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Statistical Analysis of Electrochemical Noise Records in Paintings Barrier Type

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This research presents the findings to submit to four types of paintings barrier to electrochemical noise tests using data for the treatment of statistical analysis, given its simplicity and good results obtained by them in previous work.

1. Introduction

The electrochemical noise is generally defined as random fluctuations of the potential or current observed in corrosion processes (Cottis et al 1988; Muniandy et al., 2011). The studies so far carried out by electrochemical noise technique in the field of coatings listed a large number of parameters, drawn from various methods of mathematical analysis, in which different researchers are trying to characterize the potential and current records obtained. In literature the apparent randomness of electrochemical noise records and complexity has led several authors have used very different techniques for interpretation. Of these were the analysis in time domain, time record (Kearns et al, 1996), and statistical analysis (Mansfeld et al, 1997), the analysis in the frequency domain (Zhang et al., 2007), wavelets transform (Zhao et al., 2007) methods based on chaos theory (Legat and Dolecek 1995), and others more advanced methods.
The parameters used are the mean values and standard deviations of intensity and potential, and the use of a specific parameter called noise resistance defined as the ratio of standard deviation against the potential intensity (Grundmeire et al., 2000).

2. Experimental

2.1 Materials

In this work three types of paint systems were tested: an alkyd enamel, acrylic enamel polyester enamel-resin and chlorinated rubber enamel. The four selected paints were prepared a sample of ten test pieces of each paint systems under study.
The main characteristics of the paint systems studied are shown in Table 1. All information on specifications and technical characteristics of the painting, reflected in the table as well as information about application conditions, cure times and film thickness was extracted from technical specifications of the manufacturers.

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Table 1: Painting System Specification

type of coatings	specifications supplied by the manufacturer
painting 01 Alkyd top coat red Thickness: 9.6 μm	Mean oil alkyd resin: 35,73 % color pigment: 5.70 % Additives: 1.15 % Solvents: 57.42 %
painting 02 Acrylic polyester top coat red. Thickness: 28.8 μm	Acrylic resin watered to 40 %: 32.32 % Alkyd resin diluted to 40 %: 23.70 % Polyester resin watered to 40 %: 8.62 % Pigment dye: 4.87 % Additives: 3.92 % Aromatic solvent: 26.57 %
painting 03 top coat oily resin white color Thickness 33.9 μm	Modified phenolic resin: 34.40 % Modified drying oil: 12.00 % TiO_2 pigment: 27.70 % Additives: 3.20 % Solvents: 22.70 %
painting 04 Chlorinated rubber top coat gray thickness 36.2 μm	Chlorinated Rubber Resin 10 cps: 36.30 % Pigmentation: 24.40 % Additives: 6.90 % Solvents: 32.40 %

2.2 Preparation of the test pieces

In order to ensure a good anchoring of the paint films on steel, it is degreased by side of painted with trichloroethylene.

With the purpose of obtain a uniform thickness to be utilized a standard cylindrical applicator called "K-bar". This type paint applicator consists of a stainless steel cylindrical rod on which is wound a wire of the same material of from 0.0508 to 1.524 mm which allows to have a set of bars whose application range is: 6.12 , 24, 36, 50, 60, 75, 100, 125, 150, 200, 300, 400 500 micron wet film.

2.3 Measurement Scheme

From all different schemes measurement proposed by different authors for the acquisition of electrochemical noise data (Sánchez et al., 2001) we chose a system of two identical working electrodes, connected to a zero resistance ammeter, among which we measure the current, and among a work electrode and a reference electrode connected to a voltmeter was measured voltage. These electrodes are assembled electrochemical cell, which contains the electrolyte. Both the voltmeter and ammeter are controlled by a PC which sends the data obtained from the records of noise.

2.4 Data collection and processing

The data records Voltage and current were performed with a sampling rate of 2 Hz, corresponding to two points per second.

Once obtained the different registers of noise we proceeded to the mathematical treatment thereof. The parameters were calculated for each record as follows: Mean values of potential (V) and intensity (I), Normal potential deviations ((σV) and intensity (σI) and Noise Resistance (Rn)

$$R_n = \frac{\sigma V}{\sigma I} \tag{1}$$

Noise Resistance is a useful parameter which has been shown that it is sometimes proportional to the polarization resistance, for instance when the corrosion progresses slowly (Mabbuttb et al., 2007).

3. Results and discussion

The formation mechanisms and protection of the paint film allow us to compare the different results in terms of hours of the different paintings. In the protection mechanism of the four paints tested for barrier effect takes place in this kind of protection is of great importance both the inherent permeability of the resin used as the level and type of pigments and additives used.

In this case have four paintings which can be classified according to the mechanism of film formation. Distinguish the paintings in two groups

First group: mechanism of film formation by chemical reaction with the oxygen of air: No paints 01 (alkyd) and No. 03 (oleoresinous)

Group Two: mechanism of film formation by evaporation of the solvent, paints No 02 (acrylic) and No. 04 (chlorinated rubber).

The paints film forming by the first mechanism are paintings with poor chemical resistance they tend to saponified in alkaline media, also have a poor water resistance, while forming the paint film by the second mechanism has a good chemical resistance and good water resistance.

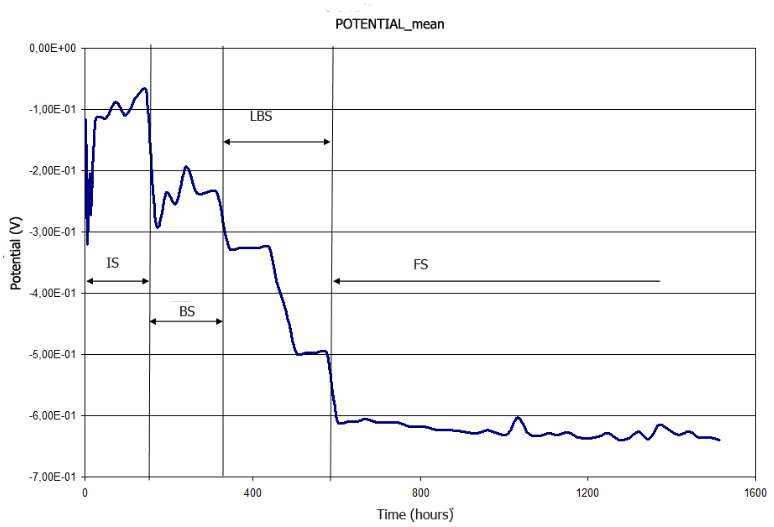

Figure 1: Paint N° 01 Mean potential variation with time

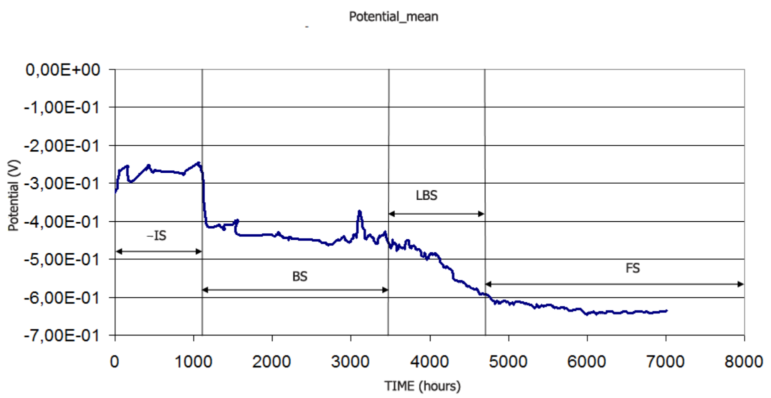

Figure 2: Paint N° 02 Mean potential variation with time

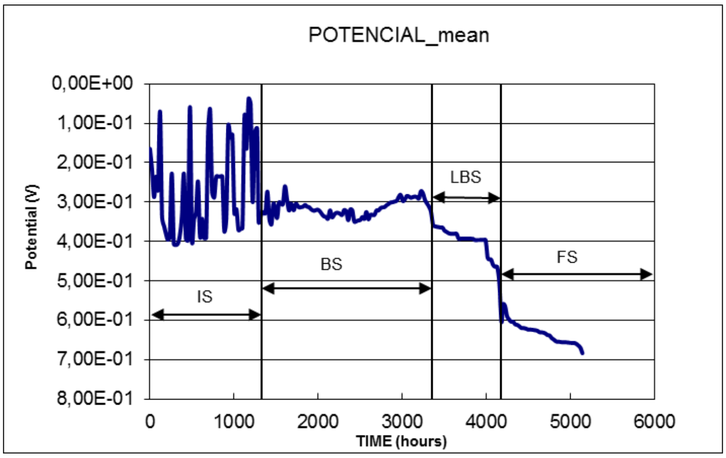

Figure 3: Paint N° 03 Mean potential variation with time

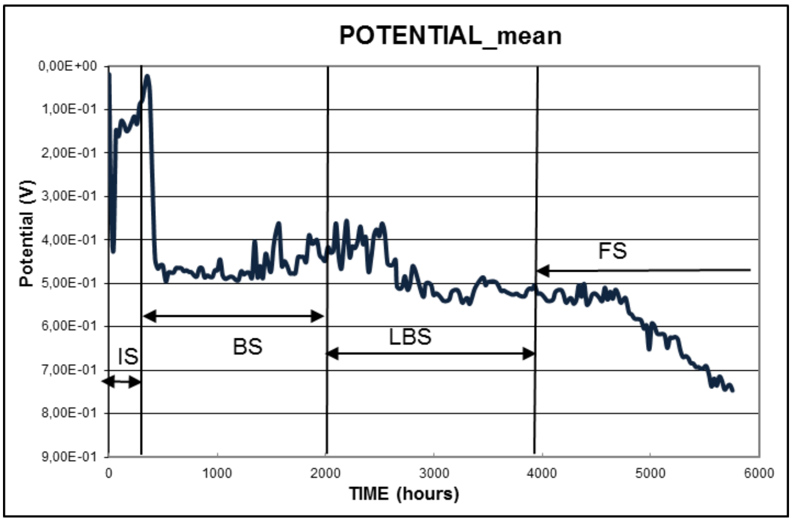

Figure 4: Paint N° 04 Mean potential variation with time

In every curve can be seen, as the coating as the potential is degraded towards a value approaching around -0.680 V, which is the potential measured in the to bare metal-electrolyte system. With this in mind, this fact can be highlighted two different behavior patterns of paint groups classified according to mechanism of film formation until the final stage reach values of corrosion potential of iron:

Paints first group (01 and 03) in which the potential corrosion measurements remain at less negative than values of potential during the step barrier effect (-0.15 to -0.28 V) and are hardly more negative when they lose -0.4 barrier effect

Paints second group (02 and 04) in which potential corrosion measurements would be more negative since to -0.4 during the step of exceeding the barrier effect -0.5 V in the stage that gradually lose their the barrier effect.

An analysis of records generated in all the systems after a transit through the iron potential corrosion, -0.660 V vs. ECSthe potential keeps evolving towards values near to those obtained in the case of measurements with bare metal a as it is deposited on corrosion products.

Making a summary it can divide the life stages of the paintings on the following:

IS: Initial Stage in which the system is soaking, usually of short duration in all systems except in the system 03, which as previous explained It is because of the presence of Titanium Dioxide (TiO_2) 27.70 % compared to other paints that do not carry this kind of pigment.
BS: Barrier Stage. Potential fluctuations in the graphics confer to a Brownian Noise appearance in all systems.
LBS: Loss Barrier Effect. The potential records appearance is similar to the previous stage,
FS: Final stage where the potential remains constant in values around the -0.700 V. In this stage the corrosion products taking preponderance and the graphics have a similar profile to the one obtained in the uncoated steel.
Table 2 compares different values of Noise Resistance of the different systems under study at different stages of degradation, with those obtained from the bare metal. In every case be observed that as the coating is degraded the value of the Noise Resistance decreases. This confirms to those that can drawn from the first studies of electrochemical noise (Skerry et al., 1991) in which high values of Noise Resistance corresponding to coatings in good condition, and low values corresponding a corrosion process advanced.

Table 2: Comparison of Noise Resistance

Stage/paint	PAINT 01	PAINT 02	PAINT 03	PAINT 04
IS	1.57E+09	2.81E+07	1.29E+09	$6.57 \cdot 10^8$
BS	5.18E+08	6.78E+06	5.94E+08	$8.56 \cdot 10^8$
LBS	1.06E+08	4.89E+06	3.95E+08	$5.36 \cdot 10^8$
FS	1.01E+08	2.95E+06	2.07E+08	$3.14 \cdot 10^8$

4. Conclusions

From the results obtained through statistical analysis of the records of potential and electrochemical noise current is deduced that the mean values of potential and noise resistance allow to study the evolution over time in the life of the barrier kind paint systems with a high level of sensitivity to the qualitative change in the system behavior paint-metal-electrolyte.

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