



An environmentally acceptable primer for galvanized steel: Formulation and evaluation by SVET

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ABSTRACT

The object of this paper was to formulate a two-pack wash primer employing aluminium phosphosilicate as active anticorrosive pigment instead of basic zinc chromate. The anticorrosive action of the primer was evaluated by the polarization technique and the scanning vibrating electrode technique (SVET). The exposed surface was then examined by scanning electron microscopy (SEM) and the surface composition determined by energy dispersive X-ray (EDX) analysis. The primer was finally integrated in a complete paint scheme whose anticorrosive performance was evaluated by the salt spray chamber and electrochemical impedance spectroscopy. The adhesion of the primer plus a painting system was also evaluated by standard ASTM D 3359-90 test method. The wash primer pigmented with zinc chromate was used as reference. Results indicated that basic zinc chromate could be replaced by the more eco-friendly wash-primer containing aluminium phosphosilicate.

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1. Introduction

Galvanized steel is widely employed as structural material in various industries. It is also employed in different constructions such as bridges, pipelines, cooling towers, home appliances, railroad electrification works, highways, etc. In brief, whenever steel is exposed to most atmospheric corroding environments, a zinc coating deposited by the hot dip process is recommended as an effective and economic mean to protect the steel substrate. Zinc coatings prevent rusting of steel by acting as a barrier against the environment and by sacrificially corroding themselves to provide cathodic protection. Zinc corrosion rate was lower than that of steel, thus improving the durability of the system. Zinc dissolution is also restrained by its own corrosion products which tend to block active sites hindering the electrochemical reactions.

The protective ability of galvanized steel may be enhanced by employing thicker zinc coatings (up to $\sim 610 \text{ g/m}^2$) or by painting the metallic surface, originating the so-called duplex systems. Painting of galvanized steel is desirable for aesthetics, as camouflage, as warning or identification marks, to prevent bimetallic corrosion, etc. Zinc painting may be avoided in rural areas but is mandatory in industrial and marine environments, not only by aesthetic reasons but also due to the poor resistance of this material to

such corrosive environments [1,2]. Paints extend the surface life of underlying zinc coating acting as a barrier against zinc reaction with environmental agents. Cracks and voids occurring in the paint are sealed by zinc corrosion products. In addition, zinc corrosion products occupy a volume only slightly greater (20–25%) than zinc while iron oxides occupy a volume several times greater than steel, thus expansive forces are reduced at the zinc/paint interface with respect to those at the steel/paint one [1,2]. The main practical problem concerning zinc painting lies in achieving good adherence of the paint system to galvanized steel. The zinc surface does not normally allow mechanical paint adhesion, however coatings can be successfully applied after galvanizing or after extended weathering [1,3]. Often adherence seems satisfactory immediately after painting but is prematurely lost as water, oxygen, etc. permeate through the coating. The failure of the duplex system is complex and depends on several factors such as surface brightness, grain size, crystallographic orientation of zinc grains, surface roughness, contaminants present on the surface, etc. [1,2,4]. Several pre-treatments were outlined to improve coatings adhesion [5]. The main function of pre-treatments for galvanized steel surfaces is to form very stable passive films or prevent the formation of unstable ones [1,2]. Pre-treatments must have the ability to form adherent films which, in turn, must resist the action of salt spray, water and humidity and also increase thermal and mechanical resistance. There exists a great variety of pre-treatments such as dip, barrier and chemical conversion coatings (phosphating, chromating, rust preventive compounds, etc.), chemical and physical vapour deposition coatings, diffusion coatings, pulsed laser deposition, etc. [6]. Many of these pre-treatments are non-priming in the sense that

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they did not contain a film forming material for further painting and the compatibility with the rest of the painting system must be checked. Many examples about the application of these pre-treatments to galvanized steel could be found in the specialized literature [7–32]. Other pre-treatments consist of the development of an adequate surface roughness by mechanical means, which can provide good surface for painting [1]. Priming pre-treatment systems contain a film forming material and are expected to act as the anchorage of the paint system [33].

The object of this paper was to develop a wash primer containing aluminium phosphosilicate by modifying a very well known formula with the carcinogenic and contaminant basic zinc chromate. This compound has the advantage of joining two inhibiting anions, phosphate and silicate. The wash primer also contained low impact solvents such as alcohols and water. The adhesion on galvanized steel was assessed employing suitable standardised adhesion tests. The anticorrosive behaviour of primed galvanized steel was evaluated by linear polarization techniques and SVET in chloride containing medium. The exposed surface, after performing SVET analysis, was studied by SEM and the surface composition determined by EDX.

2. Experimental section

The wash primer was formulated on the basis of the chromate formulation reported in Table 1. Part A of the wash primer was prepared by dispersing the components in a ball mill during 24 h. The active components of the primer are basic zinc chromate and phosphoric acid. The film forming material was polyvinyl butyral resin. The volume fraction of basic zinc chromate was replaced by aluminium phosphosilicate to formulate the alternative wash primer. Aluminium phosphosilicate was prepared according to a procedure described in the literature [34] which consisted of a low temperature synthesis leading to a compound with the formula $\text{Al}(\text{SiO}_2)_{1.5}\text{PO}_4$. The primer was applied by brushing on hot dip galvanized steel, previously degreased with hot 5% sodium carbonate. Final dry film thickness was $\sim 5 \mu\text{m}$. The panels were allowed to stand for 7 days before testing.

Coating adhesion was assessed by ASTM D 3359 standard test method. The panels to carry out this test were covered, firstly, with the primer and, then, with a painting system. This system was similar to that employed for panels exposed to the salt spray chamber and will be described below.

Anodic and cathodic polarization curves of bare galvanized steel and the primed samples were obtained at different immersion times, during 24 h. A saturated calomel electrode (SCE) was used as reference and a platinum grid as the counter-electrode. The supporting electrolyte in all electrochemical measurements was 0.05 M NaCl. The potentiodynamic scans began in the vicinity of the corrosion potential, being the scan rate 3 mV s^{-1} . Experiments were run on defect-free coatings. Measurements were carried out

with a Potentiostat–Galvanostat EG&G PAR Model 273A plus SOFT-CORR 352 software.

SVET measurements were carried out onto different samples: (a) reference chromate based pre-treatment, (b) the phosphosilicate coating and (c) bare hot dip galvanized steel. In the case of primed samples, measurements were taken around an artificial defect which was obtained by pressing a pin on the primed surface till the organic coating was completely penetrated. The pinhole area was comprised between 15 and $20 \mu\text{m}$. This area became anodic during the whole test period. The SVET instrumentation was manufactured by Applicable Electronics Inc. (MA, USA) and controlled by dedicated software. Further details can be found in the literature [35–38]. The microelectrode consisted of a platinum tip with a diameter of $40 \mu\text{m}$ and was vibrated at $20 \mu\text{m}$ of amplitude, both vertically and horizontally, at an average height of $200 \mu\text{m}$ above the surface. Each scan consisted of 400 data points obtained on a 20×20 grid on an area of $\sim 1 \times 1 \text{ mm}^2$, with an integration time of 1 s per point, which corresponded to an acquisition time of ~ 10 min. Conversion of potentials to current densities at the corroding surface was made by means of a calibration routine [38,39]. The noise level in this experiment was about $0.3 \mu\text{A cm}^2$. Results are displayed as two-dimensional plots, with iso-contour current lines as a function of the (X, Y) position in the probe scan plane. Video-microscope images are also presented for observation of the most significant features on the metallic substrate.

All the electrochemical tests were performed at room temperature, in normally aerated 0.05 M sodium chloride.

At the end of the SVET measurements, the morphology of the layer containing corrosion products was studied by Scanning Electron Microscopy (SEM) employing a PHILLIPS SEM 505 coupled with an EDAX OX PRIME 10 (Energy dispersed form, working at a fixed beam voltage of 20 kV) for semi-quantitative elemental analysis of the surface. Before SEM inspection the samples were cleaned with a soft brush to remove non-adherent corrosion products.

In order to understand the influence of a topcoat on corrosion behaviour, as measured by SVET, both wash primers were integrated in an alkyd paint system. Hot dip galvanized steel, previously degreased with boiling 5% (w/v) sodium carbonate, were coated with the primers ($5 \mu\text{m}$ dry film thickness), an anticorrosive paint ($35 \mu\text{m}$ dry film thickness) and a topcoat ($35 \mu\text{m}$ dry film thickness). Untreated galvanized steel was used as control. The composition of the anticorrosive paint, expressed as percentage by weight, was as follows: zinc molybdenum phosphate, 14.1%; non fibrous magnesium silicate, 10.6%; barite, 18.6%; titanium dioxide, 6.7; alkyd resin/white spirit (1:1), 40.6% and solvents, 9.4%. The topcoat was a commercial alkyd paint pigmented with titanium dioxide whose volume concentration was 18.0%.

A set of three panels, per each painting scheme, was put in the salt spray chamber (ASTM B 117) to evaluate the rusting degree (ASTM D 610) after different exposure times. The rusting degree was established taking into account the appearance of red oxide spots from the ferrous substrate [40]. Wet adhesion was also evaluated in the salt spray chamber by ASTM D 3359 Standard Specification). In this test, a lattice pattern with either six or eleven cuts in each direction is made in the film, reaching the substrate. Pressure-sensitive tape is applied over the lattice and, then, removed. Adhesion was evaluated by comparison with descriptions and illustrations. If no flaking has occurred classification was 5B. If flaking was higher than 65% the paint system failed to adhere on the metal surface and classification was 0B. The mean value of the obtained results was reported in this paper.

At the same time, impedance spectra of painted panels (frequency range $1.10^5 \text{ Hz} \leq f \leq 1.10^{-3} \text{ Hz}$) 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%

Table 1
Chromate based wash primer pre-treatment according to SSPC-PT 3-64 standard specification.

Part A		Part B	
Component	wt.%	Component	wt.%
Polyvinyl butyral resin	9.2	Phosphoric acid (85%)	18.5
Basic zinc chromate	8.8	Isopropanol	16.2
Magnesium silicate	1.3	Water (maximum)	65.3
Carbon black	0.1		
<i>n</i> -Butanol	20.5		
Isopropanol	57.7		
Water (maximum)	2.4		

Mixing ratio: 4 parts of A + 1 part of B (by weight).

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, in each cell, was 15.9 cm². A large area Pt-Rh mesh of negligible impedance and saturated calomel (SCE) were employed as auxiliary and reference electrodes, respectively. This electrochemical experiments were carried out at laboratory temperature (20 ± 2 °C), using a Faraday cage.

3. Results and discussion

The result of the adhesion test was satisfactory, classification 5B. No flaking has occurred in the cross-cut area; so, no adhesion losses were detected in any interface. The adhesion of the primer to the steel surface and the adhesion of the topcoats to the primer, both were satisfactory.

3.1. Polarization curves

The analysis of the polarization curve of galvanized steel (Fig. 1), at the time of immersion, showed that cathodic current was rather low ($\sim 20 \mu\text{A cm}^{-2}$) from the corrosion potential till ~ -1.3 V(SCE). This value agreed with data reported in the literature for oxygen reduction [41]. Hydrogen evolution was observed close to -1.5 V(SCE). A shoulder was observed previously to hydrogen evolution which could be originated by corrosion products reduction. A small peak was observed in the anodic branch of the polarization curve, located at ~ -1.25 V(SCE), attributable to corrosion product formation. Anodic current increased after immersion and the differences between each curve, far from the corrosion potential, are not significant.

The cathodic current observed in the case of galvanized steel primed with the chromate containing formulation (Fig. 2) was, as a general rule, low and close to $4.1 \mu\text{A cm}^{-2}$ in a wide potential interval. Hydrogen evolution was observed about -1.4 V(SCE).

The analysis of the anodic branch of polarization curves in Fig. 2, at low overpotentials, revealed that anodic currents increased with the exposure time. At high overpotentials it could be observed that

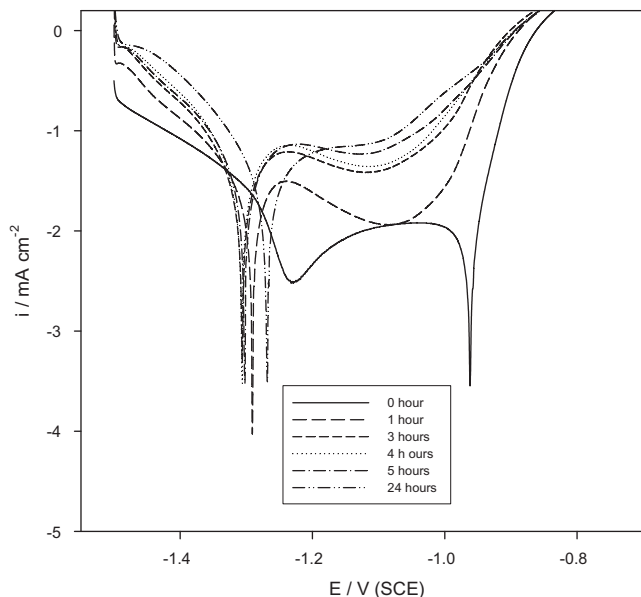


Fig. 1. Polarization curve of bare hot dip galvanized steel 0.05 M NaCl solution. Scan rate: 3 mV s^{-1} .

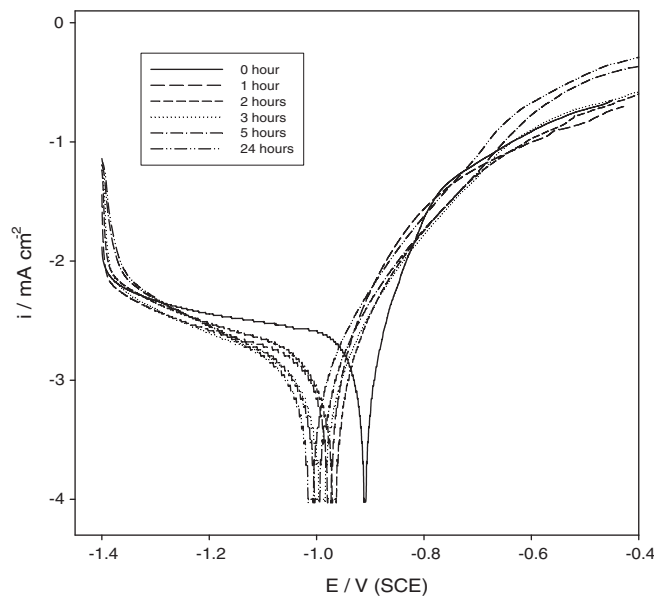


Fig. 2. Polarization curve of galvanized steel coated with the chromate primer in 0.05 M NaCl solution. Scan rate: 3 mV s^{-1} .

current decreased up to 2 h and, then, it began to increase, exhibiting the highest value at 24 h of testing. However, it seemed that the system began to lose its protective properties because current was increasing at lower overpotentials.

Examining the polarization curve of galvanized steel coated with the phosphosilicate primer (Fig. 3), at the moment of immersion, it could be appreciated that cathodic current was very small ($3.9 \mu\text{A cm}^{-2}$) from the vicinity of the corrosion potential to ~ -1.3 V(SCE). It is thought that this low current could be attributed to the deposition, onto the metallic surface, of reaction products between the primer active components and the zinc coating [42]. Something similar occurred with the dissolution reaction in the vicinity of the corrosion potential during the first hours of immersion. At higher overpotentials, anodic current began to decrease, after 2 h, matching the lowest values at 24 h.

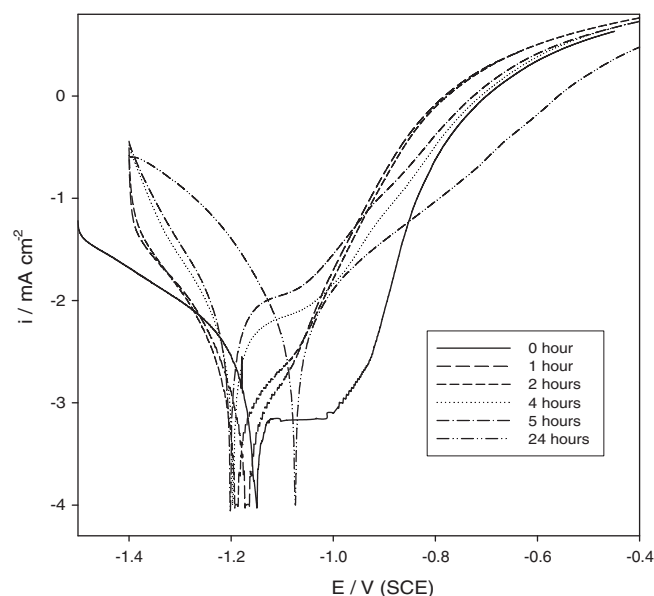


Fig. 3. Polarization curve of the of galvanized steel coated with the phosphosilicate primer 0.05 M NaCl solution. Scan rate: 3 mV s^{-1} .

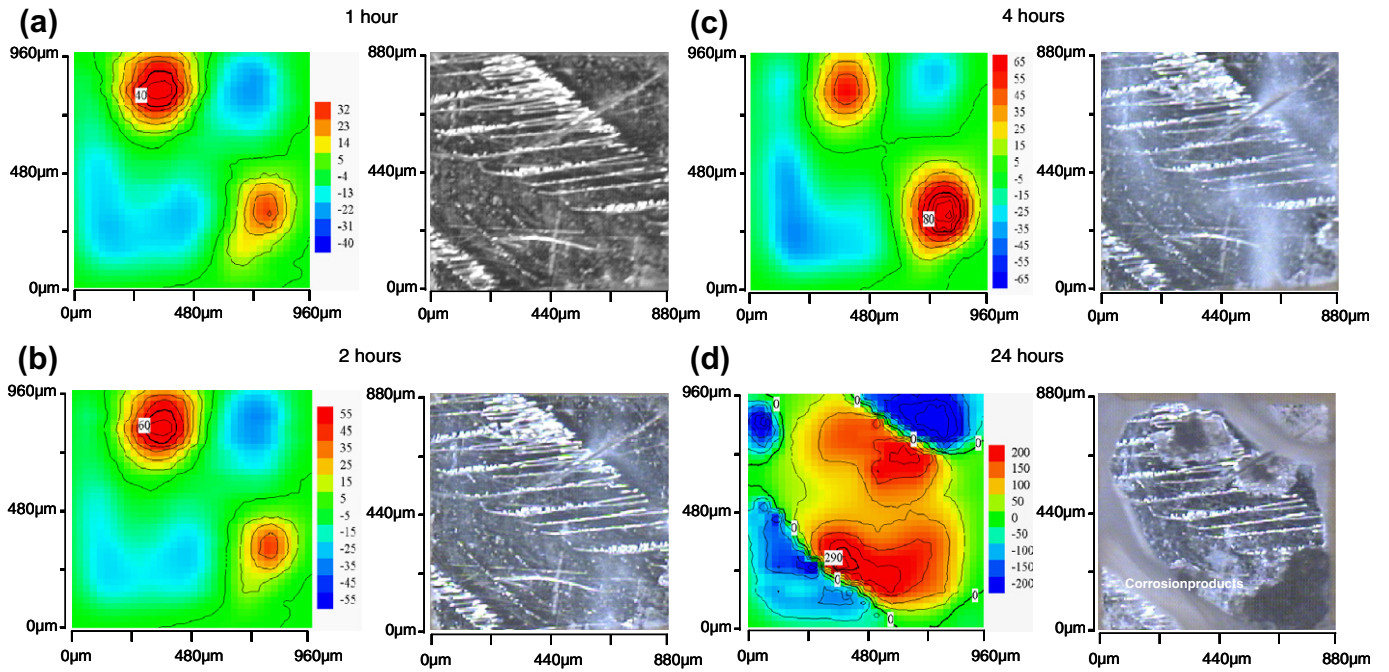


Fig. 4. Mapping of ionic currents measured over bare HDG in 0.05 M NaCl, after (a) 1 h; (b) 2 h; (c) 4 h and (d) 24 h of immersion. Current density scale in $\mu\text{A cm}^{-2}$. Scanned Area: $\sim 1 \times 1 \text{ mm}^2$. Video-microscope images of the samples are also shown.

3.2. SVET measurements

The technique is based upon the measurement of small potential variations in solution, associated to the ionic fluxes that come from oxidation and reduction reactions taking place on the active surface [36,37]. The maps of the ionic currents measured above the bare galvanized surface were made in the vicinity of well-resolved grains. The activity started in the first few minutes of immersion, with the nucleation of two anodic sites, surrounded by two cathodic areas, being the rest of the surface not active (Fig. 4). Measured currents increased approximately from 40

$290 \mu\text{A cm}^{-2}$ during one day. As time elapsed anodic and cathodic sites enlarged, current density increased and most of the surface became active. At the end of the exposure period, the precipitation of corrosion products at the grain boundaries was easily visible, close to the cathodic sites, in the video microscope image.

The chromated primed samples revealed an excellent behaviour, with full capability of healing the defect in such a way that it could not be appreciated in the SVET image. The measured current densities were extremely low, typically below $1 \mu\text{A cm}^{-2}$, with the only exception of the initial minutes, when it reached $\sim 3.3 \mu\text{A cm}^{-2}$ (Fig. 5). Sometimes, these low currents were close

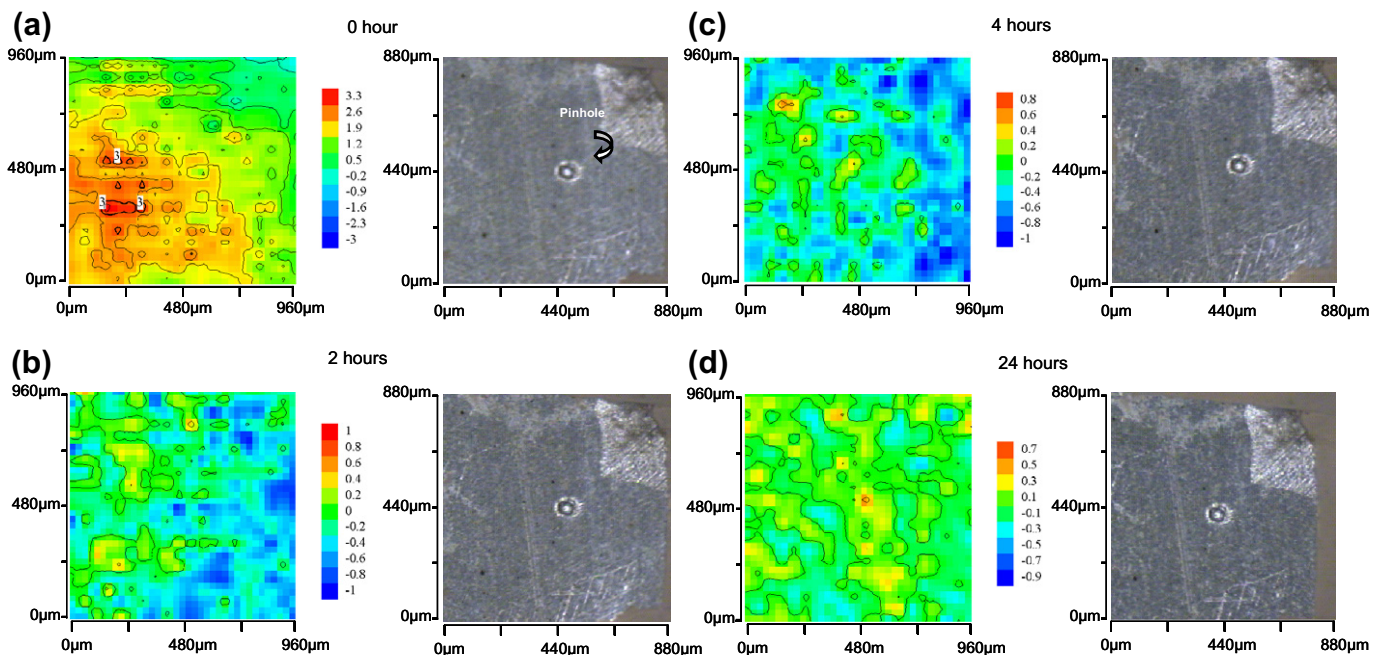


Fig. 5. Mapping of ionic currents measured over chromate primed HDG in 0.05 M NaCl, after (a) 0 h; (b) 2 h; (c) 4 h and (d) 24 h of immersion. Current density scale in $\mu\text{A cm}^{-2}$. Scanned Area: $\sim 1 \times 1 \text{ mm}^2$. The arrow points out the artificial pinhole. Video-microscope images of the samples are also shown.

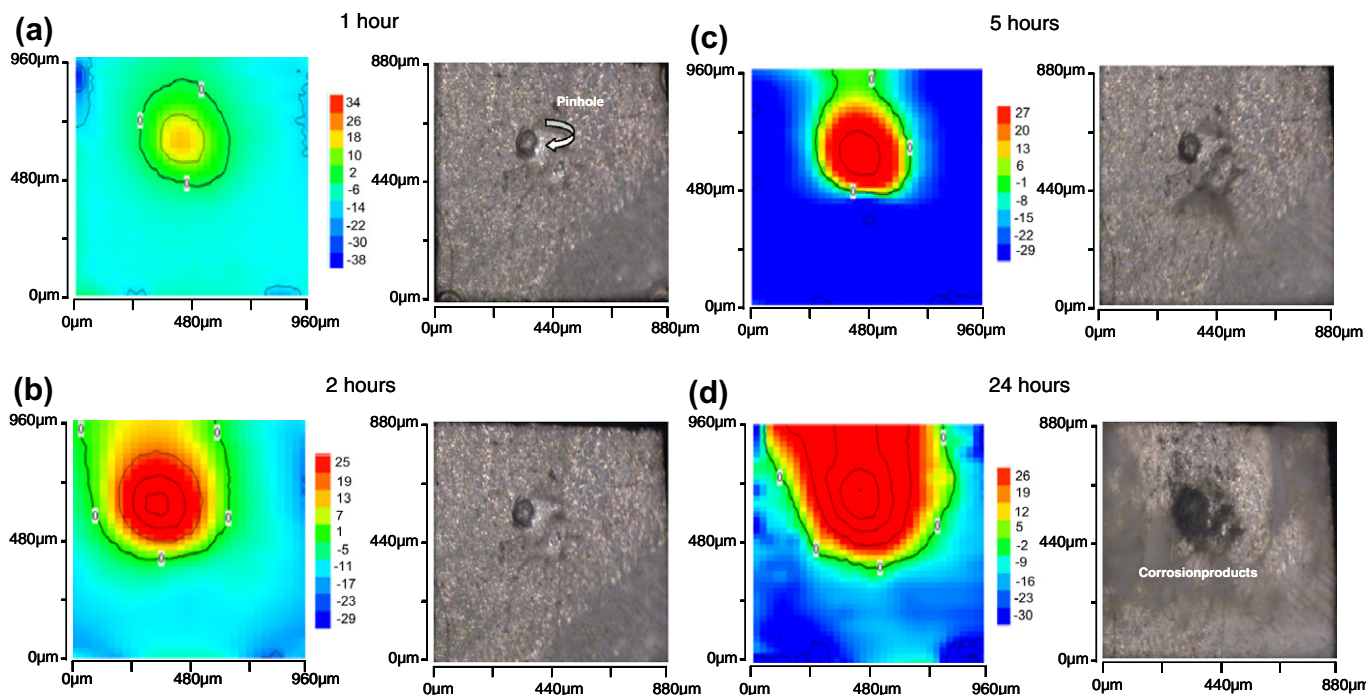


Fig. 6. Mapping of ionic currents measured over Al phosphosilicate-primed HDG in 0.05 M NaCl, after (a) 1 h; (b) 2 h; (c) 5 h and (d) 24 h of immersion. Current density scale in $\mu\text{A cm}^{-2}$. Area: $\sim 1 \times 1 \text{ mm}^2$. The arrow points out the artificial pinhole. Video-microscope images of the sample are also shown.

to the noise level of the experiment, thus indicating a low electrochemical activity. After 24 h of exposure, small anodic areas of very low intensity were detected over the exposed surface together with the corresponding cathodic sites.

Anodic electrochemical activity was detected over the defect practised on the primer containing aluminium phosphosilicate from the first minutes of immersion. However, currents were low at the beginning of the test, thus indicating certain degree of protection due to the anticorrosive pigment (Fig. 6). This fact revealed that the pre-treatment did not have the self-healing ability of the chromate one. The activity at the pinhole gradually increased with time after 2 h, but the most striking feature of the results was the high intensity of the cathodic reaction in the surrounding area which maintained during the test period. This was observed only after ~ 4 h of immersion and can easily be observed in the plot referring to 5 h, presented in Fig. 6. Towards the end of the exposure period the anodic currents also became very intense, temporarily reaching values as high as $26 \mu\text{A cm}^{-2}$. SEM inspection of the samples at the end of immersion period revealed a significant amount of corrosion products, but no delamination occurred around the defect.

Most measurements encountered in the literature using the SVET, electrochemical impedance spectroscopy or other electrochemical techniques applied to organic coatings are controlled by the barrier properties of those coatings. Further, cathodic delamination of barrier coatings is a well-known process, in which cathodic reactions take place underneath the coating and are responsible for loss of adhesion, whereas the anodic reaction proceeds underneath the layer of oxides. In the system presented, i.e., with the aluminium phosphosilicate wash-primer, the behaviour was different, with the anodic and the cathodic areas becoming separated and located at the defect and on the rest of the coating, respectively.

When compared to the chromated reference primer, the phosphosilicate primer revealed lower protective character, as observed in the SVET maps. However, the fact that both coatings retained good adhesion, in spite of the reactions occurring at the surface,

is potentially an important advantage, which means that the strong inhibiting effect of chromate may be less critical than in more resistive primers.

3.3. SEM inspection

SEM inspection and surface elemental analysis were carried out on coated areas not exposed to the saline solution and on exposed areas which included the artificial defect. The unexposed coated surface of the chromate based primer was rough, with a morphology that reflected a low thickness and also a large number of solid particles in the film. In spite of the low thickness, the film seems reasonably compact, with only a few pores whose diameters were, as an average, $\sim 2 \mu\text{m}$ (Fig. 7a). A layer of adherent corrosion products was observed around the defect, in spite of samples brushing performed before observation (Fig. 7b). There were no signs of delamination after the SVET measurements. The phosphosilicate-primed sample also had a significant amount of corrosion products on the surface at the end of exposure, but they were easily removed by brushing because fine grained phosphates may be not adherent (Fig. 8a and b).

The surface elemental analysis was performed by means of the EDX probe. The intact part of the chromate coating contained: Si = 2.8%; P: 6.9%, Cr = 2.7% and Zn = 38.4% being the rest carbon and oxygen from the polymeric material. Results are the mean of four determinations performed in different areas of the coating. It is clear that silicon came from talc incorporated to the formulation and zinc from the base metal and from primer composition. At the end of the scanning with the vibrating electrode the values reported previously did not change significantly: Si = 2.8%; P: 7.2%, Cr = 2.9% and Zn = 36.9% although a small proportion of Cl and Na from the saline solution was detected. This could be easily explained taking into account that the corrosion rate is not too high and considering that results are only semi-quantitative. The bigger particles observed in the micrographs had the same average composition as the continuous film (Fig. 10a). The moles of zinc to moles of phosphate ratio is too much higher than that corresponding

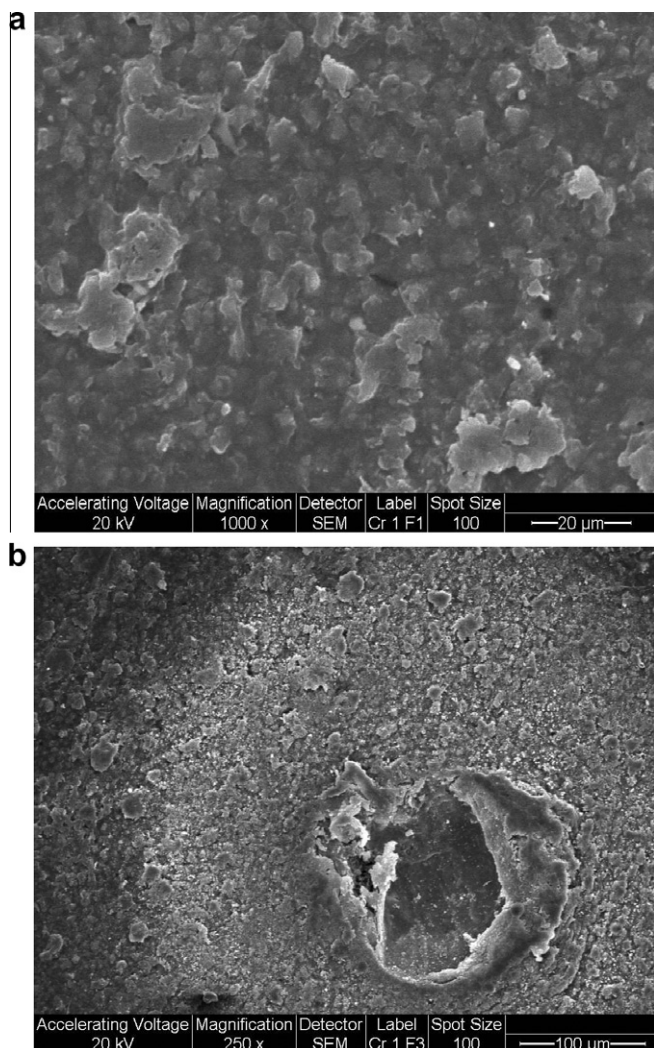


Fig. 7. SEM micrograph of the chromate primed sample in: (a) an unexposed area and (b) around the defect, at the end of the SVET test.

to zinc phosphate and reflected the influence of the base metal on the film composition.

The primer containing aluminium phosphosilicate showed similar features. The average composition of the intact film was as follows: Al = 3.8%; Si = 7.7%; P: 6.4%, and Zn = 25.8%. After the exposition to the saline solution for scanning, the surface composition did not change significantly: Al = 4.1%; Si = 7.7%; P: 6.2%, and Zn = 25.9%. The surface Si content was increased with respect to the primer formulated with zinc basic chromate due to the incorporation of aluminium phosphosilicate and Zn content was lower maybe due to a smaller attack of the base metal by the primer due to the presence of the inhibitive pigment. As in the case of the chromated sample, no delamination of the primer was observed in every case after performing the SVET analysis because of the low ionic resistance of the coating which avoided ion accumulation (especially hydroxyl ions) in certain areas, which may cause delamination. In addition, the vinyl binder may offer certain resistance to delamination as a consequence of its chemical nature.

3.4. The assessment of the anticorrosive performance of the wash primer in a complete paint system

The incorporation of both primers in true protective alkyd systems constituted by an anticorrosive paint plus a topcoat revealed

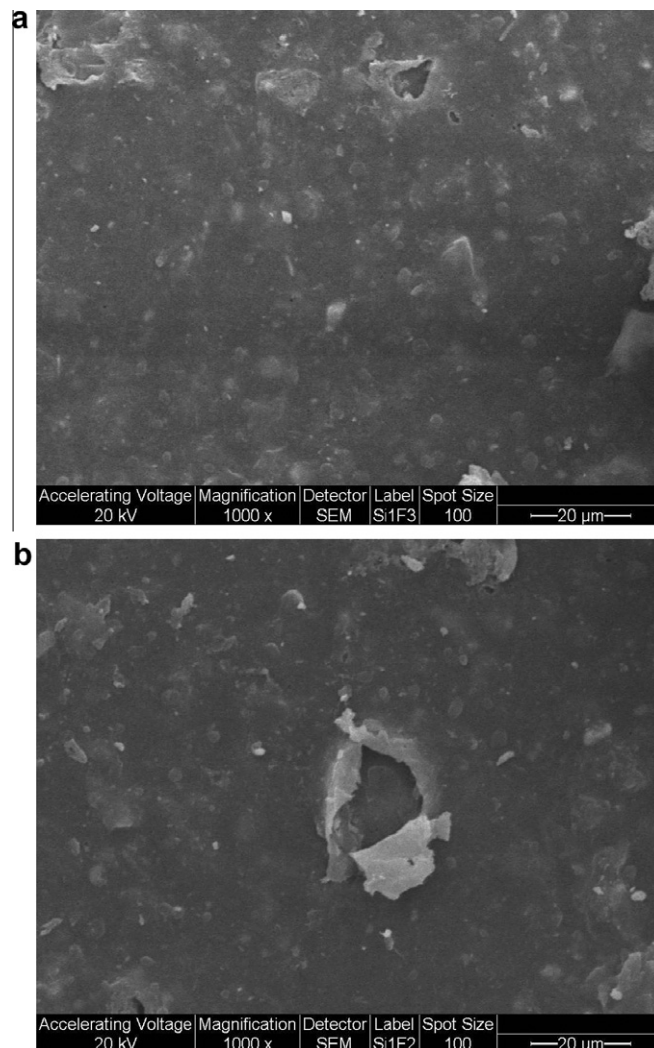


Fig. 8. SEM micrograph of the phosphosilicate primer in: (a) an unexposed area and (b) around the defect, at the end of the SVET test.

that both primers could perform adequately in the salt spray test (Table 2). It is argued that the salt spray chamber only approaches to a marine environment but results are of interest because it is a demanding exposition due to its aggressiveness. According to results in Table 2, the control panels must be retired from the chamber after 2230 h with a relatively low qualification while both primers still exhibited very good protective ability, specially that formulated with aluminium phosphosilicate. Adhesion of the painting scheme to the substrate was satisfactory either with the primer containing chromates or with that formulated with aluminium phosphosilicate. In both case adhesion was rated as 5B up to 2550 h of exposure. The rest of the test period it was found to be 4B; this means that less than 5% of the painted area exhibited loss of adhesion.

The impedance of the different paint systems was high at the beginning of essay (Figs. 9–11). In the case of the paint systems containing the wash primer with chromate (Fig. 9) or phosphosilicate (Fig. 10) it maintained, as an average, between 10^7 and $10^8 \Omega\text{cm}^2$ during the whole test period. Actually, the system containing the wash primer pigmented with aluminium phosphosilicate increased after 215 days. The high impedance of these painted panels ensured the protection of the metallic substrate. The anticorrosive behaviour of both primers resulted similar. In the case of the control (Fig. 11), the paint system without the wash

Table 2
Rusting degree (ASTM BH 610) of primed panels in the salt spray test (ASTM B 117).

Wash Primer	Exposure time (h)									
	1000	1180	1320	1780	2230	2550	2580	2600		
Basic zinc chromate	10	10	10	10	8	7	7	5		
Aluminium phosphosilicate	10	10	10	10	10	10	9	7		
Control (without inhibitor)	10	9	8	6	6	–	–	–		
^a R: rusting degree (ASTM D 610)										
Rust grade	10	9	8	7	6	5	4	3	2	1
Rusted area/%	Not rusted	0.03	0.1	0.3	1	3	10	16	33	50

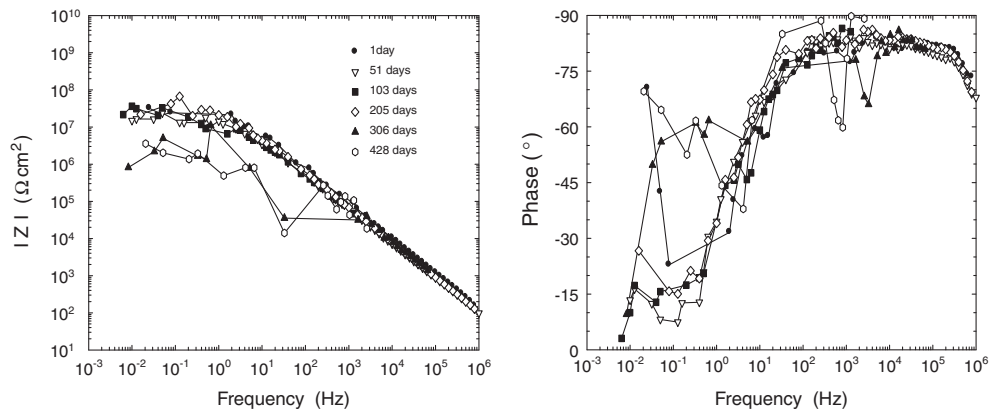


Fig. 9. Bode's plot of the galvanized steel substrate coated with the wash primer containing the basic zinc chromate and the alkyd paints. Electrolyte: 3% (w/v) NaCl.

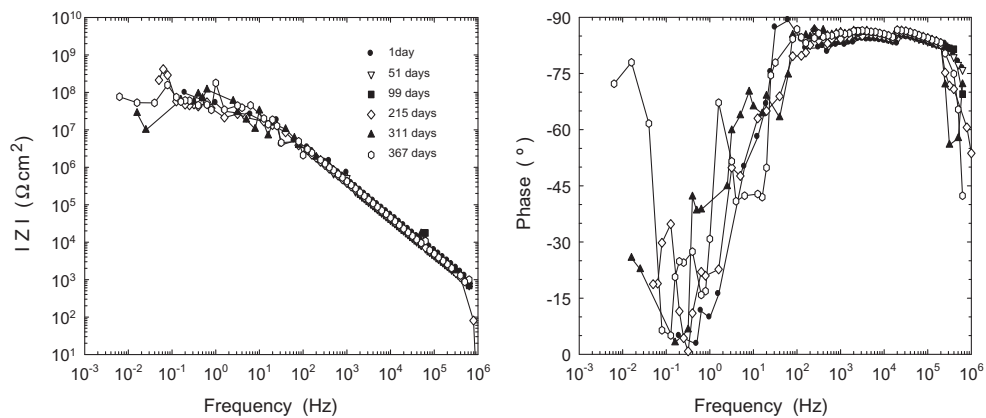


Fig. 10. Bode's plot of the galvanized steel substrate coated with the wash primer containing aluminium phosphosilicate and the alkyd paints. Electrolyte: 3% (w/v) NaCl.

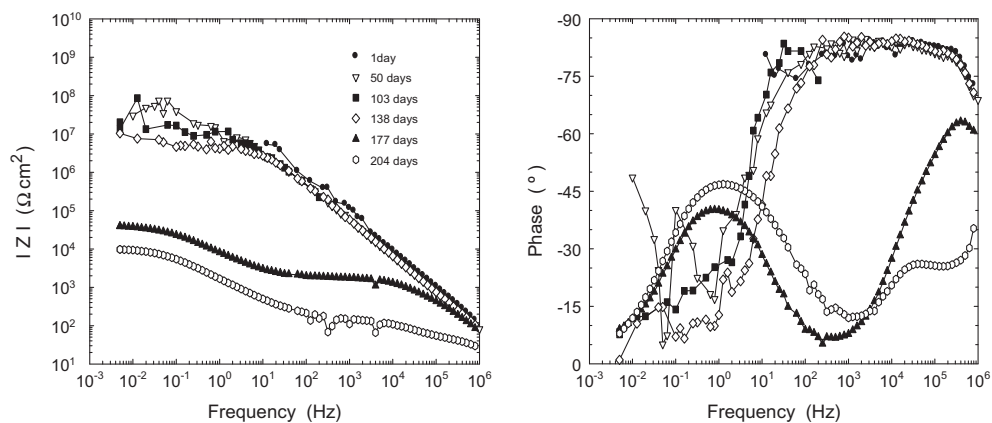


Fig. 11. Bode's plot of the galvanized steel substrate coated with the alkyd paints. Electrolyte: 3% (w/v) NaCl.

primer, the impedance of the coating begun to descend after 140 days of immersion and it lost its protective properties after 177 days.

4. Conclusions

The behaviour of a wash primer containing aluminium phosphosilicate was studied using a hot dip galvanized substrate and its behaviour compared with a reference formulation containing basic zinc chromate.

The SVET was used to assess the ionic currents flowing locally in the vicinity of a pinhole defect and revealed a steady ionic flow over the pinhole. This current was equilibrated by a cathodic process. In the case of the wash primer used as reference, the self-healing properties of basic zinc chromate could be appreciated. The primer containing aluminium phosphosilicate provided certain degree of protection at the beginning of the immersion period. SEM analysis of the exposed surfaces revealed that no delamination has occurred after SVET measurements.

Although the primer containing basic zinc chromate showed a better behaviour in SVET test, the differences observed between both primers clearly vanished when the wash primer was included in a complete paint system. Impedance measurements revealed that both wash primers had similar behaviour during the whole test period. Similar results were obtained in the salt spray test. So, it was concluded that basic zinc chromate could be successfully replaced by aluminium phosphosilicate.

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