ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF ZINC-RICH ORGANIC COATINGS ON STEEL

D. J. Frydrych and G. C. Farrington
Department of Materials Science
University of Pennsylvania
Philadelphia, Pennsylvania 19104

H. E. Townsend
Homer Research Laboratories
Bethlehem Steel Corporation
Bethlehem, Pennsylvania 18016

Abstract

Zinc-rich organic coatings are used in a wide range of applications to impart corrosion protection to steel. In this study coatings comprised of a 50 volume percent zinc-rich primer and an inorganic pretreatment layer were examined with electrochemical impedance spectroscopy during exposure to non-deaerated 0.5 N NaCl. The effects on the protective properties resulting from the pretreatment layer and from electrical post-treatment of the coating by corona discharge are reported. The data provide information about the interaction of the primer and the pretreatment, the mechanism of corona discharge treatment, and the resulting corrosion mechanisms. Impedance spectra recorded as a function of time show the breakdown of the protective properties of the coating which eventually leads to corrosion of the steel substrate.

Background

Zinc-rich organic coatings are used in a wide range of applications to impart corrosion protection to steel. In the automotive industry, a widely used coated-steel product is known as Zincrometal\textsuperscript{R} (1). The Zincrometal coating system consists of a basecoat called Dacromet\textsuperscript{R} and a topcoat called Zincromet\textsuperscript{R}. Dacromet is a water-based pretreatment consisting mainly of zinc dust and chromic

\textsuperscript{R}Zincrometal, Zincromet and Dacromet are registered trademarks of Metal Coatings International, Inc.
acid. Zincromet is a solvent-based zinc-rich primer consisting of approximately 50 volume percent zinc dust (85 weight percent) contained in a thermoplastic phenoxy resin. The total thickness of the coating is 10 to 13 microns.

Despite its widespread use in the automotive industry there is very little information in the literature describing the corrosion mechanism of Zincromet. The coating is reported to provide excellent barrier protection for steel but a low level of galvanic protection which permits rusting of the steel where it is exposed (2). It was recently reported that subjecting the coating to a high voltage treatment by corona discharge significantly increases the galvanic activity (3,4). In this study the effects on the protective mechanisms of the coating resulting from the Dacromet pretreatment and from electrical post-treatment by corona discharge are examined with electrochemical impedance spectroscopy (EIS).

Experimental

The zinc-rich primers were prepared by mixing zinc dust (St. Joe's, Grade 560, 5 μm average particle size), phenoxy resin (Shell Eponol®, #55-L-32), and an anti-settling agent in relative amounts to obtain a zinc pigment volume concentration of 50 percent. Dacromet (Metal Coatings International, Inc.) was applied onto alkaline-cleaned DQS K cold-rolled steel panels by dip-coating to give a thin coating containing approximately 0.03 mg/cm² total chromium. The Dacromet was given an initial cure by heating the panels to a peak metal temperature of 150 °C. The primers were applied with a wire-wound draw bar to Dacromet-pretreated steel and alkaline-cleaned steel and cured at a peak metal temperature of 260 °C. The thickness of the coatings was approximately 12 μm, as determined by a magnetic thickness gauge. Some samples of the primer on Dacromet-pretreated steel were electrically post-treated by corona discharge. Details of the corona discharge treatment have been described previously (3,4).

EIS measurements were conducted using either the system shown in Figure 1, or a similar configuration comprised of a Solartron 1250 Transfer Function Analyzer (TFA), Solartron 1286 Electrochemical Interface (EI), and an IBM PC/XT to control both the TFA and the EI. The experiments were conducted in unstirred, non-deaerated 0.5 N NaCl, pH = 6, in the potentiostatic mode at the corrosion potential using an AC voltage of 10 mv (rms). All
potentials were measured versus the saturated calomel reference electrode.

Results and Discussion

An electron micrograph of the surface of the Dacromet pretreatment layer on steel is shown in Figure 2. This sample was cured at the final peak metal temperature of 260 °C. The micrograph shows that Dacromet consists of a rather random array of individual and clumped zinc particles distributed on the steel surface. Careful examination of particle to particle and particle to steel interfaces shows that a thin film is binding the particles to each other and to the substrate. Scanning Auger analysis of a particle and an adjacent flat area showed that a film comprised mainly of chromium and oxygen covers both surfaces. A sputter depth profile of the two regions indicated that the thickness of the film is on the order of 1000 Å. It may be thicker at the interfaces where it is visible in Figure 2 due to wetting of the particles by the chromic acid solution.

In Figure 3 an electron micrograph of the surface of the primer applied on Dacromet-pretreated steel is shown. The surface is quite rough and many pores are visible which extend at least a short distance into the coating. A micrograph of a polished cross-section of the coating is shown in Figure 4. The particles in the primer are well-dispersed and there are no signs of settling. The Dacromet layer cannot be distinguished from the primer.

Bode plots (log |Z| and phase angle versus log w, where |Z| is the magnitude of the impedance and w is the angular frequency, rad/s) are shown in Figures 5a and 5b for the primer on cleaned steel, and the primer on Dacromet-pretreated steel with and without corona discharge (CD) treatment. The impedance spectra were recorded after one hour immersion in the electrolyte.

The corrosion potential of the primer on steel was -0.961 V. In the same electrolyte after one hour immersion, the corrosion potentials of steel and zinc sheet were -0.696 V and -1.050 V, respectively. Therefore, there was electrical contact between the steel and zinc particles in the primer. The magnitude of the impedance was very low for the primer on steel compared to the other samples. The phase angle plot shows a broad, gradual transition from an angle of 45 degrees at high frequencies to about 20 degrees at low frequencies. This behavior is probably due to the rough, porous structure of the primer which would give rise
to a wide distribution of time constants for the corrosion process. This observation, coupled with the low magnitude of the impedance, suggests that the primer itself may not be a good barrier to penetration by the electrolyte.

The largest impedance was recorded for the primer applied to Dacromet-pretreated steel. The corrosion potential fluctuated randomly around -0.57 V after one hour of exposure to the electrolyte. This indicates that there was no significant electrical contact between zinc particles in the primer and the steel substrate and the system had not yet reached a steady state. The impedance response is capacitive at all frequencies which is characteristic of an intact, insulating barrier.

In Figure 6 Bode plots are shown for Dacromet-pretreated steel, with no primer applied, after one hour immersion in the electrolyte. The sample had been cured to the final peak metal temperature of 260 °C. The corrosion potential was -0.850 V which indicates that zinc in the Dacromet was in contact with the steel substrate and the electrolyte. The magnitude of the impedance is large so the electroactive area must be small. One explanation is that zinc, and possibly steel, are exposed through very fine cracks or pores which are present in the thin chromium oxide film covering the surface. The high frequency capacitive response (phase angle = 90°) would then characterize the intact part of the film, which must be inert, and the middle and low frequency region would characterize processes occurring within the pores and at the exposed metal surface.

This description would also explain the poor galvanic and excellent barrier properties reported for the primer applied onto Dacromet-pretreated steel. The chromium oxide film would prevent zinc particles in the primer from making direct electrical contact with the steel, rendering a galvanic mechanism impossible. However, the primer is a second barrier between the steel and the environment which can limit access of corrosive species to defects present in the Dacromet. This combined effect accounts for the insulating properties of the coating as measured by the impedance technique.

The magnitude of the impedance of the primer applied to Dacromet-pretreated steel, with corona discharge treatment, is intermediate to the other two coatings (Figure 5a). The corrosion potential was -0.997 V which indicates that after corona discharge treatment zinc particles are electrically contacting the steel. The impedance is characteristic of a parallel RC circuit,
having a capacitive response at high frequencies and a frequency-independent resistive response at low frequencies.

One explanation for this behavior is that holes are formed through the primer and the chromium oxide film by corona discharge treatment which expose zinc particles in the Dacromet. In the presence of an electrolyte the holes become ionically conductive paths. In this case the resistive component would be a pore resistance and the capacitance would characterize the intact part of the coating. Another possibility is that corona discharge treatment has formed electronic paths between zinc in the primer and the steel substrate. To investigate this possibility, electrical impedance measurements of the primer on Dacromet-pretreated steel were performed before and after corona discharge treatment. The electrical contact to the coating was made by applying slight pressure to indium foil. The foil is very soft and formable and allowed good contact to be made, but insured that porosity effects would be eliminated. The results are shown in Figure 7. Before corona discharge treatment the coating is insulating and the response is totally capacitive. After the treatment the response is totally resistive, with a resistance on the order of 10 ohm-cm². This shows that electronically conductive paths are formed from the surface of the coating, through the primer and the Dacromet layer, to the steel substrate. Related studies have shown that the effect is localized, and a fairly small percentage of the zinc is affected (5). Based on this information, it is unlikely that the resistive component of the circuit is a pore resistance. It is more likely that the elements of the parallel RC circuit are the double layer capacitance and the polarization resistance associated with corrosion of zinc at the surface of the coating. The magnitude of the impedance is large because the actual electroactive area of the coating is much smaller than the apparent, exposed area.

Impedance spectra of the primer applied to Dacromet-pretreated steel, without corona discharge treatment, are shown in Figures 8a and 8b for several exposure times. Exposure to the electrolyte for 13 days results in an increase in the capacitance of the coating, measured at high frequencies, and deviation from capacitive behavior at frequencies less than 50 Hz (log w = 2.5). At frequencies less than 1 Hz (log w = 1) a Warburg-type response, characterized by a straight line with a slope of approximately -1/4 is observed in the log |Z| plot. We attribute the non-capacitive behavior to penetration of electrolyte through the primer and into defects in the
Dacromet layer. The impedance spectrum recorded after 29 days exposure has the same general shape but the magnitude of the impedance is lower at all frequencies due to continuing penetration of the coating by the electrolyte. After 76 days, red rust was visually observed at several localized spots on the sample. The impedance spectrum shows the appearance of a second, well-separated time constant at approximately 5 Hz (log w = 1.5), characterized by a maximum in the phase angle. At the lowest frequencies a Warburg-type response is still observed.

The general circuit model shown in Figure 9 can be used to explain the results. It consists of the resistance of the electrolyte, $R_{Q}$, the capacitance of the intact coating, $C_{M}$, the pore resistance resulting from penetration of electrolyte into the coating, $R_{P}$, and a general impedance element, $Z_{M}$, characterizing the reactions at the metal interface.

A schematic depicting the coating after one hour exposure is shown in Figure 10a. At this point it is likely that electrolyte has penetrated into the primer as shown by the arrows. However, it is unlikely that electrolyte has penetrated into the Dacromet layer. The circuit shown in Figure 10b, comprised only of the resistance of the electrolyte and the capacitance, describes the impedance response since $Z_{M}$ would be infinitely large.

In Figure 11a the degradation of the coating is depicted at 13 and 29 days. The electrolyte has penetrated the primer and the Dacromet layer to expose the underlying metal at localized areas. The extent of penetration would necessarily be greater at 29 days. The impedance spectra recorded at 13 and 29 days are very similar to results reported by Mansfeld et al. for polybutadiene coatings on certain types of phosphated steel (6). For that case, it was shown an equivalent circuit in which $Z_{M}$ is represented by a charge transfer resistance, $R_{T}$, in series with a general Warburg-type element, $W$ (where $W = k(jw)^{n}$), could model the results. This circuit is shown in Figure 11b. However, as discussed by the authors (6,7), there are several physical mechanisms which can explain the observed low frequency response. These include semi-infinite diffusion in pores, tangential penetration of electrolyte at the metal/coating interface, and a distribution of relaxation times resulting from heterogeneous penetration of electrolyte. All of these mechanisms are plausible for the Zincrometal coating system due to the rough, porous structure of the primer and the irregular surface structure of the Dacromet. Therefore, it is difficult to provide an
accurate physical description of the processes involved. Chemical interactions between the Dacromet layer and the electrolyte such as the solubility of the chromium oxide film and passivating effects of chromium compounds may be important at this stage of the coating breakdown (8).

We attribute the appearance of the second time constant in the spectrum at 76 days to the visually observed, localized corrosion of the steel substrate, as depicted in Figure 12a. To explain this behavior, the general model in Figure 9 may be modified as shown in Figure 12b. The impedance at the metal interface, $Z_M$, is represented by the double layer capacitance, $C_{DL}$, in parallel with a series combination of the charge transfer resistance, $R_m$, and a Warburg-type element. The high frequency time constant at 500 Hz ($\log \omega = 3.5$) would result from the interaction of the coating capacitance and the pore resistance. The time constant at 5 Hz would result from the interaction of the charge transfer resistance and the double layer capacitance. In this case the Warburg-type element is likely to be a diffusion impedance related to the corrosion process at the metal/coating interface.

Summary

Electrochemical impedance spectroscopy has been utilized to study the protective properties of a zinc-rich organic coating comprised of a pretreatment layer and a zinc-rich primer. The primer itself is porous and is active electrochemically when applied directly to steel. The pretreatment layer is responsible for the excellent barrier properties of the coating. However, it blocks zinc particles in the primer from making contact with the steel substrate, and a galvanic process is not possible. Therefore, the primer acts only as a second barrier to the corrosive environment. Electrical post-treatment by corona discharge creates electronically conductive paths between zinc in the primer and the steel substrate, which makes a galvanic process possible. Electrochemical impedance spectroscopy provides information about the breakdown of protective properties of the coating and corrosion of the steel substrate.
Acknowledgement

This research was supported by Bethlehem Steel Corporation. The authors express their appreciation to J. D. Hoffman, L. L. Hahn, S. V. Jones, D. H. VanBilliard, and C. Santos of Bethlehem Steel Corporation for their skilled technical assistance in the investigation of these coatings.

References

Figure 1. Apparatus for electrochemical impedance measurements.

Figure 2. Electron micrograph of the surface of Dacromet-pretreated steel.

Figure 3. Electron micrograph of the surface of the 50 v/o primer.

Figure 4. Electron micrograph of a cross-section of the 50 v/o primer on Dacromet-pretreated steel.
Figure 5. Bode plots of zinc-rich coated steel after 1 hour in non-deaerated 0.5 N NaCl.

Figure 6. Bode plots of Dacromet-pretreated steel with no primer after 1 hour in non-deaerated 0.5 N NaCl.
Figure 11. Models of 50 v/o primer on Dacromet-pretreated steel after 13 and 29 days exposure.

Figure 12. Models of 50 v/o primer on Dacromet-pretreated steel after 76 days exposure.
Figure 7. Results of electrical impedance measurements of 50 v/o primer on Dacromet-pretreated steel, before and after CD treatment.

Figure 8. Bode plots of 50 v/o primer on Dacromet-pretreated steel as function of exposure time in non-deaerated 0.5 N NaCl.
Figure 9. General equivalent circuit for the electrochemical impedance of coated steel.

Figure 10. Models of 50 v/o primer on Dacromet-pretreated steel after 1 hour exposure.