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Anticorrosive properties enhancement in powder coating duplex systems by means of ZMP anticorrosive pigment. Assessment by electrochemical techniques

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ABSTRACT

The effect of the addition of the anticorrosive zinc molybdenum phosphate (ZMP) with superficial modification (an organic titanate), on the corrosion resistance properties of powder coating on galvanised steel has been investigated by means of different electrochemical techniques: electrochemical impedance spectroscopy (EIS) and an accelerated cyclic electrochemical technique (ACET). Powder coating based on carboxylated polyester resin and N,N,N,N-Tetrakis-(2-hydroxyethyl)-hexanediamine (95:5) were prepared with different contents of the anticorrosive pigment ZMP (0, 1, 2.5, 10 and 15% in weight ratio to total formulation). The optimum quantity of anticorrosive phosphate pigment ZMP (maximum anticorrosive performance) was in the range 10–15%, depending on the technique applied, and can be ascribed to both barrier properties enhancement and inhibition action of the pigment. Finally, salt fog spray test was performed to confirm the electrochemical tests results.

1. Introduction

Zinc molybdenum phosphate (ZMP) seems to have become an excellent alternative to toxic inhibitive pigments because of equal or superior anticorrosive behaviour to chromates and better than non-modified zinc phosphate. This pigment belongs to the second generation of zinc phosphates that are obtained by applying an organic surface treatment to the particles, designed to enhance the continuity between the inorganic pigment and the surrounding organic binder, and blending other inorganic inhibitors like ZMP with the zinc phosphate [1,2]. ZMP pigment produces a molybdate anion (MoO_4^{-2}) that acts as an effective anodic inhibitor [3,4] whose capacity to passivate is only slightly lower than that the one of the chromate anion [5]. Among all of the molybdates-based pigments, ZMP is one of the highest reported due allegedly to a synergistic effect between the phosphate and the molybdate ions [6,7]. According to the literature [8], this dual metal pigment provides higher degree of passivation than zinc chromate under acidic conditions but inferior to that zinc chromate under alkaline conditions. Although there have been several studies to investigate the anti-corrosion efficiency of ZMP pigment [8–14], most of them are focused on protecting steel and only few examples lead with the protective effect of ZMP on hot dipping galvanised steel (HDG) [15–17].

Corrosion protection by organic coatings is considered one of the most effective and durable way for protecting HDG. The purpose is to provide additional corrosion resistance and/or an aesthetically pleasing appearance to HDG and this double protective system is commonly name as duplex. The life of a properly applied corrosion resistant duplex coating is normally greater than the sum of the lives of the two individual coatings. Typically, in a severely aggressive climate, the factor of increase is 1.8–2.0; in seawater it is 1.3–1.66 and in non-aggressive climates, the factor is 2.0–2.7 [18].

However, effective protection is only possible if the coating remains bonded to the substrate during the design life of the metallic structure. Inadequate preparation and cleaning of the zinc surface, prior to the application of a compatible paint system or powder coating, causes a lack of adhesion, which is the main cause of premature failure [19,20]. In fact, conventional processes require an initial primer or surface pretreatment [21] prior to the application of the powder coating, to facilitate adhesion to the substrate. This step implies an increase in the cost of the corrosion protection and additional environmental problems, because in many cases, chromium and other heavy metals are used. Therefore, research efforts are focused on eliminating the pretreatment step resulting in equivalent anticorrosive properties [22–28].

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The application of electrochemical impedance spectroscopy (EIS) to coated metals has been shown to be a useful technique in the study of the performance of anticorrosive coatings [22–28]. There is great interest in creating rapid assessment methods for practical applications in order to provide faster indications of corrosion processes in the surface and the interface of coated metallic substrates. Hollaender et al. [29–31] developed a rapid method for testing coated metals in food packaging. The accelerated cyclic electrochemical technique (ACET) [32–38] used in this study is based on the Hollaender method but introduce a potential relaxation step following each cathodic polarisation. Using a long potential relaxation step, the stress induced to the sample with the cycles is much higher able to increase the degradation process.

The present work will concentrate on the development of new monolayer powder coatings able to be applied on galvanised steel without pretreatments and with good anticorrosive properties. The study is based on the evaluation of powder coatings formulated with different contents of ZMP pigment by means of EIS and ACET on degreased HDG. Moreover, these techniques will provide vital information related to the anticorrosive properties of the tested powder coatings on HDG without pretreatment. Finally, this methodology will allow us to determine the optimum amount of ZMP pigment for the tested systems.

2. Experimental

2.1. Materials

ZMP pigment is based on zinc phosphate and zinc molybdate conditioned with an organic titanate in the surface. The ZMP pigment was incorporated in different contents (0, 1, 2.5, 10 and 15% of the total formulation). This material was added into the coating formulation replacing the barium sulphate and the titanium dioxide. The powder coatings were carried out starting with several saturated carboxylated polyester resins of low molecular weight and N,N,N,N -Tetrakis-(2-hydroxyethyl)-hexanediamine in a mixing ratio of 95:5. The composition of the systems comprised: 57.7% resin, 3.3% crosslinker, 3% levelling agent, 0.3% degassing agent, 0.3% polyamide wax, 0.3% PTFE wax and 1–15% ZMP pigment. The formulation was adjusted in all cases by means of the proportion of barium sulphate (0–4.7%) and titanium dioxide (19.7–30%).

2.2. Substrate/sample preparation

Samples were pre-mixed and shaken by hand until good premixing was obtained. Subsequently, the material was extruded in a double screw extruder (Werner & Pfleiderer ZSK25) and the temperature profile was set at 40, 120, 120 and 70 °C (rear to front along the extruder). The material produced was ground in an ultracentrifugal mill ZM 100 and sieved at 140 nm; thus, obtaining the different powder coatings ready for application on the steel substrates. The five different powder coatings were deposited on nine galvanised steel samples (15 cm × 7.5 cm × 0.1 cm) for each coating, previously degreased with acetone, by means of an electrostatic gun. All the coated samples were cured at 180 °C for 15 min and the thicknesses obtained were 90 ± 10 μm.

2.3. Testing methods and equipment

2.3.1. Electrochemical impedance spectroscopy (EIS)

EIS tests were carried out on the coated samples exposed to 3.5% NaCl (by weight) in deionised water. The three-electrode electrochemical cell was obtained by sticking a glass cylinder on the sample sheet and filling it with the test solution. The exposed surface area was 9.62 cm^2. A carbon sheet acted as the counter electrode and an Ag/AgCl electrode was used as the reference one. This is the most common electrochemical cell setup used in electrochemistry, although other electrode systems are developed to minimise perturbation of signals at high frequency domain when using Ag/AgCl electrode [39]. EIS measurements were performed on a ZAHNER-IM6ex electrochemical workstation. The impedance tests were carried out inside a Faraday cage over a frequency range of 100 kHz down to 10 mHz using a sinusoidal voltage of 10 mV as the amplitude in order to minimise external interference on the system.

The experimental electrochemical data were collected and analysed by using the Thales software developed by Zahner and the Medco Assay software developed by Medco.

The circuit consisted of a reference electrode, electrolyte resistance R_S, coating pore resistance R_{po}, coating capacitance C_c, polarisation resistance R_p and double layer capacitance C_{dl}. Fitting the EIS data to the circuit by means of the *Z*-view software determined the values of its passive elements, which are generally assumed to be related to the corrosion properties of the system [40]. R_{po} can be related to porosity and the deterioration of the coating, C_c to the water absorption by the coating, R_p to the polarisation resistance of the interface between the coating and the metal substrate and C_{dl} to the disbonding of the coating and onset of corrosion at the interface [41–43]. To obtain more precise fitting results, Constant Phase Elements CPE replaced capacitive elements in the equivalent circuit, giving the software values of Y_0 in units of s^n/Ω together with a parameter known as "*n*" instead of s/Ω or *F* units. Mansfeld et al. [44] reported that constant phase element parameter Y_0 could be converted into a capacitance *C* by using the following equation:

$$C = Y_0(w''_{max})^{n-1} \quad (1)$$

where w''_{max} is the angular frequency at which the imaginary part of the impedance (Z'') has a maximum in the representation of Nyquist plots.

In this study, the effective C_{dl} was calculated using the above equation because n vary in a wide range. The values used in C_c were those given by the fitting because the *n* values were always very close to 1, so no differences were detected. The chi-squared parameter of the fit was always less than 0.01.

2.3.2. Accelerated cyclic electrochemical technique (ACET)

The ACET procedure comprises a combination of cathodic polarisation (DC), potential relaxation and EIS measurements (AC). First, an EIS test is applied to the sample under the same conditions as described above. This measurement allows the present state of the test sample to be determined. Following the initial EIS measurement, the test sample is treated for a short time with a constant cathodic voltage (−4 V) for 20 min (DC) and subsequently, the relaxation time of the sample until it reaches a new steady state and the potential is once more stabilised is registered. In this case, the relaxation time was 3 h. Finally, a new EIS measurement (AC) is applied to the sample in order to determine the new state. A

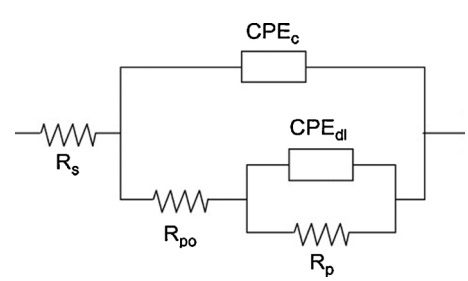

Fig. 1. Equivalent circuit used to model EIS and ACET impedance data where passive parameters (R_s = electrolyte resistance, R_{po} = pore resistance, CPE_c = constant phase element of the coating capacitance, R_p = polarisation resistance, CPE_{dl} = constant phase element of the double layer capacitance) can be defined.

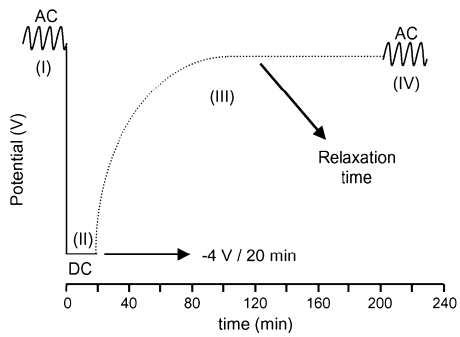

Fig. 2. ACET test schematic figure versus time.

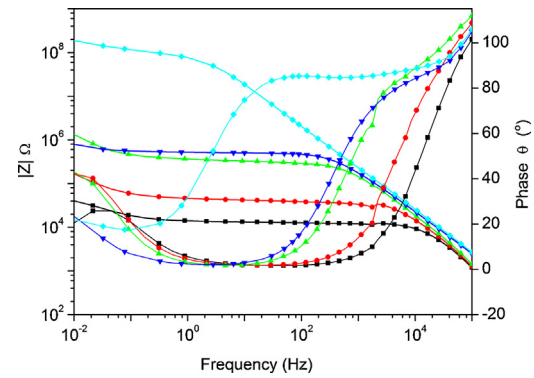

Fig. 3. Bode plot (impedance modulus and phase angle versus frequency) for polyester coatings with different ZMP content (%): 0 (■), 1 (●), 2.5 (▲), 10 (▼) and 15 (◆); applied on galvanised steel after 1176 h exposure to electrolyte (deionised water with 3.5% NaCl by weight). EIS test.

schematic representation of the ACET procedure is shown in Fig. 2. This test sequence is repeated at least six times, which means that almost 24 h are required for this procedure. The ACET procedure is completely automated on a ZAHNER-IM6ex electrochemical workstation. Experimental results obtained by EIS measurements are modelled using the equivalent circuit shown in Fig. 1 and with the same procedure described above.

2.3.3. Salt fog spray

The accelerated salt fog spray test was performed in accordance to ISO 9227:2012. In this test a scribe is performed along the coating until the bare metal is reached. The samples are then introduced in a salt fog spray chamber where a brine fog is created with 5% NaCl (by weight) water solution. The samples are collected at different periods of time and evaluated until a failure was reached (rusting penetration greater than 2 mm).

3. Results and discussion

3.1. Electrochemical impedance spectroscopy (EIS)

Fig. 3 shows a Bode plot (impedance modulus versus frequency) for 1176 h exposure of the five studied samples. The EIS test gives an idea of the processes occurring within the coating (high frequencies measurements) and those occurring at the interface (low

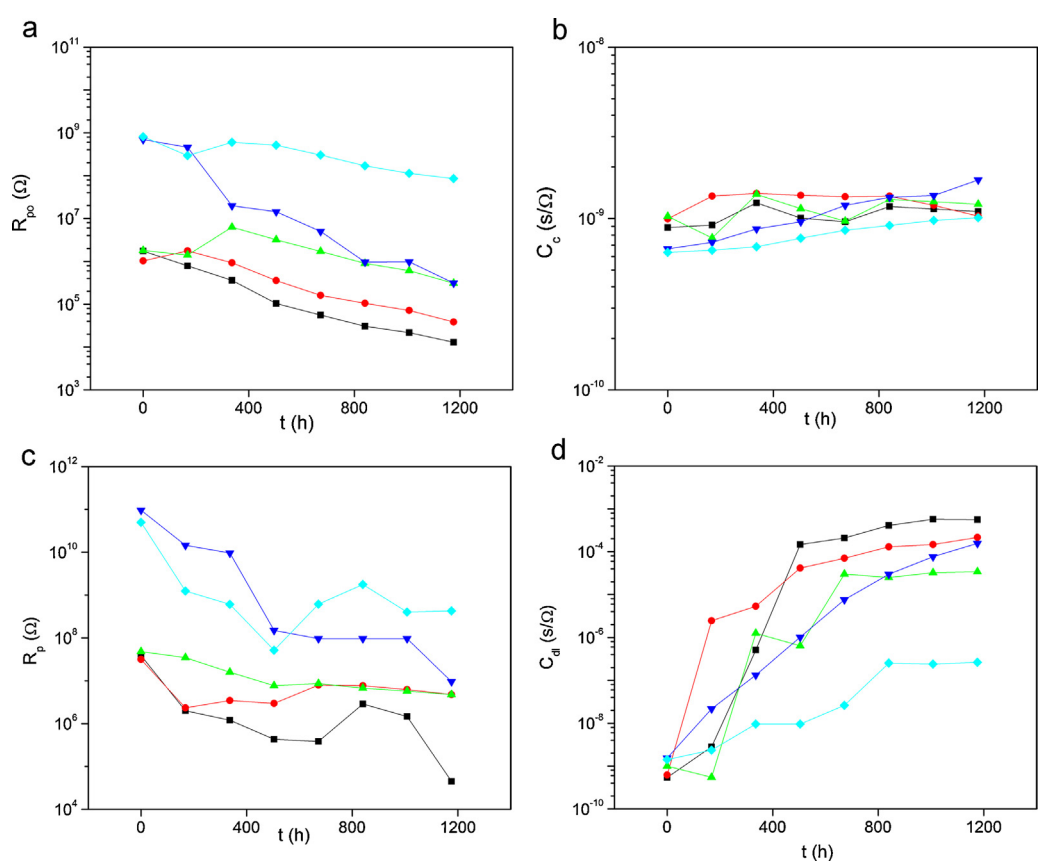

Fig. 4. (a) Evolution of pore resistance R_{po}; (b) evolution of coating capacitance C_c; (c) evolution of the polarisation resistance R_p; (d) evolution of the double layer capacitance C_{dl} vs. exposure time for polyester coatings with different ZMP content (%):0 (■), 1 (●), 2.5 (▲), 10 (▼) and 15 (◆); applied on galvanised steel after 1176 h exposure to electrolyte (deionised water with 3.5% NaCl by weight). EIS test.

frequencies measurements). Nevertheless, for samples with low porosity, this technique can require a long time to offer good results, because it is necessary that the electrolyte and the different species present in the solution pass through the coating and reach the interface to initiate the corrosion processes. From the impedance results, it can be concluded that the sample with 15% of ZMP offers the best results (highest impedance modulus and capacitive behaviour), whereas those samples without any, or with only a small amount of the additive (reference and 1% of ZMP), offer the worst result (lowest impedance modulus and more resistive behaviour). Those with 2.5% and 10% exhibit intermediate behaviour.

Results from the EIS test have been modelled with an electric equivalent circuit (Fig. 1) and its characteristic parameters determined. The evolution with immersion time of the different parameters (Fig. 4) gave information about the anticorrosive coating properties and its evolution. These figures support the results shown in the Bode plot. When adding small amounts of ZMP pigment to the reference coating, e.g., 1 and 2.5 wt%, the anticorrosion properties are not improved. The pore resistance decreases, the coating/metallic interface is far more active (R_p decreases and presents a non-stable evolution) and there is a strong increase in the coating delamination process (there is an increase in the double layer capacitance by three orders of magnitude compared with the formulation with 15 wt%). However, the incorporation of 10% and specially 15% ZMP increased strongly the anticorrosion properties. In particular, formulation of 15% showed high resistance to pore formation and the lowest water absorption due to exposition to electrolyte, even if the trend of the coating capacitance is not very clear. The values of C_c of this sample increase with time but the final value is very near (even lower) than in the rest of the samples, which is in accordance to the decrease of R_{p0} value. Moreover, it is noticeable the marked differences existing between formulated coatings at the beginning of the test (there is three-orders of magnitude increase in R_{p0} between the reference sample and the 15% ZMP sample). These results could be interpreted as an improvement of the barrier properties of the coatings due to the presence of the pigment, although significant variations in water uptake are not detected on the different samples. Beiro and del Amo [45,46] reported that variations in barrier effect of the coating could be

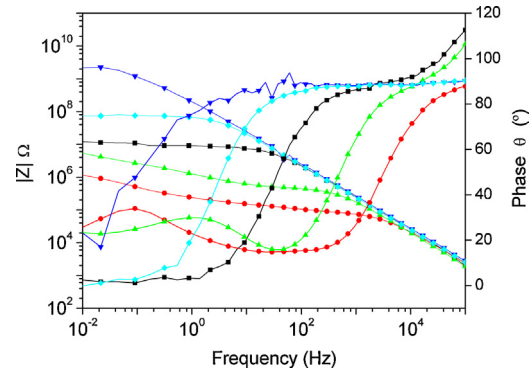

Fig. 5. Bode plot (impedance modulus and phase angle versus frequency) for polyester coatings with different ZMP content (%): 0 (■), 1 (●), 2.5 (▲), 10 (▼) and 15 (◆); applied on galvanised steel after 4 cycles of cathodic polarisations. ACET test.

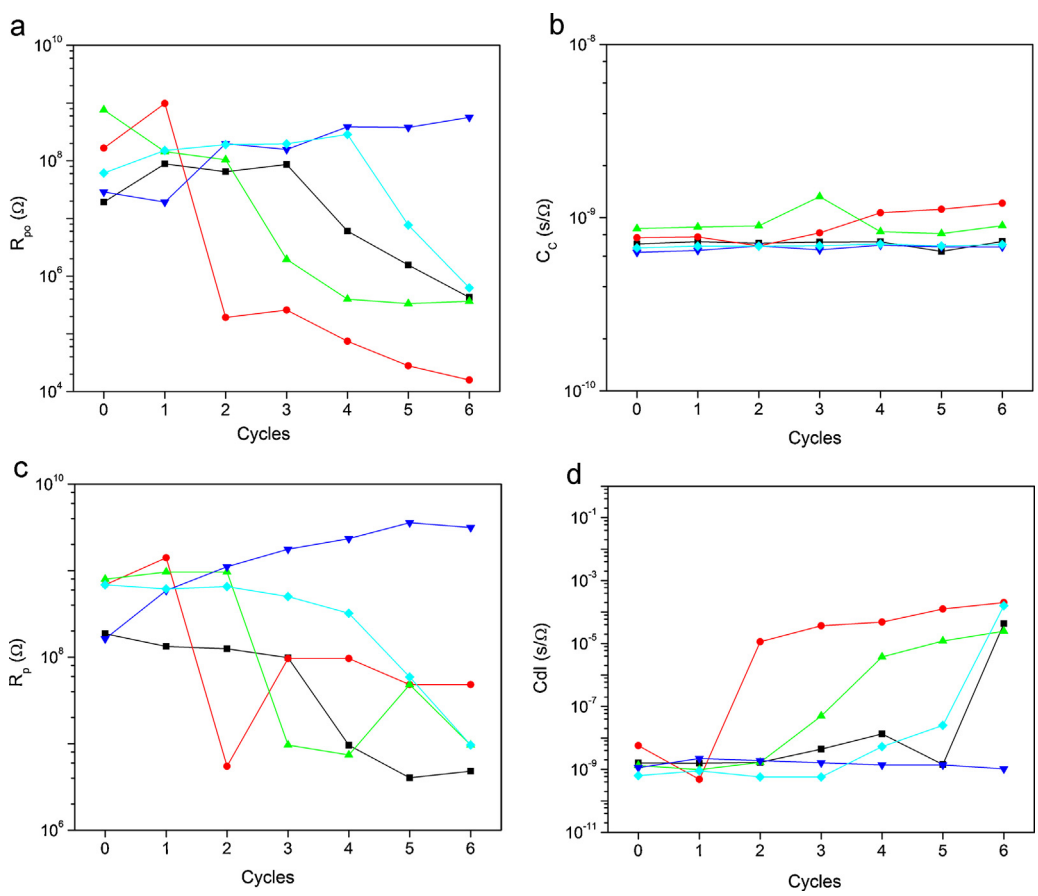

Fig. 6. (a) Evolution of pore resistance R_{po}; (b) evolution of coating capacitance C_c; (c) evolution of the polarisation resistance R_p; (d) evolution of the double layer capacitance C_{dl} vs the number of cycles for polyester coatings with different ZMP content (%):0 (■), 1 (●), 2.5 (▲), 10 (▼) and 15 (◆) applied on galvanised steel after exposure to electrolyte (deionised water with 3.5% NaCl by weight). ACET test.

ascribed to the alteration of the pigment-binder interactions when a zinc phosphate pigment was incorporated in formulations. Then, samples with 10 and 15% present an interphase quite inactive with high values of R_p and lowest values of C_{dl} (Fig. 4c and d), in particular for short testing time, that are associated with the improvement of barrier effect mentioned. When time of immersion is superior to 400 h, R_p values are maintained constant or increase probably as a result of the inhibitive action of ZMP pigment in the coating [5,15,47].

The above results show definitely that the incorporation of ZMP into the formulated systems can improve their corrosion performance and that the optimum value is achieved with an incorporation around 15 wt% of ZMP.

3.2. ACET test

Fig. 5 shows the Bode plot (impedance versus frequency) for the five tested samples after the fourth polarisation in the ACET test. It can be seen that the system including 10% of ZMP shows the best properties followed by 15% formulation. The samples including 1% and 2.5% of ZMP exhibit the worst properties. The reference presented intermediate behaviour.

In order to obtain a specific idea of the evolution of the properties with the polarisations, modelling of the experimental data of impedance can be done with the equivalent circuit of Fig. 1. Fig. 6a–d shows the evolution of the characteristics parameters of the equivalent circuit presented versus the number of cathodic polarisations applied. ACET technique is based in applying a stress on the coating because cathodic polarisation and using EIS and potential relaxation test to characterise the changes of the coating due to them. In the polarisation step the different species are forced to pass through the coating and the reaction of H_2 production is forced (if the electrolyte reaches the metallic surface), producing pores, microcracks and local delaminations. As it can be observed in modelled impedance results, the pore resistance is much higher, the interface is much less active (with higher values of R_p) and the delamination of the coating is very low for the 10% sample compared to the others, however, differences in the water content in the coatings are not detected Especially, superior anticorrosive performance of that formulation is clearly evidenced by the invariance of the C_{dl} after six cycles applied and the increasing resistance to polarisations R_p. Finally, with the ACET test, the addition of low quantities of pigment (1 and 2.5%) seems to decrease the anticorrosive properties of the reference formulation. The pigment quantity seems to have to be raised in these powder coatings to be able to enhance the anticorrosive properties probably due to their low solubility. However, sample with 15% pigment, which showed as high electrochemical performance as 10% sample in the three first polarisation cycles, tends to degrade with additional stress steps applied with resistance and capacitance values that are similar to those formulations that present the lower properties (reference, 1% and 2.5% samples).

Fig. 7 shows the evolution of the potential values versus time after six cathodic polarisations. Values of potential of the reference samples and those containing 1 and 2.5% of pigment were the minimum. This value of potential is lower than −1 V and the relaxation observed can be related to a stop of the hydrogen production because cathodic polarisation. Hydrogen production it is only allowed in the interface coating-metallic substrate during the cathodic polarisation if the electrolyte is able to arrive this area because coating permeability and adhesion to the substrate failure [32,37,38]. In the case of 15% content the potential is higher and two relaxations can be seen, one at short time related to hydrogen production stop and the other at higher times possible due to a new double layer formation. Finally sample containing 10% of pigment showed the maximum potential which can be correlated to the presence of a non-degraded coating with more dielectric properties.

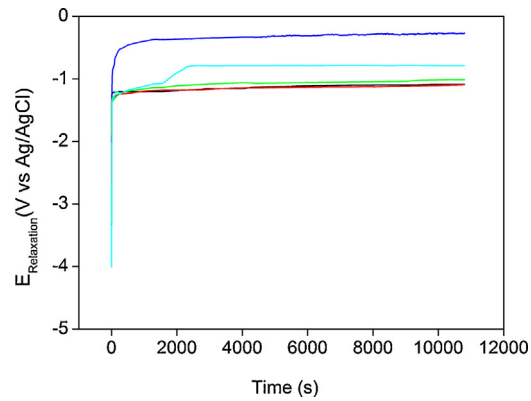

Fig. 7. Evolution of the open circuit potential (E_{OC}) versus relaxation time after exposure to six cathodic polarisations for coatings formulated with different ZMP content (%): 0 (—), 1 (▬), 2.5 (▬), 10 (▬) and 15 (▬); applied on galvanised steel after exposure to electrolyte (deionised water with 3.5% NaCl by weight). ACET test. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 8a and b shows the Bode plots (impedance modulus and phase angle versus frequency) for the reference coating. Fig. 8a corresponds to an EIS test performed over different intervals of time and Fig. 8b shows the response of the sample after different cathodic polarisations. Fig. 9a and b shows the same Bode plots as Fig. 8 but for a coating containing 10% ZMP. As can be seen in these

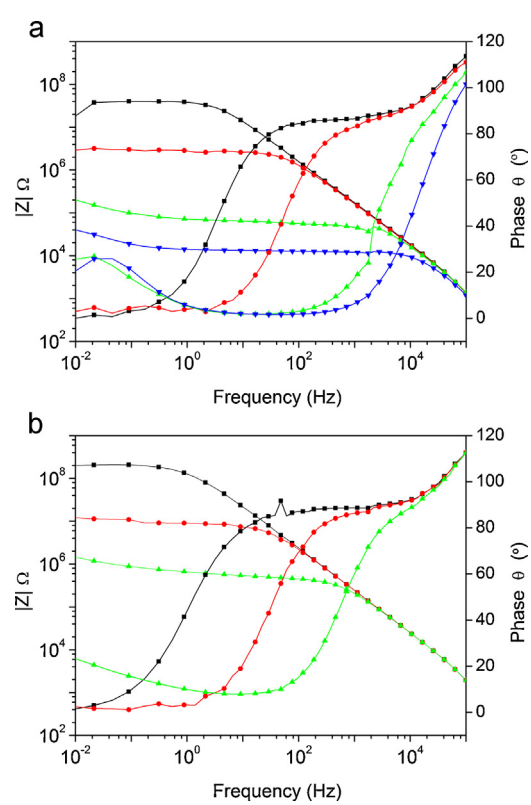

Fig. 8. (a) Bode plot (impedance modulus and phase angle versus frequency) for the reference coating (0% ZMP content) applied over galvanised steel after different exposure times: 0 (■), 168 (●), 672 (▲) and 1176 h (▼) to electrolyte (deionised water with 3.5% NaCl by weigth). EIS test. (b) Bode plot (impedance modulus and phase angle versus frequency) for the reference coating (0% ZMP content) applied over galvanised steel after different cathodic polarisations: 1 (■), 4 (●), and 6 (▲). ACET test.

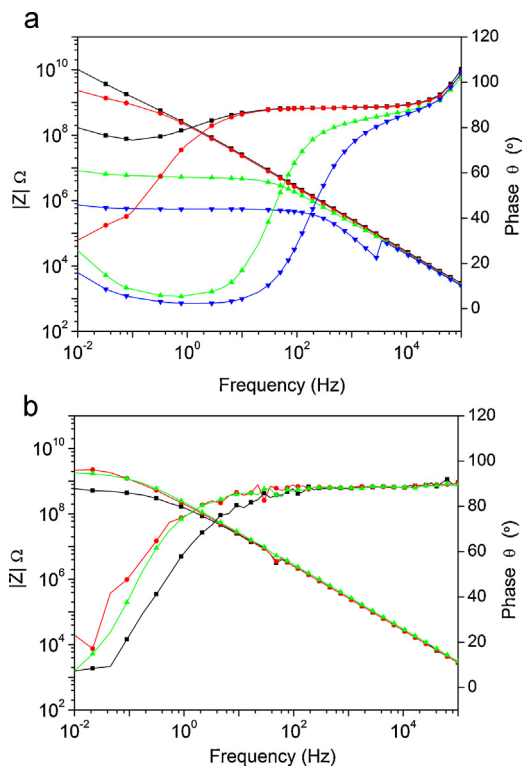

Fig. 9. (a) Bode plot (impedance modulus and phase angle versus frequency) for the 10% ZMP coating applied over galvanised steel after different exposure times: 0 (■), 168 (●), 672 (▲) and 1176 h (▼)to electrolyte (deionised water with 3.5% NaCl by weigth). EIS test. (b) Bode plot (impedance modulus and phase angle versus frequency) for the reference coating (0% pigment content) applied over galvanised steel after different cathodic polarisations: 1 (■), 4 (●), and 6 (▲). ACET test.

Bode plots, the reference coating does not have very good anticorrosion performance and its impedance decreases with both time of exposure to the electrolyte and the cathodic polarisations. The coating degradation obtained is slightly more intensive by means EIS than ACET test (impedance modulus decrease three and two orders of magnitude, respectively), although same conclusions can be extracted in both measures.

The 10% ZMP coating has a good performance and its impedance hardly changes with time or polarisations in the ACET test, showing an increase of impedance modulus with the polarisations applied that can probably related with the inhibitive action of the pigment. In contrast, impedance modulus values corresponding to different times of immersion in electrolyte for EIS test are not correlated with those represented in Fig. 9b, showing an electrochemical behaviour characteristic of a system that degrades. The discrepancy existing about the quality of 10% ZMP coating depending of the electrochemical test applied was also evident when comparing modelled parameters in Figs. 4 and 6. Differences of results between EIS and ACET tests can be related to the principal protection process that is developed in these techniques. In the case of EIS test, the very long immersion time in electrolyte can encourage the possibility of the pigment dissolution while in ACET test it is not favoured due to the limited immersion time in comparison with EIS procedure.

3.3. Salt fog spray test

Table 1 presents the time of failure (defined as the time or exposure to salt spray fog until 2 mm of delamination from the scribe is reached). Salt fog spray test showed that 10% and 15% ZMP coating are the best formulations. Similar tendency is observed in electrochemical tests, although the correlation is not as remarkable as expected. This fact can be attributed to the different mechanisms of testing between the salt fog spray and electrochemical tests [48,49]. In electrochemical procedures, the coating is not damaged and dissolution of pigments is only possible when the electrolyte is able to pass through the coating that can be a slow process. In the case of salt fog spray, the coating is damaged and the dissolution of the pigment can be clearly enhance because direct contact between the electrolyte and the pigment.

Table 1
Time to failure due to delaminated area (>2 mm) after exposure of painted panels in the salt fog spray.

Coatings	Time to failure (h)
Reference	430
1% ZMP	360
2.5% ZMP	360
10% ZMP	648
15% ZMP	648

4. Conclusions

A powder coating formulation with different contents of ZMP (0, 1, 2.5, 10 and 15%) were applied over galvanised steel. The anticorrosive properties were studied by means of electrochemical methods (EIS and ACET). The different results showed that for this type of powder coating, the anticorrosive properties were enhanced when 10 or 15% ZMP (depending on the test applied) was added due to the barrier properties improvement and the inhibitive action of the pigment. The differences between the EIS and ACET results can be possibly related to the pigment dissolution in coatings, which depends largely on the immersion time in electrolyte (ACET test presents limited immersion time in comparison with EIS procedure). Nevertheless, no variation in anticorrosive properties between samples 10% ZMP and 15% ZMP was detected in salt fog spray test.

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