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# R/S FRACTAL ANALYSIS OF ELECTROCHEMICAL NOISE SIGNALS OF THREE ORGANIC COATING SAMPLES UNDER CORROSION CONDITIONS.

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## Abstract

This work presents the electrochemical noise results obtained under chloride corrosion conditions in three different coatings (two epoxy coatings and an epoxy/polyurethane) systems. Evaluation was performed from the fractal dimension of the electrochemical noise-time series obtained using the so called Rescale Range Analysis (RRA) proposed by Hurst. The three coatings were exposed in a chloride environment and electrochemical current noise (ECN) measurements were performed. Afterwards, the fractal dimensions were calculated from the time series obtained for the three coatings. This dimension is obtained from the empirical law $R/S = (\tau/2)^H$ where R represents the difference between the maximum and minimum values of the variable, S the standard deviation of the time series, $\tau$ is the period of time measured and H the Hurst exponent between $0 < H < 1$. The calculation of the Hurst exponent and fractal dimension of the time series comes from the slope of the R/S plot. The exponent may help to

evaluate the coating resistance performance under corrosion conditions.

## Introduction

There is a variety of laboratory tests used to demonstrate the protection against corrosion conferred by coatings. Since corrosion is an electrochemical process, electrochemical testing methods which requires charge transport through coatings, has gained considerable attention during the past decade to assess the corrosion resistance properties of organic coatings.

One such method is the electrochemical noise (EN) which is a non-perturbative technique used highly successful in different corrosion conditions. EN data were collected in the form of potential and/or current time series or ensembles of sufficient length, The analysis methods of EN data include statistical and spectral techniques and visual inspection of time records [1-5]. Previous studies have suggested that EN time records contain valuable information about corrosion resistance by coatings, however statistical and visual analysis have not revealed information about mechanisms of corrosion inhibition [6]. Spectral analysis have also been used to analyse the periodicity of the structure of EN time records. The slope of the spectral density function (SDF) at higher frequencies typically has the form of $(1 / f)^{\beta}$. Different values of the $\beta$ exponent have been reported for specific modes of corrosion [2, 3, 7, 8].

Alternatively, the structure of the EN time record can be analysed in the time domain and described by the Hurst exponent H [9]. The development of fractal geometry by Mandelbrot [10] has provided mathematical tools for the analysis and characterization of the structure and scaling exponents of fractal time records. A “fractal” is an object with complex structure, revealing new details at increasing degrees of magnification. An EN time record is a “random” fractal, where the levels of detail are similar but not identical, sharing the same statistical properties. The fractal dimension $d_f$ describes the structure of a fractal, e.g., the “roughness” of an EN time record, and the fractal geometry provides the explanation for the values of $d_f$, H and $\beta$ that are observed for some of the EN time series parameters and

noise spectra. Specifically, the fractional brownian motion (fBm) technique of Mandelbrot provides the connection between the structure of the EN time record and SDF (characterized by $d_f$, H and $\beta$) and the microscopic behaviour (oxidation reactions) responsible for corrosion.

For example the Hurst exponent H which is formally related to $\beta$, reveals long-term time dependence in a time series and can be evaluated from the oscillations occurring in the data. When the variation in the time record over a specific time interval (the lag time) is proportional to the lag time raised to the power 2H, the time series is said to be fractal. The parameter 2H describes both the appearance of the time series ("roughness") and the characteristics (the "persistence" $0.5 < H < 1$, or "anti-persistence" $2H < 0.5$) of the associated physicochemical process, e.g., corrosion [11, 12].

This work presents the electrochemical noise results obtained under chloride corrosion conditions in three different coating (two epoxy coatings and an epoxy/polyurethane system). Application of fractal geometry analysis of EN time series were performed to explore the possibility to evaluate corrosion resistance characteristics of the different coatings.

## Experimental

### Coating Samples

Description of the three coatings are given in table 1. Each sample substrate consisted of a 10 cm x 15 cm mild steel AISI 1010. These steel panels were cleaned by first rinsing with deionised water, then abraded down to a roughness of 600 mesh, and finally cleaned with di-chloromethane to ensure surface uniformity conditions. The coatings were applied by hand brushing. Coated samples were allowed to cure for several weeks in a cabinet where the air was filtered and the ambient conditions were maintained at 25 °C and 45 % relative humidity. Afterwards samples were immersed in 3% chloride solution for 500 hours.

**Table 1. Characteristics of coating samples.**

| DESCRIPTION | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|
| Rugosity | 600 mesh | 600 mesh | 600 mesh |
| Coating Application | 1 layer epoxy polyamide 1 layer polyurethane aliphatic epoxy. | 2 layers epoxy paint | 2 layers epoxy varnish |
| Dry Film Thickness | 220 □m | 190□m | 143□m |

## Electrochemical Noise

To evaluate and compare the corrosion resistance of the coatings under study, and to characterise their behaviour under aggressive chloride corrosion conditions, electrochemical noise (EN) technique was used with specimens immersed in a 3% NaCl. Each measurement was done at least by duplicate, in order to observe the reproducibility.
The electrochemical noise set-up has already been described [1]. Briefly, a plexiglass cell was attached to each coated panel (electrode) and filled with electrolyte solution (3% NaCl). A surface area of approximately 7.06 $cm^2$ of each coating was exposed to the electrolyte in each cell. Nominally identical pairs of electrodes were coupled electrically through the measurement instrumentation and electrolytically by an agar salt-bridge. A reference saturated calomel electrode was placed in one of the cells for each pair of electrodes.
Potential noise was obtained against the reference electrode and the current noise between the two electrodes. The noise resistance was then calculated as the ratio of the potential noise standard deviation over the current noise standard deviation ($R_n = \sigma_v / \sigma_i$)

## Data Collection

Data were collected in the form of time records using an electrochemical system and software, that was controlled with a PC computer. The sample period was 0.5 seconds and an average value was then obtained. Every 15 seconds the procedure was repeated and

after 30 minutes an EN time series was obtained for the 7.06 $cm^2$ coated sample. The trend was removed when the EN oscillations are superimposed to a DC signal, by subtracting a linear fit from the time series. Measurements were performed for different times of immersion in the 3% NaCl solution. The time intervals were chosen because corrosion processes under coatings were expected to be fairly slow.
The initial time record was collected after 24 hours of the coated electrodes had been exposed to the electrolyte. Afterwards, time record data sets were collected less frequently over days and weeks. The immersion experiment was allowed to continue for approximately 500 hours. At this time, the cells were dismantled and the coated panels were inspected visually for blistering and rust according to ASTM procedures [13, 14].
From the EN time records, the Hurst exponent H was also calculated as to have one quantitative parameter in order to compare signals. This exponent was evaluated using the Hurst rescaled range analysis based on his empirical law proposed in 1965 [9]; $R/S = (\tau / 2)^H$ where R represents the difference between the maximum and minimum values of the variable, S the standard deviation of the time series, $\tau$ is the period of time measured and H the Hurst exponent (called K by Hurst).

## Results and Discussion

A representative example of potential, current and noise resistance time records for the three test paints after 144 hours of immersion are shown in Figures 1 to 3. The general appearance or structure of electrochemical potential and current time records appeared to be similar for the three paints, although a few transients associated to local events can be observed at the beginning and the end of the time series, for two of the samples. The average potential noise is 8E-5 V and the average current is in the order of 9E-12 A. The noise resistance time series reflects the transients observed with an observed average noise resistance of 9E6 ohms. The general structure of the time series as a function of time remained similar for the three samples.
Calculated values for noise resistance as a function of time for the carbon steel sample and the three coating samples are given in figure

4. Decreasing trend of the noise resistances for the three coatings as a function of time of exposure, associated to coating degradation was not observed [15]. Instead, during exposure to the electrolyte the noise resistance remained variable, decreasing and increasing again as a function of time, without showing a definite trend. A decrease in noise resistance could be associated to local pores, voids or defects where localized corrosion might take place, forming corrosion products and therefore increasing again its noise resistance as observed; without providing a reliable ranking of the coating corrosion resistance performance and suggesting a similar corrosion resistance properties for the three coatings. Values ranged between 1E9 ohms down to 1E4 ohms for all coating systems, with an average 1E7 ohms.

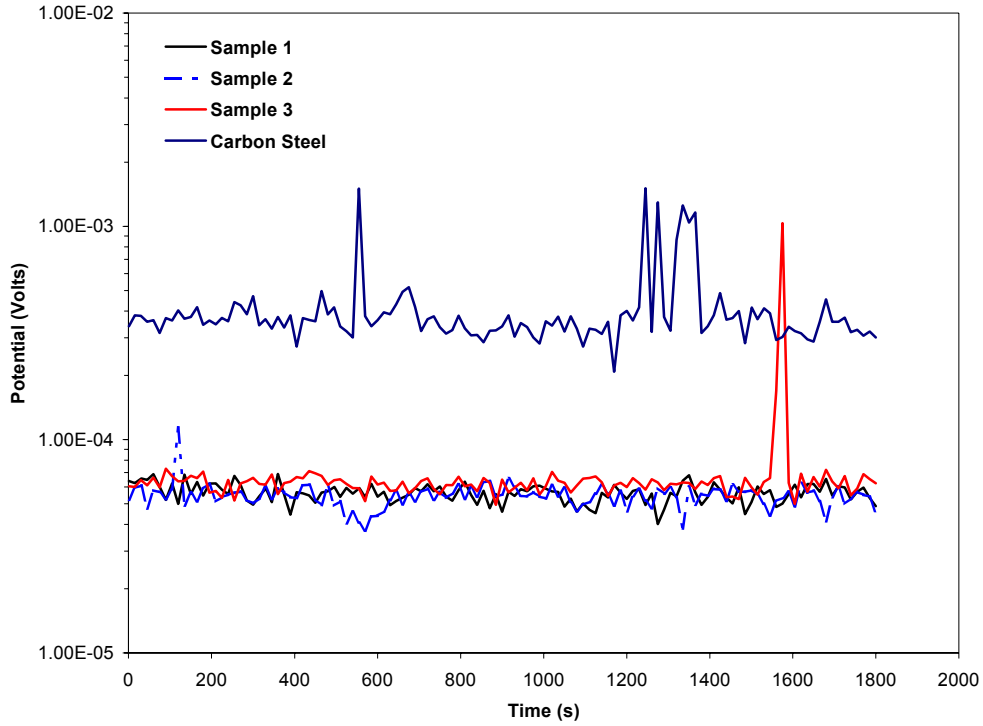


**Figure 1. Electrochemical noise potential for coated carbon steel after 144 hours of immersion in a 3 % NaCl solution.**

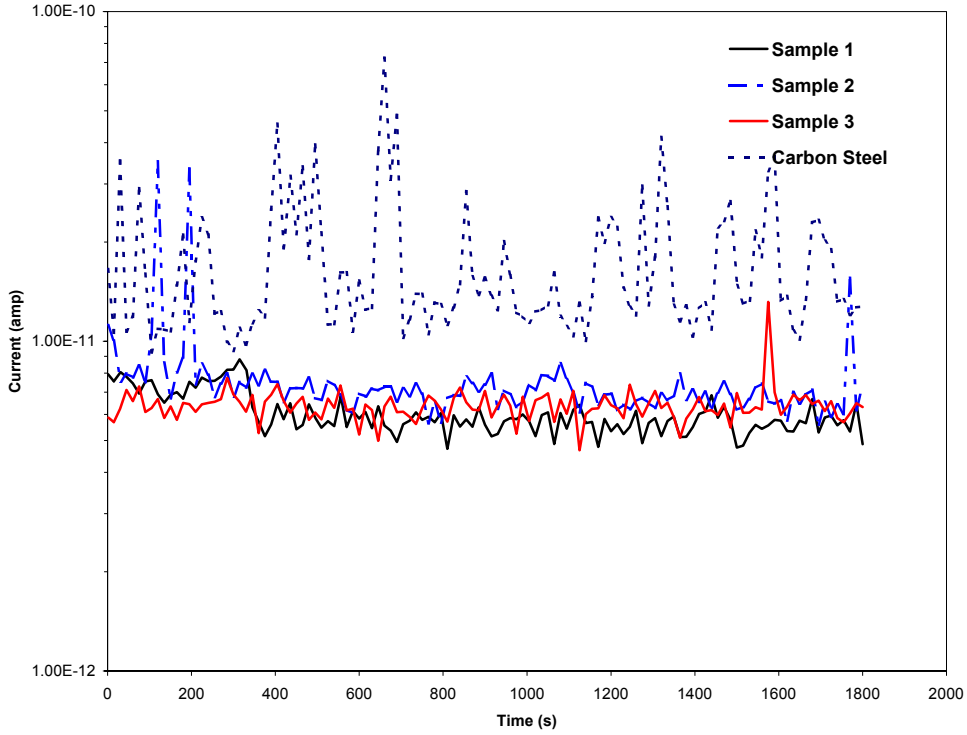


Figure 2. Electrochemical noise current for coated carbon steel after 144 hours of immersion in a 3 % NaCl solution

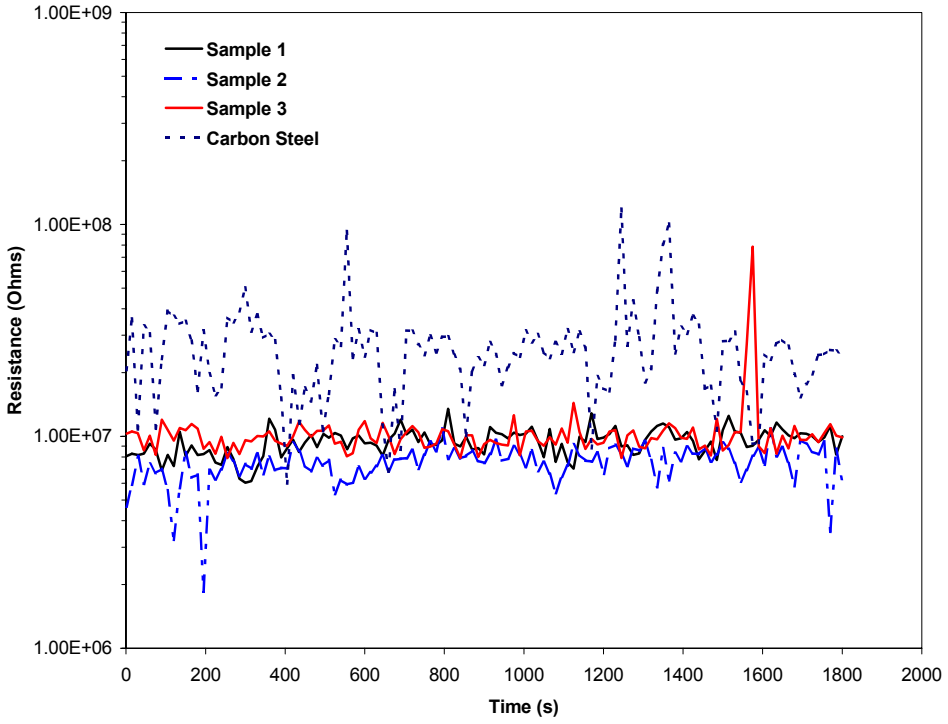


Figure 3. Electrochemical noise resistance for coated carbon steel after 144 hours of immersion in a 3 % NaCl solution.

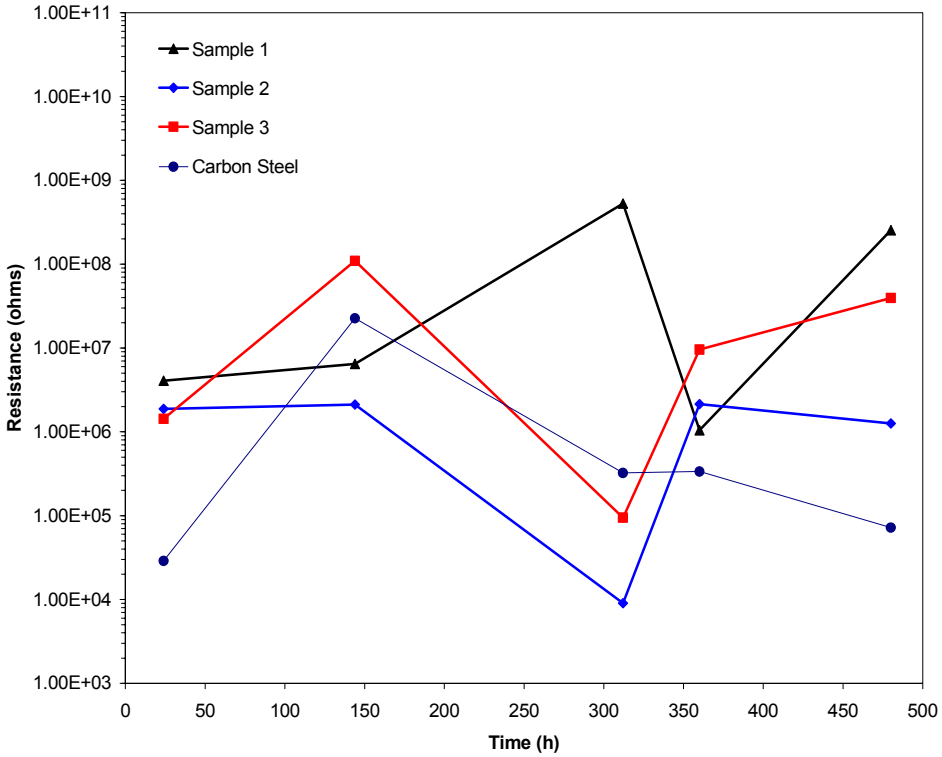


**Figure 4. Noise corrosion resistance of carbon steel and samples 1 to 3 at different times of immersion in a 3 % NaCl solution.**

Figures 5 to 8 present the rescaled range analysis for the electrochemical current noise time series obtained for different times of immersion for carbon steel and the three coating samples. The slopes of the curves represent the Hurst exponent H, which characterizes the time series structure. Depending on the 2H values, Skerry et. al. [15] proposed three protection levels to corrosion conditions, depending upon the range of 2H as follows:

a) 2H = 0–0.5 for coatings that provided good protection against corrosion.
b) 2H is initially low and increased to 0.5–1.5 during exposure for the coatings that afforded an intermediate level of protection; and
c) 2H = 1.5–2 for the coatings that offered relatively low corrosion protection conditions.

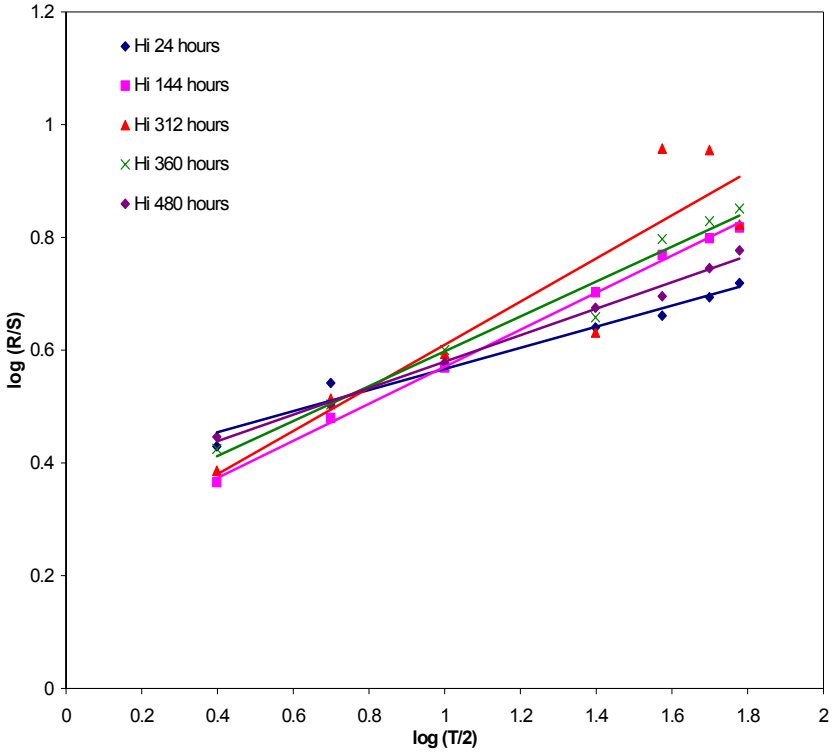


Figure 5. Rescaled range analysis at different times of immersion in a 3 % NaCl solution for carbon steel.

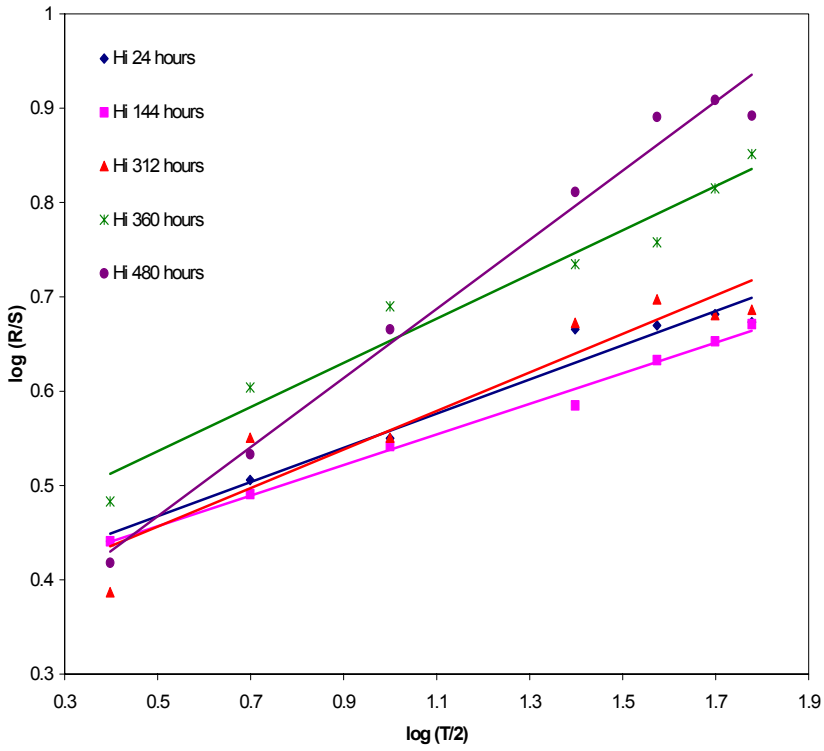


Figure 6. Rescaled range analysis at different times of immersion in a 3 % NaCl solution for coating sample 1.

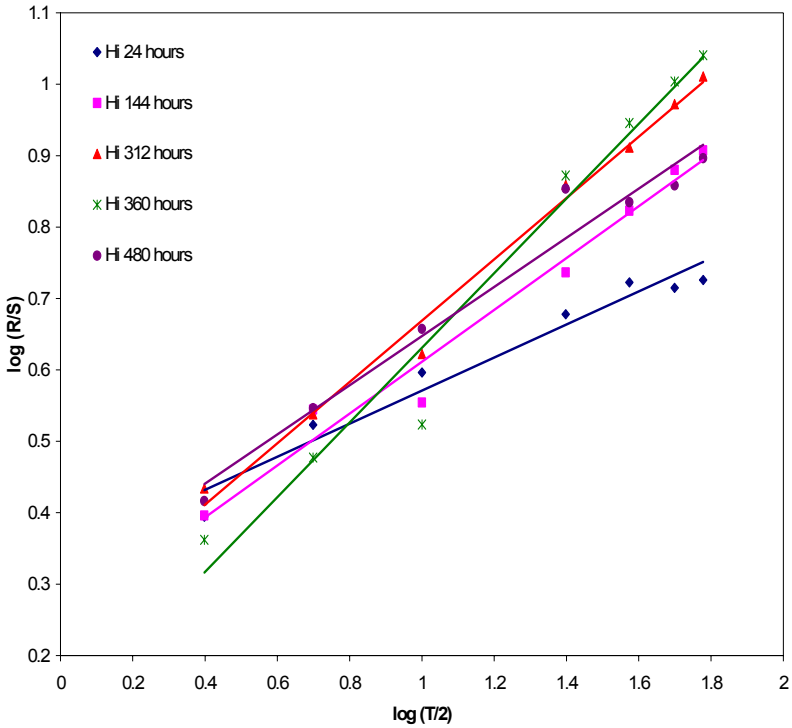


Figure 8. Rescaled range analysis at different times of immersion in a 3 % NaCl solution for coating sample 2.

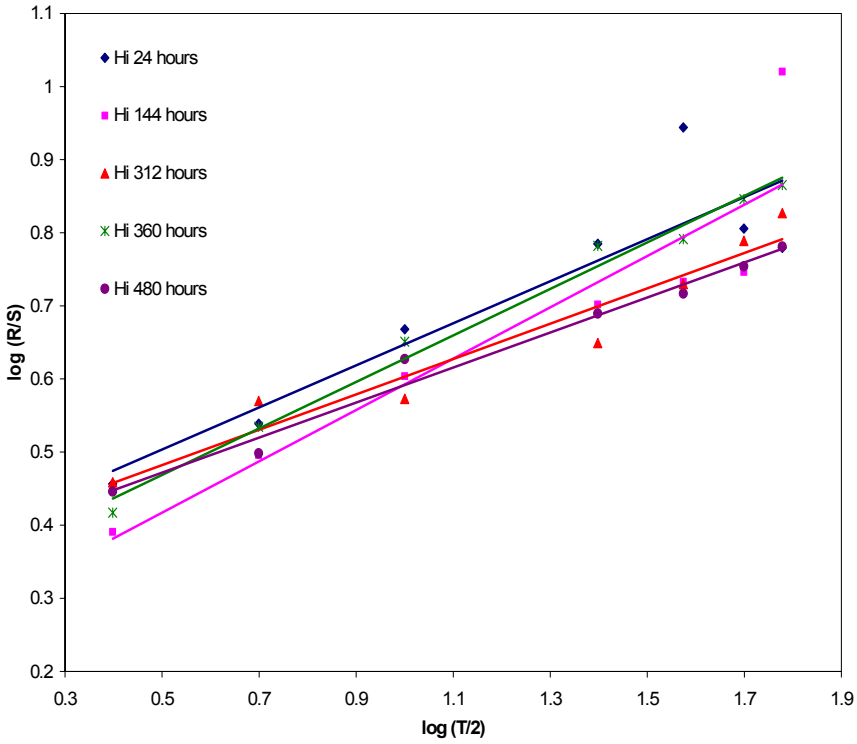


Figure 9. Rescaled range analysis at different times of immersion in a 3 % NaCl solution for coating sample 3.

From the graph the H value was obtained from the slopes. Table 2 presents the 2H values obtained from electrochemical current noise times series obtained, applying the rescaled range analysis for the three different coatings at different times of immersion. For comparison the results for carbon steel are also presented.

**Table 2. The Hurst exponent for the three coatings as a function of immersion.**

| Time of immersion | Carbon Steel 2H | SAMPLE 1 2H | SAMPLE 2 2H | SAMPLE 3 2H |
|---|---|---|---|---|
| 24 | 0.3744 | 0.3628 | 0.4632 | 0.5756 |
| 144 | 0.6568 | 0.3244 | 0.7262 | 0.7024 |
| 312 | 0.7654 | 0.4086 | 0.8588 | 0.4832 |
| 360 | 0.786 | 0.4686 | 1.046 | 0.6362 |
| 480 | 0.47 | 0.7330 | 0.6884 | 0.4788 |

According to Skerry´s proposal, and using this criteria all samples provide intermediate level of protection (case b), while samples 1 and 2 show a trend towards higher 2H values (lower protection against corrosion conditions). All show variable $R_n$ values below $10^9$ ohms $cm^2$ (good coating).Visual examination of the metal substrates revealed less corrosion attack over the metal surface in sample 3, therefore better barrier type corrosion protection properties for this coating as compared to the other two, confirming the results presented. In a previous study, the corrosion behaviour of the three paintings at different corrosion conditions were evaluated: 1000 hours Prohesion test, at immersion chloride conditions using different electrochemical techniques and visual examination. Samples were ranked and sample 1 presented blistering and samples 2 and 3 localized attack. The best performance obtained was for sample 3, as suggested by these results [16].

Persistent noise conditions (2H>1) exhibit rather clear trends with relatively little noise (has a relatively smooth or undulating appearance). If, for some time in the past a positive increment was obtained then, on the average an increase in the future will be obtained and the opposite is also true: a decreasing trend in the past

implies a continued decrease in the future. On the contrary for anti-persistent noise (2H<1), an increasing trend in the past implies a decreasing trend in the future and a decreasing trend in the past makes an increasing trend in the future probable. The time record for this case, appears very noisy and the local noise is of the same order of magnitude as the total excursion of the time record [9]. The increments of persistent noise tend to accumulate, while those of anti-persistent noise tend to cancel one another. According to the model of fractional Brownian motion, the value of 2H measures the persistence (or anti-persistence) in the increments of a time record. This persistence is presumably related to the processes generating the time record [9, 10]. For corrosion processes, the electrochemical noise and the values of 2H, are reflecting the electrochemical reactions that take place at the electrolyte/substrate interface giving rise to corrosion. If this is true, then this is the reason that 2H can be sensitive to the level of corrosion resistance provided by the various coatings [15].

Corrosion begins when aggressive ions attack a local site on the surface of the metal substrate [17]. With further ion attack, corrosion spreads gradually and oxidize adjacent sites on the metal surface [18]. On the basis of this model for uninhibited pit growth, it is expected that 2H >1 and the electrochemical noise time records would become persistent. Inhibition of corrosion, however, would be expected to reduce the persistence of the electrochemical noise (2H<1). Inhibition of corrosion may include passivity or the restriction of diffusion of aggressive ions to the substrate by a “barrier type” coating or corrosion products. The results obtained are consistent with this model, where electrochemical current noise present relatively low frequency oscillations (anti-persistent noise 2H<1) when a coating provided a high level of protection against corrosion, as suggested [15]. For carbon steel 2H initially is low with a trend to increase over time but without reaching persistency (2H>1).

Figure 10 shows the trend of the Hurst exponent as a function of the time of immersion. Except for coating 3 sample, all present a trend to increase towards persistent conditions including the steel sample, although at a lower rate (shallower slope). These allow interpretation of results according to the model previously proposed

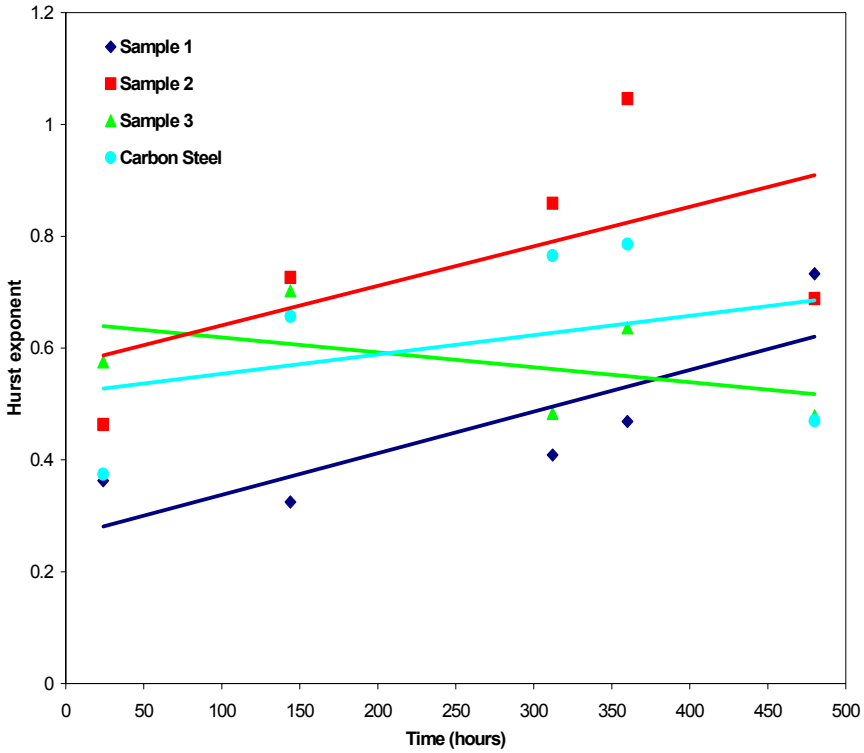


**Figure 10. The Hurst exponent trend for carbon steel and the three coating samples steel as a function of time of immersion.**

On the basis of these results it appears that the trend in the Hurst exponent, and not only the values itself can give information regarding the coating performance. Further work is needed to clarify this suggestion.

## Conclusions

The three organic coatings provide good to intermediate corrosion resistance protection to the metal substrate according to the proposed criteria. The trend in the Hurst exponent suggests that coating sample 3 offers the best anticorrosion properties of the three coatings tested.
The results obtained for the Hurst exponent demonstrate that electrochemical noise time series are fractals. It provides a tool for the interpretation of the structure of electrochemical noise data as well as a possible quantitative value to rank coating performance and corrosion mechanism.

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