M. Bengi Taysun and A. Gizli. / Hacettepe J. Biol. & Chem., 2022, 50 (3), 227-237

Research Article

Hacettepe Journal of Biology and Chemistry

journal homepage: www.hjbc.hacettepe.edu.tr

# Comparison of Accelerated Exposure Tests on Organic Coatings via Electrochemical Means

# Organik Kaplamalarda Hızlandırılmış Maruziyet Testlerinin Elektrokimyasal Yöntemlerle Karşılaştırılması

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## ABSTRACT

Organic coatings are widely employed on the protection of metallic surfaces from the effects of the corrosion. While the mechanisms of corrosion protection by organic coatings are well known, observing these mechanism's development is not possible with traditional accelerated exposure tests like salt spray (ASTM B-117) and condensation chamber (ASTM D-4585) tests. In these tests, corrosion can only be observed and evaluated after its visual clues emerge, which can be much later than the start of the actual corrosion under the coating, requiring long test durations to differentiate between samples. In this study, progress of degradation on an organic coating during two different accelerated exposure tests was investigated. Measuring electrical impedance spectra (EIS) of fresh and different levels of exposed coatings and modelling them in an appropriate equivalent electrical circuit showed the level of degradation underneath the coating. Although visual inspection did not reveal any corrosion, with EIS, corrosion was observed in just 60 hours of salt spray test exposure while 240 hours of condensation chamber test was not enough to initiate corrosion. Results showed that for the coating system tested, salt spray imparts much higher levels of degradation compared to the condensation chamber test.

**Key Words**
Corrosion, EIS, organic coating, accelerated exposure.

## ÖZ

Metal yüzeyleri korozyonun etkisinden korumak için organik kaplamalar yaygın olarak kullanılır. Organik kaplamalar ile korozyon korumasının mekanizmaları bilinmesine rağmen, bu mekanizmaların gelişiminin tuzlu sis (ASTM B-117) ve yoğuşma kabini (ASTM D4585) gibi geleneksel hızlandırılmış maruziyet testleri ile izlenmesi mümkün değildir. Bu testlerde korozyon sadece görsel emarelerin ortaya çıkmasıyla gözlenebilir, bu durum kaplama altında korozyon başlangıcından çok sonra gerçekleşebilir ve dolayısıyla numuneler arasında farkların ortaya çıkması için uzun test sürelerine ihtiyaç duyulabilir. Bu çalışmada bir organik kaplamanın iki farklı hızlandırılmış maruziyet testi etkisi altında yıpranması takip edilmiştir. Farklı sürelerde maruziyet görmüş numunelerin elektriksel empedans spektrumlarının ölçülmesi ve uygun eşdeğer elektriksel devreler ile modellenmesi kaplama altında meydana gelen yıpranmayı göstermiştir. Görsel inceleme ile herhangi bir korozyon etkisi görülmese de, EIS ile 60 saat tuzlu sis testinde korozyon başlangıcı gözlemlenmiştir, ancak 240 saat yoğuşma kabini korozyon başlangıcı için yeterli olmamıştır. Sonuçlar test edilen kaplama sistemi için tuzlu sis testinin, yoğuşma testine göre çok daha fazla yıpranma meydana getirdiğini göstermiştir..

**Anahtar Kelimeler**
Korozyon, EIS, organik kaplama, hızlandırılmış maruziyet.

**Article History:** Received: Jan 3, 2022; Revised: Mar 14, 2022; Accepted: Mar 14, 2017; Available Online: Jul 5, 2022.

**DOI:** https://doi.org/10.15671/hjbc.1052654

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## INTRODUCTION

A widespread method of protecting metallic surfaces from corrosion is to coat these surfaces with organic coatings. Organic coatings are mostly in liquid form prior to application. They, especially protective coatings, applied mostly by spray and cure on the surface to produce a complex, composite material compromised of a polymeric backbone with pigments, fillers, additives etc [1].

Corrosion is relatively rapid and linear progressing on uncoated metals, but its progress on coated specimens is nonlinear and slow moving. This presents a problem in developing, testing, and applying these coatings; how to measure the protective effect of highly corrosion-resistant coatings? To this end, accelerated exposure tests are widely employed in the coatings industry [2]. Corrosion is a complex process involving electrochemical as well as physical phenomenon such as diffusion, charge transfer etc., and it cannot be accelerated. Therefore, these tests are not really accelerated, rather they are tests that apply exaggerated exposure conditions on the specimens.

Two of these accelerated tests are salt spray (ASTM B117) and humidity chamber (ASTM D4585) tests. These can take up to several months for some highly protective coating specimens to show a difference between the samples. In most cases, the rust and associated permeability starts much sooner than any visual indication on the specimens. But with electrochemical means, namely electrical impedance spectroscopy (EIS), it is possible to measure difference between the specimens.

The real-world performance of coatings is predicted using their performance on the accelerated exposure tests. These predictions are possible thanks to the great amount of experience gained from these tests and corresponding real-world experience. Therefore, it is important to measure and parametrize the fresh and exposed coatings at different points in these tests, using electrochemical methods. This might allow prediction of performance from the fresh or lightly exposed specimens.

The ideal way to test an anti-corrosive coating would be just taking a freshly painted sample panel and just measuring its impedance. However unexposed, fresh coatings basically act as a capacitor, exhibiting very high impedances. This leads to experimental difficulties due to very low currents. Low currents might exceed some experimental setups limits and require special setups or force experimenters to use higher AC amplitudes, leaving ideal linear voltage vs current area. Besides these experimental difficulties, fresh coating poses another problem. Many anti-corrosive pigments act via dissolving into diffused water within the coating, then depositing on the surface, passivating it. Therefore, any EIS measurement taken with fresh coating might not show the effect of anti-corrosive pigments within the coating [3, 4].

The failure reason and mechanism of protective coatings is generally unknown except for the exposure intensity. Measuring EIS of fresh and different levels of exposed coatings and modelling them in an appropriate equivalent electrical circuit might show some clues and allow prediction of real-life performance of the coating, if not from fresh panels at least from the lightly exposed panels.

In this study, coated specimens were subjected to differing levels of exposure in salt spray and humidity chamber tests. The degradation on the specimens was measured using EIS and put into an equivalent electric circuit model representing the coating and corrosion process within it.

## MATERIALS and METHODS

### Substrate and application

Prepared coating was applied on 9 by 19 cm rectangular cold rolled steel panels. Panels were sanded with P280 grit sandpaper and cleaned with hydrocarbon-based cleaning thinner prior to the application. Coating was applied with spray guns to the surface in identical conditions with one coat. After application panels were left to cure at room temperature for one week.

### Preparation of the coating

For the experiments a two-pack acrylic-polyurethane coating was prepared. First component was compromised of hydroxyl functional acrylic resin, pigment, fillers, and additives. Second component was compromised of isocyanate functional resin, solvent, and additives. Molar ratio of hydroxyl groups of the first component to the isocyanate groups of the second component was 0.78. Pigment loading was 46% (v/v) and pigment volume ratio to critical pigment volume ratio was around

0.84. The coating did not include any anti-corrosive pigments.

For the preparation of the first component a pigment rich paste compromised of pigment, fillers, resin, and additives were prepared using a Eiger-Torrance Mini 250 laboratory scale dispersion mill. Then, paste was mixed with letdown mixture of resin, various additives, and solvents in a high-speed dissolver.

To prepare the second component, resin, solvents, and additives were mixed using a high-speed dissolver under nitrogen atmosphere to prevent reaction between humidity in the air with the isocyanate groups of the resin.

### Accelerated exposure tests

Salt spray and condensation cabinets were operated according to ASTM B117 and ASTM D4585 standards respectively. Samples were subjected to 60, 144 and 240 hours of exposure in both accelerated exposure tests. The rust progress was evaluated according to ASTM D610 and degree of blistering was evaluated according to ASTM D714.

### Electrical Impedance Spectroscopy (EIS) measurements

All EIS measurements were made using three electrode setup Gamry 1010E model potentiostat fitted with PTC1 paint test cell. Measurements were made between 0.01 to 100000 Hz range with ten points per decade. Electrolyte used was 3.5 wt% NaCl. Two measurements of each sample were performed, in case of discrepancy between the measurements, a third measurements were made and average of two matching measurements were taken.

## RESULTS AND DISCUSSION

### Coating

Dispersion efficiency was checked with a grindometer and maximum particle size was found to be lower than 25 µm (ASTM D1210). First and second component were mixed 4 to 1 volumetric ratio. An appropriate amount (%20 by volume) of solvent was added to this mixture to give around 20 seconds of viscosity with 4 mm DIN cup at 20°C (DIN 53211). Coating was applied to steel panels around 72 to 78 µm dry film thickness.

### Salt spray test

In salt spray test, each panel had an identical panel with a scribe. This panel aided visual observation of the coating, after prescribed test duration both panels, with and without scribe taken from the salt spray chamber and an adhesive band was applied to the scribe. This tape was pulled to observe the loss of adhesion to the substrate and the progress of corrosion underneath the coating. As shown on the Figure 1, without scribe and the subsequent pulling of the adhesive tape, initial progress of corrosion can't be seen.

The delaminated area increased as the salt spray test duration increased. On 60-hour panel, only narrow and local delamination was observed. For 144-hour panel the delamination was narrow but along the length of the scribe and for the 240-hour panel, a wide delamination exceeding length of the scribe was observed.

As for the general panel area, 60 and 144-hour salt spray panel did not show any signs of degradation. For 240-hour panel blisters with No 8 size and few in frequency (according to ASTM D714) was seen. Apart from that, it was not possible to distinguish fresh and exposed samples in salt spray test.

### Condensation chamber test

Condensation chamber panels were not scribed. Fresh, 60, 144 and 240-hour panels did not show any sign of degradation. Any distinction between the samples with visual inspection was not possible.

### EIS and modelling

While degradation of a coating can only be visually evident after a complete failure, its degradation can be tracked much earlier by EIS. Coatings are complex composite materials. But charge transfer phenomena within them can be modelled with equivalent electrical circuits. One of the most common models employed for this purpose is the Randles circuit (Figure 2) [5]. In this circuit main phenomena within the electrolyte, coating, coating-substrate interface were modelled using circuit elements such as resistors and capacitors.

Figure 3 and 4 shows total impedance through the salt spray and condensation chamber tests respectively. Total impedance values of samples show an immediate difference starting from 60 hours. The impedance value of 60-hour condensation chamber panel at 0.01 Hz is almost 5 times greater than salt spray sample at the

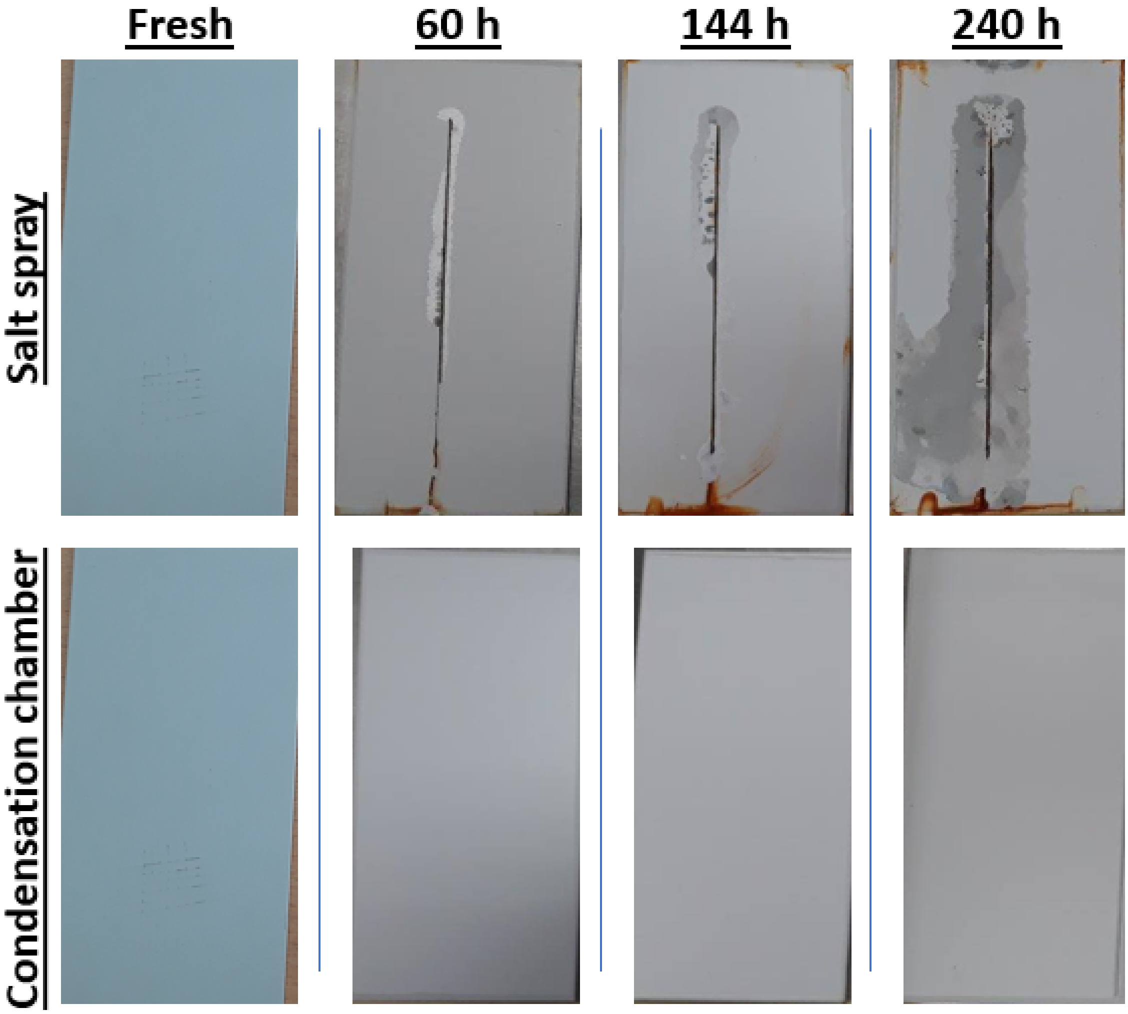

**Figure 1.** Top row: Scribed salt spray test samples, Bottom row: Condensation test samples

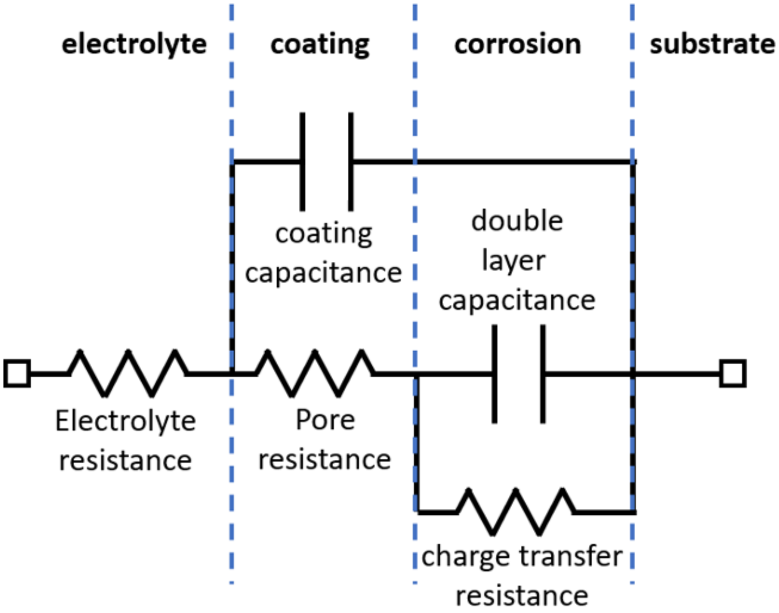

**Figure 2.** Randles cell for a damaged coating

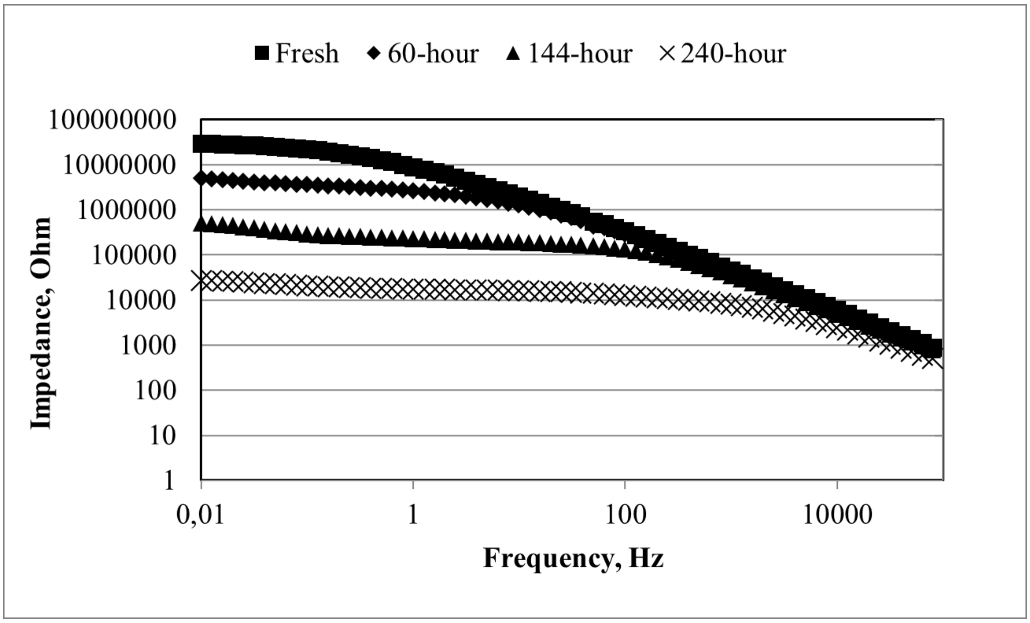

**Figure 3.** Total impedance of salt spray panels

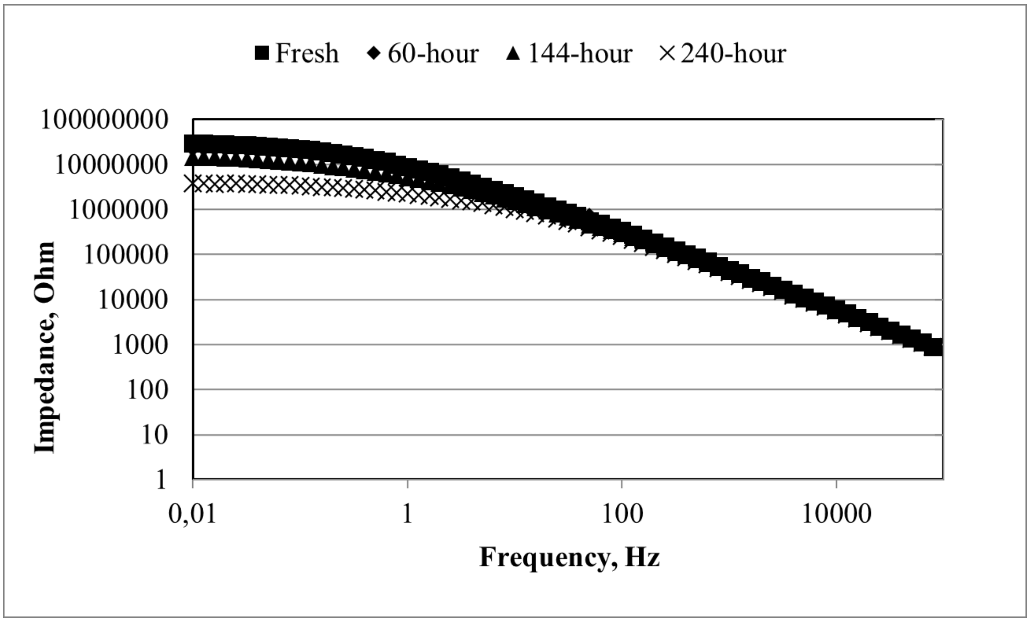

**Figure 4.** Total impedance of condensation chamber panels

same test duration. This difference increases as the test duration increase. At 144 hours, condensation chamber sample has 28 times higher impedance. At 240 hours the difference grows to 530 times.

For the medium frequency area from 1 to 1000 Hz, condensation chamber panel impedances stay relatively static, but for salt spray panels impedance drop is easy to see.

Apart from the total impedance, phase shifts of two tests also show a marked difference. For 60, 144 and 240-hour panels, condensation chamber samples did not show corrosion initiation. Their phase shift behavior suggests that coating is saturated with electrolyte and charge transfer through the coating can occur. Therefore, at this point pore resistance plays a part, still there is no corrosion.

On the other hand, salt spray test panels, starting with the 60-hour panel, show characteristic curves of corrosion initiation stage. Also, its constant phase behavior is evident on all three samples. This suggests while 240 hours of condensation chamber test is not sufficient to initiate corrosion, only 60 hours of salt spray test was enough to initiate the corrosion on the coating-substrate interface.

This observation confirmed on the Nyquist plots as well. Condensation chamber samples does not exhibit a secondary time constant, which would be evident with a second half circle on the Nyquist plots (Figure 8). But they show a gradual decrease in the total resistance, this is evident both on the Bode plots and Nyquist plots. The shrinking radii of semi-circles on the Nyquist plot shows decreasing total impedance as the test duration increases.

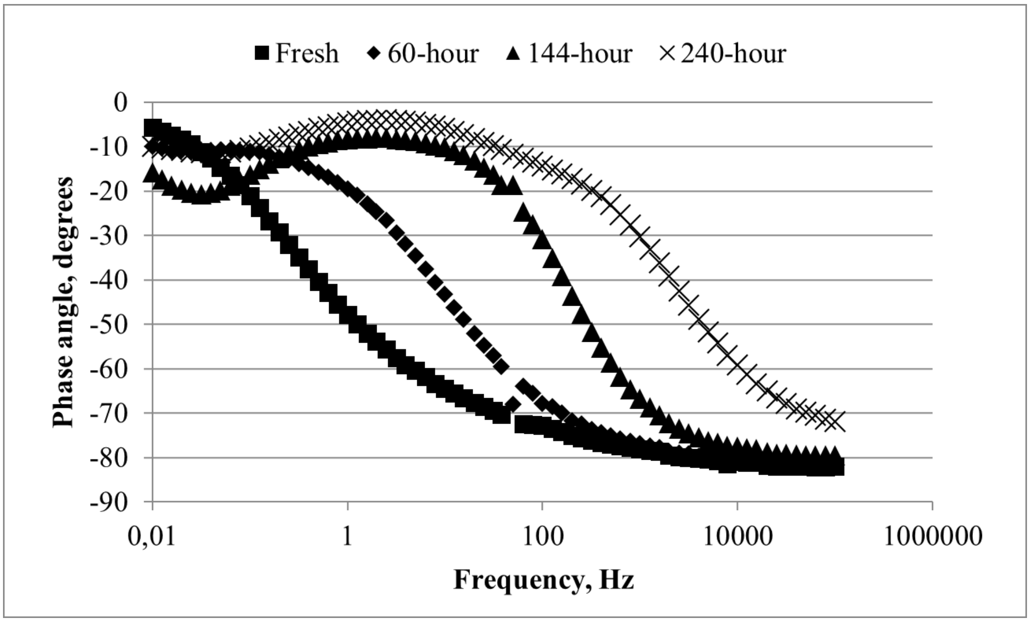

**Figure 5.** Phase shift of salt spray panels

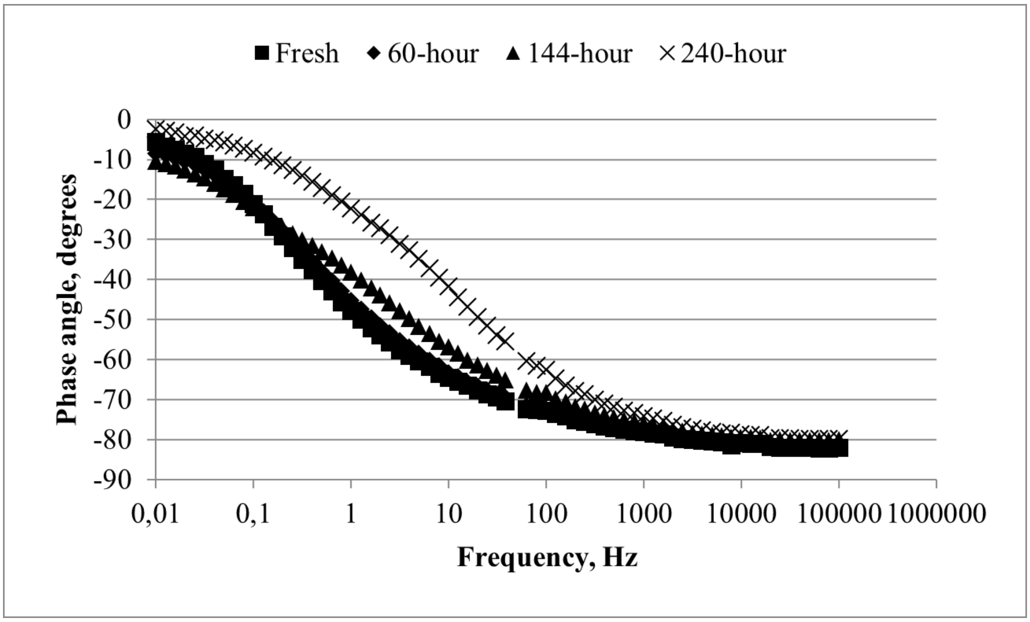

**Figure 6.** Phase shift of condensation chamber panels

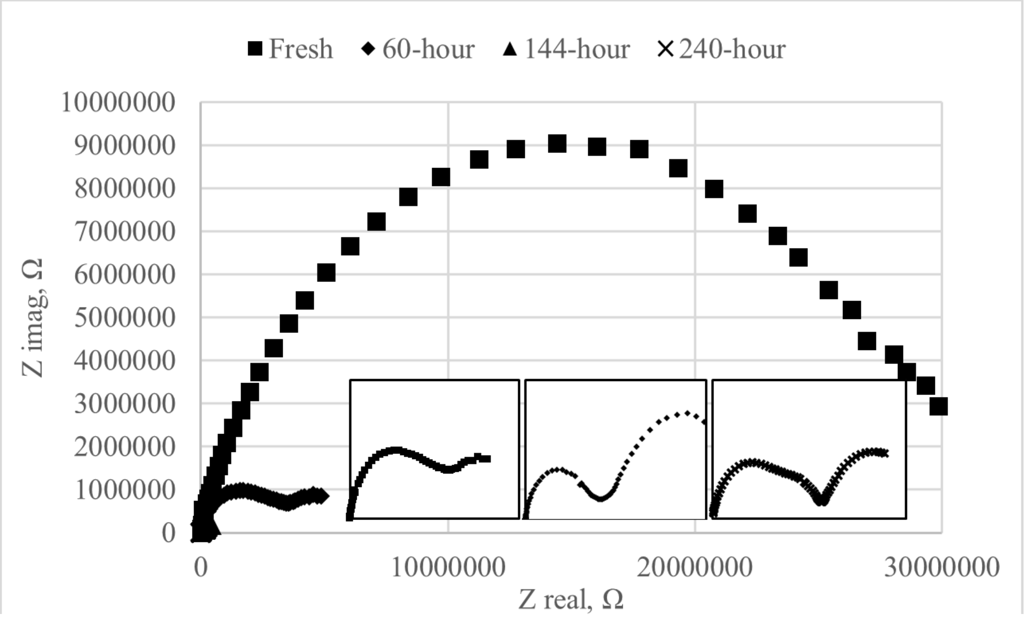

**Figure 7.** Nyquist plots of salt spray panels (inserts from left to right: 60, 144, 240-hour panels)

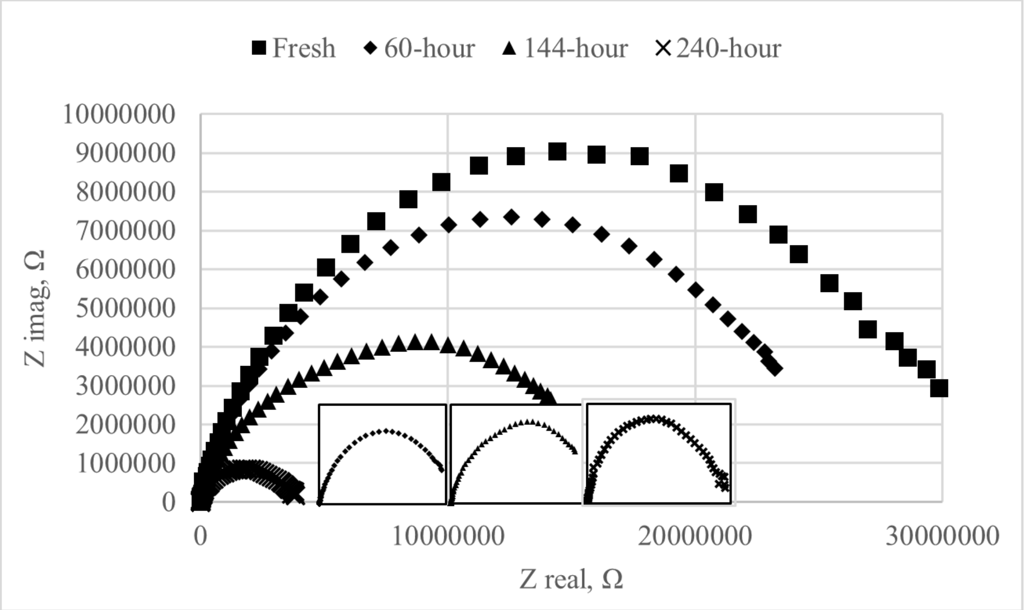

**Figure 8.** Nyquist plots of condensation chamber (inserts from left to right: 60, 144, 240-hour panels)

The decrease on the salt spray samples is much more dramatic (Figure 7). Note that Nyquist plots are not logarithmic, therefore it is much harder to represent the big difference on the resistances, inserts on the Figure 7 shows the progression of the second time constant. The second semi-circle becomes much more pronounced as the test duration increases. This shows the emergence of second time constant, namely double layer capacitance on the coating-substrate interface.

## Modelling the coating as equivalent electrical circuit

Accelerated exposure tests does not give a detailed data on the state of the coatings. Most of the times the data gained from these tests are binary, in the form of pass or fail. With proper modelling of the coating behavior, it is possible to complement data gained from the exposure tests. Modelling consists of building an equivalent electrical circuit for the coating and calculating the parameters of the model by fitting experimental EIS spectra. For proper modelling of the coating, phenomena within the coating must be generally determined. It is possible to cram many different electrical units into the models and get mathematically accurate fit. But a proper model must only include the observed or expected phenomena within the coating. To this end, placement of circuit elements representing unobserved phenomena must be avoided. In this study, impedance responses of the panels were fitted to two different models, each representing two different points on the progression of coating degradation. Figure 9 and Table 1 shows models and associated physical phenomena.

**Table 1.** Equivalent electrical circuit components and the corresponding physical phenomena

| Component | Physical phenomena |
|---|---|
| R_soln | Electrolyte resistance |
| Y0_coat | Coating capacitance |
| alpha_coat | |
| R_pore | Pore resistance |
| R_CTR | Charge transfer resistance |
| Y0_DLC | Double layer capacitance |
| Alpha_DLC | |

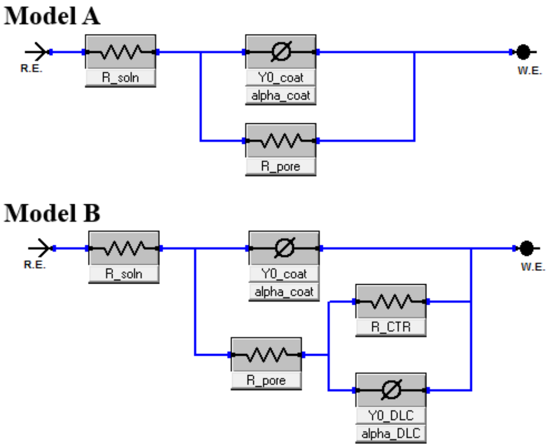

**Figure 9.** Equivalent electrical circuits

Phase diagrams and Nyquist plots of fresh and condensation chamber test samples showed only one time constant with changing phase shift through the frequency range. There was no corrosion development in these panels, therefore they are modelled using Model A. This model only represents charge transfer through the coating as pore resistance and coating capacitance.

Conversely salt spray test samples clearly showed two distinct time constants with associated phase shift characteristic, which suggest the corrosion initiation. This situation is modelled using Model B, which considers the phenomena such as double layer capacitance and charge transfer resistance at the substrate surface.

**Table 2.** Parameters for equivalent electrical circuits

| Panel | Model | R_soln | Y0_DLC | alpha_DLC | R_pore | Y0_coat | alpha_coat | R_CTR |
|---|---|---|---|---|---|---|---|---|
| | | Ω | $S\cdot\omega^{-alpha\_DLC}$ | - | Ω | $S\cdot\omega^{-alpha\_coat}$ | - | Ω |
| fresh | A | 11.6 | - | - | 24820000 | 1.648E-08 | 0.8345 | - |
| 60-hour salt spray | B | 11.6 | 2.546E-07 | 0.4489 | 1597000 | 1.198E-08 | 0.8735 | 3.638E06 |
| 144-hour salt spray | B | 11.6 | 7.596E-06 | 0.4051 | 172100 | 1.28E-08 | 0.8768 | 2.050E06 |
| 240-hour salt spray | B | 11.6 | 1.25E-04 | 0.4489 | 14090 | 9.377E-08 | 0.7572 | 2.537E04 |
| 60-hour condensation chamber | A | 11.6 | - | - | 19900000 | 1.716E-08 | 0.8324 | - |
| 144-hour condensation chamber | A | 11.6 | - | - | 11020000 | 2.458E-08 | 0.8024 | - |
| 240-hour condensation chamber | A | 11.6 | - | - | 2927000 | 2.536E-08 | 0.804 | - |

S: Siemens, ω: angular frequency, rad·s-1

In both models, capacitances were modelled as CPE (constant phase element) to allow non-ideal behavior [6].

The Table 2 shows the model parameters for each sample. The coating capacitance and pore resistance is common for all models, double layer capacitance and charge transfer resistance are only valid for salt spray test samples.

Figure 10 shows the variation of pore resistance for two accelerated exposure tests. The results show a marked difference at 60 and 144 hours between salt spray and condensation chamber. Pore resistance sharply decreases at 60 hours on salt spray and keeps decreasing. Condensation chamber samples show a similar trend in pore resistance, but their values remain much higher. The difference at 60 hours is 12-fold, and it increases to 64 and 207-fold in next intervals. The reduction on the pore resistance of the salt spray panels shows that

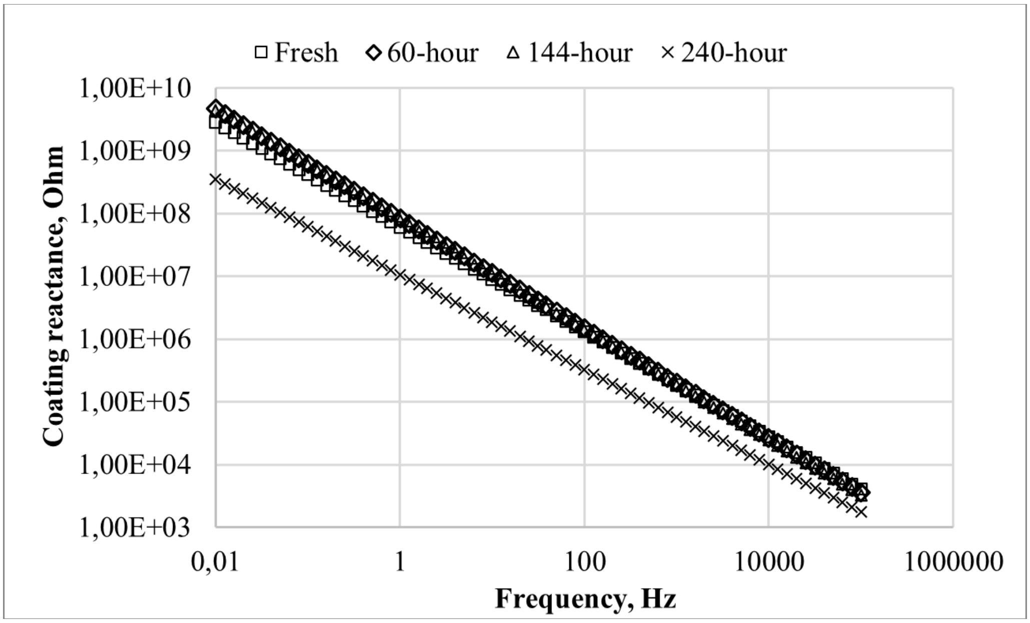

**Figure 10.** Variation of pore resistance of salt spray and condensation chamber panels

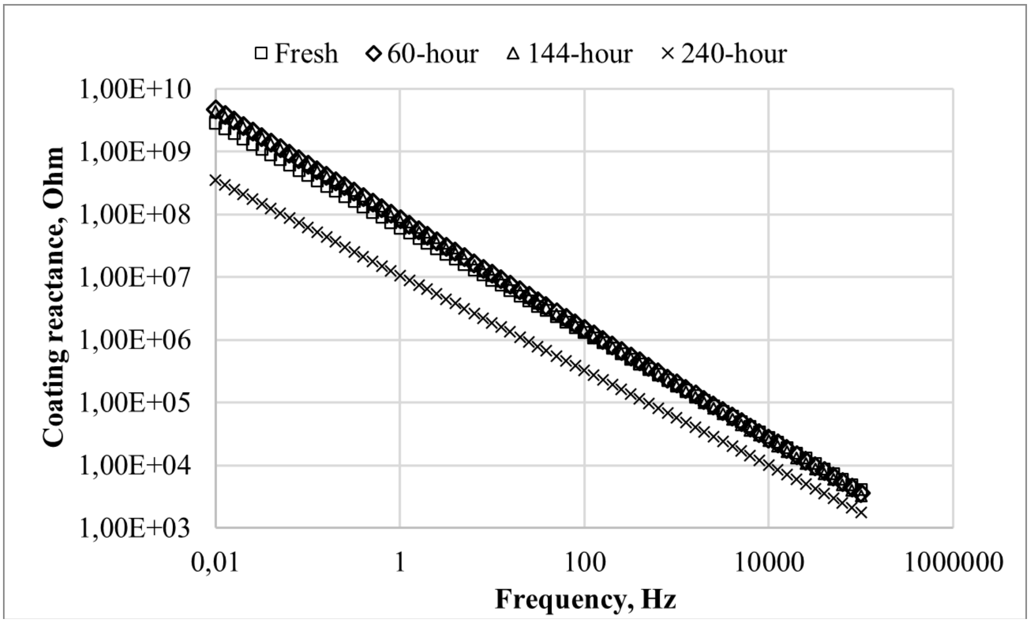

**Figure 11.** Variation of coating reactance of salt spray panels

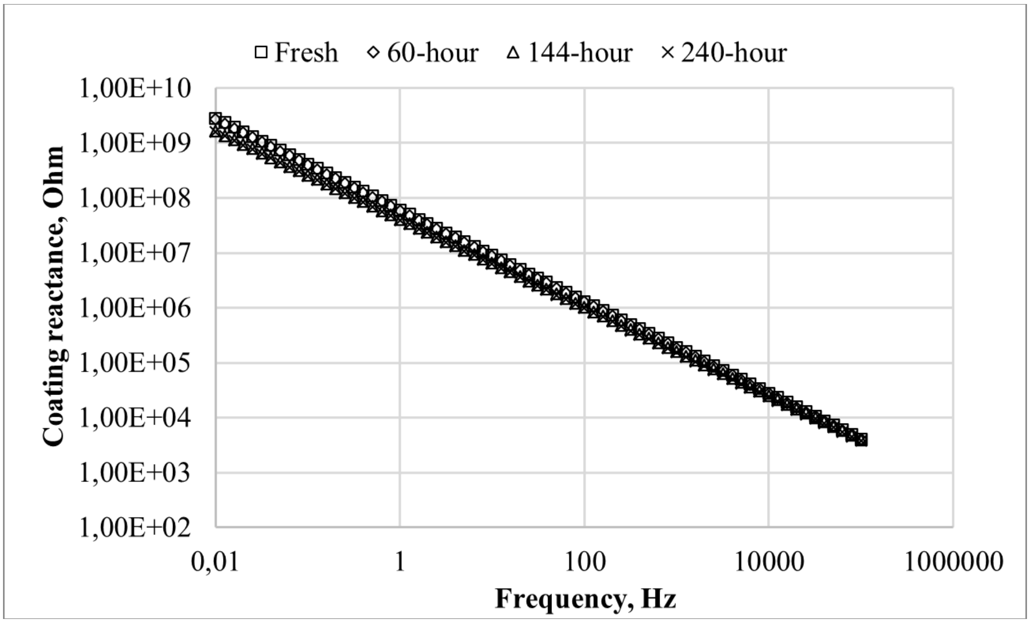

**Figure 12.** Variation of coating reactance of condensation chamber panels

in salt spray test, coating integrity degraded more than condensation chamber test.

Figure 11 and 12 shows coating reactance for salt spray and condensation chamber panels respectively. Reactance stays relatively constant for two exposure tests, except for 240-hour salt spray panel, on which it shows a marked decrease. This shows the increased capacitance of this sample. This capacitance increase most likely caused by the excessive water uptake of 240-hour salt spray panel which is also evident on the blisters observed [7].

As can be seen on the Figure 13, charge transfer resistance shows a significant decrease as the salt spray test duration increase. This decrease likely caused by the corrosion reaction on the surface. As the corrosion proceeds surface area and roughness increase, leading to lower and lower hindrance to the charge transfer to the steel substrate. Coating tested did not include any anti-corrosive pigment. Presence of an anti-corrosion pigment would likely create a passive layer. This would increase charge transfer resistance or at least slow its decrease.

Reactance caused by double layer capacitance also increases as the salt spray test duration increase. This shows the increased double layer capacitance. This is also likely caused by the increased surface area.

## CONCLUSION

In conclusion, this work shows that using EIS, it is possible to get detailed data about the coating, measure and parametrize the effects of exposure on the coating, track stages of degradation within the organic coating. Degradation that takes place within the coating was successfully tracked using EIS and detailed modelling showed that degradation and corrosion starts well before any visual sign.

Unsurprisingly, salt spray test imparts much more degradation on the organic coatings compared to condensation chamber test. For the coating system tested, corrosion was initiated in 60 hours of salt spray test duration, while 240 hours of condensation chamber test was not sufficient to initiate corrosion.

**ACKNOWLEDGEMENTS**
This project is supported by TÜBİTAK (TEYDEB 3180664).

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