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Performance of coated steel systems exposed to different media
Part I. Painted galvanized steel

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Abstract

The performance of different pre-treated galvanized steel/primer/topcoat paint systems applied on hot-dip galvanized steel sheets has been studied. Each panel was pre-treated with 5% $Fe(NO_3)_3$ + 15% H_3PO_3 solution. After this step, the panels were coated either with acrylic (AC), alkyd (AK), vinyl (VL), epoxy base-solvent (ES) or epoxy-waterborne (EW) based corrosion-inhibiting primer using zinc molybdenum phosphate as anticorrosive pigment, and with commercially available alkyd topcoat paint. Experimental behavior of these panels under standardized salt spray chamber exposure or continuous immersion in 0.5 M NaCl, 0.5 M Na_2SO_4 or 0.25 M NaCl + 0.25 M Na_2SO_4 solutions was evaluated through periodical visual inspection (blistering and rusting degrees) and EIS measurements (corrosion evolution). Initial (dry) and final (wet) paint adhesion was also determined. EIS data has been interpreted and discussed in terms of the time dependence of the electrical (paint coating) and electrochemical (steel substrate) parameters associated with interfacial processes describing the metal/paint system deterioration. According to the electrochemical properties, visual inspection and standardized tests results, the painting systems designated as AK, ES, EW, and VL presented the best overall anticorrosive behavior under immersion conditions, but all samples failed when exposed to the salt spray chamber. System AC behaved very well in 0.25 M NaCl + 0.25 M Na_2SO_4 but failed in the other media. Adhesion changes outside the tested areas showed that under immersion conditions there was lateral diffusion. Good correlation between standardized and electrochemical tests results was also obtained.
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1. Introduction

Anticorrosive protection is highly important, because corrosion reduces the strength of structural materials and this destruction involves direct and indirect losses including problems related to human safety and facts concerning natural resources conservation. In the particular case of metals, their tendency to corrode depends upon factors such as the metal surface characteristics, the metal/protective film interface, the physical, electrical and electrochemical properties of this protective film and the environmental conditions at which the system is exposed. Besides, keeping in mind the human health protection and a number of strict governmental restrictions related with the use of toxic and/or pollutant products, paint formulators have to face troubles such as

replacing toxic pigments, binders, solvents, additives [1–3] and, at the same time, to satisfy the growing waterborne based paints demands.

When steel, a metal widely used as the main structural material in different facilities, is in contact with an aggressive ambient it can corrode. Therefore, in order to delay and/or to reduce the deteriorating action of strong natural or artificial corrosive media, a number of metallic and organic coatings have been developed.

Among the metallic coatings used to protect steel against corrosion, those based on Zn or its alloys applied under different (hot-dip, electrogalvanized, etc.) deposition conditions became the most important. This is not only due to cost reasons but also mainly to the fact that the Zn based layer is electrochemically more active than the substrate, therefore, it dissolves preferentially offering cathodic protection to steel. With the same aim, when a higher protection degree of these metallic surfaces is of concern, properly chosen painting

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systems can provide a more effective corrosion-inhibiting barrier and also better aesthetic appearance [4]. The mechanism by which an organic coating protects the substrate is complex and results from different factors acting together. Thus, the paint system permeability, a property directly related with the polymeric film composition and its capacity to develop a high barrier to water, ionic and oxygen diffusion after curing, plays an important role in the metallic substrate corrosion.

Some exposure conditions are so aggressive that both protective systems (metallic + organic coatings) must be applied to get longer effectiveness. Such combination, referred to as duplex system, has demonstrated a synergistic effect when its protective properties and those provided by each coating system taken separately are compared. This better corrosion protection is attributed to the double action afforded by the Zn layer (cathodic protection + blockage of its defects by the corrosion products), and also by the pigmented paint system (barrier effect + steel corrosion-inhibition) [5]. Besides, this duplex system requires less reconditioning and repairs of coating systems after transportation and assembly on building site.

The still unsolved paint delamination or blistering trouble, due to a bad bonding at the substrate/paint interface, depends upon the chemical nature and crosslinking degree of the polymer as well as the metal substrate and its surface treatment [6]. In principle, paint adhesion can be improved by providing the substrate with a pre-treatment layer, followed by applying a corrosion-inhibiting primer + intermediate and/or topcoat paints. In line with this definition, the primer is considered the critical element in most paint systems because it is mainly responsible for preserving the metallic state of the substrate, and it must also anchor the total paint coating to the steel. Most coatings adhere to metal via purely physical attractions (e.g. hydrogen bonds) that develop when two surfaces are brought closely together [7,8]. Paint vehicles with polar groups (−OH, −COOH, etc.) have good wetting properties and show excellent physical adhesion characteristics (epoxies, alkyds, oil paints, etc.). Much stronger chemically bonded adhesion is possible when the primer can actually react with the metal, as it is the case of several pre-treatments [9–12].

Paint life depends on several factors such as the metallic substrate, the selected paint system and the paint–substrate interface [13]. Paint selection is generally based on the aggressive medium properties; the metal treatment before painting has a substantial impact on the useful life of the selected system.

Despite the extrapolation of accelerated test results to the actual coatings performance in their service life is not linear, it can supply useful information related to the rate and form of the corrosion-inhibiting system degradation. In most cases, such information can help to improve the paint formulation and/or the painting scheme design. Consequently, in the present paper a comparative evaluation of the protective performance of five pre-treated galvanized steel/painting system arrangements is reported. The corrosion resistance of these samples was tested by exposure in a salt spray fog chamber (ASTM B-117/97), while replicates of the original samples were subjected to continuous immersion in 0.5 M NaCl (in order to simulate a marine environment), 0.5 M Na_2SO_4 (urban-industrial ambient) or 0.25 M NaCl + 0.25 M Na_2SO_4 solution. Before and at the end of the exposures, paint adhesion was measured by using the tape-test (ASTM D-3359/97), while the blistering and rusting degrees were classified according to ASTM D-714-87/00 and ASTM D-610/89 standards, respectively. Electrochemical impedance measurements to determine the paint film water permeability coefficient as well as changes in the electrical and electrochemical properties of each paint/galvanized steel system were also performed.

2. Experimental

Commercial-grade galvanized steel plates (15 cm × 8 cm × 0.2 cm) were used as the metallic substrate. They were degreased by immersion in 5% Na_2CO_3 solution, rinsed with distilled water to eliminate any possible surface contamination, and then pre-treated under controlled laboratory conditions with 5% $Fe(NO_3)_3$ + 15% H_3PO_4 solution.

The anticorrosive paints (Table 1) were formulated and prepared in the laboratory. According to the literature [14,15], the primers were formulated with 30% (v/v)

Table 1
Main characteristics of the paints formulation

Paint	Resin	Solvent	Plasticizer	Pigments		
				Anticorrosive	Filler	Hiding
Acrylic	Acrylic-styrene	Water	–	Zinc molybdenum phosphate	Talc, mica, barytes	TiO_2 (rutile)
Alkyd	Medium oil alkyd	White spirit/toluene 1:1 (v/v)	–	Zinc molybdenum phosphate	Talc, mica, barytes	TiO_2 (rutile)
Epoxy$_{solv}$	Epoxy-polyamide	Xylene/MIK/butoxyethanol 13:45:42 (v/v)	–	Zinc molybdenum phosphate	Talc, mica, barytes	TiO_2 (rutile)
Epoxy$_{aq}$	Bisphenol A + bisphenol F–polyamidoamine	Water	–	Zinc molybdenum phosphate	Talc, mica, barytes	TiO_2 (rutile)
Vinyl	Polyvinyl chloride–acetate copolymer	MIK/toluene 1:1 (v/v)	Tricresyl phosphate	Zinc molybdenum phosphate	Talc, mica, barytes	TiO_2 (rutile)

Table 2
Designation and dried film thickness of the complete tested painting systems

Painting system	Anticorrosive primer	Topcoat paint	Total thickness (μm)
AC	Acrylic	Alkyd	135 ± 10
AK	Alkyd	Alkyd	120 ± 10
ES	Epoxy$_{solv}$	Alkyd	119 ± 10
EW	Epoxy$_{aq}$	Alkyd	135 ± 10
VL	Vinyl	Alkyd	110 ± 10

of phosphate anticorrosive pigment on the total pigment content, which was completed with TiO_2 (3.5%), $BaSO_4$ (3.7%), talc (3.4%) and mica (7.0%). This last pigment was incorporated in order to improve the paint barrier effect as well as to reduce the flush rusting degree caused by the waterborne paints [16]. In the water or solvent base paints the PVC was 20 and 40%, respectively. The topcoat paint was of commercial-grade type.

Because of the laboratory scale of primer paint elaboration, it was preferred to apply it by brushing; trying to maintain the same brushing application conditions for all the samples. So, after the painting systems application, the painted plates were placed in a dessicator cabinet up to complete drying. Dry film thickness (Table 2) was measured with an Elcometer 300 coating thickness gauge, using a bare sanded plate and standards of known thickness as reference.

2.1. Standardized tests

To check reproducibility, triplicate specimens of each painting system with their edges masked with a thick wax based coating were tested in a salt spray cabinet for 97 days according to ASTM B-117/97 standard. During the test, the specimen position within the cabinet was changed after each periodical (13 days) visual inspection and EIS measurement so as to neglect the possibility that the position might affect the results. The metal/paint adhesion degree on every painted steel sample was measured before and at the end of the tests according to ASTM D-3359/97 (tape-test) standard, while at the end of the tests the size and frequency of blisters as well as the rusting degree were evaluated according to ASTM D-714-87/00 and ASTM D-610/89 standards, respectively.

2.2. Electrochemical measurements

For the impedance measurements carried out before the accelerated tests initiation, and then periodically together with the visual inspections, a cylindrical clamp-on acrylic (polymethyl methacrylate) cell was positioned on the painted panel by an O-ring defining a surface area of 15.9 cm^2. An aperture in the top of this three electrodes electrochemical cell contained a Pt-Rh mesh counter-electrode with negligible impedance, oriented parallel to the working electrode (painted metal surface) and a glass-linear saturated calomel

tipped reference electrode (SCE $= +0.244$ V versus SHE) referred to as in the text, which was positioned together with the counter-electrode close to the exposed painted steel surface panel. The electrolyte was 0.5 M NaCl, 0.5 M Na_2SO_4 or 0.25 M $NaCl + 0.25$ M Na_2SO_4 solution, at pH 6.5. When samples exposed to the salt fog chamber were subjected to the periodical electrochemical measurements, these were performed after 1 h of wetting with the electrolyte formed by dissolving in distilled water the salts deposited on the sample surface. Impedance spectra were obtained from a Solartron 1255 FRA coupled to a Solartron EI 1286 and a PC, being the measurement system controlled by the Zplot® software. Impedance spectra collected starting at 10^5 Hz and going to 10 mHz were analyzed and interpreted on the basis of equivalent electrical circuits optimizing the values of the circuit parameters by using the Boukamp's program [17].

The value of the water permeability coefficient for each painted galvanized steel/solution system was also determined. The dielectric capacitance evolution was measured as a function of the immersion time until a constant value was attained. Such measurements were performed with the same equipment arrangement described above, in the potentiostatic mode and at a frequency of 2×10^4 Hz. The water permeability, diffusion and solubility coefficients were obtained with the calculus method reported elsewhere [18].

All the electrochemical experiments were carried out at laboratory temperature (23 ± 2 °C) using a Faraday cage.

3. Experimental results and discussion

A general hypothesis claimed that the application of a pre-treatment containing phosphoric acid leads to the phosphatizing of galvanized steel surfaces, which improves both the substrate/primer adhesion and the anticorrosive properties. Additionally, if an adequate paint system is also applied, the so formed protective duplex system has a synergistic effect. All these concepts were subjected to intensive studies and satisfactory protective duplex systems using solvent base paints were developed [19–24]. However, rigid environmental legislation requires more environmentally friendly systems. Therefore, their replacement by other systems with equal or even greater protective properties requires new and accelerated studies. With this in mind, the CIDEPINT has ongoing a program research, which deals with the elucidation of physicochemical phenomena occurring within and under paint coatings, encompassing defects in films, porous films, metal/coating adhesion, surface treatment and/or pretreatments, corrosion, blistered coatings and cathodic protection. In the present case, tests conducted under free corrosion conditions allowed us to carry out a comparative evaluation of the anticorrosive performance of five pre-treated galvanized steel/painting system arrangements subjected to different exposure conditions. Among these systems, the conventional solvent base paints were used as reference ones. A large amount of diverse data has been

gathered using standardized tests as well as electrochemical techniques, and then interpreted on the basis of their correlation with a number of physicochemical processes that it is thought to occur in pre-treated steel/paint film/exposure medium systems.

3.1. Adhesion measurements

Different studies have shown that in many cases the loss of adhesion is coincident with the presence of water at the metal/coating interface [17,25,26].

In the rather qualitative standardized tape-test the scales used to classify the specimens is from 0 to 5, i.e., 0 corresponds to a very poor and 5 to a very good adhesion, respectively. After dry testing, the pre-treated and painted galvanized steel sheets were subjected to the tests above mentioned. At the end of these, the panels were re-inspected and classified. In agreement with results discussed elsewhere [27], under dry testing conditions all the samples showed very good adhesion to the pre-treated galvanized steel, Table 3a and b. However, when they were exposed to the salt spray cabinet or immersion experimental conditions, the final adhesion results were mostly poor, not only at the center and edges of the panels (Table 3a), but also inside and, sometimes, outside the cell (Table 3b). The exception to this rule was the epoxy base-solvent paint (ES), whose adhesion values were almost as good as before the test initiation. On the contrary, the rest of the samples showed a clear dependence on the test conditions. Thus, the acrylic (AC) paint adhesion failed completely after the salt spray test, it was poorer after immersion in 0.5 M NaCl or Na_2SO_4 solution but slightly less after immersion in 0.25 M $NaCl + 0.25$ M Na_2SO_4 solution. In Table 3a and b can also be seen that similar changes were obtained by considering the rest of specimens. They were particularly meaningful (0B-2B) when the paint adhesion was estimated at the center and edges of the samples AC, AK and EW exposed to the salt spray cabinet, or inside the cell in samples AK (immersed in Na_2SO_4), samples AC, AK and EW (in NaCl), and samples AK and VL (in $Na_2SO_4 + NaCl$). Also minor (4B-3B) or no (5B) changes were obtained when replicates of the AC, ES, EW and VL specimens were subjected to the different experimental media.

These undesirable adhesion results could be expected, as discussed in the following paragraphs, due to the paint's permeability to water and corrosive species. However, some important differences between the initial and final paint adhesion corresponding to the outside part of the cell were also detected when their respective values were considered, Table 3b. This was interpreted as a consequence of the following mechanism: once the adhesion forces at the galvanized steel/primer interface became lower than a threshold value due to the permeating water had weakened or broken the adhesive bonds inside the cell, the liquid phase has the capacity of diffusing laterally beyond the wetting limits fixed by the cell. In such a circumstance, the size of the affected

Table 3
Paints adhesion results using the tape-test method (ASTM D-3359/97) before and after: (a) 97 days exposure to the salt spray (fog) test and (b) 90 days immersion in different electrolytes

Sample	Before the test		At the end of the test	
	Center	Edges	Center	Edges
(a) Exposure to the salt spray (fog) test				
AC	5B	5B	0B	0B
AK	4B	4B	2B	2B
ES	4B	4B	4B	5B
EW	4B	4B	0B	0B
VL	5B	5B	5B	5B

Samples	Before the test	At the end of the test	
		Inside the cell	Outside the cell
(b) Immersion in different electrolytes			
0.5 M Na_2SO_4 solution			
AC	5B	3B	5B
AK	4B	0B	0B
ES	4B	5B	5B
EW	4B	5B	5B
VL	5B	5B	3B
0.5 M NaCl solution			
AC	5B	2B	3B
AK	4B	0B	4B
ES	4B	5B	5B
EW	4B	1B	5B
VL	5B	5B	5B
0.25 M Na_2SO_4 + 0.25 M NaCl solution			
AC	5B	4B	4B
AK	4B	0B	3B
ES	4B	3B	4B
EW	4B	4B	4B
VL	5B	0B	0B

Classification	Percentage of area removed
ASTM D-3359 specifications guide	
5B	0
4B	<5
3B	5–15
2B	15–35
1B	35–65
0B	>65

area and the kinetics of the delamination process depend upon the adhesion strength that each one of the mentioned interfaces was able to develop.

Summarizing, these results suggest that the pre-treated zinc layer chemical and physical affinities to some of the tested primers were very poor after their exposure to salt spray or immersion conditions. Hence, it is apparent that such mode of adherence failure reflects the formation of few and/or weak adhesive bonds at those interfaces.

3.2. Salt spray cabinet test

Table 4a lists blistering/corrosion data obtained for intact galvanized steel/paint systems similar to those described in the above paragraph, placed in a salt spray cabinet for 97

Table 4
Paints blistering (ASTM D-714-87/00) and rusting (ASTM D-610/89) degrees after (a) 97 days of exposure to the salt spray (fog) test and (b) 90 days immersion in different electrolytes

System	Blistering size/frequency	Rusting
(a) Exposure to the salt spray cabinet test		
AC	4/D	10
AK	2/M	10
ES	2/F	8
EW	4/M	9
VL	6/F	10
(b) Immersion in different electrolytes		
0.5 M Na$_2$SO$_4$ solution		
AC	2/M	7
AK	10	10
ES	10	10
EW	10	10
VL	10	10
0.5 M NaCl solution		
AC	2/MD	6
AK	10	9
ES	10	9
EW	10	10
VL	10	9
0.25 M Na$_2$SO$_4$ + 0.25 M NaCl solution		
AC	10	10
AK	10	10
ES	10	10
EW	10	10
VL	10	10

Frequency	Size	Comments
ASTM D-714 specifications guide		
Dense, D	10	No blistering
Medium dense, MD	8	Smaller size blister easily seen by the unaided eye
Medium, M	6, 4	Progressively larger sizes
Few, F	2	

Rust grade	Percentage area rusted
ASTM D-610 specifications guide	
9	0.03
8	0.1
7	0.3
6	1
5	3
4	10
3	16
2	33
1	50

days. It can be seen that at the end of the test, samples ES and EW showed the onset of the corrosion attack (percentage of area rusted 0.1 and 0.03, respectively), while the main body of the panels AC, AK and VL remained without any visible change. In general, this whole rusting data reveals that under the current experimental conditions almost no significant difference was found when the anticorrosive+barrier protection provided by the overall coating systems was evaluated. Unfortunately, the estimation of the paints blistering degree

did not show encouraging results. All the paints failed noticeably, and a certain relationship associating the magnitude of these fails with the low paint adhesion values summarized in Table 3a was found. By comparing the experimental data contained in part (a) of Tables 3 and 4 can be seen that the poorer the paint adhesion is (e.g. 0B for samples AC and EW), the more significant the size/frequency of blistering degree (4/D and 4/M) is as function of the exposure time, environmental conditions, painting system permeability and adhesion strength to the substrate.

The mechanism of formation and growth related with the paint film blistering, which involves a number of frequencies and sizes, may be explained assuming that different amounts of water, sometimes transporting oxygen and corrosive chemicals, permeate through the organic coating up to reaching the paint/galvanized steel interface. Under these wetting conditions, and depending upon the number and magnitude of the adhesive bonds developed at such interface, these bonds could be weakened or even broken at small-localized regions where local failure of the paint film adhesion takes place. As the exposure to the aqueous electrolyte continuous, these areas grow and coalesce into larger units making that the exposed area become partial or totally delaminated. The periodical visual inspections and standardized characterizations of the painted panels allowed monitoring the starting and evolution of the blistering/corrosion processes leading to reduce the aesthetic, mechanical and protective properties of each sample.

3.3. Immersion tests in saline solution

Table 4b summarizes blistering/rusting data for intact replicates of the galvanized steel/paint systems depicted in Table 4a but, in this case, subjected to continuous immersion in 0.5 M NaCl, 0.5 M Na$_2$SO$_4$ or 0.25 M NaCl + 0.25 M Na$_2$SO$_4$ solution for 90 days. As can be seen in Table 4b, only the systems AC showed a fairly bad blistering performance (2/M in Na$_2$SO$_4$ and 2/MD in NaCl, respectively). For the rest of the test specimens (AK, ES, EW and VL), a value of 10 was obtained after their evaluations, which according to ASTM D-714 standard classification means no blistering.

The anticorrosive performance provided by the painting system AC (rust grade = 7 in Na$_2$SO$_4$, and 6 in NaCl) is indicative that in both cases the underlying steel had been exposed by dissolution of the zinc protective layer. The visual inspection results corresponding to the other coated galvanized steel panels listed in Table 4b suggest that a highly effective corrosion inhibitive action was developed by the respective paint systems.

3.4. Electrochemical measurements

Corrosion potential and impedance data as a function of the immersion time in 0.5 M NaCl, 0.5 M Na$_2$SO$_4$ or 0.25 M

$NaCl + 0.25 M Na_2SO_4$ solution have been obtained. Then, impedance data were fitted using the transfer function derived from electrical equivalent circuit models, and interpreted from their association with processes occurring within the paint film and at the metal/paint interface.

3.5. Equivalent circuit models

The painting system as well as the galvanized steel substrate deterioration takes place from processes having a complex nature. Consequently, in order to interpret and explain in electrochemical terms the time dependence of the acquired impedance data, it has been necessary to propose appropriate equivalent circuit models.

Impedance spectra provide useful information concerning the evolution of both the organic coating protective features and the kinetics of the underlying steel corrosion process as a function of the exposure time to experimental or service conditions. Thus, the dynamic character of the painting system barrier property, the anticorrosive action of specific pigments, the rust formation and also changes in the disbonded area are accounted for the time dependence of the coated steel/electrolyte impedance spectra. In general, an explanation of why and how such changes take place can be given by associating them to the resistive and capacitive parameters derived from fitting impedance data with non-linear least squares algorithms involving the transfer function of the equivalent circuit models shown in Fig. 1 [28–31]. They represent the parallel and/or series connection of a number of resistors and capacitors, simulating a heterogeneous arrangement of electrolytically conducting paths where R represents the electrolyte resistance between the reference and working (coated galvanized steel) electrodes, R_1 (resistance to the ionic flux) describes paths (pores, low crosslinking) of lower resistance to the electrolyte diffusion short-circuiting the paint film, and C_1 is the dielectric capacitance representing the intact part of the same paint film [32]. Once the

permeating and corrosion inducing chemicals (water, oxygen and ionic species) reach electrochemically active areas of the substrate, particularly at the bottom of the paint film defects, the metallic corrosion become to be measurable so that its associated parameters, the electrochemical double layer capacitance, C_2, and the charge transfer resistance, R_2, can be estimated. It is important to remark that the values of these parameters vary direct (C_2) and inversely (R_2) with the size of the corroding area. Sometimes, when the strength of the bonding forces at the paint/metal interface are affected (e.g., by wet adhesion), facilitating lateral diffusion of the electrolyte, another processes under and/or within intact parts of the coating film could be graphically and/or numerically separated [33], causing the appearance of more time constants (R_iC_i).

On the other hand, distortions observed in these resistive-capacitive contributions indicate a deviation from the theoretical models in terms of a time constants distribution 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, surface energy) and/or diffusional processes that could take place along the test [34,35]. Since all these factors make that the impedance/frequency relationship to be non-linear, they are taken into consideration by replacing one or more capacitive components (C_i) of the equivalent circuit transfer function by the corresponding constant phase element, Q_i (CPE) [17]. The CPE is defined by the following equation [36]:

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

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

Difficulties in providing an accurate physical description of the occurred processes are sometimes found. In such cases, a standard deviation value ($\chi^2 < 10^{-4}$) between experimental and fitted impedance data may be used as final criterion to define the most probable circuit.

In the present work, the fitting process was mainly performed using the phase constant element Q_i instead of the dielectric capacitance C_i. However, this last parameter was used in the following plots in order to facilitate the results visualization and interpretation.

3.6. Water permeability

From the paint film concerns, barrier and permeability properties are of great interest because they control the corrosive chemicals transport through them as well as the active pigments dissolution and supply to the metal substrate. Reliable data on water permeability, corrosion potential and
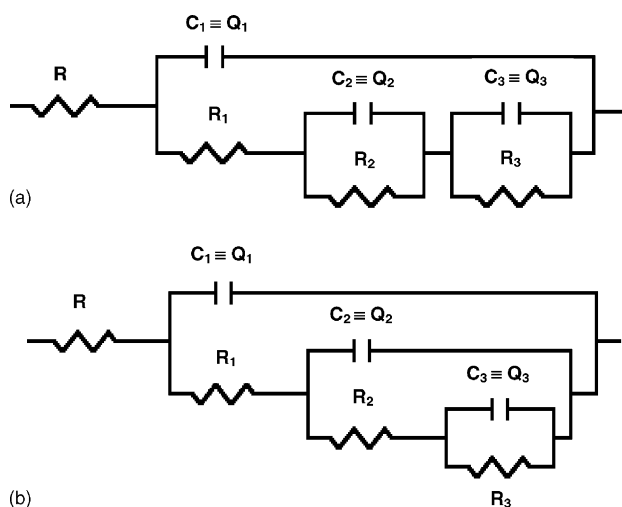

Fig. 1. Equivalent circuit models.

impedance evolution of coated metals provides valuable information to select and design the most adequate protective paint system for each practical situation.

According to Ritter and Kruger [37], it may be assumed that different amounts of water, oxygen and ions can permeate the coating in the first hours of immersion in saline solution. In the painted pre-treated galvanized panels tested,

type of anion (Cl^-, SO_4^{2-} or a mixture of both), these results may be attributed to the fact that by means of a still undetermined mechanism the SO_4^{2-} anion delays the water diffusion through acrylic-styrene base paints. Besides, by comparing the summarized in Table 5 permeability values obtained with the different paint systems immersed in each one of the electrolytes, they can be ordered as follows:

System	Lowest/anion	Intermediate/anion	Greatest/anion
AK	$0.974 \times 10^{-10}/Cl^-$	$1.58 \times 10^{-10}/SO_4^{2-}$	$1.62 \times 10^{-10}/SO_4^{2-} + Cl^-$
ES	$0.824 \times 10^{-10}/Cl^-$	$1.40 \times 10^{-10}/SO_4^{2-} + Cl^-$	$1.59 \times 10^{-10}/SO_4^{2-}$
EW	$1.80 \times 10^{-10}/SO_4^{2-} + Cl^-$	$2.30 \times 10^{-10}/Cl^-$	$2.98 \times 10^{-10}/SO_4^{2-}$
VL	$1.83 \times 10^{-10}/SO_4^{2-} + Cl^-$	$2.00 \times 10^{-10}/Cl^-$	$2.64 \times 10^{-10}/SO_4^{2-}$

a first step of such a process could be attributed to the fact that the topcoat film based on an air dried alkyd paint contain an appreciable amount of water-soluble material and tend to absorb water and swell [38]. In addition, the absorbed water has some plasticizing effect on the alkyd film structure and, as a consequence, it also facilitates the movement of molecules through the paint system.

Table 5 illustrates the effect of the electrolyte composition on the water permeability values for the test specimens. It can be seen that, under immersion conditions, the panels coated with the system AC showed the lowest value of water permeability coefficient, 3.80×10^{-10} cm^2 s^{-1}, when immersed in Na$_2$SO$_4$ solution, an intermediate one (3.92×10^{-10} cm^2 s^{-1}) in Na$_2$SO$_4$ + NaCl solution, but it cannot be measured in NaCl solution. This situation arises when the paint film water permeability is so high that its dielectric behavior does not comply the assumptions made to solve the calculation model [18]. As all the samples were identical replicates, and the main experimental difference was the

From these results it can also be inferred that besides the specific protective properties provided by each paint system, the relatively significant changes showed by the corresponding water permeability coefficient should be attributed to its dependence on the anion size, charge and/or concentration present in the electrolyte. As it was mentioned, it could change the mechanism and/or energy of interaction between the reactive polar species (polymeric components, pigment particles, etc.) within the paint film and the water molecules, which diffuse through it [39]. In Table 5 can be seen that this assumption is supported by the fact that the value of the permeability, diffusion and solubility coefficients, which are associated to the mobility of the water molecules (diffusion) and the amount of water dissolved within the coating (solubility), changed with the electrolyte composition. Unfortunately, such results contribute to make less predictable the effectiveness of the barrier properties provided by paint coatings subjected to exposures in ambient contaminated with different chemicals and, consequently, of the anticorrosive protection afforded to the underlying galvanized steel.

3.7. Corrosion potential

Rest or corrosion potential (E_{corr}) measurements for painted metals and their time dependence have been questioned with regard to their use as a technique for evaluating the anticorrosive resistance of organic coatings [40]. However, its changes as a function of the exposure time to aqueous media have been successfully used as a simple tool to study the corrosion protection afforded by organic coatings [41–44]. Depending upon the microstructure of the paint coating, especially its polymerization degree, a certain period elapses until electrolyte penetration channels are established through which the underlying metal comes into contact with the medium. So, it is not surprising that, when a compact structure and a high crosslinking level are accompanied by a high film thickness, a few days of testing are not enough time for the electrolyte to enter in contact with the base metal of coated specimens, form the electrochemical double layer, and enable the measurement of a
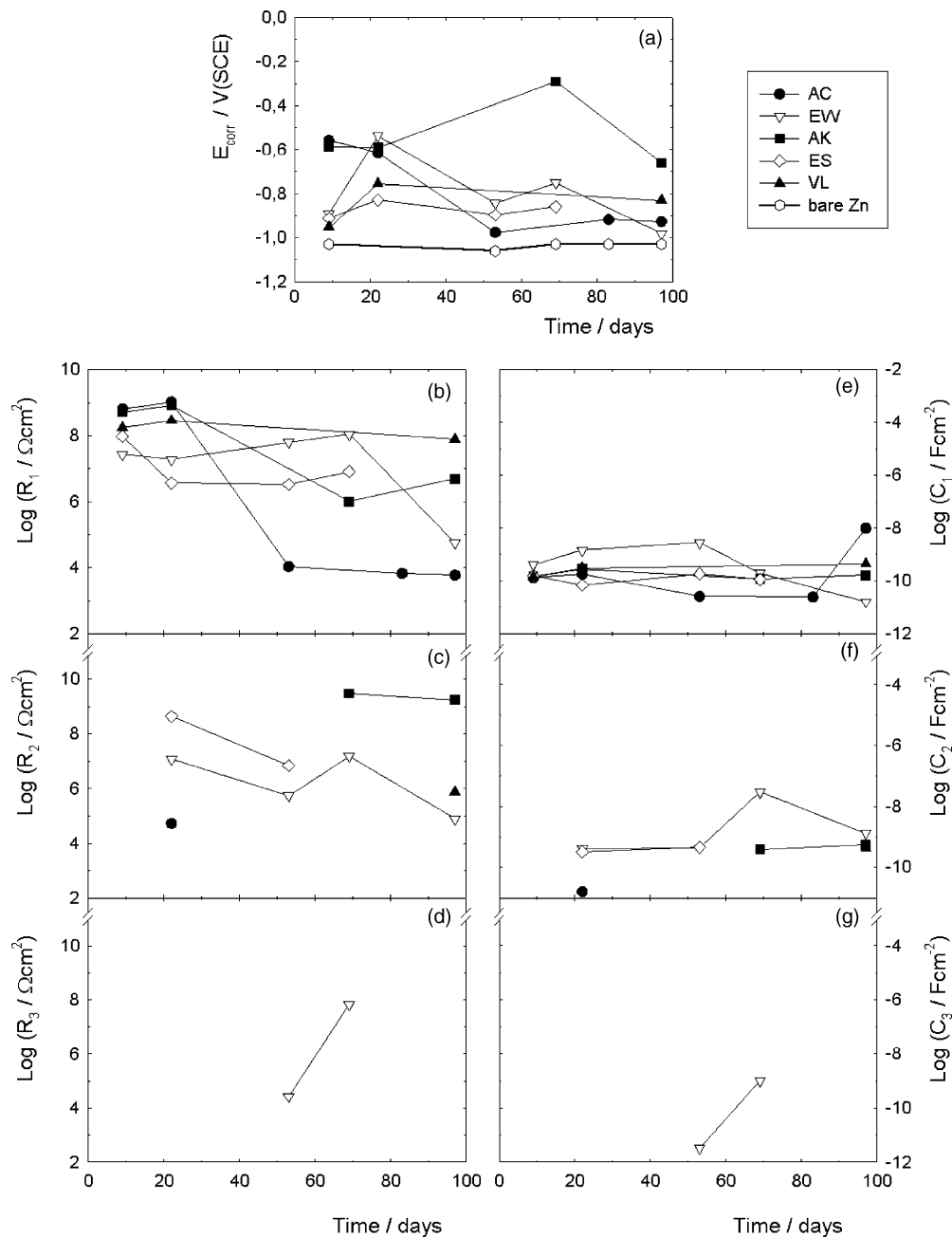
Table 5
Water diffusion (D), solubility (S) and permeability (P) coefficients of the tested paint films measured in different electrolytes

System	D ($\times 10^{10}$ cm^2 s^{-1})	S (dimensionless)	P ($\times 10^{10}$ cm^2 s^{-1})
Electrolyte: 0.5 M Na$_2$SO$_4$			
AC	9.84	0.386	3.80
AK	9.99	0.158	1.58
ES	10.9	0.156	1.59
EW	19.6	0.152	2.98
VL	23.2	0.114	2.64
0.5 M NaCl			
AC	–	–	–
AK	7.49	0.130	0.974
ES	9.69	0.085	0.824
EW	16.8	0.137	2.30
VL	20.5	0.098	2.00
0.25 M Na$_2$SO$_4$ + 0.25 M NaCl			
AC	12.0	0.327	3.92
AK	13.6	0.119	1.62
ES	10.7	0.131	1.40
EW	12.7	0.142	1.80
VL	19.9	0.092	1.83

Fig. 2. Time dependence of (a) E_{corr}, (b) $\log R_1$, (c) $\log R_2$, (d) $\log R_3$, (e) $\log C_1$, (f) $\log C_2$, and (g) $\log C_3$ of all the test specimens exposed to the salt spray chamber for 97 days.

corrosion potential. In Figs. 2a–5a the corrosion potential value of bare galvanized steel sheets exposed either to the salt spray cabinet or to the aqueous solution is showed only as a reference value.

Fig. 2a shows that during the first 20 days exposure in the salt spray cabinet the E_{corr} displacements were not uniform. They moved from their initial value with different slops towards more positive ones (samples ES, VL and EW), indicating a decreasing electrochemical activity due to the blockage of the paint pores by the zinc corrosion products, or else remained stable (samples AC and AK). Then, as the

exposure time elapsed, the potential of the coated panels either stayed almost stable or derived towards values closer to the bare galvanized steel.

From the E_{corr} values measured in all the test specimens submerged in 0.5 M NaCl solution, Fig. 3a, it is clear that there was not more than 0.25 V the difference between the bare and painted panels potentials after 4 h exposure. Then, the potential evolution was characterized by a large scattering due to its dependence on the specific protective conditions developed at the complex galvanized steel/painting system/electrolyte interfaces. The highest permeability to
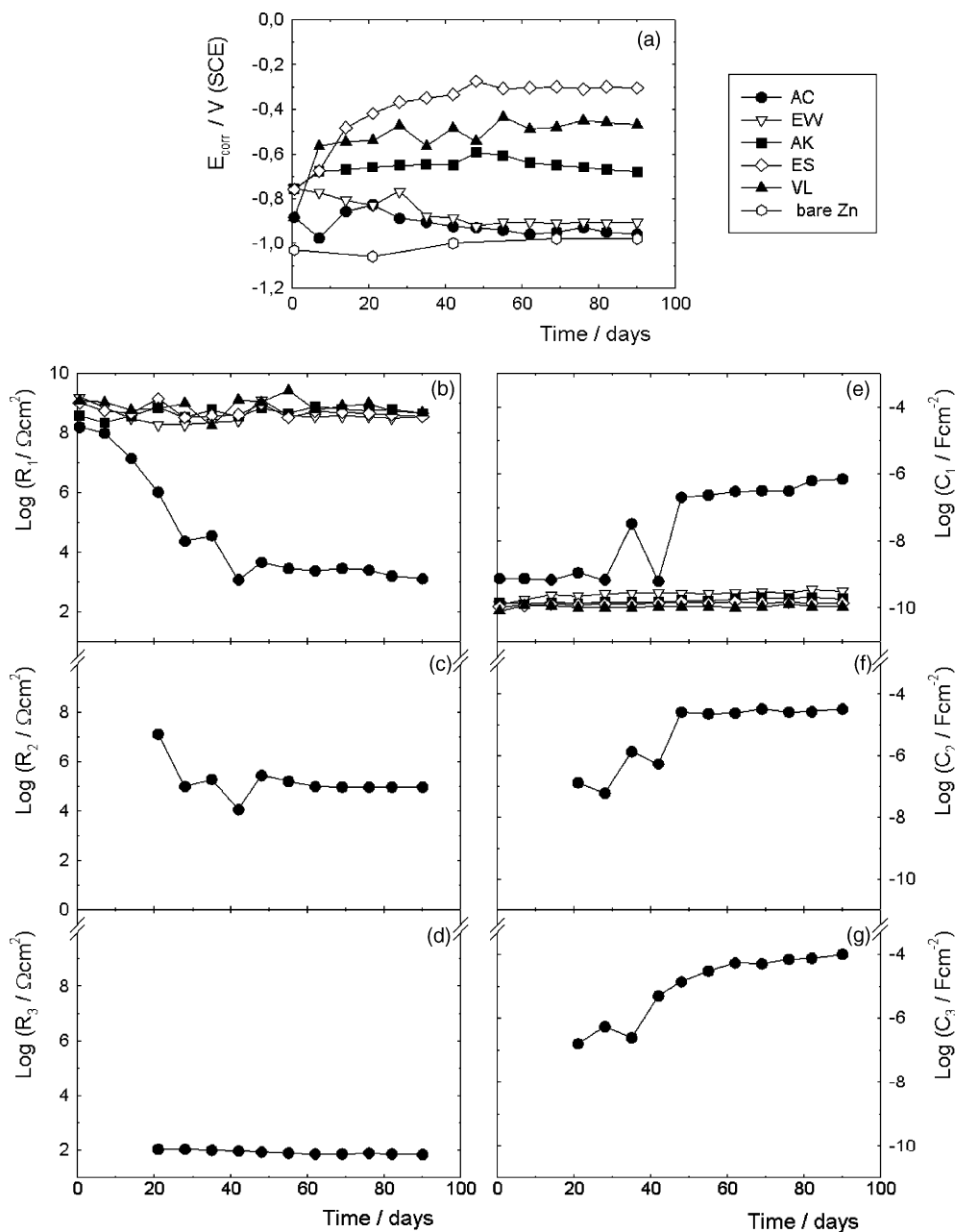
Fig. 3. Time dependence of (a) E_{corr}, (b) $\log R_1$, (c) $\log R_2$, (d) $\log R_3$, (e) $\log C_1$, (f) $\log C_2$, (g) $\log C_3$ of all the test specimens immersed in 0.5 M NaCl solution for 90 days.

water (Table 5), and probably also to other corrosive species, as well as the total loss of adhesion at the substrate/primer interface found in samples AC made possible the fast failure of the protection mechanism. This caused the E_{corr} displacement towards values close or equal than the bare metal potential in the same medium. Taking in mind that, in essence, the more negative the potential became, the more susceptible to corrosion the underlying galvanized steel surface is, the visual inspection helped to confirm that there was the characteristic orange-reddish products of steel corrosion at localized places (see Table 4b). Similar E_{corr} evolution and loss of interfacial adhesion was obtained with samples EW,

however, in this case no corrosion signal was detected; such a result was attributed to the fact that the provided barrier resistance is much better in the epoxy base primer (EW) than in the acrylic one (AC). The same figure illustrates that the E_{corr} changes in samples AK, VL and ES were initially towards more noble values, but after elapsed a certain period: ~ -0.7 V (sample AK); -0.55 V (sample VL), or -0.4 V (sample ES) was reached; thereafter, they remained stable up to ending the test. Such a behavior could be explained by assuming that, at this time, the most important but not unique form of protection, i.e. the barrier resistance supplied by the respective painting system, plus the relatively
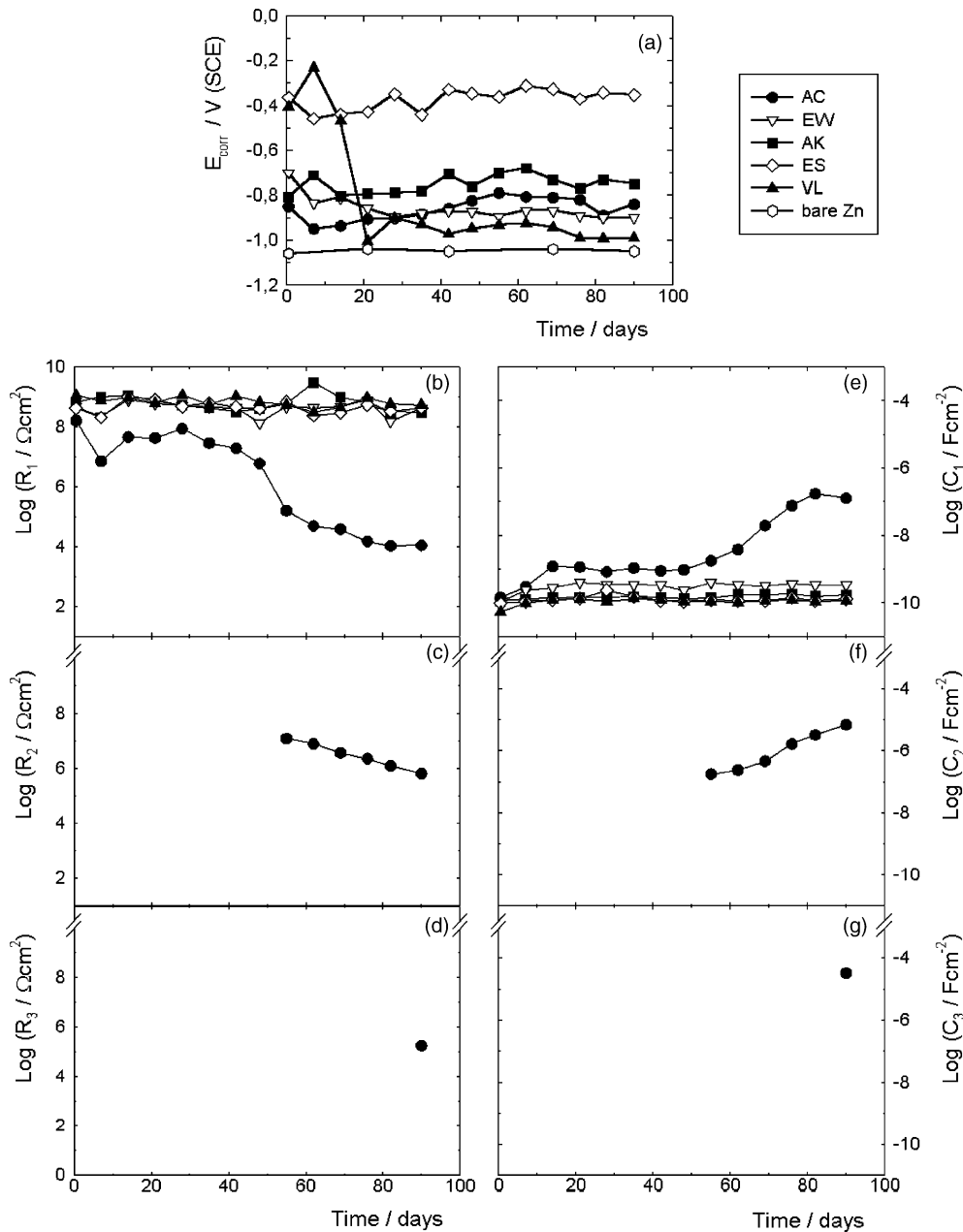
Fig. 4. Time dependence of (a) E_{corr}, (b) $\log R_1$, (c) $\log R_2$, (d) $\log R_3$, (e) $\log C_1$, (f) $\log C_2$, and (g) $\log C_3$ of all the test specimens immersed in 0.5 M Na$_2$SO$_4$ solution for 90 days.

good interfacial adhesion were effective enough as to avoid new changes in the cathodic/anodic areas relationship [45].

The time dependence of the E_{corr} corresponding to all the samples submerged in 0.5 M Na$_2$SO$_4$ or 0.25 M Na$_2$SO$_4$ + 0.25 M NaCl solution is summarized in part (a) of Tables 4 and 5, respectively. These show a well-differentiated potential value of samples ES in both electrolytes. From the beginning up to the end of the tests they remained about −0.4 V/SCE, while for the rest of the specimens the value of this thermodynamic parameter also showed small fluctuations but presumably higher electrochemical activity.

Since the main difference among the pre-treated galvanized steel/painting systems was the primer formulation used in each case, it is assumed that the magnitude of the E_{corr} displacements may be particularly associated with both the relative easiness with which the electrolytes permeate the paint films and the primers protective properties. However, and independently of the applied painting system, the metallic substrate was relatively protected from the corrosive attack throughout the tests. This conclusion arises from the fact that the corrosion potential values measured in each painted pre-treated galvanized steel panel were more noble than the corresponding potential for bare galvanized steel sheets
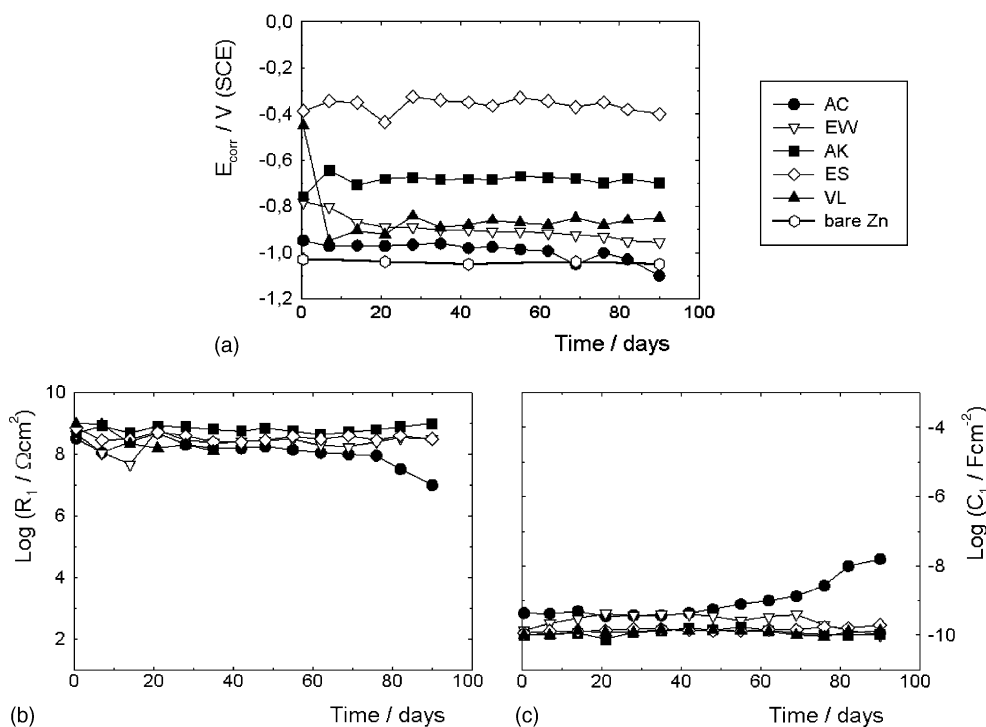
Fig. 5. Time dependence of (a) E_{corr}, (b) $\log R_1$, and (c) $\log C_1$ of all the test specimens immersed in $0.25\,M\,NaCl + 0.25\,M\,Na_2SO_4$ solution for 90 days.

subjected to the same experimental conditions. This protection may be attributed to the sum of effects such as: paint system barrier protection, substrate phosphatizing afforded by the phosphoric acid included in the pre-treatment bath formulation, pore blockage with the zinc corrosion products formed from the zinc dissolution reactions due to auto-corrosion ones and/or when it protects cathodically the underlying steel, all of them acting simultaneously. When this kind of protection is lost, or at least significantly diminished, other protective forms, as for example the exerted by the anticorrosive zinc molybdenum phosphate pigment, continue being certainly active. Several authors [46,47] suggested that both the phosphate and the molybdenum compounds contribute to the anticorrosive protective mechanism through an effective steel repassivation at the underpaint crevices and pits.

3.8. Impedance

3.8.1. Salt spray chamber exposure

Fig. 2b shows a representative plot of the impedance resistive component (R_1) corresponding to the five test specimens subjected to salt spray chamber exposure for 97 days. It can be seen that after 10 days of testing, R_1 values between 10^8 and $10^9\,\Omega\,cm^2$ were measured for all the painting systems. Elapsed 20 days, such values increased slightly (samples AC, AK, and VL), remained stable (sample EW), or declined almost two orders of magnitude (sample ES). As the exposure time went on, more significant differences between the paint films resistance to the ionic flux were arisen. As Fig. 2b illustrates, the best protective performance was afforded by

the painting system VL, for which the R_1 value stayed greater than $10^8\,\Omega\,cm^2$ during the entire test. The worst corresponded to the sample ES, whose test was interrupted at 70 days because of the appearance of few, very small but visible spots of corroded areas with orange-reddish steel corrosion products (0.1% according to ASTM D-610 standard). From intermediate (sample AK, $R_1 \approx 10^6$–$10^7\,\Omega\,cm^2$) to bad results with samples EW ($R_1 \approx 10^5\,\Omega\,cm^2$ at 97 days exposure), and AC ($R_1 \approx 10^4\,\Omega\,cm^2$ after 53 days) were also obtained. This decrease over the exposure time indicates that through the water uptake the formation and/or changes in size of the electrolyte pathways continued.

Referring to the paint films dielectric capacitance plotted as C_1 values and associated to the amount of water dissolved within the intact paint film structure, Fig. 2e shows almost no difference. As a general rule, the capacitance values of all the painting systems presented a steady state ranging between 10^{-11} and $10^{-9}\,F\,cm^{-2}$, which is a characteristic magnitude of less deteriorated organic coatings. Besides, this means that the amount of water uptake in each case could be less than 5% of the painting system volume [48] over the test.

Impedance data deconvolution shows that the second time constant, whose parameters are defined as charge transfer resistance (R_2) and electrochemical double layer capacitance (C_2), is related with a process whose contribution to the overall painted galvanized steel impedance changes dynamically as the exposure time elapses. Figs. 2c, f illustrate that there was an induction period of about 22 days exposure for samples AC, EW and ES; 70 days for AK or 97 days for sample VL, before the appearance of this time constant, which

is associated with the galvanized steel corrosion occurring at the bottom of the paint film defects. Such period was, therefore, correlated with the capacity of each painting system for delaying the corrosion inducing chemicals arrival to the galvanized steel/primer interface and, consequently, the development of the electrochemical double layer. In these figures, it can also be seen that once initiated the corrosion process, the protection systems worked of different manner. The observed behavior is explained in terms of the electrochemically reactive area related with the double layer. Thus, the strong decline showed by the ionic resistance (R_1) of system AC made that the resistive (R_2) and capacitive (C_2) components of the zinc dissolution reaction were deconvoluted after only 22 days exposure. Thereafter, they were totally masked by a mass transport process, presumably, the oxygen diffusion one under the actual experimental conditions. It is assumed that the reaction rate-determining step changed from the charge transfer (activated) to diffusion control because of the relatively fast zinc dissolution reaction ($R_2 \leq 10^4 \, \Omega \, cm^2$). Consequently, a dense and compact layer of hydrated zinc corrosion products grew and remained trapped under and/or within the paint film creating a new dielectric barrier to be permeated by the cathodic reagents before reaching the reaction surface.

The time dependence of the Faradaic parameters (R_2, C_2) corresponding to the corrosion process developed in samples AK and VL was in agreement with the changes showed by the resistive component (R_1) of the respective painting systems. Thus, the highest R_1 values measured in the alkyd topcoat/vinyl base primer (VL) system avoided the zinc corrosion for 97 days exposure, while the barrier resistance afforded by the alkyd base painting (AK) system did it for 70 days, and then maintained very slow the zinc corrosion rate ($R_2 \approx 10^{10} \, \Omega \, cm^2$). However, the alkyd topcoat/solvent base-epoxy primer system (ES) gave lower barrier resistance than the alkyd topcoat/waterborne-epoxy primer system (EW) but higher anticorrosive protection. This was attributed to the fact that the loss of adhesion suffered by the paint system EW (see Table 3a) meant an increase of the electrochemically active zinc layer and, consequently, an inversely proportional decreases of the corrosion resistance value.

The low values of the double layer capacitance ($C_2 \approx 10^{-11}$ to $10^{-8} \, F \, cm^{-2}$) make possible to infer that the electrochemically active areas under the paint coat were extremely localized. Assuming that the specific double layer capacitance of the bare metal is $C_{dl} \approx 20 \times 10^{-6} \, F \, cm^{-2}$ [49], it could be estimated that such active areas (defined as $A = C_2/C_{dl}$) ranged between 1×10^{-6} and $1 \times 10^{-3} \, cm^2$, it is to say, 0.00002–0.062% of the whole painted area [27].

Figs. 2d, g point out that the third time constant (R_3C_3) appeared precisely by fitting samples EW impedance data obtained after 53 days exposure. At this time, the charge transfer resistance (R_2) of the zinc dissolution reaction became almost two orders of magnitude less than its initial value. This means that a significant increase in the corrosion rate took place. In principle, this appearance could be

associated to the development of the above mentioned dielectric zinc corrosion products at the active zinc areas (pore bottoms). The evolution of these parameters over exposure time is consistent with this idea since R_2 should change as the exposure time does, following the evolution of the active zinc surface.

3.9. Immersion in aqueous solution

Fig. 3b shows that the ionic resistance (R_1) values, and therefore the coating integrity, of painting systems EW, AK, ES and VL in contact with 0.5 M NaCl solution were approximately stable between 10^8 and $10^9 \, \Omega \, cm^2$ meaning that along the test, the painted zinc layer stayed isolated of the saline medium, but they continuously drop in sample AC reaching $10^3 \, \Omega \, cm^2$ at 40 days. In 0.5 M Na$_2$SO$_4$, Fig. 4b, they performed similarly but, in this medium, the minimum R_1 value for sample AC was measured at 80 days. Besides, in Fig. 5b can be seen that no change in R_1 values was found when their evolution was monitored in all the test specimens immersed in 0.25 M NaCl + 0.25 M Na$_2$SO$_4$ solution.

Referring to the dielectric capacitance (C_1) values of the same paint coatings, Figs. 3e, 4e and 5e, show that the best protective behavior was again provided by the more resistive painting systems, which once the water saturation level was reached, they exhibited a quasi-steady state. The stability of the dielectric capacitance of samples EW, AK, ES and VL regardless the electrolyte was, as well as the corresponding to sample AC in 0.25 M NaCl + 0.25 M Na$_2$SO$_4$ solution, around 10^{-10} to $10^{-9} \, F \, cm^{-2}$, it was demonstrative that the intact part of the paint coating actually behaved like a dielectric capacitor throughout the immersion test. On the other hand, a clear signal of deterioration of the barrier property supplied by the system AC exposed to NaCl or Na$_2$SO$_4$ solution was illustrated by the significant increase of its capacitance, $C_1 \approx 10^{-6} \, F \, cm^{-2}$ (Fig. 3e) and $10^{-7} \, F \, cm^{-2}$ (Fig. 4e) respectively, at ending the test, although it was faster and worse in NaCl. This capacitance increase has been related in the literature to adhesion loss (delamination) at the metal/paint interface, which in turn makes easier the water accumulation.

The great stability as well as excellent protective properties inferred from the R_1 and C_1 values are interpreted as neither the test solution resistivity in the conducting pathways within the paint film nor the size of the geometric area related with the intact part of the same film changed during the immersion test in different electrolytes. Likewise, it is assumed that the protection given by the painting system AC exposed to 0.5 M NaCl or Na$_2$SO$_4$ solution failed because its poor barrier resistance cannot prevent the anion arrival to the metallic surface. These corrosion inducing chemicals, acting together with the water accumulated within and under the paint film provoked the appearance of a driving force able to overcome the activation energy of the anion diffusion process. In such circumstances, and after a certain

induction period dependent mainly on the anion characteristics has elapsed, the corrosion of the underlying zinc layer initiated. Not only is the size and electric charge of Cl^- ions less than the corresponding to $SO_4{}^{2-}$ but also greater the solubility of its reaction products. Therefore, it could be presumed that the Cl^- diffusion rate from the electrolyte bulk throughout the organic coating layer would be less affected by eventual steric and/or electrochemical interactions with the coating reactive species. An evidence that the Cl^- ions not only would arrive faster but also provoke more deterioration at the pre-treated zinc/primer interface can be seen by comparing Figs. 3c, f, and 4c, f (see also Table 4b).

The experimental results plotted in these figures corroborate that there was an induction period before the appearance of the second time constant ($R_2 C_2$), which was associated to a Faradaic process whose contribution to the overall impedance of the test specimens became meaningful as the exposure time elapses. As it was above mentioned, such period is related with the protective capacity of each paint and, consequently, with the delay to form the electrochemical double layer on the underlying metal surface. Besides the found delay was more significant in Na_2SO_4 than in NaCl solution, it can be seen that the parameters governing the zinc corrosion process (R_2 and C_2), keep an almost linear relationship with those describing the evolution of the paint film protective properties (R_1 and C_1). Thus, samples AC did not only have the lower barrier resistance but also showed the worst corrosion behavior.

Figs. 3d, g and 4d, g point out that the third time constant ($R_3 C_3$) appeared only in samples AC showing the zinc corrosion reaction. Furthermore, they also allow to observe that: (1) the time necessary for its clear definition was very much shorter in NaCl than in Na_2SO_4; (2) the resistive component (R_3) remained constant but the capacitive one (C_3) increased as a function of the immersion time in NaCl. This time constant was related to the zinc corrosion process, but as it showed a dispersion factor $n \approx 0.5$ in the constant phase element used in the fitting procedure [17], the same could be associated with an oxygen diffusion-controlled reaction usually found in zinc corrosion [50,51]. Based on this statement, it was assumed that as the electrolyte came into the slightly adhered and poorly resistive paint films, and corrosion progressed on an important fraction of the zinc layer (much more greater than at the pores bottom), the oxygen consumption at the primer/zinc interface increased [52]. Consequently, the mass transport rate through the painting system became slower than the oxygen consumption at 53 days for the less resistive system EW exposed to salt spray chamber, 20 days for system AC immersed in NaCl or 97 days in Na_2SO_4, respectively.

4. Conclusions

Of the five painting systems studied in different exposure conditions, those designated as AK, ES, EW and VL

presented the best overall anticorrosive behavior when immersed in 0.5 M NaCl, 0.5 M Na_2SO_4 or 0.25 M NaCl + 0.25 M Na_2SO_4 solution. All of these systems plus the AC one showed certain degree of rusting and/or blistering after the exposure test to the salt spray chamber.

The painting system AC presented the worst anticorrosive performance under immersion conditions in 0.5 M NaCl or 0.5 M Na_2SO_4 solutions as well as during the exposure to the salt spray chamber. In both solutions, the zinc molybdenum phosphate incorporated to the primer as anticorrosive pigment revealed to be less efficient in these very aggressive exposure conditions if the ionic resistance (i.e. barrier resistance) is poor.

The difference between initial and final results provided by the tape-test method showed that the loss of adhesion is not limited to the inside part of the electrolyte containing cell but it can spread up to certain distance due to electrolyte lateral diffusion at the paint/metal interface.

All laboratory tests involved in this work were useful in order to understand the behavior of the studied paint systems subjected to simulate but highly aggressive environments. The good correlation between standardized (blistering, rusting, adhesion, salt spray chamber) and electrochemical (impedance spectra, corrosion potential) tests allowed explaining some troubles observed in practice and, on this base, to make changes in the paint formulations to maintain their appearance as long as possible. Besides, the rather scattered results observed by comparing the anticorrosive protective properties afforded by a given painting system exposed to different media support the idea that extrapolate protective performances from an exposure condition to other is absolutely risky.

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