

High performance water-based paints with non-toxic anticorrosive pigments

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Abstract

Legal restrictions have impelled the replacement of solvent-borne resins and of toxic chromates and lead-bearing pigments in the elaboration of paints. Water-based anticorrosive paints have come a long way to improve their efficiency but their behaviour is said to be poorer than that of solvent-based paints. Nevertheless, recent advances in water-borne technologies have now resulted in improved resin systems that may be employed to produce heavy-duty coatings.

The objective of this paper is to formulate high performance water-borne paints pigmented with non-toxic phosphate inhibitors. The anticorrosive properties of the paints were evaluated by accelerated tests (salt spray and humidity cabinets) and electrochemical tests (electrochemical impedance spectroscopy, EIS). The anticorrosive properties of the pigments were also evaluated by electrochemical tests.

It was found that it is possible to formulate high performance anticorrosive paints by selecting adequate water-borne resins and ecological pigments.

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1. Introduction

The tendency towards corrosion of most strategic metals, such as steel, aluminium, zinc and galvanised steel, can be controlled in an effective manner by organic coatings. The adequate performance of organic coatings in turn depends on two main factors. It is desirable for the coating to constitute a barrier to water, ions and oxygen permeation. However, when water has passed through the coating, it is expected that corrosion inhibitors present in the coating may reach the paint/metal substrate interface and passivate the surface.

Toxicological concerns have made it necessary to replace toxic chromates and lead-bearing pigments [1]. Many attempts have been made to modify zinc phosphate because it seems that it cannot completely replace zinc chromate [2–10]. As a consequence a second generation of phosphate pigments is now available on the market [9]. The aim of this research is to employ different phosphates as inhibitors in order to check their efficiency in water-borne paints.

This paper is concerned with the protection of steel by water-borne anticorrosive paints. Water-based anticorrosive

paints have come a long way to improve their efficiency, but their behaviour is said to be poorer than that of solvent-based paints [11]. Recent advances in water-borne technologies have now resulted in resin systems that may be employed to produce high performance epoxy primers which are comparable to their solvent-borne counterparts [12].

The objective of this paper is to formulate high performance water-borne paints, pigmented with ecological inhibitors, to protect steel from corrosion. Furthermore, in order to meet environmental regulations, non-toxic phosphate inhibitors were employed. The anticorrosive properties of the paints were evaluated by accelerated tests (salt spray and humidity cabinets) and electrochemical tests (electrochemical impedance spectroscopy, EIS). The anticorrosive properties of the pigments were also evaluated by electrochemical tests.

2. Experimental

2.1. Evaluation of inhibitive properties of pigment

The inhibitive properties of the pigment were evaluated by Tafel experiments performed with SAE 1010 steel electrodes in pigment suspensions in 3% NaCl. The electrode

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was polished with no. 600 emery paper, degreased with calcium hydroxide and organic solvents, and allowed to stand in the electrolytic solution for 3 h before carrying out the electrochemical experiments. A conventional three-electrode cell was used on this occasion, with a saturated calomel reference electrode (SCE) and a platinum grid as counter electrode. The sweep amplitude was ± 250 mV, starting from the corrosion potential at a scan rate of 0.250 mV/s. Measurements were taken employing a model 273 A EG&G PAR potentiostat/galvanostat with SOFTCORR 352 software.

2.2. Paint composition, manufacture and application

The resin used was an epoxy resin based on a mix of bisphenol A and bisphenol F. The curing agent was a modified polyamide amine with a 50% solids content; it also served as emulsifier. The resin/hardener ratio was 100/120 parts by weight and their content was 78.6% by volume (v/v) of solids in the paint composition. Distilled water with pH 7 was used as solvent.

The anticorrosive pigment content employed was 5.8% (v/v) of the total solids in the paint and represented 30% (v/v) of the total pigment content, as is suggested in the literature for phosphate pigments [9,10]. To complete the pigment formula, titanium dioxide (3.5%, v/v), barium sulphate (3.7%, v/v), talc (3.4%, v/v) and mica (7.0%, v/v) were also incorporated. Mica was used due to its barrier properties and to reduce the degree of flash rusting [13]. The additives content was 2% (v/v). The selected PVC value was 20% in order to enhance the barrier effect.

Paint manufacture was carried out employing a high-speed disperser unit. Preliminary tests showed the advantage of pigment incorporation in the hardener rather than in the resin. Owing to the relatively high viscosity of the hardener, water was added first and the pigments were then incorporated in order of increasing oil absorption. Mica was added at the end of the preparation to avoid the break-up of its laminar particles.

SAE 1010 steel panels (15.0 cm \times 7.5 cm \times 0.2 cm) were sandblasted to Sa 2 1/2 (SIS 05 59 00), degreased with toluene, and then brush painted up to a thickness of 80 ± 5 μ m. The painted panels were kept indoors for 14 days before being tested.

2.3. Performance of anticorrosive paints in accelerated and electrochemical tests

The panels were placed in the salt spray cabinet (ASTM B 117) to evaluate the degree of rusting (ASTM D 610) and degree of blistering (ASTM D 714). Evaluation of the painted panels was carried out after 2000 and 4200 h of exposure. Once exposure had finished, the coatings were removed and the protective layer formed on the steel was examined by SEM and its composition determined by EDAX.

Similar panels were exposed to the humidity cabinet (ASTM D 2247) and inspected after 400 and 720 h of exposure. The degrees of blistering and rusting were evaluated according to the aforementioned ASTM standard specifications. In all the cases the tests were carried out in triplicate, determining the mean value of the results obtained.

2.4. Electrochemical measurements on painted panels

EIS is perhaps the most useful electrochemical technique for studying the behaviour of anticorrosive coatings. In this research, measurements were made with a Solatron 1250 frequency response analyser. The frequency was varied between 100 kHz and 0.01 Hz, and occasionally 1 mHz. Impedance diagrams were always obtained at the corrosion potential stabilised with a EG&G PAR 273 A potentiostat. A conventional three-electrode cell was employed. The working electrode was the coated specimen, using a calomel electrode as reference and a platinum grid as counter electrode. The electrolyte was a 3% NaCl solution. Due to the good behaviour of the anticorrosive paints tested in this study, measurements were made until important changes were observed, i.e. up to 10 months of immersion in the salt solution.

3. Results and discussion

3.1. Characterisation of pigments

The results of chemical analysis of the pigments show that their main component is zinc phosphate. The theoretical stoichiometric ratio $\text{Zn}^{2+}/\text{PO}_4^{3-}$ is 1.03. This value is lower in the case of zinc and iron phosphate because zinc phosphate is partially replaced by iron phosphate, and it is also lower for zinc aluminium phosphate due to the aluminium phosphate content. Zinc molybdenum phosphate contained molybdate anion in low proportions which was added as zinc molybdate. The $\text{Zn}^{2+}/\text{PO}_4^{3-}$ ratio is abnormally high in the case of zinc molybdenum phosphate, perhaps due to the presence of a certain amount of zinc oxide. This ratio is high in the case of basic zinc phosphate because zinc oxide was incorporated in the zinc phosphate to produce this pigment (Table 1). The presence of zinc oxide is considered beneficial for improving steel passivation [14,15]. The composition of the selected pigments coincided with specifications found in technical data sheets [16,17].

The pH of aqueous extracts of the pigments is comprised in the range of 6.20–7.80, with zinc aluminium phosphate being the most acidic pigment. Considering that steel passivation begins at pH 7 [18], these values indicate that the acid–base characteristics of the pigments do not significantly contribute to passivate the steel substrate. The phosphate content in the saturated pigment solution is, as a general rule, less than 2.5 ppm, while the zinc content ranges between 2.0 and 5.0 ppm for most of the pigments except for

Table 1
Pigment composition (wt.%)

Ionic components of pigments	Pigments				
	1, zinc phosphate	2, zinc and iron phosphate	3, zinc aluminium phosphate	4, zinc molybdenum phosphate	5, basic zinc phosphate
Phosphate (PO_4^{3-})	51.0	40.9	42.7	35.2	39.9
Zinc (Zn^{2+})	42.0	24.2	33.5	43.8	46.5
Iron (Fe^{3+})	–	17.8	–	–	–
Aluminium (Al^{3+})	–	–	2.40	–	–
Molybdenum (Mo(VI))	–	–	–	0.30	–
Loss at 100 °C	7.0	17.1	21.4	20.7	13.6

basic zinc phosphate, which is a little higher (9.3 ppm) due to its greater zinc oxide content.

Electrochemical tests revealed that all the pigments protected steel against corrosion, as may be deduced from the shifting of the corrosion potential to more positive values with respect to the blank SAE 1010 steel (E_{corr} : –650 to –700 mV vs SCE). The most positive corrosion potential value was observed for zinc molybdenum phosphate, which in turn exhibited the lowest corrosion rate. This is mainly attributed to the incorporation of Mo, which is a strong inhibitor [19,20], and to a lesser extent to the relatively high pH of the pigment suspension. The most negative value was exhibited by zinc iron phosphate, though all the values fall in a relatively narrow potential interval (Table 2).

There are significant differences among the corrosion current density values of steel in the pigment suspensions (Table 2). Zinc molybdenum phosphate and basic zinc phosphate exhibited the lowest corrosion current density, while zinc aluminium phosphate presented the highest, perhaps due to the lower pH value of the pigment suspension.

From analysis of the shape of the polarisation curves it may be deduced that the cathodic reaction is more polarised than the anodic reaction. All the pigments except zinc aluminium phosphate inhibited oxygen discharge in a similar way (Fig. 1). Zinc aluminium phosphate exhibited the highest oxygen current and the highest corrosion current density. The differences in the anodic branch of the Tafel plots are better appreciated at lower overpotentials. The most depolarised reaction is that of zinc aluminium phosphate and the lowest anodic currents were observed in the case of zinc molybdenum phosphate and basic zinc phosphate (Fig. 1).

Table 2
Corrosion potential and corrosion current intensity of SAE 1010 steel in pigment suspensions in 3% NaCl

Pigment	Corrosion potential (mV vs SCE)	Corrosion current density ($\mu\text{A cm}^{-2}$)
Zinc phosphate	–553	14.30
Zinc iron phosphate	–564	7.75
Zinc aluminium phosphate	–548	24.46
Zinc molybdenum phosphate	–515	2.6
Basic zinc phosphate	–543	3.27

As has been stated in previous reports [6,7,21], the protective layer formed on steel exposed to pigment suspensions was mainly composed of non-expansive iron oxide. In most cases small globular formations were detected, which seemed to be oxides stabilised by species constituting the anticorrosive pigment. It was thought that these formations blocked the pores in the oxide film. In the case of zinc phosphate, the presence of smaller amounts of zinc hydroxide was detected [7]. These facts are well explained by the low concentration of phosphate and inhibiting cations reported in this research.

3.2. Performance of anticorrosive paints in accelerated and electrochemical tests

Results obtained in the salt spray cabinet (ASTM B 117) after 2000 and 4200 h of testing are shown in Table 3. All the paints showed very good behaviour after 4200 h of exposure, the best scores being recorded for the samples pigmented with zinc and iron phosphate (paint 2), zinc phosphate (paint 3) and zinc molybdenum phosphate (paint 4). When the coating was peeled off, the underlying steel showed the same surface condition in all the cases, which deserved a good score, 8. The anticorrosive behaviour of all the tested paints was so good that it was not possible to establish significant differences between them. These paints provided a good service life in the aggressive salt spray cabinet, which is intended to represent exposure to marine environments. Despite the differences in the corrosion current densities

Table 3
Rusting degree (ASTM D 610) of painted panels in the salt spray cabinet^a

Paints	Hours		Under paint
	2000	4200	
1	8	8	8
2	9	9	8
3	10	9	8
4	10	9	8
5	10	8	8

^a The degrees of rusting on a painted steel surface are between 10 and 0. 10: no rusting; 9: less than 0.05% of the surface rusted; 8: less than 0.1%.

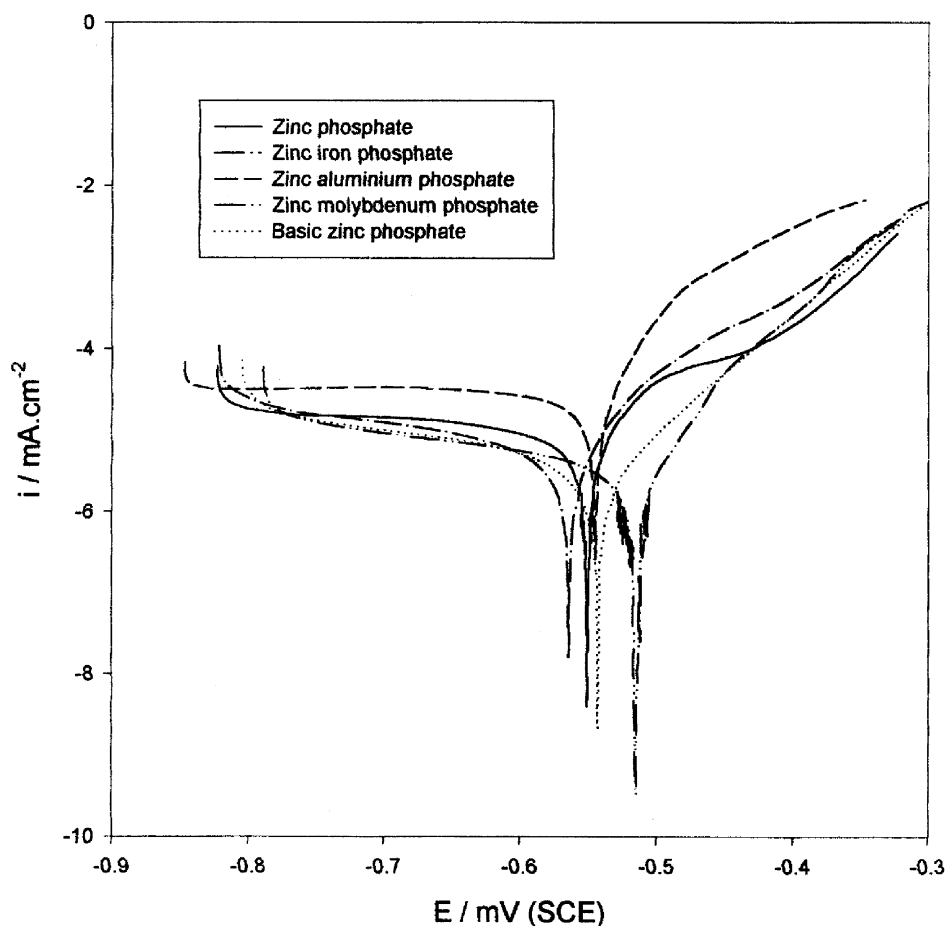


Fig. 1. Tafel plots of SAE 1010 steel electrode in pigment suspensions in 3% NaCl.

of each pigment, all of them performed acceptably in this test, and accordingly it is concluded that the binder exerted a levelling effect; compensating the differences between them.

The main component of the protective layer formed on steel beneath the coating was an amorphous iron oxide (Fig. 2a); the same kind of film encountered on bare steel in contact with pigment suspensions. In the case of pigment 3, crystalline iron oxide was detected at higher magnifications (Fig. 2b). Some globular formations began to develop when the paint was pigmented with pigment 5 (Fig. 2c). The composition of these globular formations was Cl: 33.87% and Fe: 66.13%. It is considered that these formations are precursors of future oxide spots disrupting on the paint film. In all cases an important amount of silicon (20–30%) was detected, which may come from the mica or the talc, and it was demonstrated that siliceous compounds may be beneficial to restrain corrosion resistance [22].

The paints also showed good behaviour during exposure in the humidity cabinet, and the blisters that developed on the steel surface corresponded to the smallest size, as can easily be seen by the unaided eye (Table 4).

3.3. Electrochemical measurements on painted panels

Metals protected with organic coatings are multiphase heterogeneous systems [23], in which the corrosion process is determined by the exchanges occurring at each interface. Water, ions and oxygen can penetrate through coating defects or natural channels of the polymeric matrix and reach the metal/paint interface. In this case, EIS is a valuable technique for acquiring information about the processes

Table 4
Blistering degree (ASTM D 714) of painted panels in the humidity cabinet^a

Paints	Hours	
	400	720
1	8M	8MD
2	8MD	8MD
3	8MD	8D
4	8MD	8D
5	8MD	8D

^a The numerical scale is from 10 to 0, in which 10 represents no blistering and blistering standard, 8 represents the smallest size blister easily seen by the unaided eye. The reference standards in frequency are MD (medium dense) and M (medium). ASTM D 714.

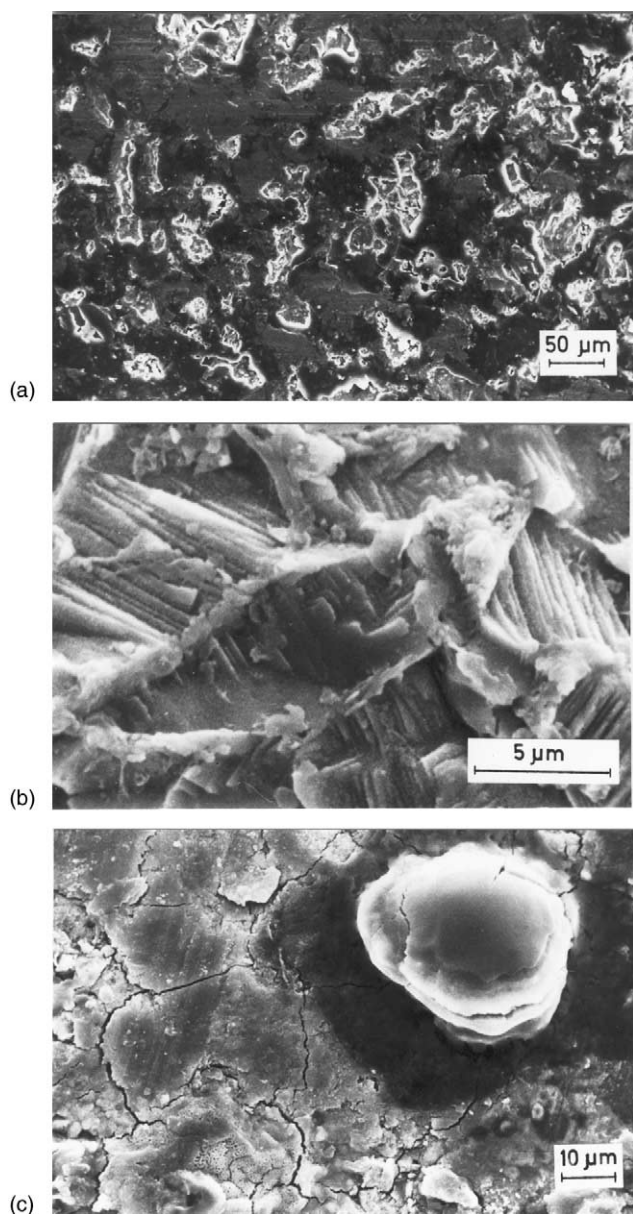


Fig. 2. Structure of protective layer developed on coated steel exposed to salt spray test for 700 h: (a) SEM micrograph of film formed on steel panel coated with paint 4 (200 \times); (b) crystalline iron oxide formed on steel coated with paint 3 (5000 \times); (c) globular formations formed on steel coated with paint 5 (1000 \times).

taking place at the coating/substrate interface. The system's response, in terms of impedance (Z), could be interpreted by means of equivalent circuits (ECs) [24–31]. A metal coated with a polymeric film exposed to an electrolytic solution is properly described by the EC of Fig. 3a. The parameter R_e is the electrolyte resistance while R_{po} is the resistance of the organic coating (conditioned by its defects) and C_c its capacitance. The charge transfer resistance (R_t) is associated with the corrosion process as well as the double layer capacitance (C_{dl}). The Warburg impedance (W) is related to diffusion processes. In this EC model the defec-

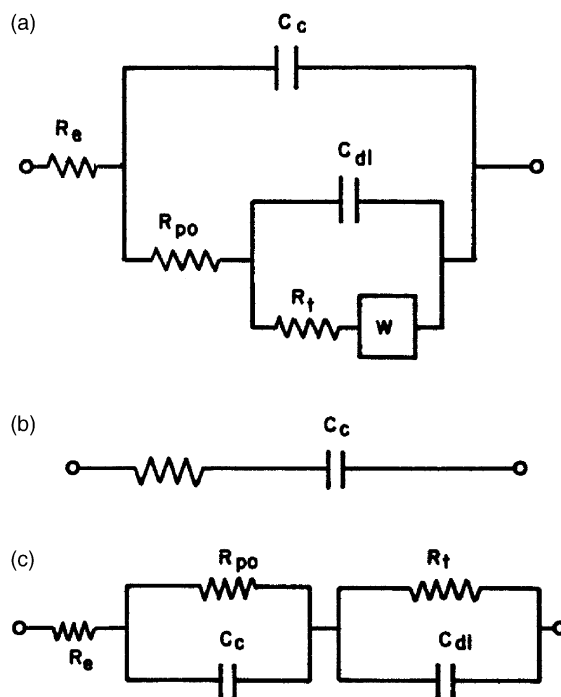


Fig. 3. ECs to interpret the response of the steel/organic coating interface in EIS: (a) defective protective coatings; (b) coatings with a very high barrier effect; (c) non-defective coatings.

tive and intact areas of the coating are in parallel to each other, and the defective fraction of the coating surface is in series with the corrosion reaction at the metal/paint interface and with possible diffusive mass transfer phenomena, represented by the Warburg impedance. For intact coatings the parameter R_{po} is high, typically $\geq 10^8 \Omega \text{ cm}^2$ [32,33], so the whole current passes through C_c and the electrochemical response of coated steel is adequately modelled by the EC in Fig. 3b. In non-defective coatings the resistors and capacitors that represent the coating and interfacial reactions must be arranged in series rather than in parallel (Fig. 3c).

The five anticorrosive paints tested in this research showed a similar electrochemical capacitive response after 24 h of immersion. This behaviour was due to the high barrier effect of the coatings and is evidenced in the Nyquist plots by a sudden increase in the imaginary part of the impedance (Fig. 4), as well as an inverse relationship between the modulus of the impedance and the signal frequency over a wide range. The value of the impedance is higher than $10^9 \Omega \text{ cm}^2$ and the phase angle close to -90° . The dispersion of measurements observed at low frequencies was due to the limitations of the measuring equipment at low frequencies.

After 7 days of exposure a semicircle is clearly defined in the Nyquist plots (Fig. 5); the values of Z , obtained from its diameter, revealed an important barrier effect, and in most of the paints Z is higher than $10^7 \Omega \text{ cm}^2$. The incorporation of water to the polymeric film enhanced its conductivity, and after 1 week the capacitive behaviour is replaced by a

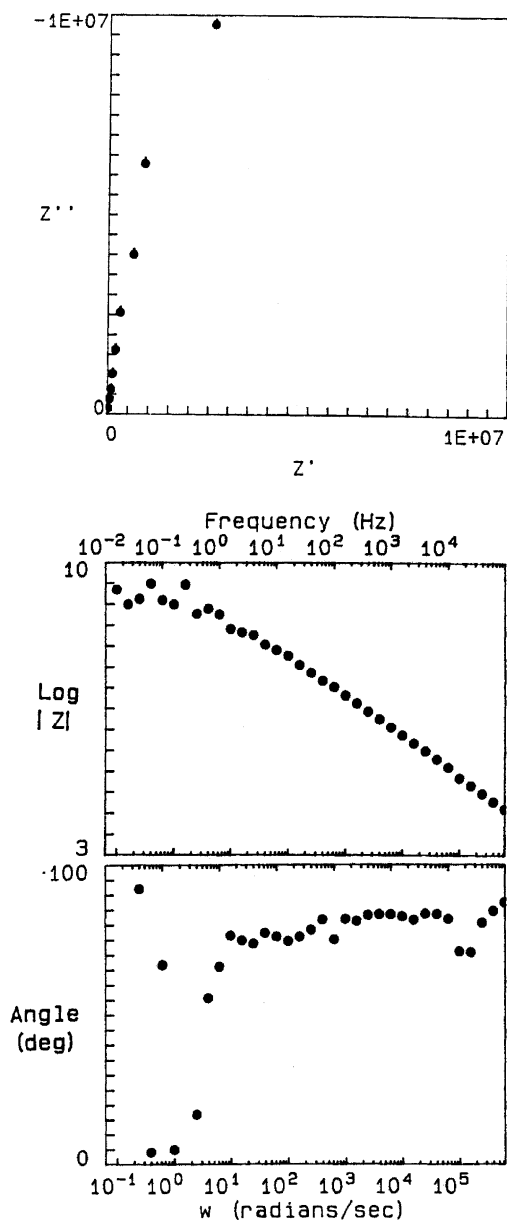


Fig. 4. Impedance plots for organic coatings (paint 3) showing capacitive behaviour in a wide range of frequencies after 1 day of immersion.

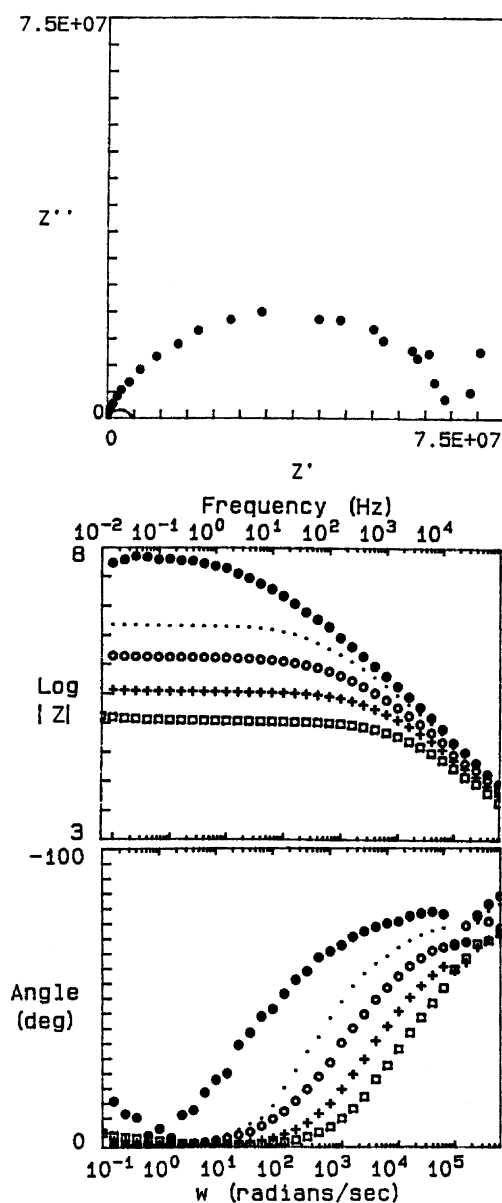


Fig. 5. Impedance diagrams of paint 5 as a function of immersion time in 3% NaCl: (●) 1 day; (⋯) 7 days; (○) 1 month; (+) 8 months; (□) 10 months.

mixed control, capacitive at high frequencies and resistive at low frequencies. However, the decrease in the barrier effect is slow and after 10 months of exposure it may drop by two or three orders of magnitude. In the case of paint 5, formulated with the least protective phosphate, the initial value of Z ($4.6 \times 10^6 \Omega \text{ cm}^2$ after 1 week) revealed the existence of a poorer barrier effect; however the resistance remained almost constant up to 200 days of immersion (Fig. 6). The decrease in Z at lower frequencies is not continuous but a certain recovery was observed in every system, in such a way that some coated panels exhibited a renewed capacitive effect. This recovery was outstanding in the case of paint 4, containing zinc molybdenum phosphate, and less important

in the case of paints 2 and 3. At the end of the test period all the paints had reached almost the same final value.

Capacitance values were found to fluctuate between 10^{-10} and $10^{-11} \text{ F cm}^{-2}$ (Fig. 7) when one semicircle is defined in the Nyquist plot. These capacitance values are typical of an intact coating which is able to protect steel by a barrier effect [33]. The best behaviour was observed for the paint formulated with zinc molybdenum phosphate, which exhibited the lowest capacitance values for a long period of time. Paints 2 and 3 also showed more resistance towards water penetration.

According to ionic resistance and capacitance values, paints 2–4 showed the best anticorrosive behaviour. These

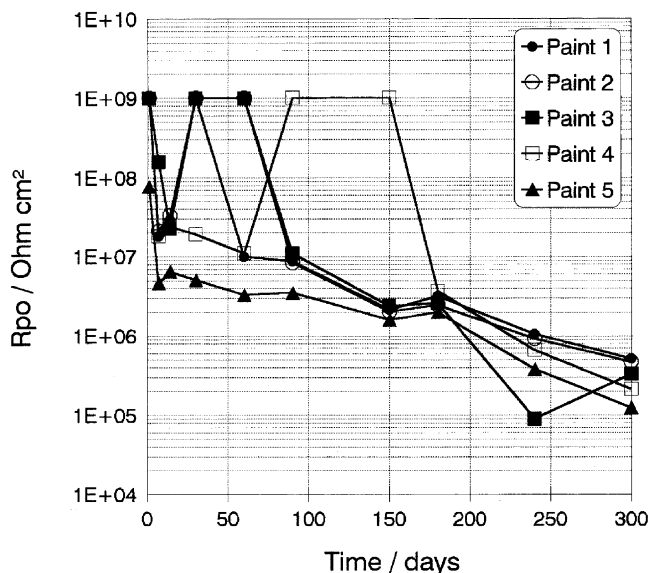


Fig. 6. Variation of paint film resistance as a function of immersion time in 3% NaCl.

results coincided with those obtained in the salt spray test, although the differences between these phosphate inhibitors are small. It is thought that these parameters (R_{po} and C_c) are adequate to evaluate the performance of the paint film.

The degradation of the coating is so slow that after 10 months of exposure a second semicircle is noticed in the Nyquist plots, which corresponded to the relaxation of the corrosion process. In this case the values of R_t and C_{dl} could be obtained (Fig. 8). The existence of this second semicircle appeared after 24 h of exposure in the zone where the paint possessed defective areas.

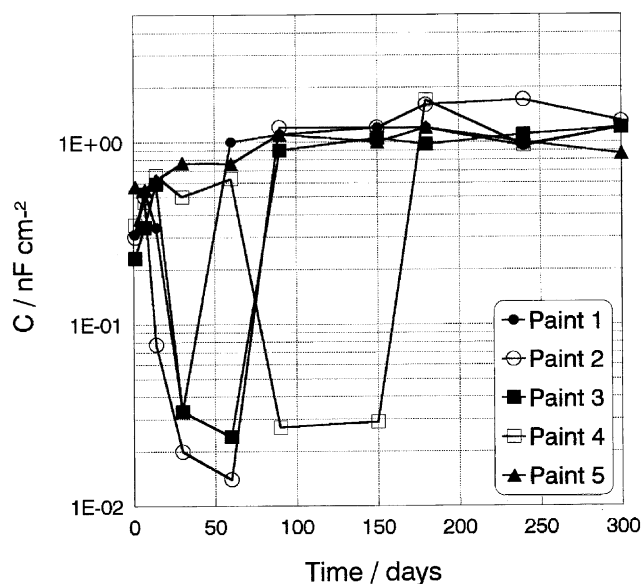


Fig. 7. Variation of paint film capacitance as a function of immersion time in 3% NaCl.

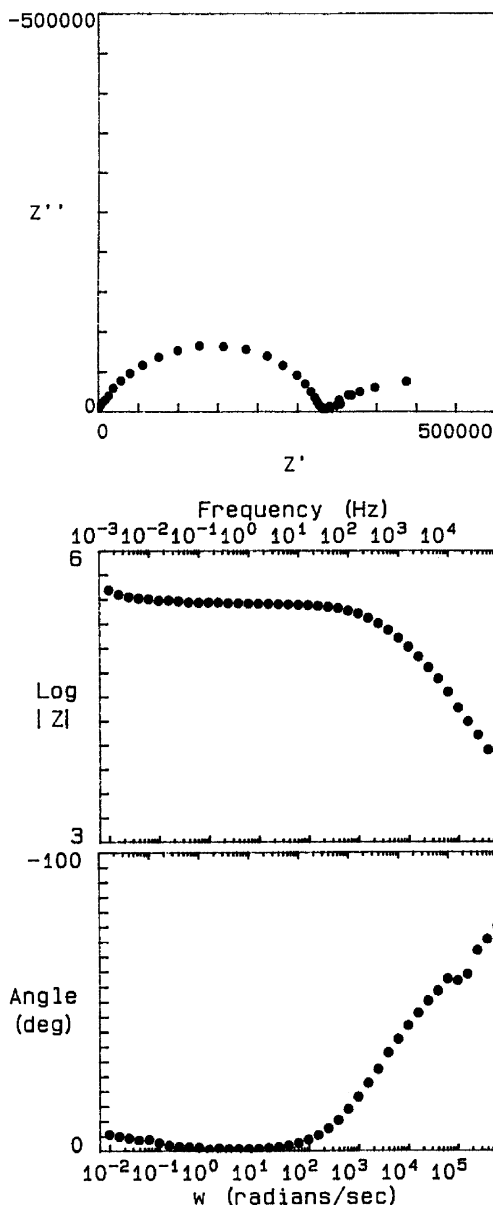


Fig. 8. Nyquist plot of paint 5 after 10 months of exposure in 3% NaCl, showing a well defined semicircle at low frequencies.

The second semicircle is appreciated at low frequencies when R_{po} descends below $10^6 \Omega \text{ cm}^2$ [24,29]. On the other hand, when R_{po} is higher than $10^6 \Omega \text{ cm}^2$ the corrosion process cause a slight irregularity in the first semicircle at the low frequency end. Charge transfer values for the different paints were found to fall between 0.4 and $1.04 \times 10^6 \Omega \text{ cm}^2$ after 10 months of exposure, indicating that steel was protected in every case.

From impedance measurements it is possible to predict, in a short time, the future performance of the coating with respect to atmospheric corrosion. In this sense the “loss factor” ($\tan \delta$) and the “break point frequency” (f_{bp}) proved to be useful parameters. The angle δ is the complement of

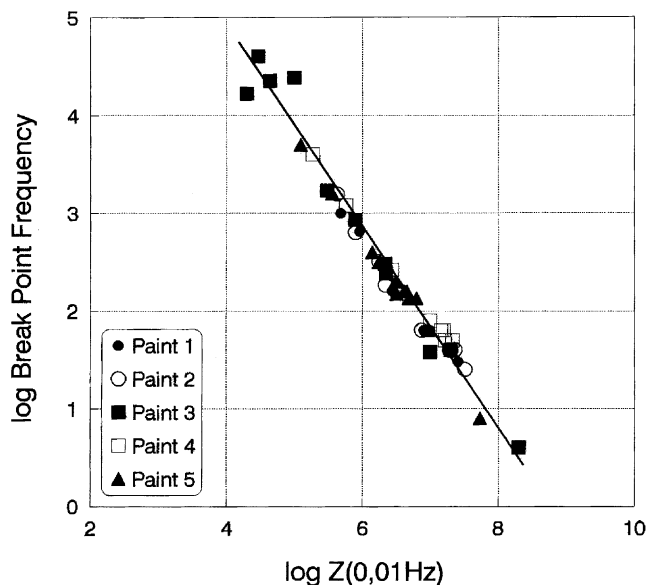


Fig. 9. Relationship between break point frequency (f_{bp}) and impedance at 10 mHz ($Z_{10\text{mHz}}$).

the dephase angle between potential and intensity current at 1 kHz frequency [34,35]; if $\tan \delta < 0.2$ after 24 h of exposure the system will show high resistance to atmospheric corrosion [35]. All the paint systems tested in this research show $\tan \delta$ values lower than 0.2. The only exception to this rule is paint 5 which had a $\tan \delta$ value equal to 0.28.

Another index which supplies qualitative information similar to the loss factor is the frequency corresponding to a phase angle of 45° , called the “break point frequency”; in this case the imaginary and the real parts of the impedance become equal. This situation corresponds to a mixed capacitive/resistive behaviour. The higher is the f_{bp} value, the lower the film impedance at low frequencies (the film resistance) will be (Fig. 9).

Both indexes, which can serve as a fast and simple control test for estimating the relative behaviour of different coatings in a medium, or the responses of one same coatings in different media, are based on the supposition that the lower the barrier effect of the coating reflected in R_{po} , the greater the $\tan \delta$ or the f_{bp} . Nevertheless, if the semicircle at high frequencies is well defined the determination of R_{po} supplies the same qualitative orientation as $\tan \delta$ or the f_{bp} and also permits quantification of resistance to deterioration. It should be borne in mind, however, that none of these indexes measure corrosion rates.

It was also proposed that the determination of the impedance at low frequencies (typically 1 or 10 mHz) could serve as a rough estimation of the charge transfer resistance (R_t) [36]. This approximation is valid in the case of uncoated metals, but for painted metals $Z_{10\text{mHz}}$ is a fairly good approximation to R_{po} , i.e. the efficiency of the barrier effect. If the barrier effect disappears, the measurement is then related to the corrosion process.

In a previous paper [37] it was demonstrated that the “loss factor” and “break point frequency” lead to equivalent qualitative estimations. This similarity can be extended to predictions based on measurement of the impedance at low frequencies, as can be seen in Fig. 9. As f_{bp} increased, $Z_{10\text{mHz}}$ decreased, R_{po} decreased, and the barrier effect of the coating is progressively lost (Fig. 5).

4. Conclusions

1. It is possible to formulate high performance anticorrosive paints by selecting adequate water-borne resin and ecological pigments.
2. All the pigments tested in this research are able to inhibit corrosion, as is evidenced by the shift in the corrosion potential and the lower corrosion rates obtained for steel in contact with the pigment suspensions.
3. The protective layer formed under the paint film was mainly composed of non-expansive iron oxide. The protective film was also enriched in silica coming from talc and mica particles.
4. The electrochemical response of painted panels indicated an initial capacitive behaviour of the coating due to a high barrier effect.
5. The barrier effect was slowly lost as time elapsed, indicating the excellent performance of water-borne epoxy paints.
6. Parameters such as $\tan \delta$, f_{bp} and $Z_{10\text{mHz}}$ can be employed for a quick prediction of the relative behaviour of a given set of paints.
7. This research demonstrated that it is possible to replace solvent-borne epoxy paints by water-based paints with excellent anticorrosive performance.

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References

- [1] T. Schauer, W.M. Liu, L. Dulog, Corrosion protective pigments: their efficiency in organic and waterborne primers, *Eur. Coat. J.* 3 (1997) 233.
- [2] J. Depireux, M. Piens, Proceedings of the 18th FATIPEC Congress, vol. 13, 1987, p. 183.
- [3] G. Meyer, Über Zinkphosphat und Bariumchromat als moderne Korrosionsinhibitoren, *Farbe + Lack* 69 (7) (1963) 528.
- [4] R. Romagnoli, V.F. Vetere, Non-pollutant corrosion inhibitive pigments: zinc phosphate, a review, *Corros. Rev.* 13 (81) (1995) 45.
- [5] J. Barraclough, J.B. Harrison, New leadless anti-corrosive primers, *JOCCA* 48 (4) (1965) 341.

- [6] B. del Amo, R. Romagnoli, V.F. Vetere, Study of the anticorrosive properties of zinc phosphate and zinc molybdophosphate in alkyd paints, *Corros. Rev.* 14 (1/2) (1996) 121.
- [7] G. Blustein, B. del Amo, R. Romagnoli, The influence of the solubility of zinc phosphate pigments on their anticorrosive behaviour, *Pigment Resin Technol.* 29 (2) (2000) 100.
- [8] L. Chromy, E. Kaminska, Non-toxic anticorrosive pigments, *Prog. Org. Coat.* 18 (4) (1990) 319.
- [9] A. Gerhard, A. Bittner, Second generation phosphate anti-corrosive pigments. Formulating rules for full replacement of new anti-corrosive pigments, *JCT* 58 (740) (1986) 59.
- [10] A. Bittner, Advanced phosphate anticorrosive pigments for compliant primers, *JCT* 61 (777) (1989) 14.
- [11] J.J. Caprari, A.R. Di Sarli, B. del Amo, Zinc phosphate as corrosion inhibitive pigment of water-borne epoxy paints used for steel protection, *Pigment Resin Technol.* 29 (1) (2000) 16.
- [12] M.A. Jackson, Guidelines to formulation of water-borne epoxy primers: an evaluation of anticorrosive pigments, *J. Protective Coat. Linings* 7 (4) (1990) 54.
- [13] S. Gee, Water-borne coatings for steel, *Surf. Coat. Int.* 80 (7) (1997) 316.
- [14] H. Leidheiser Jr., Mechanism of corrosion inhibition with special attention to inhibitors in organic coatings, *J. Coat. Technol.* 53 (678) (1981) 29.
- [15] A. Kalendová, Alkalisising and neutralising effects of anticorrosive pigments containing Zn, Mg, Ca and Sr cations, *Prog. Org. Coat.* 38 (1999) 199.
- [16] Actirox, Hispafos, Technical specifications.
- [17] Société Nouvelle des Couleurs Zinciques, Product Data Sheets.
- [18] Z. Szklarska-Smialowska, R.W. Stahele, Ellipsometric study of the formation of films on iron in orthophosphate solutions, *J. Electrochem. Soc.* 121 (11) (1974) 1393.
- [19] J.R. Ambrose, The role of molybdenum as an inhibitor of localised corrosion of iron in chloride solution, *Corrosion (NACE)* 34 (1) (1978) 27.
- [20] A.G. Gad-Allah, W.A. Badani, A. El-Rahman, N.M. Abou Romia, Kinetics of the passivation of Mo in salt solutions as inferred from impedance and potential measurements, *Surf. Coat. Technol.* 31 (2) (1987) 117.
- [21] R. Romagnoli, V.F. Vetere, Heterogeneous reaction between steel and zinc phosphate, *Corrosion (NACE)* 51 (2) (1995) 116.
- [22] M. Bennet, M. Houlton, R. Hawes, The improvement by a CVD silica coating of the oxidation behaviour of a 20% Cr/25% Ni niobium stabilised stainless steel in carbon dioxide, *Corros. Sci.* 22 (2) (1982) 111.
- [23] B. Chico, Corrosion en uniones solapadas de aceros recubiertos, Tesis doctoral, Universidad Complutense de Madrid, España, September 2001.
- [24] G.W. Walter, Application of impedance measurements to study performance of painted metals in aggressive solutions, *J. Electroanal. Chem.* 118 (1981) 259–273.
- [25] G.W. Walter, A review of impedance plot methods used for corrosion performance analysis of painted metals, *Corros. Sci.* 26 (1986) 681.
- [26] F. Mansfeld, W. Kendig, Electrochemical impedance spectroscopy of protective coating, *Werk. Korr.* 36 (1985) 473.
- [27] F. Geenen, Characterization of organic coatings with impedance measurements, Ph.D. Thesis, Technische Universiteit Delft, Netherlands, September 1991.
- [28] S. Feliu, J.C. Galván, M. Morcillo, The charge transfer reaction in Nyquist diagrams of painted metals, *Corros. Sci.* 30 (1990) 1989.
- [29] A. Amirudin, D. Thierry, Application of electrochemical impedance spectroscopy to study efficiency of anticorrosive pigments in epoxy-polyamide resin, *Br. Corros. J.* 30 (1995) 128.
- [30] P.L. Bonora, F. Deflorian, L. Fedrizzi, Electrochemical impedance spectroscopy as a tool for investigating underpaint corrosion, *Electrochim. Acta* 41 (1996) 1073.
- [31] G. Grundmeier, W. Schmidt, M. Stratmann, Corrosion protection by organic coatings: electrochemical mechanism and novel methods of investigation, *Electrochim. Acta* 45 (2000) 2515.
- [32] T. Szauer, Electrical and electrochemical resistance for the evaluation of protective non metallic coatings, *Prog. Org. Coat.* 10 (1982) 157.
- [33] C.I. Elsner, A.R. Di Sarli, Comparison between electrochemical impedance and salt spray tests in evaluating the barrier effect of epoxy paints, *J. Braz. Chem. Soc.* 51 (1994) 15–18.
- [34] Y. Sato, Mechanism and evaluation of protective properties of paints, *Prog. Org. Coat.* 9 (1981) 85.
- [35] I. Petrovich, J.M. Bastidas, S. Feliu, Comportamiento de un recubrimiento de pintura sobre acero galvanizado, Aplicación de la técnica de Impedancia, *Rev. Iberoam. Corros. Prot.* 14 (1983) 219.
- [36] K. Hladky, L.M. Callow, J.L. Dawson, Corrosion rates from impedance measurements: an introduction, *Br. Corros. J.* 15 (1980) 20.
- [37] A. Bautista, J.A. González, E. Otero, M. Morcillo, E. Almeida, Discrimination by EIS of degradation mechanisms in lap joints coated sheet, *J. Coat. Technol.* 71 (893) (1999) 61.