

## **USING EIS TO BETTER UNDERSTAND TANK LINING PERFORMANCE IN LABORATORY AND FIELD EVALUATION**

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### **ABSTRACT**

EIS (Electrochemical Impedance Spectroscopy) is being more commonly used in laboratory coating test programs and also for evaluation of coatings in field service. Typically, the impedance is measured before and after exposure to test conditions in the laboratory or service conditions in the field. The decrease in impedance is used to gain an assessment of coating deterioration and the rate of deterioration, based on the loss of barrier properties with time. This study investigated some of the variables that influence such impedance measurements, using the model system of tank linings in immersion service in oil and gas production systems. The detailed impedance information is also interpreted in terms of the coating formulation chemistry and behavior of coatings in specific service environments. The results are presented and interpreted with the objective of making reliable measurements in the assessment of coating performance in the laboratory and field.

**Keywords:** Electrochemical Impedance Spectroscopy, EIS, organic coatings, epoxy testing

## INTRODUCTION

EIS (Electrochemical Impedance Spectroscopy) has been used extensively as a laboratory-based research tool for studying the performance and deterioration of polymeric protective coatings (1-16). In recent years, the EIS technique has been used in routine laboratory testing of coatings (17, 18) where it provides an additional means by which to assess and understand coating performance. EIS measurements are also being made in the field on coatings in service in various industrial environments (19-26). In the field, EIS is potentially a method to assess coating condition, rate of coating deterioration, and remaining life, information that is valuable in planning maintenance-painting programs.

The impedance of a coating, determined by EIS, is the electrical resistance of the coating, as measured by AC (alternating current) electricity. Coating impedance can be regarded as a measure of barrier properties, or conversely, a measure of permeability to water, gases, and small-molecule corrosive species. Impedance measurements are most applicable for coating systems used in water immersion or in environments with high humidity. High performance coatings with excellent barrier properties have high impedance (ie low permeability to water). Poor performance coatings with high permeability to water have low impedance. When a coating is subjected to an aggressive aqueous environment, its impedance decreases as a function of time. The decreasing impedance is attributed to the uptake of water and an increase in permeability resulting from chemical and physical changes of the coating (5,6). Coating deterioration is attributed to deleterious irreversible changes. The resulting loss of barrier properties and influx of water promotes disbondment and the onset of underfilm corrosion. A discussion of the theory of EIS can be found elsewhere (2, 3, 5, 6, 27, 28).

The primary factor that governs the impedance of a coating is its formulation chemistry. The chemical composition strongly affects chemical and thermal resistance, mechanical strength, resistance to light, and other service-related stressors. When the coating is subsequently exposed to test or service conditions, the extent of deterioration (and loss of impedance) is related to the formulation chemistry. Compromises in coating application and cure can also reduce coating performance and accordingly reduce impedance. Secondary factors that affect impedance measurements in the laboratory and field involve such things as conditioning of the coating, elapsed time between the end of a test (or shut-down) and the impedance measurements, and coating aging. EIS measurements in the laboratory and in the field must therefore be carefully designed to ensure that representative data is obtained that can be properly interpreted.

### **Laboratory EIS Measurements**

In laboratory test programs, coatings are exposed to test conditions that approximate service conditions, or represent an accelerated version of service conditions. Coating performance is typically assessed from adhesion changes, blistering, undercreep, color change, and so on. Similarly, coating impedance can be used to evaluate coating performance. EIS measurements are particularly useful when no obvious visual change or adhesion loss has occurred during testing.

### 1) Impedance of the coating prior to testing

The initial impedance of a coating before exposure to test conditions must be determined. Most polymeric coatings have high impedance when in their "dry, water-free" state, which is independent of their inherent permeability. Therefore, to differentiate between coatings that have inherently high or low permeability to water, the coating must be hydrated prior to the impedance measurement. It has been shown, based on physical chemical calculations and impedance measurements, anywhere from 4 to 48 hours is required for water molecules to diffuse through and saturate a coating film (29-33). The specific time for a given coating is dependent upon the polymer composition, porosity, film thickness, temperature and other factors. Extended immersion time must be avoided as it can result in permanent changes and coating deterioration of low performance coatings. Determination of pre-test impedance therefore requires selection of appropriate hydration conditions ie. electrolyte, electrolyte concentration, hydration time, and hydration temperature (normally room temperature). This group of conditions then becomes the "reference conditions" against which subsequent post-test impedance measurements are compared.

### 2) Impedance of a coating in aqueous immersion at temperatures below 100°C

When the test conditions involve aqueous solutions at ambient pressure and temperatures below 100°C, coating impedance can easily be measured at actual temperature as a function of immersion time. A convenient method is the attached cell method, described below. Impedance at actual service temperature as a function of exposure time provides the best data, enabling coatings to be assessed based on their retention of barrier properties at actual service temperature.

### 3) Impedance of a coating in aqueous immersion at temperatures above 100°C

When test conditions involve temperatures above 100°C, elevated pressure, and/or noxious chemicals, measuring coating impedance is much more complex. Typically the impedance is evaluated before and after exposure to the test conditions, with the coating at ambient temperature and pressure (reference conditions). The test conditions, however, can induce large physical and chemical changes in the coating, significantly altering its permeability and impedance. Many of these changes will reverse as the coating is returned to ambient conditions. The apparent post-test impedance measured at ambient conditions would be expected to vary significantly depending upon the rate at which the changes reverse, and the elapsed time between the test and the final impedance measurements.

### 4) Measuring the impedance of coatings immersed in non-aqueous liquids

Aggressive hydrocarbon liquids can produce considerable deterioration in some coatings during service. However, most hydrocarbon liquids (eg liquid petroleum) are dielectrics with high impedance. Coatings which are immersed in such substances for testing purposes will have a high impedance either due to being "dry and water-free" or, in the case of highly permeable coatings, of being saturated with the hydrocarbon.

To use EIS to evaluate coatings in hydrocarbon service, one approach is to immerse the coating in an aqueous solution, after it has been exposed to the hydrocarbon test conditions. Any resulting increase in permeability to water is then taken as a measure of its deterioration. This procedure requires that hydration and re-equilibration times must be established, which depend upon temperature, coating formulation, and chemical resistance.

### **Field EIS Measurements**

Measuring the impedance of coatings that are in water immersion service in industrial vessels (22-24) has many similarities to laboratory test systems evaluated at elevated temperatures and pressures. The impedance is measured before the coating goes into service and again, preferably at intervals during service. Measurements during service are obtained after the vessel has been cooled, emptied, cleaned, and in some cases allowed to vent for a period of time that can result in the coating drying out. The reference conditions for the impedance measurements are therefore ambient temperature and pressure, which are typically quite different from service conditions. An analogous situation occurs when EIS measurements are made on test panels retrieved from industrial vessels. In making EIS field measurements, decisions must be made regarding the re-hydration time and electrolyte.

## OBJECTIVES

In this study, a systematic series of EIS measurements were made on four different epoxy coatings as they were taken through a series of conditions representative of those a coating passes through in a laboratory test program, or during service in an industrial vessel. These steps are:

- hydration at room temperature (to establish initial, pre-test or pre-service impedance)
- immersion at ambient and elevated temperature (to examine how impedance changes as a function of temperature and how it relates to post-test impedance at ambient temperature)
- cooling to room temperature under immersion (to simulate laboratory test completion or industrial vessel shut down)
- dry out (to assess the effects of dry out, as applicable to EIS field panel or vessel measurements)
- re-hydration at room temperature (to establish how effectively re-hydration can be accomplished after dry-out, as applicable to EIS field panel and vessel measurements)
- re-immersion at elevated temperature (assessment of the reversibility of the coating system, and if test panels can be rehydrated)
- assessment of hydrocarbon exposure (can hydration detect deterioration from hydrocarbon liquids)

The resulting data was examined with the following objectives:

- to make meaningful, accurate impedance measurements in the field and laboratory which can be correctly interpreted
- to extend the capabilities for interpretation of impedance data, specifically with respect to the coating field performance and formulation chemistry

### Epoxy Test Coatings

The coating model system used in this study was tank linings used in oil and gas production systems. The four epoxy-based coatings are all commercially available tank linings, which are marketed for immersion service, including sour oil and gas production systems. The coatings were selected on the basis of having a range of formulation chemistries, impedances, and track records in oil and gas production equipment.

The three major coating constituents that predominantly influence corrosion and chemical resistance are binders (includes curing agents), pigments, and solvents. Given that epoxy coatings were used in the present study the base epoxy resin functionality would be very important with respect to test performance characteristics. The tendency to form more highly cross-linked structures decreases in the order of epoxy novolac > Bis F<sup>1</sup> epoxies > Bis A<sup>1</sup> epoxies, with respective epoxy functionalities of approximately 2.6-3.5, 2.1 and 1.9 as illustrated in Tables 1-3 (18).

A three-dimensional network in a compact epoxy coating can be achieved using a multi-functional epoxy novolac resin. The result will invariably be a coating with superior chemical, hydrolytic and

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<sup>1</sup> Bis Phenol F, Bis Phenol A.

thermal resistance compared to a coating based on low molecular weight Bis F resins, or the di-functional Bis A types (34). Moreover, although the functionality of the epoxy resin is important, it has secondary importance in terms of the epoxy coating's final chemical resistance properties. The primary determinant for the latter is the choice of the curing agent.

Table 1 shows the base epoxy resin types and curing agents for the four epoxy coatings used in the present study. Tables 2 and 3 show the generic structures of the epoxy resins and curing agents for the four coatings (18). From molecular structure considerations, Coating A would be expected to possess the highest 3D cross-link density since it is a pure novolac epoxy co-reacted with a polycycloaliphatic polyamine curing agent.

Coating A contained a water immiscible solvent line-up (ie. solvent blend). As a result, the test exposures of water, oil and gaseous corrosives in autoclave and EIS tests may be expected to have the least effect on Coating A. In comparison, Coating B would be expected to be somewhat inferior to Coating A despite the extra film thickness (30 mils compared to 13 mils DFT (dry film thickness)) of the former system. The solventless thick film of Coating B consisted of a modified (Bis A) novolac co-reacted with three curing agents, including an adducted cycloaliphatic amine. The cross-link density, and hydrolytic and chemical resistance of the coating system is not as high as that for Coating A.

At the opposite end of the anticipated performance spectrum, Coating D had a lower 3D cross-link density given that it was a modified (Bis A) novolac co-reacted with a lower functionality cycloaliphatic curing agent. Coating D contained a water miscible solvent, namely polyethylene glycol monomethyl ether (hereinafter PGMME). While the latter is a strong solvent used to lower the viscosity of either high molecular weight epoxy resins or novolacs, its drawback would be any retention of PGMME in the cured film. The alcohol group in this solvent predisposes the coating in aqueous media to deleterious osmotic forces. General information on solvent effects can be found elsewhere (35).

Interestingly, although Coating C was also a pure novolac co-reacted with a cycloaliphatic amine, it too contained PGMME. For this reason alone, Coating C was expected to exhibit lower performance than Coating A and intermediate performance between Coating B and Coating D.

With respect to pigment content of the four coatings, Coating C was anomalous in that it contained an anticorrosive pigment, zinc phosphate. Anticorrosive pigments add little or no performance benefits to well formulated tank linings that operate at high temperatures and pressures. The presence of zinc phosphate coupled with possibly a large amount of crystalline silica pigment in Coating C, indicated that the combined pigment level was a higher percentage of the dry weight of the cured film than in the other epoxy coatings investigated. It was reasoned that with a lower proportion of epoxy coating in the dry film compared to Coatings A, B and D, Coating C might exhibit the worst performance of the four coatings.

A common denominator amongst the epoxy coatings was the use of a mobilizing agent to accelerate the reactivity of their cycloaliphatic curing agents. This was carried out using non-reactive diluents, viz benzyl alcohol in Coatings B, C and D and furfuryl alcohol in Coating A.

# Experimental

The four coatings were spray applied by a commercial applicator in accordance with the coating manufacturer's instructions. Data related to the coatings application is included in Table 1.

## EIS Cells, Instrumentation, and Measurement

EIS measurements were made using an "attached cell". An acrylic tube, typically 1 inch inside diameter, was cemented to the coated steel test panel with silicone adhesive. The tube was filled with 5% NaCl solution. Impedance was obtained for the area of coating isolated within the plastic tube. The impedance,  $Z$ , was normalized to an area of  $1 \text{ cm}^2$  and a coating film thickness of 15 mils. The impedance results are reported as  $\text{Log } Z$  for a 15 mil DFT, where  $Z$  is in units of  $\Omega \text{ cm}^2$ .

A platinum wire counter electrode and a saturated silver/silver chloride reference electrode were inserted into the solution in the acrylic tube. When an EIS measurement was made, the panel and attached cell were placed in a Faraday cage. The measuring instrumentation consisted of a Gamry Instruments PC4/750 potentiostat with EIS 300 software. Impedance ( $Z$ ) was measured as a function of frequency ( $f$ ) from  $10^5 \text{ Hz}$  to  $0.04 \text{ Hz}$ . An AC voltage of 100 to 500 mV in amplitude (rms) was used, due to the heavy film build of some of the coatings. Linearity of response was confirmed by measuring Bode plots at amplitudes down to 50 mV rms. A check showed consistent results with rms voltages of 50 mV. Bode plots ( $\text{Log } Z$  versus  $\text{Log } f$ ) were obtained, from which the  $\text{Log } Z$  value at 0.1 Hz was obtained by interpolation.

In this study, the coating impedance is reported as  $\text{Log } Z @ 0.1 \text{ Hz}$ . Selection of  $\text{Log } Z$  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  $\text{Log } Z$  at 0.1 Hz is shown in Figure 15, based on a large literature of laboratory and fieldwork on coating impedance studies (1-16).

## EIS Measurements

### 1) Dry Coatings

The impedance of a dry, non-hydrated coating was measured by introducing 5% NaCl into the attached cell and immediately measuring the Bode plot over a 5 minute interval.

Two types of dry coatings were evaluated: newly applied coatings, cured under ambient conditions and not yet immersed in water; and coatings previously immersed in water but allowed to dry out at ambient conditions, ie.  $23^\circ\text{C}$  and a relatively humidity between 30 and 40%.

## 2) Coatings Immersed in Aqueous Solutions

The attached cell doubled as both the "test vessel" and the impedance-measuring cell. The attached cell was filled with the required liquid, which served to "immerse" the coating. Coated panels with electrolyte-filled cells were placed in a convection oven. Impedance measurements were taken at intervals by moving a cell from the convection oven to the Faraday cage, immediately taking the impedance measurement, followed by placing the cell back in the oven. Impedance measurements could be readily obtained at temperatures up to 90°C (and ambient pressure) as a function of immersion time.

## 3) Coatings Immersed in Hydrocarbon Liquids

The attached cell on the coated panel was filled initially with 5% NaCl, and the coating allowed to hydrate for 7 days. The NaCl solution was then replaced with hydrocarbon liquid. At intervals when an impedance measurement was made, the hydrocarbon liquid was removed from the cell, and replaced with 5% NaCl, after which the Bode curve was immediately measured. After the EIS measurements, the 5% NaCl was immediately removed and replaced with hydrocarbon liquid. The entire operation was completed in 8 to 10 minutes.

### **Coatings Evaluated by Autoclave Testing**

The test method is based on NACE TM0185, Evaluation of Internal Plastic Coatings for Corrosion Control of Tubular Goods by Autoclave Testing. Coated test panels are exposed to simulated oil field production conditions in a small laboratory sized pressure vessel (autoclave). The performances of the coatings in the aqueous, hydrocarbon, and gas phases were simultaneously determined.

The test panels consisted of carbon steel, 4.5 by 1.5 by 0.125 inches in size, coated on one side. The test panels were hung vertically within a 1-litre Hastelloy pressure vessel fitted with a Teflon liner. The lower third of the autoclave was filled with an aqueous solution of 5% NaCl. The middle third of the autoclave was filled with a solvent mix of 1 part kerosene to 1 part toluene by volume. The top third of the autoclave was filled with sour<sup>2</sup> gas, consisting of 5% H<sub>2</sub>S, 5% CO<sub>2</sub>, and 90% CH<sub>4</sub>. The autoclave was fully immersed in an oil bath, which serves to heat it to the test temperature. The run conditions for the autoclave test were: 121°C (250°F) at 1000 ± 10 psig for 96 hrs.

The procedure for taking the autoclave from test conditions to ambient temperature and pressure was as follows:

1. 0 to 95 Minutes: Reduce the temperature from 121°C to 35°C (250°F to 95°F); pressure drops from 990 to 660 psig
2. 95 to 145 minutes: Reduce the pressure from 660 psig to 0 psig (12.8 psig/minute)
3. 145 to 200 minutes: Nitrogen purge to remove hydrogen sulfide from autoclave fluids
4. 200 to 225 minutes: Disassemble and open autoclave; begin analysis of adhesion, blistering, etc

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<sup>2</sup> Sour, defined as containing hydrogen sulfide.

## 5. 225 minutes begin impedance measurements in the water phase of test panels

The coatings were rated for adhesion and blistering (ASTM D714) immediately upon removal from the autoclave. Adhesion was evaluated using a parallel scribe method in which two cuts, 1/8 inch apart, are made through the coating to base metal. The coating between the scribe marks is pried with a utility knife and the adhesion is rated according to the following scale:

| Rating | Description                       |
|--------|-----------------------------------|
| A      | No disbondment                    |
| B      | >50% still attached               |
| C      | <50% still attached               |
| D      | No adhesion                       |
| F      | Disbondment outside scribed lines |

Acrylic tubes were bonded to the water, hydrocarbon, and gas phases of the test panels with fast dry adhesive. A 5% NaCl solution was placed in each cell and impedance measurements immediately started. All EIS measurements in the water phase were made within 1 hour of removal from the autoclave; additional measurements in all three phases were made after 24 hrs, 48 hrs, and 7 days. The coatings were then allowed to dry out at ambient temperature and pressure for 8 days, after which hydration in 5% NaCl was followed for 7 days. Untested control panels were used to obtain the initial impedance, based on hydration for 48 hrs in 5% NaCl at 23°C.

## Results and discussion

### Effect of Immersion, Dry-out, and Re-hydration

The objective of this series of measurements was to determine the impedance of the four coatings as they pass through the typical sequence of steps in laboratory testing or in service. The steps are shown in Table 4. Three sets of the four coatings (equipped with attached cells) were respectively immersed in 5% NaCl solution at 23, 65, and 90°C, and the impedance was monitored over a period of 28 days. The temperature of the coatings at 65 and 80°C were then dropped to 23°C for 14 days, still under immersion; during this time the coatings originally at 23°C were retained at 23°C for an additional 14 days. Next, the NaCl solution was removed from all of the coatings for 7 days, during which the coatings dried out under laboratory conditions (23°C, 30 to 40% relative humidity). The 5% NaCl solution was then re-introduced to each coating, and the coatings rehydrated for 7 days at 23°C. Following this, the temperature of those coatings that were originally at 65 and 90°C were returned to 65 and 90°C respectively, for 7 days.

The impedance of the four coatings was measured throughout this series of changes. The Bode plots (Log Z versus Log f) were as anticipated. Examples of some of the curves are shown in Figure 2. Coatings with high barrier properties behaved like pure capacitors, producing a straight line plot with a slope near -1. Permeable coatings had a similar straight line plot, except that the impedance levelled out in the low frequency range, reaching a slope near zero. Fine structure in the mid-frequency range,

attributed to coating disbondment (5,6, 26, 27) was not observed due to the high film build of the coatings.

#### IMMERSION AT 23°C

The results are shown in Figure 3. Prior to hydration, the impedance of all of the coatings was very high. Log Z ranged from 10.6 to 11.0, consistent with the dielectric characteristics of dry coatings. Upon contact with 5% NaCl solution, the impedance dropped rapidly for two of the coatings, particularly during the initial 24 to 48 hours as the water diffused through the coating film. After this initial hydration, the impedance either stabilized with little further change (Coatings A and Coating D), or continued to decrease slowly with time (Coating B and Coating C). A slow continuous decrease in impedance with time is presumably related to further water uptake that is related to chemical and physical changes in the film leading to increasing permeability. The data suggest that for tank lining type coatings, a hydration time of at least 48 hours should be used to establish the pre-test coating impedance.

After 42 days of immersion, the coatings were allowed to dry out for seven days. The impedance of Coatings A, B, and D returned to the original impedance values measured prior to hydration, suggesting that little deterioration or permanent change occurred from the electrolyte immersion. Coating C however, had an impedance that was 0.5 Log Z units lower after dry-out, implying that the coating was not yet fully dry or that there was a permanent change in the film resulting in different dielectric properties.

Upon subsequent re-hydration in 5% NaCl, the impedance of the coatings returned to values very similar to those after the initial 42-day hydration, indicating a high degree of reversibility. The re-hydration occurred rapidly, with stable values achieved within 24 to 48 hours of re-hydration, except for Coating B where the impedance decreased gradually with time, similar to that in the original hydration.

Given that 23°C is a mild temperature exposure and well below the T<sub>g</sub> (Glass Transition Temperature) for these coatings (18) the good coating performance in terms of hydration, re-hydration, low permeability and reversibility is consistent with the good chemical and thermal resistance of the epoxy coatings.

#### Immersion at 65°C and 90°C

The results are presented in Figures 4 and 5. As expected, the impedance of the coatings drops rapidly from the initial value (dry at 23°C) during the first 24 hours of hydration. After the initial hydration, Coatings A, C, and D (at 90°C only) showed a typical behavior, where the impedance either stabilizes or continues to decrease with time. The behavior of Coatings B and D (65°C only) was unusual, in that after the initial drop, the impedance increased during the first 10 days of immersion, after which it either stabilized (Coating B) or began to slowly decrease (Coating D). The increase in impedance is presumably related to additional curing and/or other chemical reactions at elevated temperature, which lead to reduced permeability and higher impedance.

The continued decrease of impedance in Coating D signalled that this coating was more permeable than the other coatings. To characterize this behavior further, the four coatings were treated with a Selective Adhesion Release Agent (SARA) water based chemical stripper (36). The impedance observations were consistent with the SARA studies, in that Coating D had the lowest resistance to chemical stripping. A steel plate coated with Coating D was completely stripped in 12 hours, compared to 48 hours for Coating B or softening only, or with no effect, for Coatings C and A, respectively.

The effect of temperature on the impedance of the four coatings after 28 days of immersion is summarized in Figure 6. Over the three temperatures, the ranking of the coatings, starting with the coating with the highest impedance is Coating A > B > C > D, ie the same order of resistance to chemical stripping. The only exception is Coating D, which had the third highest impedance at 23°C, but lowest impedance at 65 and 90°C. The order of performance also accords well with the molecular structures and total chemical compositions of the coatings. Significantly, it is the predicted ranking order prior to commencing the test protocol. All other things being equal, Coating A was expected to perform best and did so, largely because of its tight 3D polymeric network of cross-links and greater steric hindrance arising from a reaction between a pure epoxy novolac resin and a three ringed, polyfunctional curing agent. The presence of inert and reinforcing pigments, and water immiscible solvents in the resulting film with low free volume, augmented the performance of the cured polymer in Coating A.

After 28 days at 65 and 90°C, the temperature was reduced to 23°C for 14 days. Within 24 hours the impedance values had increased and re-equilibrated to the new temperature, either stabilizing or drifting slowly downward thereafter. These data were compared to those in Figure 3, for impedance at 23°C and 28 days of hydration (ie reference conditions). Exposure to elevated temperature had little permanent effect on the barrier properties of Coating A, as its impedance was very similar to that observed at the reference conditions. In the case of Coating B, exposure to elevated temperature appeared to actually improve the barrier properties of B, possibly due to curing reactions as outlined above. In contrast, Coatings D and C experienced a significant loss in barrier properties as a result of exposure to elevated temperatures. The impedance remained well below that observed under reference conditions (Figure 3). The extent of the permanent change was larger at 90°C than at 65°C, and larger for Coating D than for C.

Coatings D and C are not so highly cross-linked and the effect of higher temperatures would be to facilitate easier molecular segment re-orientation, which would mean their free volume was higher, and predisposition to water uptake greater.

A consideration of the role of solvent selection in these four coatings is crucial at this juncture. Solvents provide molecular lubricity and molecular mobility. They dissolve high molecular weight resins and require balancing to retain resins in solution during the curing or drying period. They must exit the coating first by evaporation and then by convection at a desirable rate. For a tank lining the solvents should be water immiscible.

Against this backdrop, an interesting common denominator to the Coating C and D formulations was the presence of a water miscible solvent, PGMME. Any entrained, water miscible PGMME solvent (in what are essentially more porous films where water could aggregate in clusters and fill the free volume)

would set up osmotic gradients and increase permeation in these coatings. In addition, polar water molecules imbibed by the coating would be inclined to orient themselves towards polar groups on the epoxy polymer itself, and associate by weak intermolecular hydrogen bonds. A hydrogen bond is a secondary valency attraction with groups such as hydroxyls, carboxyls or amines (35, 37,38). In the case of both Coatings A and B there was not only much less innocuous free volume within the 3D matrix, but no water miscible solvents and much less water uptake.

Importantly, the presence of PGMME has been shown to cause osmotic blistering in traditional potable water epoxy coatings (39). It is also worth noting that in other studies by the authors, Coating D blistered after 22 days immersion in 82°C tap water whereas Coatings A and B were unaffected (18).

During dry-out, as expected, the impedance increased significantly for each coating. The process of diffusion by which water entered the coating during immersion is reversed during the subsequent drying period. Similarly, the formation of hydrogen bonds between water and polar groups on the cross-linked epoxy reverse at varying rates. The impedance of Coatings A and B was similar to the non-hydrated pre-test values (impedance at time = 0 days). This is consistent with these coatings possessing compact, highly cross-linked and low free volume structures. In contrast, the values for Coatings C and D were considerably lower than their pre-test values, particularly for the 90°C immersion. This implies irreversible changes occurred, which resulted in an increase in permeability. That the impedance values are low for Coatings C and D is not overly surprising, especially in the case of Coating D with its lower cross-link density and likelihood of residual PGMME solvent. No blistering was evidenced for either Coating C or D.

The glass transition temperature ( $T_g$ ) is another macrophysical property that was thought to possibly differentiate the coatings based on differences in structure and cross-link densities. Selection of resin systems that yield a high  $T_g$  should help to better control the potentially deleterious penetration of liquids and gases through the epoxy coating. Prior to  $T_g$  determination, it was reasoned that the  $T_g$ 's should tend to be greatest for coatings employing higher functionality resins and curing agents, and lowest for coatings employing predominantly Bis A resins and lower functionality curing agents.

The 90°C immersion temperature falls in the upper part of the range of the  $T_g$ 's for the coatings studied. The  $T_g$ 's for the respective coatings were: Coating A at 110°C, Coating D at 108°C, Coating D at 92°C, and Coating B at 66°C (18). The transition (ie shift in baseline resulting from the change in heat capacity) was large for Coating D, moderate for Coatings B and C, but very weak for Coating A. Based on  $T_g$  data alone, any deleterious effects of exposure at 90°C might therefore have been expected in a different order; the exception to this trend was certainly Coating B. This confirms that one cannot predict coating performance based solely on a  $T_g$  measurement, a finding that underscores that laboratory tests are indicators of performance and not to be over-interpreted.

Upon re-immersion at 23°C, and the subsequent increase of temperature to 65 and 90°C, all four coatings returned to impedance values, which were relatively similar to those observed previously before dry out. During re-immersion and the respective temperature adjustments, the impedance stabilized within 24 to 48 hours.

For the tank linings under study here, the impedance observed at room temperature following exposure to elevated temperature, was a good indicator of coating performance under laboratory conditions. Those coatings with the highest impedance at elevated temperature also had the highest impedance when cooled to 23°C indicating minimal structural rearrangement and permanent change resulting from exposure to higher temperatures.

Hence, the observations are consistent with the formulation chemistry and field experience of the coatings. Coatings A and B have the best field service track records in the Alberta oil fields (40) and also have the highest impedance values in the present work.

Both the magnitude of the impedance, and the change of impedance with extended immersion time are very useful in characterizing the performance of the coatings, based on barrier properties. High, stable impedance is most desirable, as demonstrated by Coating A for example. A low impedance which is drifting downward with time is least desirable, as demonstrated by Coating C; Coating C not only had high permeability and poor barrier properties, it also appeared to undergo irreversible changes related to increasing permeability with time.

The data indicate that when impedance measurements are made on coatings in service, they should be made immediately upon shut down, before the coating dries out. Alternatively, if full dry-out occurs, the coating should be re-hydrated over a minimum period of 24 to 48 hours prior to impedance measurements.

### **Effect of Electrolyte Concentration on Coating Impedance**

When coatings are hydrated for purposes of determining pre-test impedance, an electrolyte and electrolyte concentration must be selected. In service, protective coatings are exposed to aqueous process fluids having a wide range of composition. In oil and gas production systems, produced water contains primarily sodium chloride, with salinities close to that of sea water (5% NaCl). However, geological and operational factors can result in large variations, from very low to very high (eg. 120,000 ppm or 12% NaCl). It was therefore of interest to determine the effect of electrolyte concentration on coating impedance.

The four coatings were subject to immersion in NaCl solution at four concentrations at 23°C. Impedance was measured at intervals over 40 days. The aqueous solutions, and their respective published resistivities (41) were:

0% NaCl (deionized water) ( $> 1000 \Omega \text{ cm}^2$ )<sup>3</sup>  
3% NaCl in deionized water ( $23 \Omega \text{ cm}^2$ )  
5% NaCl in deionized water ( $14 \Omega \text{ cm}^2$ )  
20% NaCl in deionized water ( $5 \Omega \text{ cm}^2$ )

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<sup>3</sup> Certification for deionized water purchased from VWR Canlab.

The results are shown in Figure 7. The impedance of the coatings is observed to decrease as the sodium chloride concentration decreases. The extent of the decrease varied with the specific coating. Coatings A and B were affected very little by electrolyte concentration, with most of the variation related to uncertainty in the measurements. The difference in impedance of the coatings between 20% NaCl and 0% NaCl, after 10 days of hydration in Log Z units was 0.75 for Coating C and 1.1 for Coating D.

With extended immersion time, the impedance either stabilized (Coating A and D) or gradually drifted downward (Coatings B and C). An exception was Coating C where the relationship between impedance and electrolyte reversed after 5 days in the 0 to 5% NaCl range. This is presumably due to other chemical reactions and physico-chemical changes which occurred with extended exposure to water.

The results suggest that bulk electrolyte does not move into the coatings, as the impedance would then be expected to decrease with increasing electrolyte concentration. Instead, the results suggest that osmotic gradients may initiate the movement of water into some of these coatings. To reiterate, entrained PGMME solvent is most likely to cause osmosis given that this solvent is water miscible and any intermolecular hydrogen bonding can be reversed to varying degrees during the subsequent drying period. The greatest osmotic pressure and corresponding negative effect to coating performance would be obtained where the coating is immersed in deionized water. Conversely, the lowest osmotic pressure would arise from immersion in 20% NaCl deionized water. As seen earlier, the fact that no blistering occurred in any electrolyte is testimony to the excellent adhesion characteristics of Coatings C and D where the adhesion values in psi would be expected to exceed the osmotic pressure generated by any entrained hydrophilic solvent.

Electrolyte concentration had little effect on Coating A, again suggesting either that osmotic effects are limited, or that the polymeric structure is highly cross-linked and rigid, and does not permit much variation in the small amount of water that can diffuse in. Coating A also had a significantly better field performance track record compared to the highly permeable coatings, consistent with a limited effect by electrolyte concentration.

These results indicate that to obtain accurate, representative results, impedance measurements should be made with aqueous solutions that are relatively close to the process fluid that will be in contact with the coating. Based on this limited amount of work this effect may be particularly significant for coatings with a high permeability (ie low impedance at ambient conditions in 5% NaCl). These data may also be useful in coating design for immersion service.

### **Effect of Hydrocarbon Solvent on Coating Impedance**

Oil and gas production fluids contain hydrocarbon liquids of a widely varying composition. The hydrocarbons consist of a mix of aliphatic and aromatic components, some of which are "condensates" or light hydrocarbons like butane and pentane. Some hydrocarbons may penetrate polymeric coatings to varying degrees, depending upon the coating and the nature of the hydrocarbon. It was of interest to

determine if deterioration from exposure to hydrocarbons could be detected by impedance, based on changes of coating permeability to water.

To evaluate this behavior, the four coatings were initially immersed in 5% NaCl solution at 23°C for 7 days. Then they were immersed in a solvent consisting of a 1:1 mix of kerosene and toluene. This simple mix is a model commonly used for the aromatic and aliphatic components of oil production fluids. The impedance was monitored for 7 days, after which the coatings were immersed once again in 5% NaCl at 23°C.

The results in Figure 8 show that the impedance of the coatings increases as the immersion time in the hydrocarbon increases (23°C). The increase is insignificant for the high impedance coatings, but very significant for the lower impedance, permeable coatings. The impedance for Coatings D and C increased from Log Z 8.3 to 9.6, and Log Z 8.8 to 10.4, respectively. After 7 days of contact with Coatings D and C, the impedance was still on an upward trend and therefore, these coatings were likely not yet equilibrated or saturated with hydrocarbon.

After hydrocarbon immersion, the coatings were returned to immersion in 5% NaCl. The coating impedance immediately dropped as water entered the coating. The impedance of Coatings A, B, and C returned to the initial values, before hydrocarbon exposure, within 2 to 7 days. In contrast, Coating D appears to have experienced irreversible change (or damage) from the hydrocarbon exposure. Upon re-introduction of electrolyte, the impedance dropped rapidly, reaching a value of Log Z =5, well below the original value of Log Z = 8.8 prior to hydrocarbon exposure. Coating D again shows that its formulation chemistry not only predisposes it to hydrolytic attack but also to degradation from hydrocarbons. In other work conducted by the authors, however, there was no visual attack of Coating D when immersed in toluene at 48°C (120°F).

The results show that when coatings are in hydrocarbon immersion service, they need to be hydrated in order to compare the impedance to the reference conditions of hydration in aqueous solution at room temperature. At room temperature the re-hydration process is relatively slow, requiring at least 2 days, and possibly 7 or more for some coatings. At higher temperatures, the equilibration would presumably be much faster. The effect of mixtures of water and hydrocarbon should be assessed to determine if the presence of water in the hydrocarbon is sufficient to hydrate the polymer. The method does appear feasible as the impedance results are consistent with the formulation chemistry and chemical resistance observed in the field service.

### **Impedance Measurements for Process Conditions at High Temperature and Pressure**

To complete this investigation, the four coating were taken through an autoclave test where they were exposed to simulated oil field conditions involving temperatures above 100°C and elevated pressure. As in the measurements below 100°C, coating impedance was measured before exposure to test conditions, after exposure to test conditions as a function of time after removal from the autoclave, through a period of dry out, and then during re-hydration at ambient conditions. The effects of gas, hydrocarbon, and aqueous phases were also evaluated.

Test panels were simultaneously exposed to 5% NaCl (bottom part of panel), a 1:1 mixture of kerosene and toluene (middle part of panel), and sour gas (5% H<sub>2</sub>S, 5% CO<sub>2</sub>, 90% CH<sub>4</sub>) (top part of panel). Test conditions were 120°C, 1000 psig for 96 hours. The impedance of the coatings in the three fluid phases was followed closely as a function of time after the panels were removed from the autoclave.

The coatings did not experience any blistering or disbondment except for Coating C, which experienced total disbondment in the hydrocarbon phase, and partial disbondment in the sour gas phase. The adhesion of the coatings was relatively good, varying between A and B, with Coating D being the only coating to have A only ratings. With its lower cross-link density, Coating D was observed to be a softer coating and less prone to chipping when pried with a knife in the parallel scribe test method. The adhesion value of Coating D is thus excellent and often apparently greater than the B adhesions recorded for more brittle Coatings such as Coating A.

The change in impedance with time after removal from the autoclave is shown in Figure 9. During the initial 48 hours after removal from the autoclave, the impedance of Coatings A and B increased somewhat, presumably due to equilibration of the coating. After 48 hours, the impedances stabilized. The change was larger for Coating B than for Coating A as expected, based on its chemistry. The impedance of the hydrocarbon and gas phases decreased after removal from the autoclave, presumably due to water uptake.

The equilibrated data (48 hrs at 23°C in 5% NaCl) for Coating A and B were compared to the pre-test impedance obtained at the reference conditions of 23°C, hydration in 5% NaCl for 48 hours. The impedance of Coating A had decreased almost 1.0 Log Z unit in the water phase, and 0.3 to 0.4 Log Z units in the gas and hydrocarbon phases, as a result of exposure to autoclave test conditions. The impedance of Coating B dropped somewhat lower than this, possibly because this film was thicker and offered slightly better resistance. In either case, only a small amount of permanent deterioration appeared to occur.

Upon dry-out the impedance of Coatings A and B increased to values similar or higher than the pre-test values. When the coatings were re-hydrated in 5% NaCl at 23°C the impedance values remained higher than the original equilibrated values. Whereas the values for Coating B stabilized after 48 hours, the impedance of Coating A had not yet equilibrated to the pre-dry-out values after 7 days of hydration.

The results for Coatings C and D were quite different. Upon removal from the autoclave, the impedance dropped with time, suggesting that the deteriorated coating was taking up additional water and had deteriorated further. The resistance of Coating D to the hydrocarbon liquid was considerably better than resistance to water and sour gas, retaining an impedance above Log Z = 9.

The relatively poor performance of Coating C could be related to the presence of zinc phosphate in the coating formulation. While it is insoluble at neutral pH, at low pH (< 5.5) unmodified zinc phosphate can become soluble (42, 43). The pH of the hot aqueous phase is low (ca. pH 4.5) due to the presence of carbonic and sulphurous acid (dissolved CO<sub>2</sub> and H<sub>2</sub>S in the water phase). Small quantities of water and gas can be drawn into the epoxy and diffuse along interstices of the zinc phosphate and binder. Thus

potentially acidic water can dissolve any soluble material and set up an electrolyte in the epoxy matrix. Since the amount of water entering the coating is small, the effective electrolyte concentration may be very high. Consequently, once again a high osmotic force could result, with the effect of pulling additional water into the coating. It should also be noted that if modified zinc phosphate is used it will potentially have hydrophilic treatments that can initiate osmotic gradients.

Extender pigments, such as barium sulfate and crystalline silica improve the protective properties of tank linings as a result of their inert qualities and reinforcing effect. In the case of Coating C, however, the overall level of pigmentation (anticorrosive and extender) is much higher than in the other coatings and, solvent arguments aside, may possibly account for its higher permeability given that a primary mechanism for water permeation is around pigment surfaces. Ordinarily, with a proper pigment volume concentration to critical pigment volume concentration (PVC/CPVC) ratio, the large permeability increase observed in Coating C would not be expected since its base epoxy resin is a pure novolac. The dull and rough textured appearance of this coating reflects the larger amount of pigment contained in the epoxy matrix compared to higher gloss coatings such as Coating A.

In either scenario, aside from structural considerations of the polymer, it can be argued that the pigment and solvent chemistries of Coating C help to account for the poorer performance of this tank lining. In contrast, Coatings A, B and D principally use barium sulfate, an inert and insoluble extender pigment noted for imparting further chemical resistance to tank linings.

Upon dry out, the impedance of Coating C increased only slightly; this was presumably due to the rapid uptake of water which was introduced for the measurement. In the following hydration the impedance continued to drop, implying further deterioration was occurring. Upon dry-out, the impedance of Coating D returned to near pre-test values. Upon re-hydration, the impedance values returned within 24 hours to the impedance observed immediately prior to dry out, showing high reversibility.

These data are consistent with the trends observed at 23, 65, and 90°C, discussed above. They are also generally consistent with the formulation chemistry described and the field experience which shows that Coatings A and B are higher performers, and consistently so, compared to Coatings C and D.

The data show that when EIS is used in the evaluation of coated panels subject to autoclave testing, test panels should be allowed to re-equilibrate to room temperature for at least 48 hours.

These data also provide valuable information for making EIS field measurements on coatings at service conditions at elevated temperature and pressure. The data show that hydration for at least 48 hours, preferably much longer, if precise data is required. Conversely, if the objective is to identify moderate to severe deterioration, a proper relative ranking of coatings can be obtained with hydration times as short as 24 hours. Coatings with significant deterioration hydrate quickly, whereas highly chemically resistant coatings hydrate slowly.

## Conclusions

EIS measurements have been shown to be particularly useful in understanding tank lining coating performance when the coatings were subjected to immersion conditions at various temperatures and a range of chemical conditions.

The impedance of four commercial epoxy tank linings was measured as the coatings were subjected to a series of conditions simulating laboratory testing (eg. autoclave testing) or industrial service. The coatings were selected on the basis of having a wide range of field performance and impedance characteristics. Based on the coatings and conditions used within this study, the results based on EIS measurements showed:

- The uptake of water and the change in the permeability of the coatings (as sensed by EIS) was consistent with key aspects of the coating's formulation chemistry. In particular, the EIS results were consistent with the combined effects of coating resins, solvent line-ups (ie blends), and pigmentation.
- The coating performance as determined by EIS measurements was generally consistent with field performance of the coatings.
- Care must be taken to adequately hydrate the coatings with the proper electrolyte when impedance measurements are made on coatings in service in the field, or on test panels retrieved from industrial vessels.
- When laboratory testing is conducted at high temperatures and pressures, care must be taken in making post-run impedance measurements at the reference conditions of ambient temperature and pressure. Sufficient time of at least 48 hours must be allowed for the coatings to re-equilibrate to the reference conditions prior to EIS measurements.
- Significant physical and chemical changes occur in the coatings under test or field conditions at elevated temperature and pressure. Many of these changes reverse at varying rates when the coatings are returned to ambient temperature and pressure. Irreversible changes can be the result of coating deterioration and loss of performance. EIS can be used as a diagnostic tool in following these processes, providing useful guidance in assessing coating performance and the effect of different formulation parameters.

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**Table 1. Epoxy Tank Linings**

| <b>Coating No.</b>                             | <b>A</b>          | <b>B</b>                   | <b>C</b>  | <b>D</b>         |
|--|-------------------|----------------------------|-----------|------------------|
| Base Epoxy Resin                               | Novolac*          | Novolac* - BisA            | Novolac*  | Novolac* - Bis A |
| Curing Agents **                               | MPCA (I)/MPCA(11) | PACM/adducted<br>PACM/TEPA | PACM      | DCH              |
| Mobilizing Agent:<br>Benzyl alcohol            | Yes               | Yes                        | Yes       | Yes              |
| Furfuryl Alcohol+A29                           | Yes               | No                         | No        | No               |
| Pigments***                                    |                   |                            |           |                  |
| BaSO4  | Yes               | Yes                        | No        | Yes              |
| TiO2   | Yes               | Yes                        | Yes       | Yes              |
| SiO2   | No                | No                         | Yes       | No               |
| Zinc Phosphate                                 | No                | No                         | Yes       | No               |
| Solvents***                                    |                   |                            |           |                  |
| PGMME  | No                | No                         | Yes       | Yes              |
| TOLUENE  | No                | No                         | Yes       | No               |
| XYLENE   | Yes               | Yes                        | No        | No               |
| Number of coats                                | 2                 | 2 (primer + topcoat)       | 3         | 2                |
| DFT, mils                                      | 13                | 30                         | 13        | 11               |
| Upper Temperature for Immersion, F             | 250-275           | 230                        | 250       | 250              |
| Sour Crude, oil environments                   | Yes               | Yes                        | Yes       | Yes              |
| Solvented or Solventless                       | Solvented         | Solventless                | Solvented | Solvented        |
| Field Service Record in Oil and Gas Production | Best              | Good                       | Uncertain | Good to Poor     |

\*Special Note: Novolac does not include Bis F in this description

\*\* Ref 18

\*\*\*Not all inclusive

Table 2. Epoxy Resins (18)

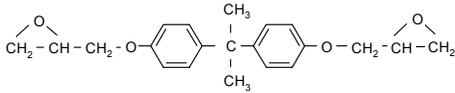
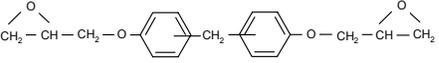
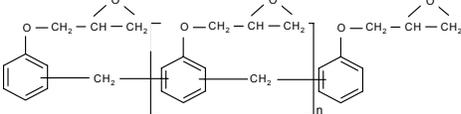
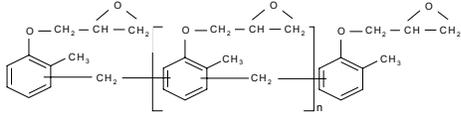
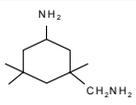
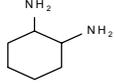
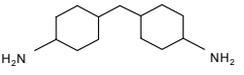
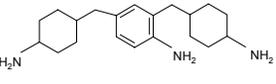
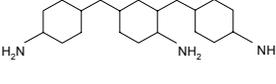
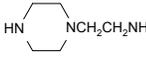
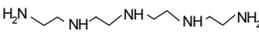
| Epoxy Resin                  | Abbreviation              | Structure  | Functionality | CAS #      |
|------------------------------|---------------------------|--|---------------|------------|
| diglycidyl ether bisphenol A | Bis A (DGEBA) (1001 Type) |  | 1.9           | 25068-38-6 |
| diglycidyl ether bisphenol F | Bis F (DGEBF)             |  | 2.1           | 9003-36-5  |
| epoxy phenol novolac         | EPN                       |  | 2.6 - 3.5     | 28064-14-4 |
| epoxy cresol novolac         | ECN                       |  | 2.7 - 5.4     | 28064-14-4 |

Table 3. Curing Agents (18)

| Curing Agents                          | Abbreviation   | Structure   | Functionality (Approx.) | CAS #       |
|--|----------------|---|-------------------------|-------------|
| isophoronediamine                      | IPDA           |  | 4                       | 2855-13-2   |
| diaminocyclohexane                     | DCH            |  | 4                       | 694-83-7    |
| 4,4-bis(para amino cyclohexyl) methane | PACM           |  | 4                       | 1761-71-3   |
| modified polycycloaliphatic polyamine  | MPCA (Type I)  |  | 6                       | 135108-88-2 |
| modified polycycloaliphatic polyamine  | MPCA (Type II) |  | 6                       | 135108-88-2 |
| N aminoethyl-piperazine                | AEP            |  | 3                       | 140-131-8   |
| tetraethylenepentamine                 | TEPA           |  | 7                       | 112-57-2    |

**Table 4. Sequence of Immersion, Temperature, Dry-out, and Re-immersion of Coatings During Which Impedance was Measured**

| Test Interval               | 0-28 days                                       | 28 – 42 days | 42-49 days         | 49 to 56 days | 56-63 days   |
|-----------------------------|---|--------------|--------------------|---------------|--------------|
|                             | Temperature of Coating During Test Interval, °C |              |                    |               |              |
| <b>23°C set of coatings</b> | 23 Immersion                                    | 23 Immersion | 23, <b>Dry out</b> | 23 Immersion  | 23 Immersion |
| <b>65°C set of coatings</b> | 65 Immersion                                    | 23 Immersion | 23, <b>Dry out</b> | 23 Immersion  | 65 Immersion |
| <b>90°C of coatings</b>     | 90 Immersion                                    | 23 Immersion | 23, <b>Dry out</b> | 23 Immersion  | 90 Immersion |

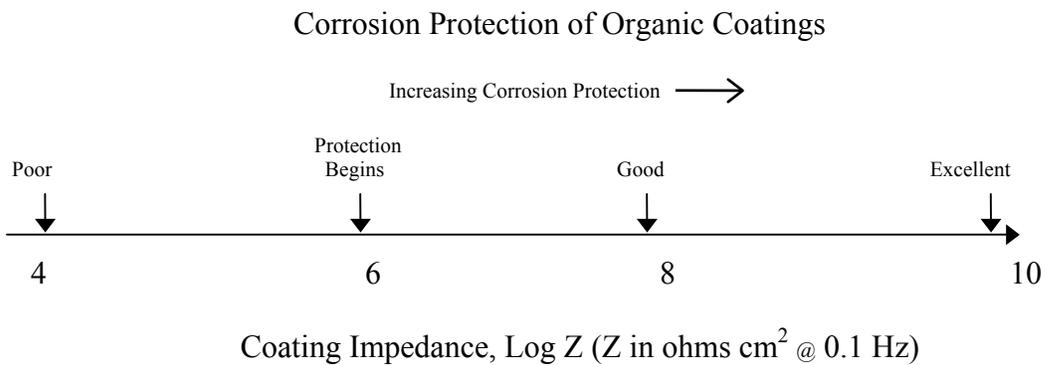


Figure 1. Interpretation of Coating Impedance Data

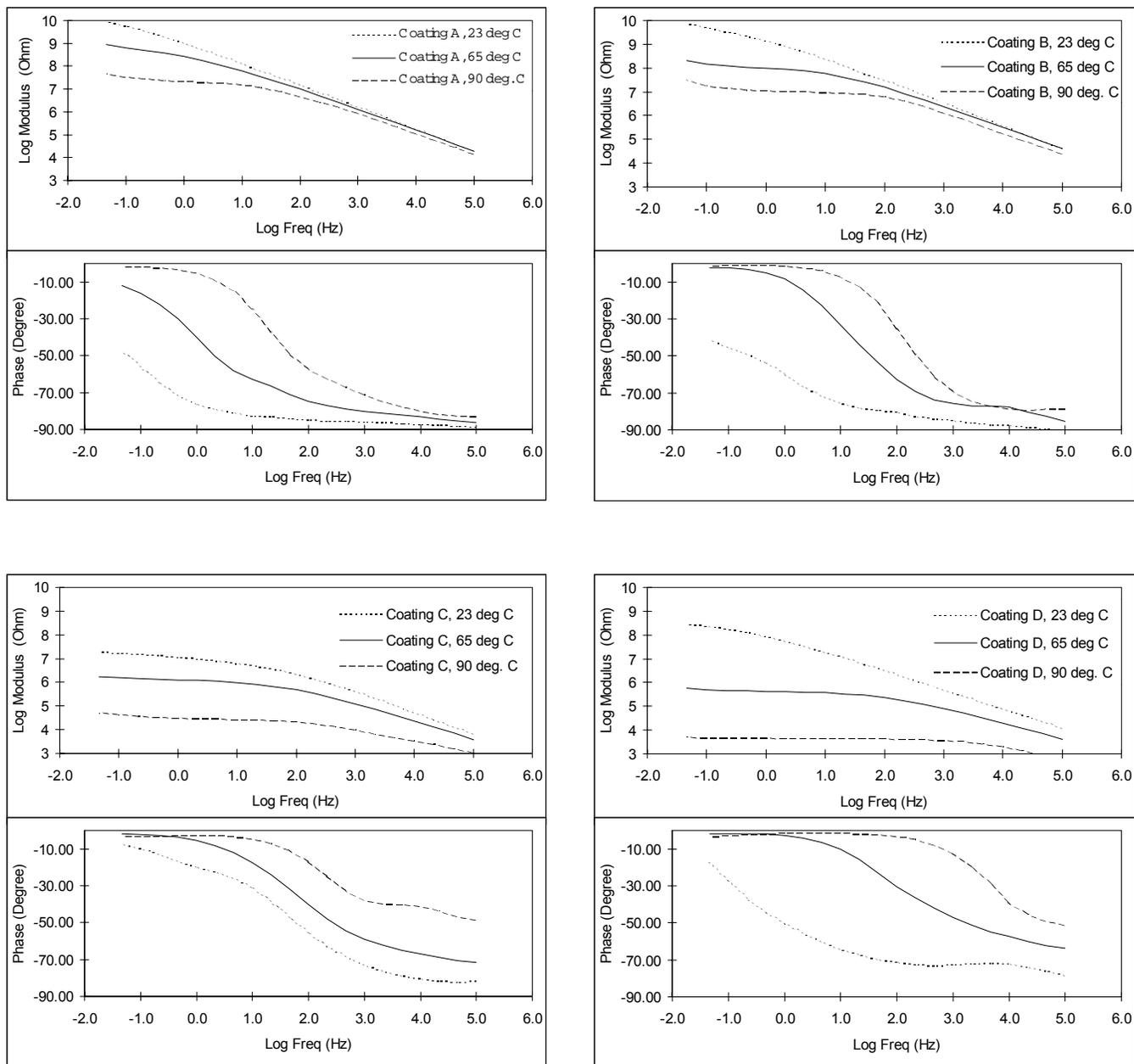


Figure 2. Bode Plots and Phase Angle of 28 day EIS Measurements

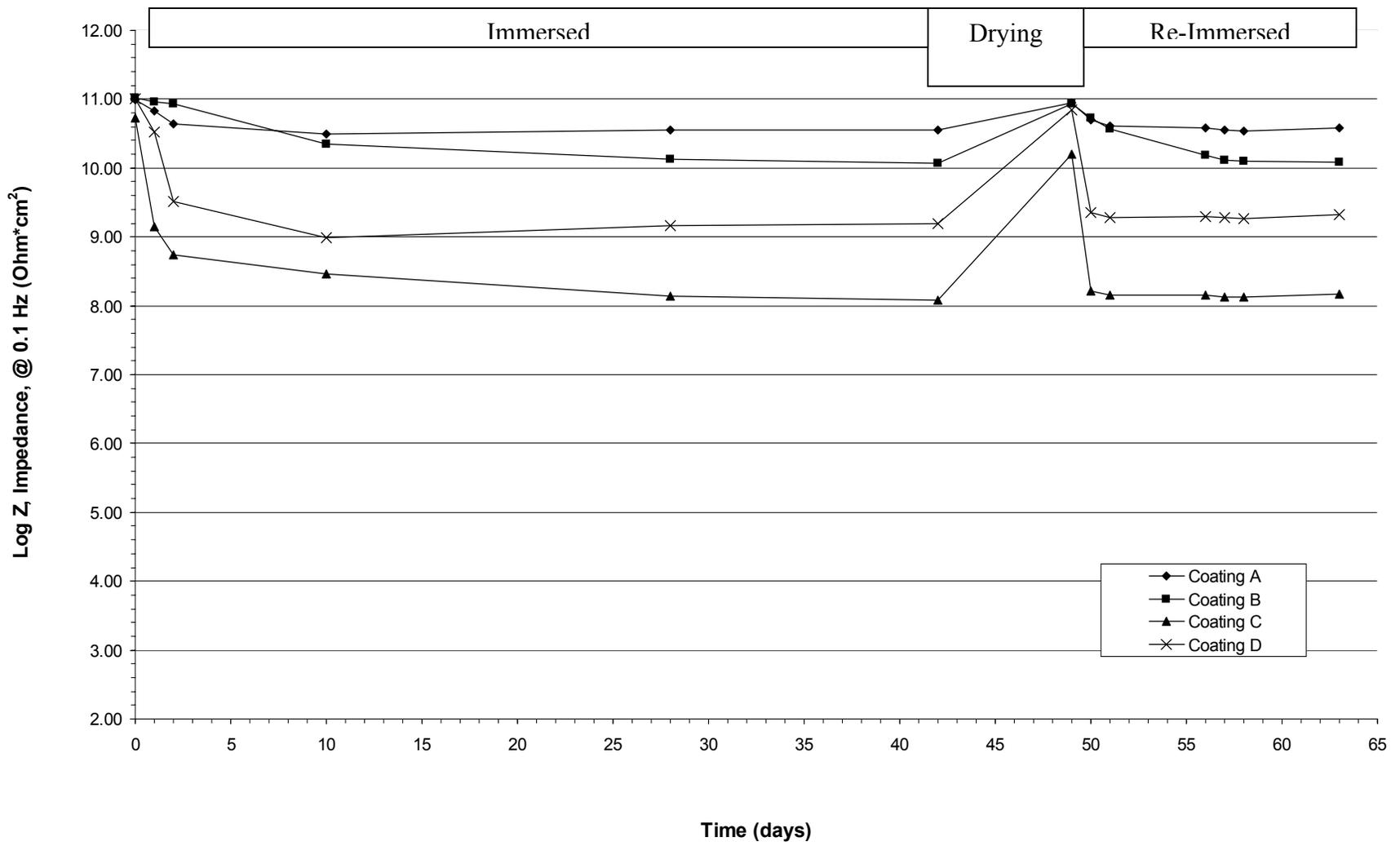


Figure 3. Coating Impedance Versus Time at 23°C

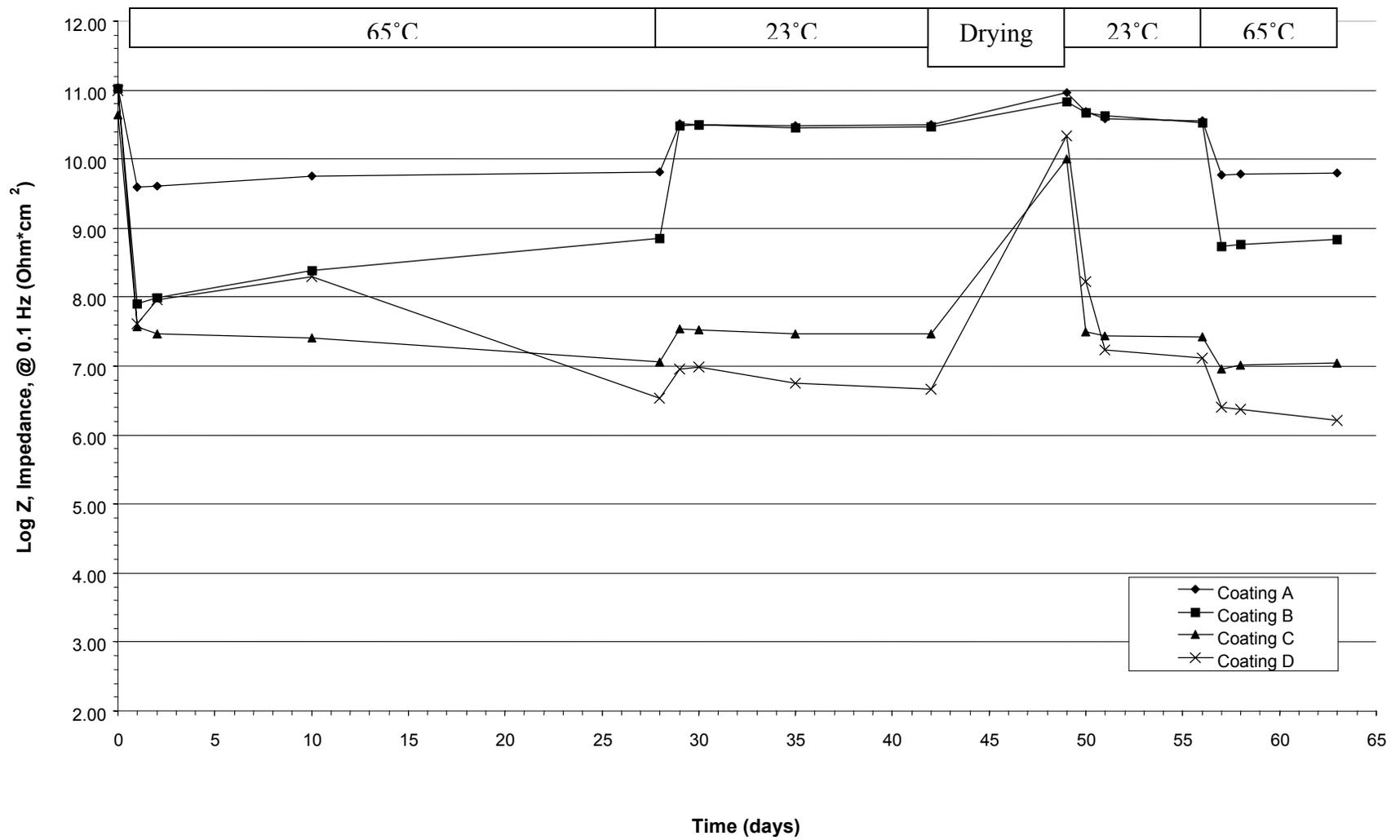


Figure 4. Coating Impedance Versus Time at 65°C

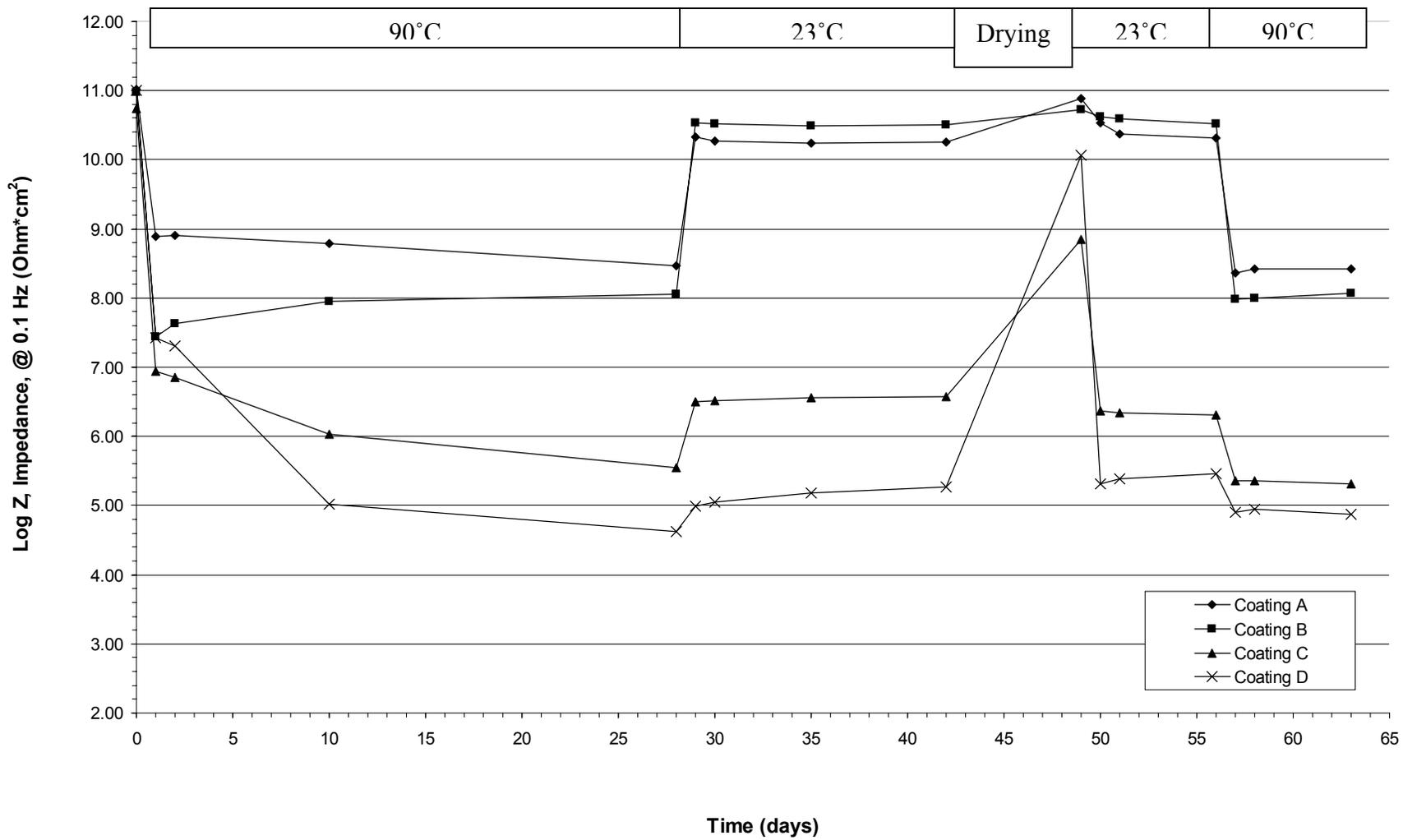


Figure 5. Coating Impedance Versus Time at 90°C

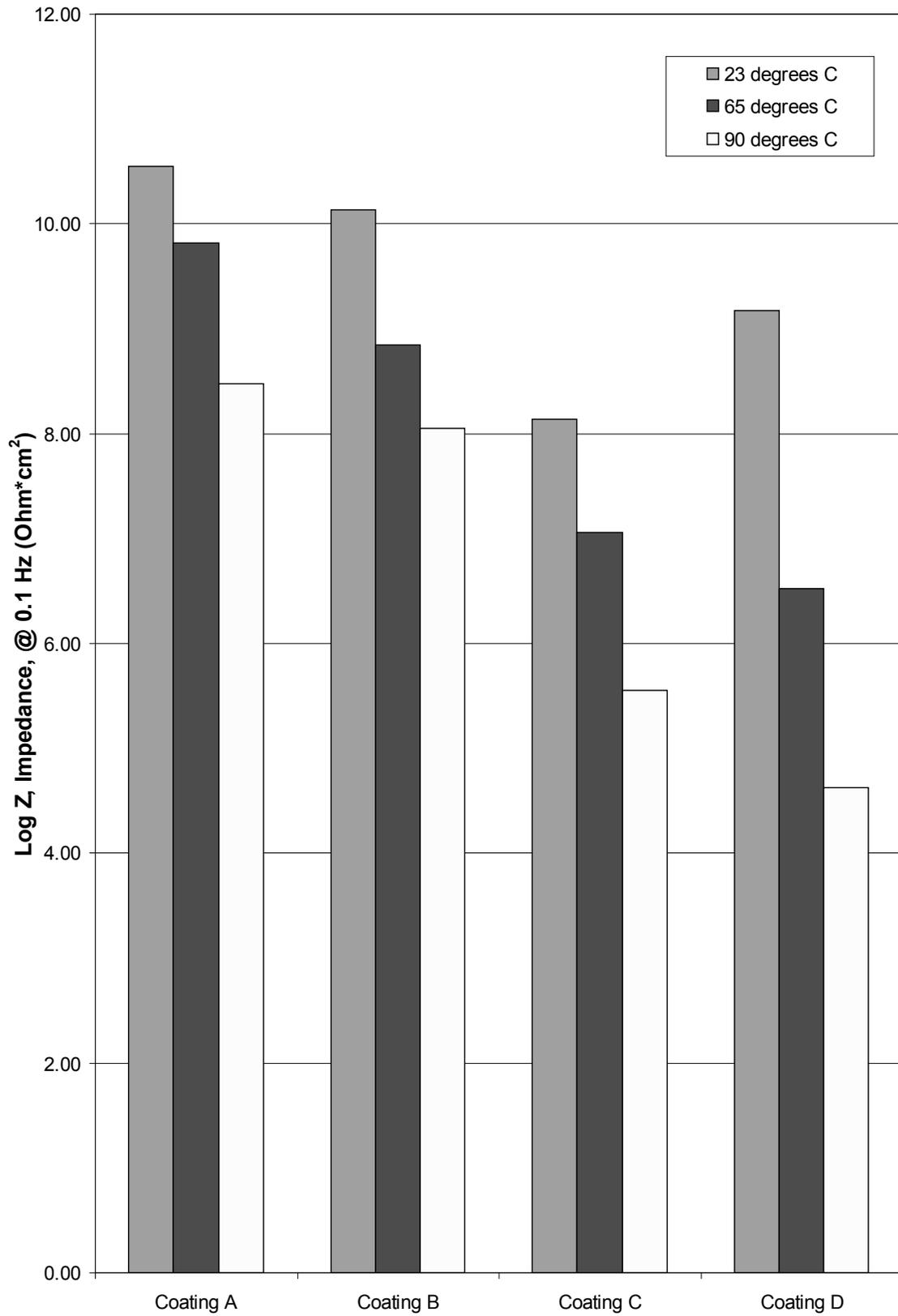


Figure 6. Coating Impedance Versus Temperature at 28 days

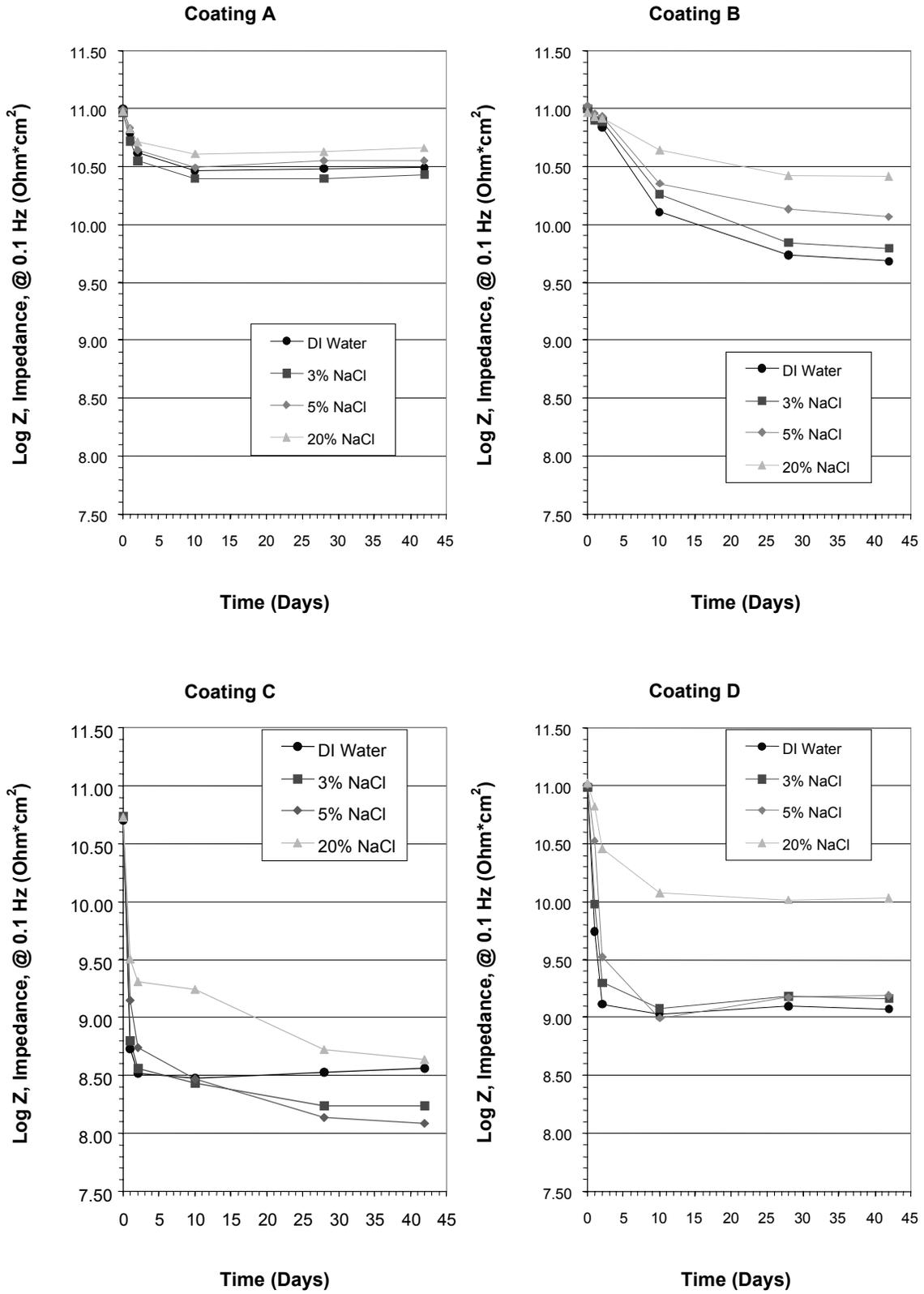


Figure 7. Coating Impedance Change Versus NaCl Concentration

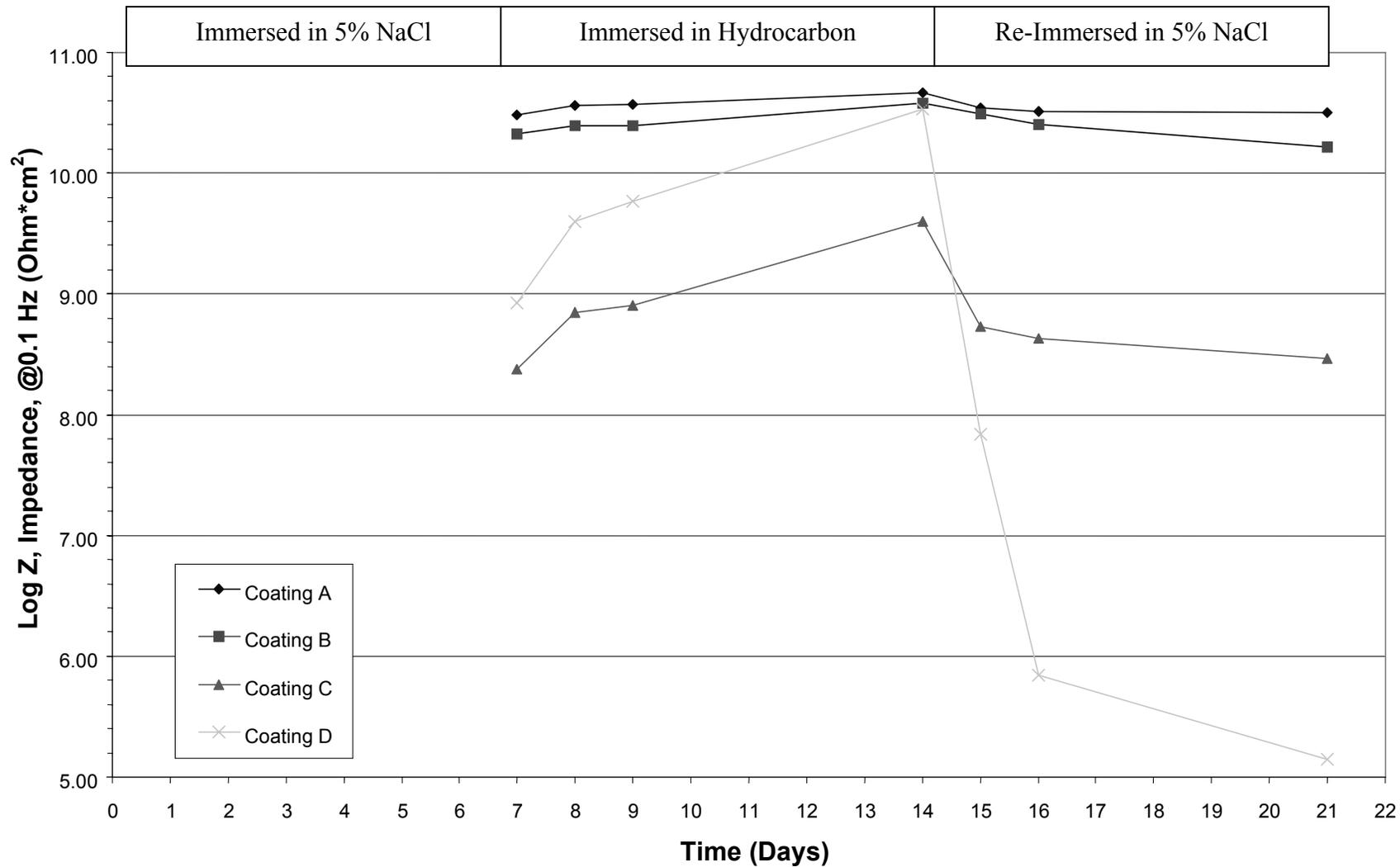


Figure 8. Coating Impedance in Hydrocarbon

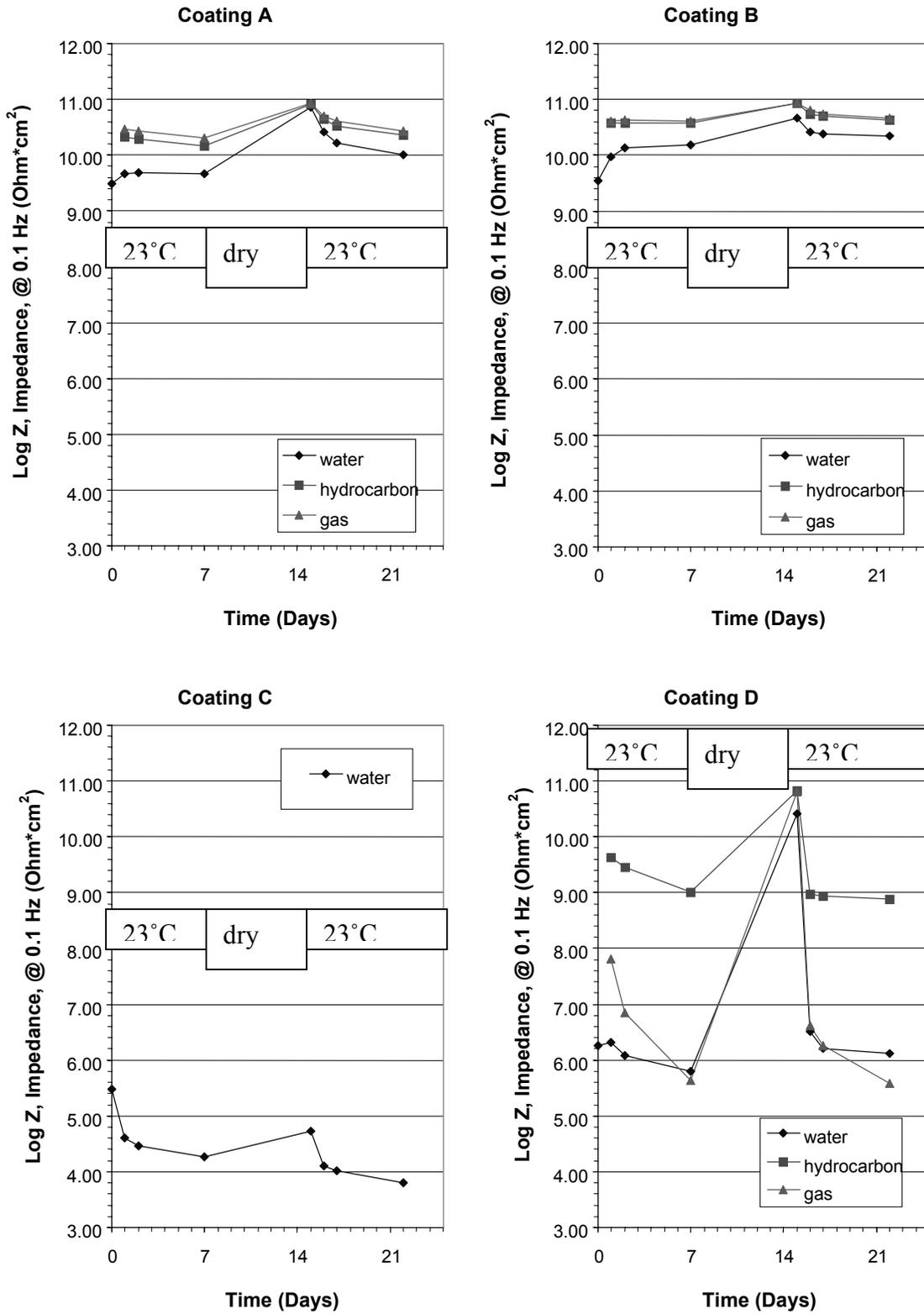


Figure 9. Coating Impedance Versus Time after Autoclave