Evaluation of Steel/Primer Based On Chestnut Tannin/Paint Film Systems by EIS

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The influence of a tannin pretreatment applied to slightly rusted steel panels on the anticorrosive performance of alkyd paint systems has been investigated using electrochemical impedance spectroscopy (EIS) and open circuit potential measurements. From EIS and corrosion potential data analysis it was found that (1) there is not a significant influence of the tannin pretreatment on the anticorrosive protection level, which depends particularly on the barrier effect afforded by the applied paint system (however, as the corrosion process starts, tannins may cause the repassivation of steel); (2) the enhancement of the protection level afforded by the tannin primer was restricted to short immersion periods and corrosive media that were not very aggressive; and (3) water uptake was not significantly affected by the presence of the tannin primer.

INTRODUCTION

The presence of corrosion products or artificially created conversion layers affects not only the protective capacity of different paint systems but also has important economic significance. Sometimes it is not possible to obtain optimum surface preparation due to economical and/or environmental reasons. Therefore, a number of coatings that provide, in principle, efficient protection to rusted and contaminated steel surfaces have been developed. Tannins are used in such coatings as corrosion inhibitors in both solventborne and waterborne paints applied on partially rusted substrates in order to reduce the need for surface cleaning efforts. They have often been referred to as rust stabilizers because they turn the active rust into quasi-inert protective compounds. Tannins are polyphenols of vegetal origin, and the positioning of hydroxyl groups in the aromatic rings makes them able to form chelates with iron. Ferric tannates of dark blue color are highly insoluble and can act as electric insulators between anodic and cathodic sites formed at the metal surface.[1-7]

Knowles et al.[8] found that a properly applied aqueous solution of tannin lasted twice as long as a phosphate coating under accelerated testing conditions. On the other hand, in external weathering, in an unsealed state, the protection afforded by tannin treatment lasts from one to three weeks. They also found that (1) the reaction was oxygen dependent; (2) iron tannate formed at anodic sites while hydrogen discharged at cathodic points on the metal surface, respectively; and (3) a tannin layer played an important role beneath a paint film.

Later, Shreir[9,10] discovered that the addition of phosphoric acid to a tannin solution has a synergistic effect, since it provides a much higher corrosion resistance than that formed by either of the constituents used alone. The phosphoric acid and tannin concentrations may reach 55% and 10%, respectively.[11] Tannins react with the metal oxide layer giving an insoluble, black, amorphous, and highly reticulated ferric tannate film, which has protective properties. This film contains free tannin and its iron content is about 2.5%.[3,5,7-12]

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

The aim of the present research was to study the anticorrosive capacity of coating systems containing a tannin primer applied to steel sheets with a slight degree of oxidation. The primed steel panels were covered with anticorrosive alkyd paint pigmented with zinc molybdenum phosphate (30% v/v) and/or a topcoat alkyd paint pigmented with titanium dioxide (20% v/v). Then, the samples were exposed to either 0.5M NaCl or 0.5M $NaClO_4$ solution. Defining t as the tannin based primer; A as the

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anticorrosive paint; and T as the topcoat paint, the protective capacity was evaluated for the following painting systems: (i) t + T; (ii) t + A; (iii) t + A + T; (iv) A + T; (v) A; and (vi) T. In view of the many applications that electrochemical impedance spectroscopy has found in coating studies,[14-18] this technique was used as a tool to compare the deterioration process of the various coating systems under test conditions.

EXPERIMENTAL DETAILS

Primer Preparation

The primer preparation was as follows: 10 mL of phosphoric acid solution (30% w/w) was added to a 6 g suspension of chestnut tannin in 40 mL of distilled water and treated according to a process whose patent has not been approved yet[19,20] to enhance its adhesive strength on steel. Chestnut tannin was selected because of its high reactivity with iron.[2] The treated tannin was filtered off to eliminate insoluble matter and mixed with a 40% aqueous solution of an acrylic resin prepared as described elsewhere.[21] Adding 2 mL of Texanol® and a flash rusting inhibitor (3 mL of 10% ammonium molybdate solution) completed the primer formulation. The system was allowed to settle for 24 hr and filtered again if necessary.

Anticorrosive and Topcoat Paints

The anticorrosive paint was formulated with a medium solventborne alkyd binder pigmented with zinc molybdenum phosphate (30% v/v) and a 0.8 PVC/CPVC ratio. Its anticorrosive performance was previously assessed.[22] The topcoat was also an alkyd paint containing 20% of solid resin (the same employed for the anticorrosive paint), 20% of titanium dioxide, and 60% of solvent (white spirit).

Paint System Application

The primer was brush applied onto SAE 1010 steel panels (15.0 × 7.5 × 0.2 cm), previously degreased with toluene, up to a thickness of 10 ± 2 μm. Test panels had a low surface roughness (average 0.78 μm) and slight rust. The low surface roughness was selected to perform the test under conditions where adhesion of the first coat would be poor. Surface roughness was measured employing a Hommel Tester model T-1000. The primed panels were kept in a laboratory atmosphere (RH 40 ± 5% and 20 ± 2°C) for seven days to ensure complete curing. They were then coated with anticorrosive and/or topcoat paints. The dry film thickness was measured with an Elcometer instrument Model 300, using a bare plate and normalized pattern standards of known thickness as reference. Mean values are shown in *Table* 1. Samples were tested in triplicate.

Table 1—Primer and Paint Films Thickness

System	Tannin Primer (µm)	Anticorrosive Alkyd Paint (µm)	Topcoat Alkyd Paint (µm)
t+T = tT	10±2	—	60±4
t+A+T = tAT	10±2	30±3	30±3
A + T = AT	—	35±3	35±3
t + A = tA	10±2	60±4	—
A	—	60±4	—
T	—	—	60±4

In order to perform the electrochemical measurements, two acrylic tubes were attached to each coated panel (working electrode) with an epoxy adhesive to get good adhesion. The geometric area for each cell exposed to the electrolyte was 15.9 cm^2. A large area Pt-Rh mesh of negligible impedance and a saturated calomel (SCE) were employed as auxiliary and reference electrodes, respectively. The electrolyte was either 0.5M NaCl or 0.5M $NaClO_4$ solution, whose pH was adjusted to 8.2 by means of sodium bicarbonate.

All impedance spectra, in the frequency range 10^{-3} Hz$\leq$f$\leq$1.10^5 Hz, were performed in the potentiostatic mode at the corrosion potential, as a function of the exposure time to the electrolyte solution, using the 1255 Solartron FRA and the 1286 Solartron EI. The amplitude of the applied AC voltage was 10mV peak to peak. The experimental impedance spectra were interpreted on the basis of equivalent electrical circuits using a suitable fitting procedure (Zplot®).

The value of the water permeability coefficient for each coated steel/electrolyte solution system was also determined. The dielectric capacitance evolution was measured as a function of the immersion time until a constant value was attained (approximately three hours immersion). Such measurements were performed in the potentiostatic mode at a frequency of 2.10^4 Hz and the water permeability coefficients were obtained with the calculus method reported elsewhere.[21] All the electrochemical experiments were carried out at laboratory temperature (20 ± 2°C) using a Faraday cage.

EXPERIMENTAL RESULTS

Water Permeation

Resistance to water permeation is a very important property of protective coatings. Data on water diffusion, solubility, and permeability coefficients corresponding to tested paint films are summarized in *Table* 2. The pretreatment film applied alone on the steel surface could not be evaluated because the high paint coating porosity gave results beyond the fitting capability of the model.[23] The main findings here are: (a) water permeation was almost always greater in $NaClO_4$ than in NaCl solutions; (b) for both electrolytes, the presence of the thin pretreatment film has a different effect on the water permeability coefficient value as a function of the paint system structure. So, when the system (AT) was used, the presence of the pretreatment coat enhanced the resistance to the water uptake (*Table* 2—Systems tAT and AT). On the contrary, when only A or T are present the influence of the tannin coat is the opposite (*Table* 2—Systems tA-A and tT-T); and (c) for both electrolytes, systems containing only A or T were more permeable than the system (AT) and that difference was two or three times greater when the tannin pretreatment was present.

Electrochemical Measurements

In order to improve our knowledge of the mechanism, by which the previously mentioned coated steel panels were protected against corrosion, corrosion potential and impedance measurements as a function of exposure time in NaCl or $NaClO_4$ solutions were carried out.

Equivalent Circuit Model: Impedance spectra provide important information related to both the organic coating deterioration evolution and the kinetics of the corrosion process suffered by the underlying steel substrate. The dynamic character of both the membrane conductivity and the corrosion products (basically rust) formation, as well as the shifts in the disbonded area, account for changes in the coated steel/electrolyte system's impedance spectra throughout the immersion time. In order to give a physical explanation of such changes, as well as to obtain a more accurate and less time-consuming curve fitting procedure from experimental impedance data, non-linear least squares algorithms and the equivalent circuit models shown in *Figure* 1 were used.[24-27] This figure represents the parallel and/or series connection of a number of resistors and capacitors, simulating a heterogeneous arrangement of electrolytically conducting paths. Thus, R represents the electrolyte resistance between the reference (SCE) and working (coated steel) electrodes. R_1 is the resistance to the ionic flux—describing paths (pores, low crosslinking) of lower resistance to the electrolyte solution penetration short-circuiting the organic coating—whose value usually is being used as a criterion of coating integrity. C_1 is then the dielectric capacitance actually representing the intact part of the paint film, whose value is associated with the water uptake.[28] Once the permeating species (water, oxygen and ions) reach electrochemically active areas of the substrate at the bottom of the paint film pores, the corrosion process became measurable so that the proper parameters, i.e., the electrochemical double layer C_2 and the charge transfer resistance R_2, can be estimated. R_2 and C_2 values vary, respectively, directly by and inversely with the attacked metallic area. Sometimes, when the strength of the bonding forces at the paint/substrate interface are affected (e.g., by wet adhesion), facilitating lateral diffusion of the electrolyte, a second faradaic process under intact parts of the coating film could be numerically separated,[29] causing the appearance of another time constant (R_3C_3).

Figures 2a and 3a show the corrosion potential (E_{corr}) dependence on the exposure time to either NaCl or $NaClO_4$ solutions, respectively. Both figures illustrate that some protective effect was afforded by the different paint films since the E_{corr} value of coated steel panels was at least 0.1-0.15 V/SCE more positive than the value expected for uncoated steel (~–0.75V/SCE) measured under similar conditions. Protection was greater in NaCl (*Figure* 2a) than in $NaClO_4$ (*Figure* 3a). Not only was the coated steel E_{corr} displacement towards more active values delayed, but also its value remained at approximately –0.3V/SCE for systems tT, AT, and T, while in $NaClO_4$ only system AT fulfilled this condition. In essence, the more negative the measured potential becomes, the more susceptible it is to corrosion in the underlying steel.

The premature appearance of the first (R_1C_1), second (R_2C_2) and, in some cases, a third (R_3C_3) loop, suggests that the performance of untreated as well as pretreated painted steel sheets was so poor that the effect of the pretreatment almost could not be detected.

Table 2—Diffusion (D), Solubility (S) and Permeability (P) Coefficients of the Tested Paint Films

System	D x 10^9 (cm^2s^{-1})	S x 10^2 (dimensionless)	P x 10^{10} (cm^2s^{-1})
		NaCl Solution	
tT	1.1192	1.921	2.149
tAT	0.9293	1.267	1.177
AT	1.0762	1.271	1.364
tA	1.4614	1.986	2.902
A	1.9073	1.255	2.393
T	1.1045	1.556	1.718
		$NaClO_4$ Solution	
tT	1.3529	1.636	2.213
tAT	0.9932	1.286	1.277
AT	1.1625	1.4898	1.730
tA	1.4408	1.979	2.851
A	1.9856	1.269	2.519
T	1.0701	2.053	2.196

Due to the low paint system thickness as well as to its relatively high water, oxygen, and ionic permeability, the coatings conductivity increased after just a few hours of immersion in the aqueous electrolytes. Therefore, the values of the resistance R_1 and the dielectric capacitance C_1 could be calculated. Almost simultaneously, the permeating species reaching the steel substrate made it possible to determine the electrochemical double layer capacitance, C_2, and the charge transfer resistance, R_2, for most samples. It is important to point out that for systems AT and A values corresponding to the equivalent parameters R_3 and C_3 were also obtained.

Information derived from impedance data suggests that the ionic resistance R_1 (*Figures* 2b and 3b) and dielectric capacitance C_1 (*Figures* 2c and 3c) dependence on exposure time indicate that a constant deterioration of the paint systems took place, particularly when submerged in the $NaClO_4$ solution. In both electrolytes, the initial R_1 value for almost all the samples was in the range of 10^6-10^8 Ωcm^2, the exception was system A when exposed to NaCl which had an R_1 initial value of $\cong 10^4$ Ωcm^2.

With increased immersion time, both plots show that the R_1 evolution was clearly different for each system and dependent on the electrolyte composition. So, when immersed in NaCl, R_1 values for samples tT, AT, and T remained almost stable up to the end of the test. For systems tAT, tA, and A the behavior was different, a more significant decrease was observed as being faster for systems tA and A. Coupled to this parameter through the time constant R_1C_1, attributed to the organic coating relaxation, the dielectric capacitance C_1 evolution shows either fluctuations between 10^{-10}-10^{-8} Fcm^{-2} for samples tT, tAT, AT, and T or a continuous increase up to $\cong 10^{-6}$ Fcm^{-2} for samples tA and A.

On the other hand, the R_1 evolution in the $NaClO_4$ solution showed that a fast and continuous decrease of the ionic resistance took place, being less significant for system AT. The corresponding C_1 time dependence also describes a rapid degradation of the paint system protective properties, since they reach values close to or, in some cases, greater than those corresponding to bare steel in the same medium. After 20 days of exposure no visual sign of

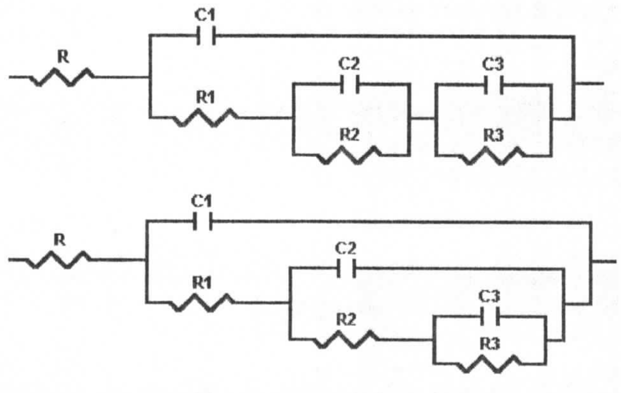

Figure 1—Equivalent circuit models.

deterioration was detected in any painted sample. Nevertheless, there was underfilm corrosion in samples AT, A, T and tT, AT, A, T exposed to NaCl or $NaClO_4$ solutions, respectively.

Figures 2d-2e and 3d-3e exhibit representative diagrams of charge transfer resistance R_2 and electrochemical double layer capacitance C_2 behavior of the painted steel sheets as a function of the exposure time in both solutions. In *Figure* 2d, it can be seen that R_2 values for systems tT, AT, and T remained oscillating around 10^6-10^7 Ωcm^2 during all the immersion period. For system tAT, the behavior is quite similar up to 70 days of immersion when R_2 decreased suddenly and approximately three orders of magnitude. In the case of system A, the resistance diminished up to 60 days of immersion and then stabilized at ~10^2 Ωcm^2. Finally, R_2 values for system tA can only be determined from 10 to 50 days of immersion and they remained approximately constant at ~10^4-10^5 Ωcm^2. On the other hand, *Figure* 3d shows that all the samples exposed to $NaClO_4$ presented a general tendency to diminish their impedance. So, for systems A and T corrosion took place just after immersion, while, for the other systems, the corrosion process began later, eight days for systems tT and AT, and 17 or 25 days for systems tAT and tA, respectively. In agreement with the described resistive changes, the evolution of the coupled capacitance C_2 shows an outstanding increase in relation with their initial values. Thus, as can be seen in *Figures* 2e and 3e, the capacitance magnitude starts around 10^{-9}-10^{-7} Fcm^{-2} (for the more resistive systems) or at 10^{-5} -10^{-3} Fcm^{-2} (for the less resistive ones). In these cases, the painted steel corrosion was so fast that the testing of the affected systems had to be interrupted.

With regard to the third time constant (R_3C_3), it is important to note that it not only appeared in painted steel panels without the tannin pretreatment, but it was also very difficult to determine if it was present. The underfilm charge transfer resistance R_3 remained almost constant at about 10^5-$10^6$$\Omega cm^2$ for sample AT and A in NaCl (*Figure* 2f), but it showed significant changes in $NaClO_4$ (*Figure* 3f). The coupled underfilm double layer capacitance C_3 either stayed stabilized (*Figure* 2g) or showed a rather increasing value (*Figure* 3g) as the exposure time elapsed.

DISCUSSION

The present work is part of an ongoing research program performed at CIDEPINT on the electrochemical phenomena occurring in and under conventional or recently developed paint films and / or paint systems covering different metallic substrates. Likewise, problems related with adhesion defects in films, porosity, metal / coating adhesion, surface preparation and / or pretreatment, blistering, and cathodic protection of painted metals are also matters of interest. So, a comparative study of the anticorrosive capacity of paint systems covering steel sheets with or without a surface pretreatment based on a tannin solution has been performed.

From the coatings point of view, barrier and permeability properties are of great interest because they control the corrosive species (water, oxygen, and ions) transport through them, as well as the active pigments dissolution and supply to the metal substrate. Reliable data on water permeability, corrosion potential, and impedance evolution of coated metals provides valuable information to select and design the most adequate protective paint system for each practical situation.

According to Ritter and Kruger,[30] it may be assumed that different amounts of water, oxygen, and ions can permeate the coating in the first hours of immersion in saline solutions. In the systems tested in this research work, such a process could be attributed to the fact that the air dried alkyd paint films contain an appreciable amount of water-soluble material and tend to absorb water and swell.[31] In addition, the absorbed water has some plasticizing effect on the alkyd film structure and, as a consequence, it also facilitates the movement of molecules through the paint system.

Table 2 shows that the water permeability values for systems tAT were lower than those for systems AT in NaCl as well as in $NaClO_4$ solutions. In principle, these results may be attributed to the fact that the higher number of coats applied to form the complete paint system improved the barrier to water diffusion.[32] However, the opposite behavior was observed when permeability values of samples tT, T and tA, A were compared. In order to explain this disagreement, it is assumed that such a result derives from the different effect that the different substrate-paint film interactions provoke on the paint film structure.[33] As can be seen in *Table* 2, the diffusion coefficient of sample tT in the NaCl solution is almost equal to that of sample T, while the solubility of the tT is higher. This difference may be attributable to the fact that the porous layer formed by the tannin primer increases the free volume within the coating and, therefore, the amount of water dissolved (solubility). Due to the chemical inertia of the pigment content in the topcoat paint, no noticeable change in the mobility of water molecules (diffusion) was measured. However, when the behavior of samples tA and A were compared a somewhat different result was found. So, while the increase of solubility was found again, it was accompanied by changes in the mobility of water molecules (diffusion). We speculate that the change of the underlying substrate, which is the main modification of the steel / coating system, could change, in some unexplained way, not only the coating structure but also the mechanism and / or energy of interactions between diffusing water molecules and, in this case, the reactive anticorrosive pigment particles within the coating film.

Corrosion potential (E_{corr}) changes, as a function of the exposure time to aqueous media, have been successfully used as a simple tool to study the corrosion protection afforded by organic coatings.[34-37] As can be seen in *Figures* 2a and 3a, the E_{corr} moved more or less quickly from their initial values towards more negative ones as a consequence of both the relatively easy electrolyte permeation, due mainly to the low paint coating thickness. However, independent of the solution corrosiveness or the applied painting scheme, the steel substrate remained relatively protected from the corrosive attack. As it was mentioned earlier, this conclusion arises from the fact that the measured E_{corr} value in each painted steel panel was more positive than that corresponding to the bare steel exposed to similar conditions (≅ -0.75V/SCE). An important fact derived from these results is that just after immersion the protection against corrosion provided by the tannin primer film was more effective in NaCl than in $NaClO_4$. According to Romagnoli et al.,[21] such protection may be attributed to both the steel surface phosphatizing afforded by the phosphoric acid present in the primer formulation and the pore blockage due to the ferric tannate formed from the chemical reaction among tannins and steel corrosion products. Later, when this kind of protection was lost, or at least seriously diminished, other protective forms such as the anticorrosive (through the zinc molybdenum phosphate pigment) and/or the barrier (provided by the alkyd resin/titanium dioxide pigment) continued being more or less active. With regard to the first case, several authors[38,39] suggested that both the phosphate and the molybdenum compounds contribute to the anticorrosive mechanism through an effective steel repassivation at the underpaint crevices and pits.

A good description of the impedance spectra was attained through the transfer function analysis using nonlinear least squares fit routines. The paint system as well as the steel substrate deterioration takes place from processes having a complex nature. Consequently, in order to both interpret and explain electrochemically the time dependence of the acquired impedance data, it has been necessary to propose appropriate equivalent circuit models. Thus, in *Figures* 2b-2g and 3b-3g, the relative performance of samples tT, tAT, AT, tA, A, and T (see *Table* 1) under immersion conditions in NaCl or $NaClO_4$ solutions is assessed by the variation of R_i and C_i with the exposure time.

Figures 2b and 3b show representative diagrams of the resistive component of the coatings impedance. The ionic resistance (R_1) values for the different paint systems immersed in NaCl were stable and approximately constant between 10^6-10^8 Ωcm^2 for samples tT-AT-T, they slowly drop to 10^5 Ωcm^2 for sample tAT and, in the case of samples tA-A the values ranged between 10^3-10^4 Ωcm^2 and they were independent of the presence of the chestnut tannin primer. On the other hand, R_1 values were strongly dependent on the presence of the topcoat. In $NaClO_4$ the behavior was completely different: a constant decrease in the R_1 values was observed, being less significant for system AT. Referring to the dielectric capacitance (C_1) values, which are associated with the amount of water permeated within and under the paint film, *Figures* 2c and 3c show that the best protective behavior was also provided by the more resistive schemes. As a general rule, the C_1 of these samples remained in the range 10^{-8}-10^{-10} Fcm^{-2}, which is a characteristic magnitude of less deteriorated organic coatings; whereas, in the rest of them and for both electrolytes, the capacitance increased gradually up to reach the normal (≅3-20.10^{-6} Fcm^{-2}) or even greater (~10^{-4}-10^{-3} Fcm^{-2}) value of the electrochemical double layer of the bare steel in these media (i.e., when the coating protective properties are totally lost).

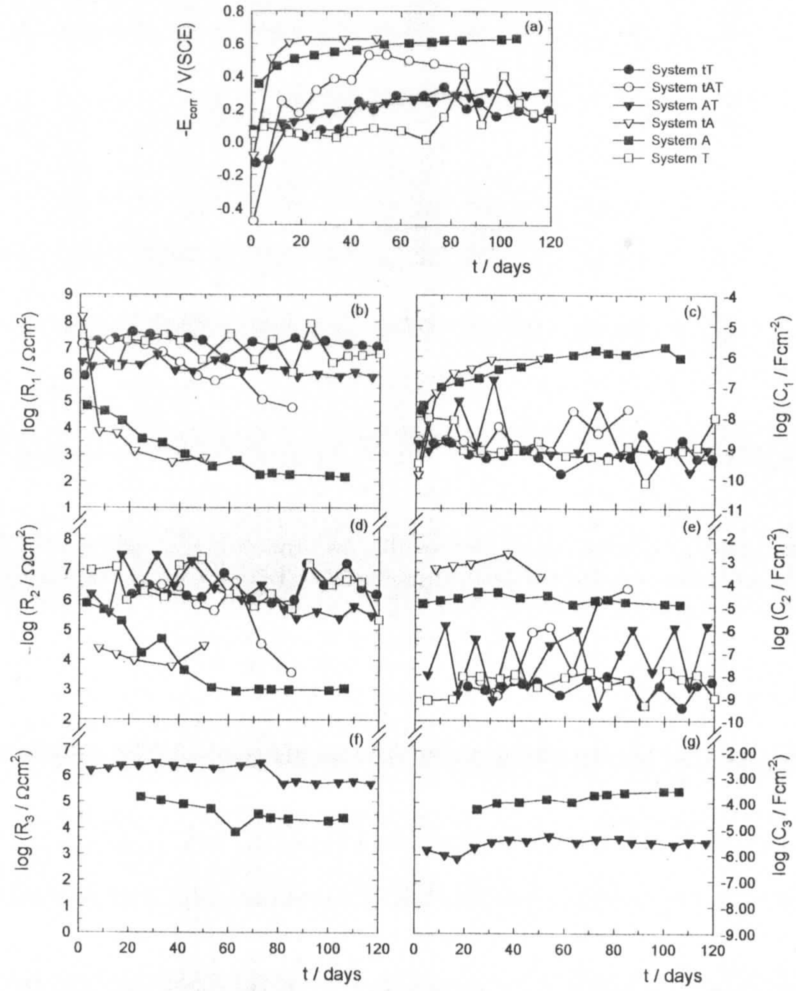

Figure 2—Time dependence of (a) E_{corr}, (b) R_1, (c) C_1, (d) R_2, (e) C_2, (f) R_3, and (g) C_3 of tested painted steel systems when immersed in NaCl.

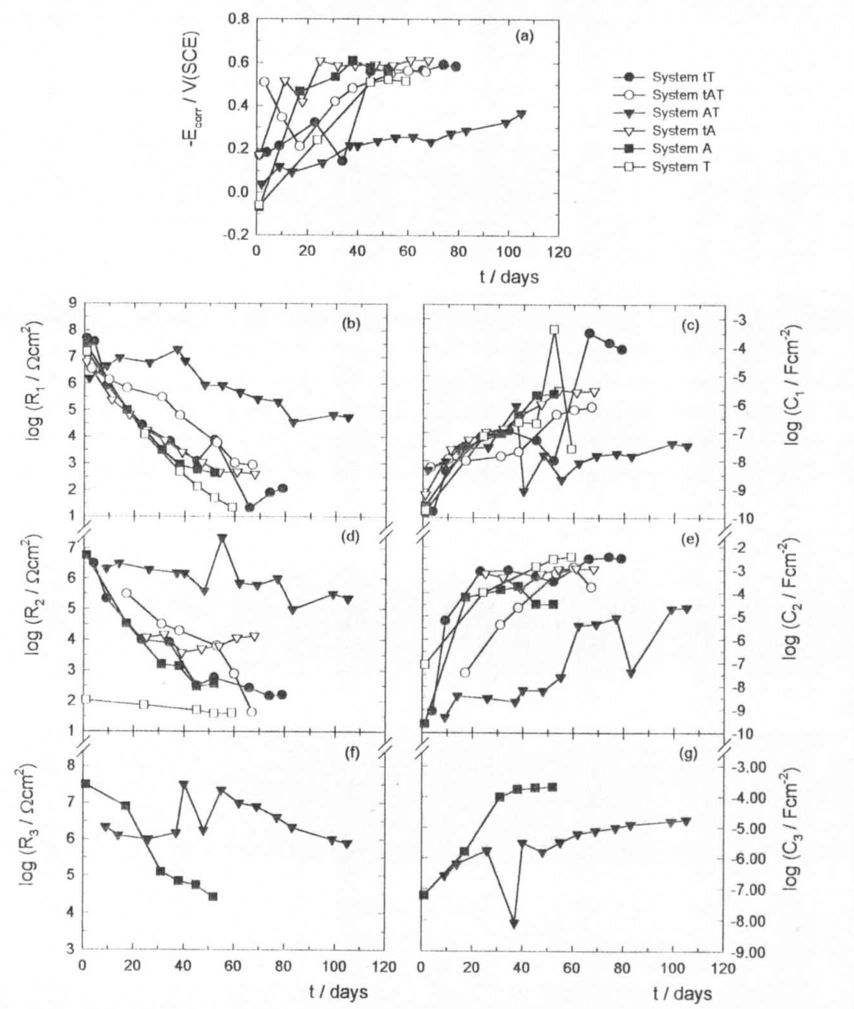

Figure 3—Time dependence of (a) E_{corr}, (b) R_1, (c) C_1, (d) R_2, (e) C_2, (f) R_3, and (g) C_3 of tested painted steel systems when immersed in $NaClO_4$.

As a general hypothesis, it is assumed that the constancy of R_1 and C_1 was mainly due to the fact that neither the specific conductivity of the test solution nor the geometric size of the areas related with the electrolyte conducting paths and the intact part of the coatings were significantly affected within the immersion time. Besides, it is also assumed that when some of the coated steel samples were exposed to NaCl, the low coating thickness and the strong corrosiveness of this electrolyte made the fast formation and gathering of insoluble steel corrosion products possible, which reacted with the tannin primer producing ferric tannate, either within and / or at the bottom of the weaker and defective paint film areas. It is thought, therefore, that the combined action of the described sealing effect and the blocking layer formed by the saponification reaction products (soaps) of the alkyd film certainly had a synergistic effect in reinforcing the paint system barrier properties. In other cases, however, such an improvement could not be effective due to either the intrinsic high porosity (i.e., poor barrier property) of the paint layer (samples tA and A in NaCl) and / or the slow rate of the reaction products development (most of the samples immersed in $NaClO_4$). Consequently, the protective system deterioration prevailed over the anticorrosive and / or sealing-type effect.

Impedance data show that the second time constant (R_2C_2) is related to a process whose contribution becomes meaningful as the exposure time elapses. *Figures* 2d-2e and 3d-3e illustrate that there was an induction period before the appearance of this second time constant, which became perceivable at the intermediate and / or low frequency range. Such a period was, therefore, correlated with the capacity of each painting system for delaying the corrosive agents' diffusion towards the steel / organic coating interface, and, consequently, the development of the electrochemical double layer. Besides, it can be seen that, in general, the mentioned delay was more significant in systems containing the tannin primer (systems tT and tAT in NaCl and tAT and tA in $NaClO_4$). Moreover, the time dependence of parameters R_2 and C_2 keeps an almost linear coherence with that related with the coating ones (R_1 and C_1). Thus, samples tA and A in NaCl as well as tT, tAT, tA, A, and T in $NaClO_4$ not only had the slower barrier resistance but also showed the worst corrosion behavior. In fact, for some samples the attack spread uniformly over the entire panel surface and was fast enough to provoke the test interruption at shorter exposure times.

The rapid loss of the effective protective properties was basically attributed to the relatively low painting system thickness and the fact that some of them are not appropriate for use under continuous immersion conditions. However, findings derived from the experimental results and the extensive search made in order to explain differences in their anticorrosive performance could have important applications.

When the rusting kinetics corresponding to treated and untreated samples was compared, the slower rate measured in the treated ones was attributed to the fact that the tannin primer contributes effectively to the anticorrosive mechanism provided by the zinc molybdenum phosphate. Natural tannins perform their corrosion inhibition action forming structurally amorphous iron tannates.[4,40,41] Those are mainly ferric tannates, which, together with other reaction products, block the active sites at the steel surface, protecting it through the kinetics hindering mechanism.[3,4,42,43] In addition to this corrosion inhibitive effect, when the applied coating formulation contained zinc molybdenum phosphate, steel corrosion protection was enhanced. This pigment protects steel by precipitation of a ferric phosphate layer, which is partially adhered to the metallic surface. Loose ferric phosphate contributes to seal the paint film pores. Another factor providing greater charge transfer resistance at the steel / alkyd-based paint interface is the formation of soaps by the reaction of the pigment with the alkyd resin.[44-47]

Figures 2f-2g and 3f-3g point out that the third time constant (R_3C_3) appeared only for samples without tannin primer. Besides, they also show that (1) the time of appearance in both electrolytes was different, being shorter in both $NaClO_4$ (system A) or in NaCl (system AT); (2) the time constant value remained almost constant in NaCl but not in $NaClO_4$; (3) diffusional control was associated to a faradaic process taking place at the steel / paint interface where intact parts of the paint system are weakly adhered to the steel panel; and (4) as R_3 and C_3 values depend respectively directly and indirectly on the electrochemically active area, the experimental results allow one to infer that the delaminated area either did not change (NaCl) or else increased ($NaClO_4$).

CONCLUSIONS

- Water uptake was not significantly affected by the presence of the tannin primer. Its value was strongly dependent on the electrolyte as well as on the barrier properties of the applied anticorrosive system.
- In electrolytes that were not very aggressive, the presence of the tannin primer delayed the corrosion process due to the formation of ferric tannates at the interface.
- The enhancement of the protection level afforded by the tannin primer was restricted to the first weeks of immersion, after which no influence was detected.
- The anticorrosive protection level depends particularly on the barrier effect afforded by the applied paint system rather than on the tannin pretreatment presence. However, as the corrosion process starts, tannins may cause the repassivation of steel.
- The protective performance of the tested anticorrosive systems was more effective when exposed to NaCl than to $NaClO_4$ solutions.

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