Study of the anticorrosive behaviour of epoxy binders containing non-toxic inorganic corrosion inhibitor pigments

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Abstract

The anticorrosive performance of epoxy coatings pigmented with non-toxic corrosion inhibitors pigments was investigated in this work. The coatings used contained the following pigments: zinc phosphate (ZP), zinc phosphomolybdate (ZPM) and zinc calcium phosphomolybdate (ZCPM). For comparative studies epoxy coatings with the following compositions were made up: one only with filler (CRG); one without pigments, varnish (VR) and other with zinc chromate (ZC) pigment. The corrosion inhibitor performance of the coatings was evaluated by immersion tests in 0.01 mol L^{-1} NaCl aqueous solutions and accelerated tests in a salt spray chamber. The corrosion inhibitor performance of the samples was monitored using open-circuit potential (E_{oc}) measurements and electrochemical impedance spectroscopy (EIS) technique. Complementary tests were carried out using water vapour permeability of free-standing films and thermogravimetric (TG) analysis. The permeability test showed that the addition of the studied pigments did not modify the barrier properties of the free-films in comparison that pigmented with chromate. Thermal analysis indicated that the addition of the pigments improved the thermal stability of the coatings and it suggested a resin/pigment interaction. The total immersion tests and salt spray tests demonstrated that the barrier properties of the coatings pigmented with the inhibitors were not degrading as much as that pigmented with ZC. Therefore, all the three pigments could replace ZC as an anticorrosive pigment in similar conditions to those described here. The best corrosion inhibitor performance in the total immersion test was presented by the ZPM and ZCPM coatings while in the salt spray test the corrosion inhibitor performance of all the three pigmented coatings was similar, suggesting that only in the less aggressive test is possible to detect any difference between the coatings with the non-toxic pigments.
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1. Introduction

It is widely known that organic coatings have many technical and economic advantages for the protection of metal materials against corrosion. The protection mechanism is associated to the barrier effects added to the action of anticorrosive pigments present in the coating. The most traditional anticorrosive pigment is zinc chromate, because the efficiency of this compound for corrosion protection of steel has been long proven. However, this pigment is toxic, contributing to environmental contamination, allied to the fact that it represents a risk to human health, particularly during the production process and paint removal operations [1,2]. Additionally, regulations for the protection of the environment and human health have resulted in efforts to develop more environmentally acceptable coatings. This has stimulated, during the last decade, research to develop a new generation of anticorrosive pigments, called "environmentally friendly", which have been proposed to replace the toxic anticorrosive pigments in paint formulations [3].

Zinc phosphate (ZP) is the most commercially successful non-toxic inhibitive pigment used in paint formulations. Furthermore, the use of phosphates does not represent an excessive cost and their application is even easier than other proposed alternatives, such as those pointed out in Ref. [4]. The corrosion inhibitor performance of primers pigmented with ZP has been studied by accelerated tests and field exposure to marine and industrial environments, but their anticorrosive action is not yet fully understood. In accelerated tests, the anticorrosive performance of these coatings was lower than when a long outdoor exposure test was employed. This fact was related by the authors to the low solubility of ZP and its coarse crystalline structure [5–9].

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In order to improve the protective action of the "environmentally acceptable" coatings, a second generation has been developed aiming to combine, in a synergistic manner, the corrosion inhibition properties of phosphates and molybdates, called phosphomolybdate pigments. However, there is little information in the literature about the anticorrosive performance of coatings pigmented with these pigments [1,10–12].

It is necessary to point out here that, despite the literature reports consider the phosphate-based pigments to be "environmentally acceptable", ZP is classified as "not hazardous" for human health under the United States' regulations; however, it is considered "very toxic in an aquatic environment", according to the regulations of the United States and the European Union. Thus, ZP-based pigments cannot necessarily be qualified as "environmentally friendly" products.

Thus, the aim of this work is to evaluate the anticorrosive performance of organic epoxy coatings pigmented with the following non-toxic pigments: ZP, zinc phosphomolybdate (ZPM) and zinc calcium phosphomolybdate (ZCPM). The analysis is based on immersion tests in $0.01\,mol\,L^{-1}$ NaCl aqueous solutions and accelerated tests in a salt spray chamber. Similar studies were also carried out with epoxy coatings pigmented zinc chromate (ZC), for comparison. The corrosion inhibitor performance of the samples was monitored by open-circuit potential (E_{oc}) measurements and electrochemical impedance spectroscopy (EIS) technique. Complementary tests were carried out using water vapour permeability of free-standing films and thermogravimetric (TG) analysis.

2. Experimental

The coatings were especially formulated for this work using diglycidyl ether of bisphenol A epoxy resin as binder and the following commercial pigments: zinc potassium chromate (ZC), tetra-hydrate ZP, ZPM and ZCPM, supplied by Moly-White Pigments Group. Also the following compositions were made up: only with filler (CRG) without pigments, and with varnish (VR).

In order to compare the behaviour of all the studied pigments, the coatings were pigmented with 12% (w/w) of active pigment and the ratio of the pigment volume concentration (PVC) and critical pigment volume concentration (CPVC) was between

0.70 and 0.78. Features of the five coatings studied are given in Table 1.

SAE 1010 steel panels (100 mm × 150 mm and 80 mm × 90 mm) were used as substrates. The metallic surfaces were previously sandblasted to white metal and degreased with toluene. The coatings were applied with an air spray gun. The total primer thickness for each system was about 100 μm. Selected samples were intentionally scribed aiming to evaluate the corrosion beneath the film and, consequently, to assess the effectiveness of the active pigments in impeding the advance of corrosion beyond the scribe. Free-standing films were also prepared under the same conditions as the metal-coated samples.

2.1. Corrosion tests

In order to evaluate the anticorrosive performance of the coatings being studied, two sets of painted panels were prepared. One with a horizontal scribe, made with a carbide lath tool to scratch through the paint to expose the bare uncoated substrate and the other set without a scribe.

Scratched painted panels were tested in a salt spray chamber according to ASTM B117 Standard Practice. After each 250 h, the panels were withdrawn from the chamber, immersed in 0.01 M NaCl and characterized by EIS technique at E_{oc}, at room temperature ($\cong 27\,°C$). The electrochemical impedance measurements were carried out in the non-scratched zone of the painted panels. After this stage, the panels were washed with water Milli-Q and then returned to the chamber. Another set of scratched samples was immersed in 0.01 M NaCl to monitor the E_{oc} of the scratch zone. The EIS technique was also used to monitor the anticorrosive performance of the non-scratched coatings under total immersion in the same electrolyte.

The electrochemical cell consisted of a PVC tube glued to the surface with an exposed area of about $22\,cm^2$. The working electrode was the coated sample; a saturated calomel electrode (SCE) was used as reference electrode and a platinum grid as the counter electrode. All the impedance spectra were obtained with an Autolab PGSTAT30 controlled by the Frequency Response Analyzer software (FRA) using a frequency range between 2.5 mHz and 40 kHz and with an amplitude of the sinusoidal voltage signal of 10 mV. All impedance measurements were carried out in a Faraday cage in order to minimize external interference

Table 1
Basic description of tested paints (w/w)

Components	Chemical composition of the studied paint					
	ZPM	ZCPM	ZP	ZC	CRG	VR
Zinc phosphomolybdate	12.0	–	–	–	–	–
Zinc calcium phosphomolybdate	–	12.0	–	–	–	–
Zinc phosphate	–	–	12.0	–	–	–
Zinc chromate	–	–	–	12.0	–	–
Talc	15.4	15.4	15.4	15.4	27.0	–
Titanium dioxide	11.4	11.4	11.4	11.4	11.8	–
Aditives	3.0	3.0	3.0	3.0	3.0	–
Solvents	14.8	14.8	14.8	14.8	14.8	17.62
Epoxi resin/polyamide (4/1 ratio)	43.37	43.37	43.37	43.37	43.37	82.38
Λ (PVC/CPVC)	0.70	0.71	0.78	0.72		

on the studied system. All corrosion tests were performed in, at least, duplicate. At the end of the immersion tests, the loss of adhesion (ASTM D714) evaluation of blistering (ASTM D3359) and underfilm corrosion were evaluated.

2.2. Complementary tests

Water vapour permeability measurements were performed according to ASTM D1653 (water method). Free-standing films ($\cong 100\ \mu m$) were cut in circular plates with 6-cm diameters.

The thermal gravimetric analysis was performed with a Shimadzu TGA-5OH in a synthetic air atmosphere with a heating rate of $10\ ^\circ C\ min^{-1}$. The temperature of the experiments ranged between 25 and $200\ ^\circ C$. Small discs of about 10 mg were cut from the free films to be used in these experiments.

3. Results and discussion

The determination of the water vapour permeability through free-standing films is important to evaluate coating properties, because the presence of an aqueous solution in the coating can activate the corrosive process [13,14].

Time dependence of water vapor permeability through the free-standing film is displayed in Fig. 1. The results show that the mass loss values for all the studied films were very close, indicating that the corrosion tests were started with all the studied samples presenting similar barrier properties, which was expected since all the coatings were formulated with similar PVC/CPVC ratios. Additionally, the pigmented samples presented slightly higher permeability than VR. This is because the addition of pigment into the polymeric structure increases the voids and capillaries between the pigment particles facilitating permeation. Some research has been carried out on the relationship between pigmentation and permeability [15,16]. All authors observed that the pigment/binder interaction is very important. So, TG was performed to note possible pigment/binder interactions (Fig. 2).

Fig. 2 shows the thermal gravimetric curves obtained in an oxidative atmosphere for all the free-standing films formulated. The thermal behaviour of the primers was evaluated up to $200\ ^\circ C$, since epoxy resins are not stable at temperatures beyond this. These curves show that the mass of all the films remains approximately constant until around $60\ ^\circ C$, followed
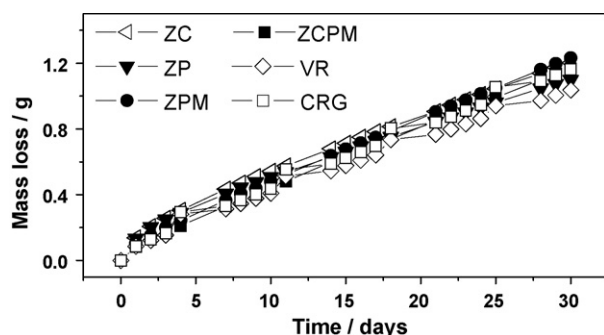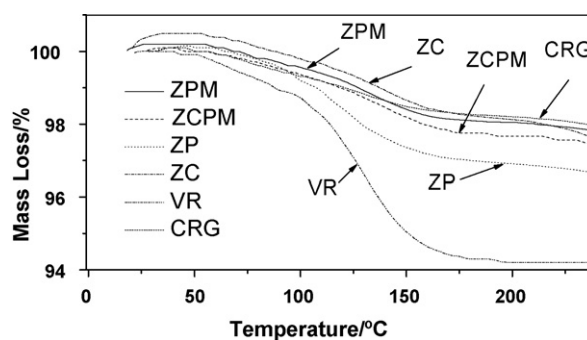

Fig. 2. Thermogravimetric curves obtained for free-standing films ZC, ZPM, ZCPM, ZP, CRG and VR.

by a decrease until the end of the test. These results are in close agreement with those previously published in the literature [17]. According to Rosu et al., the thermal degradation from $60\ ^\circ C$ is related to the breaking of the esteric links with CO_2 elimination. At higher temperatures, the decomposition of the epoxy resin continues with scission of small molecules and cyclization.

As was expected, due the absence of pigmentation, the sample with the highest mass loss was VR. Additionally, among the pigment free films the one with ZP presented the worst thermal stability; however, there was no significant difference in the thermal behaviour between the CRG, ZPM, ZCPM and ZC films. These results indicate that the addition of the pigments improves the thermal stability of the primers, suggesting a resin/pigment interaction, which can influence the painting performance as an anticorrosive coating. A possible explanation for the observed thermogravimetric behaviour of the paint pigmented with ZP is related to the thermal instability of the tetra-hydrate ZP.

Fig. 3 shows the variation of the E_{oc} of the scratched samples with immersion time in 0.01 M NaCl. According to Vasconcelos et al. [18], the E_{oc} measurements are related to the electrochemical processes taking place in the scratched zone. In this graph all samples studied presented a fast decline in the E_{oc} values in the first 5 h of immersion. After 24 h of immersion, the E_{oc} val-

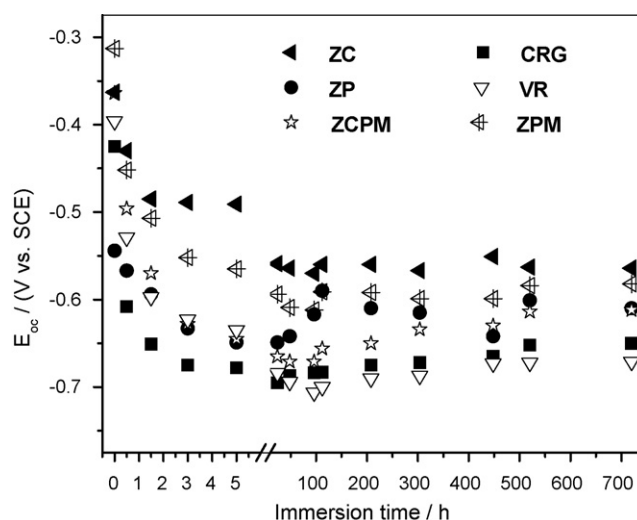Fig. 1. Water vapor permeability graphs of free-standing films according to ASTM D1653.

Fig. 3. Monitoring of the E_{oc} of scribed samples as a function of immersion time in 0.01 M NaCl aqueous solution.
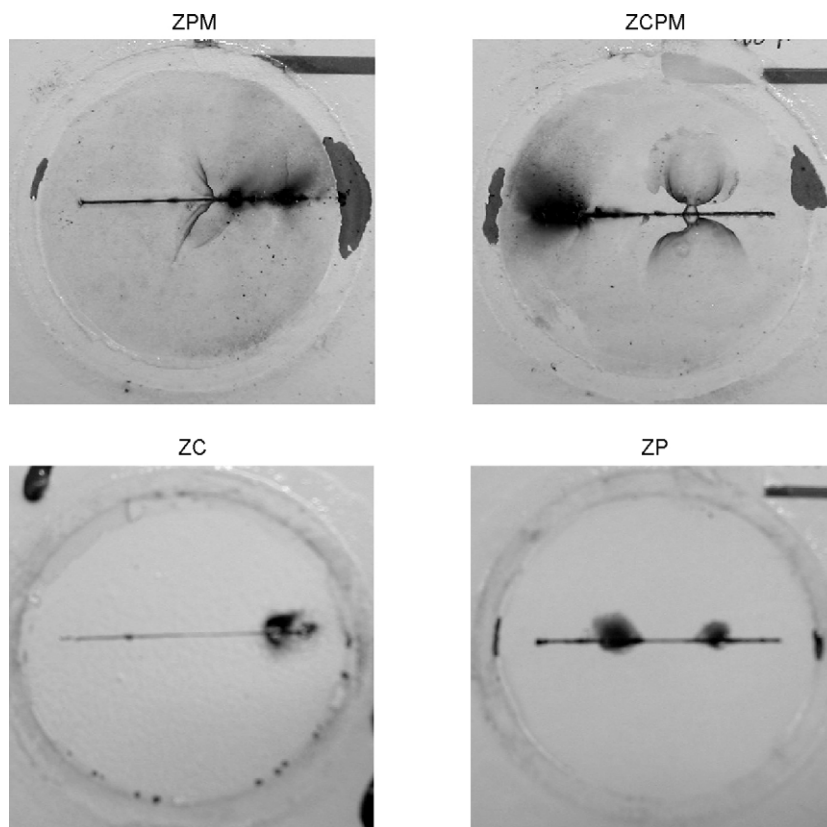
Fig. 4. Visual aspects in the scratch region of the samples after monitoring of E_{oc} with time (60 days) in 0.01 M NaCl solution.

ues of the ZC and ZPM samples reached a minimum value and remained stable until the end of the test period. On the other hand, the E_{oc} values of the ZP and ZCPM samples reached minimum values with 24 and 96 h of immersion, respectively, followed by an increase until reaching a plateau. These results suggest that all the inhibitor pigments presented a passivating effect in aqueous medium after, at least, 24 h of immersion. Similar E_{oc} behaviour presented by ZP and ZCPM samples is reported in the literature for epoxy coatings pigmented with Ca/silica in comparison to coatings pigmented with chromate [18].

Additionally, the lowest E_{oc} values were presented by the VR and CRG coatings, which were similar throughout the whole immersion test, indicating that the fillers do not have inhibiting corrosion properties. Further, the coatings pigmented with ZC and ZPM presented the highest and similar E_{oc} values, which is related to the pigments passivating effect.

The pictures shown in Fig. 4 correspond to the visual aspects of the scratched samples after monitoring of E_{oc} with time (60 days) in 0.01 M NaCl solution. After the end of the immersion test, rust was present in the scratched regions for all studied samples, however, only the VR and CRG samples showed a significant amount of blistering. The pictures of the VR and CRG samples are not shown in Fig. 4.

Fig. 5 shows the impedance diagrams of non-scratched samples tested in 0.01 M NaCl solution. For each sample, diagrams obtained at 2, 576 and 1224 h of immersion are shown. Initially ($t_{imm} < 6$ h), all the studied samples exhibited a similar capacitive behaviour that is typical for non-defective coatings [19]. With

24 h of immersion, the impedance diagram of all the samples studied presented a clearly defined semicircle. In the ZC and ZP samples, a second loop appeared at low frequency, which is associated to some degradation of the coating [18,19].

The loop in the high-frequency range is attributed to electrolytic resistance through the coating defects (R_p), characterizing the barrier properties of the coating, in parallel with the double-layer capacitance (C_{dl}) [18,19], which is usually considered to provide information about the degree of water permeation through the coating. These two values were obtained from impedance diagrams in order to monitor the modifications of the coating properties with the immersion time and the corrosion protection given by the different coatings studied. The values of R_p were determined by extrapolation of the loop at high frequencies to the real axes, while the capacitance values were calculated by $C_{dl} = (2\pi R_p f)^{-1}$, where f is the frequency of the maximum values of the high-frequency capacitive loop. The evolution of the coating resistance and coating capacitance with the immersion time are shown in Fig. 6.

At the beginning of the immersion tests, the coating resistance values (Fig. 6a) were similar for all studied coatings and they decreased during the first day of immersion, reaching a plateau at the end of the first day of immersion, except for the coating pigmented with chromate which shows a slight decrease in coating resistance throughout the whole immersion test. Additionally, the coatings pigmented with the non-toxic pigments presented higher coating resistance values in comparison with the coating pigmented with chromate. These analyses are in close agreement
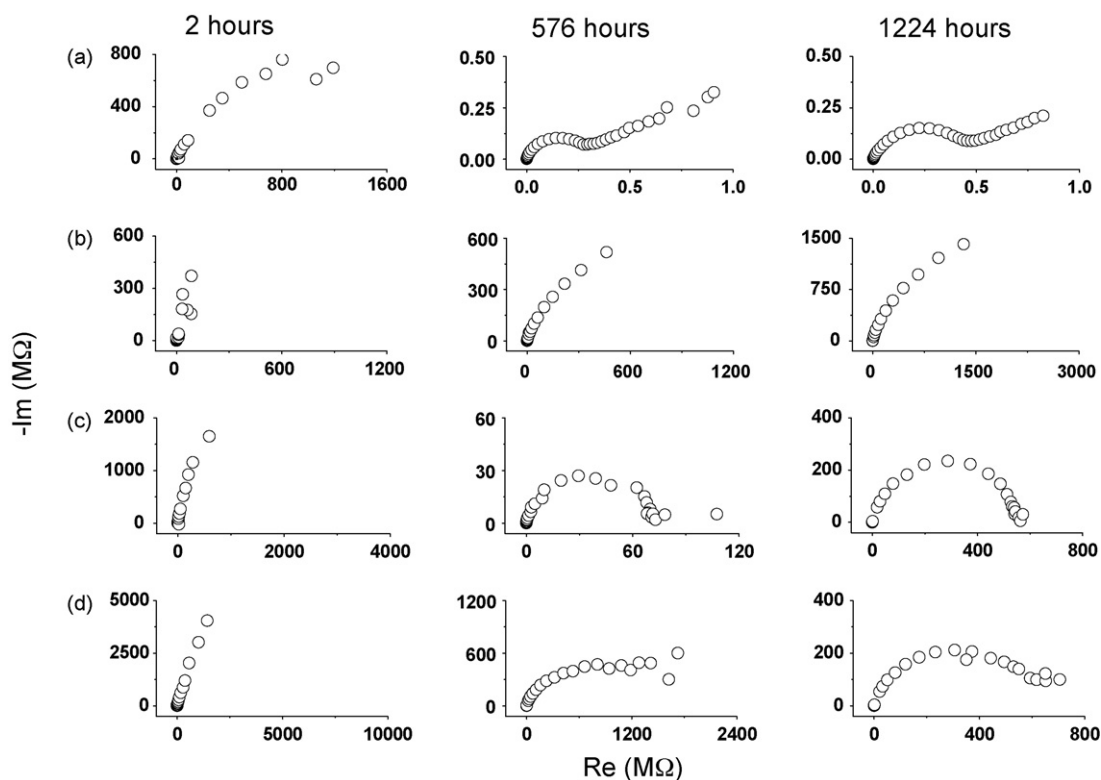
Fig. 5. Nyquist impedance diagrams obtained at E_{oc} for non-scratched ZC (a), ZPM (b), ZCPM (c), and ZP (d) samples immersed in 0.01 M NaCl aqueous solution.
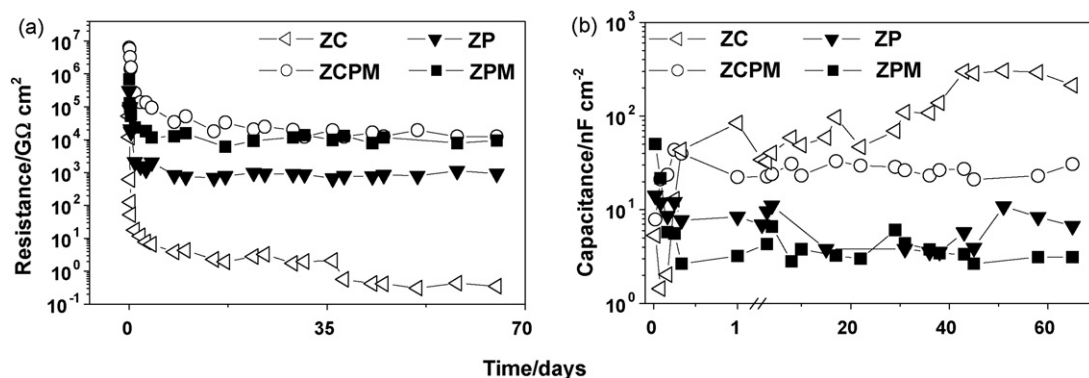

Fig. 6. (a) Resistance and (b) capacitance as a function of immersion time in 0.01 M NaCl for coatings pigmented with: ZC (◁), ZP (▼), ZCPM (○) and ZPM (■).

with results reported in the literature [19], where a comparison of the corrosion behaviour of epoxy coatings pigmented with ZP and zinc chromate is shown. According to Corfias et al. [19], the coating resistance decreases during the immersion test due to the solubility of the pigments, which leach from the coating resulting in large pores in the coating. The solubility values of the studied pigments are shown in Table 2.

As pointed out in Section 1, pigmented organic coatings posses an inhibitive corrosion function associated to their barrier properties as well to the presence of inhibitor pigments in the coating. For the ZC coatings, there is a large experimental evidence showing that organic coatings pigmented with zinc chromate presents an effective corrosion inhibitor performance, despite the decrease of its barrier property with the immersion time, due to its relative high solubility. Thus, the EIS data sug-

gest that if the pigment is relatively soluble and mechanistically effective, such as ZC, the barrier property is less important in determining the overall corrosion inhibitor performance for this coating. On the other hand, for the coating pigmented with non-toxic pigments, the EIS data show that the barrier properties is the most important factor in the corrosion inhibitor performance

Table 2
Solubility of the studied pigments

Pigment	Solubility, g ($\times 10^{-1}$ L^{-1} H$_2$O)
ZC	0.085
ZP	0.026
ZPM	0.002
ZCPM	0.001

of these coatings, since all the non-toxic pigments present low relative solubility and high-coating resistance value.

Fig. 6b shows that the capacitance of ZC and ZCPM increased during the first day of immersion, which is expected according to the literature [14], being related to the water uptake in the coatings through the defects presenting in the coating. Additionally, ZCPM reached a plateau after 1 week of immersion, which is explained as a consequence of saturation of the polymeric matrix [14], while ZC continued increasing for 70 days, which is probably related to the interfacial (double layer) contributions. In the case of the ZP and ZPM paintings, the capacitance values decreased in the first hour of immersion, attaining approximately constant values after 1 day of immersion. According to Vasconcelos et al. [18], this fact can be related to the interfacial phenomena.

The anticorrosive performance of the samples was also evaluated in a salt spray chamber (ASTM B117). The impedance diagrams of the samples taken from the salt spray chamber presented the same profile obtained in the immersion test (Fig. 5). The variation of the resistance values with exposure time in the salt spray is shown in Fig. 7. Different from the results obtained in the immersion test, the samples presented a reduction in the resistance values during the salt spray test, evidencing the aggressiveness of the conditions of the accelerated tests. The salt spray test result of the ZC sample was similar to that obtained in immersion test, while there was no significant difference between the ZCPM, ZP and ZPM samples. Concerning
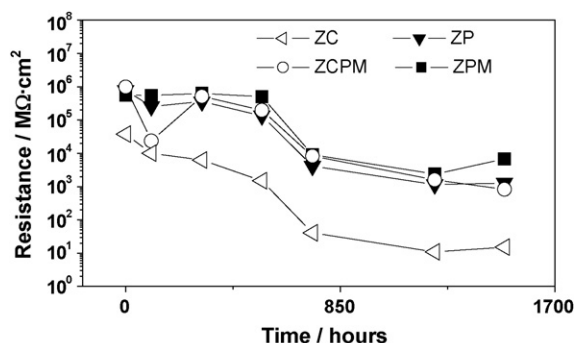

Fig. 7. Variation of resistance as a function of exposure time in salt spray.

the visual aspect of the samples, in the non-scratched region no significant change was observed. Fig. 8 shows the visual aspect in the region of the scratch after 1600 h in the salt spray chamber. As can be seen, the ZC sample had the best visual aspect. The ZP, ZCPM and ZPM samples also had satisfactory results despite the aggressiveness of the salt spray test. Towards the end of the test, a little rust in the scratch and some points of blistering in the region close to the scratch in the ZP, ZPM and ZCPM samples appeared.

Table 3 shows the blistering degree and adhesion results for the samples after immersion and salt spray exposure. This table clearly shows that the highest blistering degree and loss of adhesion was presented by the VR and CRG samples. Concerning the
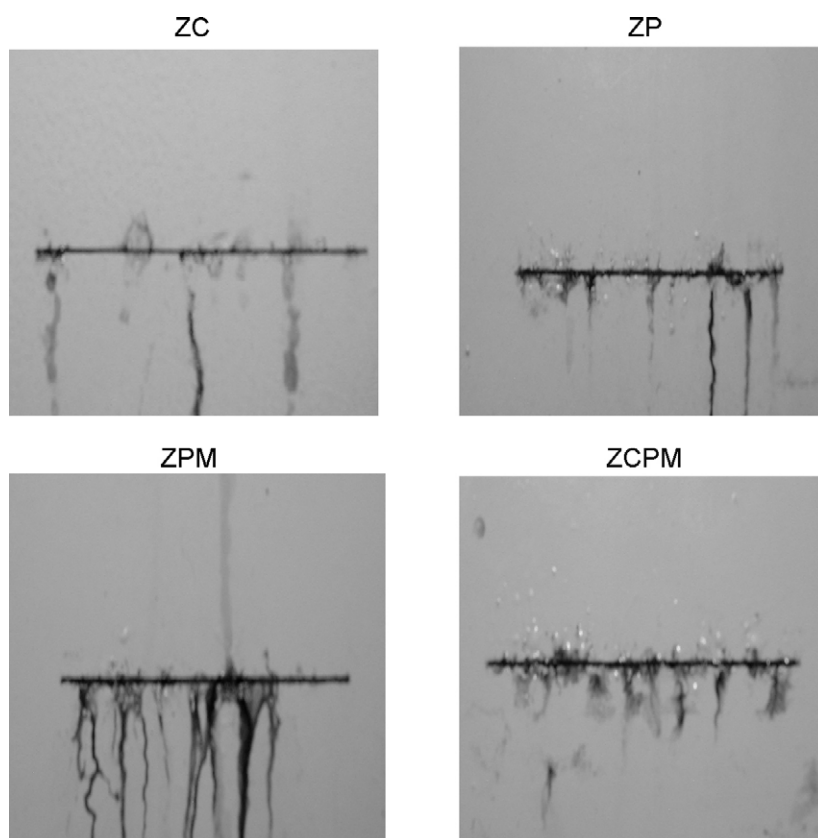

Fig. 8. Visual aspects of the scratched line samples after the 1500 h in the salt spray.

Table 3
Blistering degree (ASTM D714) and adhesion test (ASTM D3359) after the immersion and salt spray exposure

Sample	Immersion test			Salt spray test		
	Blistering evaluation	Adhesion test	Time (h)	Blistering evaluation	Adhesion test	Time (h)
ZPM	–	5B (0%)	1560	–	5B (0%)	1500
ZCPM	–	5B (0%)	1560	–	4B (5%)	1500
ZP	–	5B (0%)	1560	–	4B (5%)	1500
ZC	–	5B (0%)	1560	–	5B (0%)	1500
CRG	8F	2B (35%)	1560	8F	1B (65%)	1500
VR	4F	3B (15%)	528	6F	3B (15%)	1500

other samples, it was not possible to distinguish the behaviour between them for the immersion test, only for the salt spray test. This fact can be explained by the high aggressiveness of the salt spray test.

4. Conclusions

The permeability test showed that the addition of the studied pigments did not modify the barrier properties of the free-films in comparison that pigmented with chromate. Thermal analysis indicated that the addition of the pigments improved the thermal stability of the coatings and it suggested a resin/pigment interaction. The total immersion tests and salt spray tests demonstrated that the barrier properties of the coatings pigmented with the inhibitors were not degrade as much as that pigmented with ZC and that all the three pigments could replace ZC as an anticorrosive pigment in similar conditions to those described here. However, the best corrosion inhibitor performance in the total immersion test was presented by the ZPM and ZCPM coatings while in the salt spray test the corrosion inhibitor performance of all the three pigmented coatings was similar, suggesting that only in the less aggressive test is possible to detect any difference between the coatings with the non-toxic pigments.

References

[1] B. Del Amo, R. Romagnoli, V.F. Vetere, J. Appl. Electrochem. 29 (1999) 1401.
[2] R.B. Hayes, Cancer Causes Control 8 (1997) 371.
[3] J. Sinko, Prog. Org. Coat. 42 (2001) 267.
[4] L.S. Hernández, B. del Amo, R. Romagnoli, Anticorros. Methods Mater. 46 (1999) 198.
[5] G. Blustein, B. del Amo, R. Romagnoli, Pigment Resin Technol. 29 (2000) 100.
[6] R. Romagnoli, V.F. Vetere, Corrosion 51 (1995) 116.
[7] J.A. Burkill, J.E.O. Mayne, JOCCA 9 (1988) 273.
[8] M. Beiro, A. Collazo, M. Izquierdo, X.R. Nóvoa, C. Pérez, Prog. Org. Coat. 46 (2003) 97.
[9] M. Mahdavian, M.M. Attar, Prog. Org. Coat. 53 (2005) 191.
[10] G. Adrian, A. Bittner, Anticorros. Pigments 58 (1986) 59.
[11] C. Simpson, Chemtech 24 (1997) 40.
[12] A.O.S. Leite, W.S. Araujo, I.C.P. Margarit, A.N. Correia, P. Lima-Neto, J. Braz. Chem. Soc. 16 (2005) 756.
[13] E.P.M. van Westing, Ph.D. Thesis, Technical University Delft, Delft, The Netherlands, 1992.
[14] F. Deflorian, L. Fedrizzi, S. Rossi, P.L. Bonora, Electrochim. Acta 44 (1999) 4243.
[15] B. Liu, Y. Li, H. Lin, C. Cao, Corros. Sci. 44 (2002) 2657.
[16] N.S. Sangaj, V.C. Malshe, Prog. Org. Coat. 50 (2004) 28.
[17] D. Rosu, C.N. Cascavaf, C. Ciobanu, L. Rosu, J. Anal. Appl. Pyrolysis 72 (2004) 191.
[18] L.W. Vasconcelos, I.C.P. Margarit, O.R. Mattos, F.L. Fragata, A.S.B. Sombra, Corros. Sci. 43 (2001) 2291.
[19] C. Corfias, N. Pébère, C. Lacabanne, Corros. Sci. 41 (1999) 1539.