



Evaluation of eco-friendly anticorrosive pigments for paints in service conditions

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ABSTRACT

The performance of different replacements for chromates was studied. The anticorrosive properties of seven phosphate-based pigments, a calcium-exchange silica and a ferrite were assessed by electrochemical techniques and formulating solvent-borne paints with epoxy and alkyd resins. Paints contained 30% by volume of anticorrosive pigment, with respect to the total pigment content.

The anticorrosive performance of paints was evaluated by accelerated tests (salt spray chamber) and electrochemical essays (corrosion potential and ionic resistance). Outdoor exposure tests were carried out in an urban-industrial environment during 8 years.

The anticorrosive performance of the tested paints showed that there is not a clear relationship between the laboratory tests and the outdoors exposition and that none of them, by themselves can predict the behaviour of the paint under service. However, electrochemical essays with pigments may give an orientation about pigment performance in anticorrosive paints. As a general rule, if the pigment reduces notably steel corrosion rate and generates a rather high apparent polarization resistance a good anticorrosive performance may be expected.

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1. Introduction

Organic coatings are a widespread method to protect steel against corrosion. Coatings protect metals from the adverse effects of atmospheric agents by two main mechanisms: a barrier effect and surface passivation. These two effects are in series, only after the coating is penetrated by water, oxygen and electrolytes, the anticorrosive pigments begin to act passivating the surface [1].

Classical anticorrosive paints normally contained inhibitors based on hexavalent chromium or lead compounds. The employment of these compounds is being restricted because they contaminate the environment and cause health problems to humans [2]. Regulations in different countries, led to an intense research to find out alternative pigments of low toxicity and with the same performance as the old ones.

The use of zinc phosphate in anticorrosive paints is widespread and has been well documented [3–7]. Although zinc phosphate gives good results, in certain cases, it proved to have lower anticorrosive performance than zinc chromate [4,5]. As a consequence, a second pigment generation based on zinc phosphate was introduced by modifying it with molybdenum or aluminium [4,8]. Finally, a third generation arose by substituting the phosphate anion by polyphosphates (tripolyphosphate, pyrophosphate, etc.)

[9–17]. Both pigment series are claimed to have better anticorrosive behaviour than zinc phosphate.

Although phosphate pigments dominate the market, many other inhibitors were developed for improved anticorrosive protection. Ferrites and ion-exchange pigments are acquiring increasing importance as alternative products. These inhibitive substances have not been studied as deeply as phosphates; but, in many accelerated tests they exhibit better performance than zinc phosphate [10,18–24].

Ferrites have the general formula XFe_2O_3 ($X = MgO, ZnO$ or CaO) or YAl_2O_3 ($Y = CaO, ZnO$) and a spinel structure [10,18–20]. Ferrites can act as barrier pigments or by neutralizing the action of corrosive substances that diffuse through the coating [21]. In this last case, the reaction between the fatty acids present in the resin and the anticorrosive pigment forms soaps which harden and seal the coating. Besides, the metallic substrate is passivated by the alkaline media generated by the hydrolysis of the pigment [10].

The protection of the metallic surface by paints with exchange pigments is claimed to be due to the growth of a silica film onto the metal surface and calcium ions, exchanged from silica particles, which migrate towards the metal-coating interface. The resulting film is impermeable to humidity and ions, preventing corrosion. However, it seems that protection depends more on the high pH provided by the pigment than on other of its properties [23–27].

The protective ability of coatings is currently evaluated by electrochemical and accelerated essays. These last ones often simulate extreme environments such as the marine one or high humidity environments. However, in most cases, there is not a good cor-

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Table 1
Anticorrosive pigments main chemical composition.

Pigment		Chemical composition (% by weight)
ZP	Zinc phosphate	36.3% zinc, 52.5% phosphate, 8.7% de sodium; $Zn_3(PO_4)_2$
ZMP	Zinc molybdophosphate	43.7% zinc, 35.4% phosphate, 0.26% molybdenum
Zpp	Zinc polyphosphate	24.4% zinc, 47.6% phosphate and 2.1% sodium; $NaZn_2(P_3O_{10})$
Capp	Calcium polyphosphate	22.3% calcium, 69.7% phosphate, 2.3% sodium; $NaCa_2(P_3O_{10})$
Alpp	Aluminium polyphosphate	3.4% aluminium, 24.3% zinc, 8.2% silica; 64.1% phosphate
ZPy	Zinc pyrophosphate	31.7% zinc, 49.4% phosphate, 0.7% de sodium; $Zn_2(P_2O_7)$
ZHy	Zinc hypophosphite	69.7% zinc, 22.8% phosphate, 7.5% hypophosphite
CaEx	Calcium-exchange silica	5.25% calcium, 77.93% insoluble silica, 1.14% active silica
CaFt	Calcium ferrite	79.5% zinc, 20.0% calcium

relation between laboratory tests and the coating performance under service conditions. This lack of correlativity is due to the oversimplification made in accelerated tests about the aggressive environment where the coating will be exposed. Only a few variables such as high temperature, high humidity, presence of aggressive ions, U.V. radiation are normally taken into account in laboratory tests.

The aim of this work was to evaluate a selected series of corrosion protective pigments in outdoors conditions. The selected phosphate pigments were zinc phosphate (ZP), zinc molybdenum phosphate (ZMP), three different polyphosphates (zinc, calcium and aluminium tripolyphosphates, Zpp, Capp and Alpp, respectively), zinc pyrophosphate (ZPy) and a pigment based on zinc hypophosphite (ZHy). As alternative non-phosphate pigments, calcium-exchange silica (CaEx) and calcium ferrite (CaFt) were chosen. The results showed that accelerated and electrochemical tests are complementary and none of them by themselves can predict the behaviour of the paint under service (Table 1).

2. Experimental

The electrochemical behaviour of a SAE 1010 steel electrode in a suspension containing 5 g of the corresponding pigment in 0.025 M sodium perchlorate was studied. Steel corrosion potential was measured with respect to the saturated calomel electrode (SCE), during 4 h and after 24 h of immersion. Steel polarization resistance was also measured with (R_p^{IR}) and without IR-drop (R_p) compensation in a three electrode cell. The reference electrode was SCE and the counterelectrode a platinum grid. The sweep amplitude was ± 20 mV, starting from the corrosion potential at a scan rate of 0.166 mV/s. Measurements were taken employing the 273A EG&G PAR Potentiostat/Galvanostat plus SOFTCORR 352 software.

Pigments performance was also assessed in anticorrosive paints. The materials used to form the paint films were an epoxy-polyamide resin and a medium oil alkyd (50% linseed oil, 30% o-phthalic anhydride, 8% pentaerythritol and glycerol, and 12% pentaerythritol rosinat) resin. The solvent mixture was xylene/methyl isobutyl ketone/butoxyethanol (13/45/42%) in the case of the epoxy resin and white spirit for the alkyd. The anticorrosive pigment concentration was, in every case, 30% v/v, with respect to the total pigment concentration. The complementary pigments were titanium dioxide, barium sulphate and talc. The composition of the pigment mixtures is shown in Table 2. The PVC/CPVC (Pigment Volume Concentration/Critical Pigment Volume Concentration) ratio

Table 2
Composition of the pigment mixtures (% by volume).

	Zp	ZMP	Zpp	Capp	Alpp	ZPy	ZHy	CaEx	CaFt
Anticorrosive pigment	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Titanium dioxide	12.0	12.0	14.4	14.4	12.0	12.0	12.0	12.0	14.4
Barium sulphate	29.0	29.0	36.1	36.1	29.0	29.0	29.0	29.0	36.1
Talc	29.0	29.0	19.5	19.5	29.0	29.0	29.0	29.0	19.5

was 0.8. Pigments were dispersed in the vehicle employing a ball mill with a 3.31 jar for 24 h to achieve an acceptable dispersion degree.

Paints were applied by brush on SAE 1010 steel panels (15.0 cm \times 7.5 cm \times 0.2 cm), previously degreased with toluene, up to a thickness of 80 ± 5 μ m.

A set of three panels was placed in the salt spray chamber (ASTM B 117). Rusting (ASTM D 610) and blistering (ASTM D 714) degrees were evaluated as a function of time.

Ionic resistance between the painted steel substrate and a platinum electrode was measured in the cell obtained by fixing an acrylic tube, 2 cm diameter, on the painted specimen and filling it with 0.5 M sodium perchlorate. Measurements were carried out employing an ATI Orion, model 170, conductivity meter at 1000 Hz. The corrosion potential was measured in the same cell, against SCE, with a high impedance voltmeter.

Another set of panels, with a suitable top-coat, total film thickness 100 ± 5 μ m, was placed at 45° , facing north, in the outdoor station of CIDEPINT, located at La Plata, Argentina ($34^\circ 54'S$ and $57^\circ 55'W$), in an urban-industrial environment. The characteristics of the station in terms of average temperature, relative humidity, winds and annual rain, according to the months and the years, are shown in Figs. 1–3.

Electrochemical measurements were also done on panels after 8 years of outdoor exposure. In this case, the samples were removed from the exposition site and the corrosion potential as well as the ionic resistance were measured employing the same cell described before. After the measurement, the samples were placed back outdoors.

3. Results and discussion

Results of electrochemical tests can be seen in Table 3. After 4 h of immersion, steel in contact with calcium polyphosphate had a corrosion potential more negative than that of the steel immersed in the supporting electrolyte (blank). The same results were obtained with calcium ferrite while in the case of aluminium and zinc polyphosphates, the corrosion potential was similar to the blank. However, only steel in the blank test rusted. This fact evidenced that the metal activity was similar in all these cases but the presence of the pigments induced the formation of a protective film [9,13]. The corrosion potential of the steel immersed in the other pigments' suspensions was at least 70 mV more positive than the blank and they never reached uncoated steel corro-

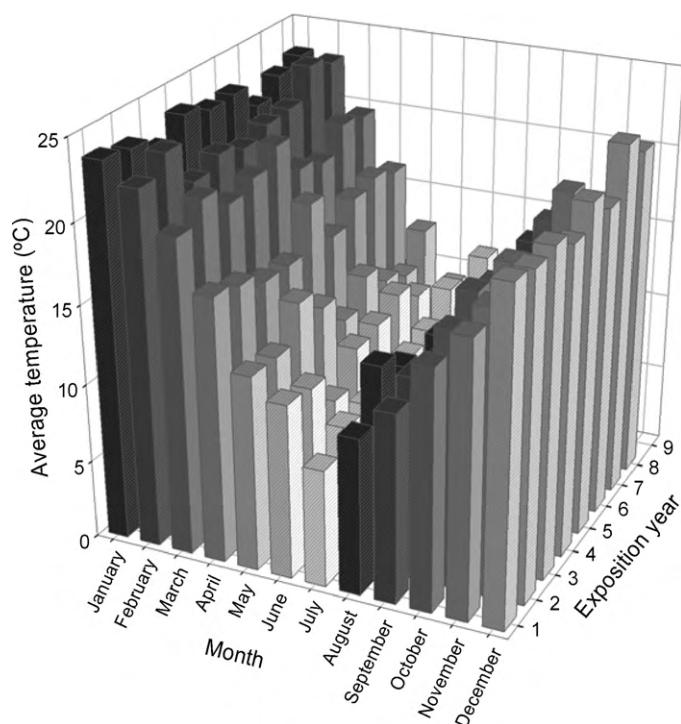


Fig. 1. Average temperature as a function of the month and the year of exposure.

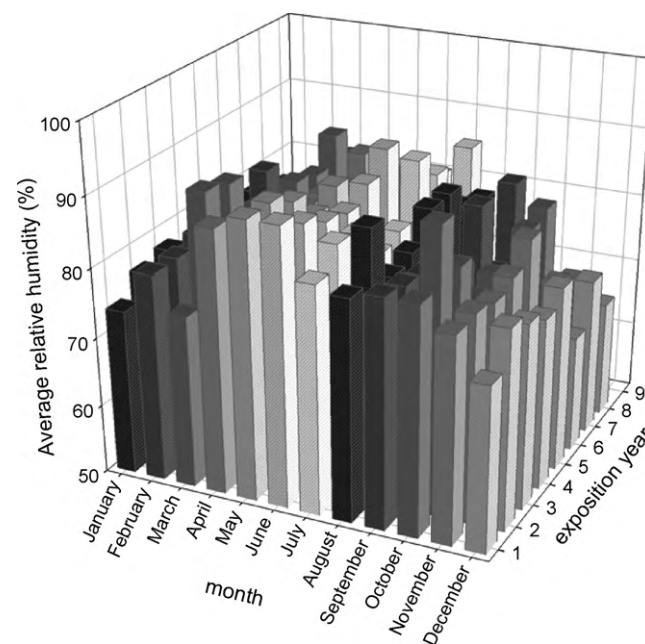


Fig. 2. Average relative humidity (%) as a function of the month and the year of exposure.

sion potential, although the values decreased during the essay (Figs. 4 and 5).

The higher values of R_p with respect to R_p^{IR} indicated that some additional protection was obtained due to the barrier properties of a film formed on the substrate. This film was composed by non-expansive iron oxides as in the case of the phosphate-based pigments, or by silica when CaEx was employed [9,13,24,25,28]. For each pigment, the ratio $R_p^{IR}/R_{p_{blank}}^{IR}$ was, at least, 7 and maybe as high as 25, thus indicating an important reduction in the corrosion current due to anticorrosive pigments.

The ratio R_p/R_p^{IR} was higher or equal to 2 for steel immersed in the ZP, ZMP, Zpp or ZPy suspensions while in the case of Capp, Alpp, ZHy, CaEx and CaFt is lower than that value, indicating that the film formed on steel was not very protective (Table 3).

Results obtained with the epoxy coated panels in the salt spray cabinet (Table 4) show that phosphates have an acceptable behaviour because after 1000 h the rusted area was $\leq 0.1\%$. The best anticorrosive protection, after 2000 h of exposition, was obtained with zinc molybdenum phosphate (ZMP), aluminium polyphosphate (Alpp) and the calcium-exchange silica (CaEx); the painted surfaces had neither corrosion points nor blisters. The worst anti-

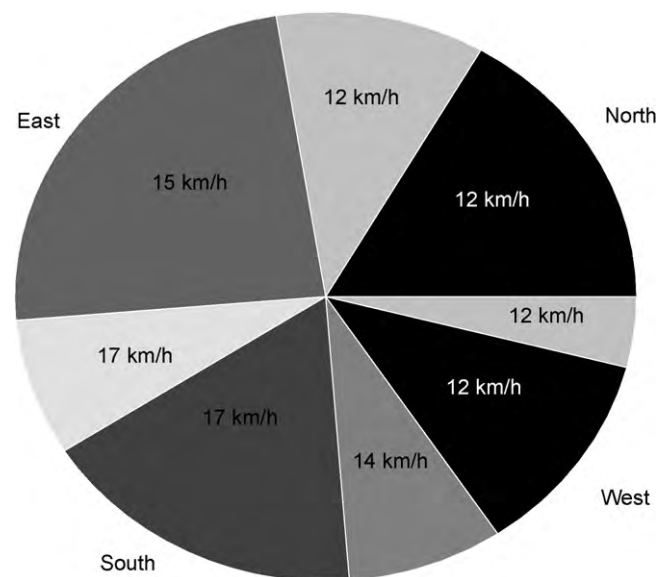


Fig. 3. Relative frequency, direction and average speed of the winds.

Table 3

Polarization resistance with and without IR compensation and corrosion potential of the steel immersed in the pigment suspensions.

Pigment	4 h		24 h			
	E (mV)	E (mV)	R_p ($k\Omega cm^2$)	R_p^{IR} ($k\Omega cm^2$)	$R_p^{IR}/R_{p_{blank}}^{IR}$	R_p/R_p^{IR}
ZP	-464	-690	3.5	1.1	3.7	3.2
ZMP	-372	-445	11.5	4.8	16.0	2.4
Zpp	-548	-622	7.6	2.1	7.0	3.6
Capp	-639	-623	4.9	2.7	9	1.8
Alpp	-510	-665	3.0	7.5	25.0	0.4
ZPy	-481	-531	10.1	5.1	17.0	2.0
ZHy	-419	-546	6.9	4.0	13.3	1.7
CaEx	-441	-535	8.8	6.2	20.7	1.4
CaFt	-617	-683	0.8	1.3	4.3	0.6
Blank	-558	-635	0.2	0.3	1	0.7

R_p : polarization resistance without IR compensation; R_p^{IR} : polarization resistance with IR compensation.

Table 4
Rusting (R) and blistering (B) degrees of the epoxy painted panels during salt spray test.

Pigment	240 h		700 h		1000 h		2000 h			
	R	B	R	B	R	B	R	B		
ZP	10	10	10	10	10	10	8	10		
ZMP	10	10	10	10	10	10	10	10		
Zpp	10	10	9	10	8	10	–	–		
Capp	10	10	9	10	9	7F	–	–		
Alpp	10	10	10	10	10	10	10	10		
ZPy	10	10	9	10	9	10	7	10		
ZHy	10	10	10	10	10	10	7	2F		
CaEx	10	10	10	10	10	10	10	10		
CaFt	6	6M	–	–	–	–	–	–		
Rusting degree (ASTM D 610)										
Rust grade	10	9	8	7	6	5	4	3	2	1
Rusted area/%	No rusted	0.03	0.1	0.3	1	3	10	16	33	50
Blistering degree (ASTM D 714)										
Frequency	Dense, D		Medium dense, MD				Medium, M		Few, F	
Size	10		8				6, 4		2	
Comments	No blistering		Smaller size blister easily seen by unaided eye				Progressively larger sizes			

corrosion performance was obtained with calcium ferrite (CaFt) which failed after 240 h of exposition (corrosion degree: 6, blistering degree: 6M).

Panels painted with the alkyd coatings had lower performance due to the intrinsic lower resistance of alkyd binders. Only panels coated with anticorrosive paints containing ZMP, ZPy, ZHy and CaEx were classified with a 9 or 10 after 1000 h in the salt spray cabinet. Panels coated with the other paints presented, at that time, more than 0.3% of the surface rusted (qualification 7 or less), blisters or serious adhesion problems (Table 5).

As the protection usually depends not only on the pigment but also on the binder [9,24,25], the best results were obtained with the epoxy resin except when calcium ferrite was used. CaFt has better performance with the alkyd resin due to the neutralization of its acidic components and consequent soap formation [18,21,25].

The corrosion potential of painted panels as well as the ionic resistance (R_i), after 1 and 30 days of immersion in 0.5 M NaClO₄, can be seen in Table 6. Full barrier properties of a coating are attained when $R_i > 10^6$ k Ω cm² and this effect is completely lost when the $R_i < 10^2$ k Ω cm² [29]. All the epoxy paints, except those formulated with ZMP and CaFt, showed a certain barrier effect because R_i was higher than 2×10^3 k Ω cm² after 1 day of immer-

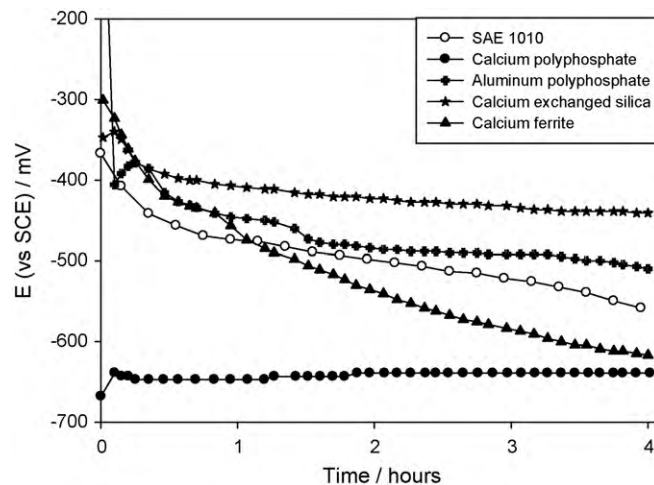


Fig. 5. Corrosion potential of SAE 1010 immersed in non-zinc based pigments.

sion. After 30 days of exposure, the epoxy paints with ZPy and ZHy lost their barrier properties while the others epoxies maintained a certain barrier protection. The same happened with the alkyd paints, being the exceptions the paints pigmented with ZMP and CaEx. Most of alkyds lost their barrier properties after 30 days except that formulated with ZHy.

It can be seen that an important change took place after 4–5 years of outdoor exposure (Table 7). Up to that time, the protection

Table 5

Rusting (R) and blistering (B) degrees of the alkyd painted panels during salt spray test.

Pigment	240 h		700 h		1000 h		2000 h	
	R	B	R	B	R	B	R	B
Zp	10	10	7	2D	–	–	–	–
ZMP	10	10	10	10	10	10	9	6F
Zpp	10	10	8	6D	–	–	–	–
Capp	10	10	9	4F	6	^a	–	–
Alpp	10	10	9	10	7	10	–	–
ZPy	10	10	10	8F	10	8F	7	8F
ZHy	10	10	10	10	9	10	9	6F
CaEx	10	10	10	10	10	10	10	8F
CaFt	10	10	10	8F	6	2D	–	–

^aDelaminated paint, serious adhesion problems.

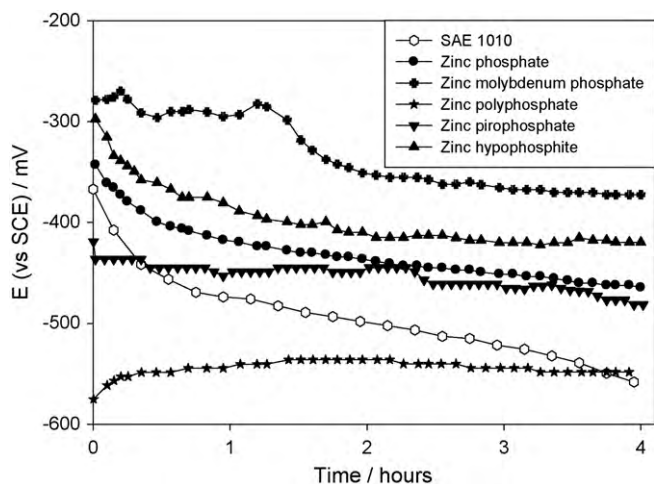


Fig. 4. Corrosion potential of SAE 1010 immersed in zinc-phosphate-based pigments suspension.

Table 6Corrosion potential and ionic resistance of the painted panels after 1 and 30 days in NaClO₄ 0.5 M and after 8 years outdoor.

Pigment	1 day				30 days				8 years			
	Epoxy paint		Alkyd paint		Epoxy paint		Alkyd paint		Epoxy paint		Alkyd paint	
	E (mV)	Ri (kΩ cm ²)	E (mV)	Ri (kΩ cm ²)	E (mV)	Ri (kΩ cm ²)	E (mV)	Ri (kΩ cm ²)	E (mV)	Ri (kΩ cm ²)	E (mV)	Ri (kΩ cm ²)
ZP	-180	50,000	68	6976.7	-422	12,000	-521	1.07	61.5	2803	-	-
ZMP	-295	100	36	300	-266	7.5	-223	2.70	Unstable	>300,000	Unstable	>300,000
Zpp	-236	75,000	-136	6521.7	-367	50,000	-432	0.49	-194.2	168	88.8	97.4
Capp	-420	50,000	101	2631.6	-220	21,428.6	-165	17.1	-	-	-	-
Alpp	-120	25,000	60	27,272.7	-505	5660.4	-581	352.9	N/E	N/E	Unstable	9817
ZPy	-475	6,000	-125	2381.0	-561	729.9	-291	5.34	-430	7.3	-	-
ZHy	-218	10,000	137	42,857.1	-525	73.9	-441	1 034	-	-	-	-
CaEx	-150	11,800	-160	10.0	-150	12,100	-630	0.33	-	-	-	-
CaFt	-161	413.8	-43	5263.2	-648	2.1	-580	0.58	-	-	-	-

N/E: the paint was not evaluated.

Table 7

Rusting degree of the painted panels after outdoors exposition.

Pigment	2 years		4 years		5 years		6 years		7 years		8 years	
	Alk*	Epx#	Alk*	Epx#	Alk*	Epx#	Alk*	Epx#	Alk*	Epx#	Alk*	Epx#
ZP	N/E	10	-	10	-	10	-	10	-	10	-	10
ZMP	10	10	10	10	10	10	10	10	10	10	10	10
Zpp	10	10	8	10	8	10	8	9	8	9	8	9
Capp	10	10	10	10	5	10	-	5	-	-	-	-
Alpp	10	10	10	10	10	10	10	10	9	9	9	8
ZPy	10	10	10	10	5	10	-	10	-	10	-	9
ZHy	10	10	6	10	-	8	-	5	-	-	-	-
CaEx	10	10	10	10	10	5	-	-	-	-	-	-
CaFt	N/E	7	-	-	-	-	-	-	-	-	-	-

N/E: the paint was not evaluated; Alk*: alkyd paint; Epx #: epoxy paint.

was due to the top-coat barrier properties but as they were lost, water, oxygen and ions reached the paint–metal interface and the protection depended, from that time, on the properties of the active anticorrosive pigment. If the protection afforded by the anticorrosive coating was poor, the metal corroded easily and in a shorter time.

Among the phosphates, ZP and ZMP exhibited the better performance with the epoxy resin because neither corrosion points nor blisters were seen on the painted surfaces after 8 years of exposition to an urban–industrial environment. Zpp, Alpp and ZPy gave good protection to the substrate (qualification 9 after 8 years) but, the rest of the phosphate-based pigments, failed after 6 years outdoors (qualification ≤ 5).

In the case of the alkyd paints, only ZMP, Zpp and Alpp had a good performance during 8 years outdoors; none or few corrosion dots were detected and blisters were absent. The other paints did not surpass 5 years of testing (qualification 5 or less).

Paints formulated with calcium-exchange silica, although with good results in the accelerated test, only protected steel during the first years of outdoor exposition. The epoxy paint qualified 5 after 5 years while the alkyd after 6 years. Calcium ferrite failed very soon, due to the poor protective ability of the pigment.

Electrochemical tests performed on the painted panels exposed outdoor showed that after 8 years the paints kept their barrier properties ($Ri > 2 \times 10^3$ kΩ cm²) except in the case of Zpp ($Ri \sim 10^2$ kΩ cm²) and ZPy ($Ri < 10$ kΩ cm²; Table 6). In the case of ZP, ZMP and Alpp, the barrier properties were due to the anticorrosive paint because, as it was said before, the top coat has been completely penetrated after 4–5 years of exposition.

4. Conclusions

1. Not all the pigments proposed as replacement for zinc chromate protected steel in a suitable form.

- Accelerated tests as well as electrochemical ones are complementary and none of them, by themselves, can predict the behaviour of the paint under service. However, a high ratio Rp_{pigm}^{IR}/Rp_{pigm} with a high value of Rp_{pigm} seems to be convenient to achieve a suitable substrate protection.
- Zinc molybdenum phosphate, zinc polyphosphate and aluminium polyphosphate had good protective behaviour, independently of the resin employed in this paper. Zinc pyrophosphate only showed good anticorrosion behaviour in the epoxy paint.
- Calcium ferrite had a low performance in outdoor tests despite the resin employed.

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