Coating Evaluation and Validation of Accelerated Test Conditions Using an In-Situ Corrosion Sensor

G.D. Davis, L.A. Krebs,† and C.M. Dacres—DACCO SCI, Inc.*

An in-situ corrosion sensor was used to obtain electrochemical impedance spectroscopy (EIS) measurements on coated panels under a variety of accelerated laboratory test conditions as well as ambient exposure at a Florida beach. Three studies are reported. The first compared the sensor (EIS) measurements taken in a salt fog chamber to those obtained using a clamp-on cell and the conventional remote electrode/immersion approach. For coatings with minimal edge defects, the two methods gave equivalent results. For coatings with edge defects, the sensor was able to detect the defects provided the surface was wet, as in the salt fog chamber. In contrast, the conventional approach was unable to detect defects unless they were within the confines of the clamp-on cell. In the second case, sensor measurements were used to compare coating degradation during salt fog, a cyclic corrosion test, humidity, and immersion to that occurring at a Florida beach. The cyclic corrosion test showed an excellent correlation with beach exposure while the salt fog and other test showed very little correlation, suggesting that the cyclic test is more valid for discriminating coating performance for seacoast exposure. The sensor also indicated that the test could be shortened by up to 40% without significantly reducing the validity of the test. In the final example, a series of primers and appliqués were evaluated using the cyclic corrosion test. The sensor EIS results allowed a discrimination between the materials sets even though there was little or no visual difference between the specimens.

INTRODUCTION

Evaluation of coating performance is important to both coating developers and end users who need to screen available coatings for their applications. The best test of the corrosion performance of a coating is ambient, service conditions. Unfortunately, the coating degradation under these conditions must be very slow for any coating of practical interest. Accelerated exposures and/or laboratory testing are commonly used to evaluate coatings in a reasonable time frame. However, the use of accelerated tests raises the issue of validity of the test—do the coatings or materials degrade in the laboratory with the same mechanisms as they do in the field? An additional issue is quantification of the early stages of degradation. Visual inspection is the most common means of evaluating a coating's performance. Such evaluation is only semi-quantitative and requires significant coating degradation and substrate corrosion, which can take a relatively long time for good coatings. Thus, there is a need for a means to detect and quantify the early stages of coating degradation to allow for the quicker evaluation and screening of coatings.

Electrochemical impedance spectroscopy (EIS) has been used to detect coating degradation in the laboratory.[1-5] Very good correlation has been shown between short-term EIS data and long-term coating performance in seawater, demonstrating the technique's predictive capabilities. Traditionally, EIS measurements have required immersing the specimen (or an area of the specimen) into an electrolyte. Such immersion at best is inconvenient and time consuming and can result in artifactual damage to the specimen even for short immersion times.[6]

A recently developed in-situ corrosion sensor allows EIS measurements to be acquired under ambient or test conditions and can be used to predict coating performance before any visual deterioration.[7-10] One particularly useful ability of the sensor is to obtain the exact same measurements under different conditions, such as beach exposure and different laboratory accelerated testing exposure. This al-

*10250 Old Columbia Rd., Columbia, MD 21045. E-mail: davis@daccosci.com; AlKrebs@erols.com; and dacres@daccosci.com.
†Present Address: Anderson Materials Evaluation, 1405 South Rolling Rd., Baltimore, MD 21228.

lows a correlation of the different exposures to determine which laboratory tests best duplicate field exposure. Although such comparisons have been previously reported using visual observations, weight loss measurements, analysis of corrosion products, or other semiquantitative or late-stage measurements,[11-15] direct comparisons of different exposure conditions using a quantifiable measure of coating degradation from the very early stages have not been possible. The ability of the in-situ sensor to obtain EIS measurements under these different conditions has permitted such a correlation.

Two versions of the sensor are available and were used in the investigations reported here. The first is a permanent sensor electrode that is applied to the coating surface. An electrical lead is then connected to the electrode. This version is particularly useful for monitoring inaccessible areas or taking repeated measurements in an accelerated test chamber. The second is a hand-held sensor probe that is pressed against the coating surface when measurements are acquired. This version is useful for inspecting a number of specimens or structures in service that do not have a permanent sensor applied. For both versions, electrical connection to the substrate completes the electric circuit.

Three studies are reported here. The first involves a comparison of EIS results obtained using the permanent sensor and traditional clamp-on cell measurements of painted panels exposed to salt fog. The second involves a comparison of different accelerated laboratory tests with beach exposure in Florida. The final study demonstrates the usefulness of the sensor in materials screening.

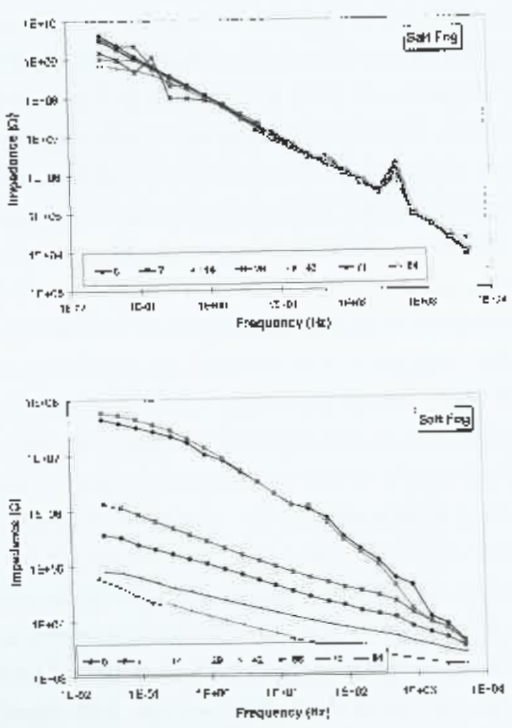

Figure 1—Impedance spectra of a very good coating (top) and a poor coating (bottom) during salt fog exposure. The legend gives the exposure time in days.

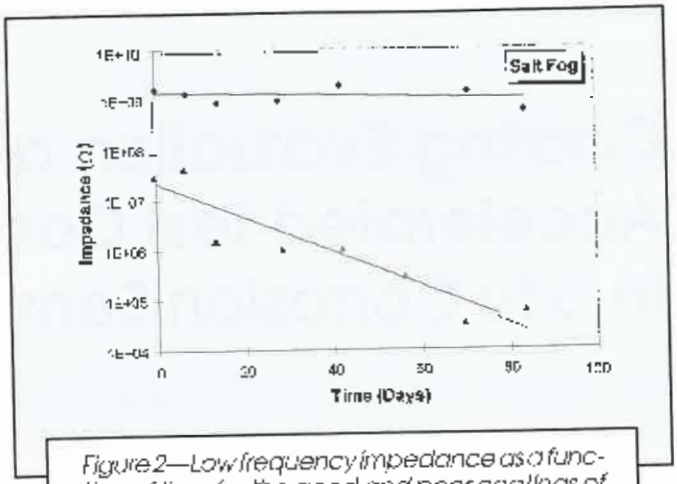

Figure 2—Low frequency impedance as a function of time for the good and poor coatings of Figure 1.

EXPERIMENTAL

To compare EIS measurements taken with the permanent sensor with those taken with conventional flat cell technology, a series of 2024 aluminum panels with aerospace grade primers were tested in salt fog exposure (ASTM B 117). Sensor measurements were taken while the panels were in the test chamber by snaking the lead wires outside of the chamber for connection to the Gamry PC3 potentiostat. The sensor lead was connected to the counter and reference electrode connections of the potentiostat. The working electrode connection was attached to the substrate. The frequency was typically swept from 0.1 to 10^4 Hz.

The conventional EIS measurements were taken by removing the specimens from the chamber, attaching a clamp-on cell, filling it with 5% NaCl solution, inserting counter and reference (standard calomel electrode, SCE) electrodes, and acquiring data using the same potentiostat and parameters used for the sensors. The measurements were begun a few minutes following set up; because the specimen was already in equilibrium with the salt fog environment, no equilibration time was necessary. The cell was then emptied and removed; the specimen was rinsed, and then returned to the salt fog chamber. Total time of immersion exposure was less than 30 min.

For comparison of the different accelerated laboratory tests and field exposure, a variety of coatings were prepared on 2219 aluminum using a spontaneous polymerization process.[16-20] In this process, the panel is immersed in a monomer solution. The panel's surface promotes polymerization of the monomer with the result after drying being a thin, protective coating with few defects. Conventional coatings were also used for comparison. A total of over 100 coatings were evaluated. These exhibited a wide range of performance, as desired for comparisons of different exposure conditions.

Four accelerated exposure tests were used with the spontaneous polymerized coatings, although not every coating was subjected to each test. The four exposure tests were: salt fog or spray (ASTM B 117), cyclic corrosion test, humidity exposure (ASTM D 2247), and water immersion (ASTM D 870).

The standard and most common accelerated test is salt spray, which is often specified but rarely corresponds well to service degradation. The salt fog exposure was 2000 hr.

The other principal exposure is based on the Ford cyclic corrosion test that was developed for evaluation of the perforation resistance of painted steel; the test development and procedures have been reported elsewhere.[22-24] Other automotive companies have similar cyclic tests, differing in detail of exposure conditions. The exposure period was 100 cycles (each business day corresponds to one cycle.) We modified the test to reflect the coastal conditions at the Kennedy Space Center (KSC): immersion in artificial seawater whose pH is reduced to 4 by adding HCl to simulate the acid precipitation caused by rocket motor exhaust (15 min), ambient drying (1 hr, 45 min) 90% humidity at 50°C (22 hr), and ambient exposure to UV or artificial solar radiation (weekends and holidays).

High humidity (100% RH, 50°C, 30 days) and immersion (38°C, 168 hr) exposures were also used for some coatings. However, these tests were not very discriminating; i.e., they were easy for the coatings to pass and were not used for all coatings.

Field exposure was conducted at the Kennedy Space Center's beach corrosion site. Panels were mounted on racks inclined at approximately 30°. The racks faced the ocean, approximately 30 m away from the high tide line of the Atlantic Ocean.

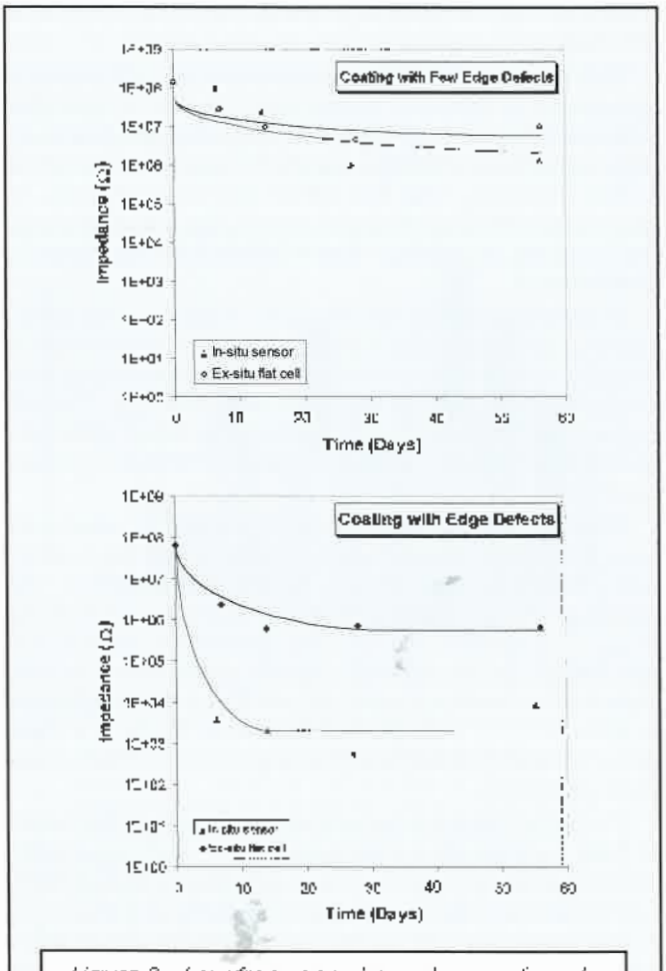

Figure 3—Low frequency impedance of coatings exposed to salt fog and inspected using the in-situ sensor and the ex-situ clamp-on cell.

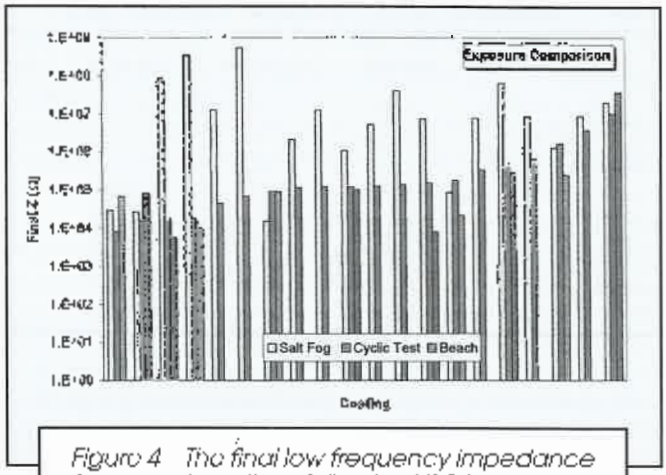

Figure 4 The final low frequency impedance for several coatings following KSC beach, salt fog, and cyclic corrosion test exposures. The coatings are ordered in increasing cyclic test values.

In a separate test, a series of appliqués and primers were evaluated as part of a materials screening process. Steel substrates were used. The appliqué specimens were only subjected to the cyclic corrosion test. Here H_2SO_3 was used to lower the pH and represented acid precipitation from stack gases.

For the latter two studies, the hand-held version of the corrosion sensor was used. It was pressed against the coating surface using a drop of ultrasonic couplant, which tends to improve the signal-to-noise ratio of the data. For the salt fog and cyclic corrosion tests, data were generally taken every two weeks; for the humidity test, data were generally taken every week; for immersion, every several days. For the beach site, data were taken at three- to four-month intervals. Specimens were removed from the test chambers for EIS measurements. In the case of the cyclic corrosion test, measurements were taken during the dry cycle. For some of the primer / appliqué specimens, measurements were taken with this schedule; for others, measurements were only taken before and after the complete exposure test.

Data were generally analyzed using the geometric mean of the lowest frequency decade of points. This region of the impedance spectrum (Bode magnitude plot) is very sensitive to coating degradation and can vary by several orders of magnitude. Other analyses involving phase angles or equivalent circuit modeling have proven useful in other systems, such as composites or adhesive bonds,[25,26] but did not provide significantly more information than the simple low-frequency impedance for these coatings studies.

RESULTS AND DISCUSSION

Each coating exhibited degradation as reflected in the impedance spectrum measured by the in-situ corrosion sensors. This is most easily indicated by the low frequency impedance that can decrease by several orders of magnitude during exposure. Accordingly, this parameter was chosen to track coating performance. *Figure 1* shows that a

Table 1—Correlation Matrix for Different Corrosion Tests

	Salt Fog	Cycle 1E7	Cycle 25	Cycle 50	Cycle 75	Cycle 100	Humidity	Immersion	KSC
Salt Fog	1								
Cycle 1E7	0.078	1							
Cycle 25	0.45	0.36	1						
Cycle 50	0.018	0.035	0.46						
Cycle 75	0.056	0.73	0.062	0.014	1				
Cycle 100	-0.12	0.67	-0.3	0.0037	0.90	1			
Humidity	0.40	0.21	-0.10	0.27	-0.19	0.18	1		
Immersion	-0.040	0.21	0.69	0.31	-0.28	-0.28	0.30	1	
KSC	-0.038	0.89	0.76	0.96	0.98	0.97	-0.13	-0.32	1

very good coating remains capacitive in nature (slope of –1 in this log impedance vs. log frequency Bode plot) with high impedance at low frequencies. In contrast, a poor coating exhibits a sharp decrease in impedance at low frequencies. Detailed analysis of the spectral shape (not discussed here) indicates corrosion occurring under the coating.

By using the low frequency impedance, the performance of the coatings was tracked and comparisons were made between different coatings and between different exposure conditions. As an example, the low frequency impedances of the two coatings in *Figure* 1 are given in *Figure* 2. As a rule of thumb, the low frequency impedance of a good coating will be $10^8\ \Omega$ or higher; that of a poor coating will be $10^7\ \Omega$ or lower. The impedance of the good coating remains above $10^8\ \Omega$ throughout the exposure period. That of the poor coating is much lower at the beginning, quickly decreases to $10^6\ \Omega$, and continues to decrease over the course of the test.

As part of the validation of the in-situ sensor, direct comparisons were made for panels exposed to salt fog conditions using the sensor and conventional clamp-on cell approaches. *Figure* 3 shows examples of two primers—one that is uniform and defect-free and one that has several edge defects. EIS measurements obtained on the first specimen are essentially identical for the in-situ sensor and the clamp-on cell indicating that the two spectra taken with the two approaches are equivalent. The differences seen for the second specimen can be explained based on the area of inspection of the two methods. With the clamp-on cell, the EIS measurements reflect on the area of the specimen under the cell where the electrolyte is in direct contact with the coating. For this specimen, the primer is good in the middle of the panel. With the in-situ sensor, the inspection area depends on the wetness of the surface. Because the measurements were taken inside the salt fog chamber, the surface is wet and there exists a conductive pathway from the sensor electrode to the edge defects (and ultimately to the substrate). Thus, the sensor is able to monitor the entire face of the specimen and detect the edge defects.

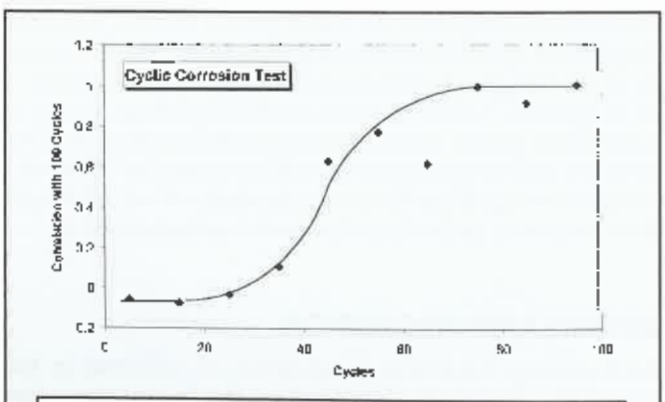

Figure 5—Correlation of interim sensor measurements with results at the end of the cyclic corrosion test. This correlation includes all coatings tested

Other experiments have shown that when the surface is dry, the sensor inspection area is much smaller and localized near the electrode. In contrast, on a wet surface, the sensor was able to detect a coating defect up to 4.5 meters away. Thus, the inspection area of the sensor can be controlled by controlling the degree and extent of wetness of the structure.

By comparing EIS measurements of nominally identical specimens in different accelerated laboratory tests and ambient Florida beach exposure, degradation of the coatings under those conditions can be compared to determine which laboratory tests best reflect service conditions. As described in the Experimental section, this was performed for a variety of coatings that exhibited a wide range of performance.

A common finding for almost all of the coatings tested was that they did well in high humidity and water immersion. Because these tests were not very discriminating, they were discontinued and not used for all coatings. The salt fog and cyclic corrosion test, on the other hand, allowed a distinction between highly protective coatings and poor coatings.

The final low frequency impedance for a series of coatings following Florida beach exposure, salt fog testing, and cyclic corrosion testing is given in *Figure* 4. The coatings are ordered in increasing impedance following the cyclic corrosion test. It is clear from the figure that the salt fog values are randomly placed and that there is little correlation between the two sets of values. Although there is some scatter with the beach results, there is a clear general trend that the beach values increase with increasing Ford values.

This correlation is more quantitatively seen in the matrix of *Table* 1, which shows the population correlation coefficients[47] for the different exposure conditions. Included are correlations with the humidity and immersion tests, as well as intermediate cyclic corrosion test results. The number associated with the values (e.g., cycle 25) is the number of cycles on which the measurements were taken (interpolations were used if measurements were not taken on a given

day). For cycle IE7, the data represent the number of cycles for the low-frequency impedance to decrease to 10^7 Ω. Previously, that parameter was shown to correlate with corroded area at the end of the test (100 cycles) of panels with different automotive coatings.[6,9]

The most notable finding in *Table 1* is that the salt fog test shows almost no correlation with the beach results, that is, coating performances from the two exposures are independent of each other. A similar random relationship is seen between the beach results and those of humidity and immersion exposures. In contrast, an excellent correlation is seen between the beach exposure and the cyclic corrosion test. Both the complete cyclic corrosion test results and intermediate results at 75 cycles and 50 cycles show a strong relationship with KSC results. A slightly less, but still very good, correlation is observed using the time for the impedance to decrease to 10^7 Ω criterion.

The finding that the salt fog test does not correlate well to many ambient or field exposure conditions is not new. Many other groups have reported the same conclusion.[11-15] In general, cyclic tests give improved performance rankings compared to the static salt fog test—materials that do well in the cyclic corrosion tests tend to do well under field conditions. However, the previous studies have primarily used weight loss or visual appearance to compare the different exposures. Such measures are only semiquantitative and can require significant coating degradation, especially in the case of good, undamaged coatings. The corrosion sensor results presented here allow for a quantitative comparison of the early stages of degradation.

A more complete correlation study of all cyclic corrosion test results (not just the ones with KSC exposure upon which *Figure 4* and *Table 1* are derived) shows that increasingly good correlation with final results is seen after ~60 cycles, but that 40 cycles and below do not provide enough material degradation to allow coating evaluation (*Figure 5*). Such data suggest that the test could be shortened from the standard 100 cycles by ~40% with little loss in confidence in the results.

In a subsequent evaluation of primers and appliqués, the cyclic corrosion test was used for materials screening. A series of three film appliqués and six primers, plus no primer (designated as primer #7) were tested. A few combinations were monitored at approximately two-week intervals during the exposure. EIS measurements of all panels were taken before and after the complete exposure period. The change (decrease) in the low frequency impedance measurements for all appliqué/primer combinations is given in *Figure 6*. Although there was little visual difference between the different specimens following the test, the EIS measurements clearly allowed a discrimination to identify the most protective combination. Primers #1 and #2 were more protective than any of the other primers while appliqué #1 was significantly better than the other two appliqués. In fact, the combinations of primers #1 or #2 with appliqué #1 exhibited no decrease in low frequency impedance over the course of the accelerated exposure and are predicted to give the best performance in service.

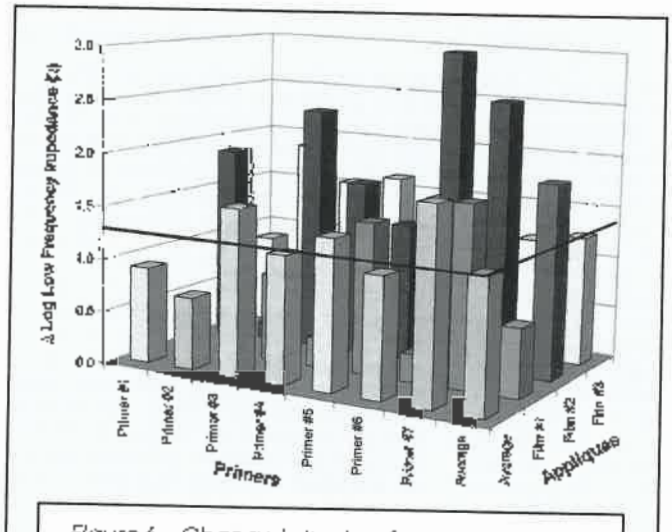

Figure 6—Change in the low frequency impedance as a result of 100 cycles of the cyclic corrosion test. In this figure, a low value (small change) represents a good coating system. The interior bars correspond to the individual primer/appliqué systems. The bars at the right are the average values for all primers for a given appliqué. The bars at the front are the average values for all three appliqués for a given primer. The corner bar with the heavy lines is the average of all material sets.

CONCLUSIONS

The in-situ corrosion sensor obtains equivalent EIS measurements to those obtained by the conventional remote electrodes/immersion approach. A distinct advantage of the sensor approach to the conventional approach is that EIS measurements can be taken under nonimmersed conditions, including salt fog, humidity, and laboratory or field ambient conditions. This flexibility allows the early stages of coating degradation to be monitored and allows comparison of different exposure conditions. Coatings and materials sets can be screened and selected based on quantitative EIS results instead of waiting for visual indications of severe coating degradation and substrate corrosion. In the study reported here, the cyclic corrosion test correlated very well with Florida beach exposure while the salt fog, humidity, and immersion tests showed very little correlation. Furthermore, by tracking coating degradation from the early stages, the data suggest that the 100-cycle corrosion test could be shorted by up to 40% without affecting the validity of the results.

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References

(1) Scully, J.R., *J. Electrochem. Soc.*, 136, 979 (1989).

(2) Tait, W.S., "Using Electrochemical Impedance Spectroscopy to Study Corrosion Behavior of Internally Coated Metal Containers," JOURNAL OF COATINGS TECHNOLOGY, 61, No. 768, 57 (1989).

(3) Scully, J.R., in *Corrosion Testing and Evaluation: Silver Anniversary Volume. ASTM STP 1000*, Baboian, R. and Dean, S.W. (Eds.), American Society for Testing and Materials, Philadelphia, PA, p. 351, 1990.

(4) Murray, J.N. and Hack, H.P., Corrosion90, Paper 140, NACE, Houston, TX, 1990.

(5) Mansfeld, F., Kendig, M.W., and Tsai, S., *Corrosion*, 38, 478 (1982).

(6) Davis, G.D., Dacres, C.M., and Krebs, L.A., *Materials Performance*, 39 (2), 46 (2000).

(7) Davis, G.D. and Dacres, C.M., "Electrochemical Sensors for Evaluating Corrosion and Adhesion on Painted Metal Structures," U.S. Patent 5,859,337 (January 12, 1999).

(8) Davis, G.D. and Dacres, C.M., "Portable Hand-Held In-Situ Electrochemical Sensor for Evaluating Corrosion and Adhesion on Coated and Uncoated Metal Substrates," U.S. Patent 6,054,038 (April 25, 2000).

(9) Davis, G.D., Dacres, C.M., and Krebs, L.A., "IDS-Based *In-Situ* Sensor for the Early Detection of Coating Degradation and Substrate Corrosion," Corrosion2000, Paper 275, NACE, Houston, TX, 2000.

(10) Krebs, L.A., Davis, G.D., and Dacres, C.M., "Monitoring Moisture Intrusion and Coating Degradation in the Field," Corrosion2001, Paper 1430, NACE, Houston, TX, 2001.

(11) Lyon, S.B., Thompson, G.E., and Johnson, J.B.,"Materials Evaluation Using Wet-Dry Mixed Salt-Spray Tests," STP 1133, ASTM, Philadelphia, PA, p. 20 (1993).

(12) Potschel, M., Jr., "SAE ACAP Division 3 Project: Statistical Evaluation of Accelerated Corrosion Test Results and Correlation with Two-Year, On-Vehicle Field Results," *Proc. 5th Automotive Corrosion & Prevention Conf.*, SAE, Warrendale, PA, p. 179, 1991.

(13) Skerry, B.S., Alavi, A., and Lindgren, K.L., "Environmental and Electrochemical Test Methods for the Evaluation of Protective Organic Coatings," JOURNAL OF COATINGS TECHNOLOGY, 60, No. 763, 97 (1988).

(14) Townsend, H.E., McClune, D.C., Neville, R.J., Granata, R.D., and Schumacher, W.A., "Progress by the Automotive and Steel Industries Toward an Improved Laboratory Cosmetic Corrosion Test," *Proc. 5th Automotive Corrosion & Prevention Conf.*, SAE, Warrendale, PA, p. 73, 1991.

(15) Appleman, B.R., "Predicting Exterior Marine Performance of Coatings from Salt Fog: Two Types of Errors," *J. Protective Coatings Linings*, October, p. 134 (1992).

(16) Agarwal, R. and Bell, J.P., *Polym. Prep. Am. Chem. Soc. Div. Polym. Mater. Sci. Eng.*, 73, 341 (1996).

(17) Agarwal, R. and Bell, J.P., *Polym. Eng. Sci.*, 38, 299 (1998).

(18) Zhang, X. and Bell, J.P., *J. Appl. Polym. Sci.*, 62, 1303 (1996).

(19) Zhang, X. and Bell, J.P., *Mater. Sci. Eng.*, A257, 273 (1998).

(20) Agarwal, R. and Bell, J.P., *J. Appl. Polym. Sci.*, 76, 875 (2000).

(21) Zhang, H., Davis, G.D., and Bell, J.P., "Formation and Properties of Spontaneously Polymerized Fluorocoatings on Aluminum," *Polym. Eng. Sci.*, 41, 1970 (2001).

(22) Hospadaruk, V., Huff, J., Zurilla, R.W., and Greenwood, H.T., *Trans. SAE* 87, 755 (1978).

(23) Ford Laboratory Test Method, BI-23-1, April 30, 1981.

(24) Holubka, J.W., Chun, W., and Dickie, R.A., *J. Adhes.* 30, 173 (1989).

(25) Davis, G.D., Thayer, K., Rich, M.J., and Dzal, L.T., "Inspection of Composite and Metal Adhesive Bonds with an Electrochemical Sensor," *J. Adhes. Sci. Technol.*, 16, 1307 (2002).

(26) Davis, G.D., Krebs, L.A., and Dacres, C.M., "Sensor to Detect Moisture/Degradation of Composites and Adhesive Bonds," *Proc. 46th Inter. SAMPE Symp.*, SAMPE, Covina, CA, p. 20 (2001).

(27) Microsoft Excel CORREL function.