

Improvement of anticorrosive performance of phosphate-based alkyd paints with suitable additives

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Abstract The purpose of this investigation was focused on reducing the content of zinc phosphate in anticorrosive paints by means of the incorporation of low quantities of selected soluble corrosion inhibitors. The article describes the anticorrosive behavior of alkyd paints containing reduced levels of zinc phosphate, zinc oxide, and some soluble compounds used as additives (e.g., sodium polyphosphate, sodium phosphate, and sodium benzoate). Anticorrosive solvent-borne alkyd paints were formulated with a zinc phosphate content of 10% by volume (v/v) with respect to the total pigment concentration. In all cases, the PVC/CPVC (pigment volume concentration/critical pigment volume concentration) ratio was 0.8. Experimental paints, applied on sandblasted SAE 1010 panels, were evaluated by accelerated tests (salt spray cabinet) and electrochemical measurements (electrochemical impedance spectroscopy, EIS). The results show that the additions of small amounts of soluble corrosion inhibitors to low content zinc phosphate paint formulations enhance their performance in a very remarkable way. Perhaps, the most outstanding feature is that the employment of soluble additives allowed the reduction of the zinc phosphate content with concomitant savings.

Keywords Anticorrosive paints, Phosphate pigments, Soluble additives, Electrochemical impedance spectroscopy

Introduction

Corrosion protection of metals and the replacement of toxic compounds in paint formulations are the most important ambitions claimed in the field of paint technology. In this sense, the elimination of classical anticorrosive pigments (e.g., lead and chromate compounds) in paints is of great interest.

Many compounds have been suggested as possible replacements for chromates and lead compounds, but zinc phosphate and related substances became the leading substitutes for toxic inhibitors. Three generations of phosphates were introduced in the market, with zinc phosphate as the precursor. A second generation of phosphate pigments was developed by modifying zinc phosphate adding suitable cations, such as molybdenum or aluminum, or by reducing the particle size. The third generation is concerned with the substitution of the phosphate anion by the tripolyphosphate one.^{1–25}

As a general rule, it can be stated that the protective action of zinc phosphate is due to the formation of an iron oxyhydroxides film on the steel substrate, which is non-expansive in nature.^{1,26} The polarization of cathodic areas by the precipitation of sparingly soluble salts, which strongly adhere to the surface, also contributes to metal passivation.^{2,26,27}

Usually, the zinc phosphate load in high performance anticorrosive paints is ~30% v/v of the total pigment content.^{6,9,10,23–26} As it will be discussed later, poorer results were obtained when lower zinc phosphate contents were employed. However, this content could be reduced following two different ways. Blends of zinc phosphates with other non-toxic corrosion inhibitors can be used to give similar or better anticorrosive performance and, simultaneously, to reduce the phosphate content.²⁸ In this sense, zinc phosphate has been combined with borates and molybdates with improved results^{3,29} and, more recently, formulations

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containing phosphate/polyaniline and phosphate/molybdenyl-modified zeolites were reported in the literature.^{30,31} The employment of suitable additives, particularly organic inhibitors, which often act synergistically, was also of great concern and it is reported in current literature.^{28–38} Zinc nitrophthalate, zinc benzoates, metallic sulfonates, phosphonic acids and their derivatives, amines salts of succinic acid, etc., were incorporated to paint formulations with success.

The incorporation of soluble compounds in anticorrosive formulations containing zinc phosphate to enhance their anticorrosive properties or to avoid the flash rusting process is documented in the literature.^{39–41} However, the soluble compounds content must be limited because their leaching by water penetrating the pores of the coating would greatly increase coating permeability with the concomitant loss of the protective properties of the paint.^{42–44} In brief, if soluble compounds are used at very low concentration (e.g., as additives), it is possible that the anticorrosive performance of paint system could be enhanced.

The purpose of this investigation was to reduce the zinc phosphate content, in alkyd paints, by means of the incorporation of low quantities of selected soluble corrosion inhibitors (e.g., sodium phosphate, sodium polyphosphate, and sodium benzoate). The inhibitive properties of these compounds were known from many years ago^{2,27,45–53} and they were utilized by the authors to precipitate certain anticorrosive pigments in the past.^{22–25,54–57} We hypothesize that the incorporation of soluble corrosion inhibitor to the paints formulations would enhance their anticorrosive performance and this fact would allow reducing zinc phosphate content without impairing the coatings protective ability.

Anticorrosive alkyd paints containing low content of zinc phosphate, zinc oxide and the selected corrosion inhibitors were formulated and their performance was evaluated in the salt spray chamber and EIS.

The results showed that zinc phosphate content could be reduced with the addition of the soluble active compound, but the performance of the paint depends on the nature of the additives.

Experimental section

Composition, manufacture, and application of paints

The resin employed to formulate solventborne alkyd paints was a medium oil alkyd (50% linseed oil, 30% *o*-phthalic anhydride, 8% pentaerythritol and glycerol, and 12% pentaerythritol resin). The [®]ALKYPOL 352/50 resin employed to carry out this research was provided by POLIDUR S.A. from Argentina. For all paints white spirit was used as solvent. The PVC/CPVC

(pigment volume concentration/critical pigment volume concentration) relationship was 0.8 as suggested elsewhere.^{9,10}

The anticorrosive pigment load was 10% v/v of the total pigment content and titanium dioxide, barium sulfate, and zinc oxide were incorporated to complete the pigment formula. All pigments were dispersed for 24 h in the vehicle, employing a ball mill, to achieve an acceptable dispersion degree.

Three soluble additives were selected to be incorporated to the previous formulation to enhance its anticorrosive properties. From now on, paints will be numbered according to the soluble additive employed in each case. Paint 1 contained sodium polyphosphate; paint 2 was formulated with sodium benzoate; sodium phosphate was the additive for paint 3; and paint 4 was the reference paint. In every case Merck[™] reagents grade chemicals were used. The composition of the paint 4 could be seen in Table 1. In order to elaborate the paints 1–3, soluble additives, 2% v/v, were incorporated to paint 4 and, then, dispersed during 1 h.

Solventborne paints were chosen to assess the anticorrosive behavior of these additives because their behavior was very well documented for many years and the alkyd resin was selected because its use is widespread. The selected zinc phosphate content was low and it cannot ensure, by itself, an appropriate anticorrosive performance. It is also important to point out that this content is just one-third of that recommended in the literature for adequate protection.^{2,6,9,10}

Prior to painting, SAE 1010 steel panels were sandblasted to Sa 2 1/2 (SIS 05 59 00) and degreased with toluene. Then, paints were applied on steel panels (15.0 × 7.5 × 0.2 cm) by brushing to reach a dry-film thickness of 80 ± 5 μm. Painted panels were kept indoors for 14 days before testing.

Anticorrosive performance evaluation of paints through accelerated tests

Salt fog chamber

For each type of paint, a set of three panels, coated only with the alkyd paint (without topcoats), was placed in the salt spray chamber according to ASTM B 117 specification (Table 2).⁵⁸ Rusting and blistering degrees were evaluated in relation to ASTM standards,^{59,60} i.e., ASTM D-610 and ASTM D-714, respectively; as function of the exposure time.

Table 1: Composition of paint 4 as vol%

Zinc phosphate	Titanium dioxide	Barite	Zinc oxide	Alkyd resin	White spirit
2.2	4.3	7.9	7.9	49.3	28.4

Table 2: Salt spray chamber test (ASTM B 117)

Rusting degree (ASTM D 610) of painted steel panels ^a						
Time (h)	360	720	1080	1440	1800	2160
Paints	1	----- No rusted -----			9	8
	2	8	7	----- Out of test -----		
	3	----- No rusted -----		9	8	7
	4	10	8	7	----- Out of test -----	

^a Rusting degree (ASTM D 610)										
Rust grade	10	9	8	7	6	5	4	3	2	1
Rusted area (%)	No rusted	0.03	0.1	0.3	1	3	10	16	33	50

Electrochemical tests

Impedance spectra of painted panels (frequency range $1 \times 10^5 \text{ Hz} \leq f \leq 1 \times 10^{-3} \text{ Hz}$) were performed in the potentiostatic mode, at the corrosion potential (E_{corr}). Measurements were carried out as a function of the exposure time in 3% NaCl using the 1255 Solartron FRA and the 1286 Solartron EI. The amplitude of the applied AC voltage was 0.010 V peak to peak. Two acrylic tubes were attached to each coated panel (working electrode) with an epoxy adhesive; the geometric area exposed to the electrolyte was, in each cell, 15.9 cm². A large area Pt–Rh mesh of negligible impedance and saturated calomel (SCE) were employed as auxiliary and reference electrodes, respectively. The experimental impedance spectra were interpreted on the basis of equivalent electrical circuits using a suitable fitting procedure developed by Boukamp.⁶¹ The electrochemical experiments were carried out at laboratory temperature ($20 \pm 2^\circ\text{C}$), using a Faraday cage. Simultaneously, corrosion potential values were recorded as a function of immersion time.

Results and discussion

Salt spray test

As general rule, the performance of tested paints is regarded as satisfactory if they maintain a good qualification after 500 h of exposure. In this sense, all paints assessed in this work satisfied this criterion but there are significant differences between the tested paints which depend on the nature of the soluble compound employed (Table 2).

The anticorrosive performance of coatings containing sodium polyphosphate (paint 1) and sodium

phosphate (paint 3), were clearly superior to that obtained with zinc phosphate alone (paint 4). The incorporation of sodium benzoate into the paint formulation had a deleterious effect on its anticorrosive behavior (paint 2).

Paint 1 obtained a qualification 8 after 2160 h of testing. Likewise, paint 3 behaved adequately but achieving qualification 7 in the same period of exposure. In contrast, paints 2 and 4 displayed a poorer behavior, getting a qualification 7 after 720 and 1080 h, respectively. As it was expected, a very low zinc phosphate content could not provide a satisfactory anticorrosive behavior.^{9,10,26,62} In change, formulations containing 30% v/v of zinc phosphate, with respect to the total pigment content, were reported to undergo 1700 h of testing previous to failure.²⁶ It is clear that the incorporation of sodium phosphate and sodium tripolyphosphate to the paint formulation improved paints performance in such a way that lower zinc phosphate loadings gave a similar behavior to that obtained with 30% of zinc phosphate. Hence, it was concluded that the zinc phosphate content could be reduced only if the suitable anticorrosive additives (e.g., polyphosphate and phosphate anions) are added to the paint formulations.

It is well known that polyphosphate and phosphate anions restrained steel corrosion by generating a thin protective oxides film.^{2,27} It was thought that the presence of phosphate species, from soluble additives, in the pore solution, at the metal/paint interface, controlled the onset of the corrosion at the active sites of the base metal. An atypical behavior was detected when benzoate anion was employed as an anticorrosive additive. Benzoate ion hydrolyzes in water like any weak acids do, generating a fraction of benzoic acid in the pore solution of the coating. This fraction is higher at the anodic sites due to their acidic pH and this fact

would prevent the formation of a protective layer of ferric benzoate.⁵⁴ On the other hand, ferric phosphates could precipitate at lower pH values.

As a general rule, it can be said that alkyd paints did not blister during their time in the salt spray chamber, but that paint 2 blistered prematurely.

The good anticorrosive performance of paints 1 and 3 could be attributed to the inclusion of phosphate species in the anticorrosive paint formulation.

Electrochemical impedance spectroscopy

Equivalent circuits

Impedance spectra provide useful information concerning the evolution of both the organic coating protective properties and the kinetics of the underlying steel corrosion process, as a function of the immersion time in the selected electrolyte. The point of view adopted in this article was that of Amirudin and Thierry⁶³ in the sense that visual observation of the spectra could not indicate the exact number of time constants involved in the degradation of the organic coating subjected to a corrosive environment. The number of these constants must be determined by data analysis rather than by visual observation of spectra. Fortunately, appropriate equivalent circuit has been proposed to describe the behavior of painted metals (Fig. 1); these circuits were discussed previously by several authors.^{63–68} Experimental impedance data are usually fitted with non-linear least squares algorithms, involving the transfer function derived from the equivalent circuit models, to obtain circuit parameters.^{69–72}

The impedance of a high-quality, non-defective organic coating is that of a dielectric capacitor with a frequency dependence expressed by the following equation:

$$Z_c = -j/wC$$

However, as the coating degrades, an in-phase component develops as a result of shorting the organic coating capacitance with a parallel resistor. This resistor represents the development of ionic conducting paths which may occur through microscopic pores or virtual pores defined by low cross-linking regions in the polymer with concomitant high ionic transport.^{72–77} Thus, R_s represents the electrolyte resistance between the reference and working (coated steel) electrodes, R_1 the resistance to the ionic flux through paths short-circuiting the paint film, and C_1 the dielectric capacitance of the intact part of the same film (Fig. 1a).

Once the permeating and corrosion-inducing chemicals (water, oxygen, and ionic species) reach the electrochemically active areas of the substrate, particularly the bottom of the paint film pores, metallic corrosion takes place and its associated parameters, the double-layer capacitance (C_2) and the charge transfer resistance (R_2) can be obtained from the fitting

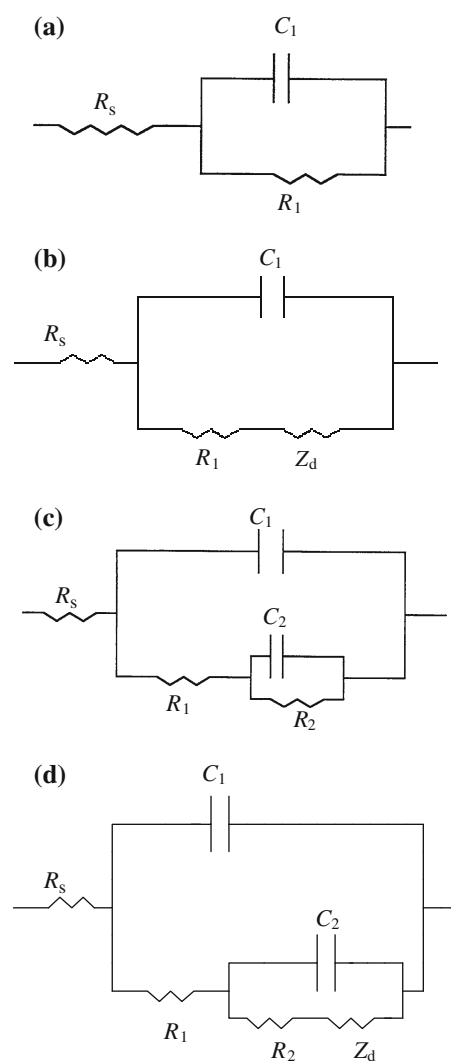


Fig. 1: Equivalent circuits to interpret the response of the steel/organic coating interface in EIS: (a) intact coating, (b) a coating with a diffusion process across it, (c, d) a coating where the faradaic process associated with corrosion started

procedure. It is important to remark that R_2 and C_2 values vary inversely and directly, respectively, and with the size of the attacked metallic area. There is almost a unanimous opinion that a polymer-coated metal is represented by the circuit in Fig. 1(c) when water penetrates the coating and reaches the metal. It is also agreed that the general impedance may include the Z_d , the mass transfer (Warburg) impedance⁶³; Fig 1(b) and (d).

Distortions observed in these resistive–capacitive contributions indicate a deviation from the theoretical models due to either lateral penetration of the electrolyte at the steel/paint interface (usually started at the base of intrinsic or artificial coating defects), underlying steel surface heterogeneity (topological, chemical composition, and surface energy), and/or

diffusional processes that could take place along the test.^{78,79} Since all these factors cause the impedance/frequency relationship to be non-linear, they are taken into consideration by replacing the capacitive components (C_i) of the equivalent circuit transfer function by the corresponding constant phase element Q_i (CPE), thus obtaining a better fit of data.^{61,63} The CPE is defined by the following equation⁸⁰:

$$Z = \frac{(j\omega)^{-n}}{Y_0}, \quad (1)$$

where Z is the impedance of the CPE ($Z = Z' + Z''$) (Ω), j is the imaginary number ($j^2 = -1$), ω is the angular frequency (rad), n is the CPE power ($n = \alpha/(\pi/2)$) (dimensionless), α is the constant phase angle of the CPE (rad), and Y_0 is the part of the CPE independent of the frequency ($s^2 \Omega^{-1}$).

The accuracy of the fitting procedure was measured by the χ^2 parameter obtained from the difference between experimental and fitted data; the most probable circuit was selected providing that $\chi^2 < 10^{-4}$. In the present work, the fitting process was mainly performed using the phase constant element Q_i instead of the dielectric capacitance C_i .

Electrochemical tests

The corrosion potential (E_{corr}) evolution of coated steel panels immersed in 3% NaCl solution is shown in Fig. 2. Differences between these paints became visible from the beginning of the test. E_{corr} values of panels coated with paints 1 and 3 were displaced to more positive values, indicating that good protection with these paints was achieved during, at least, 9 months. Paint 2 failed from early days showing an E_{corr} close to that presented by bare steel in similar exposure conditions. Hence, it could be concluded that sodium

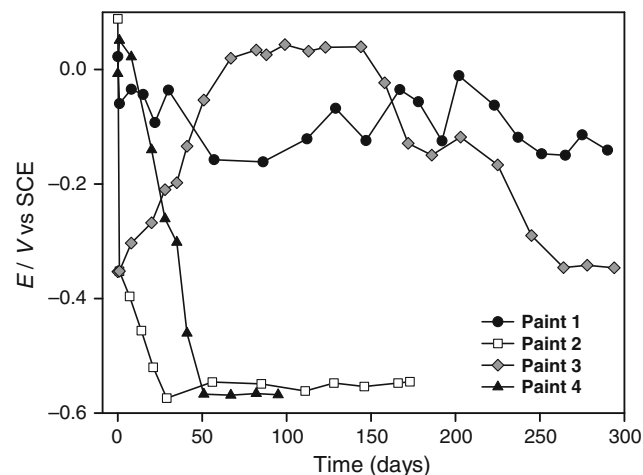


Fig. 2: Corrosion potential of coated steel immersed in 3% NaCl solution

benzoate did not provide an additional inhibitive effect to this paint. Paint 2 behaved as paint 4, which formulated with a low phosphate content, provided a poor anticorrosive performance.^{6,23–26}

In view of these results, it is believed that phosphate and polyphosphate anions, offered a satisfactory anticorrosive action due to the initial passivation of the steel substrate while the phosphate pigment (e.g., zinc phosphate) provided protection in the long term. These results were confirmed by means of EIS measurements.

The analysis of Bode's revealed that paint 1 had a high impedance throughout the entire test period. The values assumed by the phase angle revealed the existence of a resistive–capacitive behavior (Fig. 3). In change, paint 2 showed an initial impedance value higher than $10^7 \Omega \text{ cm}^2$ which decreased several orders of magnitude after 1 day of immersion (Fig. 4), thus indicating the absence of an effective anticorrosive protection. As in the case of paint 1, water reached the metal substrate from the beginning of the test period and at least two time constants were perceivable. The impedance of paint 3 was very high for 51 days of immersion but it descended although its value ranged 10^6 – $10^7 \Omega$ for a long period of time. The phase angle showed a similar behavior to the previous cases (Fig. 5). Finally, paint 4, containing only 10% of zinc phosphate, showed a slightly better behavior than paint 2 but the protective properties were impaired as time elapsed and after 67 days they were practically lost (Fig. 6).

After the examination of Bode's plots, the fitting procedure was carried out to determine the time constants involved in the coatings degradation process. As no pure capacitive behavior was observed in any case, the circuit employed to fit experimental data was that of Fig. 1(c). The exponent “ n ” in Eq. (1) was comprised between 0.5 and 0.8, so it was concluded that a CPE (Q_i) could describe appropriately the dielectric properties of the film and the capacitance of the double layer.

It is reported in the literature that an acceptable barrier effect is attained when $R_1 > 10^8 \Omega \text{ cm}^2$, and a residual protective effect is still present if R_1 ranged between 10^6 and $10^7 \Omega \text{ cm}^2$.^{66,81–83} As it can be seen in Fig. 7, with the exception of paint 2, the others showed a high barrier effect ($R_1 \sim 10^8$ – $10^9 \Omega \text{ cm}^2$) which was maintained for paint 1, but was lost after a few days of immersion in the case of paint 3 and 4. However, paint 3 conserved a residual barrier effect ($R_1 > 10^6 \Omega \text{ cm}^2$) during all the test period and paint 4 lost its barrier properties after 50 days of immersion. The oscillating behavior observed for paints 1 and 3 was attributed to pore blocking with corrosion products which, temporarily, enhance the steel protection. On the other hand, the dielectric properties of paints 1 and 3 ($Q_1 \sim 10^{-8}$ – $10^{-9} \text{ F cm}^{-2}$) corresponded to non-damaged films.^{66,82,83} Again, the poorer behavior was obtained when sodium benzoate was employed as additive, since the values of Q_1 , $\sim 10^{-6} \text{ F cm}^{-2}$, similar

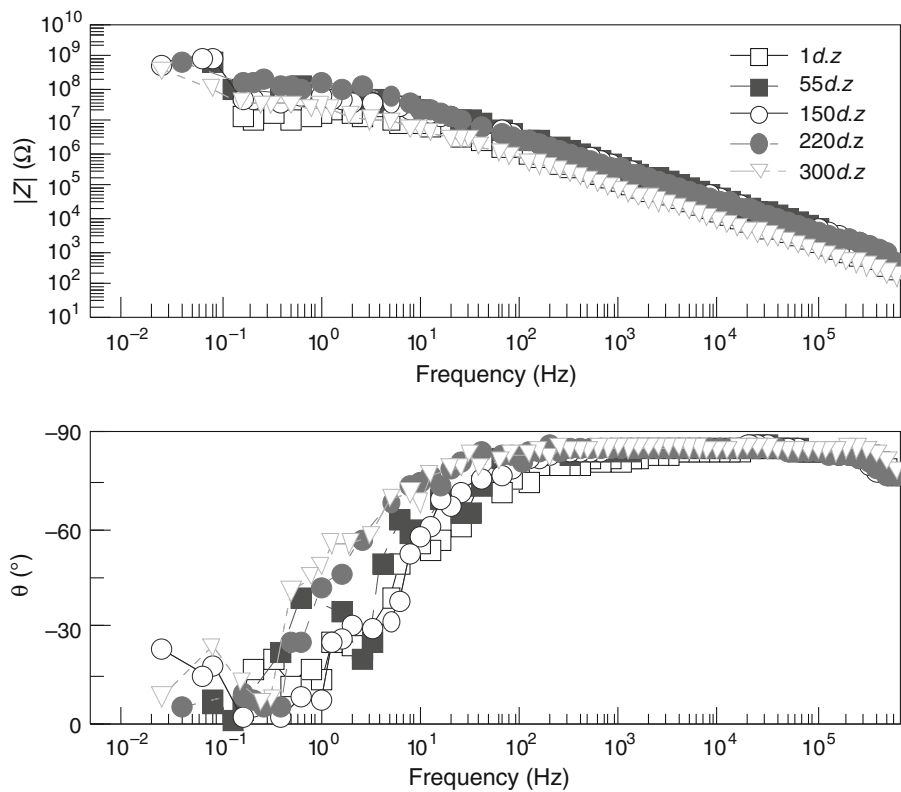


Fig. 3: Bode plots for paint 1 immersed in 3% NaCl solution

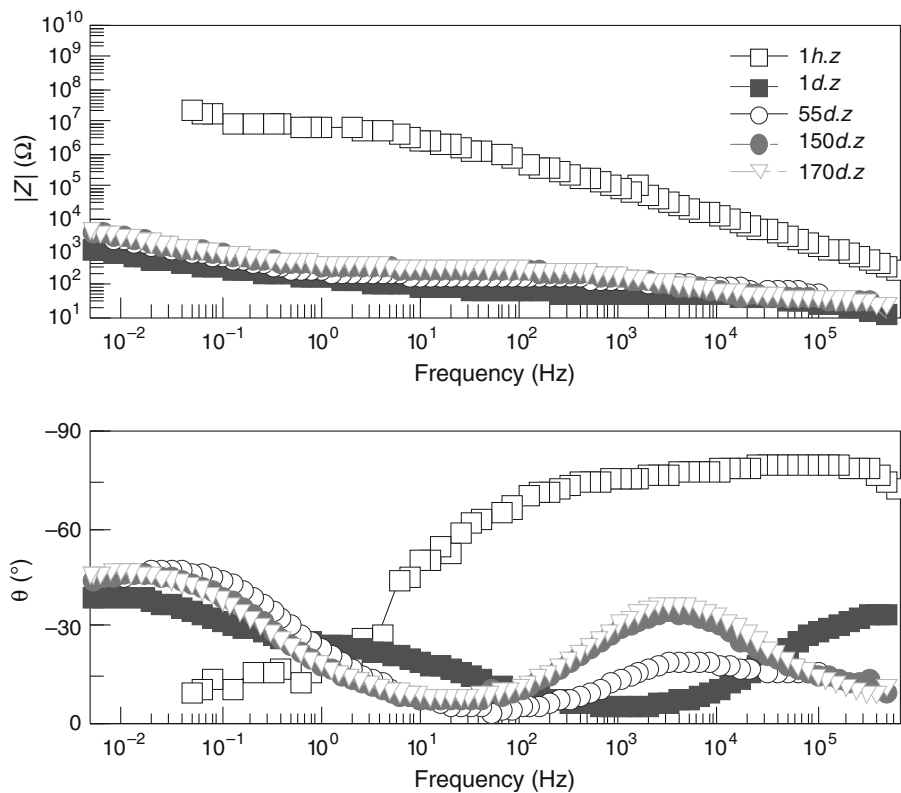


Fig. 4: Bode plots for paint 2 immersed in 3% NaCl solution

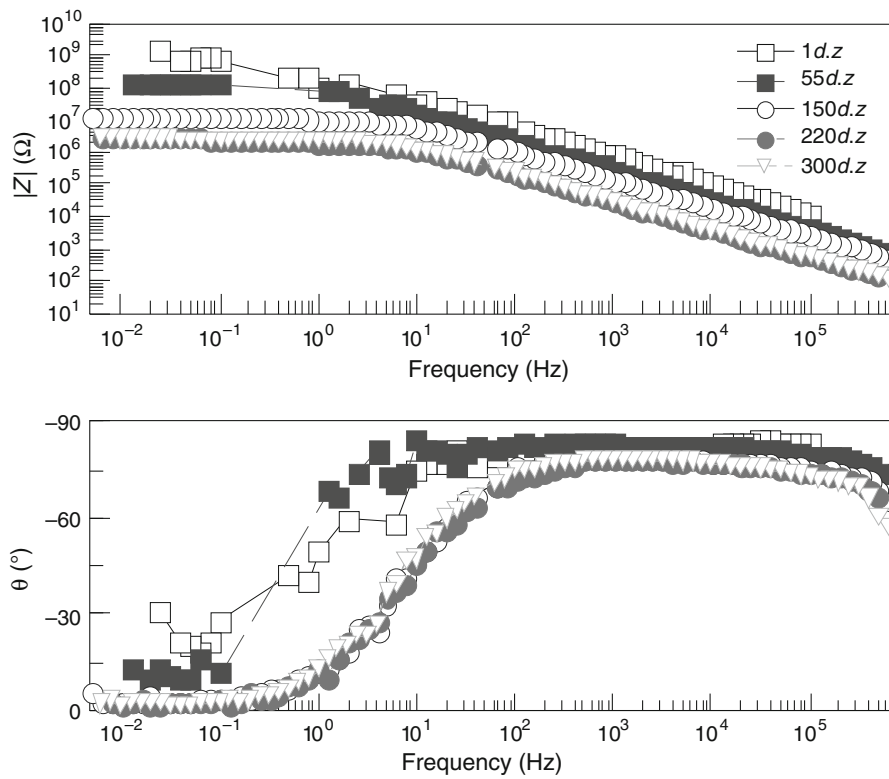


Fig. 5: Bode plots for paint 3 immersed in 3% NaCl solution

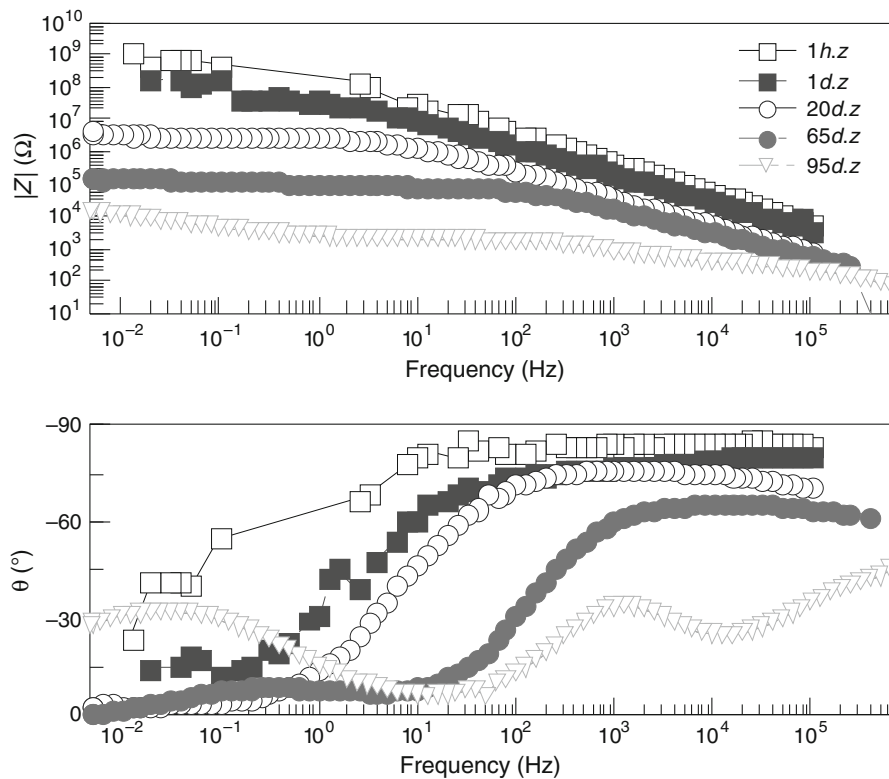


Fig. 6: Bode plots for paint 4 immersed in 3% NaCl solution

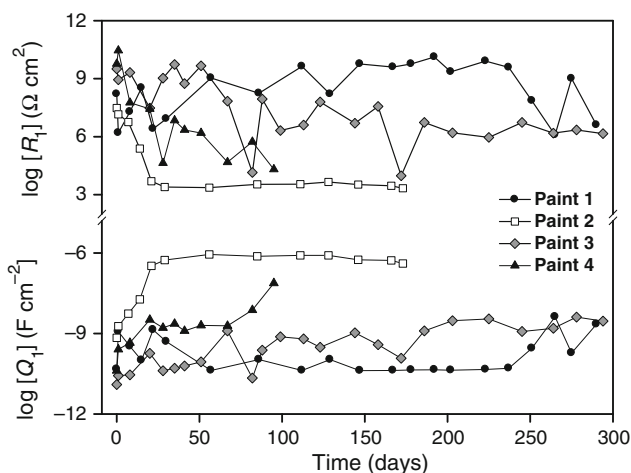


Fig. 7: Fitting parameters (R_1 and Q_1) of coated steel immersed in 3% NaCl solution

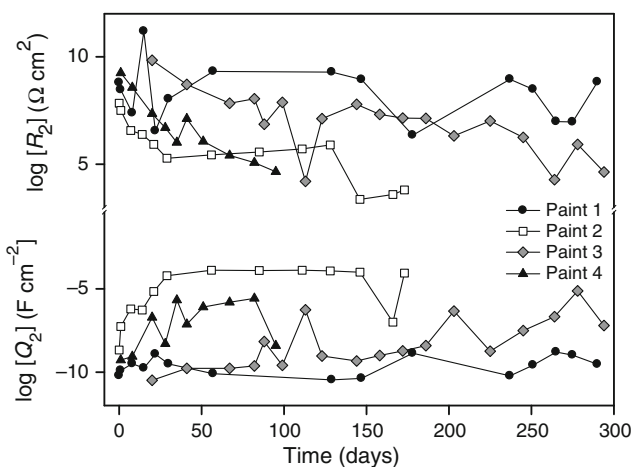


Fig. 8: Fitting parameters (R_2 and Q_2) of coated steel immersed in 3% NaCl solution

to the electrochemical double-layer capacitance of bare steel, are indicative of a total loss of paint barrier properties and delamination at the steel/paint film interface.

As can be seen in Fig. 8, the parameters associated with the faradaic process, R_2 - Q_2 , showed an important inhibition of the corrosion process in the case of paints 1 and 3. It is perceptible that R_2 ranged between 10^7 to $10^{10} \Omega \text{ cm}^2$ for these paints during, approximately, all the test period. This fact was attributed to the existence of an almost negligible electrochemical active area due to the initial steel passivation provided for the soluble phosphate species combined with the less important but also effective barrier effect afforded by the paint. The charge transfer resistance of paints 2 and 4 was some orders of magnitude lower than that of the above-mentioned paints, revealing a significant

progress of the corrosion process which, in turn, was originated by the low phosphate content and the poor anticorrosive behavior of sodium benzoate.

The capacitance of the electrochemical double layer (Q_2), coupled to the charge transfer resistance (R_2), remained between 10^{-8} and $10^{-10} \text{ F cm}^{-2}$ for paints 1 and 3; such a behavior confirmed the assumptions made to interpret R_2 (Fig. 8). On the contrary, the rest of the painted samples showed rather low Q_2 values after few days of immersion due to the progress of corrosion process associated with a large electrochemically active area.

The oscillating behavior of R_2 - Q_2 values could be attributed to dynamic changes in the surface covering degree with a protective layer of corrosion products.

Conclusions

1. Soluble anticorrosive additives could improve paints anticorrosive performance if they are selected adequately.
2. Sodium phosphate and sodium polyphosphate could improve the anticorrosive performance of alkyd paint formulations with reduced zinc phosphate contents.
3. The electrochemical response of painted panels indicated that initial steel passivation was achieved when suitable additives were employed in combination with zinc phosphate.
4. There was good correlation between salt spray tests, corrosion potential measurements, and EIS test.
5. The most interesting feature is that soluble additives allowed for the reduction of the zinc phosphate content in anticorrosive paints to a third of the recommended value without diminishing paint performance. As a consequence, more cost-effective paints could be formulated with less environmental impact.

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