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


INTRODUCTION

Evaluation of coating performance is important to both coating developers and end users who need to assess 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 perform the same as 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 quicker evaluation and screening of coatings.

Electrochemical impedance spectroscopy (EIS) has been used to detect coating degradation in the laboratory.23 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 artificial damage to the specimen even for short immersion times.4 A recently developed in-situ sensor allows EIS measurements to be acquired under ambient or test conditions and be used to predict coating performance before any visual deterioration.23,25 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 allows a comparison of the measurements under the same conditions, which can be used to compare the sensor's performance with other methods.26,27

In summary, EIS has been used extensively to evaluate coating performance in laboratory conditions.23 However, there is a need for a more practical method to evaluate coating performance under real-world conditions. The in-situ sensor developed by DACCO SCI, Inc. allows for the acquisition of EIS measurements under ambient or test conditions, providing a practical method to evaluate coating performance before any visual deterioration.23,25 This allows for a more accurate prediction of coating performance under real-world conditions, which can be used to improve the selection and application of coatings.26,27
A correlation of the differences in exposure to determine which laboratory tests best duplicate field exposure. Although such comparisons have been previously reported using visual, weight loss measurements, analysis of corrosion products, or other semi-quantitative or late-stage measurements, 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 sensors 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 that is permanently connected 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 use of the sensor in materials screening.

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 applying the load wires outside of the chamber for connection to the Gamry CP3 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 100 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 setup, because the specimen was already in equilibrium with the salt fog environment. No equilibration time was required. The cell was then emptied, the specimen 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. In this process, the panel is immersed in a monomer solution, observations, weight loss measurements, analysis 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. The exposure tests were: salt fog or spray (ASTM B 117), cyclic corrosion test, humidity exposure (ASTM D2247), and water immersion (ASTM D870).

The standard and most common accelerated test is salt spray, which is often specified but rarely corresponds well to service exposures. The salt fog exposure was 200 hr.

The other principal exposure is based on the Ford cyclic corrosion test that was developed for evaluation of the performance resistance of painted steel; the test development and procedures have been reported elsewhere. 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 by 4-7 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 (32°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.

In a separate test, a series of applicators and primers were evaluated as part of a materials screening process. Steel substrates were used. The applicated specimens were only subjected to the cyclic corrosion test. Here H2SO4 was used to lower the pH and represent 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 a resistant coupling agent, 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 test, 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/applicator specimens, measurements were taken with this schedule; for others, measurements were only taken before and after the complete exposure test.

Data were generally acquired 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 ceramics or adhesives, but this did not provide significantly more information than the simple 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
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very good coating remains capricious in nature (slope of 1, zero intercept) and it is therefore not possible to predict coating properties from high impedance at low frequencies. In contrast, a poor coating exhibits a sharp decrease in impedance at low frequencies. Detailed characterization of these coatings (not discussed here) indicates corrosion occurring under the coating.

By using the low frequency impedance, the performance of the coatings over the entire frequency range can be assessed. As an example, the low frequency impedance of the coatings in Table 1 is given in terms of the real and imaginary components. The results are shown in Figure 3. The data in Figure 3 show that the impedance of the coating is increasing with frequency, which is consistent with the expected behavior of a capacitive coating. The data also show that the coating impedance is decreasing with frequency, which is consistent with the expected behavior of an inductive coating.

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 is that it allows for the determination of the coating performance at the surface of the sample, without the need for an electrolyte. The data in Figure 3 show that the coating impedance is decreasing with frequency, which is consistent with the expected behavior of an inductive coating. The data also show that the coating impedance is decreasing with frequency, which is consistent with the expected behavior of an inductive coating.
very good coating remains capacitive in nature (slope of -1) in high frequency impedance), but with a bath (not shown) the capacity decreases with high frequency impedance. In contrast, a poor coating exhibits a sharp decrease in capacitance at low frequencies. Contamination with water and ammonium nitrate indicate a coating occurring under the coating.

By using the low frequency impedance, the performance of the coatings can be evaluated. For this type of coating, the sensitivity of the coating to the electrode to the defect is related to the total impedance of the coating. Thus, the sensitivity of the coating to the defect is the total impedance of the coating.

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 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 and the coating surface conditions can be correlated to determine the coating performance. The current 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 characteristics.

A common finding for almost all of the coatings tested was that they did well in high humidity and water immers. Because of the wide variation in the results, they were not considered and are not included in the discussion. The salt fog and cyclic corrosion test, on the other hand, allowed a direct comparison between highly protective coatings and poor coatings.

The final low frequency impedance for a series of coatings is the cyclic corrosion test 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 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 correlation coefficients for the different exposure conditions. Included are correlations with the humidity and immersion tests, as well as intermediate tests. The matrix shows the correlation coefficients that one would expect to see for the data sets shown. The majority of the correlation coefficients are the average values for all coatings for a given test. The second row are the average values for all coatings for a given test. The third row are the average values for all three tests for a given test. The correlations between the data sets are the average of all test conditions.

CONCLUSIONS

The EIS measurements show correlation to those observed using the conventional remote electrodes and immersion apparatus. A distinct advantage of this method is the sensor approach to the conventional approach is that EIS measurements can be taken under nonimmersed conditions, including salt fog, humidity, and field conditions. This flexibility allows the testing of coatings that are not environmentally stressed. For example, the measurements can be taken outside the field condition. 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 measuring the coating degradation from the early stages, the data suggest that the 100-cycle corrosion test could be shortened by up to 40% without affecting the validity of the results.

ACKNOWLEDGMENTS

We would like to thank Patricia Johnson and Louis McDowell of NASA and Joe Curran of Dynatec for help with the beach exposures and Jim Bell of the University of Connecticut for supplying the compartmentalized test systems. We would also like to thank Ray Dickie for insight into the Ford cyclic test. We acknowledge the helpful assistance of Craig Beck and Tom Long on the running of the laboratory tests. This work was funded in part by NASA under contract NASS-99083.
June 2002 Subcommittee Reports of ASTM Committee D01

The summer meeting of the American Society for Testing and Materials (ASTM) Committee D01, on Paint and Related Coatings, Materials, and Applications was held June 16-19, 2002 at the Wyndham Philadelphia at Princeton Hotel, Philadelphia, PA.

Highlights

Two significant highlights from this meeting were (1) discussions on how one can make the Memorandum of Understanding (MOU), signed in 2000 by E. A. Przech for D01 and J. P. Benches for ISO/TC 35, truly functional, and (2) the scarcity of representatives from many major paint manufacturers. This can be illustrated by comments made regarding the D01.27-23 meeting. One attendee stated that "the paint and coating industries have a standard that does not reflect how we work, or how we try to stay with ISO/TC 35 (9/97). This is a difficult area and we do not want to beRules that are not in our opinion. Also, he said, "I did not see the condition of our members, or the lot of expertise or experience at this meeting. I think this would be interest in a particular ES coatings guide. We may want to consider recruiting other specialists to participate."

Interactions between D01 and the U.S. Environmental Protection Agency (USEPA) continues. At the D01.21.13 meeting, the USEPA will issue new regulations to require the reporting of HAPs and VOCs at points tested on indoor parts as a result of the RCRA.

If you're not a D01 member, contact T. S. Przylucki (tsp@american.org). He will e-mail the minutes you request.

Dates and Locations of Future Meetings

Jan. 12-15, 2003 - Ft. Lauderdale, FL
June 8-11, 2003 - Cleveland, OH
Jan. 11-14, 2004 - Ft. Lauderdale, FL
June 15-16, 2004 - Las Vegas, NV
Jan. 9-12, 2005 - Ft. Lauderdale, FL
June 13-16, 2005 - Baltimore, MD

DIVISION I ADMINISTRATION

Subcommittee D01.06 International Liaison

J. C. Weaver, Chair

I. Weaver wrote that his official report will include his letter to have the D01/ISO/TC 35 Coordinators be included in ASTMUS, and a new contact W. Stickel will not be authorized to test why ISO/TC 35, publication in their new standards, may be unduly influenced by their standards and the responsibility of ISO/TC 35. Weaver wrote that D01/ISO/TC 35 will be working with D01 next June in Cleveland. He said ISO/TC 35 has six working groups: SC 1, SC 2, SC 9, SC 10, SC 12 and SC 14. He said the National Association of Corrosion Engineers (NACE) and ASTM has TAG affiliations with SC 12 and SC 14. Weaver reported that D01/ISO/TC 35 is working on the "Paints and Varnishes" Induction Kit, which does not require an ASTM commitment. G. Waer will contact equipment suppliers to determine their position. The subject will be discussed at the D01.90 meeting in January.

Subcommittee D01.08 Environmental Concerns

J. C. Berry, Chair

W. Clinton reported on the VOC trade-in for emission reduction, which will be held only once this year, compensated by the Federation of Societies for Coatings Technology and held during their International Coating Exhibition (ICE). E. A. Przech reported no new programs have been made on a new edition of Manual 4 "Determination of VOC in Paints..." (To upgrade it to include information on regulations for hazardous air pollutants) Voluntary programs are needed to help and editor got the program started. S. Brunel, of France, presented their work in determining the carbon values from volatile Emission Control. In a D01.21 meeting, he announced, based on the results obtained at their laboratory, they will be working on improving the test method. J. C. Berry reported D01.51 hopes for "juxtaposition" of meetings with the Mid-year meeting in June. Saltman was not present to report on the status of the Agency's programs on hazardous air pollution regulations for paint use facilities. It is clear that this was not possible. However, the Agency has missed the first deadline established in the 1990 Act. The NACE and ASTM has TAG affiliations with SC 12 and SC 14. Weaver reported that D01/ISO/TC 35 is working on other standards, which will allow more time for the Federal rules to be completed and avoid 30 new (and likely different) requirements gains from the 30 states.

R. J. Nilner reported EPA will not publish a "Paints Production Waste Labeling." Until after NQCA was primarily responsible for persuading EPA that such a requirements was unnecessary. He reported the EPA's Reactivity Reporting Workshop Group, held in its 4th year, hopes to publish an Advanced Notice of Proposed Rulemaking (ANPR) within the next year. The ANPR will identify the alternatives which have been identified by the Agency's Memorandum of Understanding with the U.S. EPA, and then to develop a joint standard that will be of assistance to the Agency.

ISO has published the standard dealing between ASTM and ISO test methods developed in D01 in their most recent volumes. The standard has not been made by D01 on whether to proceed with publishing the standard in the ASTM volumes in this time due to the many technical differences between the methods.

K. S. Silva presented an agenda outlining ballot actions taken in ISO/TC 35 since the January 2002 meeting. D. Bredero reported the specifics, in each event, each ballot received a standard that it has established as its final standard for those industries. The next step for EPA is to compare the work. The States and EPA are working to ensure that will allow more time for the Federal rules to be completed and avoid 30 new (and likely different) requirements gains from the 30 states.

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