Protective coatings are applied to many industrial steel structures for corrosion control. Polymeric coatings act as a barrier, separating the metal structure from a corrosive service environment. They reduce the access of corrosive species to the metal substrate and interrupt the flow of electric current required for the steel corrosion processes. A key attribute in the performance of protective coatings is, therefore, a low permeability to ions, water, gases, and other corrosive species of the service environment.

EIS is a technique well suited for evaluating coating permeability or barrier properties based on the electrical resistance of the coating. The impedance of a coating is related to the nature of the polymer, its density, and its fillers. EIS has been used widely in the laboratory for determining coating performance and for obtaining quantitative kinetic and mechanistic information on coating deterioration. The impedance of a coating is observed to decrease as a function of time of exposure to a corrosive environment. The decrease in impedance is observed to be related to the loss of barrier properties and the onset of under-film corrosion. In laboratory studies of various generic types of coatings, the relative performance of different coatings could be determined well in advance of the visible effects of deterioration; these studies also showed a good relationship between coating impedance and coating field performance. A review of the application of EIS in the evaluation of coatings has been published recently.

In recent years, EIS has been adapted to evaluate coatings that are in service on industrial structures and equipment. Field measurements have been made on car paint on seven-year-old automobiles and coatings on field structures; marine coatings on underwater structures; alkyd and chlorinated rubber coatings on steel structures; ballast tank coatings inside U.S. Naval ships; epoxy tank linings in oil production equipment and phenolic coatings in rail cars; fusion-bonded epoxy (FBE) coatings on transmission pipelines; epoxy coatings systems on highway bridges; and a variety of industrial structures including protective coatings on aircraft.

The objectives of this article are to describe the theory and methodology of the EIS technique, to present an example of the use of EIS in a laboratory coating evaluation program, and to review recent progress in field evaluation of coatings in industrial service.

**Basis of EIS Measurements**

**Definition of Impedance**

The protectiveness of a polymeric coating is related to its electrical resistance. That is, protection increases as electrical resistance increases, where an electrical resistance of at least $10^6$ to $10^7 \Omega \text{ cm}^2$ is required for reasonable corrosion protection ($\Omega = \text{ohm}$). Modern high-build polymeric coatings can have electrical resistances of $10^{11} \Omega \text{ cm}^2$ or greater.
The resistance across a polymeric coating film is measured using DC electrical methods. From Ohm's law, resistance \( R \) is defined as

\[
R = \frac{V}{I}
\]

where \( V \) is the applied DC voltage and \( I \) is the measured DC current.

The impedance across a coating film is measured using AC electrical methods. The analogous equation in AC electricity for impedance, \( Z \), is

\[
Z = \frac{V_{ac}}{I_{ac}}
\]

where \( V_{ac} \) is the applied AC voltage and \( I_{ac} \) is the measured AC current.

Polymer coatings and electrochemical corrosion processes both have an inherent resistance and capacitance character. AC methods can identify and quantitatively measure the individual resistance and capacitance elements, as described below in the discussion of equivalent circuits. DC methods measure the net resistance only of a coating. Therefore, AC electrical techniques normally provide considerably more information on coatings and under-film corrosion processes than DC methods.

In EIS analysis, the coating film and under-film corrosion processes are regarded as a system of resistors and capacitors. The magnitude of the coating impedance varies with frequency, depending upon the respective resistances and capacitances. Capacitors cause a phase shift between input voltage and output current, an effect readily measured by AC methods. Normally a simple inspection of impedance data provides a good indication of the coating's barrier properties.

**EIS Measurements: Cells, Instrumentation, and Data Presentation**

The impedance across a coating film is measured with the use of an electrochemical cell (Fig. 1). Two common cell designs are shown schematically in Fig. 2. The “attached cell” consists of a plastic tube cemented to a coated metal panel. The attached tube is filled with an electrolyte (such as 5% NaCl). A counter and reference electrode are inserted into the solution. The reference electrode, typically a silver/silver chloride electrode, is used to apply a controlled AC voltage across the coating film. The counter electrode, typically platinum or another inert material, is used to measure the resulting AC current across the coating film. The area inside the plastic tube is the area of the coating for which impedance is measured. A picture of the attached cell and EIS instrumentation is shown in Fig. 1.

The attached cell is particularly convenient when coating impedance is measured as a function of time under immersion conditions. The cell can be placed in a convection oven to obtain measurements at elevated temperature. Non-flat surfaces can be accommodated. A variant of this is the clamp cell, which is similar to the attached cell except that the cell is clamped on rather than cemented to the panel.

A second cell design (called the flat cell, EG&G Princeton Applied Research), also shown in Fig. 2, has the same components as the attached cell but is more suited for pre- and post-run evaluation of coated panels that have been exposed to actual or simulated process conditions, e.g., noxious fluids at elevated temperature and pressure. Coated panels of a wide range of sizes and coating thicknesses can be accommodated in either cell.

**Data Output and Interpretation**

The impedance of a coating is measured as a function of frequency from \( 10^5 \) Hz to 0.001 Hz or less. An AC voltage ranging from 5 to 500 mV in amplitude (rms) is applied to the coating. The resulting AC current (including phase shifts) is measured, and the impedance derived. For coatings analysis, the most useful output format for the data is a Bode plot, consisting of a Log-Log plot of the impedance (Log \( Z \)) versus frequency (Log \( f \)) and a semi-Log plot of phase angle shift (Phase) versus frequency (Log \( f \)). Inspection of the Bode plot readily provides very useful information on coating performance.

High-performance coatings with good barrier properties behave as pure capacitors with a simple, readily recognized response. The equivalent circuit and impedance response is shown in Fig. 3. The circuit is a simple capacitor, \( C_{coat} \). The Log \( Z \) plot is a straight line with a slope of -1. The phase shift of a capacitor is 90°. At low frequencies in the range of 0.1 to 0.001 Hz, the coating impedance falls in the range of \( 10^9 \) to \( 10^{11} \) \( \Omega \) cm².
Permeable coatings, where the permeability is due either to inherent properties or deterioration, have a slightly different equivalent circuit. A resistance element, $R_{coat}$, appears parallel to $C_{coat}$ (Fig. 3). The plot of impedance versus frequency now has a region in which the impedance levels off (plateaus) at low frequency (i.e., $10^7$ ohm cm$^2$ at 0.1 Hz), as shown in Fig. 4. The phase shift varies between 0 and 90° in the resistance and capacitance active frequency ranges, respectively.

When corrosion and disbondment are occurring at the coating/metal interface, an additional circuit element appears in series with the coating resistance, $R_{coat}$. The equivalent circuit and response are shown in Fig. 5. The “corrosion” element consists of the polarization resistance, $R_{pol}$, which can be related to the corrosion rate of the base metal, and a double layer capacitance, $C_{dl}$ (parallel to $R_{pol}$), which results from the aqueous electrolyte in contact with the metal surface.\(^5,6,26,27\)

Information about the barrier properties (and relative permeability) of a coating is obtained from the low frequency part of the Bode plot. To facilitate analysis of the data and assessment of coating performance, Log Z at 0.1 Hz is read from the plots by interpolation. The Log Z value at 0.1 Hz is tabulated or plotted and used as the basis of comparison between coatings. It is also used for monitoring the change in a coating’s impedance as a function of exposure time to a test environment. Selection of Log Z at a frequency of 0.1 Hz is somewhat arbitrary but represents a compromise between speed of analysis and selection of a frequency at which the performance of different coatings can be easily distinguished.

Anticipated performance of a coating based on Log Z at 0.1 Hz is shown in Fig. 6. This summary figure is based on the large literature of EIS laboratory and fieldwork on coatings.

**EIS in the Laboratory: Evaluation of Liquid Pipe Coatings**

**Background**

Protective coatings, in conjunction with cathodic protection, are used to control external corrosion on oil and gas transmission pipelines. In new construction, lengths of pipe that are externally coated in a shop are welded together in the field. The resulting girth welds and related ancillary components such as flanges, risers, and tees are coated in the field with liquid coating products. Pipe coating technology has been rapidly advancing and improving, with continual introduction of products.

Many pipeline owners conduct laboratory test programs as the first step in the evaluation and qualification of new products for use on their pipelines. The test programs normally include an assessment of cathodic disbondment resistance, wet adhesion, impact resistance, flexibility, and hardness, among other tests specific to the owner’s line. In our laboratory, EIS measurements have been included in many of these test programs as an additional means of assessing coating performance. The following is an example of the EIS measurements made in such a test program and their use in the selection of the best pipe coating.

**Laboratory Methods**

Six liquid pipeline coatings, assigned name codes from A to F, were evaluated. Coated test panels, 4 x 4 x 0.25 inches, were prepared by the respective coating manufacturers and submitted to our laboratory for testing. The liquid products were a mix of 99 to 100% solids epoxies and polyurethanes.

EIS measurements were made using the attached cell method. Acrylic tubes, 1.5 in. (3.7 cm) in diameter, were cemented to the coated panels and filled with 5% NaCl solution. The tubes were closed with stoppers and placed in a convection oven at 65°C (149°F). This temperature was somewhat higher than the service temperature and accelerated the test. At intervals of 1, 4, 7, 14, and 28 days, the panels were temporarily removed from the oven.
coating. Over the duration of the measurements, little subsequent change was observed, suggesting that the barrier properties were stable and that little to no change or deterioration was occurring at the test conditions.

The behavior of coating D (Fig. 8) was quite different from coating A. After one day, the Bode plot for coating D was very similar to that for coating A. However, at subsequent intervals, the impedance decreased significantly. In the low frequency range, the impedance reached a limiting value, which was almost independent of frequency. This coating was acting like a resistor and capacitor in parallel, like the model in Fig. 4. The data suggest that this coating was becoming increasingly permeable with time, with a significant loss of barrier properties.

To observe the change in impedance for each coating as a function of time, Log Z at 0.1 Hz was read from the Bode plots. These data are plotted as shown and the impedance of the coating within the area of the attached tube was determined. A silver/silver chloride reference electrode and platinum counter electrode were used. Measurements were made in duplicate for each coating.

Results and Discussion

The Bode plots obtained at the various time intervals are shown in Figs. 7 and 8 for coatings A and D, respectively. Note that in the raw data, the impedance values have not been corrected for the cell area of 11.4 cm².

The Bode plot obtained for coating A after one day was characteristic of a high-performance coating with very low permeability. The coating behaved like a capacitor, generating a straight line with a slope of -1. After 4 days, there was a small drop in the coating impedance at low frequency, producing some curvature in the Bode plot. Based on simultaneous gravimetric and EIS studies, this initial drop in impedance is attributed to the uptake of water, which reduces the impedance of the coating.
The impedance measurements were corrected to a 1 cm² area.

The data in Fig. 9 show that coatings A, C, and F have similar behavior and outstanding barrier properties under the test conditions. The Log Z impedances are in the range of 10 to 11. There is no discernible downward trend, suggesting the coatings all have very low permeability, low water uptake, and very little deterioration with time. Based solely on impedance measurements, these coatings would be anticipated to be highly protective, particularly under the milder service conditions of many pipelines (e.g., moist soil at 5 to 15 C [41 to 59 F]).

Coating B had a somewhat low impedance initially, which dropped further to Log Z = 8 over seven days of immersion. With a Log Z of 8, this coating has an appreciable permeability to water and electrolyte but is still in the impedance range in which corrosion protection is provided. Of significance is that the impedance stabilized after seven days with little further change, suggesting that after the initial hydration and related chemical changes, little further change or deterioration occurred.

Coatings D and E had relatively high initial impedances, with Log Z > 10. Their impedance dropped significantly, however, over the first seven days of immersion. The data in Fig. 9 show that the impedance continued to decrease slowly with time and would be anticipated to eventually approach the range of Log Z = 6 to 7, below which significant corrosion protection is lost. Based on EIS data only, these coatings would be anticipated to have the poorest long-term field performance of the products evaluated.

Correlation of EIS data with field performance is not available at this time because of the newness of the products. However, data are being collected and will be presented at a future time.

In service, the impedance of the pipe coatings would be anticipated to change with time, probably in the manner of the laboratory test as shown in Fig. 9. The magnitude and rate of change in impedance with time might be used as a means to assess the rate of coating deterioration and remaining coating life.

### EIS Field Measurements

EIS has been used primarily as a laboratory technique. In recent years, however, the use of EIS as a field technique has been under development, with EIS measurements...
Evaluation of Tank Linings in Oil Field Production Vessels

Background

EIS measurements were made on a test separator and a manway cover from a produced water storage tank located in a conventional oil production facility in Alberta. The units were coated internally with an epoxy tank lining and had been in service for two years. The objective was to assess the condition of the epoxy coating, for which there was relatively little field experience.

Impedance of the Epoxy Coating before Service

The impedance of the new coating was measured on laboratory panels. When the coating was hydrated in 5% NaCl solution at 23 C (73 F) for 24 hours before measurement, the impedance was Log Z = 9.2 (0.1 Hz). When the panel was hydrated at 60 C (140 F) in 5% NaCl for seven days, the impedance dropped to Log Z = 8.8 (0.1 Hz). These values were relatively low for a new epoxy tank lining that had not been in service, compared to other products with which we are familiar.

Field Measurements

The test separator is used to measure the volumes of oil, water, and gas being produced from one or more oil wells. It is therefore exposed to raw, unprocessed petroleum fluids. The maximum operating temperature of the vessel was 60 C (140 F). Based on visual inspection, the coating inside the test separator was in good condition. The average impedance of the coating in the oil phase was Log Z = 8.4 and in the water phase was 7.6. The impedance in the water phase was lower than in the oil phase, as expected, because water is typically the primary source of coating degradation. The field measurements suggested that although the coating in the separator was still protective, considerable deterioration had occurred over the two years of service, in

Two examples of EIS field measurements are presented here. They consist of measurements on an epoxy tank lining in an oil field application and on FBE coatings on transmission pipelines. Modifications of laboratory equipment and methods were made to facilitate the field measurements. This involved development of field-useable cells, extended cabling, a portable power supply, and development of measurement verification techniques. Bode plots were recorded, and the impedance (Z) at 0.1 Hz was read from the plots and reported as Log Z. The field data were compared to samples of new coatings on laboratory panels to assess the protectiveness and degree of deterioration.

![Fig. 8: Pipe coating D: Bode Plots. 5% NaCl at 65 C. Impedance (Z) uncorrected for cell area of 11.4 cm²](image)

![Fig. 9: Summary of impedance, Log Z (Z @ 0.1 Hz in Ω•cm²) as a function of immersion time at 65 C in 5% NaCl for liquid pipe coatings.](image)
Analysis

The EIS measurements on the epoxy tank lining, summarized in Table 1, suggested that it was not providing a high degree of protection initially and that it was deteriorating relatively rapidly in view of the mild service. The EIS results were later found to be consistent with field experience. The coating was subsequently found to have poor performance in other vessels at other facilities and was gradually replaced with other epoxy coatings.

Pipeline Coating Field Measurements

Background

EIS measurements were made on four operating pipelines that were coated with FBE.22 The FBE coatings ranged from 5 to 20 years in age in a range of environments. The objective of the EIS measurements was to determine the integrity of the FBE and the extent of deterioration since installation. Integrity of the FBE, in conjunction with an effective cathodic protection system, is considered essential to preventing corrosion and stress corrosion cracking on transmission pipelines.

Observations

Field measurements were made based on the availability of pipelines through scheduled digs. Details regarding the pipeline, environment, age, and condition of the coatings are shown in Table 2. The site locations, all within Canada, were as follows: #1 in the Northern Prairies; #2 and #3 in moun-
tainous terrain; and #4 in the Rocky Mountain foothills.

The five-year-old FBE at Site #1 was in excellent condition visually with no blistering, cathodic disbondment, or other signs of deterioration. The impedance was Log Z ≥ 8.9, the measuring limit of the instrumentation. In comparison, the impedance of new FBE on a lab panel was Log Z = 9.7 (after 24 hours of hydration in 5% NaCl at 23 C [73 F]).

Similarly the 19-year-old FBE at Site #2 was in excellent condition, with no blistering, cathodic disbondment, or soil abrasion. The finish was slightly rough and uneven, presumably because of the coating application methods of 19 year ago. The impedance of the FBE was Log Z ≥ Log 8.7, the measuring limit of the instrumentation. The impedance of the new, current-day version of the FBE was Log Z = 9.7.

At site #2, a portion of the FBE adjacent to the girth weld had poor adhesion. Small sheets of coating several inches in size could be pried from the pipe surface with a knife. No metal loss or corrosion under the poorly bonded coating was visible. The impedance of a free film of the disbonded FBE was measured in the laboratory and observed to be Log Z = 9.6, almost identical to newly applied FBE. Based solely on impedance measurements and visual observations, it was concluded that the barrier properties of the FBE had deteriorated little, if at all, in 19 years of service. The free film measurements showed that the barrier properties were retained even when the adhesion was low. The good performance is probably due to the mild environment, i.e., an up-slope with good drainage.

At site #3, the FBE had been in service for 8 years after being stored outdoors for 22 years. The FBE showed extensive blistering at the 9 to 12 o’clock position. The impedance of intact areas of the coating was Log Z = 6.9. The impedance of areas with intact blisters was Log Z = 5.2. Therefore, this coating had moderate to poor barrier properties, which were attributed to UV deterioration from outdoor storage prior to installation.

The 21-year-old FBE at site #4 was blistering extensively over all of the pipe surface. The FBE had poor adhesion, and superficial corrosion was observed on the pipe exterior. The impedance of intact areas of the coating was Log Z = 8.4. The impedance of blistered areas ranged from Log Z = 6.2 to 7.4. In spite of the blistering, the coating had moderate to relatively good barrier properties. The extensive blistering was attributed to inferior application procedures.

Conclusions
This article has described several uses of EIS for evaluating critical properties (barrier properties and permeability) of protective coatings under laboratory or field conditions. In particular, the manner in which coating impedance decreased with time was used as a means to monitor coating protectiveness and deterioration.

EIS was used to monitor the barrier properties of six pipe coatings in laboratory performance testing and to assist in the evaluation and selection of pipe coatings for field use. The behavior of the six coatings varied widely, ranging from little to no change in impedance with time (best performance), to a continual decrease in impedance with time (poorest performance). Since similar changes in impedance would be anticipated to occur in service, impedance might be used as a means to assess the rate of coating deterioration and remaining coating life.

Several examples were also presented where EIS was used to evaluate the protectiveness and extent of deterioration of coatings that were in service in industrial applications, i.e., oil field production equipment and transmission pipelines externals.

Some additional possible examples of applications are as follows:

- determining the degree of water permeation of a coating subject to accelerated laboratory testing (to assess the validity of the accelerated test and to establish practical times for test duration),
- comparison of the degree of permeation or film breakdown in accelerated and natural exposures, and
- comparison of the increase in permeability of coatings applied to rusted or previously painted surfaces.

Ultimately, the value of this technique will be judged on its capability to provide better and earlier information on coating lifetimes. This information could assist manufacturers, specifiers, and users in providing more cost-effective protection to the myriad of structures affected by corrosion.

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