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Remarks on the formulation of water-borne primers and their performance assessed by EIS☆

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ABSTRACT

In this work the effect of several constituents on the performance of water-borne anticorrosive primers was investigated. The behaviour of four resins (acrylic, styrene-acrylate, alkyd and epoxy-ester) was compared with their respective primers. The acrylic formulation was further used to investigate the influence of the pigment volume concentration (PVC), type and quantity of inert pigments and fillers, and anticorrosive pigments. The corrosion protection was assessed by electrochemical impedance spectroscopy (EIS) with samples immersed in 3 % NaCl aqueous solution. The primers presented very low barrier properties but those incorporating anticorrosive pigments showed high charge transfer resistance. Good results were obtained in natural weathering tests and when the primers integrated a paint scheme with a topcoat.

1. Introduction

Modern paints are highly effective in extending the durability of metal structures exposed to various environments [1–3]. The most reliable systems are solvent-borne, formulated with synthetic resins, which are responsible for most of the paint properties, including adhesion, as well as mechanical, chemical, and weathering resistances. The corrosion protection of metal substrates is further enhanced by the inclusion of anticorrosive pigments.

Most of the best performing systems had to be reformulated to comply with governmental regulation due to health and environmental concerns. Red lead, zinc yellow, and other chromate-based pigments that were used for decades [4,5] have been replaced by a variety of synthetic phosphates, primarily zinc phosphate with and without modifications, and by cation exchange silicas [5–7]. The traditional solvent-borne systems undergone changes to decrease or replace their volatile organic compounds (VOCs) [8–10]. Nowadays powder and high solid coatings are good alternatives in industrial applications [11,12] whereas water-borne paints also found a place in the *do-it-yourself* and home markets [13,14].

For many applications, water-borne paints are the main substitutes for the traditional products [3,15–18]. Their advantages include a low VOC content, reduced odour, non-flammability and easy cleanup with just water. Additionally, the rheology of the water-borne systems can be engineered to imitate the well-established applicability and processability of the solvent-borne systems. The resins are designed to be dispersed, emulsified or dilutable in water. However, the polarity of water complicates formulation, requiring a variety of additives to enhance paint performance. Many additives, such as wetting and dispersing agents, defoamers, thickeners, and rheology modifiers, are hydrophilic or surfactant-like, which can increase water sensitivity. These additives remain in the dry film, potentially facilitating water ingress and significantly increasing the total water absorption of the paint film, thereby compromising its protective properties.

This study investigated the impact of various formulation constituents on the anticorrosive performance of water-borne primers. Initially, the protective behaviour of four different resin types was compared to primers prepared according to manufacturer-recommended formulations. Subsequently, one formulation was modified to explore the effects of pigment volume concentration (PVC), as well as the type and quantity of inert pigments, fillers (extenders), and anticorrosive pigments. Corrosion protection was evaluated using electrochemical impedance spectroscopy (EIS), and the performance predicted by EIS was compared with results from natural weathering tests.

2. Experimental

2.1. Paint formulations

The samples investigated in this work are summarised in Fig. 1.

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a) Resins

Four water-borne resins were studied: an acrylic dispersion, a styrene-acrylate dispersion, an epoxy ester emulsion and an alkyd emulsion. The resins were applied to carbon steel substrates with a spiral applicator. The emulsions were applied as received while for the dispersions the mixture in Table 1 was necessary to achieve a non-defective continuous film.

b) Primers

Primers were produced with the above resins following formulations recommended by the resin manufacturers. The formulations are presented in the Supplementary Material together with the lists of constituents.

c) Effect of the pigment volume concentration (PVC)

PVC is the ratio of the volume of pigments (and fillers) to the total volume of the paint film. To study the influence of the PVC, two primers were manufactured based on the acrylic formulation, one with PVC = 10 % and the other with PVC = 50 %. The volume proportion between the pigments and fillers was kept unchanged. From the mixture between the two paints, a series of primers was prepared with PVC between 10 and 50 %.

d) Influence of inert pigments and fillers (extenders)

In order to observe the influence of inert pigments and fillers, the acrylic formulation was modified, and three primers were manufactured with PVC = 25 %, each with only one of the following constituents: iron oxide, talc, and barite. A mixture of the three with the same volume proportion (33 %/33 %/33 %) was also prepared. No anticorrosive pigment was incorporated into these primers.

e) Influence of anticorrosive pigments

To evaluate the performance of non-toxic anticorrosive pigments as alternatives to traditional ones (*e.g.*, red lead and chromates), primers with PVC of 25 % and 45 % solids by mass were produced based on the acrylic formulation. Three anticorrosive pigments were tested: zinc phosphate (ZP), amorphous silica with calcium cation exchange capacity (ES), and Zn/Sr/Ca phosphosilicate (PS). The pigments were incorporated in varying amounts, around the values recommended by the manufacturers: 6 %, 9 %, and 12 % for ZP; 2 %, 5 %, and 7 % for ES; and 2 %, 4 %, 6 %, and 10 % for PS. A direct comparison can be made for primers with anticorrosive pigments close to 6 %. In each case, the anticorrosive pigment replaced part of the inert pigments maintaining a constant PVC. Adjustments were also made to the proportions of resin, pigments, and fillers to ensure that, in addition to maintaining the PVC, the overall paint solids content and the volumetric ratios between talc, barite, and iron oxide remained constant.

Table 1
Mixture for obtaining a good film from the aqueous dispersion resins.

Constituent	Parts by weight
Resin (acrylic or styrene-acrylate)	100
Coalescing solvent (butylglycol)	5
Defoamer 1	1
Flash-Rust inhibitor (15 % $NaNO_2$ in water)	5

2.2. Paint fabrication

For each primer 1 kg of product was fabricated. The pigments dispersion was made with a propeller disperser at a peripheral rotation speed of 5–8 ms^{-1} for 15–20 min. In all cases the degree of pigment dispersion was around 6 in the Hegman scale. The let-down was done with the same disperser, but at a slower speed (3 ms^{-1}), for 10–15 min, adding the paste with the pigments to the resin followed by the successive addition of the other constituents. Quality control parameters (pH, degree of pigment dispersion, density, viscosity and solids content) were measured at the end of fabrication and in the following day. Variations in the viscosity and stability of the paint were monitored for a few weeks.

2.3. Paint application

The primers were applied to 0.8 × 102 × 152 mm^3 Q-Panel S-46 SAE 1010 low carbon cold-rolled steel panels (Q-Panel Company, Cleveland, Ohio, USA) using a conventional spray-gun system. The panels were previously abraded and cleaned with acetone. The coatings dried in a controlled environment (20 °C, 55 % relative humidity) for 7 days. The average thickness of the dry film was measured with a Elcometer 456 coating thickness gauge and was 50 ± 5 μm, determined after seven days, in a series of three measurements in fifteen different locations of each panel.

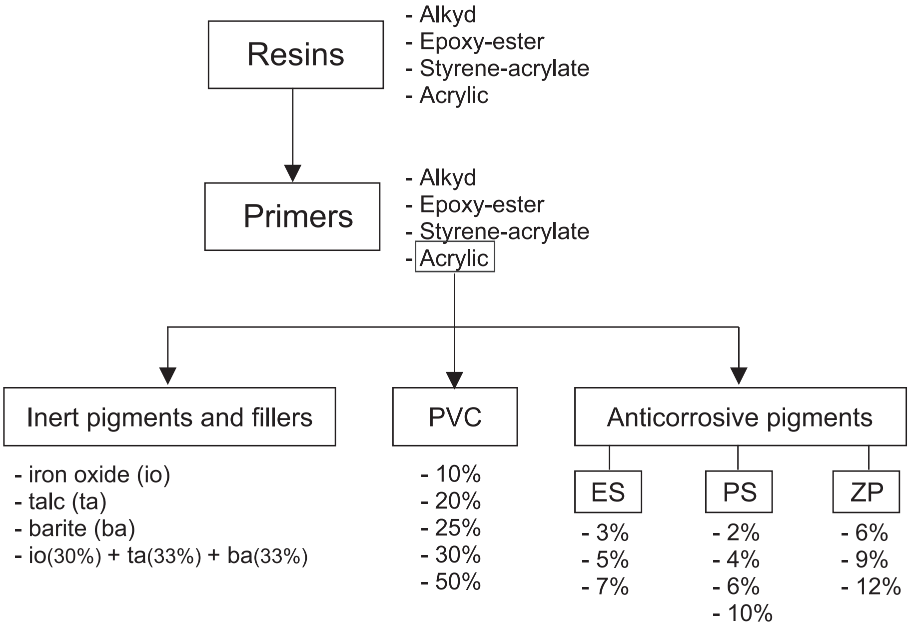

Fig. 1. Summary of samples tested in this work.

2.4. *Electrochemical impedance spectroscopy*

The electrochemical cells for the impedance measurements were assembled by gluing polymethyl methacrylate tubes to the painted panels with epoxy glue. The tubes were 7 cm high and had an internal area of 10.2 cm^2. This was the area of the panel exposed to the test solution (working electrode). The tubes functioned as reservoirs, which were filled with 3 % NaCl aqueous solution (Merck, p.a.). A Ag|AgCl|1 M NaCl reference electrode and a platinum counter electrode completed the 3-electrode set-up. The cells were introduced into a Faraday cage

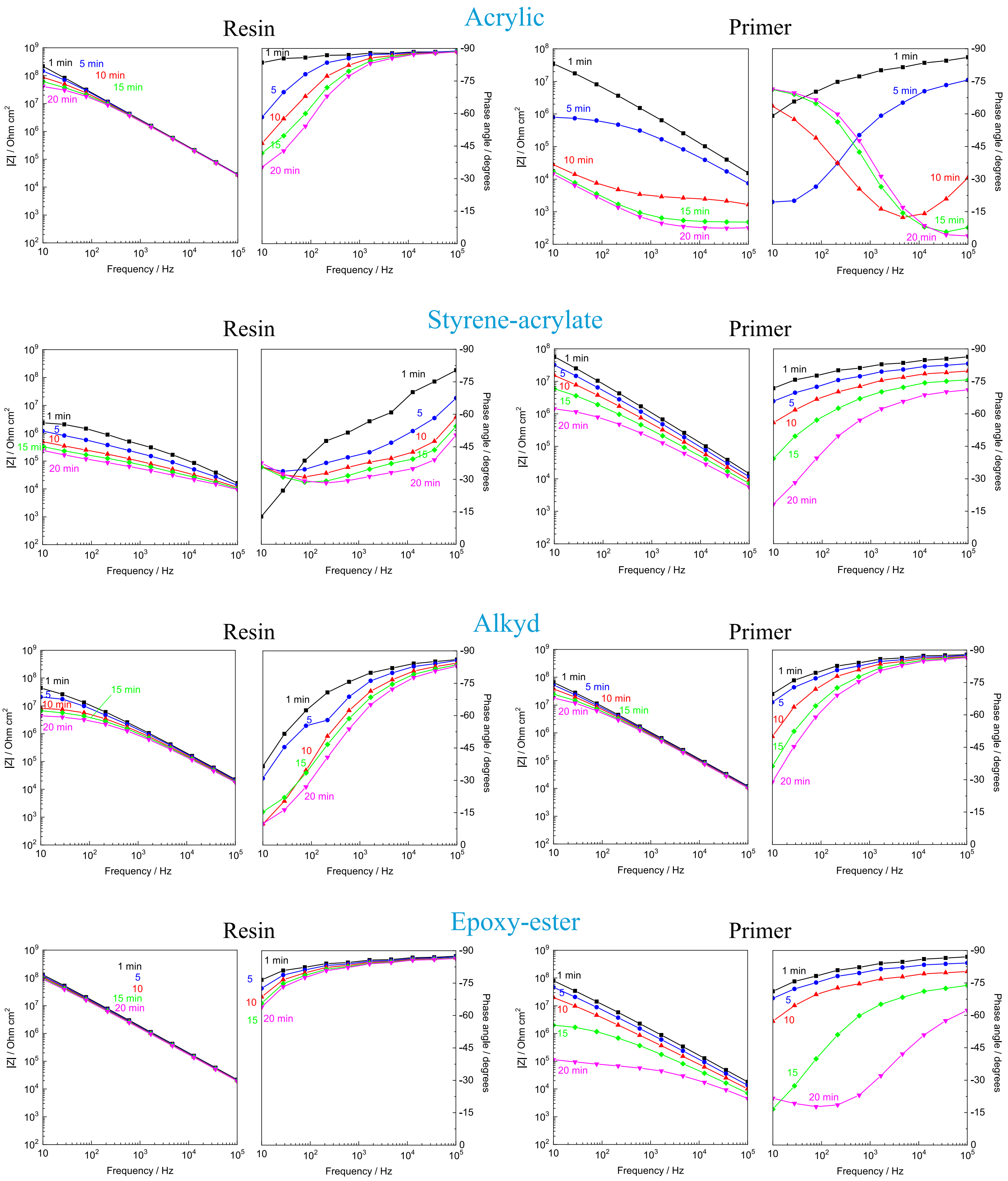

Fig. 2. Bode plots depicting the impedance response of steel panels coated with aqueous resins or primers, during the first 20 min of immersion in 3 % NaCl.

and connected to an Autolab PGSTAT20 potentiostat/galvanostat (Eco Chemie, The Netherlands) coupled with an Autolab FRA2 frequency response analyser module. The system was controlled by the FRA 2 program.

The measurements were made at the open circuit potential (OCP) with a sinusoidal potential of 10 mV_{rms}, sweeping frequencies from 100 kHz to 1 or 10 mHz and recording 7 frequencies for decade with logarithmic distribution.

3. Results

3.1. Resins and primers

This study began by evaluating the protective performance of four water-borne resins and their corresponding primers. Fig. 2 presents the Bode plots of the impedance response, measured every 5 min during the first 20 min of immersion in a 3 % NaCl solution. The spectra were obtained over a narrow frequency range with a limited number of points to enable rapid data acquisition. This approach was necessary to capture the rapid transition observed in most samples, from high impedance with a capacitive response to low impedance with a resistive response.

An exception was noted for the epoxy-ester resin, which exhibited an almost purely capacitive behaviour during the initial minutes of immersion. Similarly, the acrylic resin displayed a capacitive response at the start, but a resistive plateau gradually appeared at lower frequencies. This resistive plateau was even more evident in the alkyd resin. In contrast, the styrene-acrylate resin showed a much faster impedance decline, with response from the substrate already in the first minutes of exposure. The primers formulated with these resins presented varying behaviour. The styrene-acrylate and alkyd primers outperformed their corresponding binders, displaying higher impedance values and slower rates of change over time. Conversely, the acrylic and epoxy-ester primers showed the opposite trend, with weaker performance compared to their respective binders. The epoxy-ester primer is in fact a hybrid system because it also contains a styrene-acrylate resin added to improve the flow properties and hardness. This addition seems to compromise the barrier properties provided by the epoxy-ester resin.

The acrylic primer demonstrated a rapid evolution in its impedance response. Initially, it exhibited capacitive behaviour during the first minute of immersion. By the fifth minute, the response had transitioned to a combination of capacitive behaviour at higher frequencies and resistive behaviour at lower frequencies. After 10 min, the behaviour shifted again, becoming primarily resistive at higher frequencies and capacitive at lower frequencies. This progression reflects a rapid decline in the primer's impedance, indicating a significant loss of its barrier properties.

The impedance of the resins and primers after three days of immersion is shown in Fig. 3. The epoxy-ester and alkyd resins maintained high impedance, with the paint film capacitance (C_f) dominating at higher frequencies, and the pore film resistance (R_{pore}) –the resistance of the solution within the pores and defects of the paint film – appearing at intermediate and lower frequencies. No evidence of substrate activity was detected.

In contrast, the dispersions (acrylic and styrene-acrylate resins) displayed poorer performance, with the pore film resistance appearing at higher frequencies. This resistance was surprisingly low and could be mistaken for R_s, the resistance of the bulk solution between the working electrode (WE, the sample) and the reference electrode (RE). In these experiments, R_s was consistently around 14 Ohm cm^2, as seen in the spectrum of bare steel in Fig. 2 a) and remained relatively unchanged across experiments since the same 3 % NaCl solution was used, and the distance between the RE and WE was kept constant.

The capacitive response observed at middle and lower frequencies corresponded to the double-layer capacitance at the steel surface exposed at the bottom of pores and defects or in areas where the paint had delaminated. Among the primers, only the alkyd resin demonstrated good performance. The inclusion of styrene-acrylic resin in the epoxy-ester primer decreased its barrier properties. Over longer immersion times, the impedance response of all systems showed no significant differences, as the impedance decreased rapidly during the initial days of immersion.

3.2. Effect of the pigments and fillers

Next, to analyse the impact of pigments and fillers on anticorrosive performance, the acrylic formulation was modified by varying the

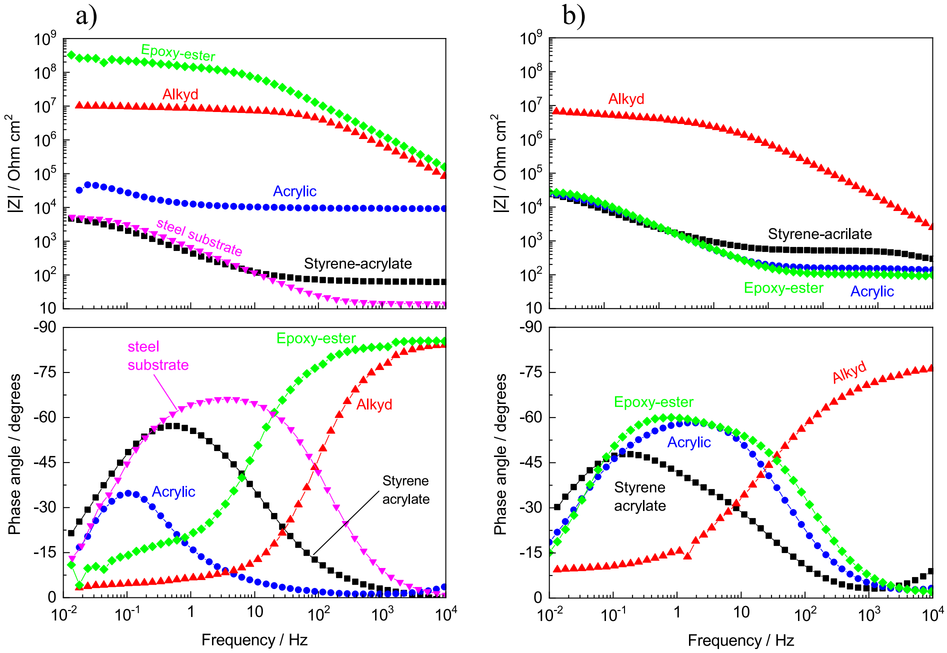

Fig. 3. Bode plots of the impedance measured on steel panels coated with aqueous a) resins or b) primers, after 3 days of immersion in 3 % NaCl. The spectrum of the bare steel substrate was measured after 3 h of immersion.

pigment volume concentration (PVC) and the type and quantity of inert pigments and fillers. The corresponding impedance plots are presented in Fig. S1 (Supplementary Material). Adjusting the PVC from 10 % to 50 %, or the type and quantity of inert pigments and fillers resulted in primers with R_{pore} ranging from 100 to 1000 Ohm cm^2, lower than the value for the binder alone. The impedance at low frequencies lied in the interval 2–10 kΩ cm^2, showing no improvement in performance. Typically, the barrier properties of a paint improve as pigment content increases, up to the critical pigment volume concentration (CPVC). At this point, the binder is just sufficient to fill the spaces between pigment particles. Beyond this critical concentration, the paint becomes porous and loses its barrier characteristics [19,20]. In this study, the pore resistance of the film didn't follow the trend. R_{pore} decreased steadily as the pigment volume increased.

Primers with a PVC of 25 % were formulated using different inert pigments and fillers: iron oxide with spherical particles approximately 0.3 μm in diameter, talc with a lamellar shape and an average size of 5 μm, and barite with a granular form and a mean size of 6 μm. The best performance, reflected in greater R_{pore} and higher impedance at low frequencies, was achieved by the primer containing lamellar particles. The poorest results were observed with the primer incorporating only the small spherical particles.

These findings can be attributed to the structural influence of lamellar particles, which create a longer and more tortuous path for water and ions to traverse before reaching the metallic surface. Altering the mineral constituents of the primer did not significantly impact the performance of the acrylic formulation. However, the addition of anticorrosive pigments markedly changed the impedance response of the primers.

3.3. Effect of anticorrosive pigments

Fig. 4 shows the impedance response of acrylic primers containing different anticorrosive pigments after three days of immersion. While the barrier properties remained low ($R_{pore} \approx 100$ Ohm cm^2), higher impedance values were observed at intermediate and low frequencies, where the substrate's signal dominates. The primer with exchange silica (ES) exhibited a response similar to previous systems, characterized by a single time constant but with a higher low-frequency impedance. The differences between loading levels of 3–7 % were minimal.

In contrast, the primers containing Zn, Sr, and Ca phosphosilicate (PS) and zinc phosphate (ZP) displayed significantly higher impedance and two distinct time constants at intermediate frequencies, one attributed to the formation of a surface layer and the other the corrosion process. For primers with PS, the impedance increased proportionally with the amount of incorporated inhibitor. For ZP, however, the best performance was observed at the lower loading level (6 %), with impedance decreasing as the pigment concentration increased. Fig. 4 d) shows the surface of the primer containing 6 % zinc phosphate after three days of immersion. A few blisters are visible, and partial removal of the paint revealed corroded spots only beneath the blistered areas.

3.4. Numerical fitting with equivalent electrical circuits

The impedance response was numerically analysed using suitable equivalent electrical circuits. Fig. 5 illustrates the sequence of equivalent

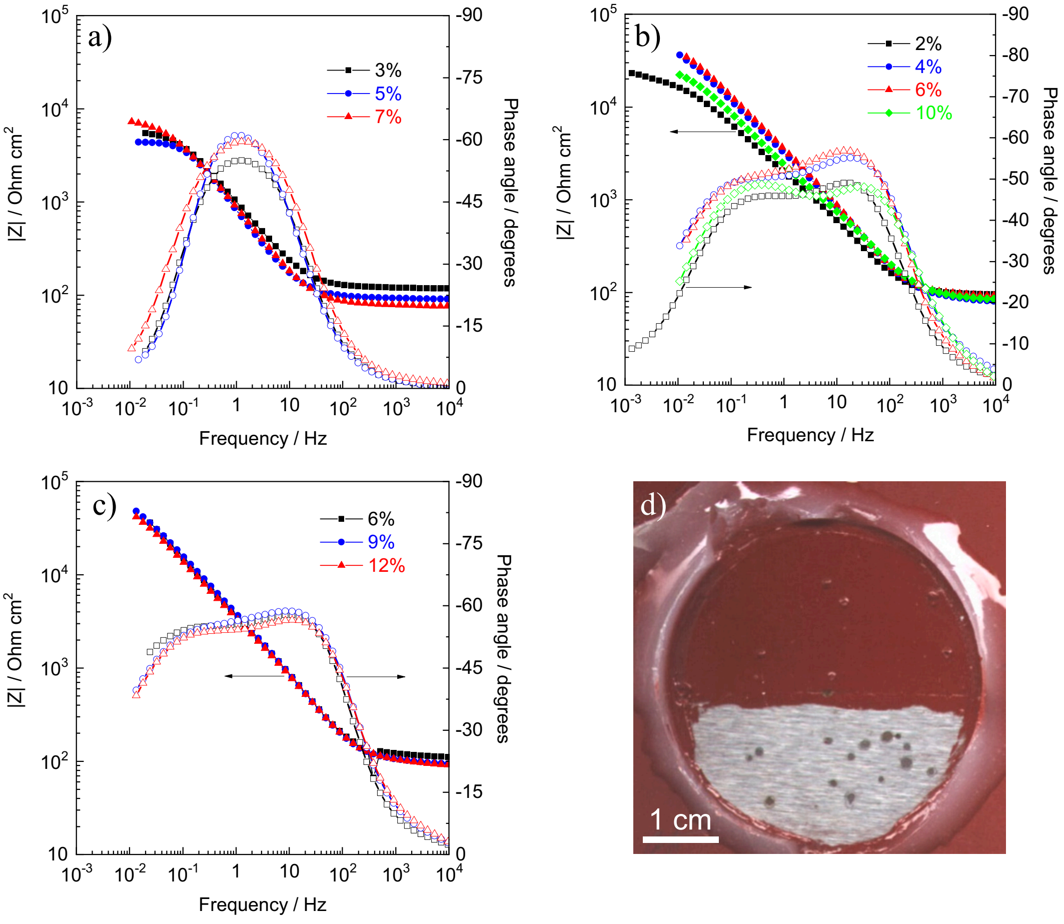

Fig. 4. Bode plots illustrating the impedance response of acrylic primers with various anticorrosive pigments after 3 days of immersion in 3 % NaCl: a) calcium exchange silica (3 %, 5 %, and 7 % by weight), b) zinc, strontium, and calcium phosphosilicate (2 %, 4 %, 6 %, and 10 % by weight), c) zinc phosphate (6 %, 9 %, and 12 % by weight), d) Visual appearance of the acrylic primer containing 6 % zinc phosphate after 3 days of immersion.

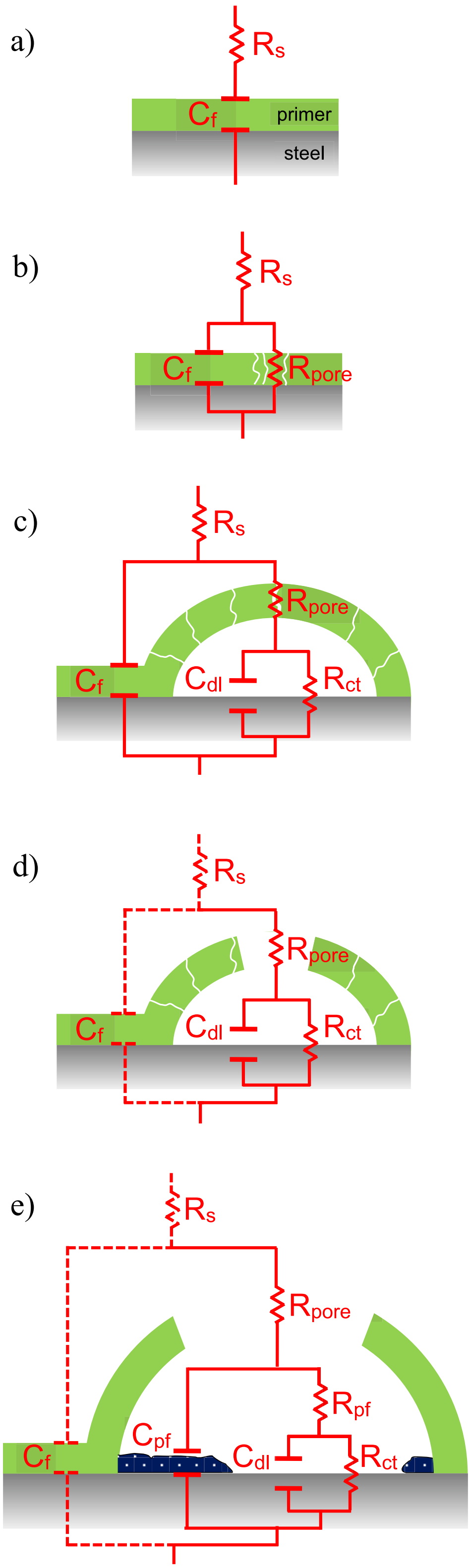

Fig. 5. Equivalent electrical circuits used to interpret the impedance response of painted steel panels: a) intact film exhibiting a purely capacitive response, b) first pores with conductive pathways through the coating, c) corrosion occurring beneath the paint film, d) highly porous paint film where the time constant associated with the coating is no longer detectable, e) appearance of a intermediate time constant resulting from the deposition of corrosion products, eventually with protective properties.

circuits that describe the evolution of impedance response of a coated metal during its exposure to an aqueous corrosive medium [21,22]. Circuit a) represents the purely capacitive response measured when the coating behaves as a simple dielectric material. Here, C_f denotes the capacitance of the organic film applied on steel. If the impedance is sufficiently high, the solution resistance, R_s, is not visible in the spectrum. An example of this stage is seen in the spectra of the epoxy-ester resin in Fig. 2. As ions from the environment enter the paint film, opening conductive pathways to the substrate, a resistive response emerges at lower frequencies, corresponding to the resistance of the solution within the pores and defects (R_{pore}). This response requires the use of Circuit b). Examples include the spectra of the alkyd resin and primer, as well as the acrylic resin, and the styrene-acrylate and epoxy-ester primers shown in Fig. 2. As the number and size of these pathways increase, R_{pore} decreases. In time, the solution reaches the metal substrate at the bottom of the pores, leading to the formation of an interfacial double layer (C_{dl}). The electrochemical dissolution of steel can now start and an associated resistance to charge transfer (R_{ct}) appears. Both C_{dl} and R_{ct} give rise to a new time constant in the impedance spectrum, which becomes described by Circuit c). In this study, the coatings were highly permeable to water and ions, causing R_{pore} to drop rapidly to values close to R_s, and C_f to become undetectable. Circuit d) represents this condition, exemplified by the spectra of the acrylic and styrene-acrylate resins and primers, as well as the epoxy-ester primer shown in Fig. 3. In some cases, such as those in Figs. 4 b) and c), a layer of corrosion products or a protective surface layer (passive film) promoted by the anticorrosive pigments introduce an additional time constant (C_{pf} and R_{pf}), represented by Circuit e).

The spectra were numerically fitted with the ZView software (Scribner Associates, USA), using constant phase elements (CPEs) in place of capacitances. The Brug equation [23,24] was used to convert the CPE values to capacitances. The values of C_{dl} and R_{ct} for primers containing different pigments and fillers are presented in Fig. 6. The C_f could not be measured, and the R_{pore} values were consistently low and with minimal variation across samples, as presented above. The charge transfer resistance R_{ct} of primers without anticorrosive pigments, as well as the primer containing exchange silica, was similar, about one order of magnitude higher than that of the bare substrate. In contrast, primers containing phosphosilicate (PS) and zinc phosphate (ZP) demonstrated significantly higher R_{ct}, confirming the beneficial effects of their addition. Optimal performance for PS was observed at intermediate loading levels, whereas ZP performed best at the lowest concentration tested (6 %). At higher ZP concentrations, R_{ct} decreased. The variation of C_{dl} was almost inverse of the verified for R_{ct}. C_{dl} is proportional to the delaminated area of the paint film, and higher values denote higher delamination. As expected, the primers containing anticorrosive pigments, particularly ZP and PS, exhibited the best results.

A common feature of these water-borne primers was their very low barrier properties. Modifying the pigmentation did not yield substantial improvements. The results suggest that additives such as wetting and dispersing agents, stabilizers, and thickeners significantly influence performance. Their hydrophilic nature renders the films prone to water absorption. Additional experiments confirmed this effect: primers formulated with higher amounts of these additives experienced a faster drop in impedance, further demonstrating their detrimental impact.

3.5. *Effect of drying and atmospheric exposure*

After completing the EIS measurements and removing the solution, the samples exhibited low hardness and weak adhesion to the substrate. However, these properties were restored after the film dried, which required only a few hours. The results in Fig. 2 demonstrated a rapid water absorption. These last observations point to an equally fast desorption process. This prompted additional experiments to evaluate the primer's performance under alternating immersion and drying cycles. Fig. 7 illustrates the variation in C_f and R_{pore} for the acrylic primer

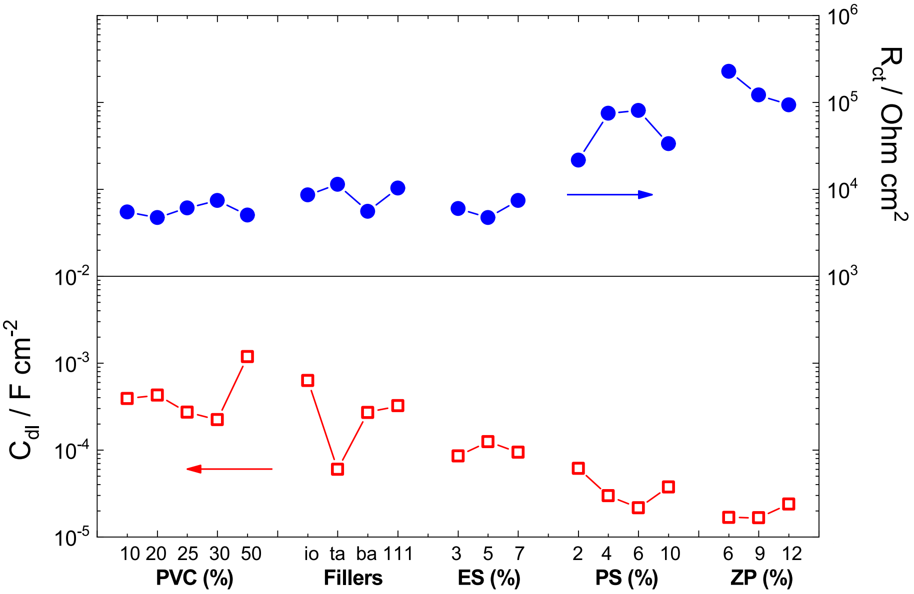

Fig. 6. R_{ct} and C_{dl} values of various acrylic primer formulations after 3 days of immersion in 3 % NaCl: pigment volume concentration (PVC), iron oxide (io), talc (ta), barite (ba) and a mixture of 33 vol% of iron oxide, talc and barite (111), exchange silica (ES, 3, 5 and 7 wt%), phosphosilicate (PS, 2, 4, 6 and 10 wt%) and zinc phosphate (ZP, 6, 9, 12 wt%).

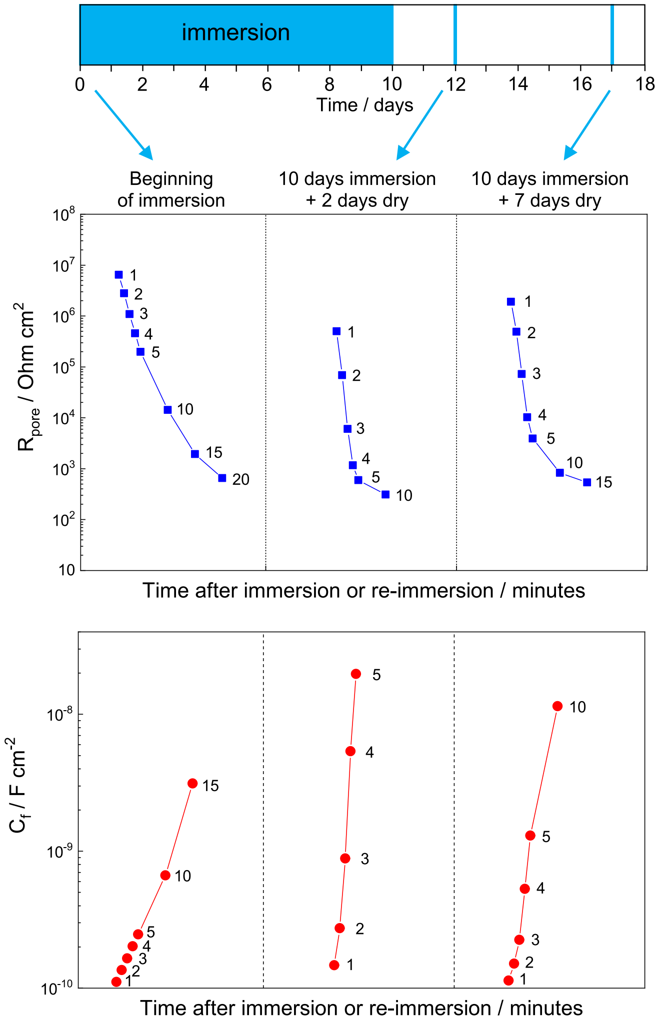

Fig. 7. Variation of pore resistance (R_{pore}) and film capacitance (C_f) in an acrylic primer in the beginning of immersion and after drying.

containing 6 % zinc phosphate in the first minutes of immersion at the three different moments. The first moment corresponds to the beginning of immersion. The second moment was measured after 10 days of immersion followed by 2 days of drying. The third moment corresponds to 7 days of drying after the initial 10 days of immersion. The results revealed a rapid decrease in pore resistance and a corresponding increase in paint capacitance during the initial exposure cycle. The behaviour and the values observed in the second and third stages were comparable to those of the initial immersion, indicating the primer's ability to absorb and desorb water efficiently and the reversibility of these processes. These results indicate that the primer might perform better in non-immersion conditions like atmospheric exposure.

To validate this hypothesis, steel panels were coated with the acrylic primer containing 6 % zinc phosphate and exposed outdoors for five years in an environment between rural and industrial. Areas of the panels were further coated with either a commercial water-borne acrylic topcoat or a commercial solvent-borne alkyd topcoat. Fig. 8 a) shows a panel after five years of exposure, while Fig. 8 b) presents the metal surface after removing the organic layer using 2-pyrrolidinone. For comparison, Fig. 8 c) depicts the uncoated backside of the steel panel. Despite its poor performance under immersion conditions—where blisters formed in less than three days—the primer exhibited significantly better results in outdoor exposure. After five years, the coated surface remained largely intact, with rust limited to the scratches left by adhesion testing. Notably, there was no delamination propagating from these scratches. Small blisters were visible across the surface, appearing as tiny dark spots in Fig. 8 b). When comparing the regions beneath the different topcoats, no discernible difference was observed between the area with the water-borne acrylic topcoat and the region with only the primer. However, the solvent-borne alkyd topcoat showed superior protection, with almost no visible corrosion, despite its poor adhesion to the primer. Fig. 8 c) shows the high level of corrosion in the uncoated back of the panel. It serves to better judge the performance of the water-borne primer. Although it performed poorly in immersion tests and had low impedance values, its real-world performance over five years of atmospheric exposure demonstrated good protective capabilities.

A final comment about the anticorrosive pigment used. Steel panels with a similar primer but without anticorrosive pigment exhibited higher level of rusting on the surface of both organic layer and substrate (See Fig. S2 in Supplementary Material). Thus, the good performance

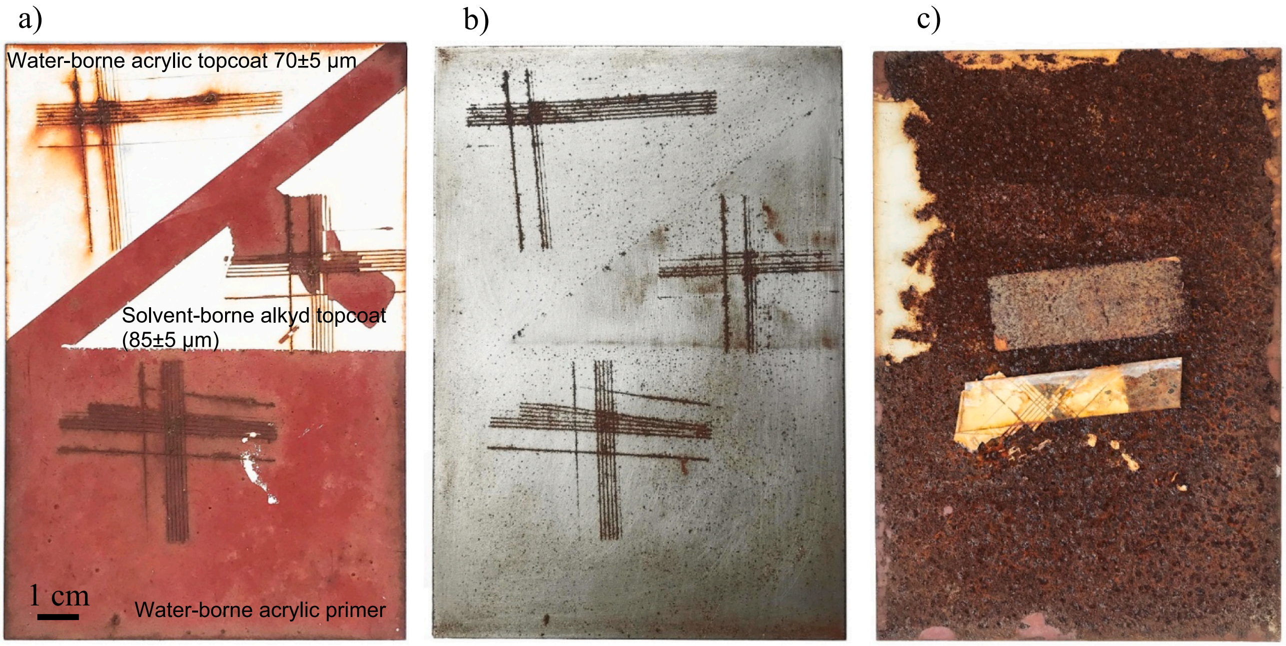

Fig. 8. a) Steel panel coated with acrylic primer (35 ± 5 μm) with 6 wt% zinc phosphate after 5 years of outdoor exposure, b) metal substrate after removing paint layer, c) unpainted backside of the steel panel.

observed during the outdoor exposure tests can be largely attributed to the presence of zinc phosphate in the formulation. The zinc phosphate employed in this study was a basic grade, with the particle surface modified only to facilitate its incorporation into water-borne systems. Advanced variants, such as mixtures and co-precipitated products, are available in the market and are designed to enhance solubility and

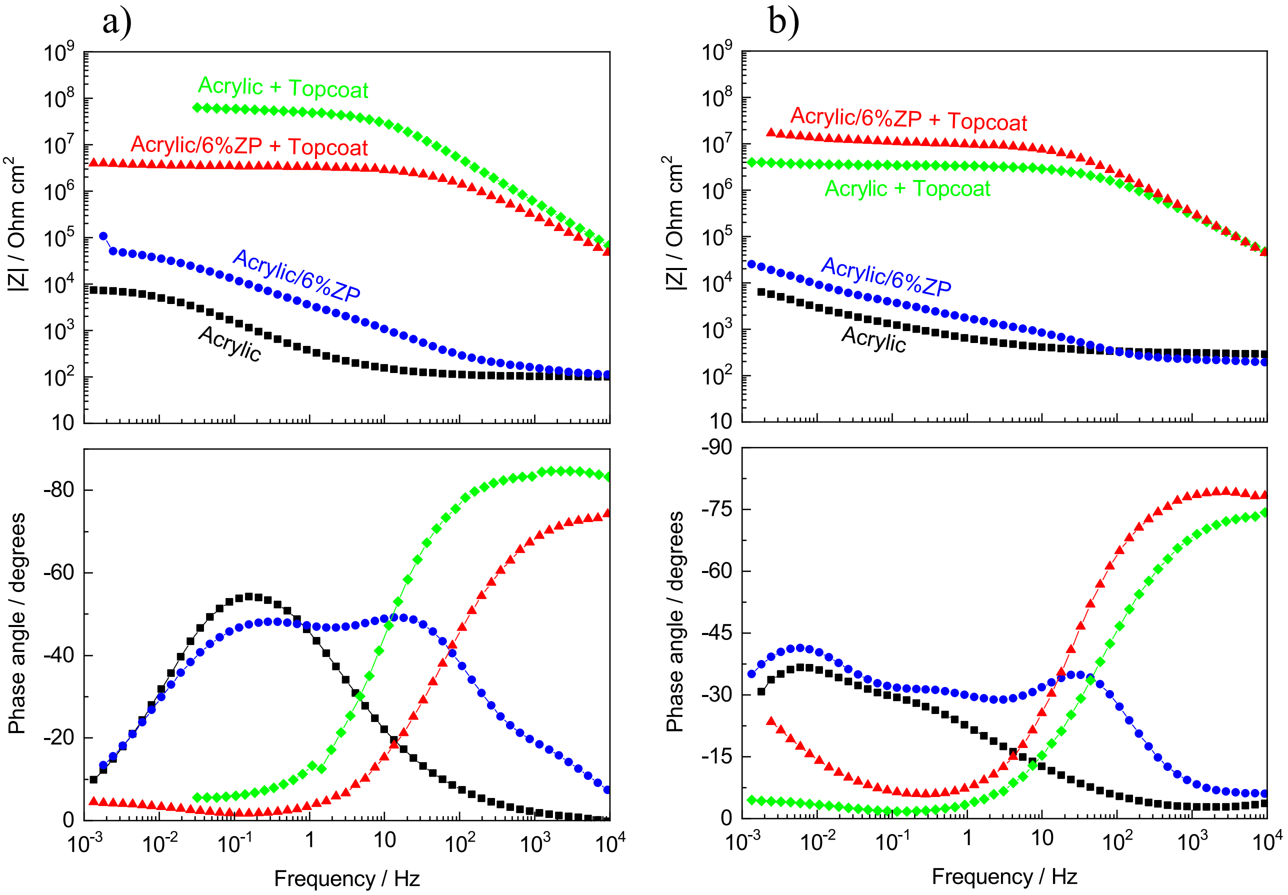

Fig. 9. Impedance response of an acrylic primer, with and without anticorrosive pigment (6 % ZP), in combination with an aqueous alkyd topcoat after (a) 3 days and (b) 30 days of immersion in 3 % NaCl.

efficacy. M.J. Austin [5] noted that these modifications improve the action of zinc phosphate in accelerated corrosion tests, such as salt spray tests, but they seem to provide no difference in cases of real exposure. This difference is likely due to the higher solubility of the modified pigments, which enables them to act more quickly, providing immediate protection in accelerated tests. In long-term real-world conditions, where the degradation processes occur more gradually, the simpler zinc phosphate appears to perform equally well.

3.6. Primer in paint schemes

Primers are not intended to function independently but rather to serve as a smooth, adherent base for a midcoat or topcoat. Consequently, their true performance is better assessed by evaluating a complete paint system that includes the primer and topcoat, which mirrors the actual conditions during service. The impedance of such systems with an aqueous alkyd topcoat is presented in Fig. 9. In these combinations, the impedance was significantly higher and remained high even after 30 days of immersion for both the acrylic primer with and without anticorrosive pigments. Interestingly, the system incorporating the primer without active pigments initially displayed the highest impedance. However, this value declined more rapidly over time compared to the system containing anticorrosive pigments. These results underline the importance of evaluating full paint schemes, as the presence of a topcoat can drastically improve overall performance. Additionally, the slower impedance decay of the system with anticorrosive pigments highlights their contribution to the long-term stability of the coating system.

4. Discussion

4.1. Sensitivity to water

This study began by comparing four water-borne resins and the anticorrosive primers formulated from them. In most cases, the impedance of films applied to steel substrates declined rapidly, with an even faster decrease observed in most primers. Modifying the mineral constituents of the acrylic formulation had minimal impact on performance. Talc, owing to its lamellar structure, slightly improved the barrier properties, but the effect was modest. While anticorrosive pigments did not enhance barrier properties, they significantly increased the charge transfer resistance.

The constituents of water-borne paints are inherently hydrophilic due to their need for water compatibility, rendering the dry films sensitive to moisture. These systems are engineered to emulate the application characteristics of solvent-borne paints, often through the use of specialized thickeners and rheology modifiers. However, it has long been argued that water-borne paints are fundamentally different systems, and efforts to replicate the rheology of solvent-borne formulations are misguided and a key factor hindering the progress of water-based technology [25]. Baking the dried films might be a potential method to mitigate the detrimental effects of their hydrophilic constituents.

These water-borne films exhibited both rapid water absorption and desorption, which can be advantageous in atmospheric conditions where rain alternates with drying periods. Notably, panels coated with the primer and exposed outdoors for five years demonstrated unexpectedly good corrosion protection, contrary to the low impedance results obtained in laboratory tests. The low barrier properties may be needed for the activation of anticorrosive pigments. In a complete paint system, the topcoat ensures the barrier effect, while the primer provides active pigments to inhibit corrosion.

4.2. EIS analysis

The impedance results revealed systems with rapid water absorption and a swift decline in barrier properties. These are characteristics typically associated with coatings offering poor protection. However, the primers performed significantly better in atmospheric exposure than predicted by the laboratory EIS experiments. This discrepancy highlights that permanent immersion may not have been the most appropriate testing medium for coatings intended for atmospheric conditions. As reminded by Appleman [26], any corrosion test involves four key elements: (i) the type of sample, (ii) the method of inducing degradation (test environment), (iii) the approach to degradation assessment, and (iv) the analysis and reporting of data. In this study, aspects (iii) and (iv), concerning the EIS methodology, were relatively straightforward. However, aspects (i) and (ii) require closer consideration. The sample preparation followed the standard practices for the intended application of these primers, but factors such as pre-treatment, coating thickness, and the number of layers can significantly change results.

More critically, the testing environment – constant immersion in 3 % aqueous NaCl – played a pivotal role. This medium is a standard for EIS testing and ranking coated metals but is primarily suited to marine coatings that remain submerged throughout their service life. For the primers examined in this study, which are highly water-sensitive and designed for atmospheric exposure, a cyclic testing regime would likely provide a more representative and accurate evaluation of their performance.

5. Conclusions

This study investigated four water-borne resins and anticorrosive primers formulated from them. Primers based on aqueous dispersions performed poorly during immersion in 3 % NaCl. Modifying a dispersion formulation by adjusting the PVC, as well as the type and quantity of pigments and fillers, resulted in only minor performance improvements. Upon initial immersion, the dispersion-based systems exhibited rapid water absorption and a swift decline in film pore resistance. Remarkably, after removal from immersion, these systems showed fast water desorption and recovery of film resistance and adhesion. The inclusion of anticorrosive pigments significantly increased charge transfer resistance, thereby enhancing corrosion resistance. Performance under natural weathering conditions far exceeded expectations based on EIS results. Additionally, the primers performed well when incorporated into a primer-topcoat system.

CRediT authorship contribution statement

A.C. Bastos: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.porgcoat.2025.109095.

Data availability

Data will be made available on request.

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