

An evaluation of coil coating formulations in marine environments

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Abstract

This paper describes the activities carried out between 1996 and 1999 by the Group 6 “Coil Coating” in the frame of the Patina Network (Anticorrosive Protection in the Atmosphere), sponsored by CYTED. It includes the work accomplished by Science and Technology Institutions of the Ibero-American region on different painting systems supplied by Production Sectors of companies of participating countries. Twelve coil coating systems of varied protective characteristics were exposed outdoors, at three different marine atmospheric conditions of the MICAT Ibero-American Test Stations Network (CYTED). Steel, galvanised steel and Galvalume[®] samples coated with any of the painting systems built up with and without incision were used. In each case, the paint coating deterioration was evaluated according to ISO 4628-1 to ISO 4628-6, ISO 4623 and ASTM D-3274 standards. Results found after 12, 24, 36 and 42 months are discussed, in function of the aggressive agent characteristics of the test environment. These results are compared with those found in a salt spray chamber test, showing similar behaviour. Electrochemical impedance spectroscopy (EIS) was also applied on replicated samples of each material after different exposure periods, to evaluate deterioration of the metallic substrate/organic coating systems in the ambient conditions tested.

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1. Introduction

Coil coating or pre-painting steel is a novel and one of the most advanced steel anticorrosive protection technologies, developed to promote the use of steel in the most varied environmental conditions. It consists of a metallic base and a thin organic coating of uniform quality and excellent in-service performance, applied in a coil coating process. The metallic substrate is steel, although frequently used galvanised or pre-coated with some Zn-containing alloys, for extra protection, thus ensuring an important performance improvement. In fact, this electrochemically active metallic coating provides an additional protective layer, which increases not only isolation between the steel and its environment, but also, upon its preferential corrosion, it ensures steel cathodic protection if some localised defect of the organic outer film allowed access of corrosion agents to the metal.

Among the main metal substrates used in the coil coating process, galvanised steel and Galvalume[®] or Cinalume[®] (steel/55% Al–1.5% Si–Zn alloy) should be mentioned. In both cases, the Zn content in the coating layer preferentially dissolves in corrosive environments providing cathodic protection to the underlying steel.

Coil coating starts by successive joining of coils pairs feeding the process, with or without a Zn base coating on steel. Treatment with cleaning products optimises painting adhesion by chemical conversion under strict control of the parameters, ensuring uniformity of the process. The steel sheet enters a painting chamber where special rotating rubber roller applicators paint either one or both sides. The most widely spread coil coating systems consist of an epoxy base coating and another siliconised or fluorocarbonate polyester special topcoat layer, which renders higher protection against corrosion and an attractive (coloured) aspect, admitting further panel formability operations.

After painting, the sheet enters a furnace where hot air cures the organic coating film giving the paints the appropriate hardness, adherence and flexibility for further processes. On leaving the furnace, the painted sheet is cooled with

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de-mineralised water, followed by quality control. Through polyethylene film application it achieves protection before subsequent formability processes. Finally, a winding machine re-rolls the painted sheet to complete the coil coating production.

This work reports yearly results of 12 coil coating formulations applied for protection of steel panels exposed to five different marine atmospheres of Ibero-America, and in salt spray chamber. The tests were carried out by members of the Group 6 of Patina Network (Anticorrosive Protection in the Atmosphere), in the frame of the XV Sub-program “Environmental Impact on Materials”, sponsored by CYTED, in the 1996–1999 period.

2. Experimental

The 12 coil coating systems described in Table 1 were exposed to the five outdoor test stations which ambient characteristics and corrosivity are shown in Table 2. The same materials have also been tested in a salt spray test chamber to determine the type and magnitude of failures observed for different exposure times, as compared to those found in the marine test stations with up to 42 months of exposure.

After atmospheric exposure for 12, 24, 36 or 42 months replicated coated panels of A₁–A₆ materials were characterised by electrochemical impedance spectroscopy (EIS) and compared to non-exposed samples. For the impedance measurement, a cylindrical clamp-on acrylic (polymethyl methacrylate) cell was positioned on the panel covering a surface area of 15.9 cm². This cell contained a Pt-Rh mesh auxiliary electrode oriented parallel to the painted metal surface. An aperture in the top of the cell contained

a glass-lineal saturated Ag/AgCl-tipped reference electrode, positioned together with the counter-electrode. The electrolyte was 3.5% (w/v) NaCl solution (pH 8.2). The electrochemical experiments were carried out at laboratory temperature (20 ± 2 °C) in a Faraday cage, after 1 h immersion in the electrolyte. A Solartron 1255 FRA coupled to a Solartron electrochemical interphase 1286 and a PC were used. Measurements were accomplished at the potentiostatic mode and the amplitude of the applied ac voltage was 15 mV peak to peak. Impedance data collected starting at 10⁵ Hz and going to 1 × 10⁻³ Hz were interpreted on the basis of equivalent electrical circuit models using the fitting procedure developed by Boukamp [1].

The performance observed for the 12 materials in the different atmospheres was discussed according to the metallic coating presence and composition, and the base and topcoat paint coatings.

3. Results and discussion

Deterioration level of the organic coatings, with and without incision [2], caused by their exposure to three natural and also to the simulated salt spray laboratory atmospheres was evaluated by application of ISO 4628/82-1 to ISO 4628/82-16 [3–8] and ASTM D-3274 [9] standards.

Representative data involving size and density of failures were estimated on the basis of the proposal made by Keane et al. [10] and shown in Table 3. Value 0 was assigned to the absence of failure and 5 to complete damage, according to the ISO scale of 4628/82-1 standard [3]. For visualising the incidence of blistering degree, corrosion, estimated percentage of damaged area, etc., both in the body of the sample

Table 1
Characteristics of the tested materials

Paint system code	Metallic coating	Thickness of coating (μm)	Paint							Total thickness, E (μm)
			Base			Finishing				
			Vehicle	Pigment ^a	E (μm)	Vehicle	Pigment	Colour	E (μm)	
A ₁	Galvalume [®]	20	Epoxy	Ti, Cr, Co, Al	4	PVDF	Al, Ti, Fe, Si	Light blue	20	44
A ₂	Zn	20	Epoxy	Fe, Cr, Zn, Ti	6	PVDF	Fe, Zn, Si	Blue	17	43
A ₃	Zn	20	Epoxy acrylic	Si, Fe, Ti	6	Polyester siliconised	Fe, Si, Pb	Red	17	43
A ₄	Galvalume [®]	20	Polyester	Fe, Si, Ti	5	Polyester siliconised	Fe, Si, Al, Ti	Light blue	17	42
A ₅	Galvalume [®]	20	Epoxy	Fe, Si, Ti	4	PVDF	Al, Si, Ti	Red	19	43
A ₆	Galvalume [®]	20	Polyester	Ti, Si, Al	5	Polyester	Ti, Si, Al	White	18	43
CH ₁	–	–	Epoxy	Fe, Si	15	Polyester	Ti, Fe, Al, Si	Beige	15	30
CH ₂	–	–	Epoxy	Fe, Si	15	Polyester	Fe, Si	Brown	15	30
E ₁	Zn	20	Polyester	Ti, Al, Si	20	Polyester	Ti, Al, Si	White	15	55
E ₂	Zn	25	Polyester	Ti, Cr, Si, Al	20	Polyester siliconised	Fe, Si, Ti, Ca	Red	10	55
E ₃	Zn	20	Epoxy aminepl.	Fe, Ti, Si	20	PVDF	Fe, Al, Si	Green	16	56
E ₄ ^b	Zn	25	–	–	–	Alkyd melamine	Ti, Si, Al	White	25	50

^a Elements detected through EDX, in decreasing order of relative abundance.

^b NILU (Norway).

Table 2
Ambient characteristics and corrosivity of the three outdoor test atmospheres

Country	Station	Atmosphere	T (°C)	RH (%)	TOW (%)	Rain (mm per year)	[SO ₂] (mg m ⁻² per day)	[Cl ⁻] (mg m ⁻² per day)	Corrosion rate (first year) (μm per year)		Sun radiation ^a (K J cm ⁻² per year)	Sun hours (h per year)
									Fe	Zn		
Argentina	Jubany	Marine–polar	-2.7	84	29.3	278	Neg.	16.50 ^b	37.3	1.89	284	434
Uruguay	Punta del Este	Marine	16.5	78	53.8	823	3.95	143.5	49.0	1.89	568	2348
Venezuela	La Voz	Marine–desertic	34.7	92	48.3	398	29.90	374.8	922	26.5	490	3073

Data from the book “Mapas de Iberoamérica de Corrosividad Atmosférica” [4].

^a Data 1996–1998.

^b Estimated through the Cl⁻ content in water monthly collected in pluvionivograph of the Jubany base station (1993–1995, 1998).

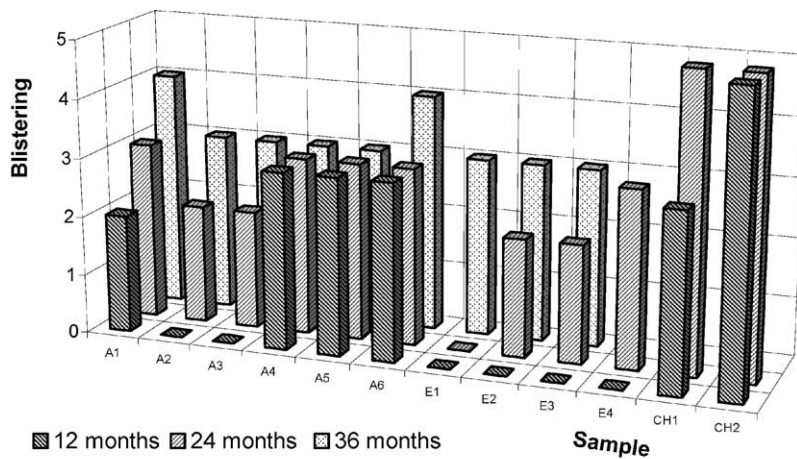
Table 3
Deterioration degree as a function of failure size and density

Density	Size				
	1	2	3	4	5
S1	1	1	1	1	2
S2	1	2	2	2	3
S3	2	2	3	3	4
S4	3	3	4	4	5
S5	4	4	4	5	5

and at the incision, bar diagrams showing the failure magnitude for the different materials and yearly test times were plotted. Bar diagrams illustrating the painting systems blistering degree in two marine atmospheres and during the salt spray test are shown in Figs. 1 and 2.

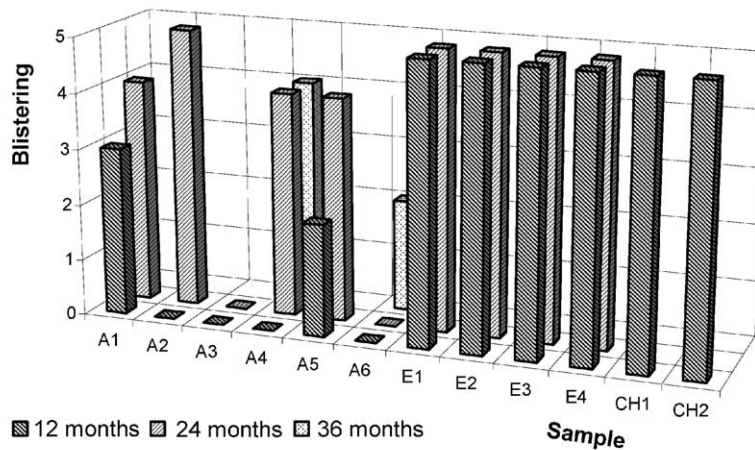
Among the painted panels characteristics that changed during the natural as well as during the accelerated test, blistering and corrosion, both at the incision, were the most significant. Next, corrosion in the sample body, away from the incision and edges, suggested each painting system defects (porosity, low cross-linking density, adhesion fails, etc.), and also the reactivity of the corresponding metallic substratum to the distinct atmospheres.

Comparative results for the 12 protective systems exposed at three outdoor stations (Jubany, Punta del Este and La Voz), conditions for different times, as well as the best and the worst behaviour for the three sets of coatings, are shown in Table 4. Times required for blistering and corrosion initiation during exposure to salt spray chamber are included in Table 5. Ionic resistance for testing periods included the final



(a) Punta del Este Station

CH1- CH2 were removed at 24 months because the coating failure was over 25% of the area



(b) La Voz Station

CH1- CH2 were removed at 12 months and E1-E4 at 24 months because the coating failure was over 25% of the area

Fig. 1. Blistering at incision vs. exposure time.

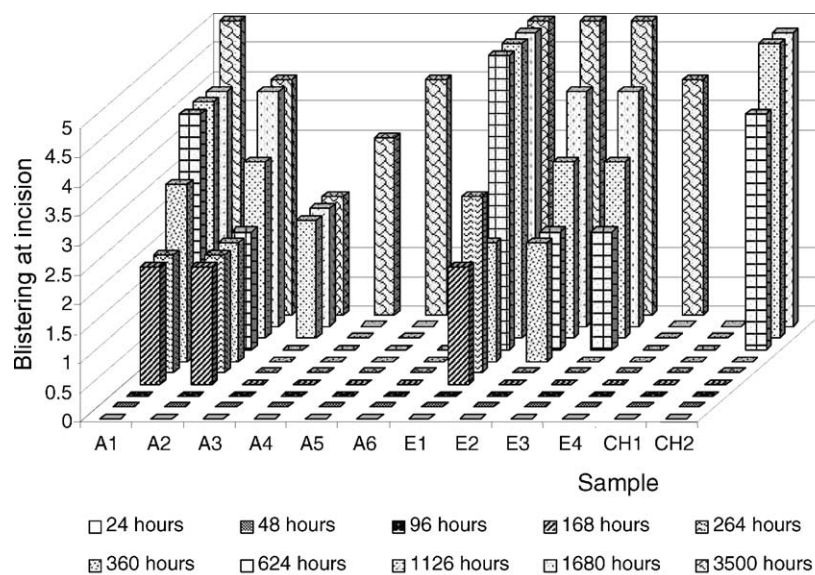


Fig. 2. Blistering at incision for different salt spray test periods.

Table 4
Results after yearly exposure in the three outdoor test stations

Behaviour	Failure	Test station (Country)		
		Punta del Este (Uruguay)	La Voz (Venezuela)	Jubany (Argentina)
Best	Final exposure time (months)	36	42	42
	Blistering in incision	A ₆ and E ₂	A ₆	A ₂ and E ₄
	Corrosion in incision	E ₂	A ₆	E ₄
	Blistering in body	A ₃ –A ₆	A ₆	A ₂ –A ₅ ; E ₁ –E ₄
	Corrosion in body	A ₁ –A ₆ ; E ₂ –E ₄	A ₆	A ₁ –A ₆ ; E ₁ –E ₄
Worst	Final exposure time (months)	23	12	12
	Blistering in incision	CH ₂ ^a	CH ₂	CH ₂
	Corrosion in incision	CH ₂ ^a	CH ₂	CH ₂
	Blistering in body	CH ₁ and CH ₂	CH ₂	CH ₂
	Corrosion in body	CH ₁ and CH ₂	CH ₂	CH ₂
Main failure		Blistering in incision	Flaking	Corrosion in incision

^a Observations: retired when coating failure is >50% (at 23 months).Table 5
Salt spray chamber—time to failure initiation (h)

Paint system code	Blistering		Corrosion		Observations
	Body	Incision	Body	Incision	
A ₁	–	168	–	–	Test finished at 3500 h; best behaviour A ₂ ; worst behaviour A ₁ ; also in protected edges in A ₄ and A ₅
A ₂	1128	168	–	–	
A ₃	–	1128	–	–	
A ₄	–	3500	–	–	
A ₅	–	3500	–	–	
A ₆	–	3500	–	–	
CH ₁	624	128	–	24, red	Test finished at 1680 h; similar behaviour in CH ₁ and CH ₂
CH ₂	264	360	–	24, red	
E ₁	624	168	–	–	Test finished at 3500 h; best behaviour E ₃ and worst behaviour E ₂ ; blistering and white corrosion also in non-protected edges
E ₂	624	360	–	–	
E ₃	3500	624	–	1128, white	
E ₄	1128	3500	–	–	

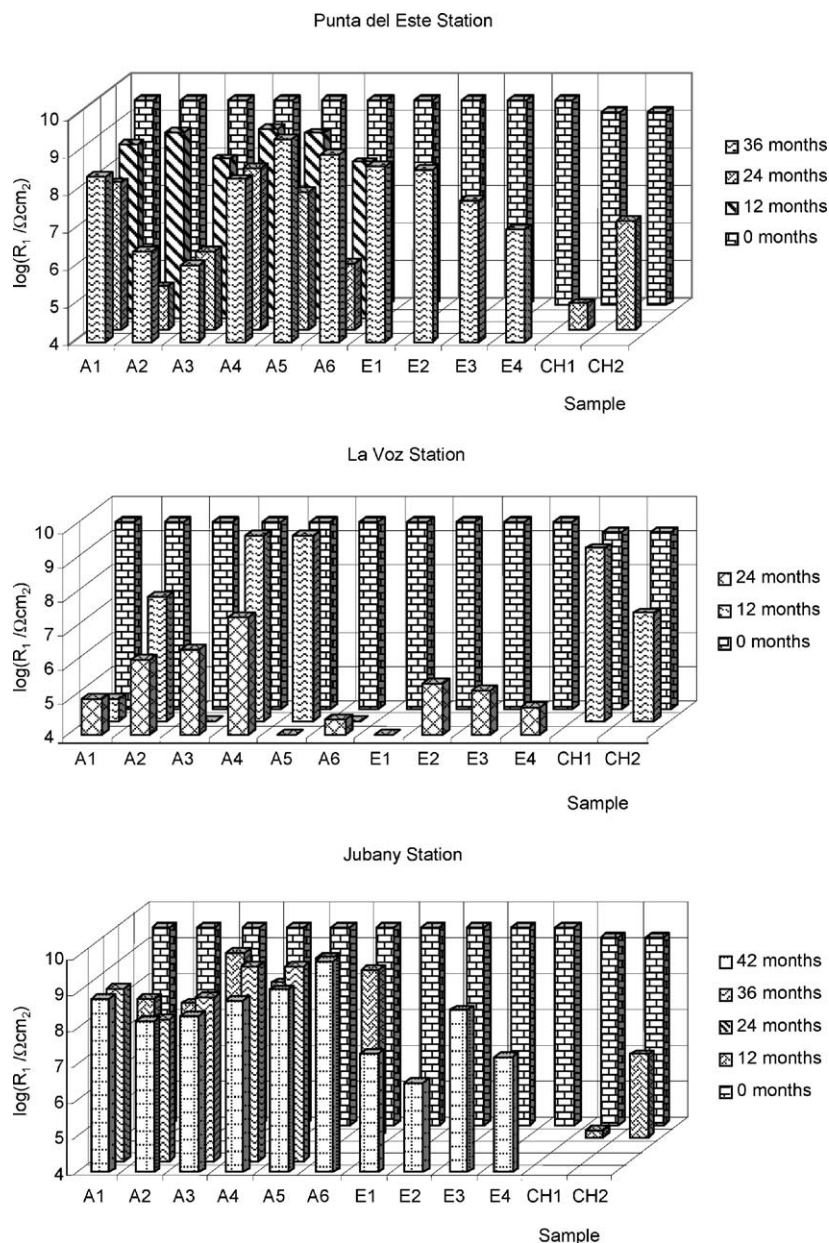


Fig. 3. Ionic resistance vs. outdoor exposure.

of 42 months, are summarised in Fig. 3. Besides, EIS results derived from measurements applied yearly to A₁–A₆ naturally weathered panels in the same test stations are shown in Fig. 3.

3.1. Atmospheric exposure

The many atmospheric parameters interacting with the tested materials include the fraction of exposure time designed as “time of wetness” (TOW) [11] as one of the controlling factors of the weathering process. The sun radiation is synergistic on the TOW’s effects, enhancing deterioration of pigments and polymer components of the paint coating in combination with their washing off effects.

Oxygen permeation through all painting systems provides the necessary element for the main cathodic reaction in neutral electrolytes.

Among the environmental variables defining the type and magnitude of the metal attack in different natural atmospheres, Cl⁻ and/or SO₂ air contaminants are the most frequently mentioned [12]. They substantially increase the aggressiveness of aqueous media, accelerating the corrosion reactions at the metal/organic film interface.

The organic coating porosity as much as the aqueous phase osmosis and conductivity, increasing with the salt accumulation, are non-visible driving forces for the corrosion nucleation on the underlying metal(s) and further organic coating degradation. Gloss loss and colour changes,

sometimes added to chalking, are the initial surface evidences of the weathering process.

Once corrosion starts on the steel panels only protected by an organic coating system (samples CH₁ and CH₂), growing blisters appear and a rapid deterioration occurs at the incision and edges. Conversely, the galvanised steel and Galvalume[®] panels only show slow white corrosion, even in the most aggressive environments. When the Zn-containing metallic coating locally wears off completely at the incision and edges, its cathodic protection disappears, and orange-reddish corrosion points can be seen due to the base steel attack. Away from the borders, corrosion and blistering occur slower than at the incision because the mass transport process (water, oxygen and ionic species) involved takes place through the intact part of the paint films.

The strong effect of sun radiation was appreciable when comparing the datum at Jubany (284 KJ cm⁻²) with those obtained in the other marine atmospheres of similar corrosiveness on bare plain carbon steel and Zn, as seen in Table 2. Moreover, both the screen effect of the thick ice layer accumulated on the samples during most of the exposure period and the very lower TOW estimated according to ISO 9223 standard for this polar station could also be considered causes of minimising the sun radiation effect on degradation of all the organic coating systems. However, in previous papers dealing with Jubany polar atmosphere, it was demonstrated that the TOW, as defined and estimated according to ISO 9223 standard [11], is less than half of the real-time during which test samples are in contact with liquid water [13,14]. Even the low mean temperatures could be another apparent cause. But it could also be ruled out when considering the corrosion rates of bare metals determined in Jubany. Then, these two last parameters do not offer significant arguments to justify the exceptionally good performance of all the tested coil coating formulations in the Antarctic Jubany station.

In La Voz station, where the samples faced north (southern hemisphere) and the sea, the intense winds provided a very interesting effect for analyses. Predominant winds reached the samples from NW and more intensely from NE, constituting not only an important source of marine salts but also a mechanically aggressive factor itself, due to their erosive action. This effect, evaluated by exposure of bare carbon steel AISI 1010 for 3 years, caused an attack penetration of 1500 μm per year while the measured average electrochemical corrosion rate for the same type of substrate was 922 μm per year. SEM metallographies of the more damaged edges and incision in all the tested systems showed evidence of attack initiation and propagation due to the wind erosive effect, not only on the organic but also on the metallic coatings [15].

3.2. Salt spray test

ASTM B-117 [16] and ISO 7253 [17] are the international standards most generally applied to follow this test,

evaluate samples state and express results for different exposure times. Results are shown in Table 5.

3.3. Electrochemical impedance spectroscopy

When there is no electrolyte solution within the metal/organic coating interface, neither electrochemical double-layer formation nor faradaic reactions occur; therefore, the only information that can be obtained from impedance spectra is related to the dielectric properties of the organic coating. A first interpretation of the complex plane plot may be described by a transfer function corresponding to an equivalent circuit built up from a series combination of the electrolyte resistance (R_s) with the paint film dielectric capacitance (C_1).

As the exposure time goes on, the amount of permeating water, oxygen and ionic species increase the paint coating conductivity, becoming measurable the resistance (R_1) coupled to the dielectric capacitance C_1 . In such conditions, the impedance diagram and equivalent circuit, together with information about the membrane ionic resistance (R_1 , which describes paths of lower resistance short-circuiting the organic coating) and the dielectric capacitance (C_1 , the value of which is associated with the water uptake), can be obtained. Once the permeating species reach the metallic substrate corrosion processes may start, causing the emergence of a second time constant due to the relaxation of the electrochemical double-layer (C_2) and the charge transfer resistance (R_2) proper of a faradaic process, related as $1/R_2$ with the corrosion rate. The characteristic impedance spectra and corresponding equivalent circuit modelling the tested coated metal systems in 3.5% NaCl solution are shown in Fig. 4 [18].

3.4. Materials ionic resistance versus exposure time

In previous papers, this type of electrochemical analysis was applied for 12 and 24 months exposure [19,20].

EIS is a very useful technique to evaluate this low thickness but high performance formulations developed to protect steel in the most aggressive natural and simulated conditions [21–24]. The results for all the considered materials after different natural exposition periods are presented in Fig. 3.

Ionic resistance (R_1) values for the organic coatings ranged from $10^3 \Omega \text{ cm}^2$ for weathered samples up to greater than $10^8 \Omega \text{ cm}^2$ for non-exposed ones. These resistance values are inversely related to the average cross-section of the conductive pathways between the metal and the electrolyte. Therefore, they suggest that penetration of the paint by the electrolyte solution after 12–42 months exposure to different atmospheric media was highly dependent on both the painting system formulation and the aggressiveness conditions. Accordingly, the lower values obtained coincided with large rust spots on the specimens, confirming their poor barrier and anticorrosive properties under the experimental conditions.

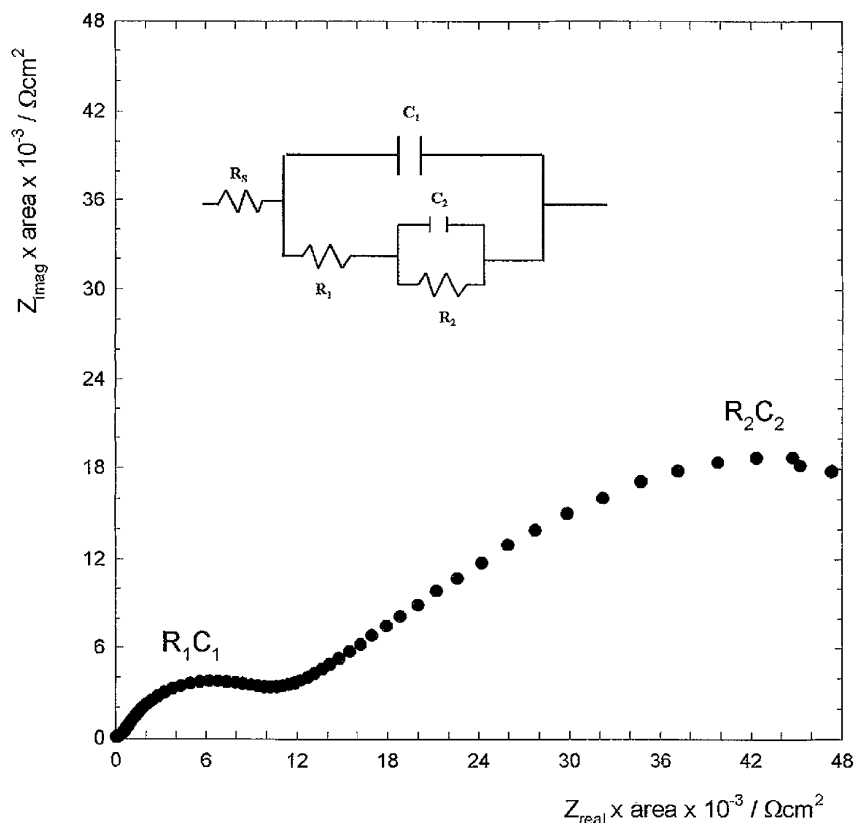


Fig. 4. Complex plane plot for combination R_s with two time constants R_1C_1 and R_2C_2 .

The high anticorrosive protection found in samples where $R_1 > 10^8 \Omega \text{ cm}^2$ was attributed to the great influence of the mechanism described by the barrier and insulating effect model (i.e. the paint capacity for delaying the aggressive species diffusion up to the metal/paint interface), added to an effective corrosion-inhibiting action of the base coating pigments. In agreement with this mechanism, it was assumed that the metal surface effectively maintained isolation not only from the natural atmospheres to which the samples were exposed, but also from the 3.5% NaCl solution during EIS measurements.

After the first yearly period and for the three test stations, the EIS results showed a clear decrease of the organic coating resistance with time for samples A_1 – A_6 . On the contrary, after the second year in the most aggressive atmosphere of La Voz station the coating resistance increased for samples A_1 , A_3 and A_6 , due to the blockage of the intrinsic and/or extrinsic paint defects by the Zn corrosion products accumulated from the metallic coating dissolution. For other painting systems applied on metallic pre-coated steel and also for replicate samples but in milder marine test sites, either continuously decreasing or oscillating values were determined for longer periods. Such a performance is a consequence of the formation of new ionic conductive paths through the organic film and/or the defects blockage by the Zn corrosion products, respectively.

Except in the marine polar Jubany station, and in spite of very different atmospheric variables (yearly mean T , sun radiation intensity and sun hours, SO_2 and Cl^- deposition rates, etc.) in the rest of stations, the paint blistering at the incision was the main failure in all the protective systems (Fig. 1). Changes with time in the magnitude of this failure for all the samples showed that the most significant environmental parameters were $[\text{Cl}^-]$ and sun radiation (Table 2). In spite of the great difference among those marine atmospheres, the other ambient characteristics did not show a significant correlation with the magnitude of the damage variation. By comparing changes of the coating ionic resistance as a function of the exposure time at each one of the outdoor stations (Fig. 3), it could be inferred that (a) at Jubany, A_i samples showed the best performance. All of them maintained good protective level for 42 months and oscillating R_1 values, while E_i and CH_i samples lasted 24 and 12 months, respectively, reaching $R_1 < 10 \Omega \text{ cm}^2$. In good agreement with the absence of colour change and the lowest gloss decrease, as compared with the rest of the atmospheres, it could be attributed to the low sun radiation accumulated and sun hours during each test period; (b) at La Voz station, the performance of all the protective systems was worst. They lasted up to 24 months and R_1 values became $< 10^5 \Omega \text{ cm}^2$ for systems A_i and E_i , while for those built up from non-metallic coated steel (CH_i) the measured

R_1 values reached up to $10^7 \Omega \text{ cm}^2$ due to gathering of steel corrosion products; (c) at Punta del Este station, both A_i and E_i samples lasted for 36 months showing oscillating values of $R_1 \geq 10^6 \Omega \text{ cm}^2$, while CH_i samples showed faster deterioration rate with $R_1 \leq 10^6 \Omega \text{ cm}^2$ at 24 months exposure.

4. Conclusions

1. The best performance of the tested coil coating materials subjected to atmospheric exposure was observed in test stations with the lowest aggressiveness, this being mainly determined by the pollutant content.
2. Experimental results provided by natural atmospheres and the salt spray chamber test showed that each material appeared as the best or the worst, depending on the type of failure (blistering, corrosion, gloss, colour, etc.) evaluated.
3. Painting system thickness greatly affected the outdoor behaviour. Therefore, the relative values of dispersion observed among the different painting systems tested could have introduced some uncertainty when the relative anti-corrosive performance as a function of the exposure time was compared. All experimental data showed clearly the following:
 - Thicker painting systems decreased the susceptibility to blistering in the sample body.
 - In all laboratory tests as well as in natural environments, the most frequent failures occurred were corrosion and secondly blistering, both at the incision.
 - After the exposure in different atmospheres, the experimental results obtained for samples CH_1 showed a better anticorrosive performance when considering the steel panels without metallic pre-coating. This was attributed to an enhanced barrier effect afforded by the Ti and Al pigments added to this paint formulation; its light colour should also have reduced the sun radiation effect as compared to the dark CH_2 samples.
 - Ionic resistance values obtained from EIS correlated well with the characteristics observed during visual inspection. So, if it is considered that $R_1 \geq 10^7 \Omega \text{ cm}^2$ provides a good protection level, after 42 months exposure in Jubany all A_i samples had good behaviour; in La Voz only sample A_4 attained that condition after 24 months exposure, and finally in Punta del Este all the Galvalume[®] metallised samples showed good protective performance after 36 months.
 - After 42 month's outdoor test, among the samples designed A the best performance was shown by formulation A_4 and the worst was A_5 , while among those designed E the best performance was shown by formulation E_3 , followed by E_2 . The worst was observed for E_4 .
 - Metallic Zn-based coatings increased the time for reddish corrosion products appearance in edges and

incision during salt spray chamber test. They promote pore blockage in organic coatings, but when Zn corrosion was intense organic coating disbonding took place. This also occurred in natural environments.

- When the samples were exposed to natural outdoor or at the accelerated salt spray tests, the factors controlling coil coating failures were different due to: (1) the strong effect of sun radiation on the organic coatings during natural exposure mainly at La Voz, secondly at Punta del Este and the lowest at Jubany; and (2) the continuous 100% TOW in salt spray test promoted the formation of less protective Zn corrosion products than those formed during the alternated dry/wet periods provided by natural outdoor exposures.

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