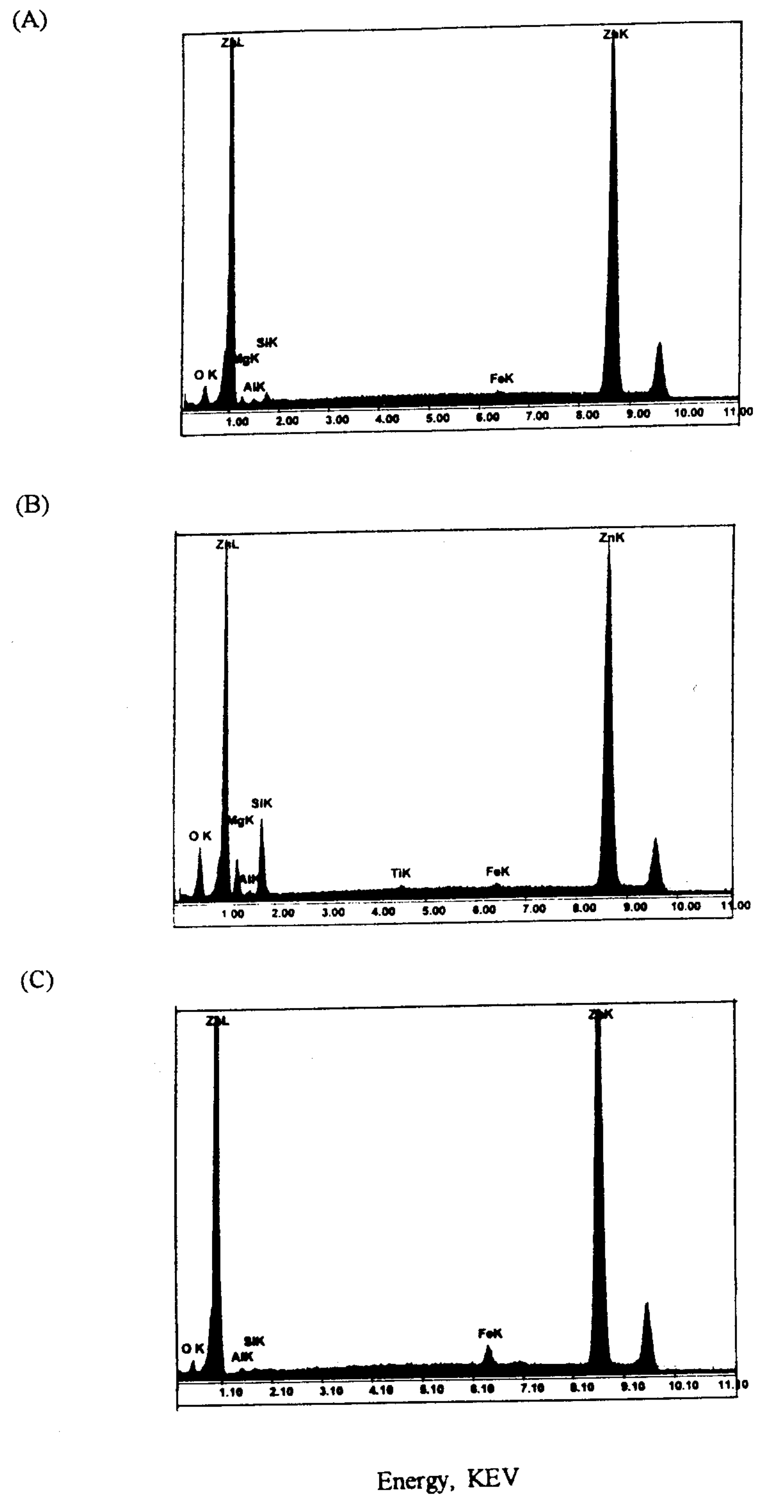


Figure 4. Energy dispersive X-ray analysis of pigment for Systems A, B, and C.

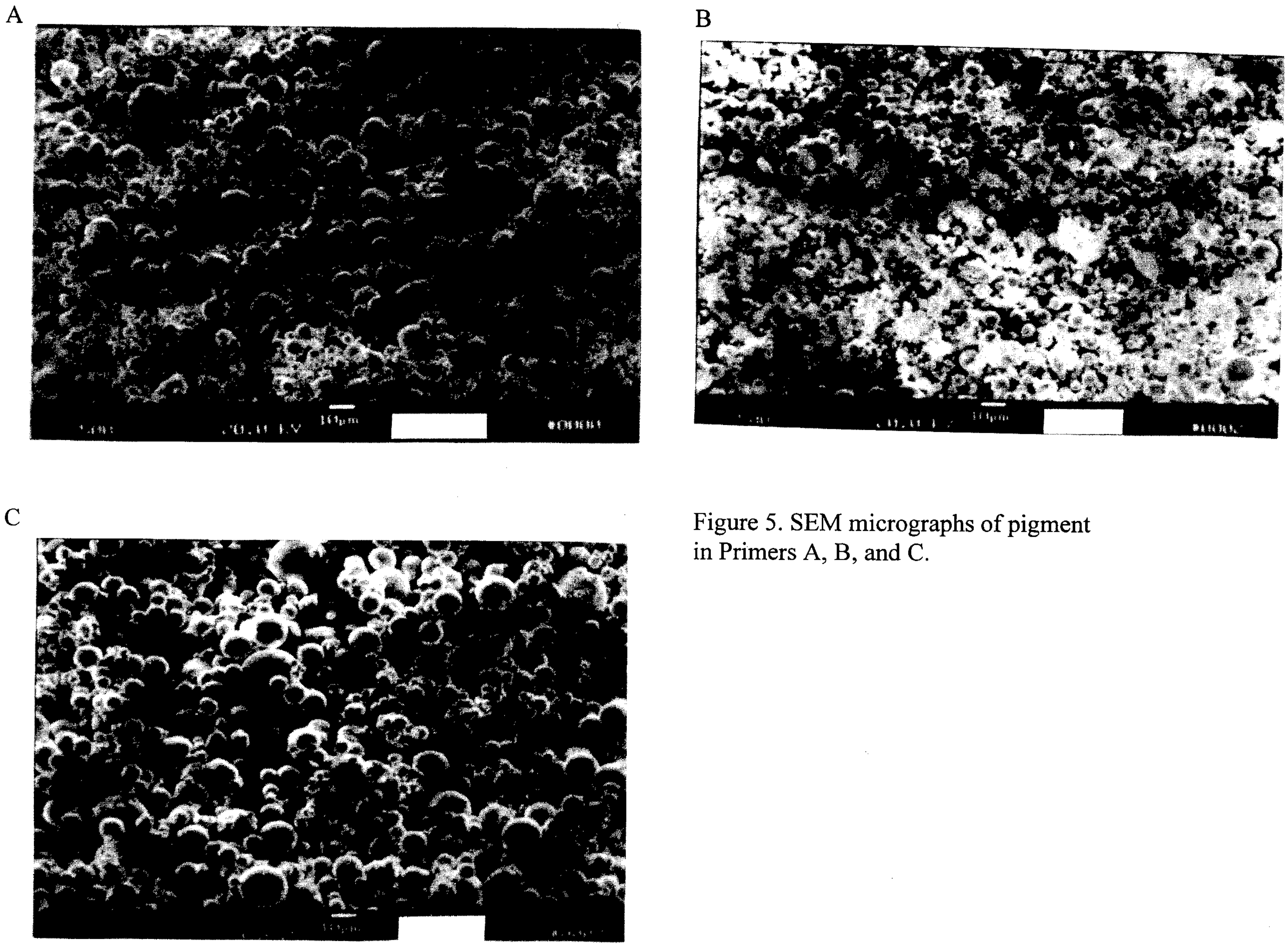


Figure 5. SEM micrographs of pigment in Primers A, B, and C.

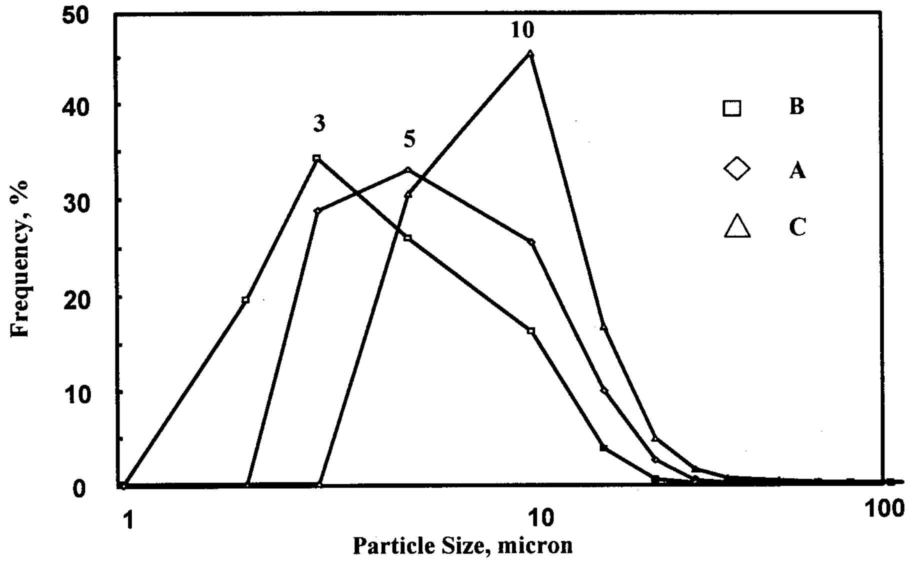


Figure 6. Particle size distribution of pigment in Primers A, B, and C.

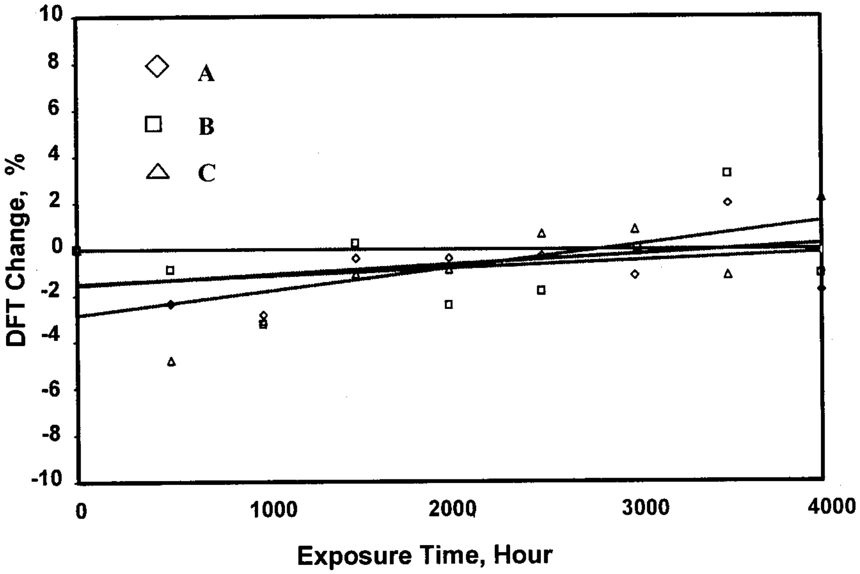


Figure 7. Plot of total dry film thickness of Systems A, B, and C versus laboratory test time.

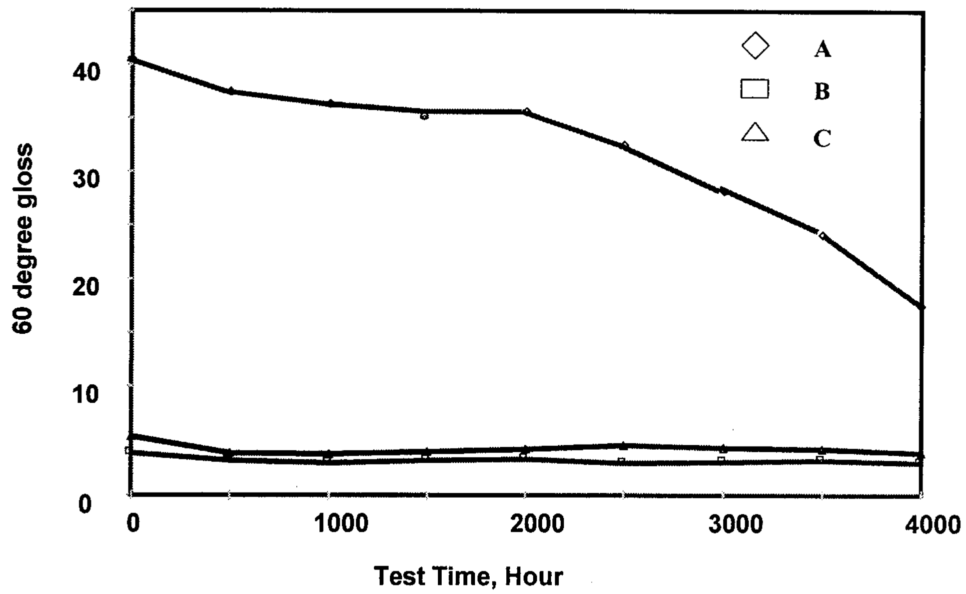


Figure 8. Plot of topcoat gloss of Systems A, B, and C versus laboratory test time.

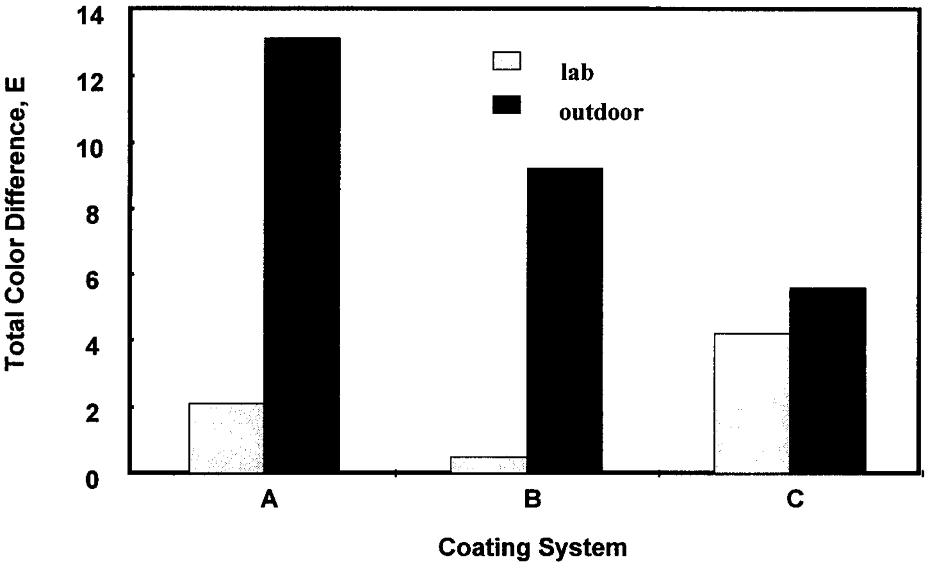


Figure 9. Color difference of topcoat of Systems A, B, and C.
after 4,000-h laboratory test and 2-yr outdoor exposure.

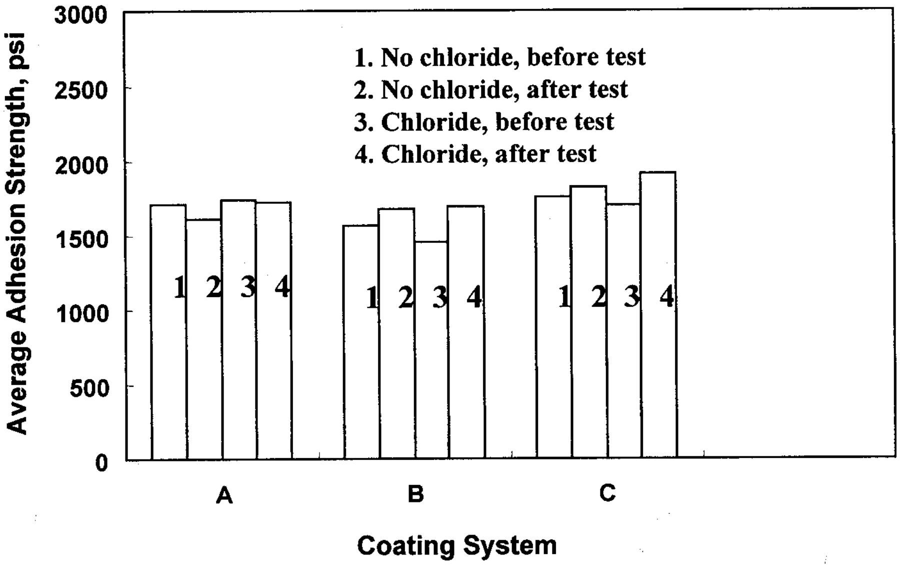


Figure 10. Adhesion strength of MC-urethanes over SP 10 surfaces and chloride-doped SP 10 surfaces before and after 4,000-h laboratory test.

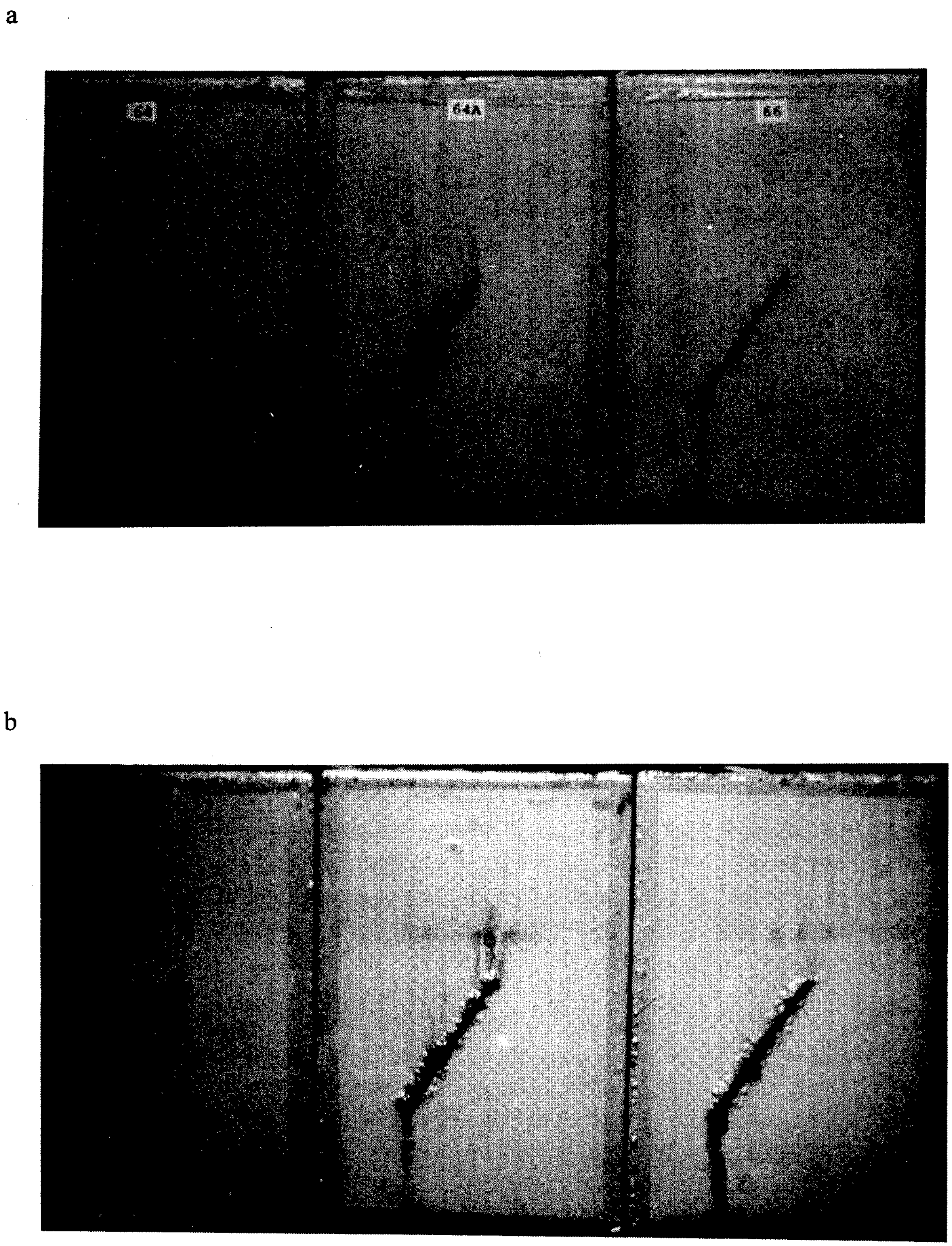


Figure 11. Coating conditions of MC-urethane System A over SP 10 (a) and over chloride-doped SP 10 (b) surfaces after 4,000-h laboratory test.

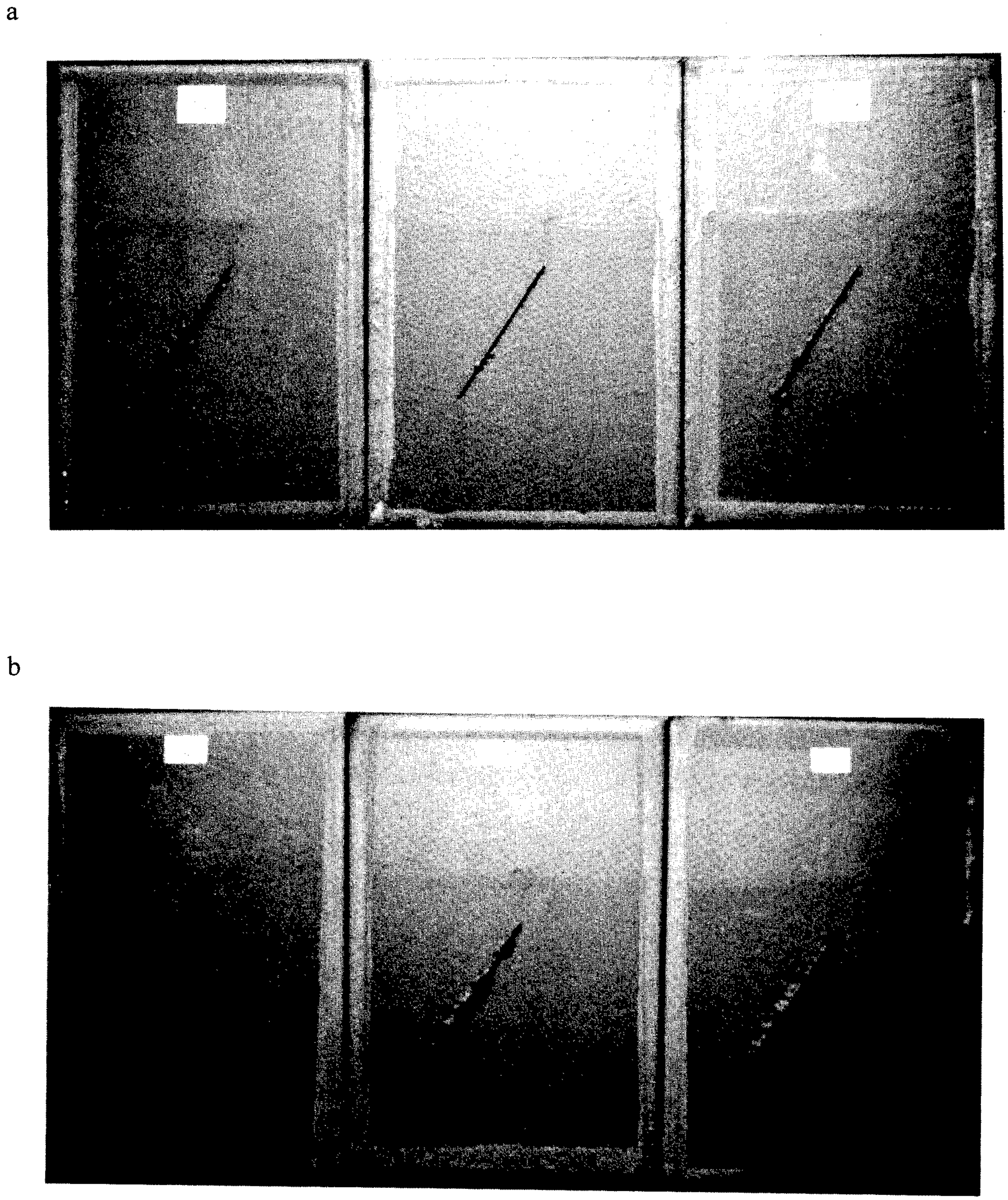


Figure 12. Coating conditions of MC-urethane System B over SP 10 (a) and over chloride-doped SP 10 (b) surfaces after 4,000-h laboratory test.

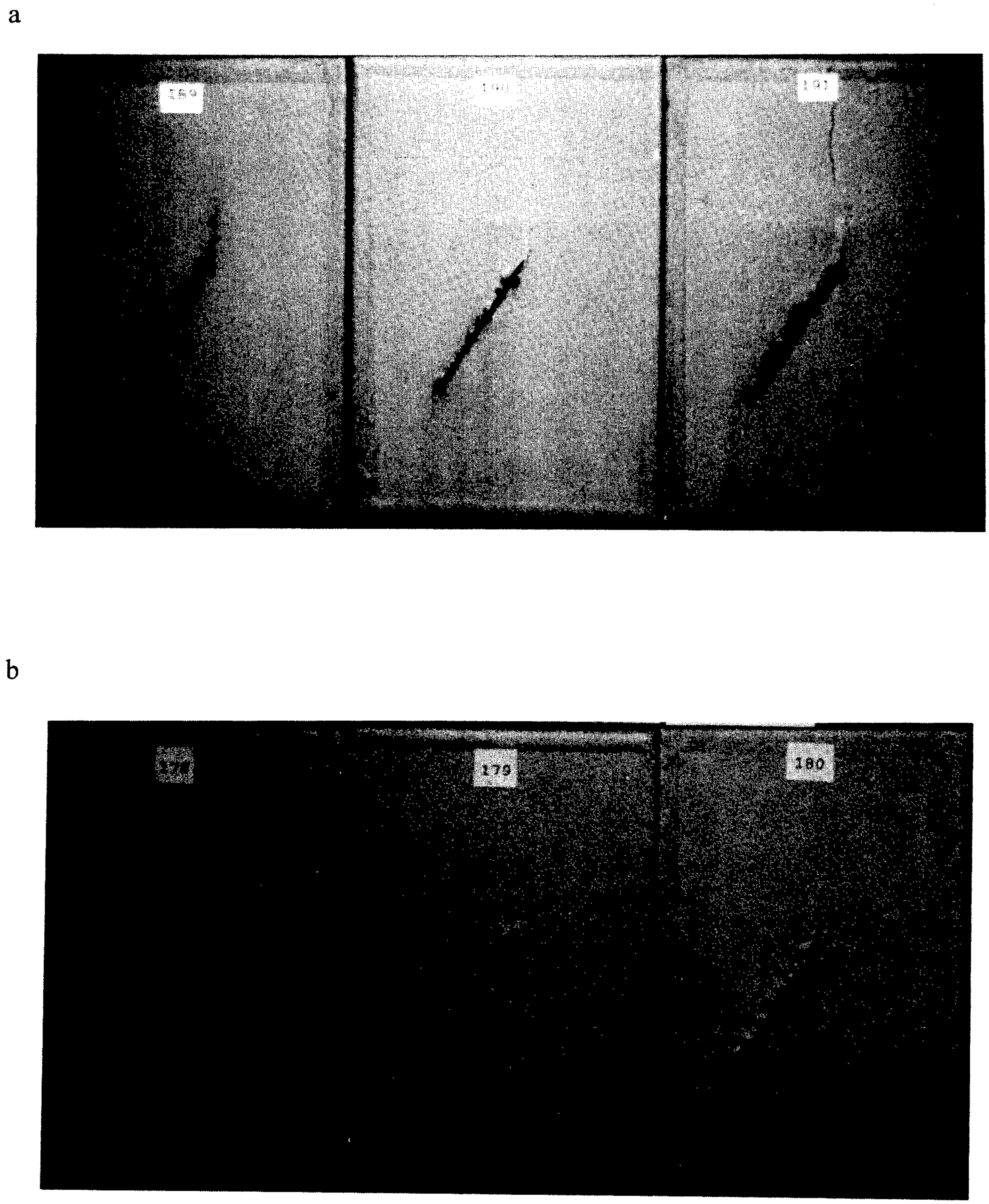


Figure 13. Coating conditions of MC-urethane System C over SP 10 (a) and over chloride-doped SP 10 (b) surfaces after 4,000-h laboratory test.

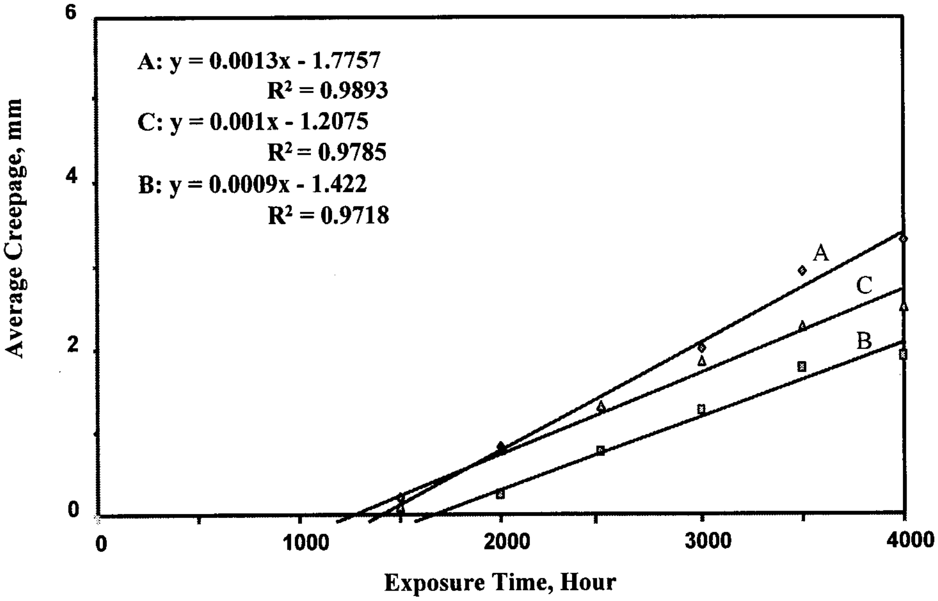


Figure 14. Plot of scribe creepage versus laboratory test time for MC-urethane systems over SP 10 surfaces.

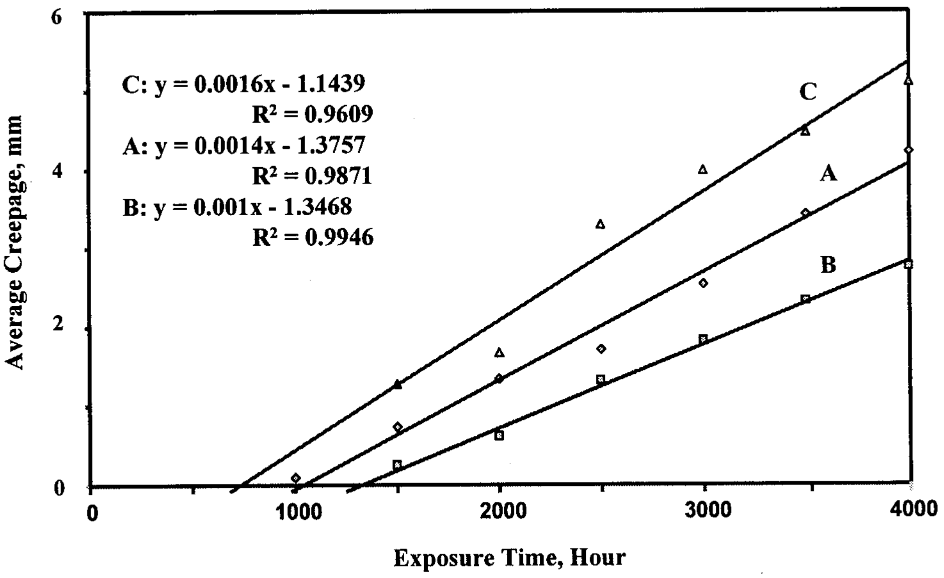


Figure 15. Plot of scribe creepage versus laboratory test time for MC-urethane systems over chloride-doped SP 10 surfaces.

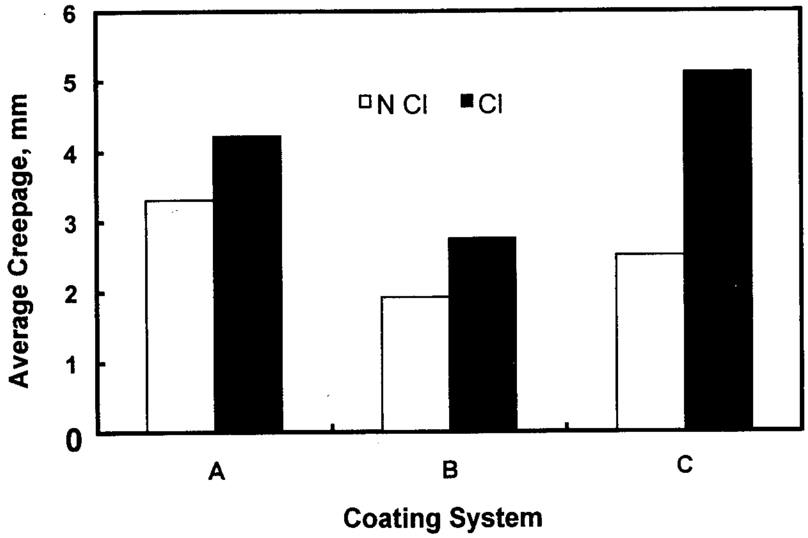


Figure 16. Scribe creepage of MC-urethanes over SP 10 and chloride-doped SP 10 surfaces after 4,000-h laboratory test.

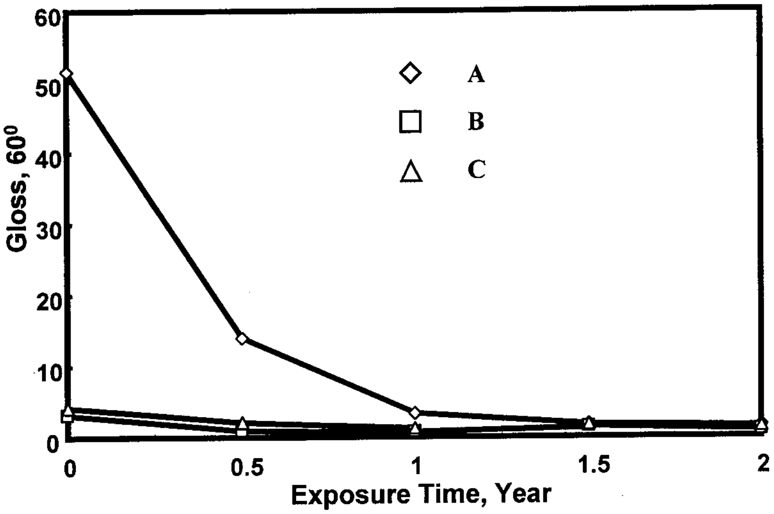


Figure 17. Plot of topcoat gloss of Systems A, B, and C versus outdoor exposure time.

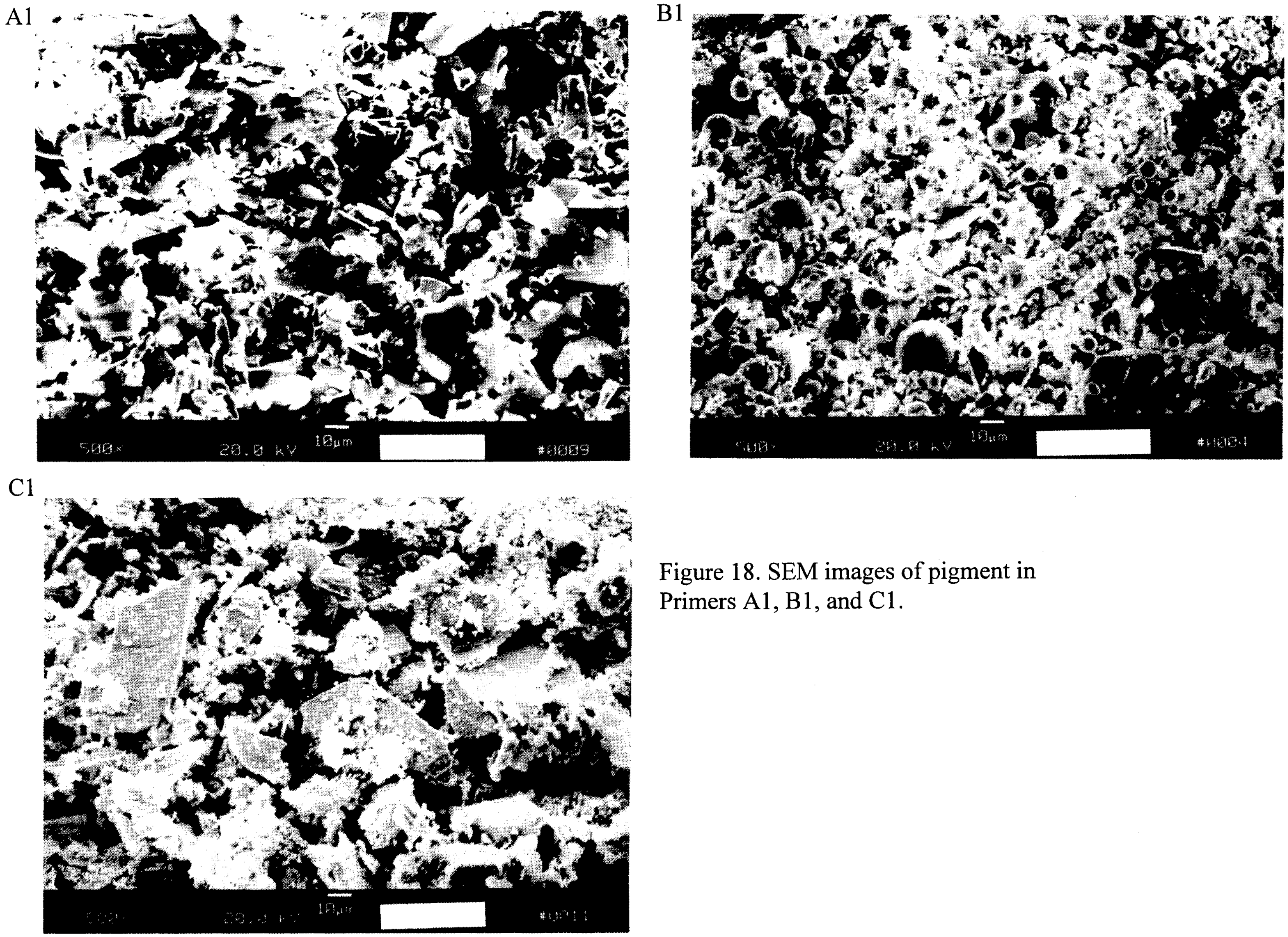


Figure 18. SEM images of pigment in Primers A1, B1, and C1.

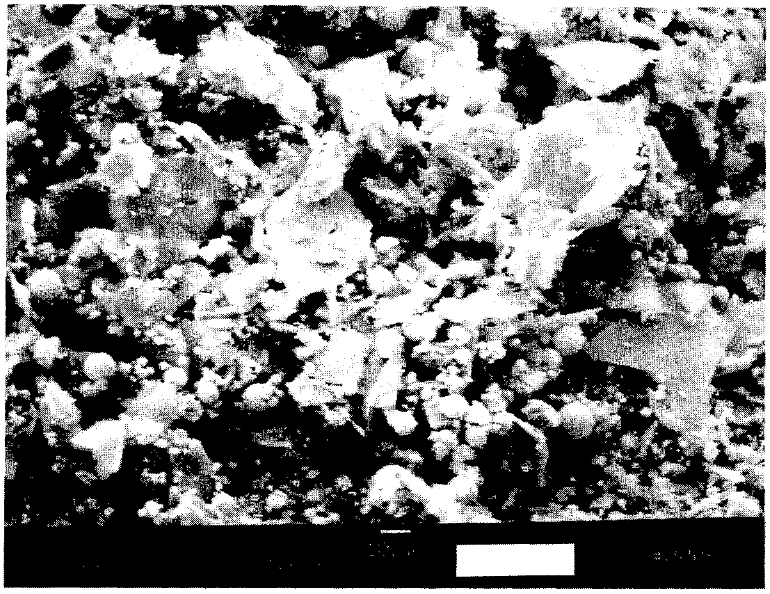


Figure 19. SEM micrograph of pigment in Primer C2.

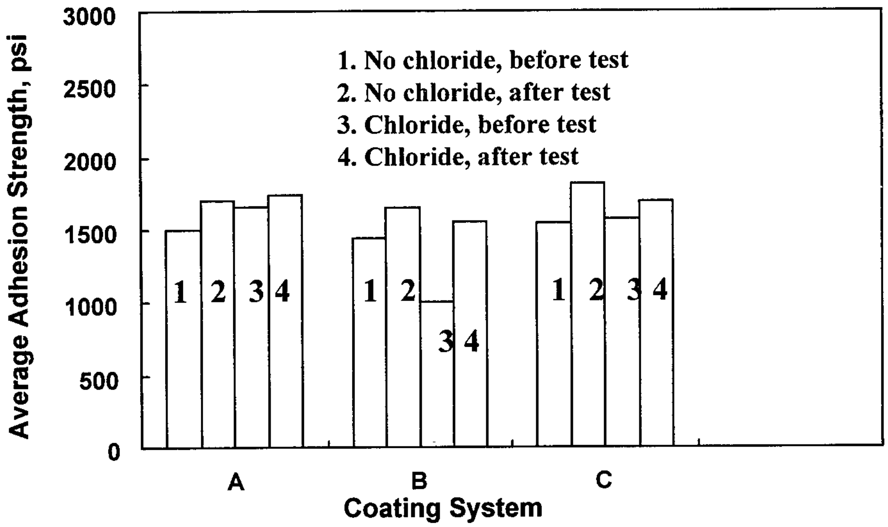


Figure 20. Adhesion strength of MC-urethane systems without sealer over SP 3 surfaces before and after 4,000-h laboratory test.

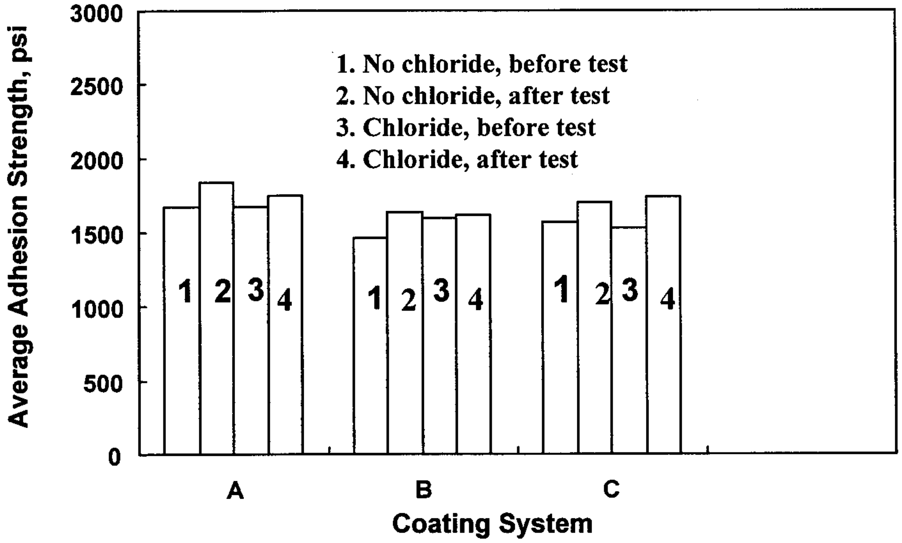


Figure 21. Adhesion strength of MC-urethane systems with sealer over SP 3 surfaces before and after 4,000-h laboratory test.

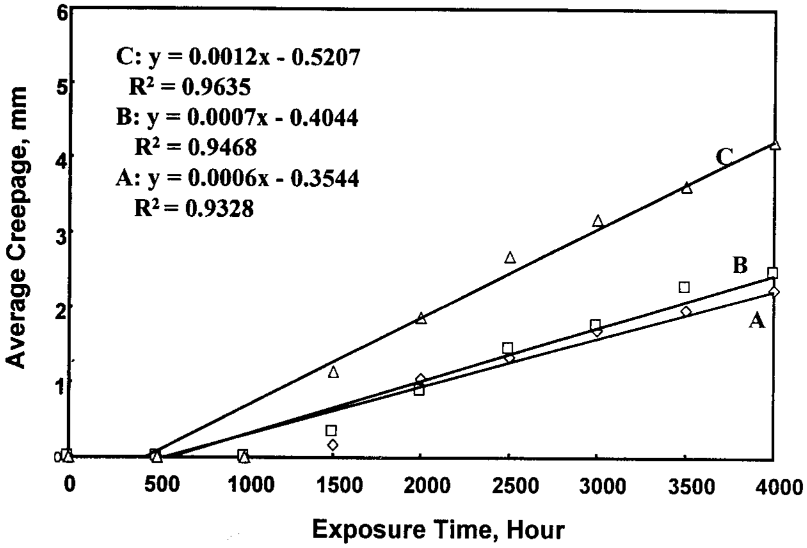


Figure 22. Plot of scribe creepage of MC-urethane Systems A1, B1, and C1 over SP 3 surfaces versus laboratory test time.

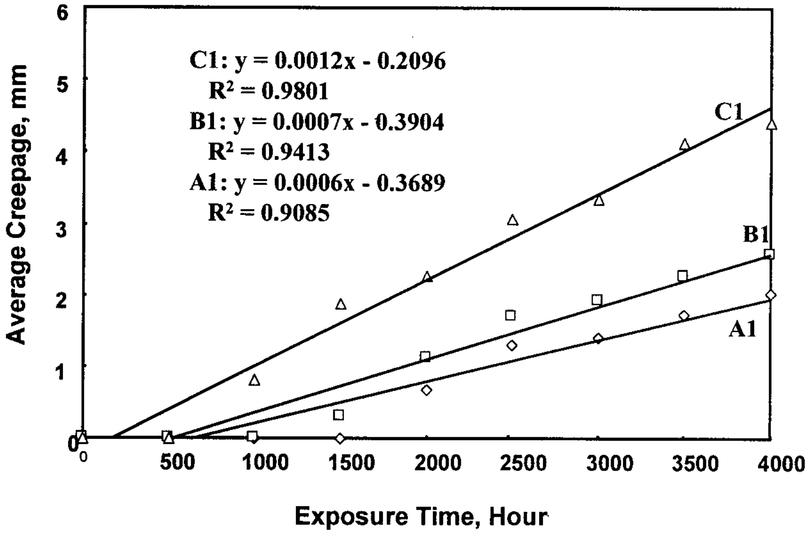


Figure 23. Plot of scribe creepage of MC-urethane Systems A1, B1, and C1 over chloride-doped SP 3 surfaces versus laboratory test time.

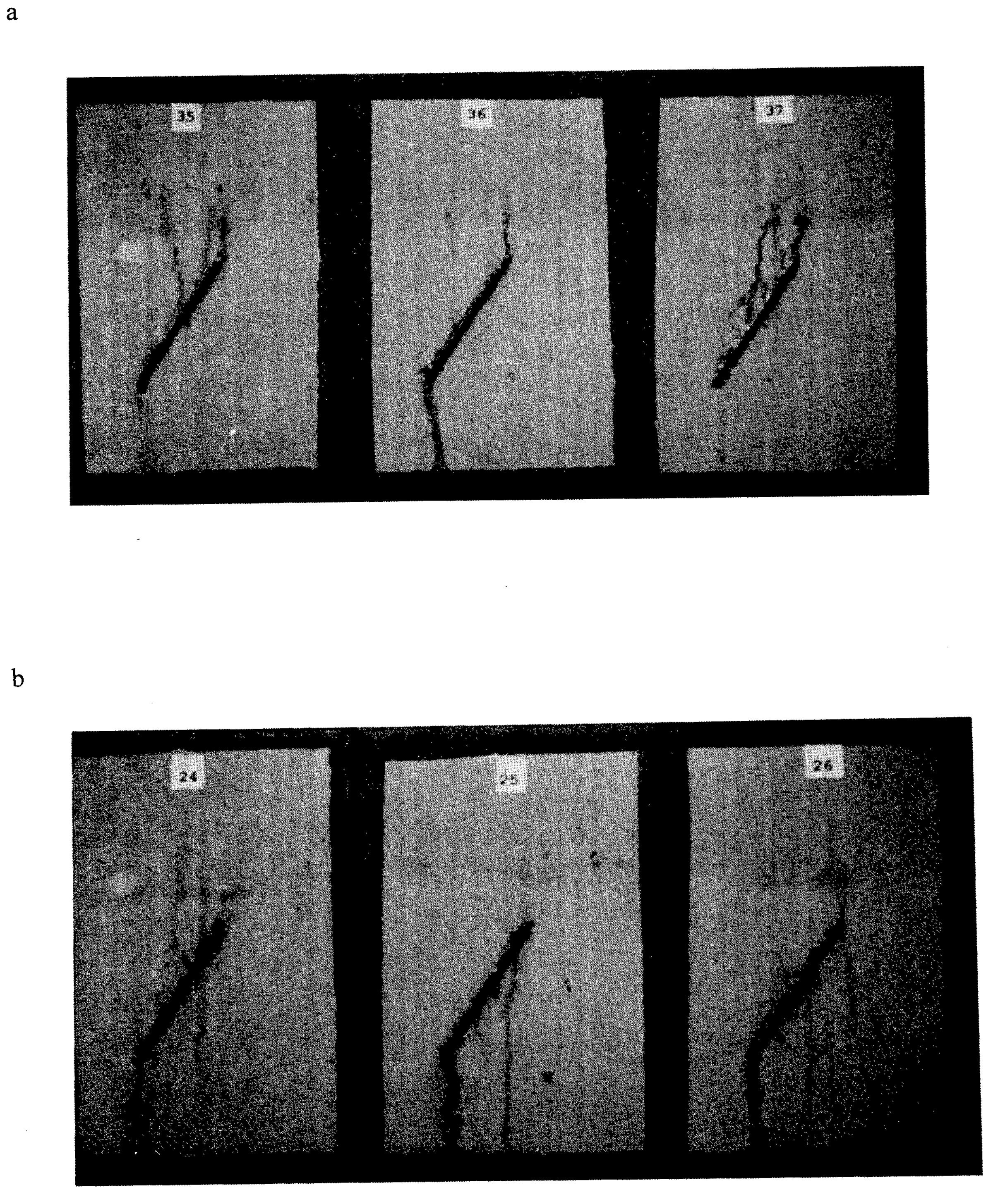


Figure 24. Coating conditions of MC-urethane System A1 over SP 3 (a) and over chloride-doped SP 3 (b) surfaces after 4,000-h laboratory test.

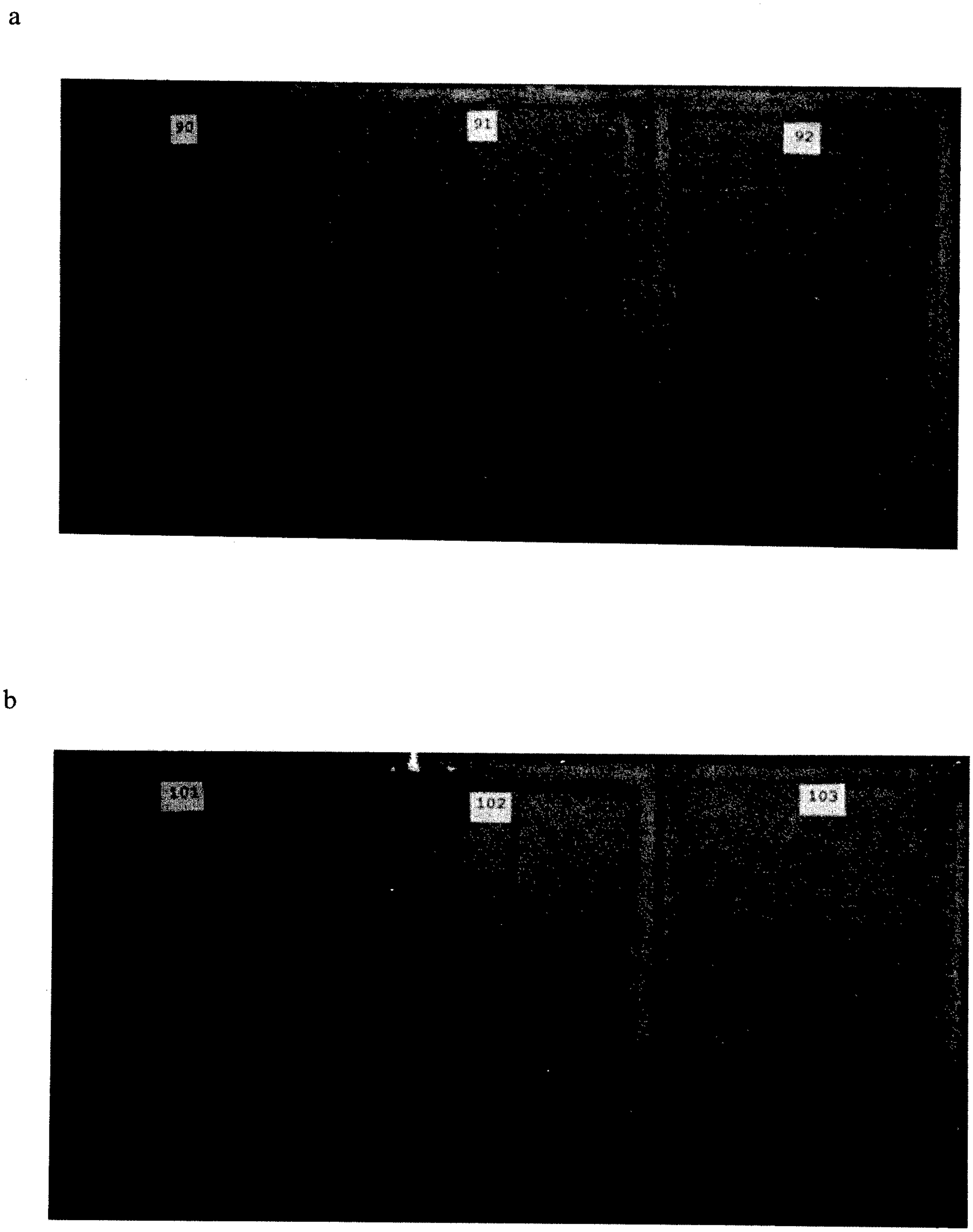


Figure 25. Coating conditions of MC-urethane System B1 over SP 3 (a) and over chloride-doped SP 3 (b) surfaces after 4,000-h laboratory test.

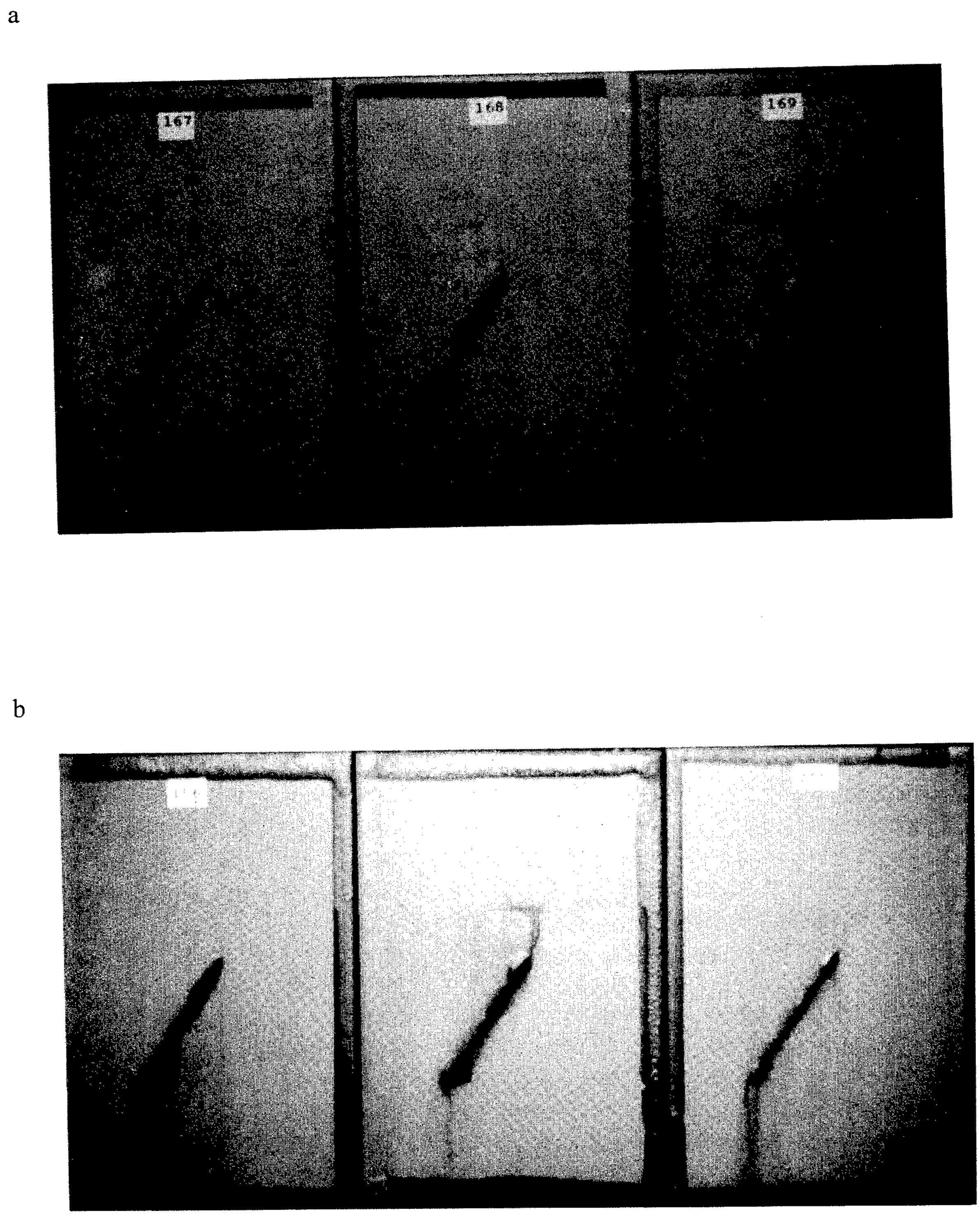
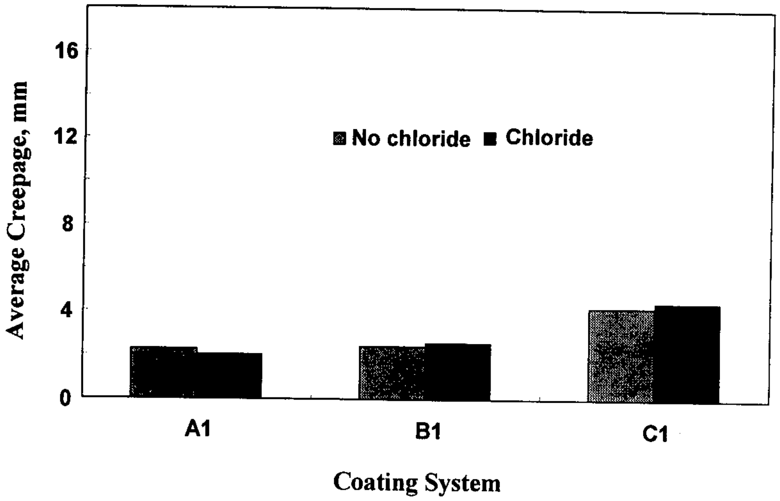


Figure 26. Coating conditions of MC-urethane System C1 over SP 3 (a) and over chloride-doped SP 3 (b) surfaces after 4,000-h laboratory test.

(a) Without sealer



(b) With sealer

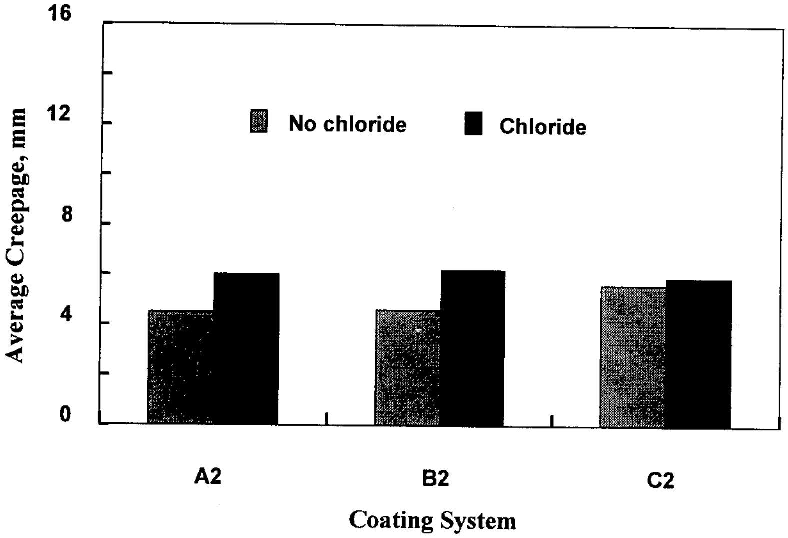


Figure 27. Scribe creepage of MC-urethanes without sealer (a) and with sealer (b) over SP 3 and chloride-doped SP 3 surfaces after 4,000-h laboratory test.

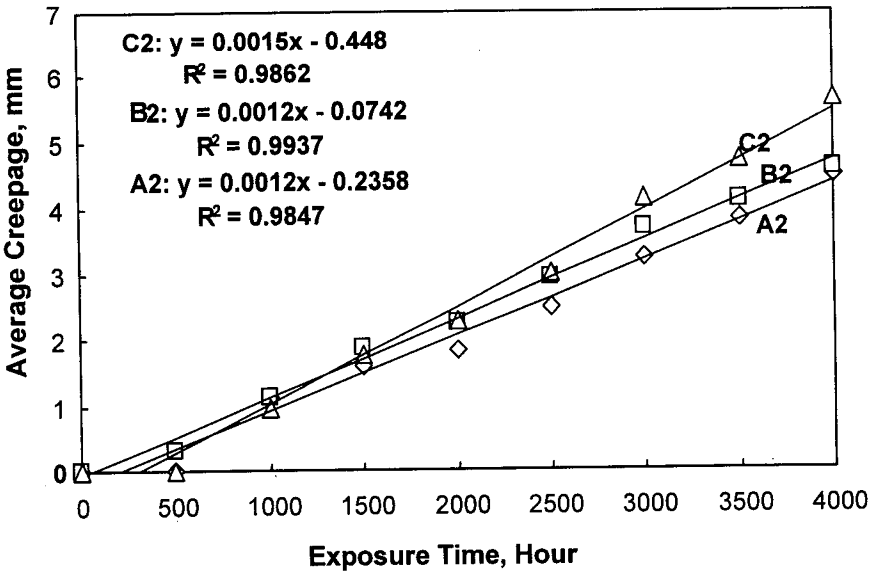


Figure 28. Plot of scribe creepage of MC-urethane Systems A2, B2, and C2 over SP 3 surfaces versus laboratory test time.

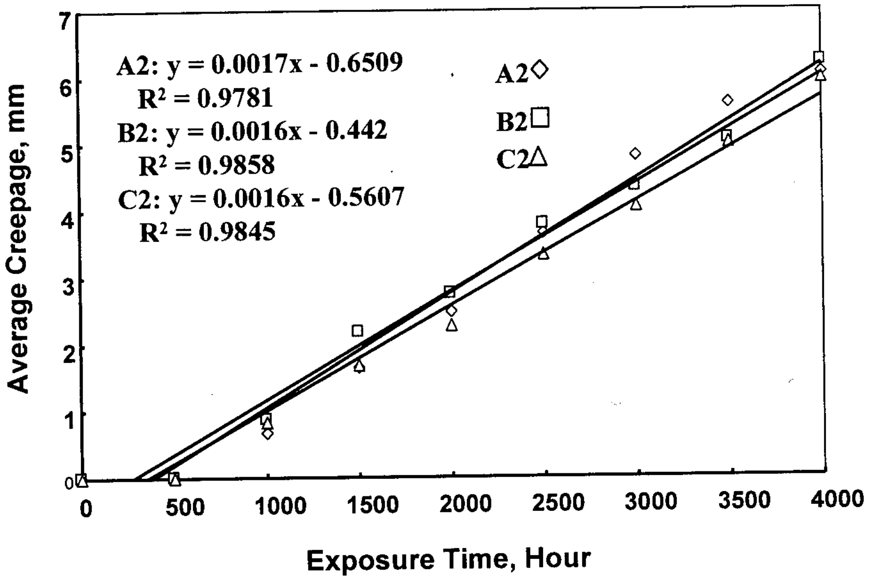


Figure 29. Plot of scribe creepage of MC-urethane Systems A2, B2, and C2 over chloride-doped SP 3 surfaces versus laboratory test time.

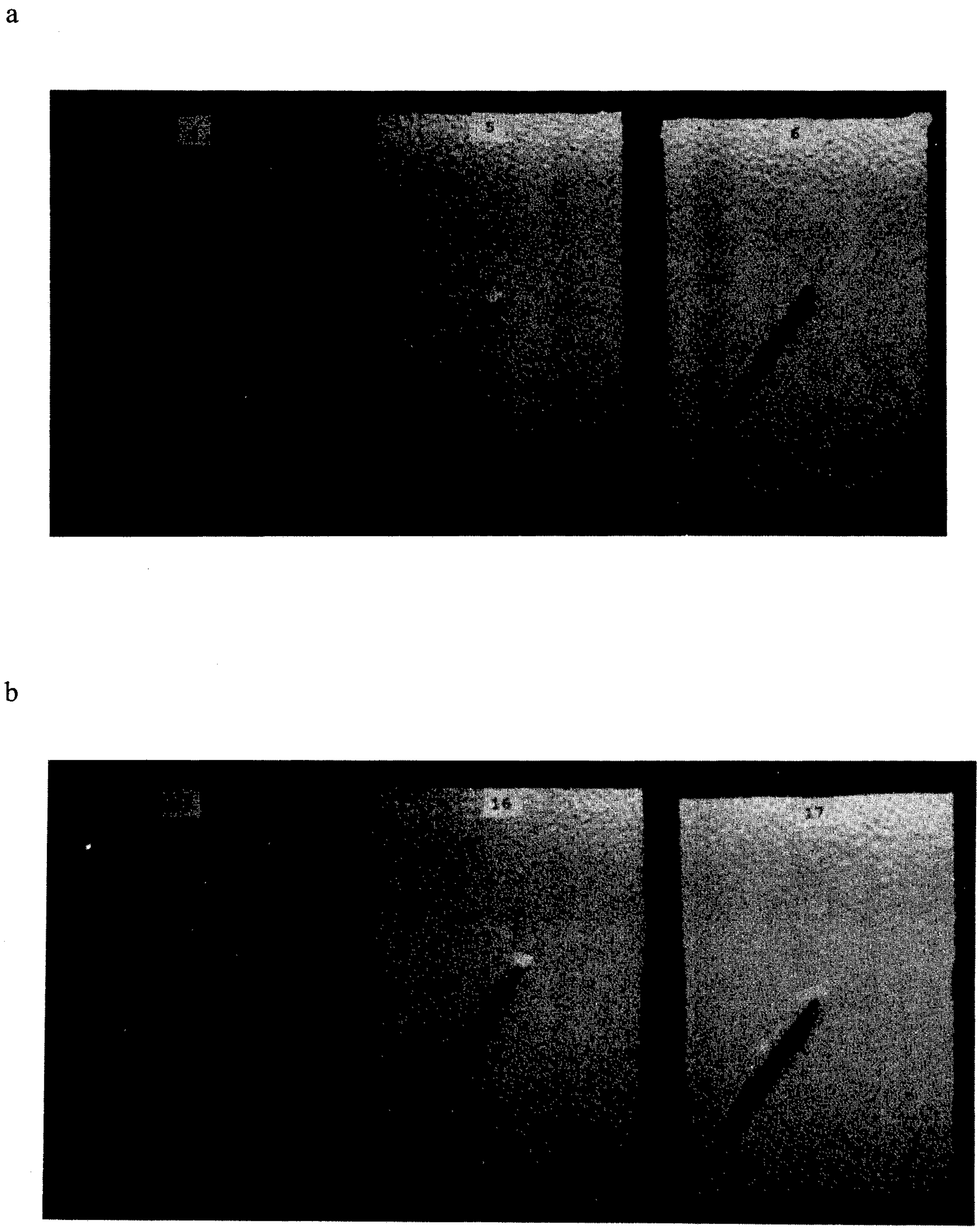


Figure 30. Coating conditions of MC-urethane System A2 over SP 3 (a) and over chloride-doped SP 3 (b) surfaces after 4,000-h laboratory test.

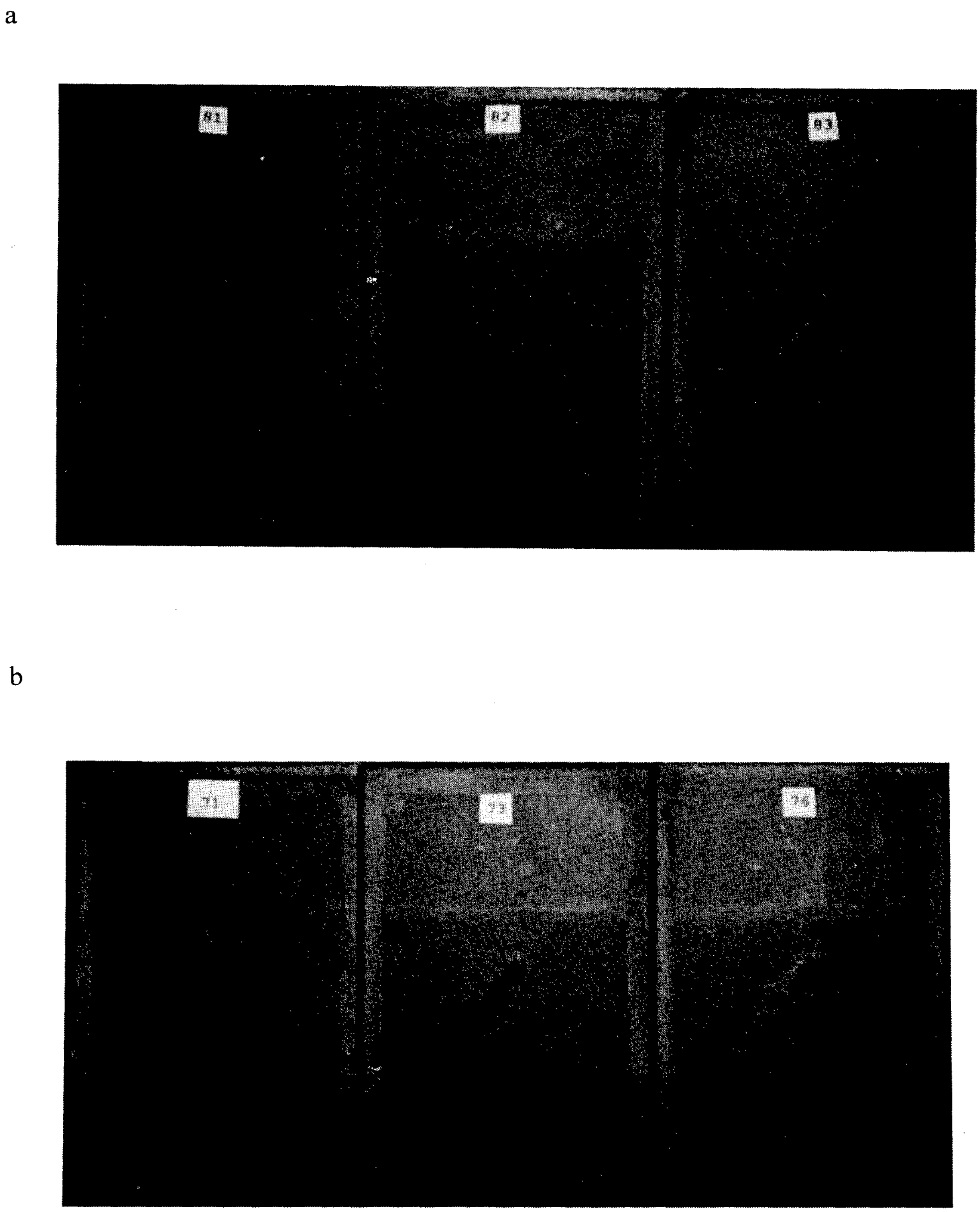


Figure 31. Coating conditions of MC-urethane System B2 over SP 3 (a) and over chloride-doped SP 3 (b) surfaces after 4,000-h laboratory test.

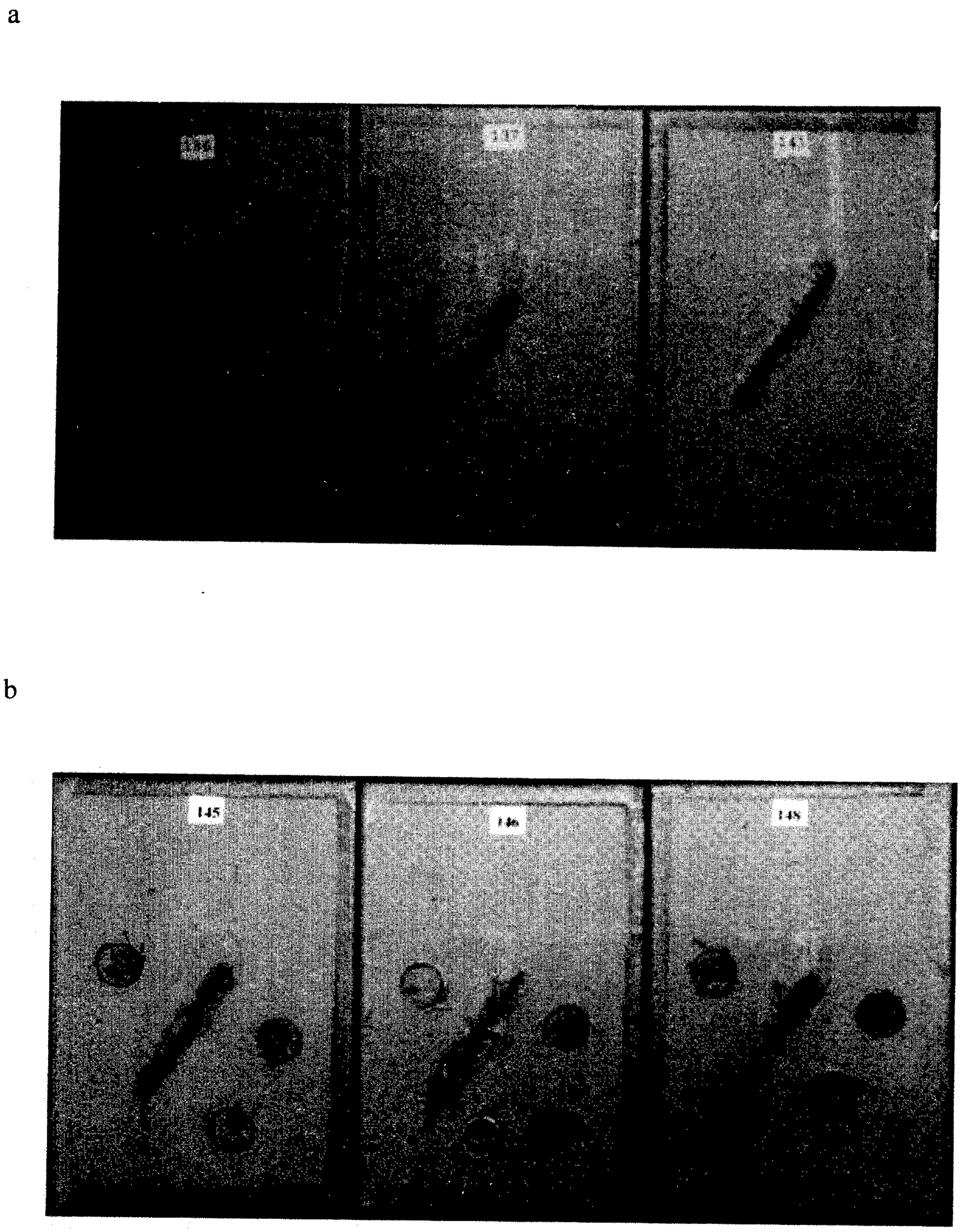


Figure 32. Coating conditions of MC-urethane System C2 over SP 3 (a) and over chloride-doped SP 3 (b) surfaces after 4,000-h laboratory test.

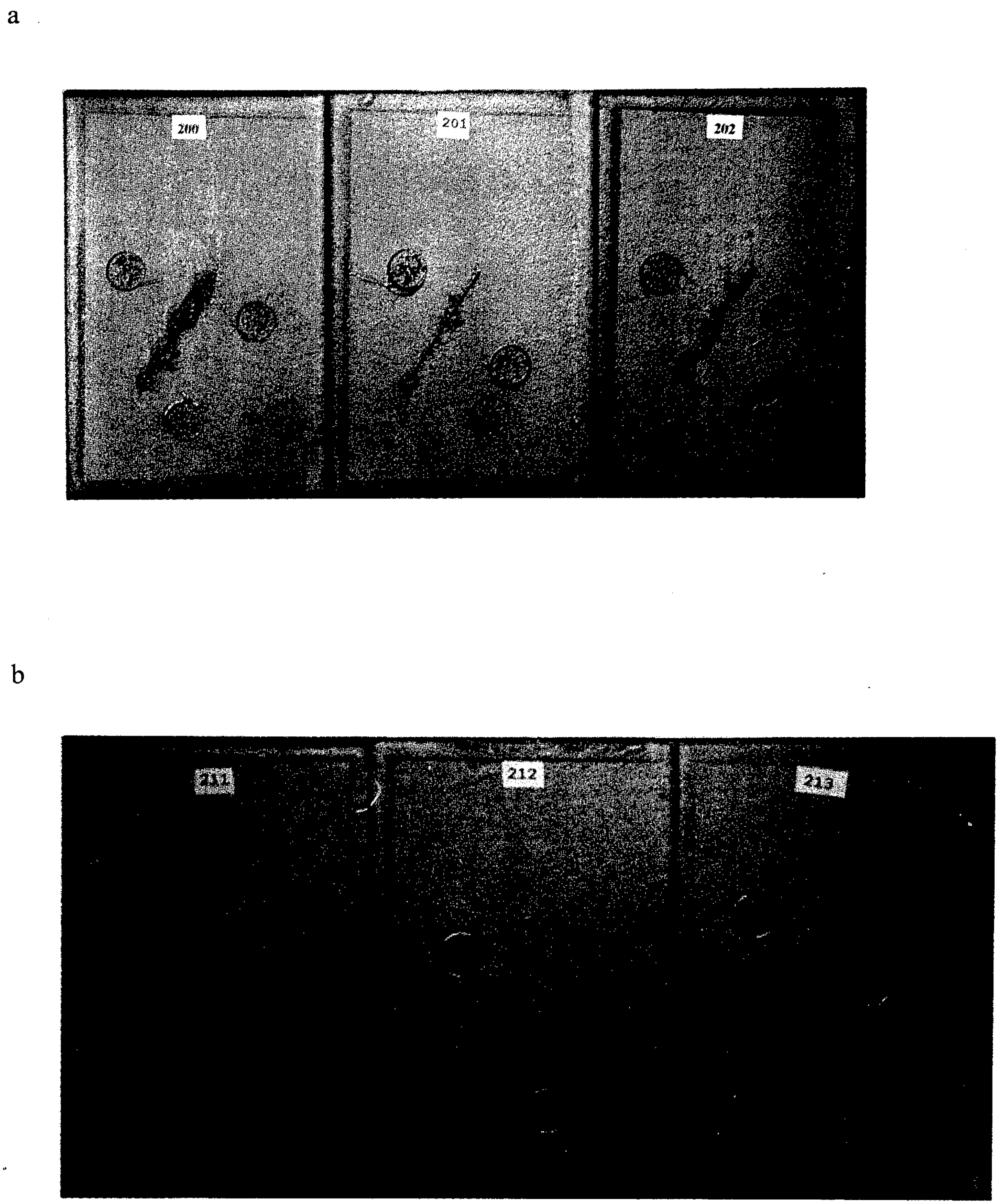


Figure 33. Coating conditions of MC-urethane System C3 over SP 3 (a) and over chloride-doped SP 3 (b) surfaces after 4,000-h laboratory test.

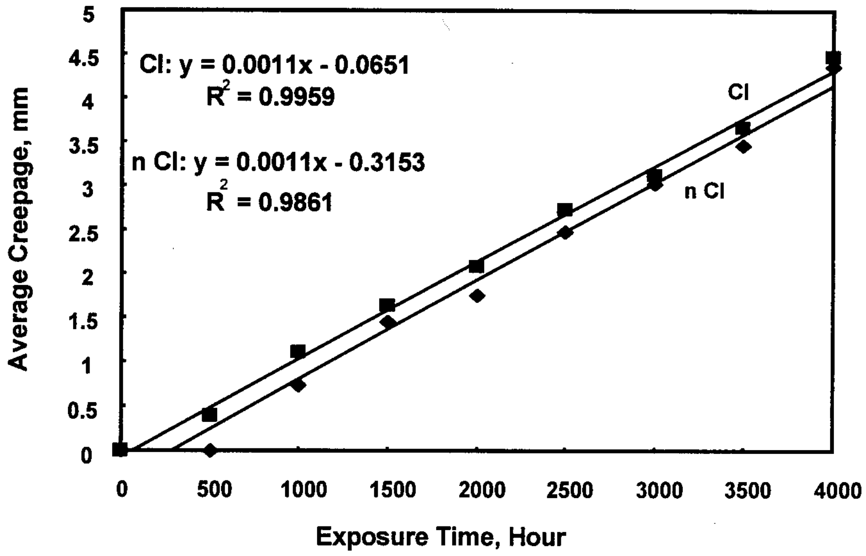


Figure 34. Plot of scribe creepage of System C3 over SP 3 and chloride-doped SP 3 surfaces versus laboratory test time.

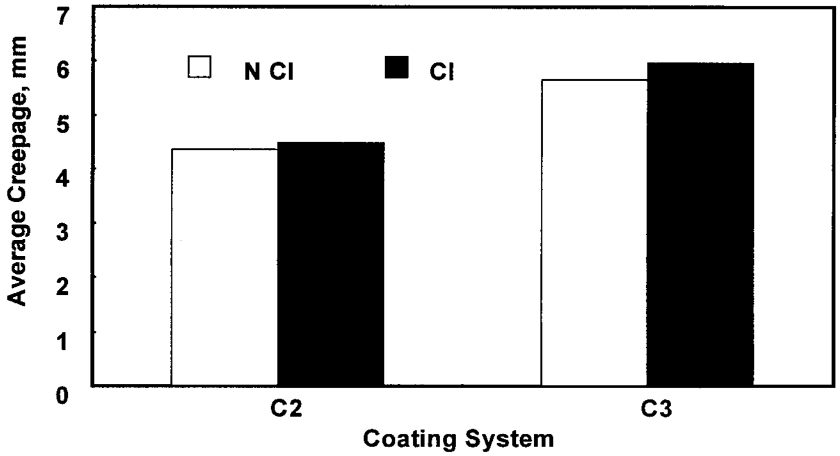
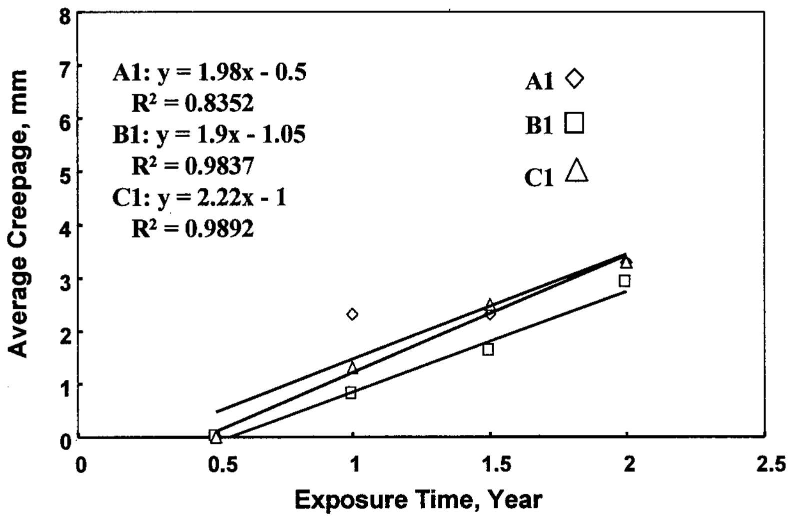


Figure 35. Scribe creepage of Systems C2 and C3 over SP 3 and chloride-doped SP 3 surfaces after 4,000-h laboratory test.

(a) Without chloride



(b) With chloride

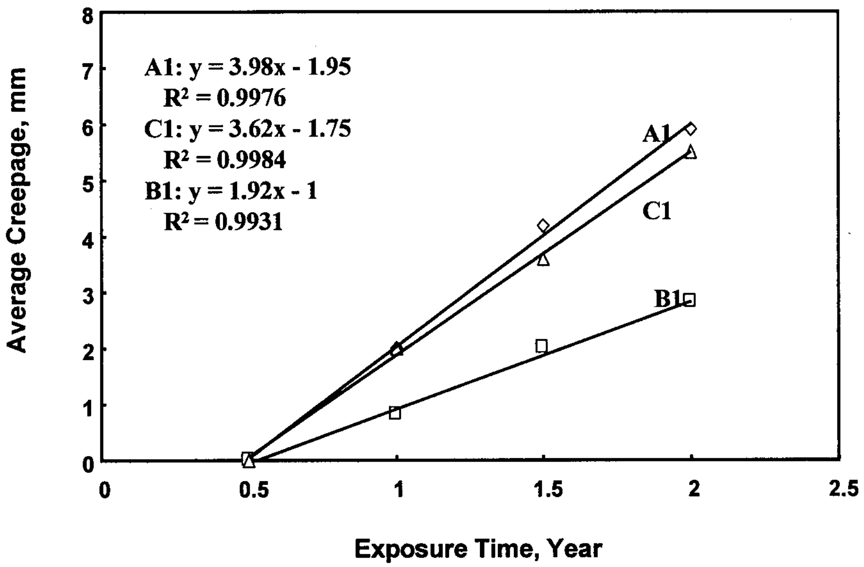


Figure 36. Plot of scribe creepage of MC-urethanes A1, B1, and C1 over SP 3 (a) and over chloride-doped SP 3 surfaces (b) versus outdoor exposure time.

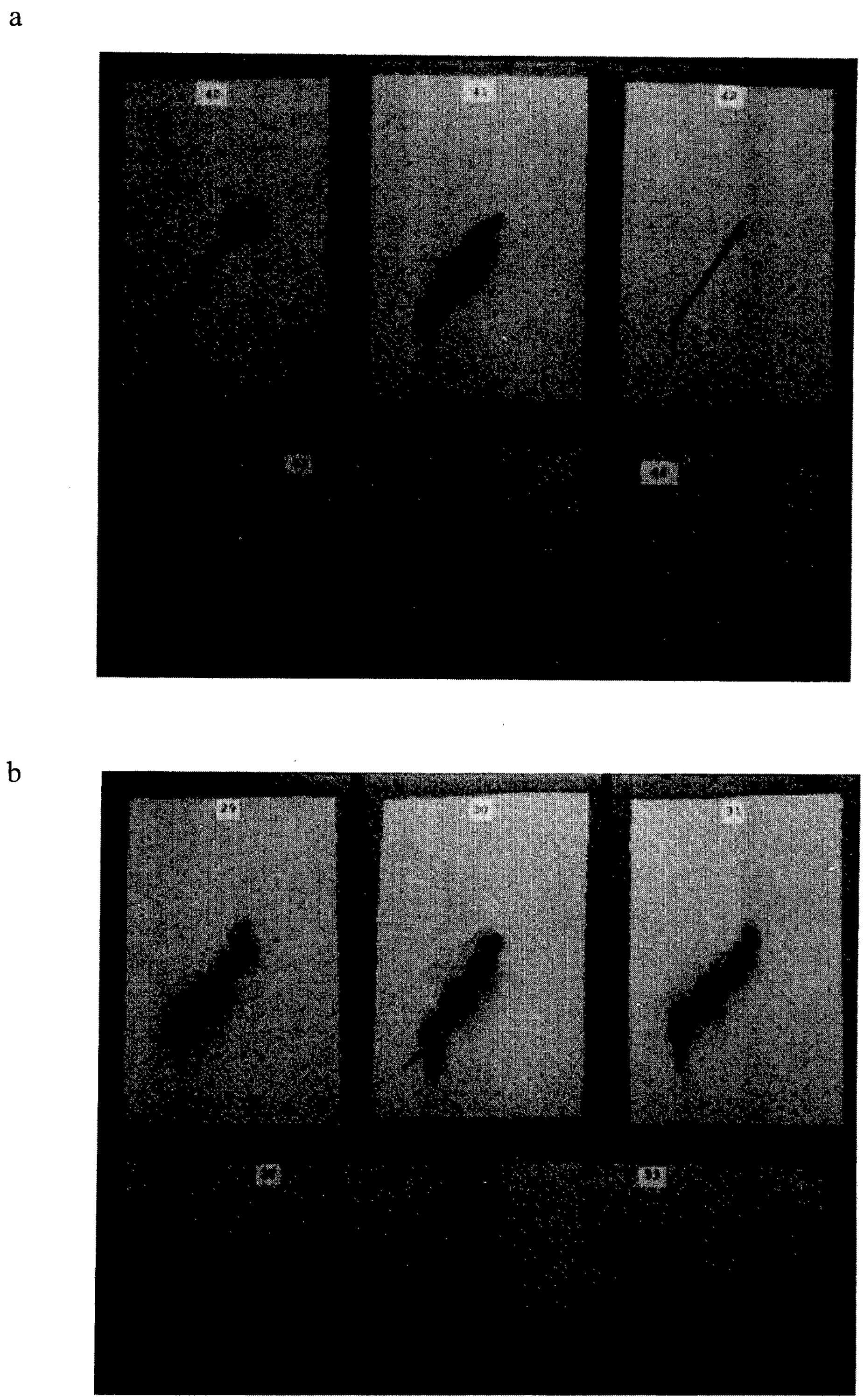


Figure 37. Coating conditions of MC-urethane System A1 over SP 3 (a) and over chloride-doped SP 3 (b) surfaces after 2-yr outdoor exposure.

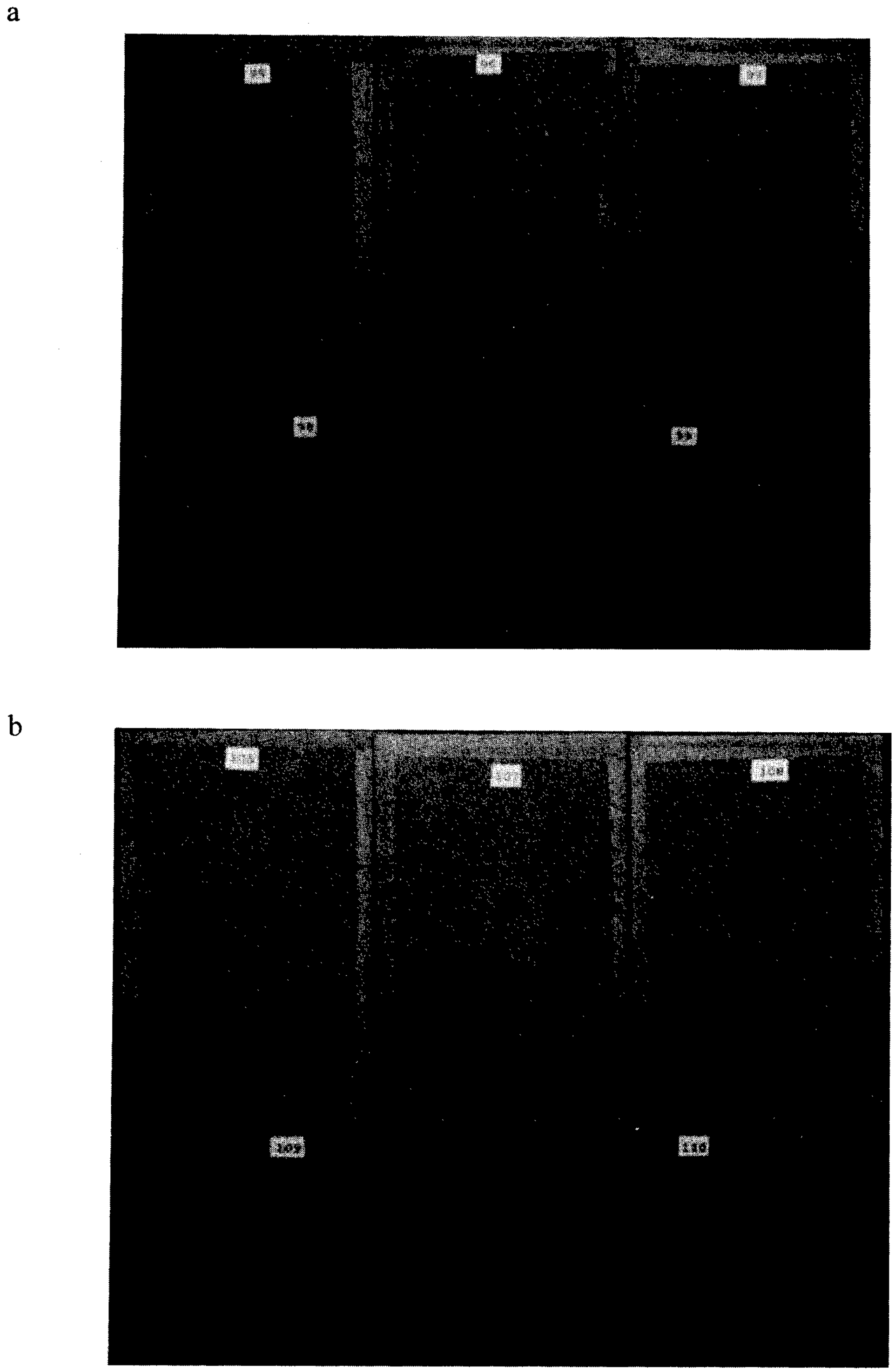


Figure 38. Coating conditions of MC-urethane System B1 over SP 3 (a) and over chloride-doped SP 3 (b) surfaces after 2-yr outdoor exposure.

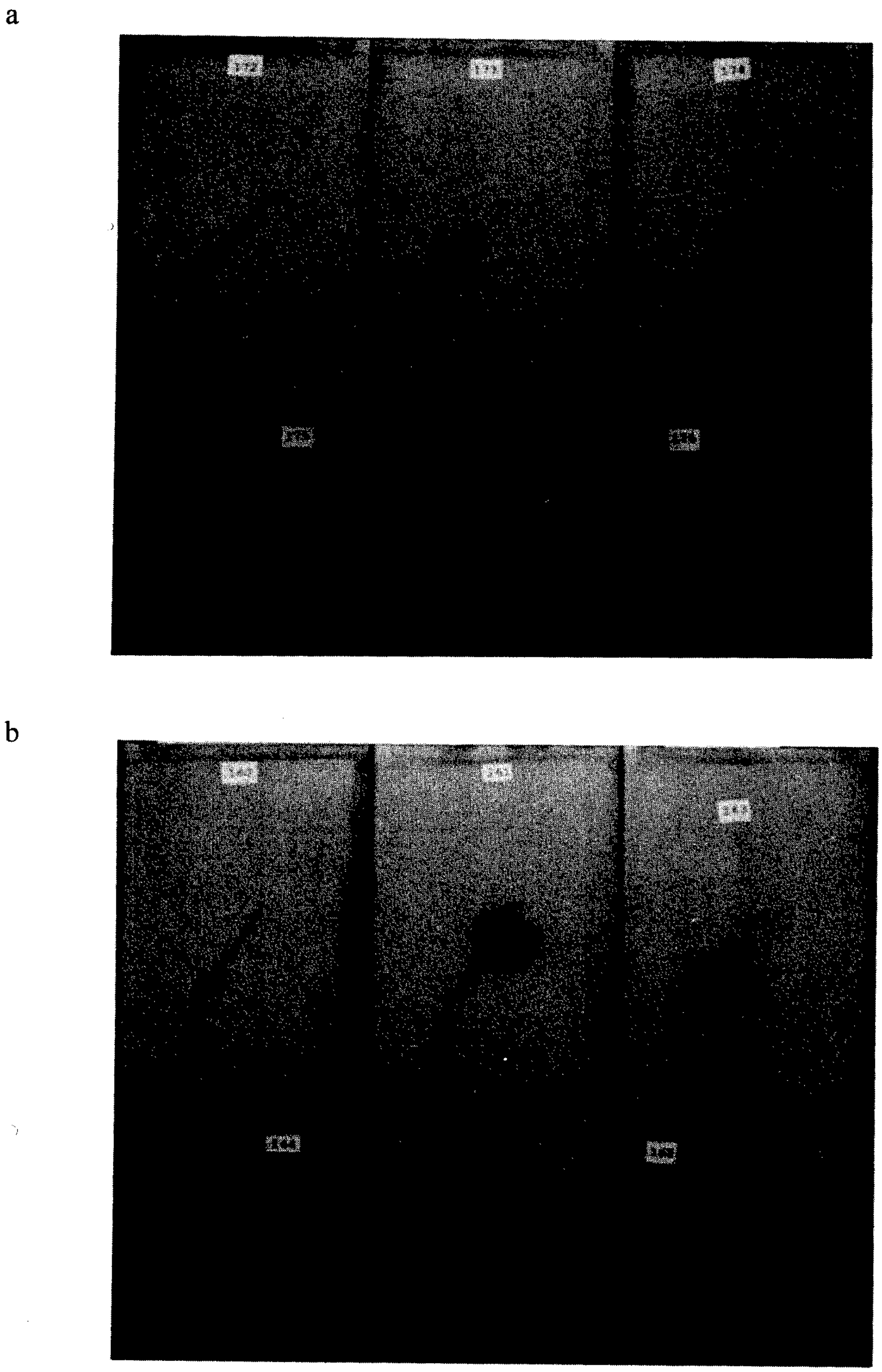
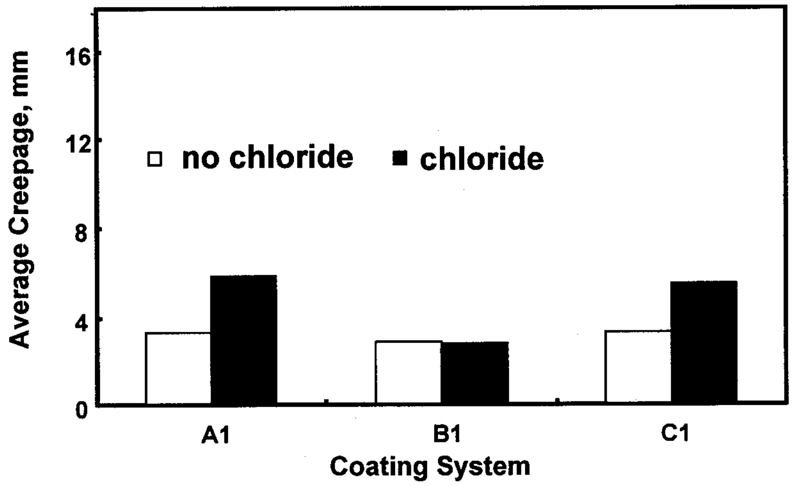


Figure 39. Coating conditions of MC-urethane System C1 over SP 3 (a) and over chloride-doped SP 3 (b) surfaces after 2-yr outdoor exposure.

(a) Without sealer



(b) With sealer

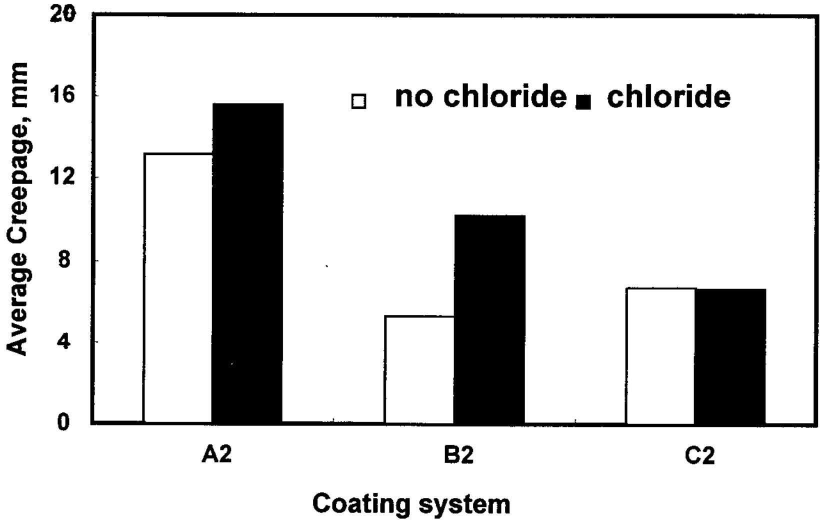
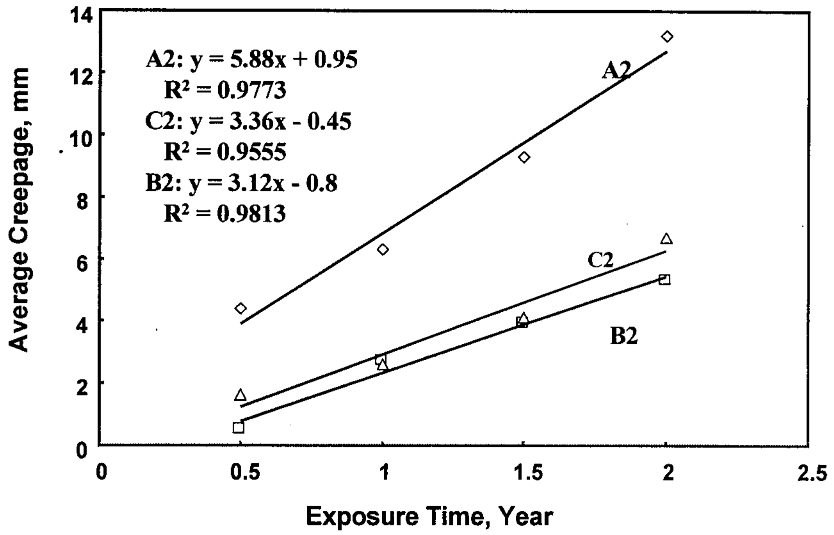


Figure 40. Scribe creepage of MC-urethanes without sealer (a) and with sealer (b) over SP 3 and chloride-doped SP 3 surfaces after 2-yr outdoor exposure.

(a) Without chloride



(b) With chloride

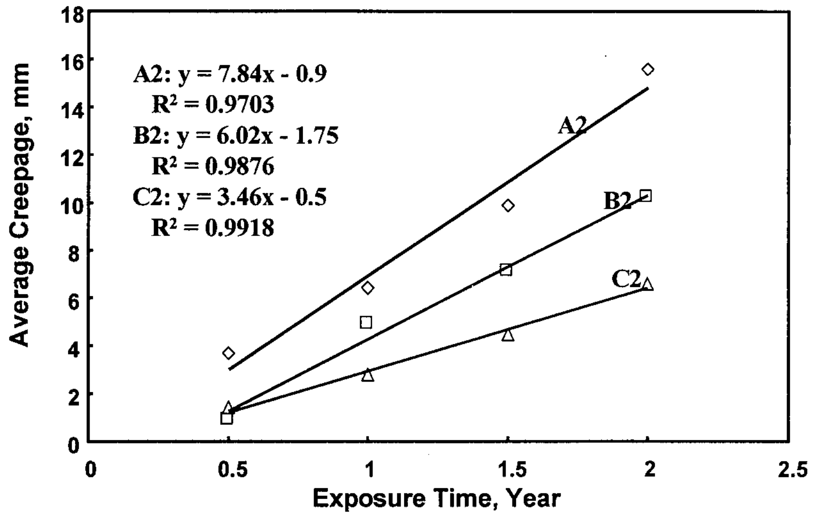


Figure 41. Plot of scribe creepage of MC-urethanes A2, B2, and C2 over SP 3 (a) and chloride-doped SP 3 (b) surfaces versus outdoor exposure time.

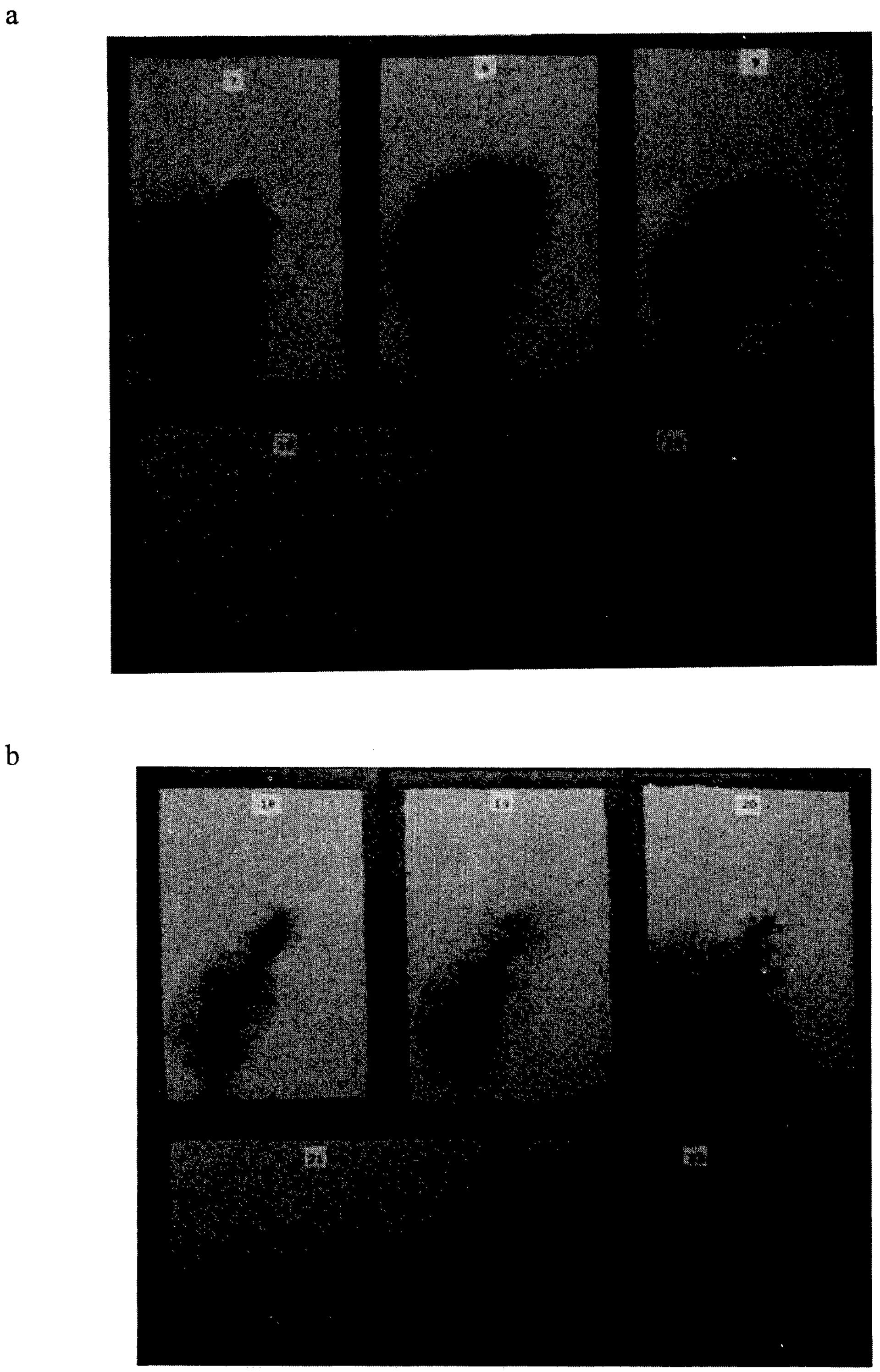


Figure 42. Coating conditions of MC-urethane System A2 over SP3 (a) and over chloride-doped SP 3 (b) surfaces after 2-yr outdoor exposure.

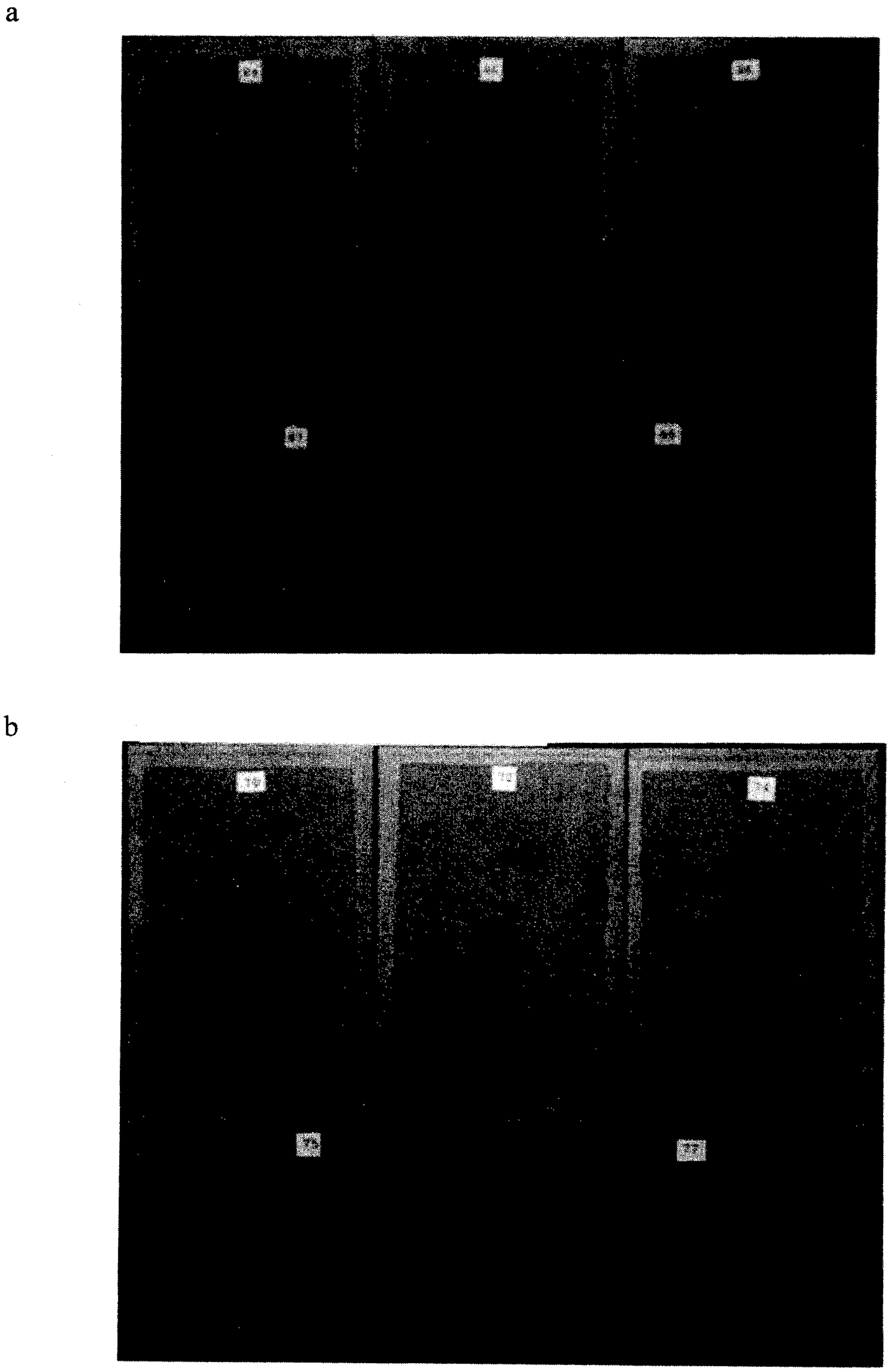


Figure 43. The coating conditions of MC-urethane System B2 over SP3 (a) and over chloride-doped SP 3 (b) surfaces after 2-yr outdoor exposure.

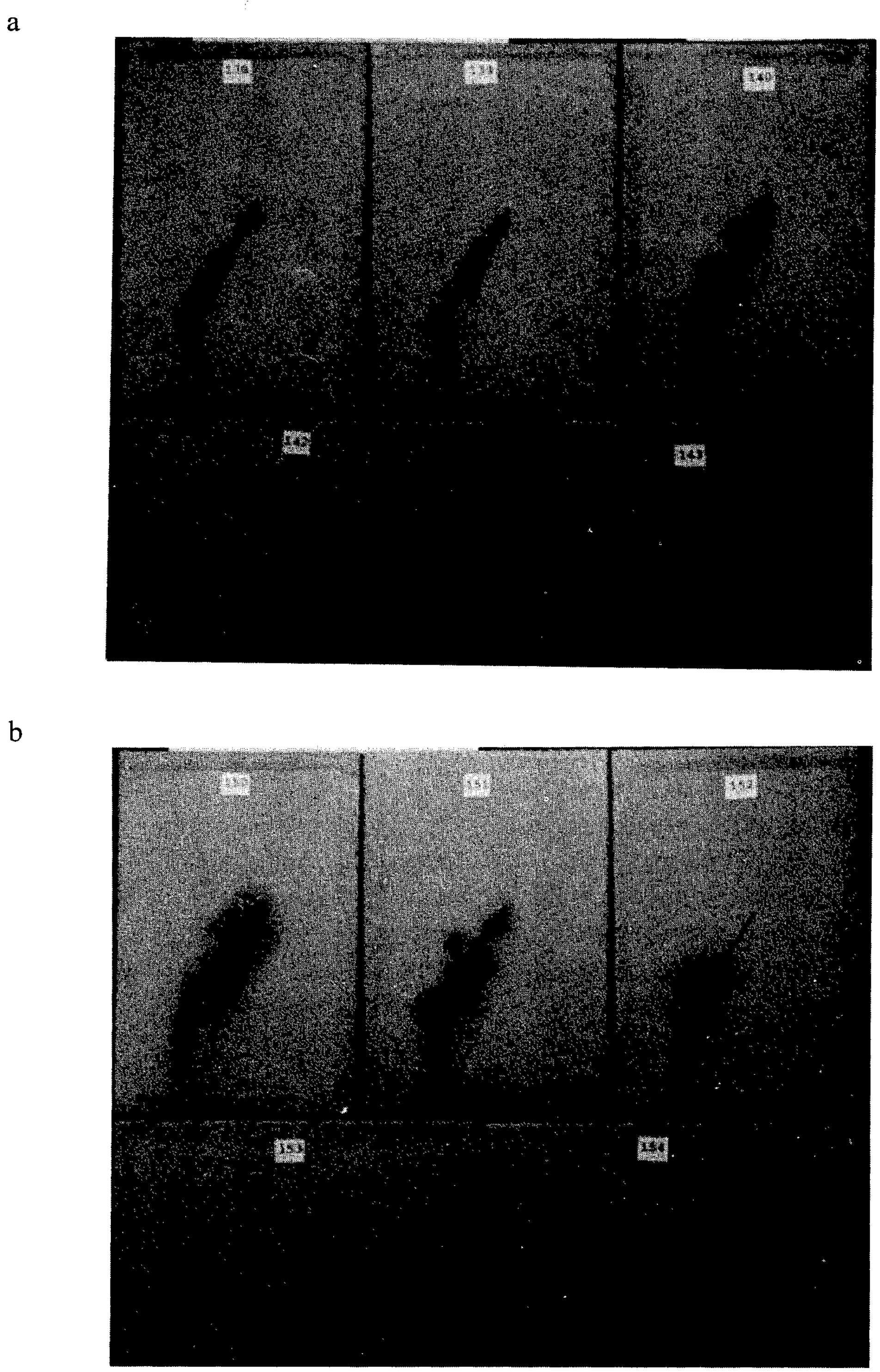


Figure 44. Coating conditions of MC-urethane System C2 over SP 3 (a) and over chloride-doped SP 3 (b) surfaces after 2-yr outdoor exposure.

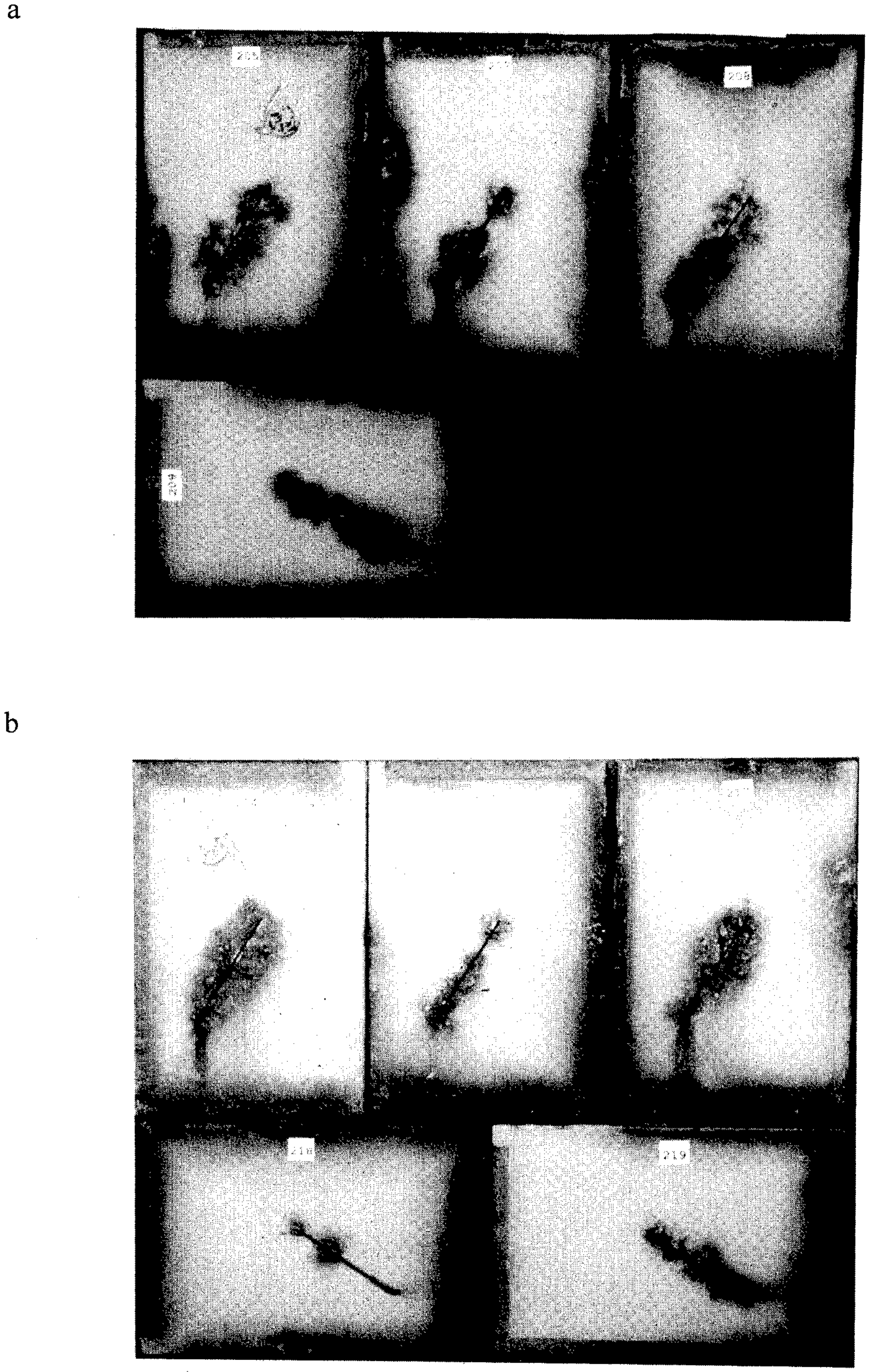


Figure 45. Coating conditions of MC-urethane System C3 over SP 3 (a) and over chloride-doped SP 3 (b) surfaces after 2-yr outdoor exposure.

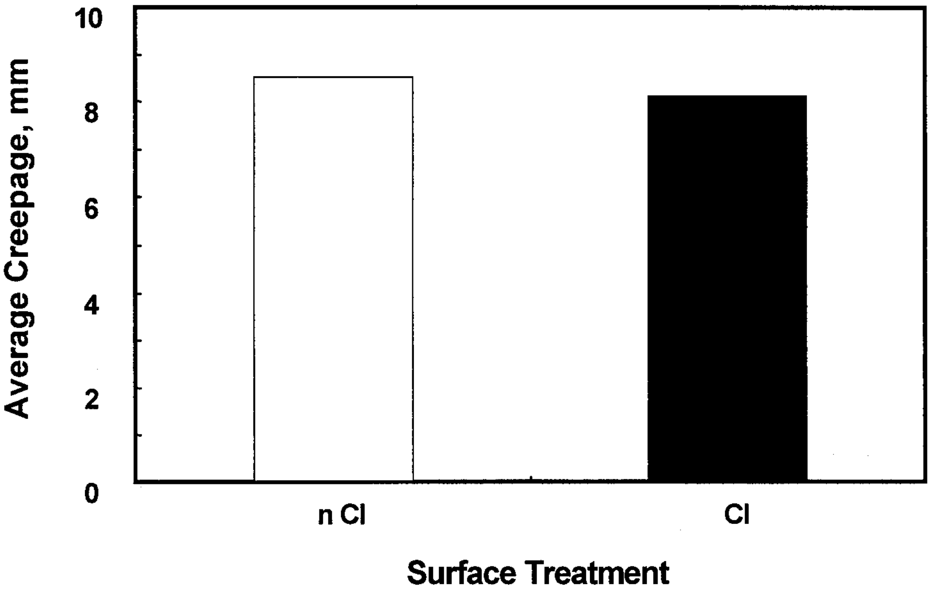


Figure 46. Scribe creepage of MC-urethane System C3 over SP 3 and chloride-doped SP 3 surfaces after 2-yr outdoor exposure.

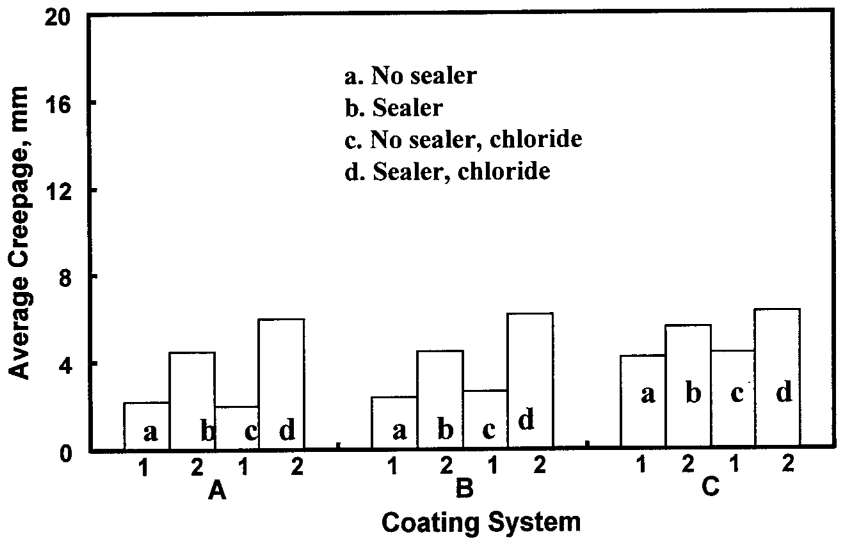


Figure 47. Comparison of scribe creepage of MC-urethane systems without sealer and with sealer over SP 3 and chloride-doped SP 3 surfaces after 4,000-h laboratory test.

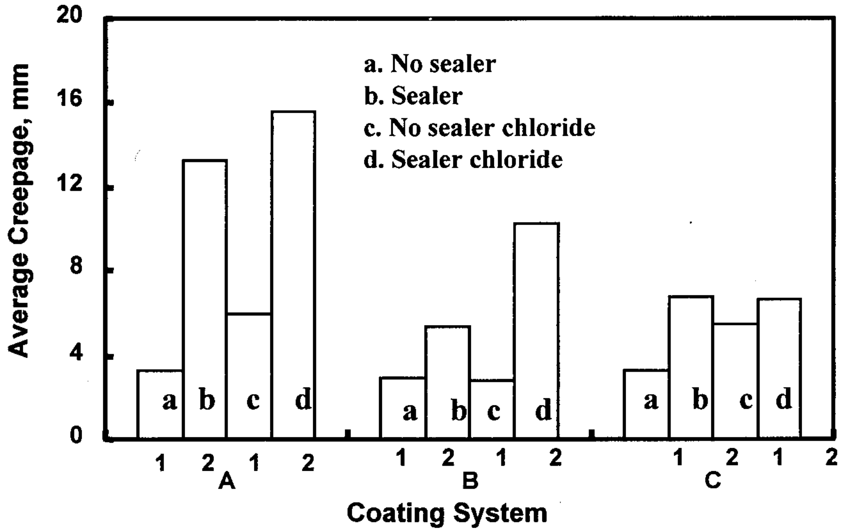


Figure 48. Comparison of scribe creepage of MC-urethane systems without sealer and with sealer over SP 3 and chloride-doped SP 3 surfaces after 2-yr outdoor exposure.