EMPLOYING ELECTROCHEMICAL IMPEDANCE IN PREDICTING CORROSION EVENTS

By **Tony Gichuhi**,
Andrew Balgeman,
Shonda Prince,
Caitlin Wagner,
Shannon O'Brien,
and **Amanda Adams**
HALOX, USA

In 1990, the federal highway authority gave the I-35W Mississippi River Bridge a rating of "structurally deficient," citing significant corrosion in its bearings. The need for better screening and detection of corrosion in our infrastructure was heightened by the collapse of this bridge in Minneapolis in 2007. Predicting corrosion events or coating failures and pitfalls can be done using non-invasive electrochemical techniques such as electrochemical impedance spectroscopy (EIS). In this article, EIS is used to monitor the performance of direct-to-metal (DTM) coatings on steel over a period of time. The authors also attempt to correlate EIS spectral responses to well known accelerated techniques such as ASTM B117 salt spray and Prohesion G85A5.

Presented at the 2011 CoatingsTech Conference, sponsored by ACA, March 14-16, in Rosemont, IL.

INTRODUCTION

Significant effort and money is expended each year in fighting corrosion. The costs associated with combating corrosion in a variety of fields from oil and gas pipelines to infrastructure to transportation (land, air, sea, and space) have forced scientists to innovate faster and more accurate techniques to study corrosion processes. In this regard, much has been done in researching alternative accelerated corrosion methods aside from the traditional salt spray and cyclic corrosion tests which can allow scientists to predict and identify corrosion long before it leads to catastrophic events. The ability to probe coatings in service using electrochemical techniques represents a divergence from the norm. Protective coatings are designed to withstand corrosion and provide some safety guarantee that the coating will provide adequate protection for a period of time. While it is true that the time to failure

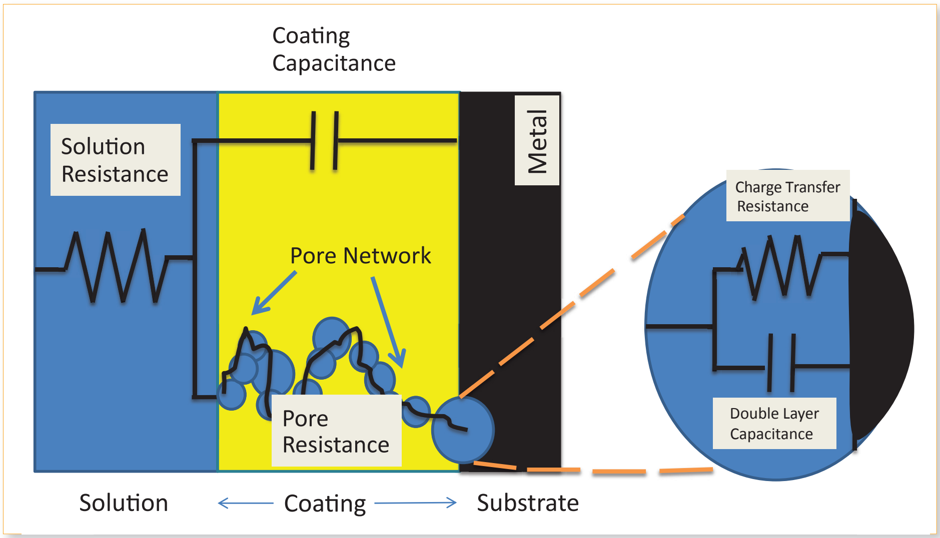


Figure 1—Schematic of pore network and pathway for a coating applied to a metal substrate.

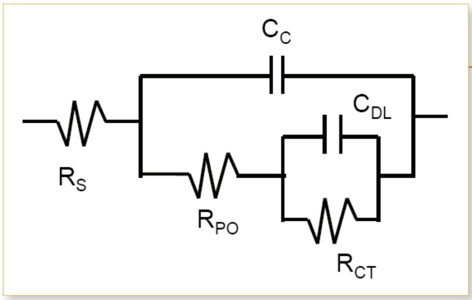


Figure 2—Equivalent circuit diagram for a damaged coating.

is often arrived at by trial and error, it stands to reason that the ability to accurately screen and predict which coatings will perform well and which coatings will fail during service is of paramount importance. Several electrochemical techniques are employed today to interrogate coatings and identify potential defects or pitfalls.

In this article, the authors attempt to interrogate the electrochemical impedance of various direct-to-metal (DTM) waterborne coatings and use impedance changes as a determinant of which coatings will provide the best protection in a highly corrosive environment. The electrochemical impedance allows one to accelerate the corrosion process and amplify the impact of corrosion, and provides a sensitive measurement for corrosion occurring underneath a coating.[1] Electrochemical impedance rapidly provides information on the physical and electrochemical behavior of the coating in question. While EIS relies on the permeability of the coating to an electrolyte necessary to initiate the corrosion processes, it can also provide information on the adhesion characteristics of the coating. Good wet adhesion is paramount to good corrosion protection. Changes in a coating will be apparent in EIS long before any visible changes such as blistering can be observed.[2] Several features in the electrochemical response can be used to provide information on the deterioration or lack thereof of the coating. For instance, changes in the overall impedance can be driven by changes in the pore resistance. For example, the pore resistance in a coating will vary from one corrosion inhibitor to another depending on their ability to inhibit the corrosion processes. Changes in the coating capacitance indicate that the coating is absorbing water and is therefore more likely to corrode as the water migrates to the metal substrate. By measuring the electrical behavior of the coating sandwiched between the substrate and the solution, we can track the corrosion process on a micro scale. Increasing the exposure time of the coating to the solution allows water to penetrate through the pore network, leading to an increase in corrosion. A high impedance measurement, coupled with good adhesion, is desirable for any anticorrosive coating.

The objectives of this research were fourfold:

- Determine if EIS can predict early coating failure, i.e., can we use EIS to predict coating performance in a corrosive environment?
- Determine if there is a correlation between the EIS response and salt spray and Prohesion cabinet results
- Determine if the coating deterioration or failure mode via EIS mimics the cabinet test results
- Determine if, by using EIS, we can shorten the screening time of multiple DTM coatings designed for anticorrosion purposes.

The resistance to the transport of water and oxygen through the coatings pores is referred to as the pore resistance.[2] This pore resistance can be magnified or attenuated by the anodic and cathodic activity of corrosion inhibitors present in the film. We can correlate changes in the coating to the changes in the impedance (Z). As shown in *Figure* 1, the coating sandwiched between the metal substrate and the electrolyte can be represented by an electrical circuit. Equivalent circuit modeling (see *Figure* 2) is used to determine the various electrochemical elements of the coating such as coating capacitance (C_c), pore resistance (R_{po}), solution resistance (R_s), coating double layer capacitance (C_{dl}), and charge transfer resistance (R_{ct}).

This article highlights research aimed at identifying which coatings will provide good corrosion resistance by screening more rapidly with EIS. EIS will be able to save time to screen these coatings using accelerated corrosion test cabinets. Our desire is to be able to quickly predict the good

Table 1—Waterborne Direct-to-Metal Coating Matrix

System	Description (DTM)	Type	pH	KU Visc.	ICI Visc.	Weight Solids	Volume Solids	VOC (g/L)
A	Coating A	Acrylic Gloss DTM	9.22	59.4	0.3	46.3	34.8	222
B	Coating B	High Solids Styrene Acrylic	7.46	63.1	0.9	56.5	43.1	158
C	Coating C	Acrylic Dispersion	9.26	93.0	0.7	41.1	28.0	356
D	Coating D	Acrylic DTM	8.79	68.6	0.6	47.2	36.7	118
E	Coating E	Vinyl Acrylic DTM	7.83	64.3	0.8	42.5	27.7	123
F	Coating F	High Gloss Acrylic	8.87	67.9	0.8	44.7	33.7	212
G	Coating G	High Gloss DTM	9.46	57.6	1.4	40.6	28.9	258
H	Coating H	Acrylic DTM Enamel	8.12	79.3	1.4	43.9	41.9	30
I	Coating I	Acrylic Latex	8.43	51.5	0.5	45.6	37.4	240
J	Coating J	High Gloss Acrylic DTM	9.38	80.4	0.3	46.3	34.9	103
K	Coating K	High Performance Acrylic Gloss	9.25	88.9	1.4	51.0	38.5	200

and bad coatings among various waterborne DTM coatings applied to untreated low carbon steel and exposed to salt solutions. EIS responses were compared to salt spray and Prohesion results after a period of time. A summary of the DTM coatings evaluated is provided in *Table* 1. For the sake of simplicity, only room temperature air-dried coatings were considered in this study. EIS was conducted at room temperature although the influence on temperature (thermal cycling) on impedance and pore resistance cannot be ignored. No corrosion inhibitors were included in any of the coatings studied. A common flash rust inhibitor was included in all the systems to overcome the flash rusting issue. No attempts were made to optimize the DTM formulations provided by various resin suppliers. In other words, the authors tested the DTM paint formulations without making further adjustments to the supplied formulations.

The actual DTM formulations are not included here. Following coating application, all paints were air dried under normal laboratory conditions (20–25°C, 45–55% RH) for one week. After air drying, all panels were subjected to the EIS electrolyte solution at the same time for the same period. As the authors were interested in being able to predict the corrosion processes faster using EIS, salt spray and Prohesion tests were also employed and panels compared periodically. The problem with cabinet tests, of course, is that they require a long time. Formulators are well aware that no laboratory test method can accelerate or completely mimic the deleterious effects of atmospheric exposure. However, EIS can observe the deterioration of the coating long before visual defects appear.

EXPERIMENTAL

Paint Formulations and Test Substrates

All DTM paint formulations were made according to their manufacturer's guideline formulations. In this study, 11 formulations (labeled A through K) of acrylic, styrene, or vinyl acrylic polymers were included. No corrosion inhibitors were included in the formulations tested. A flash rust inhibitor, 0.5% of total formula weight of a 10% aqueous $NaNO_2$ solution, was used in all cases to ensure the panels did not flash rust and skew the results. Several physical properties such as pH, KU viscosity, ICI viscosity, weight, and volume solids as well as VOC were noted.

ACT (ACT Test Panel Technologies, Hillsdale, MI) dull matte finish cold rolled steel, untreated 1008 panels were the primary substrate for this research. Panels were wiped with MEK prior to the coating application using draw down bars. Panels were visually inspected for flash rusting after one hour. Due to the differences in viscosity in the formulations, a range of applicator bars was used to ensure that the final dry film thicknesses all fell between 2.5–3.0 mils (62.5–75 microns).

All coatings were air dried for seven days before beginning the EIS measurements. All coatings were tested in duplication. All EIS panels were unscribed.

Figure 3—Electrochemical impedance spectroscopy setup.

Electrochemical Impedance Spectroscopy

A Gamry PC3 with ECM8-channel multiplexer, running the Gamry Framework version 4.30 was used. A cylindrical cell filled with the electrolyte with an exposed surface area of about 14 cm^2 was employed. A three electrode—including the substrate— electrochemical cell assembly was used as shown in *Figure* 3. The electrolytes chosen were 5% NaCl and 0.05% NaCl/0.35% NH_4SO_4 to mimic the cabinet solutions. EIS curves were obtained after one hour (initial), 24 hr, 48 hr, and 168 hr. Prior to obtaining EIS curves, the open-circuit potentials (Eoc) were measured after making contact with coated samples exposed to the electrolyte. The EIS experiments were then run after samples had reached a steady state signaled by a stable open circuit potential (Eoc).[3]

Cabinet Accelerated Corrosion Tests

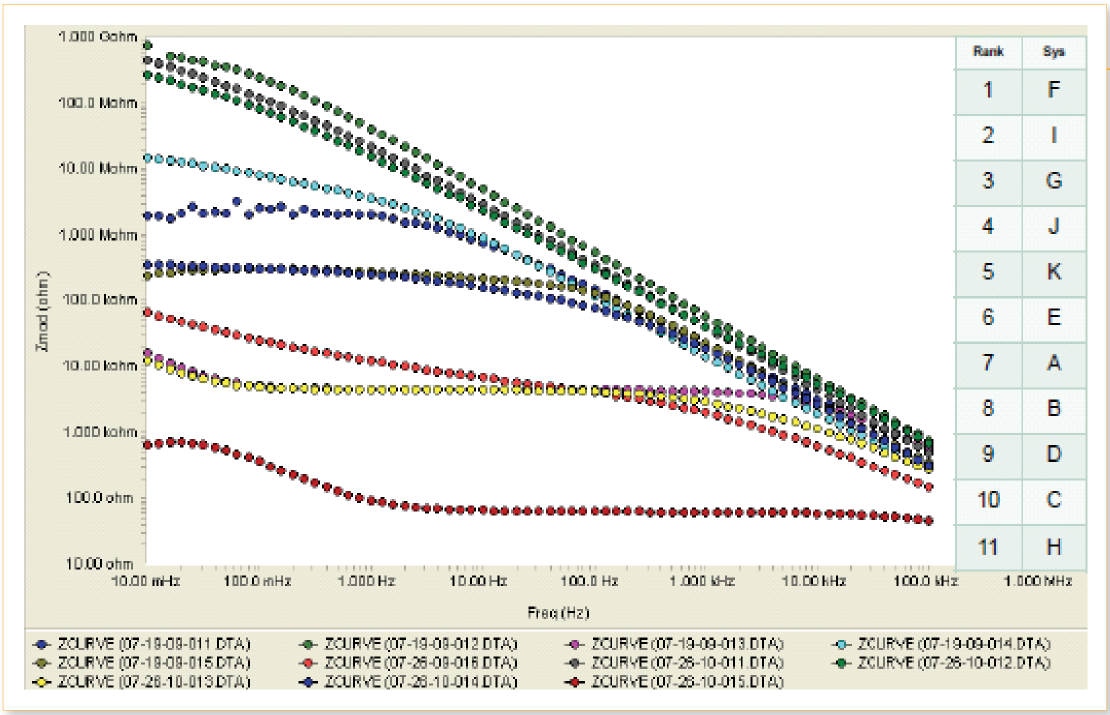
In addition to EIS testing, ASTM B117 salt spray cabinets (5% NaCl, 35°C, 100% RH) were used on a different set of scribed test panels. ASTM G85A5 Prohesion experiments were also run to correlate the response from EIS. In Prohesion, the samples are subjected to a 0.05% NaCl and 0.35% NH_4SO_4 electrolyte. Whereas salt spray is a static test, Prohesion is cyclic, incorporating a one-hour salt mist at ambient temperature and a one-hour drying stage at 35°C.

RESULTS AND DISCUSSION

Electrochemical Impedance Performance

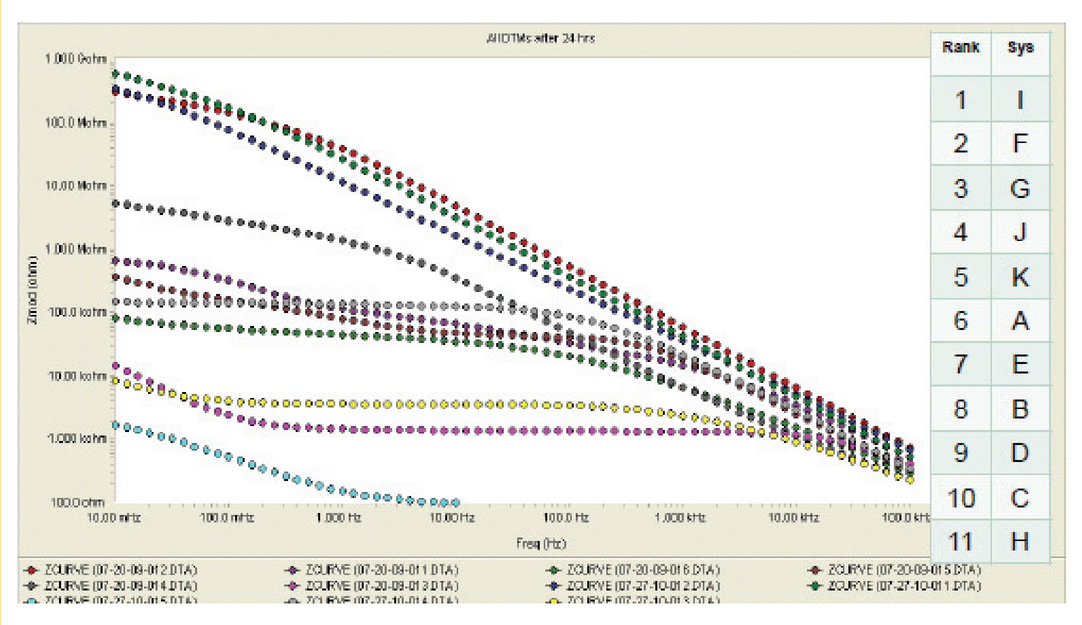
Eleven DTM coatings were evaluated using EIS. Bode plots were obtained after the initial setup (one hour), 24, 48, 72, and 168 hr later. All 11 coatings were compared on a single Bode plot. The impedance at low frequency (0.1 Hz) was used as the key performance indicator for each coating. A high impedance value was indicative of a superior performing coating with good barrier properties. The impedance was also monitored as a function of exposure time. Impedance responses were tracked for the best performing coatings and compared to accelerated cabinet corrosion results. Overall, the best performing systems in EIS were also the best performing coatings in salt spray and Prohesion. For interpretation purposes, a rough impedance qualification scale was used to rank the best coatings. The resistive properties can be ranked as follows: $> 10^8$ Ω.cm (excellent); $10^7 – 10^8$ Ω.cm (good); $10^6 – 10^7$ Ω.cm (fair); and below 10^6 Ω.cm (poor).[4]

EIS results indicate that three of the 11 coatings (F, I, and G) showed very good resistance after one-hour immersion. This data indicates that the coatings are highly resistant to electrolyte and ionic penetration, particularly in the case of direct-to-metal enamels where such properties are desirable.[5] *Figure* 4 shows the initial Bode plots for all 11 systems. The low frequency (0.1 Hz) impedance was used to rank the 11 coatings. After 24 hr, Systems



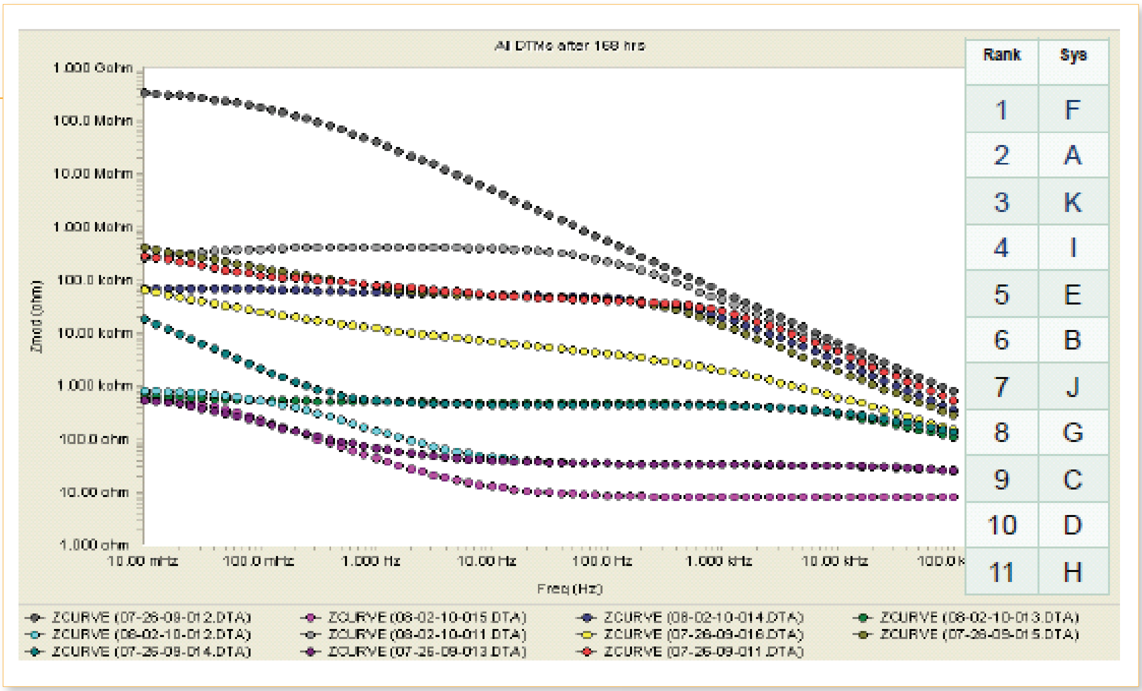
Rank	Sys
1	F
2	I
3	G
4	J
5	K
6	E
7	A
8	B
9	D
10	C
11	H

Figure 4—Initial Bode plots for all DTM coatings.



Rank	Sys
1	I
2	F
3	G
4	J
5	K
6	A
7	E
8	B
9	D
10	C
11	H

Figure 5—Bode plots for all DTM coatings after 24 hr.



Rank	Sys
1	F
2	A
3	K
4	I
5	E
6	B
7	J
8	G
9	C
10	D
11	H

Figure 6—Bode plots for all DTM coatings after 168 hr.

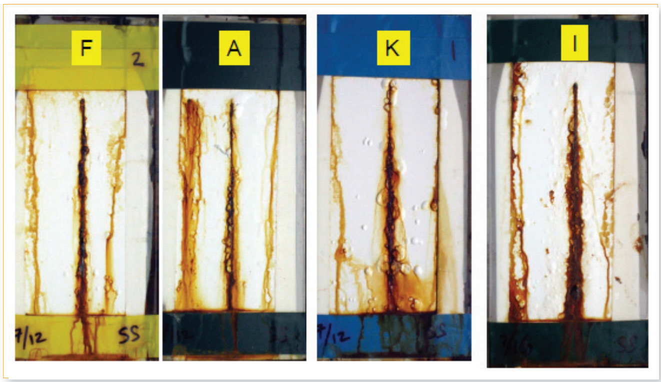


Figure 7—Neutral salt spray data after 504 hr.

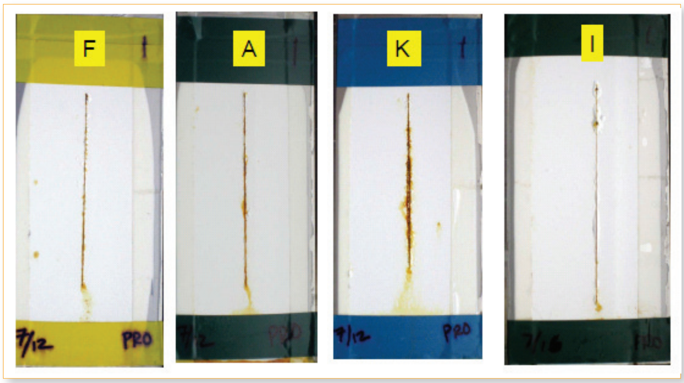


Figure 8—Prohesion data after 504 hr.

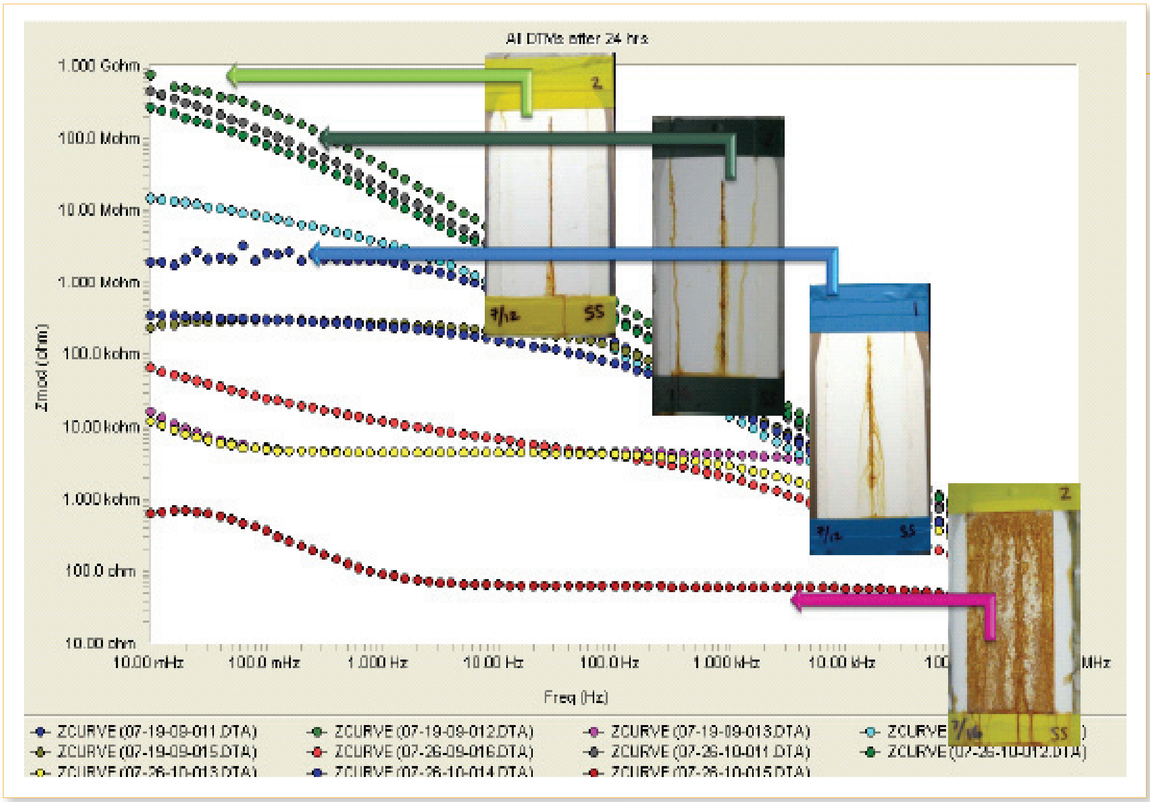


Figure 9—Overlay of EIS response and salt spray results after 24 hr.

I, F, and G showed the best performance once again. These coatings registered impedances between 100 MΩ and 1 GΩ. See *Figure* 5.

Figure 6 shows Bode plots for all 11 systems after 168 hr of immersion. Once again, the low frequency impedance was used to determine the best coatings. System F showed the best performance after one week. This was the only coating whose impedance was still well above 10^8 Ω.cm. The rest of the coatings were below 10^6 Ω.cm.

Cabinet Accelerated Corrosion Results

Figure 7 shows accelerated corrosion results following 504 hr of neutral salt spray exposure (ASTM B117). Systems F, A, K, and I showed the best performance after the three weeks of exposure correlating well to the EIS response after 168 hr. Coating F was by far the best performing coating in terms of corrosion undercutting and blister resistance.

Figure 8 shows accelerated corrosion results following 504 hr of Prohesion exposure (ASTM G85A5). Coating F showed the best overall performance after the three weeks of Prohesion exposure correlating well to the EIS response after 168 hr and salt spray response after 504 hr.

The authors attempted to overlay cabinet accelerated corrosion results to the EIS responses after 24 hr as a means to predict the best and worst performing coatings in a quick manner. It is evident that the coatings that showed the highest corrosion resistance in salt fog and Prohesion also demonstrated high impedance in EIS. The impedance rankings shown in the EIS curves after 168 hr matched up well with the cabinet results, supporting the assertion that EIS can be used to predict corrosion behavior in these types of coatings.

Correlation of Cabinet vs. EIS Response

The authors attempted to correlate cabinet results to EIS results. Although correlation appears to exist between the results of electrochemical impedance and cabinet test methods, one can only conclude that one system is more degraded than the other by ranking these coatings relative to one another. The correlation is determined by comparing the spread of rust along the scribe for scribed panels. The scribed area is deliberately scored (mechanical damage) to induce anodic corrosion and study the adhesion properties of the coating. Cabinet tests do not provide quantitative data about the coating compared to EIS. The data can only be used for a limited range of applications. Therefore, different applications require different test methods.[6] *Figure* 9 shows the correlation overlay of EIS responses and salt spray results after 24 hr of exposure. One can conclude from these data that the best system in EIS also shows the least amount of corrosion spread from the cabinet test. The worst coating in the cabinet test was quickly confirmed by EIS. The degradation mechanism of these DTM coatings can be better understood by employing several other conventional tests useful for the quantification of the physicochemical properties of the coatings (for example, tensile strength, elongation, hardness, and resistance against impact, abrasion, temperature, and chemicals). These tests have proven to be paramount in determining which coatings are suitable for a specific environment, based on reliable quantitative data.[6]

CONCLUSIONS

EIS is a useful and versatile electrochemical technique for studying DTM coatings over steel substrates. The EIS response tracked well with actual cabinet corrosion tests. In this article, we considered coated samples over cold rolled steel and how we can predict and rank which paints would perform well in accelerated corrosion cabinets such as salt spray and Prohesion chambers. We used the low frequency impedance (Z) response as an indicator of the coating's anticorrosion performance and showed agreement between coatings with high impedance after one week and those with good corrosion resistance after three weeks in the corrosion cabinets. The best overall coating performance was realized within the first 24–48 hours of EIS screening. The worst performing coating was also identified within the same timeframe. In conclusion, EIS not only acts as a detector of a coating's quality, but it can also be used as a predictor of the coating's long-term performance. Finally, as many authors have confirmed, the relatively short period of testing with EIS provides reliable data for long-term coating behavior.[7-14] CT

References

1. Electrochemical Tests—http://corrosion-doctors.org/Electrochem/Techniques. (Accessed website on December 12, 2010.)
2. Loveday, D., Peterson, P., and Rodgers, B., "Evaluation of Organic Coatings with Electrochemical Impedance Spectroscopy: Application of EIS to Coatings," *JCT CoatingsTech,* 1 (10), 88-93 (October 2004).
3. Loveday, D., Peterson, P., and Rodgers, B., "Evaluation of Organic Coatings with Electrochemical Impedance Spectroscopy: Protocols for Testing Coatings with EIS," *JCT CoatingsTech*, 2 (13), 22-27 (February 2005).
4. Bierwagen, G., Tallman, D., Li, J., and He, L., "EIS Studies of Coated Metals in Accelerated Exposure," *Prog. Org. Coat.*, 46, 148 (2003).
5. Dubowik, D.A. and Lucas, P.A., "A Novel Water-borne Epoxy Resin for Zero-VOC, Two-Component Coatings," *J. Oil & Colour Chemists' Assn.,* 84, A3, 126 (2001).
6. Sonke, J. and Bos, W.M., "Scientific Methods for Qualification and Selection of Protective Coatings," *J. Protective Coatings & Linings* (June 2008).
7. Mansfeld, F. and Kendig, M.W., *Electrochemical Impedance Tests for Protective Coatings, Laboratory Corrosion Tests and Standards,* p. 122-142, 1985.
8. de Wit, J.H.W., van der Weijde, D.H., and Ferrari, G., Chapter 19 in *Organic Coatings of Corrosion Mechanisms in Theory and Practice,* Second Edition, Marcel Dekker, 2002.
9. van Westing, E.P.M., "Determination of coating performance with impedance measurements," PhD Thesis, TU Delft, The Netherlands (1992).
10. Amirudin, A. and Thierry, D., "Application of electrochemical impedance spectroscopy to study the degradation of polymer-coated metals," *Prog. Org. Coat.,* 26, 1-28 (1995).
11. Kendig, M., Mansfeld, F., and Tsai, S., "Determination of the Long Term Corrosion Behavior of Coated Steel with AC Impedance Measurements," *Corr. Sci.,* 23, 317 (1983).
12. Kendig, M., Jeanjaquet, S., Brown, R., and Thomas, F., "Rapid Electrochemical Assessment of Paint," *J. Coat. Technol.*, 68, No. 863, 39 (1996).
13. Murray, J.N. and Hack, H.P., "Testing organic architectural coatings in ASTM synthetic seawater immersion condition using EIS," *Corrosion*, Vol. 48, No. 8, p. 671-685 (1992).
14. Kendig, M. and Scully, J., "Basic Aspect of Electrochemical Impedance Application for the Life Prediction of Organic Coatings on Metals," *Corrosion*, NACE, January (1990).

AUTHORS

Tony Gichuhi, **Andrew Balgeman**, **Shonda Prince**, **Caitlin Wagner**, **Shannon O'Brien**, and **Amanda Adams**, HALOX®, USA, a div. of Hammond Group, 1326 Summer St., Hammond, IN 46320; tgichuhi@halox.com.