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The combined role of inhibitive pigment and organo-modified silica particles on powder coatings: Mechanical and electrochemical investigation

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ABSTRACT

The addition of organo-modified silica particles (OSP) to powder coating containing zinc molybdenum phosphate pigment (ZMP) has been investigated. The OSP were directly incorporated at different concentrations (1, 2.5, 3.5 and 4.5 wt%) in a polyester powder monolayer coating with 10 wt% ZMP. The adhesion and anticorrosion properties were evaluated by means of adhesion studies and different electrochemical techniques: electrochemical impedance spectroscopy (EIS) and an accelerated cyclic electrochemical technique (ACET). The optimum quantity of OSP that gave maximum anticorrosive performance of the coating system was determined (1.0%), however two opposite effects of addition on the coatings led to a reduction of anticorrosive properties for higher contents. Finally, the electrochemical behaviour of the optimized combined system was compared to the effects achieved when both additives were separately added to powder coatings by means of an additional electrochemical test.

1. Introduction

Corrosion protection by powder coatings is considered one of the most environmentally friendly mechanism to protect metallic substrates as they are essentially free of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) [1]. Today powder coatings do not provide sufficient corrosion resistance for some applications yet, but some studies have demonstrated its superior performance in many aspects when compared to liquid coatings [2,3]. Initial primers or surface pretreatments prior to applying the coating are usually designed to facilitate adhesion to the substrate [4–6]. Although improved corrosion properties of these systems have been demonstrated, their two-step application involved an additional cost and entails environmental problems because in many cases chromium and other heavy metals are used [7]. Therefore many efforts in the field of metal protection are focused on the development of new materials to both simplify the protection system and be more environmentally friendly than traditional anticorrosion procedures.

Zinc molybdenum phosphate (ZMP) pigment has been proposed as an excellent alternative to toxic inhibitive pigments because of equal or superior anticorrosive behaviour to chromates and better than zinc phosphate [8–10]. Certainly, zinc phosphate pigment has been strongly criticized by some coatings manufacturers for not providing the corrosion resistance required by standard specifications [11], so the development of new generations of zinc phosphate pigment with enhanced anticorrosive properties has become a necessity. ZMP 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 [12,13].

In another attempt to find environmentally safer alternatives to traditional methods in the field of corrosion control of metals, organosilane technology emerged in the last decades as a coupling agent substitute to replace chromate conversion coatings [14–17]. Nowadays continuous research on these advanced materials has led to new and different protection systems designs. Zhang et al. studied the direct incorporation of silane monomers into epoxy coatings [18]. Van Ooij group reported an improvement by incorporating silanes directly on a polyurethane resin system to obtain a 'superprimer' with outstanding adhesion and corrosion protection properties [19]. Further advances were also proposed by other authors consisting of the combination of montmorillonite nanoparticles or rare earths in silane sol–gel coating to enhance barrier properties and to achieve higher thickness and densification

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Table 1
Composition in weight (%) of the formulated coatings.

Nomenclature	Ref.	10 ZMP	2.5 OSP	1.0 Comb	2.5 Comb	3.5 Comb	4.5 Comb
Polyester resin	57.7	57.7	57.7	57.7	57.7	57.7	57.7
Crosslinking agent	3.3	3.3	3.3	3.3	3.3	3.3	3.3
TiO_2	30.0	24.7	30.0	23.7	22.2	21.2	20.2
Barite	4.7	0.0	2.2	0.0	0.0	0.0	0.0
Flow ag.	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Levelling ag.	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Degassing ag.	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Pol. wax	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Tef. wax	0.2	0.2	0.2	0.2	0.2	0.2	0.2
ZMP pigment	0.0	10.0	0.0	10.0	10.0	10.0	10.0
OSP	0.0	0.0	2.5	1.0	2.5	3.5	4.5

[16,20–22]. Other recent studies report the development of hybrid coatings based on a silane functionalized epoxy resin to improve corrosion resistance [23].

In our recent investigation organo-modified silica particles with silanes were directly incorporated in different contents as an integral additive in a polyester powder monolayer coating to assess adhesion properties on galvanized steel without pretreatment [24]. The results determined the optimum concentration in 2.5 wt% due to the improvement in the adhesion and electrochemical properties of the coatings. In a further investigation, the optimum concentration of ZMP in the same polyester coatings applied on galvanized steel was also determined by means of electrochemical techniques [25]. The enhancement of anticorrosion properties when ZMP is added was attributed to both the improvement of barrier properties and the inhibitive action of the pigment.

In this study, the organo-modified silica particles (OSP) and zinc molybdenum phosphate pigment (ZMP) were simultaneously incorporated in a polyester system with the aim to combine the effects achieved when they were separately added to monolayer powder coatings in previous works. First, an optimum concentration of the combined system was determined by electrochemical, adhesion and salt fog spray tests. Finally, an additional electrochemical study was performed to investigate the possible existence of synergistic effect between the OSP and ZMP formulations.

2. Experimental

2.1. Materials

The coatings were developed from a saturated carboxylated polyester resin of low molecular weight (Reafree 8585 from Cray Valley Iberica, S.A.) to combine with a hydroxyalkylamide crosslinker (Primid-XL 552 from EMS-GRILTECH). Inorganic fillers and other additives used were titanium dioxide (Kronos 1171), barite (R-2 from Miber Minerales Roset), a flow agent (Additol from Cytec-Liquid Coatings Resins & Additives), a levelling agent (Cray-Vallac-PC from Cray-Valley Ibérica), a degassing agent (benzoin from DSM Special Products), a surface hardener (Licowax PE 520) and a teflon wax (Ceridust 9610F from Clariant).

ZMP pigment used in this work is based on zinc phosphate and zinc molybdate conditioned with an organic titanate in the surface (Nubiorox 106 supplied by Nubiola). The ZMP pigment was incorporated in a fixed content of 10% of the total formulation. The silane was a commercial additive consisting of trifunctional organosilane (alkyl-triethoxysilane) grafted to the surface of amorphous silica particles (reference ESQUIM DL-8302/7, supplied by Esquim S.A., Barcelona). Different concentrations of the additive (OSP) were incorporated into the formulations replacing the inorganic filler (TiO_2) except in the 2.5 OSP formulation that replaces the barite.

Table 1 summarizes the compositions of the samples studied in this work.

2.2. Substrate/sample preparation

Samples were premixed and hand-shacked before extruding in a single screw extruder (Haake Rheomex 254). The extrusion temperature was set to 100 °C, the residence time was approximately 1 min and the torque generated was 20 Nm. After that, the materials were ground in a Moulinex Mill MX843 and sieved through a mesh size of 140 μm. The five different powder coatings were deposited over galvanized steel substrates, 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. Scanning electron microscopy (SEM)

The morphology of the coatings was observed by scanning electron microscopy (LEO 440i SEM) with a digital image acquisition. Samples studied were obtained from coatings detached from the substrates after cryofracturing. The back-scattered and secondary electron images were complemented by appropriate chemical information from energy dispersive X-ray analysis (EDS) acquired as point and/or line scans.

2.3.2. Mechanical tests

2.3.2.1. Impact resistance test. Impact test was performed in accordance to ISO 6272-2:2002. The operation principle of the impact tester is a 1 kg dart mass that drops down from different heights up to 1 m and impacts the back of the painted panel to result in its rapid deformation. Coating resistance to impact may be determined from observing whether the film cracked or peeled off.

2.3.2.2. Cross-cut test. Paint adhesion was investigated in accordance to ISO 2409:2007, using a cutter with six blades that makes 2 mm square lattice cuts wide on the coating film. The cuts were made through the coating film with steady motion using just sufficient pressure on the knife. The samples were visually evaluated to detect any delamination of the film. The classification of the delaminated film was based on the criteria and standard stipulated in the ISO 2409:2007.

2.3.2.3. Adhesion test. Adhesion test was performed in accordance to ISO 4587:2003. Specimen preparation procedure for adhesion test consists on the deposition of the coatings with different adhesion promoter contents between two rectangular and degreased steel substrates, as was prepared in previous works [26], and cured at 180 °C for 30 min. After the curing process, the samples were tested using an Instron Universal Test Machine 4469 H 1907 with a load cell of 50 kN at a crosshead speed of 1 mm/min. Data of load and

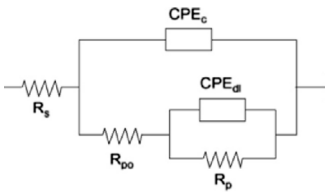

Fig. 1. Equivalent circuit used to model EIS and ACET impedance data where passive parameters (R_s = electrolyte resistance, R_{po} = pore resistance, CPE_c = constant phase element of the coating capacitance, R_p = polarization resistance CPE_{dl} = constant phase element of the double layer capacitance)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

deformation was registered. Shear stress was obtained dividing the shear force by the cross-sectional area. Fracture modes were evaluated by means of an optical microscope. Five specimens of each formulation were prepared and tested.

2.3.3. Electrochemical impedance spectroscopy (EIS)

The effect of adding the OSP on the anticorrosive properties of the formulated powder coatings was evaluated by EIS tests. A three-electrode system was used, in which the sample without coating acts as the working electrode, an Ag/AgCl electrode is the reference electrode and a Pt electrode is the counter-electrode. The area of the painted metal surface was defined by a cylindrical open PVC tube (9.62 cm^2 delimited circular area) that contained an aqueous electrolyte solution (3.5 wt% NaCl). EIS measurements were performed on a ZAHNER-IM6ex electrochemical workstation. A sinusoidal AC perturbation of 10 mV amplitude coupled with the open circuit potential was applied to the metal/coating system inside a Faraday cage in order to minimize external interference with the system. The EIS tests were performed in the frequency range from 100 kHz to 10 mHz. All measurements were conducted at room temperature (≈25 °C). The experimental electrochemical data were collected and analyzed using the Thales software developed by ZAHNER and the Medco Assay commercial software developed by Medco S.L., respectively.

An equivalent circuit model most widely used by many authors to analyze organic paint systems to protect metals [27–31], shown in Fig. 1, was employed to analyze the EIS spectra. The circuit consisted of a working electrode (metal substrate), a reference electrode, electrolyte resistance R_S, coating pore resistance R_{po}, coating capacitance C_c, polarization 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 [32]. 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 polarization 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 [33–35]. To obtain more precise fitting results, constant phase elements CPE (represented here as C) replaced capacitive elements in the equivalent circuit, giving the software values of capacitance in units of s^n/Ω together with a parameter known as "n" instead of s/Ω or F units. Hsu and Mansfeld [36] 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 varies 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.

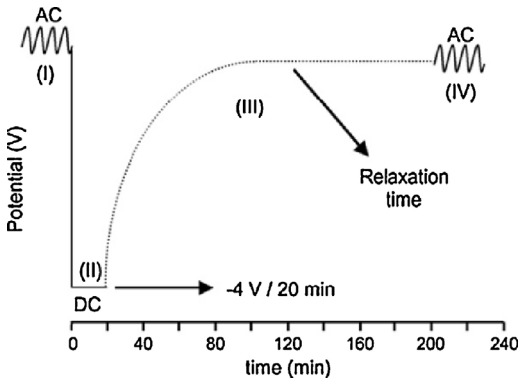

Fig. 2. ACET test schematic figure versus time.

2.3.4. Accelerated cyclic electrochemical technique (ACET)

The ACET procedure comprises a combination of cathodic polarization (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 stabilized 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 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.

2.3.5. 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. Powder coatings morphological characterization

Fig. 3a and b shows the 4.5 comb thermoset cross section at 500× and 1000× magnification obtained by SEM in backscattered electron mode, respectively. All formulated coatings showed the heterogeneous structure typical of organic powder coatings that is shown in the microscopic image and significant differences were not detected between them. Two predominant phases are visually identified in Fig. 3a, a darkest phase that can be attributed to polymeric matrix and a clearest one that corresponds to zinc phosphate molybdate (ZMP) particles forming aggregates, as it was revealed by the presence of C, O, P, Ti and Zn in EDS analysis performed in one of them (Fig. 3b and c).

Moreover, when the OSP is added to the formulated systems in different contents, single particles cannot be detected visually in

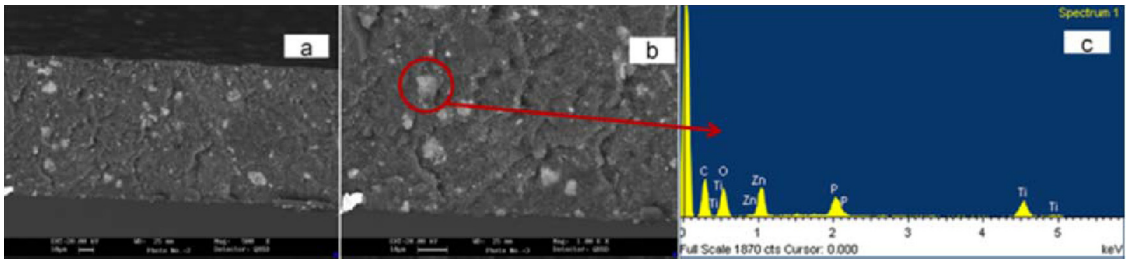

Fig. 3. SEM pictures at (a) 500× magnifications and (b) 1000× magnification for the 4.5 comb coatings detached from the substrate. (c) EDS analysis of an aggregate.

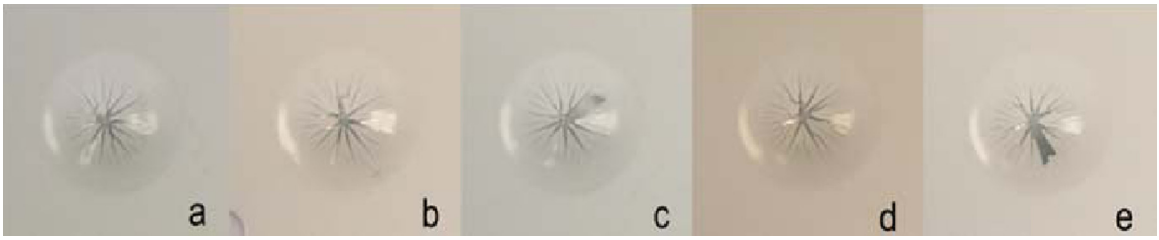

Fig. 4. Impact resistance pictures of the formulated coatings: (a) 10 ZMP, (b) 1.0 comb, (c) 2.5 comb, (d) 3.5 comb and (e) 4.5 comb.

the SEM-pictures of any of the coatings indicating a high rate of dispersion as well.

3.2. Mechanical and adhesion properties of the powder coatings

Fig. 4 shows the pictures of the five samples after the impact test from a height of 100 cm with a dart of 1 kg. It can be observed a similar behaviour between all systems studied, regardless of the OSP content. All samples presented slight radial cracking and degree of delamination in the area impacted. According to these results, variation in fracture resistance or tenacity by using different contents of the OSP is not detected in the coatings. In the cross-cut test, adhesion measured resulted high in all samples because the edges of the cuts were completely smooth without detachment in the intersections of the lattice, even when they were inspected under a magnifier.

Fig. 5 shows the breaking shear stress (σ_{shear}) needed to pull apart two pieces of galvanized steel glued together by the four combined systems formulated in the adhesion test. The results shown indicate that the σ_{shear} was slightly decreased from the 10 ZMP coating when 1.0 wt% of OSP is added to the formulation (1.0 comb), although conclusions of this result cannot be extracted because the obtained standard deviation for the 10 ZMP as a consequence of various factors involved in the performance of the test [24]. However, maximum shear stress seems to be stable or to increase proportionally with the OSP content for higher percentages, indicating that one of both of these phenomena are occurred: the OSP incorporation could reinforce the polymeric matrix or the adhesion to the substrate has been increased. Considering that, on the one hand, σ_{shear} is just a measure of the adhesion when failure occurs at the interface between the organic coating and the substrate (adhesive failure) and, on the other hand all samples exhibited a mixed-mode failure (adhesive and cohesive failure), the increased shear stress cannot be attributed to a single phenomenon.

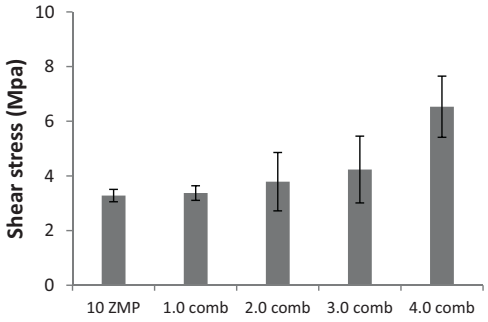

Fig. 5. Breaking shear stress of the coatings formulated in adhesion test.

3.3. Electrochemical characterization

Fig. 6 shows the Bode plot (impedance modulus versus frequency) for 840 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 frequencies measurements). From the impedance results, it can be observed that the sample with 1.0 comb offers the best results (highest impedance modulus and capacitive behaviour), whereas those samples with higher contents show lower impedance modulus, more resistive behaviour, which means that are degraded at a greater or lesser extent.

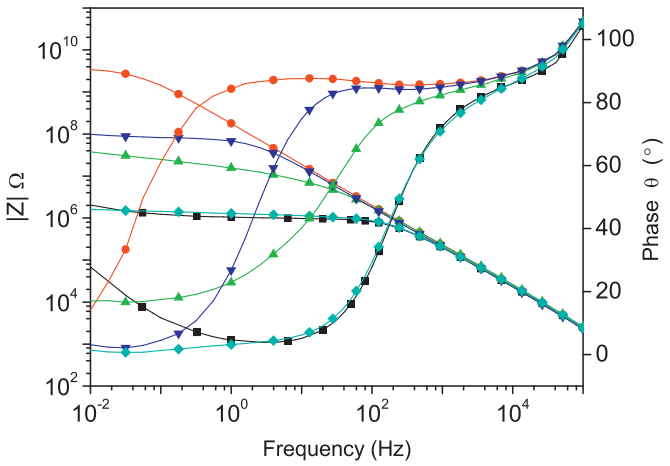

Fig. 6. Bode plot (impedance modulus and phase angle versus frequency) for polyester coatings: 10% ZMP (■), 1.0 comb (●), 2.5 comb (▲), 3.5 comb (▼) and 4.5 comb (◆); applied on galvanized steel after 840 h exposure to electrolyte (deionised water with 3.5% NaCl by weight). EIS test.

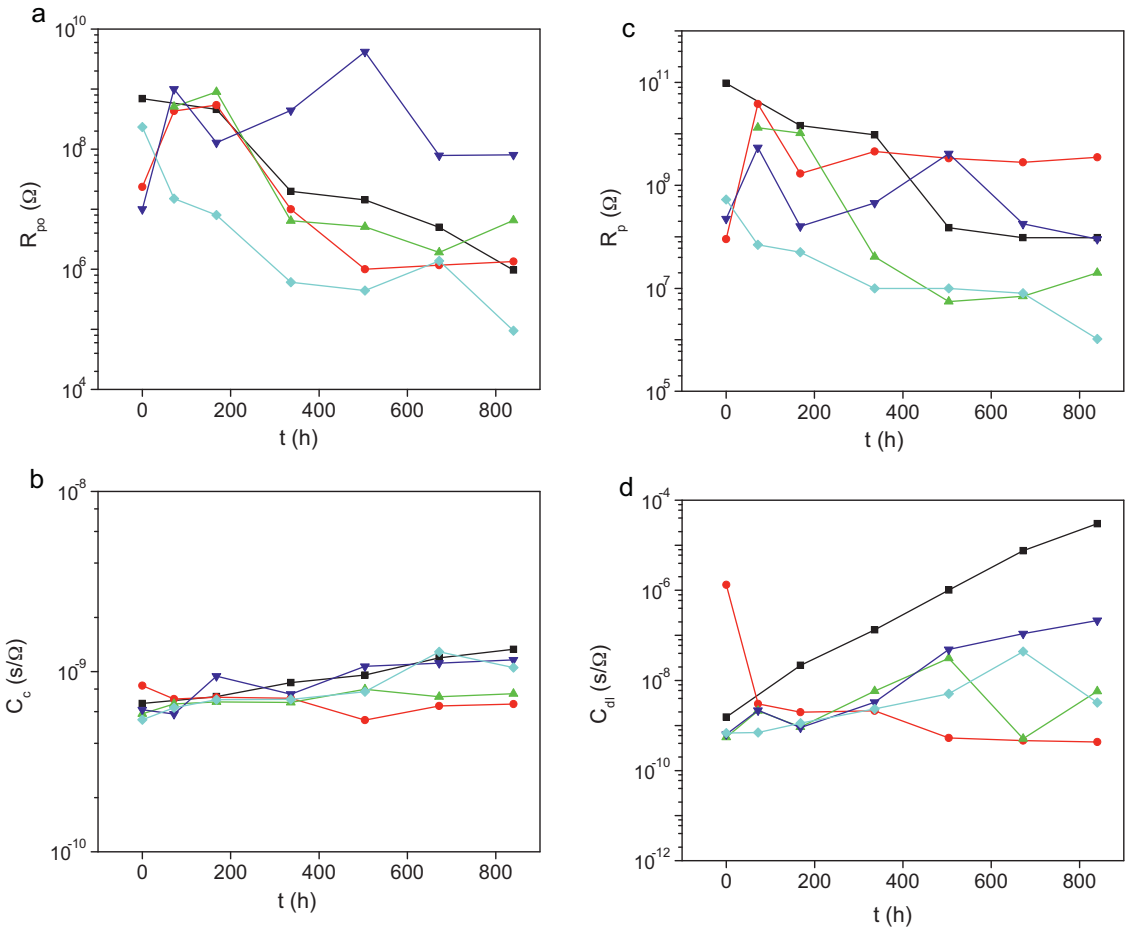

Fig. 7. Evolution of: (a) pore resistance R_{po}; (b) coating capacitance C_c; (c) polarization resistance R_p; (d) double layer capacitance C_{dl} vs. exposure time for polyester coatings: 10% ZMP (■), 1.0 comb (●), 2.5 comb (▲), 3.5 comb (▼) and 4.5 comb (◆); applied on galvanized steel after 840 h exposure to electrolyte (deionised water with 3.5% NaCl by weight). EIS test.

Results from the EIS test have been modelled with an electric equivalent circuit (Fig. 1) and its characteristic parameters determined (Fig. 7a–d). The evolution with immersion time of the different parameters shows a decrease in R_{po} values for all the samples in time of contact to electrolyte that is an indicative of pore formation due to the coatings degradation, although the trend of the coating capacitance with OSP concentration is not very clear. In contrast to these results, C_c values demonstrate a slight decrease in water uptake for combined systems with respect to the 10 ZMP coating. The sample with lower content of OSP (1.0 comb) presents a quite inactive interphase with high values of R_p and lowest of C_{dl} for all testing time, but for highest contents the anticorrosion properties are aggravated because the interphases are more active (R_p decreases with non-stable evolution and C_{dl} presents fluctuations).

Fig. 8 shows the Bode plot of the five coatings after the fourth polarization in the ACET test. It can be noted that degradation achieved in this test is lower than that achieved in 840 h of contact in EIS test because coatings present high impedance modulus and capacity response in almost all frequencies and significant variations are not found between them.

In order to assess the ACET results in all cycles of polarisations, experimental data of impedance were also modelled with the equivalent circuit of Fig. 1.

Fig. 9a–d shows the evolution of the characteristic parameters of the equivalent circuit presented versus the number of cathodic polarisations applied. From these plots it can be concluded that incorporating OSP to the ZMP system involved, in almost all concentrations, the decrease of the pore resistance and led to a less active interphases between metal and coatings (with higher values of R_p). Although there are no significant differences in the water content in the coatings, the pore resistance and polarization resistance is lower by one or two orders of magnitude, the interface is

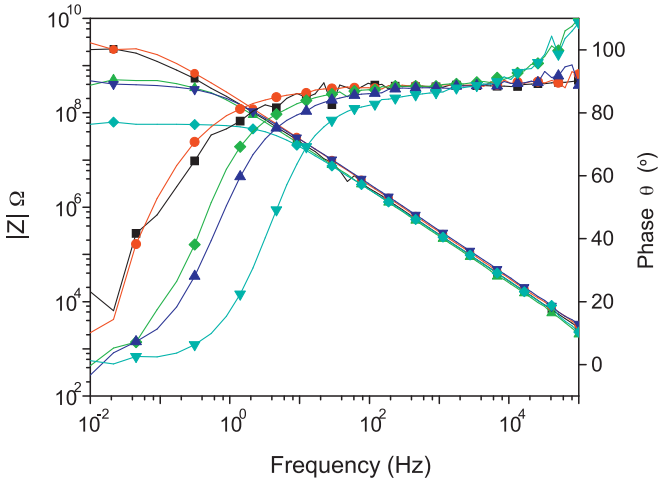

Fig. 8. Bode plot (impedance modulus and phase angle versus frequency) for polyester coatings: 10% ZMP (■), 1.0 comb (●), 2.5 comb (▲), 3.5 comb (▼) and 4.5 comb (◆); applied on galvanized steel after 4 cycles of cathodic polarisations. ACET test.

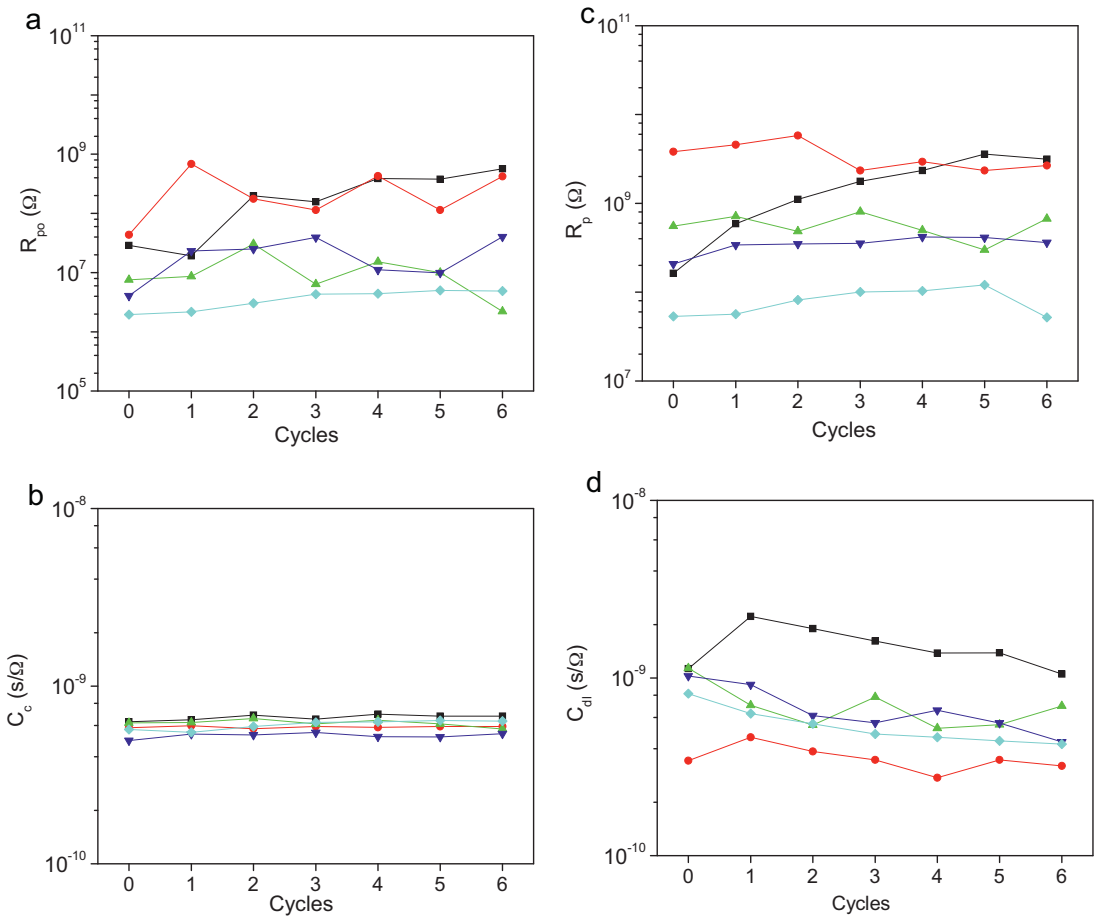

Fig. 9. Evolution of (a) pore resistance R_{po}; (b) coating capacitance C_c; (c) polarization resistance R_p; (d) double layer capacitance C_{dl} vs. the number of cycles for polyester coatings: 10% ZMP (■), 1.0 comb (●), 2.5 comb (▲), 3.5 comb (▼) and 4.5 comb (◆); applied on galvanized steel in the ACET test.

much more active (with lower values of R_p) and the delamination process is intensified in all cycles of polarization for coatings with 2.5 wt% content or higher with respect to the 10% ZMP coatings. Nevertheless, a superior anticorrosive performance of 1.0 comb system could be expected because present high and very stable R_p values for all cycles of polarisations and without coating delamination process (C_{dl} remains stable in lowest values for all cycles of the test). These results indicate, on the one hand, the existence of two opposite effects when OSP are introduced: the deterioration of barrier properties of the coatings and the stabilization of substrate-coating interphase, and on the other that the stabilization of the interphase component seems to compensate the slight increment of permeability when the additive is incorporated to coating in low quantities.

Finally, the evolution of the modelled parameters obtained in both electrochemical techniques is simultaneously analyzed by eliminating the time variable in EIS test and polarisations number in the case of the ACET test in order to analyze readily the properties of the five coatings formulated and to find the optimum content. Fig. 10a–d shows the equivalent circuit passive parameters at conditions in which degradation of coating is produced and the ZMP and OSP action can be subjected to evaluation, e.g. after 840 h of exposure to electrolyte for the EIS test and after 4 cycles of cathodic polarisations in the ACET test. It can be seen that when the OSP has been added to a system that contains 10% ZMP barrier properties are modified when its concentration exceeds 1.0 wt% (1.0 comb system) although this effect is not reflected in the coating capacitance values obtained (Fig. 10a and b). However, the optimal combined system can be easily established for 1.0 wt% of OSP by observing the R_p and C_{dl} evolutions (Fig. 10a and b). Enhanced performance of this combined formulation is possibly due to the presence of both pigment that increases the inhibitive corrosion properties [25] and OSP in low contents to allow the adhesion to the substrate but without greatly altering barrier properties or permeability of the coating [24].

Electrochemical results strengthen the idea that OSP incorporation to coatings can lead to an embrittlement of their microstructure influencing on their barrier properties but in turn improving polarization resistance and avoiding delamination as it was found in some samples. This interface stabilization could be correlated with the results obtained in the adhesion test shown in Fig. 5 (although they cannot be completely attributed to an adhesion enhancement due to the mix failure mode of the samples, as was mentioned above). However, overall anticorrosive performance is strongly reduced when OSP content is superior to 1.0 wt% indicating a maximum content, above which microstructure of the coatings is possibly altered allowing the electrolyte and the different species present in the solution pass through the coating and reach the interface to initiate the corrosion processes.

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 to detect the OSP effect in barrier properties of the sample while in ACET test it is not favoured due to the limited immersion time in comparison with EIS procedure. Immersion time effect in coating degradation process can be

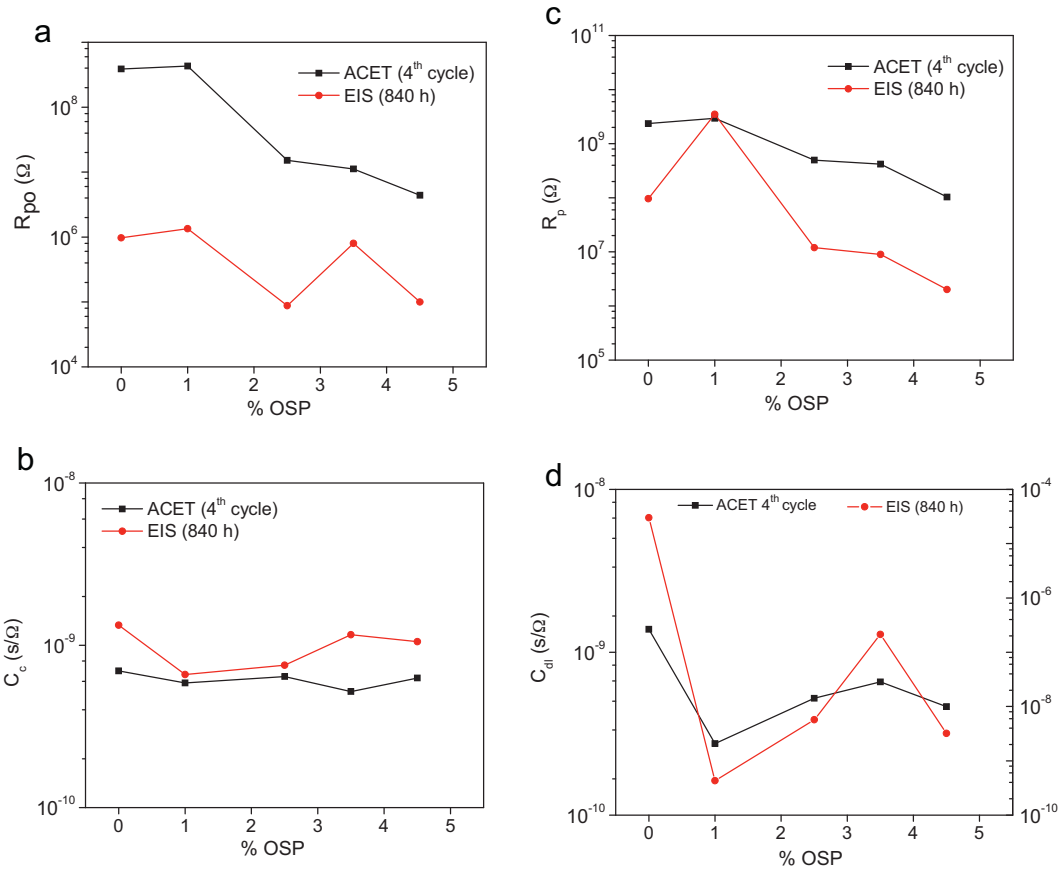

Fig. 10. Evolution of: (a) pore resistance R_{po}, (b) coating capacitance C_c, (c) polarization resistance R_p and (d) double layer capacitance (C_{dl}) versus the OSP content in coatings with 10% of ZMP in the ACET test-4 cycles (■) and EIS-840 h (●).

also detected in C_{dl} values obtained (Fig. 10c), where the action of the additives in the substrate-coating interphase are more intensified in the EIS test than in the ACET test (different scales on the *y*-axis are used to show correctly the C_{dl} fluctuations).

3.4. Salt fog spray test

Table 2 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 ZMP coating without OSP is the best formulation and that the higher concentration of additive the properties conferred to the samples are worsened. A similar tendency was observed in electrochemical tests except to the 1.0 comb coating, therefore the correlation is not as remarkable as it was found in our previous work [25]. This fact can be attributed to the different mechanisms of testing between the salt fog spray and electrochemical tests [37,38]. 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 enhanced because of direct contact between the electrolyte and the pigment.

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

Coatings	Time to failure (h)
10 ZMP	648
1.0 Comb	504
2.5 Comb	504
3.5 Comb	504
4.5 Comb	312

3.5. Study of synergistic effect

In order to evaluate the possible existence of a synergistic effect between the corrosion inhibitor (ZMP) and the organo-modified silica particles (OSP) an electrochemical comparative study was performed. Fig. 11 presents the modelled parameters evolution with polarization cycles applied in the ACET test for the combined coating that has offered superior electrochemical performance (1.0 comb) in this investigation and for optimized individual systems that are obtained in our previous works, i.e. 2.5 OSP and 10 ZMP), all of them compared with a reference coating without ZMP and OSP in its composition. It can be seen that separate incorporation of the two additives results in improved properties of the reference coating, being the ZMP inclusion the effect that raise more significantly R_{po} and R_p values. Moreover, if these systems are compared with optimum combined sample (1.0 comb) it can be clearly observed an anticorrosion properties improvement with similar values of R_{po} to the 10 ZMP coating and R_p and double layer capacitance lower and more stable that the rest of the formulations studied. It is stressed that high performance of ZMP coating was ascribed to both barrier properties and inhibitory action enhancement. Hence, OSP incorporation needs to be in low percentages to a formulation containing the ZMP inhibitor to achieve a synergistic effect between the two additives.

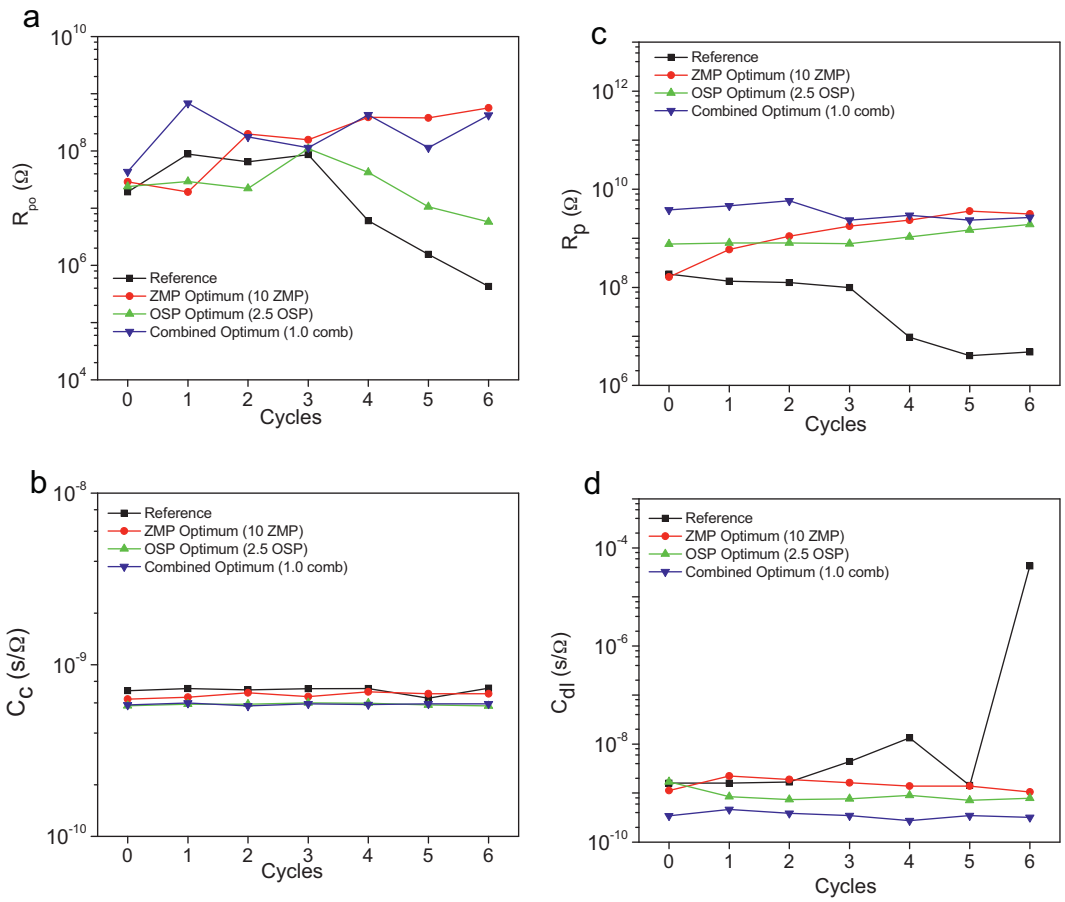

Fig. 11. Evolution of: (a) pore resistance R_{po}; (b) coating capacitance C_c; (c) polarization resistance R_p; (d) double layer capacitance C_{dl} vs. the number of cycles for polyester coatings. Evaluation of synergistic effect.

4. Conclusions

Combined powder coating formulations with different contents of OSP (0, 1, 2.5, 3.5 and 4.5%) and containing all of them 10 wt% zinc molybdenum phosphate pigment (ZMP) were studied. The results show that all samples with OSP lead to an improvement in the adhesion properties determined by adhesion test. Anticorrosion performance was improved when 1.0% additive was incorporated but showing decrease in properties when this content was exceeded and then constituting an optimum combined coating. The deterioration of barrier properties of the monolayer coatings and the stabilization of substrate-coating interphase are probably the two opposite effects of OSP addition that lead to a reduction of anticorrosive properties for higher contents. Finally, an additional accelerated electrochemical test showed that this coating that combines both additives offers best results than those formulated with the additives separately, revealing a synergistic effect between them.

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