

Physical and Electrochemical Behavior of Epoxy Coatings Submitted to Drastic Thermal Ageing

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With the purpose of evaluating commercial coatings in a short term, many authors report the behavior of coatings through accelerated cyclic tests which start at the lowest temperature and increases up to the highest one. This work presents a drastical thermal ageing cycle for a commercial epoxy coating with an inhibitor pigment. Films applied on low carbon steel and substrate-free films have been evaluated. Both films have been continuously immersed in a 3% wt sodium chloride solution, and heated at four temperature values starting with the highest one of 85 and decreasing each 20 degrees (65, 45) down to 25 °C (24 hours in each temperature). Substrate-free films were sampled and electrochemical measurements on painted samples were carried out when the temperature decreased every 24 hours. Analyses of EIS, EN scanning electronic microscopic (SEM), infrared spectroscopy (IR) and differential scanning calorimeter (DSC) were carried out to look for signs of deterioration in the films. The obtained results are discussed in this paper.

Keywords: drastic thermal ageing, EN, organic coating, corrosion

1. INTRODUCTION

Both chemical and physical accelerated aging of organic coatings submitted to multiple thermal and immersion shocks have been reviewed for many years. This has been done because coatings on metal systems support a cyclic thermal weathering which is related to temperature fluctuations in daily and seasonal cycles[1]. Previous documents have shown the behavior of organic coatings after one or several immersion heating step cycles. The authors suggested that at the beginning of the immersion, it

is impossible to estimate the protective properties of organic coatings because the analysis in this stage is limited to the changes in the capacitance of paint which is only due to electrolyte absorption. The former cannot be very often correlated to the corrosion performance[2,3]. Changes in environmental temperature affect coated metal in two ways: by the inducing thermal stresses in the system and by changing the mechanical properties of the viscoelastic coating[4,5,6]. The final effect of physical ageing and chemical degradation is the loss of the coating capacity to relax stresses. Therefore, a mechanical damage to the coating (micro-cracks) and the delamination of the metallic base may occur[4,5]. When the coating is submitted to the accelerated ageing cycles increasing the temperature on steps of approximately 20°C, this kind of heating allows coating to adapt itself to the aggressive conditions. This is because the polymer chains relax while the temperature increases and the electrolyte can be absorbed. These phenomena caused plasticization of the coating when the cycle finished. The damage was physical because the coating tried to go back its original properties. Only after several cycles the coating shows signs of mechanical damage (micro-cracks)[7,8,9]. In this paper, the electrochemical and the SEM measurements of both, free and applied films of a commercial epoxy coating pigmented with zinc chromate (inhibitor properties) are reported. This coating has been submitted to a drastic ageing cycle by combining the immersion in brine and by heating it at four temperatures. When the first evaluation was at 25°C the temperature started to increase immediately and drastically until it reached 85°C (above the T_g of the coating). The temperature was kept for 24 hours. Eventually, the temperature decreased on steps of 20 °C keeping each step for 24 hours and developing an evaluation in situ. Coating degradation had been monitored by means of the changes in capacitance, resistance, physical damage (detected by SEM) and chemical damage (FTIR and DSC).

2. EXPERIMENTAL

Experiments of immersion-heating cycles at four different temperatures, using both films applied in low carbon steel and free-substrate films, have been developed.

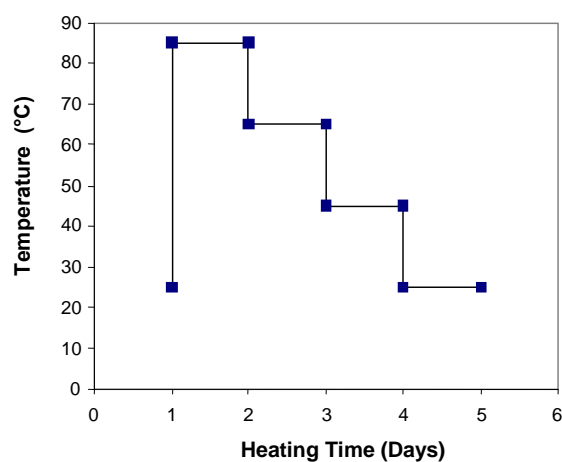


Figure 1. Drastic immersion-heating cycle.

The immersion-heating cycles are shown in figure 1. Each point indicates where the electrochemical measurements and sampling of films were made.

A commercial pigmented zinc chromate epoxy coating, obtained from two components: epoxy and amide was used. Epoxy coatings were selected because they are recommended for marine immersion. They also have a high glass-transition temperature (T_g) of approximately 61.35°C. Therefore, a damage resulting from these cycle temperature changes was not expected. The pigment was selected due to its inhibitor properties. The coating was prepared according to the manufacturer's recommendations to obtain the films. Electrochemical evaluations were done while the coating films were submitted to the ageing process. SEM, DSC and FTIR analyses were carried out later.

2.1. Free-substrate films

Commercial epoxy paint was prepared according to the manufacturer's instructions. Paints were applied with a razor on a sheet of glass, obtaining films with a homogeneous average dry thickness (60 μm). Paints were cured for 3 days at 25 °C and were taken off the glass for ageing experiments. The films were heated for 24 hours at each temperature and then, sampled when the heating cycle finished in order to analyze them at SEM, DSC and FTIR.

2.2. Films applied on steel

These samples were used for electrochemical measurements. Sheets of low carbon steel AISI 1010 (UNS 10100) of 5 x 2.5 x 0.15 cm were prepared. The substrate was submitted to a manual surface preparation with abrasive paper 240 (SSPC-SP-2) and later degreased with acetone (SSPC-SP-1). The paints were applied on the steel with a razor to obtain films with average thickness values of about 24 μm . The painted steel sheets were submitted to immersion-heating cycles, at four temperatures, keeping the sheets at each temperature for 24 hours and doing electrochemical measurements at the beginning and at the end of each cycle.

2.3. Electrochemical measurements

The tests were made in a potentiostat GillAC of ACM Instruments. Impedance measurements were carried out by using a NaCl 3 % wt solution as an electrolyte. A vertical cell with a saturated calomel electrode (SCE) as the reference and a graphite bar as the auxiliary electrode were employed. The amplitude applied was 50 mV, and the frequency range from 10^4 to 10^{-1} Hz. EN measurements were made using an electrolyte of NaCl 3 % wt, employing a vertical cell with a two nominally identical working electrodes arrangement. In addition to a calomel saturated electrode as a reference[10], was employed. The frequency sampling was 2 points/sec, obtaining 2048 readings. These results were analyzed statically and the trend was removed in order to get the Noise Resistance (R_N), which can be compared with Polarization Resistance (R_p)[11,12] and the location index (LI).

3. RESULTS AND DISCUSSION

3.1. Electrochemical Evaluations

The irreversible damage on the coated substrates could be observed after only one ageing cycle. The EIS Bode plot in figure 2, shows that since the first heating, the coating had failed, because the first value of impedance modulus was too high ($10^{11} \Omega\text{-cm}^2$), and it was the expected value for epoxy coatings[6]. . So, when the temperature increased drastically, that value decreases down to $10^5 \Omega\text{-cm}^2$. It did not try to recover the original value while the cooling stages were carried out. This behavior could be due to the rigidity of the epoxy coatings. This is because when the heating occurred on stages, the polymer chains can get relaxed. However, in this case the heating was immediate and the polymer could not be plasticized. It did not resist the aggressive conditions and broke.

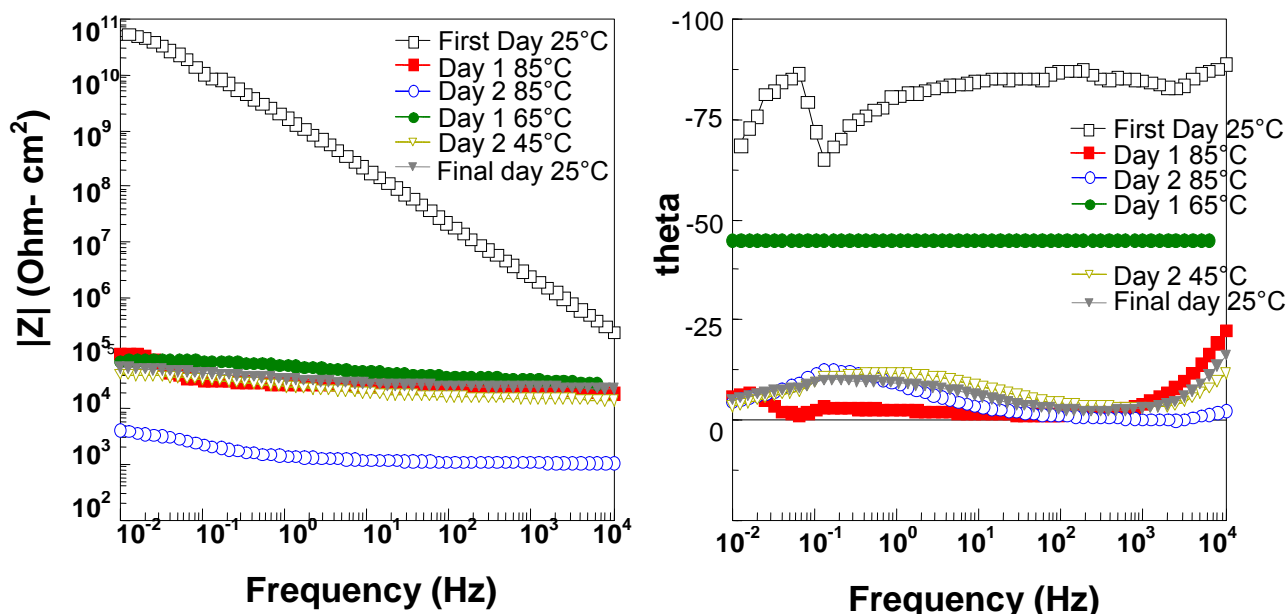


Figure 2. Bode plot of coating measured at the most critical temperatures trough a drastic and complete immersion heating cycle

When the EIS high frequency data (these data belong to the phenomena the coating went through.) They were simulated using a Randless circuit. The protective properties, coating capacitance (C_c) and a coating resistance (R_c) were obtained. Figure 3 shows that the C_c behavior was the expected one for the modulus of impedance. Because the initial value was about $10^{-11} \text{ F-cm}^{-2}$, it was the expected value for an intact epoxy coating. When the drastic heating started, this parameter increased up to $10^{-9} \text{ F-cm}^{-2}$, which is acceptable. But after 24 hours at 85°C , the parameter increased up to $10^{-3} \text{ F-cm}^{-2}$. This value cannot be considered as a double layer one. When the cooling started, the C_c decreased by one order of magnitude. And, it continued around $10^{-5} \text{ F-cm}^{-2}$ until the cycle finished.

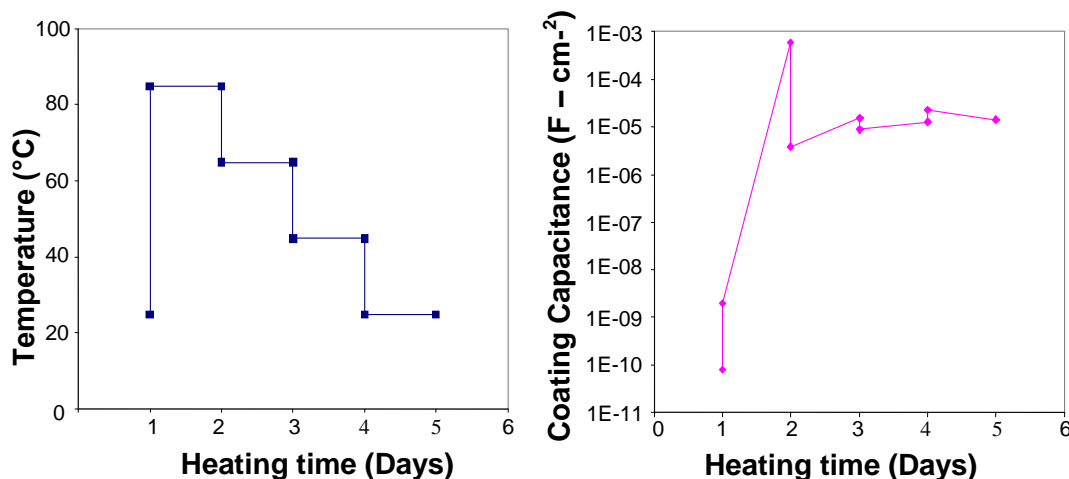


Figure 3. Coating capacitance trough a drastic immersion heating complete cycle.

The resistance of the painting revealed in Figure 4 showed the same tendency of the diagram of Bode. This property decreased from the first heating coming down six orders of magnitude and after 24 hours, it diminished one more order. When the cooling initiated, the resistance tried to increase again; however the damage was already done when the temperature descended. It ended with a value of an order of 10⁻⁴ Ω-cm². With these values of Rc and Cc, it is possible to affirm that the coating had been fractured. The cracks gave as result the electrolyte access and the establishment of the double electrochemical layer, and this would be considered a delamination[13,14,15].

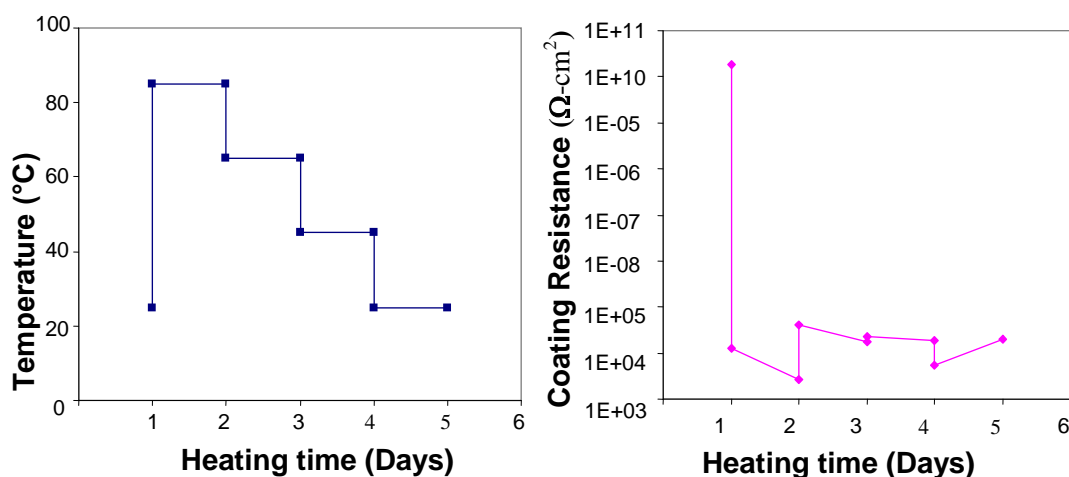


Figure 4. Coating resistance trough a drastic complete immersion heating cycle

The small increase observed on Cc and Rc plots could be due to the releasing of inhibitor pigment, which could react with the metal surface forming some passivating products. Nevertheless, the damage was catastrophic because the coating broke so the exposed area was too big and the inhibitor action of pigment was not enough to protect the metal.

EIS results indicate that in this kind of cycle, similar behaviors in the first and the last day would not happen, as they would be expected. In addition, the signals on EN measurements changed drastically since the heating initiated. This fact is very evident in the plots of the original (crude) signal (Figure 5), as well as in the signal plots with a removed trend (Figure 6). There are three graphs obtained in the most important points in both figures. Points of corrosion of a possible breaking of the coating layer would be expected consequently, according to the evaluated results with EIS. In fact, at the points located with the letter *b* in both figures, it can be observed that the coating formed crevice. This is deduced clearly due to the fall and quick recovery of both, the potential and the current. Indeed, this is more evident in figure 6[16,17]. A potential fall observed in point *c* in the same figure could correspond to a puncture. Perhaps this behavior is due to the hardening of the paint film and to the possible adhesion of passivating products which could be deposited in the crack, covering it partially.

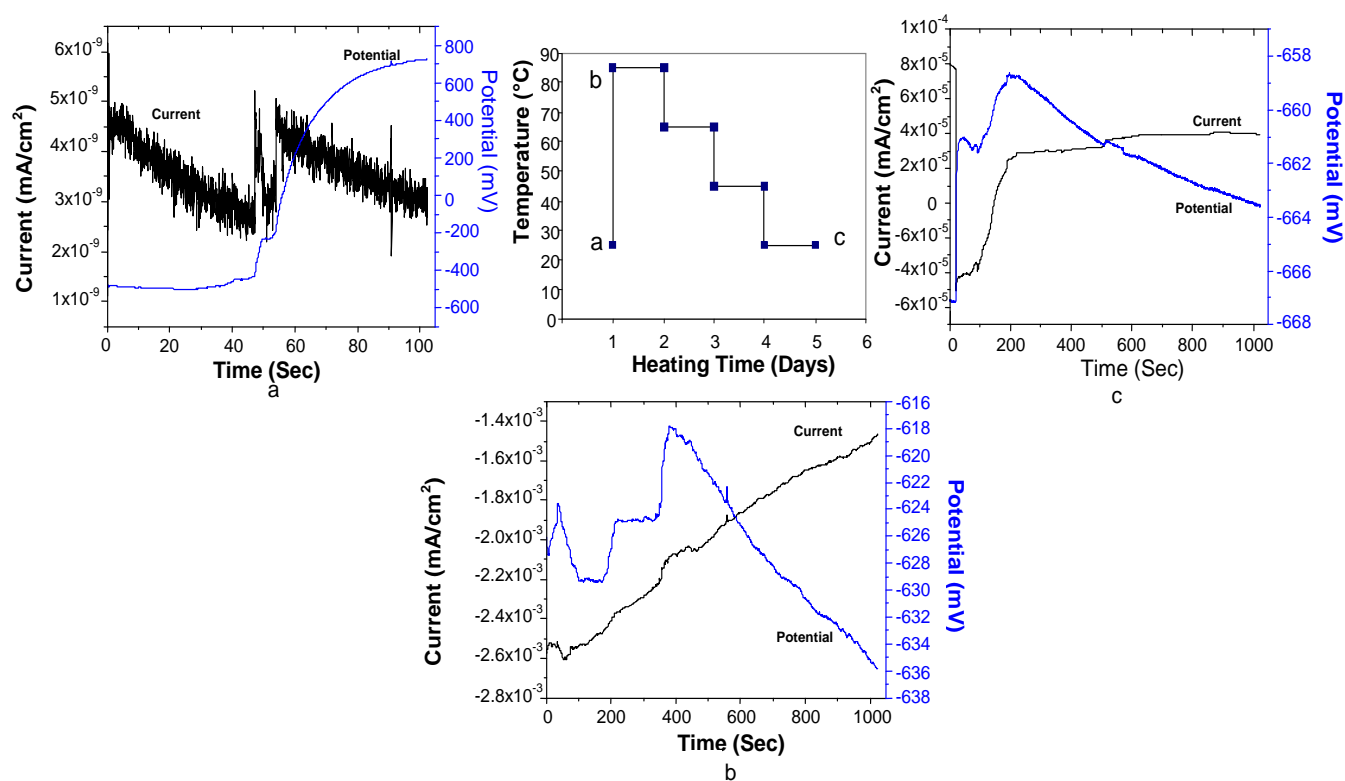


Figure 5. En graphs (original trend signal) of coating through a drastic complete immersion heating cycle. (the letters indicate when the measurement was performed.)

By going through the analysis of the noise resistance (Figure 7), the predicted phenomenon by impedance was observed. As the paint was not able to plasticize by itself, it succumbed to the first thermal shock. Therefore, not even the zinc chromate could protect it because, although it tried to increase to the R_n when the cooling started, it was impossible that it recovered at least two orders of magnitude..

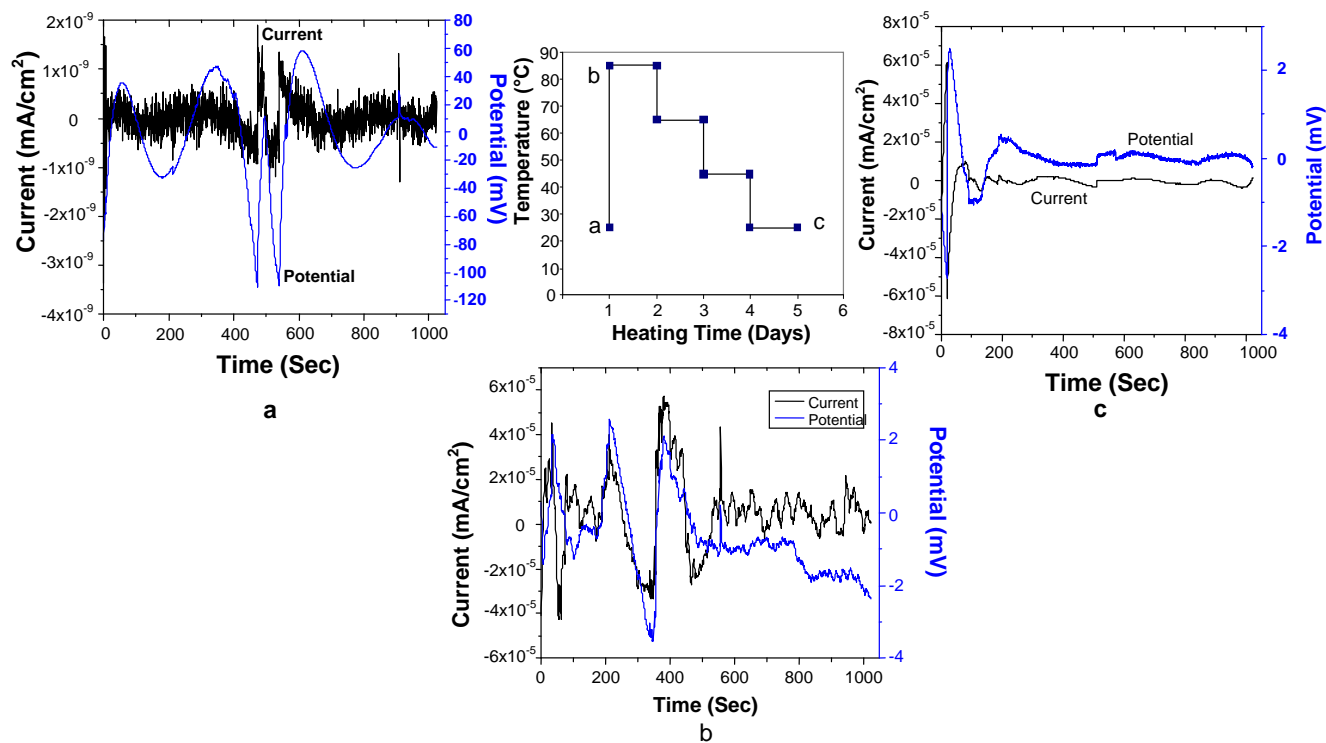


Figure 6. En graphs (trend removed signal) of red coating through a drastic complete immersion heating cycle. (the letters indicate when the measurement was performed.)

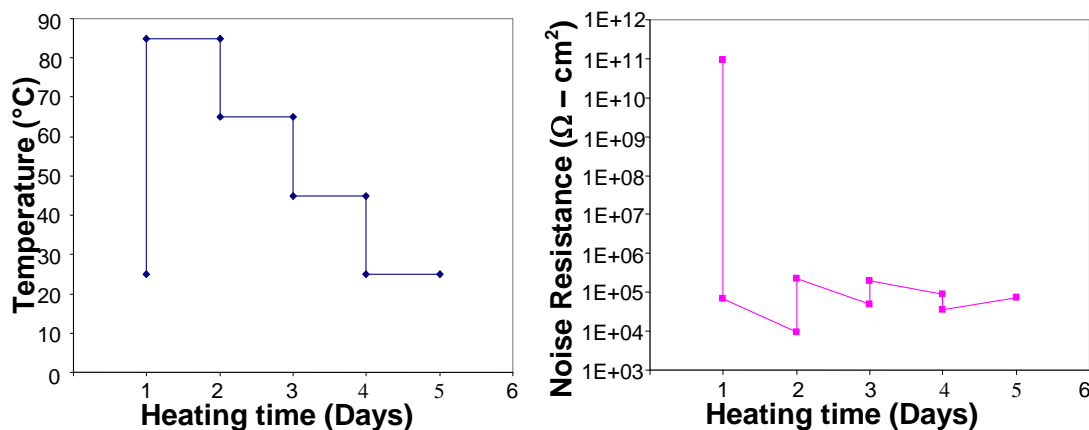


Figure 7. Noise resistance of the coated metal trough a drastic complete immersion heating cycle.

The location index (LI) obtained for this coating varied between 0.1 and 1.0 throughout the cycle and it is shown in figure 7. The initial values of the LI were closer to a mixed corrosion. After the first heating the parameter almost reached 1.0. This indicated the formation of located corrosion due to a possible formation of a crack, since the film did not support the heating and it was broken in some sections. When the cooling started, the LI decreased to smaller values, almost 0.1. This revealed a mixed corrosion because the not broken sections of the film got relaxed while they were heated and could almost cover the location of the holes[17,18]. In addition, the crack was also being covered by

corrosion products. Although they are not passivating, they could help the metal cover itself, whereas paint tried to do the same thing[19]. After 24 hours at each temperature the polymer was stabilized, but it did not stop relaxing. On the contrary, when the temperature decreased, the polymer was contracted and perhaps the passivating products were deposited in certain zones leaving others without covering. Therefore, the IL increased. When the cycle concluded, IL increased until almost 1.0 which definitely indicated that the paint had broken.

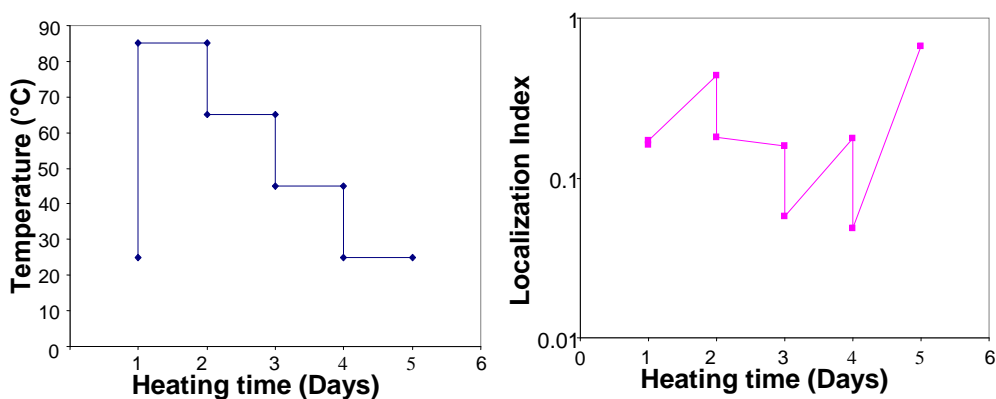


Figure 8. Variation of location index of the coated metal trough a drastic complete immersion heating cycle.

3.2. Physics and chemical Evaluations.

The free-substrate films were analyzed before and after the cycle. Figure 9 shows the micrographs obtained by SEM of the coating before aging and after completing the drastic cycle (Figures a, and b respectively). Some holes shown in figure b, corresponding to possible collapsed blisters, were caused by thermal shocks. By looking at these photographs, it is possible to affirm that all the holes were due to the thermal shock, as it was revealed in the electrochemical techniques.

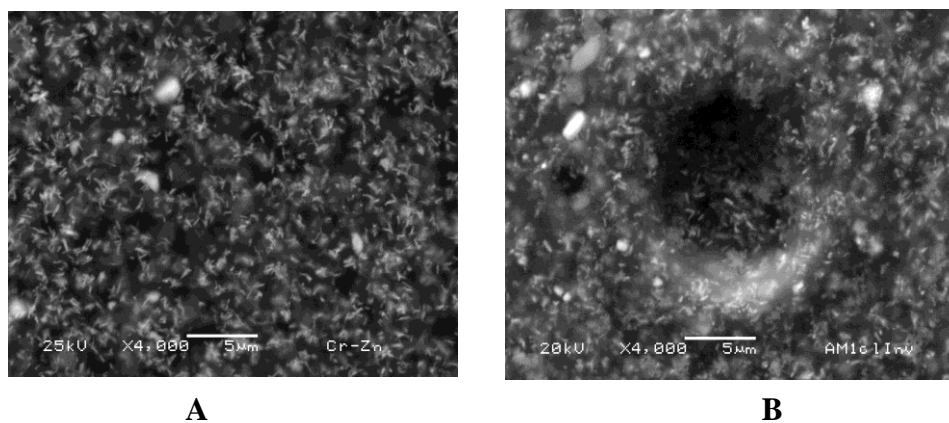


Figure 9. Sem photographs of the coating free-substrate film: a) film not aged and b) film after a drastic complete immersion heating cycle.

When the DSC analyses were carried out to verify the degradation according to the Tg (figure 10), an increase in both glass transition temperatures of the aged film could be observed. The coating showed two values of Tg because it is an epoxy paint obtained by the reaction of two comonomers (two components): epoxy-amide.

It is known that polymers become more rigid and fragile when Tg increases. In this case, this increase on Tg was the result from the breaking of the film. Because the heating was so fast, the paint did not have time to absorb the enough water to get plasticized.

Thus, the resin chains could not relax making that coating did not support the thermal shock and broke itself. In fact, with the previous results: the photographs obtained by SEM, and the electrochemical characterization, the rupture of the paint films applied to the steel had already been demonstrated.

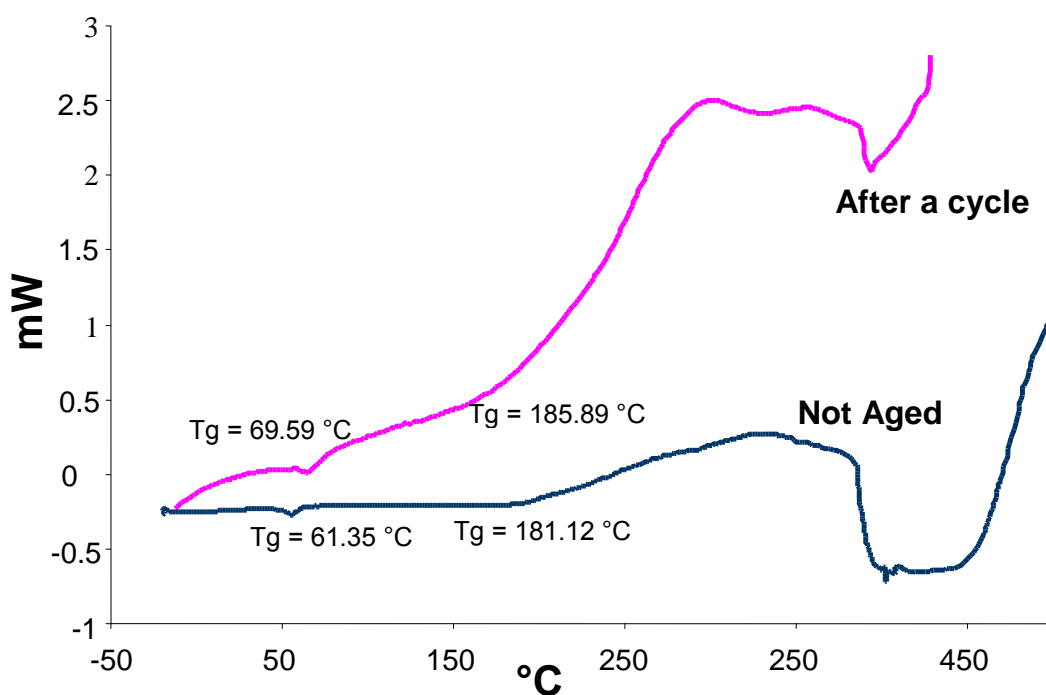


Figure 10. Dsc plot of the coating free-substrate film not aged and the film after a drastic complete immersion heating cycle.

When the effects of the aging with the FTIR technique were analyzed and, which spectra is in figure 11, the most evident result was the decrease in the intensity of the band of the group hydroxy. This confirms the previous result of DSC, that the coating did not absorb the enough amount of water. Therefore, it did not reach plasticizing itself and broke. Also, a slight decrease in the residual monomer bands was observed (groups amide located in 1500cm^{-1}). Moreover, there was a little decrease in the typical bands of the epoxy located around 2900 and 1600 cm^{-1} . These are more evidences of the undergone degradation.

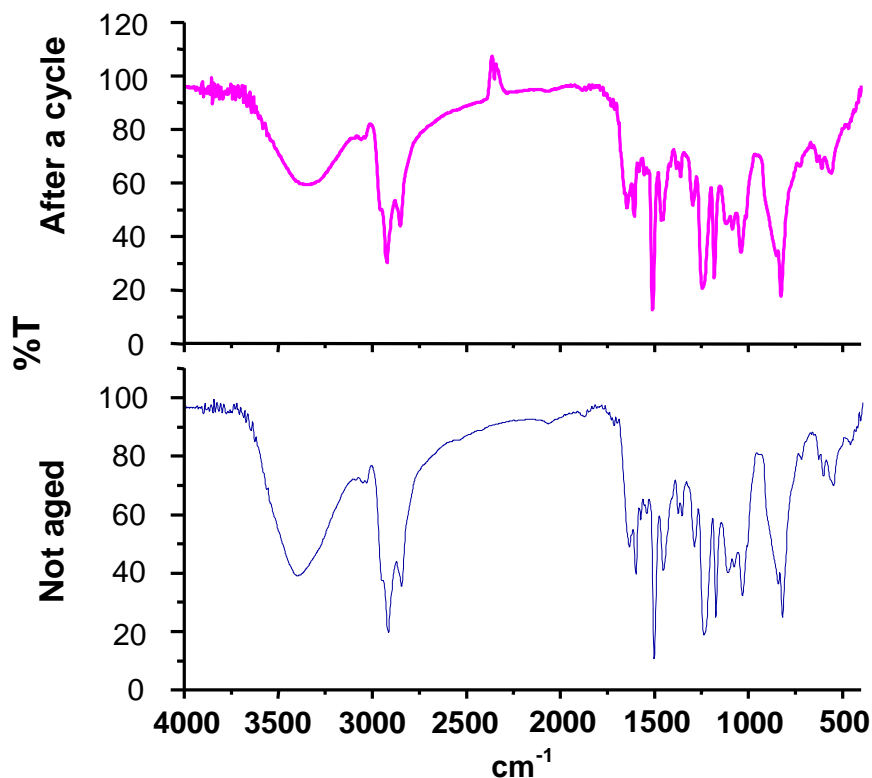


Figure 11. Ftir spectra of the coating free-substrate film not aged and the film after a drastic complete immersion heating cycle.

With these cycles of aging, it was verified that it was unnecessary to submit these coatings under a drastic thermal shock because the extreme high temperatures degrade them both, physically and mechanically. Chemical aging signs were also revealed. Although the paint arrives to its own point of irreversible fault in an extremely short time, it is not recommendable to make this type of aging if it is needed a more precise monitoring of the degradation mechanism and the phenomena that occur (such as plastization, leaching of pigments, passivating product forming, etc.)

4. CONCLUSIONS.

The drastic aging in situ cycle with NaCl degraded coating almost instantaneously. This was because the paint did not support the drastic initial increase of the temperature. It was enough just a single heating to provoke the paint fault. The immediate deterioration caused by the ageing cycle, promoted the creation of defects in the films (fractures, collapsed blisters, etc). Although the drastic cycle degraded the paint films physically and mechanically, without allowing them to recover, there was no chemical aging considerable. This was because alterations in the functional groups of the resin were not revealed. In this type of aging, the inhibitor effect of pigment in the metallic surface was not observed, because the damage in the films was so drastic that even chromate was not able to protect the zones that were free of coating.

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