

Evaluation, Using EIS, of Anticorrosive Paints Pigmented with Zinc Phosphate

L S Hernández, G García, C López*, J J Carpio*, B del Amo** and R Romagnoli**

Institute of Metallurgy, UASLP, Av. Sierra Leona N° 550, 78210 San Luis Potosí, México.

*Corrosion Program, U.A. Campeche, Av. Agustín Melgar s/n, 24030 Campeche, México.

**Cidepint, Research and Development Center for Paint Technology, 52 entre 121 y 122, 1900 La Plata, Argentina.

Introduction

Due to their excellent corrosion inhibiting properties, both red lead and hexavalent chromate based pigments have been used in organic coatings for a long time. In spite of their widely recognised toxicity and the legal restrictions imposed on their use, they cannot be entirely eliminated from formulations even though there is an increasing trend towards reducing their content in anticorrosive paints used for industrial maintenance. Regardless of the many efforts that have been made to replace these toxic pigments, the replacement compounds that have been proposed have in only a few cases become as effective, as has been claimed.¹⁻⁴ Accordingly, such use has not generalised. It is perhaps a measure of the efficiency of the traditional pigments that they still held approximately 50% of the US market in 1990.⁵

One of the substitutes that has often been employed in the formulation of environmentally acceptable anticorrosive primers is zinc phosphate.^{1,6} Its anticorrosive mode of action is not yet fully understood. According to a recent review:⁶ "the protective action of zinc phosphate results from phosphatization of the metal substrate and the formation of complex substances with the binder. These substances react with corrosion products to yield a layer that adheres strongly to the substrate. More recent studies, have shown that the protective action is due to the formation of a film of iron oxyhydroxides on the steel. This involves the polarisation of cathodic areas by the formation of sparingly soluble basic salts that adhere to the surface. These salts may contain the phosphate anion. The low solubility of zinc phosphate and its extremely coarse crystalline structure could affect the formation of the protective layer".

Zinc phosphate is able to be used with all types of binders. When added to resins it improves both the drying and the adhesion to the metal substrate.⁷ However, very different experimental results have been obtained with this pigment: accelerated tests gave bad results but long-term outdoor exposure tests were encouraging.⁶ New phosphate-based pigments have been developed to replace zinc phosphate. One of these modifications is micronised zinc phosphate which has acquired an increasing significance since it disperses better, settles less and the amount used in the paint may be reduced. This is probably due to the smaller particle size and the surface changes produced during the micronisation process.

An excellent starting point for appraising the usefulness of substitutes for toxic anticorrosive pigments, is to control the

ratio of the pigment volume concentration (PVC) to the critical pigment volume concentration (CPVC). The correct choice of PVC with respect to the CPVC of the paint system, is an essential consideration in designing coatings of all kinds.⁸ Most of the important physical properties, (including gloss, hiding power (opacity), permeability, flexibility and scrubability), most of the mechanical properties, many of the optical properties (except colour) and many of the electrical properties of a paint film are dependent on the PVC/CPVC ratio. This ratio was named by Bierwagen and Hay⁹ as the reduced pigment volume concentration and is represented by the Greek letter lambda (Λ).

Electrochemical impedance spectroscopy (EIS) has proved its value in the evaluation of the performance and degradation of coated metals in contact with electrolyte solutions. EIS is very useful because it provides the possibility of investigating systems with a high resistance owing to their dielectric properties, and, moreover, it is also possible to detect, at a very early stage, the onset of the corrosion process and to determine the corrosion protective mechanism of active pigments.¹⁰ A large number of impedance studies of painted metals under conditions of permanent immersion has been published. According to Felio and co-workers,¹¹ values representative of the impedance parameters of the metal/paint system and their changes with time provide valuable information of the degradation system. In addition a quantitative method of making performance comparisons of different paint systems is made available.

The purpose of this work was to compare the protective capacity of two series of anticorrosive primers, pigmented with different contents of micronised zinc phosphate. As the binder, two vinyl resins were employed: VAGD resin, a partially hydrolysed vinyl chloride – vinyl acetate copolymer, which adheres on a wash primer; and VMCC resin, a carboxyl modified terpolymer resin, that can be applied directly on steel. The performance of both paint series was assessed by EIS combined with adhesion, salt spray and humidity chamber tests.

Experimental

Composition and Paint Preparation.

As the anticorrosive pigment, micronised zinc phosphate was used. Its morphological characteristics were outlined in previous papers.^{12,13} Paints were prepared with 8, 16 and 25% of micronised zinc phosphate of total pigment content by weight, at Λ ratios of 0.8, 0.9 and 1.1. Although it is not

usual to employ $\Lambda = 1.1$, in anticorrosive paints, this ratio was included in assessments of the anticorrosive pigment performance, with a minimum contribution of the binder barrier effect. Paints were formulated from similar pigment mixtures including Fe(III) oxide and barytes. These materials do not have anticorrosive properties, rather their role was to provide hiding power in the case of the Fe(III) oxide, and to act as an inert extender in the case of barytes. The experimental formulations are shown in Table 1.

Two homologous series of anticorrosive primers were prepared using the two commercial grades of vinyl resins. The first series, identified as 1-9, included VAGD resin, a partially hydrolysed vinyl chloride – vinyl acetate copolymer. The second series, identified as 1V-9V series, was made with VMCC resin, a carboxyl modified vinyl chloride terpolymer. Vinyl resins most widely used in coatings are vinyl chloride – vinyl acetate copolymers that can be modified, as in this case, with hydroxyl groups to improve the compatibility of the copolymer with other resins such as epoxies and alkyds; or with maleic acid to enhance the adhesion to the substrate.¹⁴ By changing the vinyl chloride – vinyl acetate ratio and the degree of polymerisation degree various polymers with different properties can be obtained. The vinyl acetate concentration influences the copolymer solubility. A high vinyl chloride content produces films of low permeability and high water and chemical agents resistance.

The polymeric film formers were each used a solvent mixture containing methyl isobutyl ketone, xylene and butyl acetate at a ratio 10/20/70 by weight. Tricresyl phosphate was added as plasticizer, being the vinyl resin/plasticizer ratio 4/1 by weight.

Paint assembly was prepared in a laboratory using a ball mill of 3.3 litre jar capacity. First, the resin solution was added and then the pigment. Dispersion took place for 24 hours.¹⁵

Preparation of the test panels.

The 15 × 7.5 × 0.2 cm specimens, used as the metallic substrate, were cut from SAE 1010 steel plates. The surface, (initial grade A), was sandblasted to Swedish Standard SIS 05 59 00/67 Sa 2 1/2 and then vapour degreased with toluene. The paint series 1-9 (with VAGD resin) were brush applied over specimens previously coated with a wash primer (SSPC-PT 3-64 specification). Paint series 1V-9V were brush applied directly over the bare steel. The average dry film thickness was determined as $60 \pm 5 \mu\text{m}$ with the aid of an electromagnetic gauge, using a bare sanded plate and standards of known thickness as reference. Samples, thus prepared, were kept in the laboratory atmosphere for 24 hours before the start of the tests.

Laboratory Tests

Electrochemical impedance spectroscopy.

The impedance measurements were carried out at ambient temperature with a three electrode arrangement and at the rest potential of the coated sample. The surface area

Table 1: Composition of paints tested (g/100 g).

Component	Paints								
	1	2	3	4	5	6	7	8	9
Zinc phosphate	5.7	10.9	16.3	6.1	11.7	18.1	6.4	12.4	18.7
Ferric oxide	33.3	29.0	24.8	35.6	30.9	26.4	37.5	32.8	28.3
Barium sulphate	32.5	28.2	24.3	34.7	30.3	26.0	36.6	32.3	27.7
Vinyl resin	22.8	25.5	27.7	18.9	21.7	23.6	15.6	18.0	20.2
Tricresyl phosphate	5.7	6.4	6.9	4.7	5.4	5.9	3.9	4.5	5.1
Zinc phosphate content, (%)	8.0	16.0	25.0	8.0	16.0	25.0	8.0	16.0	25.0
PVC/CPVC (L)	0.8	0.8	0.8	0.9	0.9	0.9	1.1	1.1	1.1

of the painted samples (9.1 cm²) exposed to the electrolyte, (a 3% NaCl solution, pH = 7.0), was confined by means of a short piece of glass tubing attached to the coated steel surface using a silicon rubber adhesive. On each specimen, two cylindrical tubes were fixed. The cell contained a graphite electrode, as the counterelectrode and a saturated calomel electrode (SCE) as the reference. Impedance spectra were collected in the potentiostatic mode, using a Schlumberger 1250 frequency response analyser (FRA), operated under microcomputer control. The FRA was connected to the electrochemical cell through a PAR 273 potentiostat. A sinusoidal signal of 10 mV was applied over a frequency range from 100 kHz to 1 MHz. Impedance measurements were made for all the paints, after different exposure times in the electrolyte of up to 576 hr.

Salt spray testing (ASTM B 117-90).

Before the test, a cross scratch, penetrating through the coating, was made in all specimens, following ASTM D 1654-92 standard, in order to evaluate the protection provided in the presence of a paint film failure. The test was carried out in triplicate and determining the mean value of data. The oxidation grade was assessed according to ASTM D 610-85 standard, after 500 hours exposition.

Humidity chamber (ASTM D 2247-87).

Another sample batch similar to that described above was placed in a humidity chamber, (100% relative humidity and $38 \pm 1^\circ\text{C}$), for 500 hours. The blistering grade was assessed according ASTM D 714-87 standard.

Adhesion (ASTM D 4541-89).

The pull-off test was carried out in triplicate using an Elcometer 106 portable device.

Results and Discussion

Figure 1 shows the impedance spectra obtained from the coated electrodes after 1 hour immersion in the sodium chloride solution. Reproducible data were obtained from the two cells on each coated steel specimen. The Bode plots of the 1V-9V paint series show two characteristic segments. The high-frequency, straight line region, representing a capacitive behaviour has a slope close to unity, indicating that the modulus Z is inversely related to ω . At lower frequencies, the straight line bends so as to become a line approximately parallel to the abscissa; the impedance is independent of frequency, indicating a $|Z|$ resistive value. 9V, 3V, 7V and 6V paints (except 7V paint, all with 25% of zinc phosphate) showed a gradual transition from capacitive to resistive behaviour and total coating resistance values (R_f) at the lowest frequencies around 10^9

Figure 1: Electrochemical impedance spectra after 1 hr immersion in a 3 % NaCl solution for steel electrodes coated with paints containing micronized zinc phosphate in VMCC vinyl resin (1V–9V) or in VAGD vinyl resin (1–9).

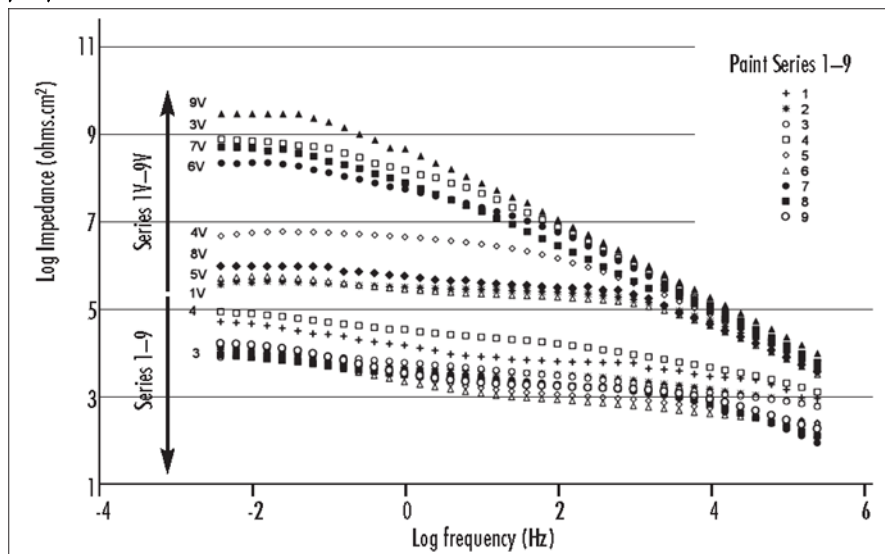


Figure 2: Example of complex plane plot for paints with the highest Rf values. Paint 3V after 1 hr immersion in a 3 % NaCl solution.

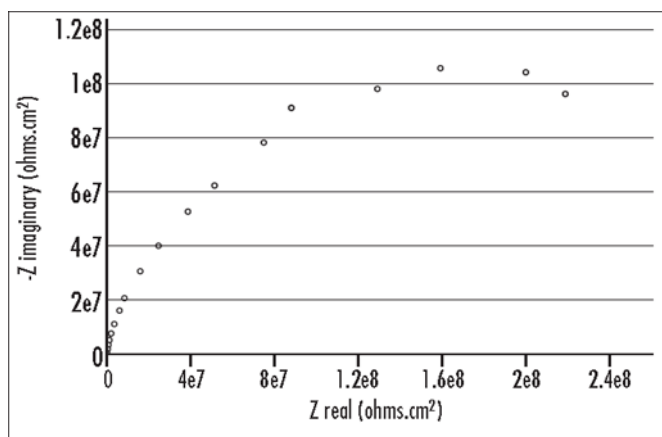
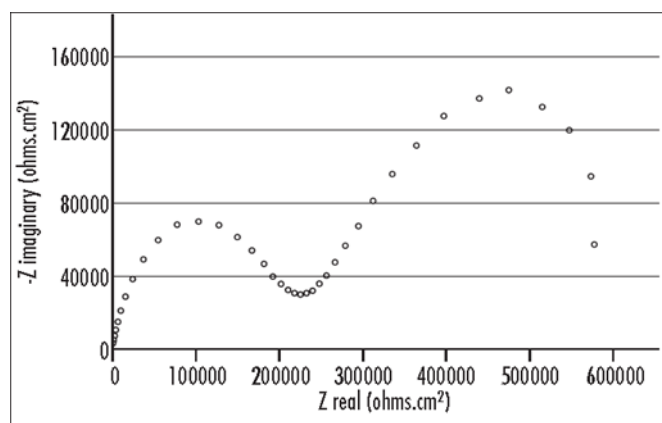


Figure 3: Example of complex plane plot for paints with middle Rf values. Paint 5V after 1 hr immersion in a 3 % NaCl solution.



$\Omega \text{ cm}^2$. Throughout the text, R_f will indicate the Bode plots extreme values considered as total coating resistance, since, eventually, they will represent the sum of the coating resistance, charge transfer resistance and solution resistance. The complex plane plots of these four paints depict an incomplete semicircle which contains information of

the coating properties and suggests that the electrolyte has started to permeate through the coating, see Figure 2. The corresponding electrical equivalent circuit is a Randles simple circuit,¹⁶⁻¹⁹ a combination in series of the solution resistance with a parallel arrangement containing the ionic resistance (R_i) and the coating capacitance (C_p). Conversely, 4V, 8V, 5V and 1V paints showed a relatively sharp capacitive-resistive transition and R_f values which are progressively low, between 10^7 and $10^5 \Omega \text{ cm}^2$. The complex plane plots for these paints depicted a complete semicircle at high frequencies and only a portion of a second semicircle at the lowest frequencies, see Figure 3. The corresponding electrical equivalent circuit had two time constants¹⁶⁻¹⁹ indicating that the electrolyte permeates through the coating and that the oxidation and reduction electrochemical

processes have started to happen in the coating/steel interface. Thus, the high frequency time constant is the result of the coating capacitance (C_p) and ionic resistance (R_i) interaction and the low frequency relaxation time is given by the charge transfer resistance (R_t) and the double layer capacitance (C_d).²⁰

The value of $10^5 \Omega \text{ cm}^2$ provides a distinct zone between both paint series. All R_f values for the 1-9 series are lower than $10^5 \Omega \text{ cm}^2$, ranging from $\sim 8.9 \times 10^4$ to $6.9 \times 10^3 \Omega \text{ cm}^2$ for 4 and 3 paints, respectively, causing an overlap in the R_f values and in the whole spectrum range. These low resistance values indicate that the coatings possessed inherent porosity and that a substantial amount of electrolyte had penetrated the pores in the coating.¹⁶ The lack of linearity of the high-frequency segment of some spectra has been associated with a continuous state of change of the coated steel samples due to electrolyte uptake.²¹ This paint series showed another response model so long as the coating capacitance-resistance transition was shifted to higher frequencies (i.e. $> 10^4 \text{ Hz}$). The complex plane plots also showed two poorly defined semicircles and much less Z imaginary and Z real values, Figure 4, than those measured for the 4V-1V paints.

The impedance spectra after 576 hours of immersion, are shown in Figure 5. In order to facilitate interpretation, some spectra of 1V-9V paint series were omitted. Even so, the spectra and R_f values of both paint series overlap. R_f values range from $\sim 2.8 \times 10^4$ to $1.7 \times 10^3 \Omega \text{ cm}^2$, for 9V and 7 paints respectively. This suggests that the electrolytes has penetrated the coatings and that corrosion of the metallic substrate has taken place extensively. It also indicates that the organic coatings were no longer acting as a protective layer. The decrease of resistance, throughout the frequency range studied, with increasing time of immersion, suggests that water ingress was uniform throughout the coating and not localised.¹⁶ These assertions were verified by inspecting the immersion zones. Highest R_f values paints (3V, 6V, 9V), showed less rust, with blisters only in some areas of the immersion zone, but none had burst. In the rest of the paints, although some had fewer blisters like those of paint 5, blisters were, on the whole, in the immersion zone and some of them were burst, with abundant rust around

them. This inspection was carried out using a low magnification stereoscope.

It can be seen, in Figure 5, that only four paints, including the three paints of 1V-9V series which contained 25% of zinc phosphate, showed the coating capacitive-resistive

Figure 4: Example of complex plane plot for 1-9 paint series, lowest Rf values. Point 4 after 1 hr immersion in a 3 % NaCl solution.

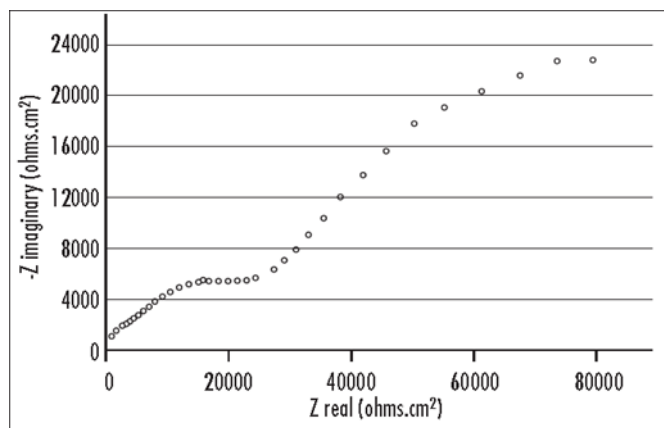


Figure 5: Electrochemical impedance spectra after 576 hr immersion in a 3 % NaCl solution for steel electrodes coated with paints containing micronized zinc phosphate in VMVC vinyl resin (1V-9V) or in VAGD vinyl resin (1-9).

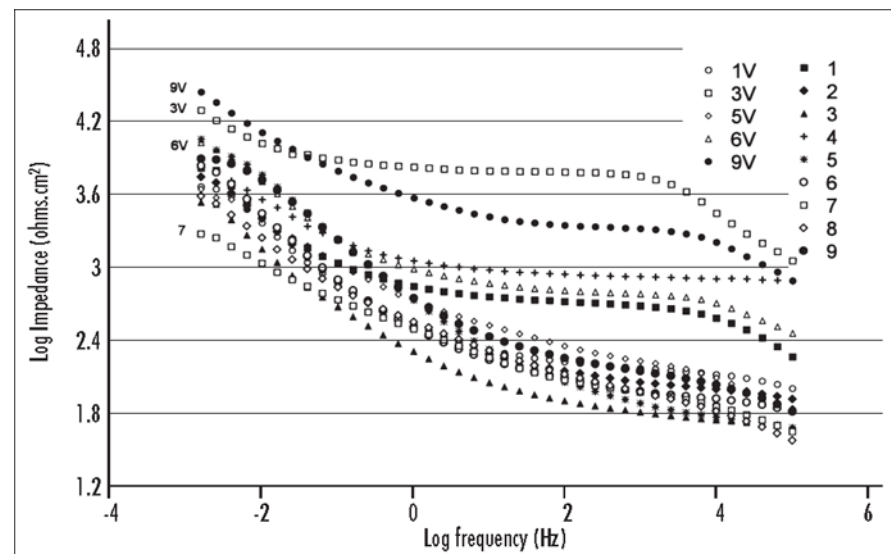
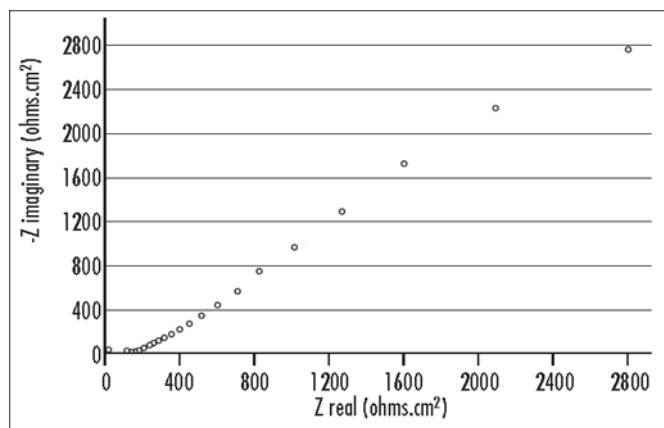


Figure 6: Appearance of Warburg impedance for paint 1V after 576 hr immersion in a 3 % NaCl solution.



transition in the frequency range of the plot. For the other paints, this transition had moved toward even higher frequencies.²² At lower frequencies, all paint responses bent upward showing a linear increase in $\log |Z|$ as $\log f$ decreases. This additional low frequency component of the impedance spectra has been identified as the onset of substrate corrosion. However, in this plot it represents the Warburg impedance (diffusion tail) as a consequence of a diffusion controlled corrosion process at the paint/steel interface. Figure 6 proves the appearance of this kind of impedance for 1V paint, after 576 hours of immersion. The highest Rf values paints (9V, 3V, 6V) showed a poorly defined semicircle followed by the diffusion tail. The 1-9 paint series depicted the diffusion tail alone, as it was already observed after 24 hours. The shape of the diagrams did not change from this time to the end of the immersion time, only the Z imaginary and Z real values became progressively lower.

As for the low Rf values showed in Figure 5 for 1V-9V paint series after 1 hour immersion, the specimens with the highest Rf values decreased about five orders of magnitude after 576 hours exposure, indicating an increasing ionic conductivity for the coatings and lower protective properties, as a result of electrolyte penetration (Figure 7).

On the contrary, for 1-9 paint series, the decrease was of about one order of magnitude or less. The values were very low after only 1 hour of immersion and stayed at this low range during the whole test period, as can be seen in Figure 8. It is worth noting that the evolution of the corrosion potential (E_{corr}) showed a behaviour very similar to that of the Rf, ie, initially for the 1-9 paint series, E_{corr} values were between -376 and -628 mV/SCE. The E_{corr} values far from ~ -650 mV/SCE, the known free corrosion potential of uncoated steel under equivalent environmental conditions, shifted rapidly and continuously in the negative direction, reaching a value near to -650 mV/SCE in only 72 hours and remained in this range until the 576 hour test period. On the other hand, E_{corr} values for 1V-9V paint series, at the beginning ranged from 85 to -358 mV/SCE, growing slowly to the negative side. After 576 hours all the E_{corr} values were equal to the free corrosion potential of the steel, except that of the 3V paint E_{corr} (-566 mV/SCE).

The associated increase in capacitance as a function of time, as a consequence of the electrolyte penetration into the coating, is difficult to assess due to the uncertainty in the calculated capacitance values. This is due to the higher degree of deterioration shown by most of the paints, after scarcely 24 hours of immersion (Figures 7 and 8). Practically, the paint film capacitance can be calculated only on paint films that have not been damaged too much. Several researchers have determined paint capacitance ratio after very long exposure times, on badly damaged films, and/or at lower frequencies,^{21,23} so, what they really have determined is the double layer capacitance. Actually, in order to continue measuring the capacitance of a deteriorated paint, it would be necessary to use much higher fre-

Figure 7: Variation of Rf values as function of time for paint series 1V–9V.

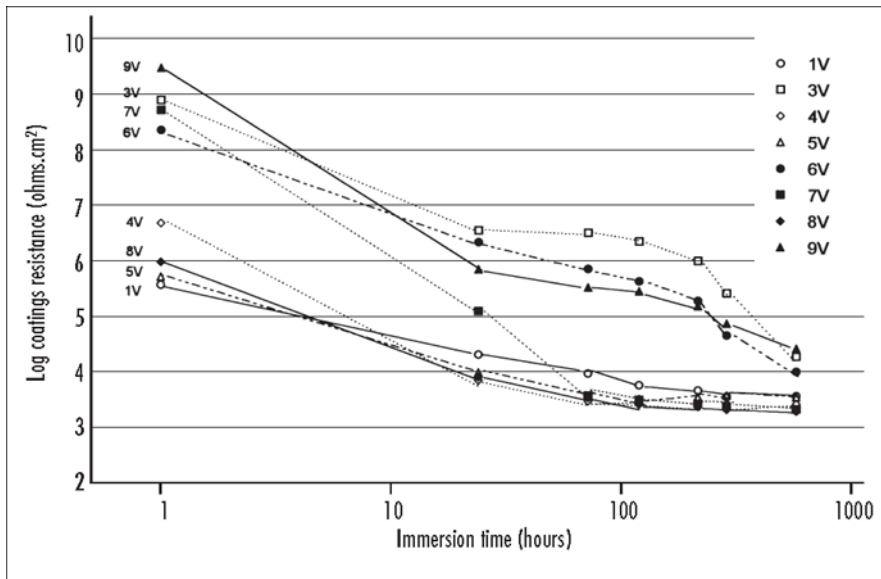


Figure 8: Variation of Rf values as function of time for paint series 1–9.

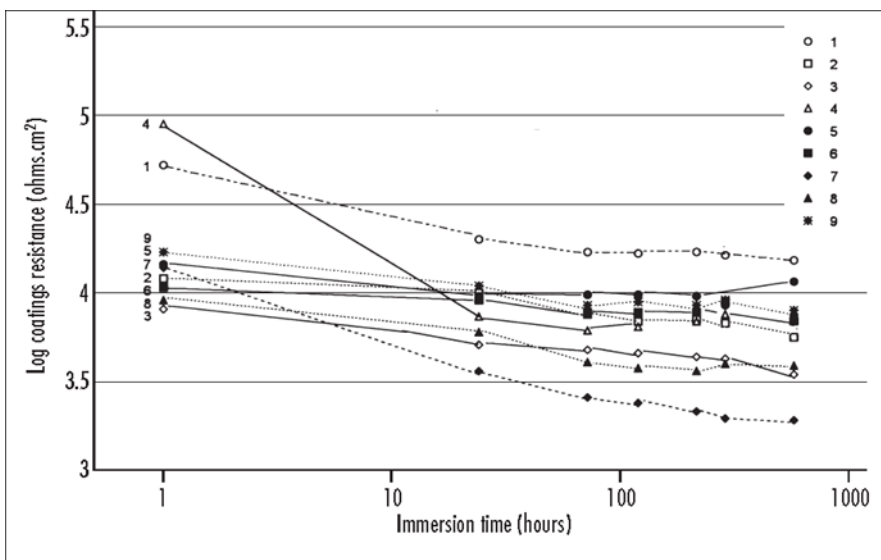
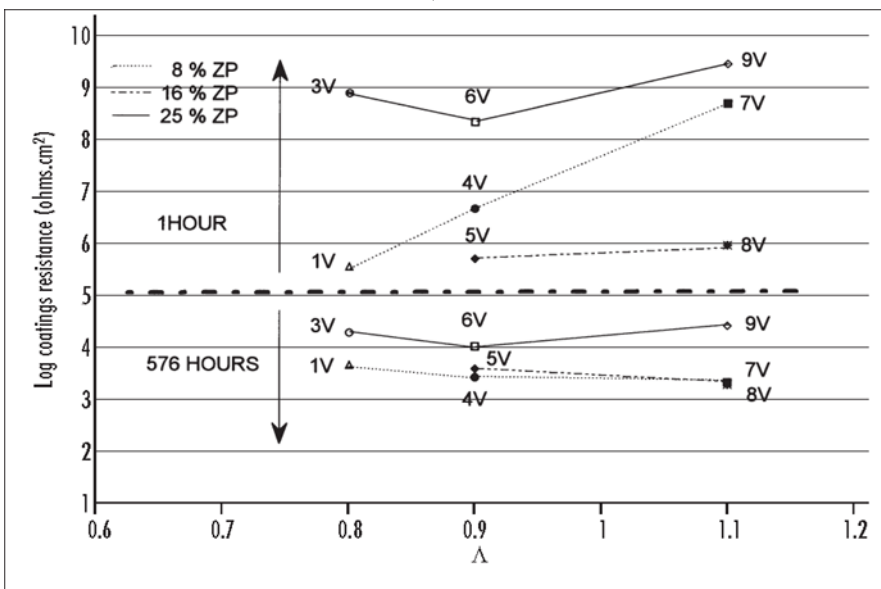


Figure 9: Coating resistance vs Δ ratios for the 1V–9V paint series after 1 and 576 hr immersion testing.



frequencies than those permitted by the measuring equipment used.²⁴

Sometimes it is possible to calculate the paint capacitance if, previously, the ionic resistance has been determined as the length of the chord enclosed by the points at which the high frequency semicircle cuts the real axis, in a complex plane diagram. However, as noted earlier, only paints with 25% of zinc phosphate showed this high frequency semicircle up to 576 hours. The plot of capacitance for the above mentioned paints as function of time showed a trend of continuous increase of capacitance after immersion. A capacitance stabilisation period (constant value) after some hours It was not observed, indicating a continuous electrolyte uptake. This behaviour is similar to that given by a coated electrode with an artificial intentional defect.¹⁹

From the EIS results provided, it is apparent that the only mechanism that is common in the metallic substrate protection is a barrier effect, although the high porosity of 1-9 paint series just at the beginning of the immersion and the increasing porosity of the 1V-9V paint series as function of time it was noticed. Chemical protection by build-up of solid compounds that plug the pores did not occur. The electrochemical mechanism which involves the build-up of permanently passive conditions at the metal surface was hindered by the action of chloride ion which formed soluble ion complexes of iron which may diffuse away and are converted to insoluble rust products.¹¹ The exact nature of the pores in the organic primers is not clear. These pores could be macroscopic flaws created during the application or curing process, or they could be microscopic defects with tortuosity associated with amorphous polymer tangles, or even flaws due to poor attachment of pigment particles to the resin.²⁵

The damage to both paint series may be increased by the fact that tricresyl phosphate is a highly hydrolysable substance due to its high polarity.²⁶ As a result of this, the film becomes very permeable to water, oxygen and ions which increased the conductivity of the solution and facilitated at the interface the cathodic reaction of oxygen ionisation, complementary to the metallic dissolution process.

With regard to the effect of the Δ ratio on the performance of the paints,

Figure 10: Coating resistance vs Λ ratios for the 1–9 paint series after a) 1 hr and b) 576 hr immersion testing.

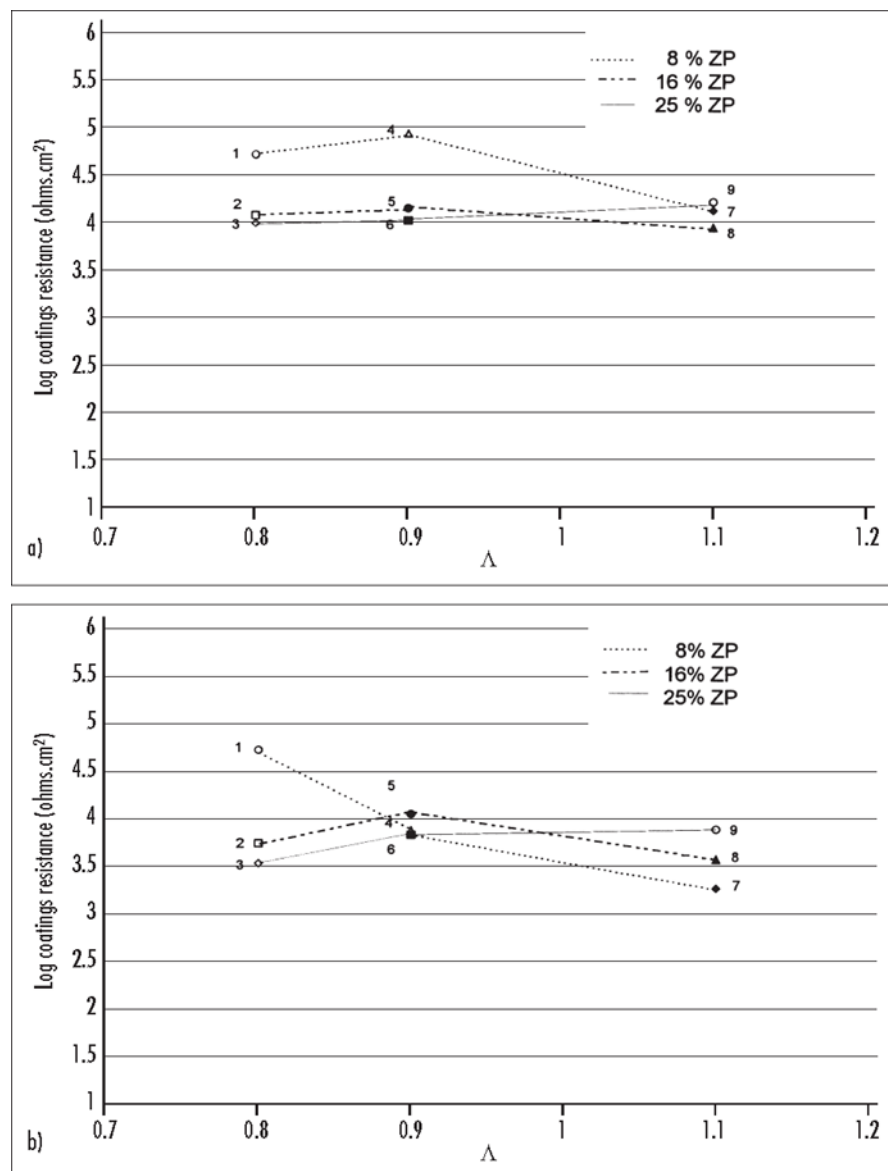


Figure 9 shows R_f values plotted against such a ratio after 1 and 576 hours immersion, for the 1V–9V paint series. It can be seen clearly that after 1 hour of immersion, the lines for the three contents of zinc phosphate went up as the Λ ratio increased from 0.9 to 1.1. The behaviour for the paints with 8% of zinc phosphate shows as a straight line. After the 576 hours test period, the paints with 25% of zinc phosphate continued showing the highest R_f values, including 9V paint with a $\Lambda = 1.1$. In contrast, the other two paints with the same Λ ratio exhibited the lowest R_f values even though these were very similar to the values of the other paints. A minimum for 6V paint with a $\Lambda = 0.9$ can be seen at both test periods. For the 1–9 paint series, the R_f values were already low after 1 hour of immersion and diminished further after 576 hours of immersion, as can be seen in Figure 10.

The good results yielded by the 9V paint, with $\Lambda = 1.1$, are in conflict with the results that were expected and with those reported by Skerry et al.²² In alkyd primers containing either zinc chromate or barium metaborate as inhibitors, Skerry et al.²² found that the R_f values sharply diminished when the Λ ratio changed from 0.8 to 1.1 (~ from 10^9 to $10^4 \Omega \text{ cm}^2$) and the paints with $\Lambda = 1.1$ quickly

deteriorated with respect to paints with $\Lambda < 1.0$. So far, it is not known why this behaviour occurs with $\Lambda = 1.1$, is not unknown considering that, when $\Lambda > 1.0$, there are voids in the film with part of the pigment particles not in contact with the binder.⁹ It could be due to the small particle size of the micronised zinc phosphate and its interaction with the more acidic resin (VMCC). By successively diminishing of the particle size, the active area is increased in such way that its anticorrosive action becomes more effective.

As for the importance of the micronised zinc phosphate, a 25% content showed the highest R_f values. Leblanc et al.² claimed that the zinc phosphate protective action clearly increases with the concentration, being, in some cases, better than that of the zinc chromate. They obtained the best results with a PVC of 40%, although they did not report the paint Λ ratios they used. They mention that the damage at the paints cuts was much reduced and that the paint films showed excellent adhesion to the substrate.

The results obtained in the salt spray chamber and in the humidity chamber, both after 500 hours of testing, are shown in Table 2. In the salt spray test none of the paints depicted blistering during the test. The anticorrosive protection achieved with the VMCC resin was more pronounced than that obtained with the VAGD resin. This increased with the higher zinc phosphate contents. Again, it can be seen that paints with 25% of micronised zinc phosphate and Λ ratios of 0.8–0.9, gave the smallest oxidation. Thus, 3V and 6V

paints showed the best anticorrosive performance. 9V paint also showed good anticorrosive performance, but not as good as that indicated by the impedance test. A similar trend was observed with paints numbers 3, 6 and 9 although the protection capacity was smaller.

Table 2: Results of salt spray and humidity chamber tests both after 500 hours exposure.

PAINT	Salt spray test Oxidation (ASTM D 610-85)		Humidity chamber test Blistering (ASTM D 714-87)	
	1–9 SERIES	1V–9V SERIES	1–9 SERIES	1V–9V SERIES
1	2	5	8MD	6M
2	3	5	8MD	6M
3	4	8	8M	6F
4	4	5	8M	8D
5	4	6	8F	8MD
6	5	8	8F	8F
7	4	4	8F	8F
8	4	5	8F	8F
9	5	7	8F	8F

Table 3: Results of initial paint adhesion by pull-off method, ASTM D 4541 – 89, in MPa. Values are the average of 3 determinations.

Paint	Series	
	1 – 9	1V – 9V
1	1.08	1.18
2	1.08	1.27
3	1.18	1.27
4	1.18	1.37
5	1.27	1.37
6	1.37	1.47
7	0.88	0.98
8	0.98	0.98
9	1.08	1.18

1 MPa = 145 psi = 10.2 Kg/cm².

After 500 hours of exposure in the humidity chamber, the blister grade for paints 6 to 9, in both paint series, was the same: only a few small blisters (8F). For the other paints, the amount of blistering per unit area increased when the A ratio diminished. Slightly better behaviour of paints number 3, with 25% of micronised zinc phosphate, with respect to paints numbers 1 and 2 was observed.

Results of the adhesion test are shown in Table 3. Adhesion is lower for paints formulated with VAGD resin than for paints formulated with VMCC resin. The adhesion increased when the A ratio increased from 0.8 to 0.9. However, the adhesion diminished when the mentioned ratio was 1.1 and the zinc phosphate content lower than 25%.

Conclusions

All tests employed point to the better behaviour of the paints formulated with the acidic resin (VMCC) than with the VAGD resin. Furthermore, paints containing 25% of zinc phosphate by weight and a A value = 0.8-0.9, showed the best anticorrosive performance in the EIS, salt spray and adhesion tests. Similar paints, but with A = 1.1, showed the highest coating resistance values after 576 hours immersion in a 3% NaCl solution. These results were not confirmed by the traditional laboratory tests.

With exception of the increase in Rf values, for paints with VMCC resin, containing 8% of zinc phosphate by weight after 1 hours immersion, for both paint series, the corrosion protective properties were not greatly affected by the A ratios.

Using parameters derived from impedance data, the total coating resistance at the lowest frequencies is easily and unambiguously determined, whereas the calculations of paint capacitance values must be done carefully in order not to mistake them for the corresponding values of the double layer.

Again, the important role of the binder in paint formulation has been proven. It can be seen from this work using the same inhibitor pigment, that for the same pigment blends and even two types of vinyl resins, the two paint series prepared had very different electrochemical responses, at least in the beginning of the immersion test, although they became very similar later.

Acknowledgements

The authors are grateful to CONACYT (Consejo Nacional de Ciencia y Tecnología, México, contract 3025-A9306); to

CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina) and to CIC (Comisión de Investigaciones Científicas de la Provincia de Buenos Aires) for their sponsorship to do this research. They wish to thank J. M. Miranda for assistance in preparation of the manuscript.

References

1. Goldie BPF, *JOCCA*, **70**, (9), 257-267, 1988.
2. Leblanc O, Llovensà X and Martorell C, "Un estudio sobre la eficacia de los pigmentos anticorrosivos", Colores Hispania, S.A., Barcelona, 1981.
3. Koskiniemi MS and Conti WJ, *Pinturas y Acabados Industriales*, **38**, (229), 28-31, 1996.
4. Escudero J, *Rev. Iber. Corros. y Prot.*, **15**, (3), 43-46, 1984.
5. Hare CH, "Protective Coatings. Fundamentals of Chemistry and Composition", Technology Publishing Company, Pittsburgh, Pennsylvania, 1994, p 343.
6. Romagnoli R and Vetere VF, *CIDEPINT-Anales*, 249-264, 1994.
7. Meyer G, *Farbe+Lack*, **71**, (2), 113-118, 1965.
8. *ibid* 5, p6.
9. Bierwagen GP and Hay TK, *Prog. Org. Coat.*, (3), 281-303, 1975.
10. Rammelt U and Reinhard G, *Prog. Org. Coat.*, (24), 309-322, 1994.
11. Feliu S Morcillo M and Feliu Jr S, *Surface Coatings Inter.*, **78**, (8), 338-341, 1995.
12. Romagnoli R and Vetere VF, *Corrosion Reviews*, **13**, (1), 45-64, 1995.
13. Hacticox Hispafos, pigmentos anticorrosivos no tóxicos y eficaces. Especificación técnica, Colores Hispania, S.A., Argentina, 1995.
14. *ibid* 5, p85.
15. Giúdice C Benítez JC and Rascio V, *JOCCA*, **63**, (3), 151, 1980.
16. Lin C, Nguyen T and McKnight ME, *Prog. Org. Coat.*, (20), 169-186, 1992.
17. Feliu S, Galván JC and Morcillo M, *Corros. Sci.*, **30**, (10), 989-998, 1990.
18. Tsai CH and Mansfeld F, *Corrosion*, **49**, (9), 726-737, 1993.
19. Deflorian F, Miskovic-Stankovic VB, Bonora PL and Fedrizzi L, *Corrosion*, **50**, (6), 438-446, 1994.
20. Cavalcanti E, Ferraz O and Di Sarli AR, *Prog. Org. Coat.*, (23), 185-200, 1993.
21. Chen C-T and Skerry BS, *Corrosion*, **47**, (8), 598-611, 1991.
22. Skerry BS, Chen C-T and Ray CJ, *J. Coat. Tech.*, **64**, (806), 77-86, 1992.
23. McIntyre JF and Hang L, *Corrosion*, **50**, (1), 26-38, 1994.
24. Feliu S, private communication, October 1996.
25. Cohen SM, *J. Coat. Tech.*, **68**, (859), 73-81, 1996.
26. Di Sarli AR, Schwiderke EE and Podestá JJ, *JOCCA*, **73**, (1), 18-23, 1990.