

# EFFECT OF THE PAINT APPLICATION METHOD ON ADHESION AND CORROSION RESISTANCE OF AN ALKYD COATED STEEL

*EFEECTO DEL METODO DE PINTADO EN LA ADHESION Y RESISTENCIA A LA CORROSION DE ACEROS RECUBIERTOS CON PINTURA ALQUIDICA*

**P. R. Seré<sup>1</sup>, D. M. Santágata<sup>2</sup>, C. I. Elsner<sup>3</sup>, A. R. Di Sarli<sup>4</sup>**

## SUMMARY

*The influence of the paint application method (spinning (Sn), rolling (R), brushing (B) and spraying (Sy)) on the behaviour of steel/alkyd coating/aqueous aggressive medium systems was analyzed. Experimental results obtained from electrochemical and standardized tests allowed to conclude that: a) all intact coated samples showed a high resistance to the strong aggressive medium of the salt spray cabinet; b) cross scribed ones only show corrosion at and close to the cross; c) from the electrochemical point of view, the corrosion potential, ionic and charge transfer resistance evolution on immersion time suggests that the alkyd paint applied by the four different methods used have relatively good protective properties, in the order  $Sy > R \cong Sn > B$ , at the present environmental conditions.*

**Keywords:** *paint application methods, adhesion, corrosion resistance, alkyd paint, carbon steel, salt spray test, electrochemical impedance.*

## INTRODUCTION

Paints have been used for many years to protect steel against corrosion. The effectiveness of the coating depends upon many factors. Some of them provide relatively little protection even under rather mild exposure conditions. Others will provide complete protection for many years even under severe conditions.

Until about 30 years ago, it was assumed that the mechanism by which coatings protect steel was acting as a barrier keeping water and oxygen away from the surface of the steel and so that preventing the occurrence of the corrosion process. Then, based on the paint film's water and oxygen permeability values, it was confirmed that the uptake of these species into the interface was higher than its rate of consumption in the corrosion process of the uncoated steel [1]. Since this means that the mechanism of protection could not be the barrier effect of

---

<sup>1</sup> Becario CIC, UNLP

<sup>2</sup> Becario CIC

<sup>3</sup> Miembro de la Carrera del Investigador del CONICET, UNLP

<sup>4</sup> Miembro de la Carrera del Investigador de la CIC

the coating, it was proposed that the electrical conductivity of the coating must be the controlling variable of the corrosion process. Therefore, presumably, high conductivity coatings would have less protective performance than low conductivity ones. In practice, that is truth except for very low conductivity coatings which present no relationship between conductivity and corrosion protection [2,3].

Funke et al [4-7] found that an important factor which had not been sufficiently considered was the adhesion of the coating to the steel in presence of water. They proposed that water permeating through an intact film could detach some films from the steel, that is, the film could have poor "wet adhesion". In such a case, water and oxygen, dissolved in the water, after they permeated through the film, would be in direct contact with the steel surface. In this way, all the elements necessary for corrosion would be present in the water layer, and in direct contact with the anodic and cathodic areas on the surface of the steel. Therefore, if the wet adhesion is poor, corrosion protection will be poor in any case; however, if the wet adhesion is quite good, a low rate of water and oxygen permeation may delay the loss of adhesion and then, for many practical conditions, an adequate corrosion protection level was obtained.

On the other hand, a paint or coating, as supplied, is not a finished product. It fulfils its function only when applied to the substrate. In a most basic sense, coating application can be described as getting the paint from the can to the surface being coated. There are a number of ways of accomplishing this, and often the type of paint material determines the selection of the most appropriate method. Besides, proper application is a critical point of the paint system. The proper use of an application method utilized to apply the paint or coating, can have a definite effect on the time required, the appearance of the finished job, the performance of the applied product and the total cost of the job.

With regard to the performance of the applied coating the application method can have a marked effect, especially when it is subsequently exposed to adverse environments. The choice of the application method may, in general, be dependent on some of the following considerations: 1) where the coating is applied; 2) the object being painted; 3) the objects' location; 4) the objects' configuration; 5) the number of units being coated; 6) the time available to do the job; 7) the surrounding environment; 8) the type of paint used; 9) the skill of the applicator and 10) the budget of the job.

A survey of the literature showed that it is difficult to find specific information about the effect of the paint application method on the behaviour of steel/organic coating/aqueous medium systems, at least from an electrochemical point of view. Consequently, the objective of the present work was to begin its study by using four (brushing, rolling, spraying and spinning) application methods of a commercial alkyd paint on carbon steel sheets. The painted electrodes, exposed to NaCl solutions, were assessed with respect to water and oxygen permeability as well as impedance and corrosion potential evolution as a function of immersion time. Besides, the pull-off and tape adhesion tests as well as salt spray cabinet standardized procedures were also performed.

## **EXPERIMENTAL PROCEDURE**

Each sample substrate consisted of a (10x10x0.3 cm) carbon steel test panel, whose percentual chemical composition was: C (0.16); Mn (0.54); Si (0.05); S (0.01); P (0.01), Fe

being the difference. The surface was sandblasted to ASa 2<sup>1/2</sup>-3 (Swedish Standard SIS 05 59 00/67); its roughness, measured with a Hommel Tester mod. T 1000, was 2.04±0.24 µm. Then, the steel sheets were cleaned with toluene to ensure surface uniformity and coated with a commercially available alkyd paint using either the brushing, rollering, spraying or spinning method. During the drying period the coated plates were kept in a desiccator at a constant temperature (30±2 °C). The dry film thickness was measured with an Elcometer instrument mod. 300, using a bare plate and standards of known thickness as reference; its mean values are shown in **Table 1**.

**Table 1**  
**Average thickness of the tested alkyd films**

<b>Paint Application Method</b>	<b>Average thickness (µm)</b>
BRUSHING (B)	24±3
ROLLERING (R)	27±3
SPINNING (S <sub>n</sub> )	24±1
SPRAYING (S <sub>y</sub> )	28±2

For all the electrochemical measurements, two acrylic tubes were attached to each coated panel (working electrode) with an epoxy adhesive in order to get good adhesion. The geometrical area for each cell exposed to the electrolyte was 15.9 cm<sup>2</sup>. A large area Pt-Rh mesh of negligible impedance and a saturated calomel (SCE) were employed as auxilliary and reference electrodes, respectively. The electrolyte solution was 3% NaCl solution at a pH of 8.2.

All impedance spectra in the frequency range 10<sup>-3</sup> Hz ≤ f ≤ 6.10<sup>4</sup> 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 Frequency Response Analyzer and the 1286 Solartron Electrochemical Interface, the amplitude of the applied AC voltage was 10 mV peak to peak. Data processing was accomplished with an Olivetti PC and a set of programs developed by Boukamp [8].

The value of the water permeability coefficient of the coated steel/electrolyte solution systems above described was determined from measurements of the dielectric capacitance performed in the potentiostatic mode at a frequency of 2.10<sup>5</sup> Hz and the calculus method showed elsewhere [9] while the oxygen one was obtained applying a DC electrochemical technique developed at the CIDEPINT [10]. In it, the samples in contact with a 3% NaCl solution saturated with either oxygen, air or nitrogen were polarized cathodically at a potential value which assures a mass transport control of the oxygen reduction reaction. All the electrochemical experiments were carried out at laboratory temperature (20±2 °C).

Besides the mentioned electrochemical techniques, the **anticorrosive** behaviour of these systems was also evaluated by the salt spray cabinet method (ASTM Standard B-117/85) (exposure time: 750 hours for non-scratched samples and 300 hours for cross scribed ones). On the other hand, before and after exposure tests, the adhesion strength of the four

steel/alkyd paint systems was determined through the **Pull-off strength** (Elcometer mod. 106 tester, ASTM D-4541/85) and the **Tape test** (ASTM D-3359/92a, Method B) standardized procedures. The porosity of the paint films was determined by means of the ASTM Standard D-3258-80 (1992)<sup>61</sup>.

## RESULTS

### Electrochemical tests

Fig. 1 shows the changes observed in the DC corrosion potential ( $E_{corr}$ ) of the coated electrodes for a 45 days immersion period. It is evident that initially samples B (brushing),  $S_n$  (spinning) and R (rollering) exhibited corrosion potentials which became more negative (active) as time elapsed, while that corresponding to sample  $S_y$  (spraying) remained almost unvariable. In essence, the more negative the measured potential becomes, the more susceptible to corrosion is the underlying steel surface.

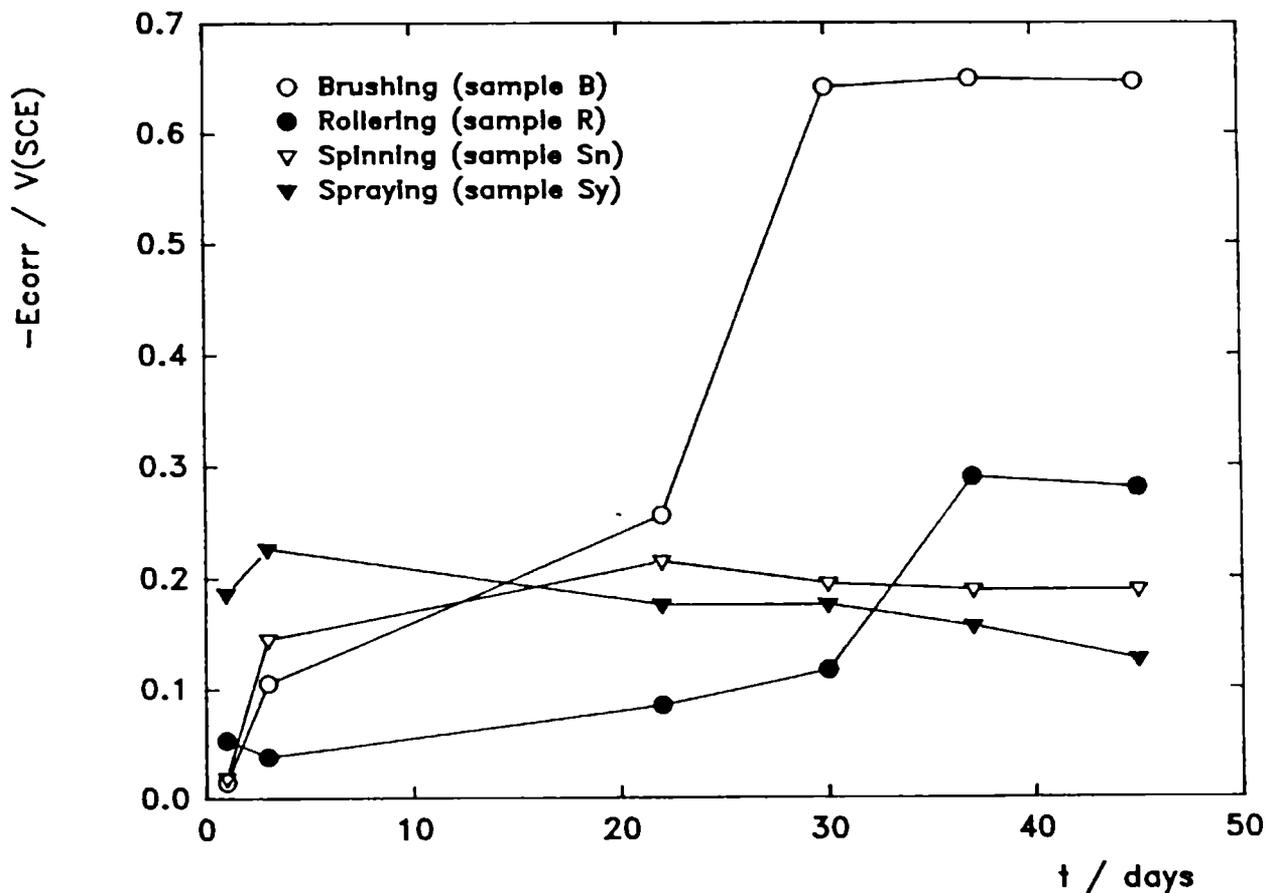
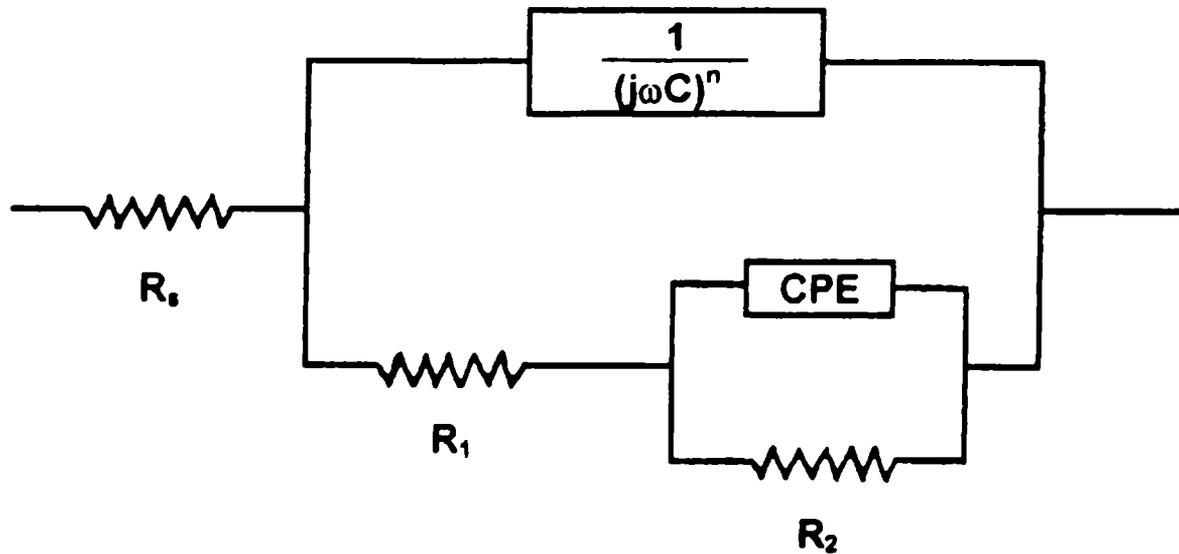


Fig. 1.- Corrosion potential ( $E_{corr}$ ) vs. immersion time ( $t$ ).

The samples B assumed a limiting value in the order of ca. -0.68 V/SCE after only 30 days immersion. This approaches the value expected to be taken up by uncoated carbon steel if measured under similar circumstances. In contrast, samples  $S_n$  and R appear to approach, or in the case of sample  $S_y$ , remained at much more noble potentials, but after an initial period of rapid deterioration.

The impedance spectra were analyzed using the analogous circuit shown in Fig. 2. In this circuit, as the exponent  $n \rightarrow 1$  in all tests, it was assumed that the corresponding passive component was a dielectric capacitance  $C$ ; likewise, the solution resistance was not drawn

because its value was compensated by the measurement equipment in each run. **Figs. 3 - 4** illustrate the impedance results as a function of the immersion time for the four steel/alkyd/3% NaCl solution systems investigated in this work, which differ according to the paint application method employed.



**Fig. 2.- Analogous circuit used for EIS modelling.**

Due to the small alkyd film thickness as well as to its water, oxygen and ionic permeability, just after few hours immersion in the electrolyte, the coating conductivity increased. Thus, the resistance  $R_1$  (which describes paths filled with electrolyte solution of lower resistance shortcircuiting the organic coating) associated with the dielectric capacitance  $C$  (whose value is related to the water uptake), can be obtained applying non-linear squares fitting algorithms to the impedance data. Almost simultaneously, the permeating species reached the metallic substrate causing the emergence of the electrochemical double layer capacitance ( $Q$ ) and the charge transfer resistance ( $R_2$ ) characteristics of the faradaic process and assumed to be inversely proportional to the coated steel corrosion rate.

Information derived from impedance data suggests that both ionic resistance  $R_1$  (**Fig. 3a**) and dielectric capacitance  $C$  (**Fig. 3b**) dependence on exposure time indicate that a constant deterioration took place in the case of samples B but  $R_1$  values remained either oscillating in the  $10^7$ - $10^5 \Omega\text{cm}^2$  range for samples  $S_n$  and R and grown up just to stabilization at the same order of magnitude for samples  $S_y$ ; coupled to this parameter through the time constant  $R_1C$ , corresponding to the alkyd coating relaxation, the dielectric capacitance ( $C$ ) evolution shows either fluctuations between  $10^{-8}$ - $10^{-10} \text{Fcm}^{-2}$  for samples  $S_n$  and R, a significant decrease up to stability at the same range for the sample  $S_y$ , and finally a continuous increase up to  $10^{-6} \text{Fcm}^{-2}$  for sample B. Assuming that the capacitance change is due to the water uptake, the application of the Brasher and Kingsbury equation [11] gives about 7-9 % water absorption in the alkyd samples after 3 hours immersion, **Fig. 5**.

**Fig. 4a** illustrates the highly fluctuating behaviour of the charge transfer resistance ( $R_2$ ) with the immersion time. Changes of  $R_2$  values between  $10^6$  and  $10^3$  for samples B denotes either a progress or a blockage of the active metal surface beneath the alkyd paint film as  $R_2$  decreases or increases, respectively. Correspondingly, as it is shown in **Fig. 4b**, the electrochemical response of the double layer capacitance (which was best fitted using a constant phase element,  $Q$ ) follows an undulating evolution as the time elapsed.

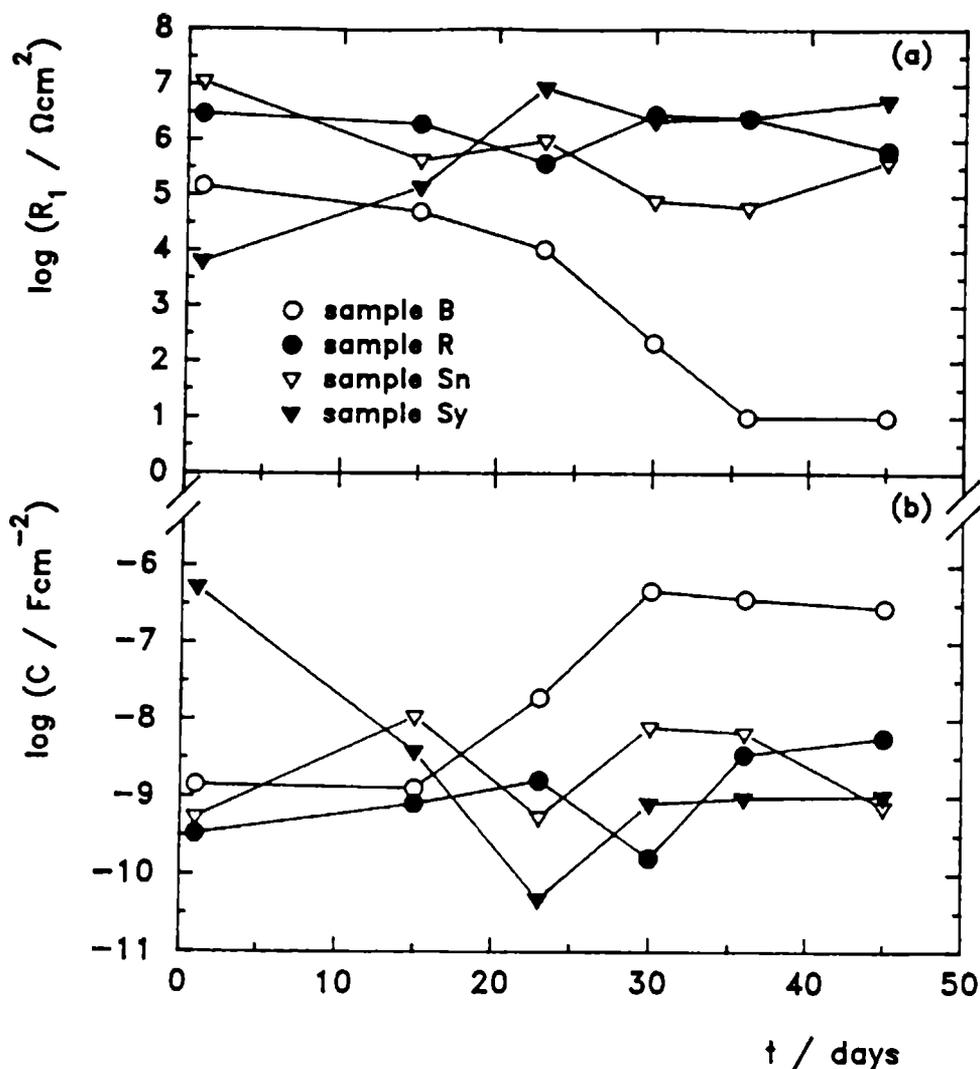


Fig. 3.- a) Ionic resistance ( $R_1$ ) vs. immersion time ( $t$ ); b) Dielectric capacitance ( $C$ ) vs. immersion time ( $t$ ).

Concerning the effect of the paint application method on the coating paint water and oxygen permeability the results are included in **Table 2**. The values of the water permeability coefficient in the alkyd coatings were calculated from measurements of the parallel capacitance as a function of immersion time and using a linear regression of the Carpenter equation [9], while the oxygen ones were determined polarizing cathodically the coated steel, exposed to the electrolyte solution saturated with either nitrogen, air or pure oxygen, and measuring the limiting current for each case [10]. Thus obtained, the values of the water permeability coefficients ranged from a minimum of  $3.92 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  for sample B to a maximum of  $7.03 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  for sample R, whilst the oxygen ones from  $3.56 \times 10^{-7}$  for sample B to  $7.98 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  for sample  $S_y$ .

**Table 2**

**Average water and oxygen permeability coefficients  
of the tested alkyd films**

Sample	$P_{\text{H}_2\text{O}} \times 10^{11} (\text{cm}^2 \text{s}^{-1})$	$P_{\text{O}_2} \times 10^7 (\text{cm}^2 \text{s}^{-1})$
B	3.92	3.56
R	7.03	4.40
Sn	5.80	7.69
$S_y$	6.88	7.98

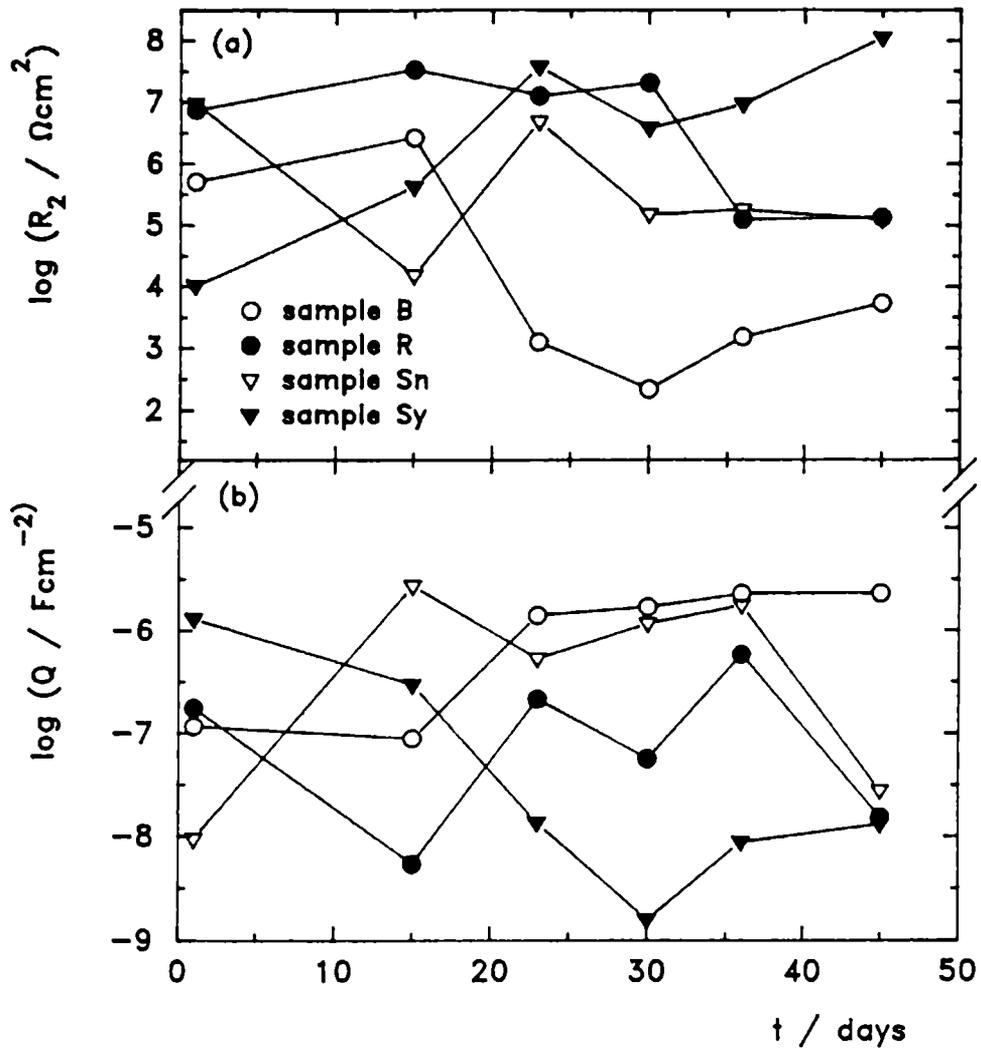


Fig. 4.- a) Charge transfer resistance ( $R_2$ ) vs. immersion time ( $t$ ); b) Double layer capacitance ( $Q$ ) vs. immersion time ( $t$ ).

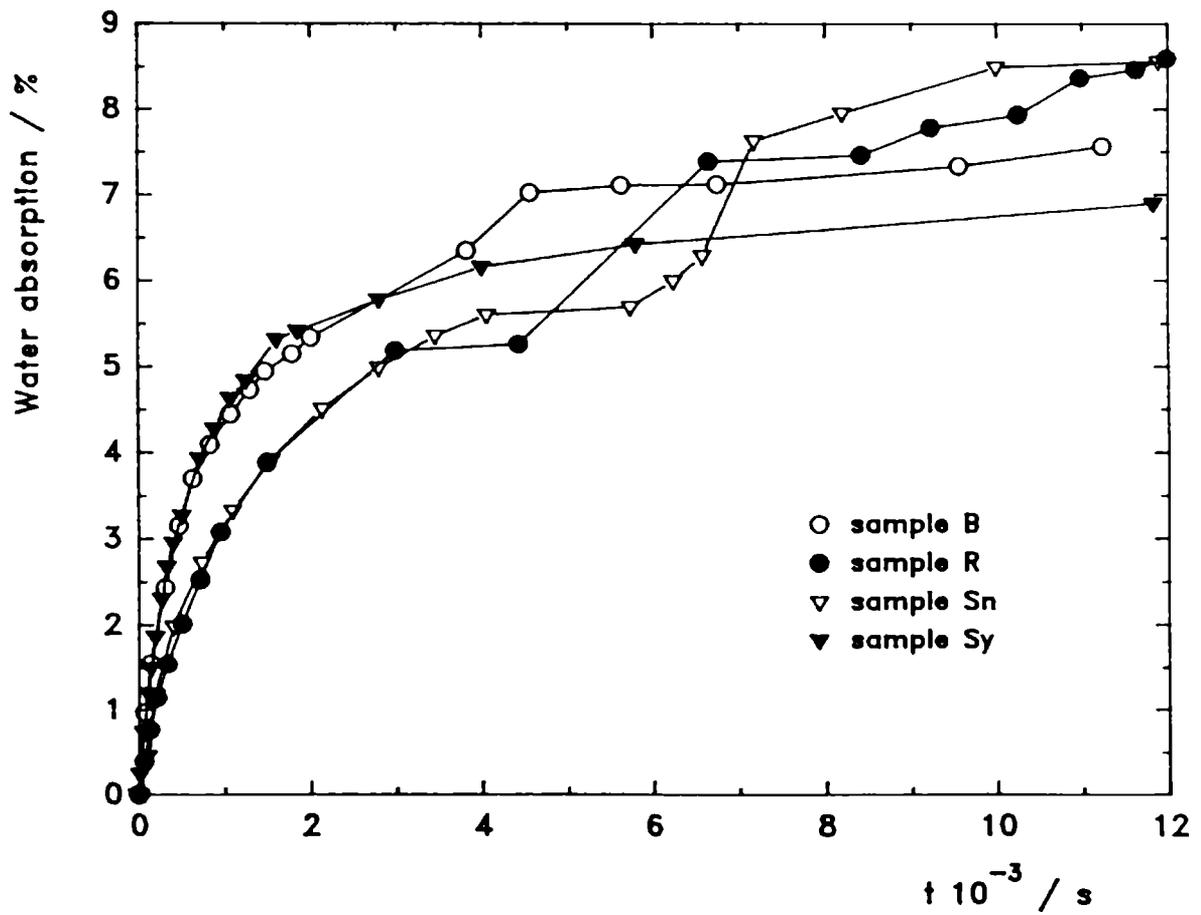


Fig. 5.- Evolution of water uptake for 3 h. immersion.

## Salt spray cabinet and Adhesion Tests

**Fig. 6a** shows steel panels coated by the different application methods with the alkyd paint after an exposure time of 750 h in the salt spray chamber. The intact films show neither corrosion products nor coating defects on the main body of the panels. Slight rusting and blistering were noticeable at the vertical edges of the panels; this was due to a defective wax used there. **Fig. 6b** shows similar panels but with a cross scribe in the coating through the steel substrate. After 300 h in the salt cabinet chamber, the photographs illustrate that areas with intact paint coating have no corrosion, while those at and close to the cross scribe have been corroded severely.

**Fig. 7** and **Tables 3 - 4** give the average level of the steel/alkyd film adhesion strength before and after the salt spray cabinet test carried out for 750 h for intact coatings and 350 h for scribed ones. Such values were obtained using the pull-off (**Figs.7 a-b**) and the tape test (**Tables 3 - 4**) standardized procedures. In both cases it can be seen that except for the corroded areas, i.e. at and close to scratched zones, where adhesion ranged from poor to bad, the adhesion strength show neither meaningful changes nor corrosion after exposure (see **Fig. 6**).

**Table 3**

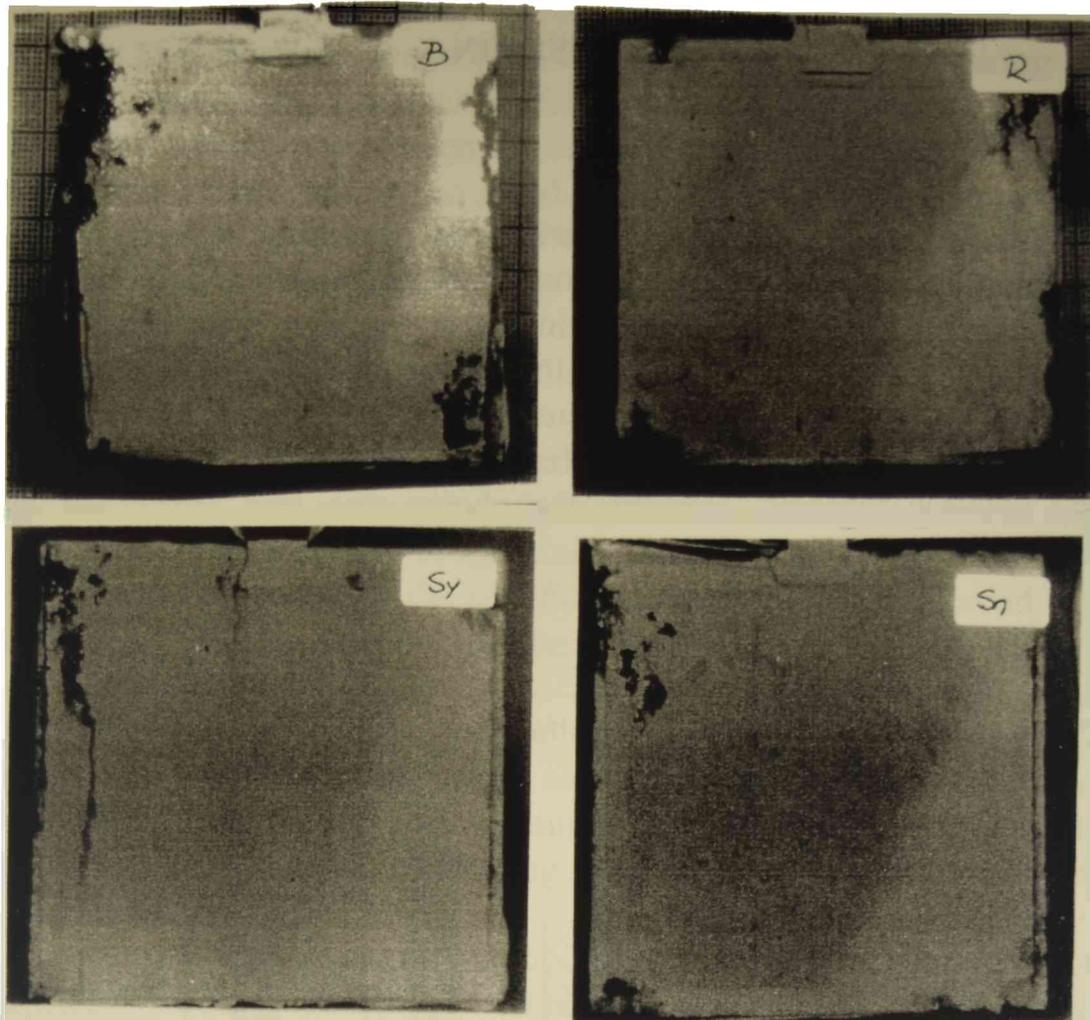
**Tape test adhesion results (ASTM D 3359-92a, Method B) after the salt spray cabinet test for non scratched samples**

	sample B	sample R	sample Sn	sample Sy
before testing	5B	5B	5B	5B
non corroded areas	5B	5B	4B	4B
nearby corroded areas	1B	1B	1B	1B
corroded areas	0B	0B	0B	0B

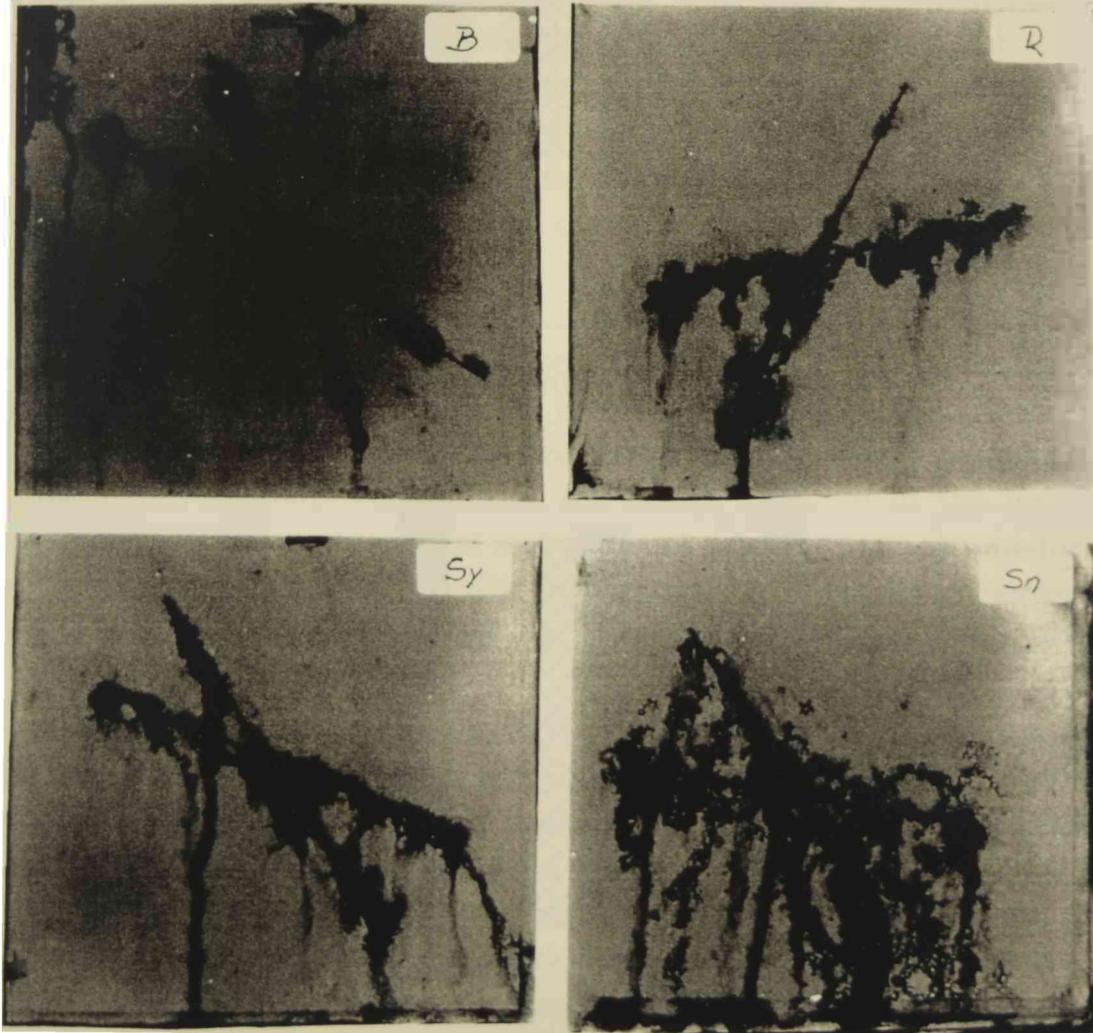
**Table 4**

**Tape test adhesion results (ASTM D 3359-92a, Method B) after the salt spray cabinet test for scratched samples**

	sample B	sample R	sample Sn	sample Sy
on the scratch	0B	0B	0B	0B
5mm from the scratch	1B	0B	0B	0B
10mm from the scratch	4B	0B	0B	0B
15mm from the scratch	4B	4B	0B	1B
20mm from the scratch	4B	4B	0B	4B
30mm from the scratch	4B	4B	0B	4B
40mm from the scratch	4B	4B	1B	4B



(a)



(b)

Fig. 6.- Visual inspection after exposure in the salt spray cabinet a) intact samples; b) scratched samples.

## DISCUSSION

### Electrochemical measurements

This work is part of a continuous investigation of electrochemical phenomena under paint coatings, clasp defects in films, porous films, metal/coating adhesion, surface preparation and/or pretreatments, blistered coatings and cathodic protection. The coating used here was a commercially available alkyd paint. In spite of the fact that in practice this paint is only a part of a painting scheme, it was considered interesting to use it individually to evaluate if the paint application method has any effect on the protective properties of carbon steel/alkyd/NaCl solution systems. Besides, the choice was also supported by the rapid electrochemical response of such a system.

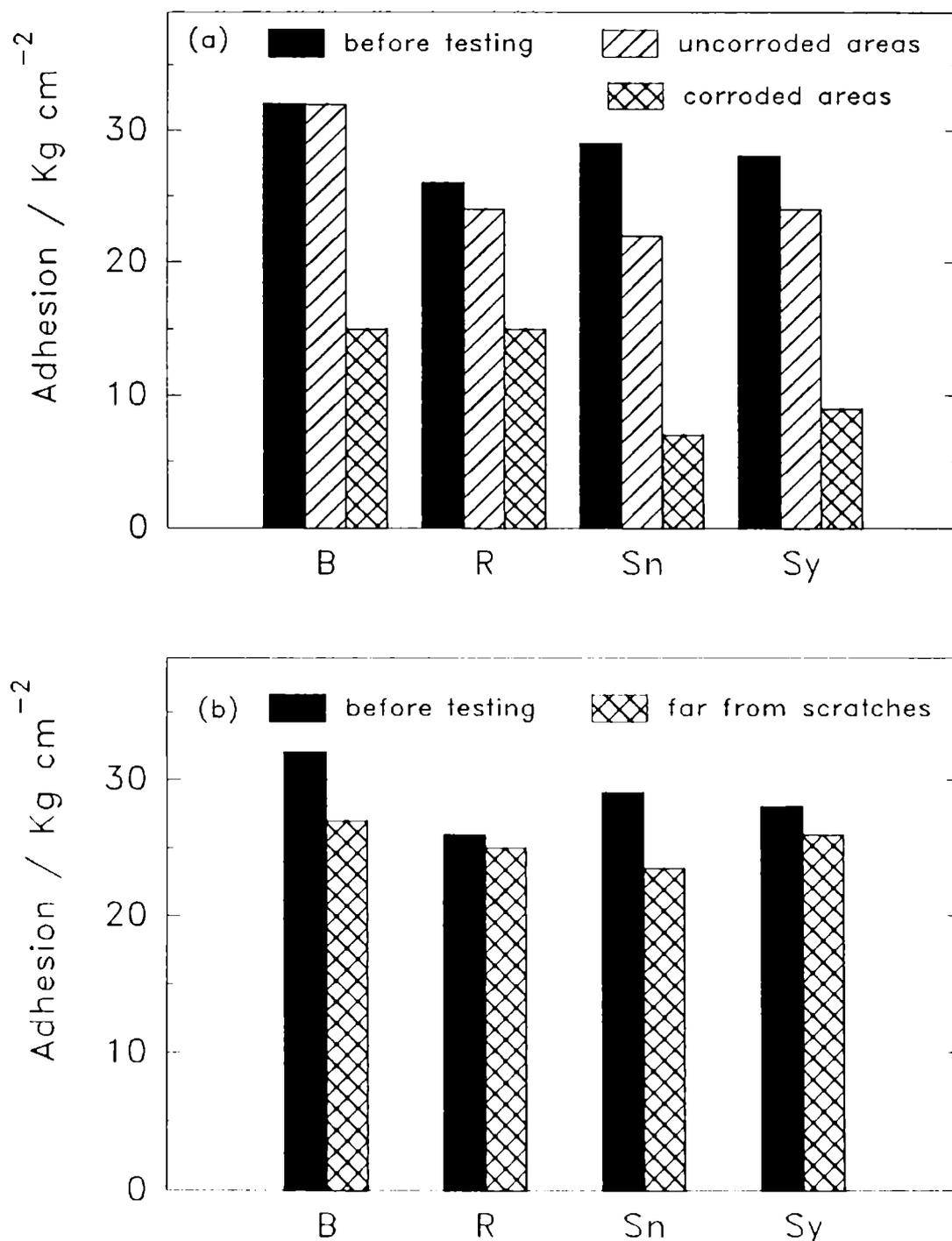


Fig. 7.- Adhesion strength for a) non scratched and b) scratched samples before and after exposure in the salt spray cabinet.

According to Ritter and Kruger [12], it may be supposed that during the first stage of immersion in NaCl containing solutions, different amounts of water, oxygen,  $\text{Na}^+$  and  $\text{Cl}^-$  can permeate the paint coating. In the systems used here, such a process could be attributed to the fact that the air dried alkyd coating contained some unreacted polar groups which developed hydrophilic characteristics when exposed to aqueous solutions; consequently, this condition facilitated permeation. Besides, the relatively great amount of water absorbed by the alkyd paint coating has some plasticizing effect on the internal structure with consequent easy movement of molecules through the coating film.

Thus, during the first hours of immersion in 3% NaCl solution the corrosion potential ( $E_{\text{corr}}$ ) for the four alkyd/steel systems was between 0.018 and 0.18 V/SCE, **Fig. 1**. The more noble values for samples B,  $S_n$  and R than for sample  $S_y$  were attributed to an initial higher barrier effect, presumably added by the significant adhesion forces, afforded by these samples. As the test goes on, however, it is evident the sample's B potentials approach values close to the free corrosion potential characteristic of uncoated carbon steel under equivalent environmental conditions. Such a trend support the assumption of an increasing electrochemical activity at the steel surface along the test, caused by the water, oxygen and ionic species diffusion through the coating paint with a rate and to an extent determined by the physicochemical characteristics of the painting scheme/metallic substrate interactions.

The amount of water absorption by alkyd paint films, obtained from the electric capacitance measurements, against immersion time is illustrated in **Fig. 5**; this shows that sample  $S_y$  gives the lowest value. The other samples have a higher water uptake in the order of  $R \cong S_n > B$  after about 3 h immersion. In particular, samples' B values increased rapidly as the paint film began to deteriorate and peel-off from the metal and the corrosion process progressed. Although the water uptake for sample  $S_y$  was less than for samples R and  $S_n$ , it can be observed in **Fig. 8** that the adhesion force on the metal surface became weak, causing the paint film peel-off but no steel corrosion. Consequently, the steep increase of water absorption in samples  $S_n$  and R seems to be due to water collected at the steel/alkyd paint interface.

Impedance spectra contain valuable information about the electrical coating paint parameters and kinetics of the corrosion process taking place on the metallic substrate. Due to the dynamic character of corrosion products formation and the metal/coating paint interaction forces, the impedance spectra of carbon steel/alkyd film/3% NaCl solution systems change throughout the exposure time. Nevertheless, the complex nature of the interfacial processes have been studied through mathematical and physical models that account for the impedance data measured at such interfaces. Basically, a good description of the experimental impedance can be obtained in terms of a transfer function analysis using non-linear fit routines.

The analogous circuit model used in order to explain the impedance data is shown in **Fig. 2**. A first interpretation of the complex plain plot establishes that it may be described by a transfer function corresponding to an equivalent circuit built up by the electrolyte resistance ( $R_s$ ) in series with the parallel combination taking into account the high frequency time constant due to the coating paint capacitance (C) and the ionic resistance ( $R_1$ ) interaction, while the low frequency relaxation time would be given by the charge transfer resistance ( $R_2$ ) and the electrochemical double layer capacitance (Q). The distortions occurred in the resistive-capacitive contribution at low frequency (reason by which the double layer capacitance was best fitted using a constant phase element (CPE), Q), indicate a deviation from the ideal behaviour in terms of a distribution of time constants due to tangential penetration of

electrolyte at the metal/paint interface, surface inhomogeneities and/or roughness effects [13,14]. By fitting the transfer function associated to the most probable circuit, these factors were taken into consideration through the CPE.

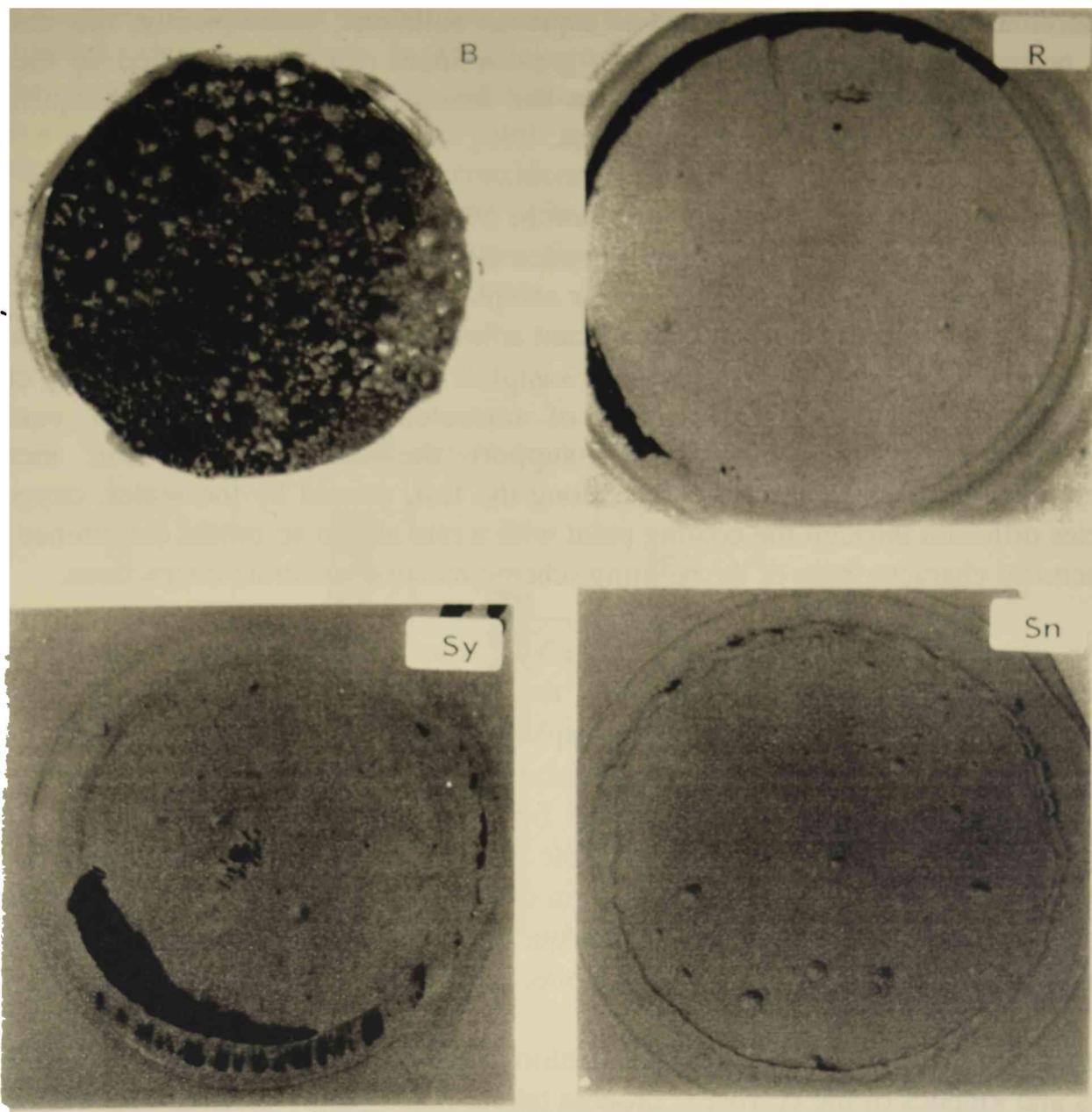


Fig. 8.- Visual inspection after EIS measurements

As can be seen from **Fig. 3**, the ionic resistance for sample B decreased with the exposure time; since its value is mainly determined by the geometric size of the defects filled with the electrolyte solution and the specific conductivity of the test solution, these results suggest that the electrolyte paint film penetration increased with exposure time and confirm those shown in **Fig. 5**. Recognizing that the coating is free from corrosion inhibitors, it is assumed that the very low  $R_1$  values obtained for these samples, agree with the appearance of large corrosion spots on the coated specimens (**Fig. 8**), prove of their poor protective properties under the present environmental conditions. Such a behaviour is particularly attributable to one disadvantage of the brushing application method, it does not produce a very uniform film thickness nor low pores density; both of these factors allow the  $Cl^-$  concentration threshold for steel corrosion be rapidly attained at the base of the paint defects causing an initial localized corrosion which, in turn, promotes a local coating delamination. As the immersion time increases, these areas grow and coalesce until the overall area in contact with the electrolyte shows substrate corrosion and coating disbonding.

The remaining samples (R, S<sub>n</sub> and S<sub>y</sub>) exhibited a well differentiated performance. For samples S<sub>y</sub>, the increase of the ionic resistance (R<sub>1</sub>) values up to about 25 days immersion indicates an increase of the barrier effect afforded by the organic coating presumably enhanced by the formation of an underfilm and, therefore no visually identified, blocking layer due to reaction products (soaps) of the alkyd film. On the other hand, the R<sub>1</sub> values for samples R and S<sub>n</sub> does not greatly differ showing certain stabilization in the range 10<sup>5</sup>-10<sup>7</sup> Ωcm<sup>2</sup> for 45 days immersion. The relatively good anticorrosive protection of these samples was also attributed to the mechanism described by the barrier and insulating model (i.e., the film capacity for delaying the diffusion of aggressive ions to the steel/alkyd paint interface).

Referring to the paint dielectric capacitance (C) dependence on the immersion time **Fig. 3b**, the results document that, in general, there was an undulating performance, which depends on the coating deterioration degree. For sample B the capacity (C) increases gradually to attain the normal value range of an electrochemical double layer (between  $\approx 3$  and  $30 \times 10^{-6}$  Fcm<sup>-2</sup>) when the protective properties are totally lost (sample B) and for the other samples C remains oscillating within the range 10<sup>-8</sup>-10<sup>-10</sup> Fcm<sup>-2</sup>, which is characteristics of somewhat deteriorated organic coatings.

Changes in R<sub>2</sub> (**Fig. 4a**) denote the progress of the active (corroding) metal surface under the alkyd film when either R<sub>2</sub> decreases (due to an increase of the steel/electrolyte solution contact area) or increases (which is caused by the insulating effect due to the accumulation of corrosion and paint degradation products). Again, the protective properties, in the order S<sub>y</sub> > S<sub>n</sub>  $\approx$  R, were higher than those corresponding to sample B, although differences between S<sub>n</sub>-R and B tend to diminish as the test proceed. Correspondingly, the parameter (Q) representing the double layer capacitance followed an undulating evolution as the time elapsed, **Fig. 4b**. Such evolution can provide information about the extent of the underfilm steel/aqueous solution contact area as a consequence of the progressive coating disbonding [15].

With respect to delamination without corrosion in the case of samples S<sub>y</sub>, S<sub>n</sub> and R, it may envision that the initial oxygen and water permeation through the coating develop small localized regions where local delamination of the paint film takes place. As the continuous exposure to the electrolyte goes on, these zones grow leading to their coalescence into larger units until the total exposed area became delaminated. Likewise, the visual evidence of corrosion absence (**Fig. 8**) on these samples could be explained taking into account that spinning, rolling and spraying methods give smoother, more uniform and non-porous films than brushing does. It was assumed, therefore, that the slower rate of Cl<sup>-</sup> permeation due to the development of negative charges in the paint structure, which restricts the permeation of ions with the same charge sign when exposed to aqueous electrolytes, added to the lack of direct pathways (pores, pinholes, etc) through the paint film, avoids that the chloride concentration threshold for the underlying steel corrosion would be reached [16-18].

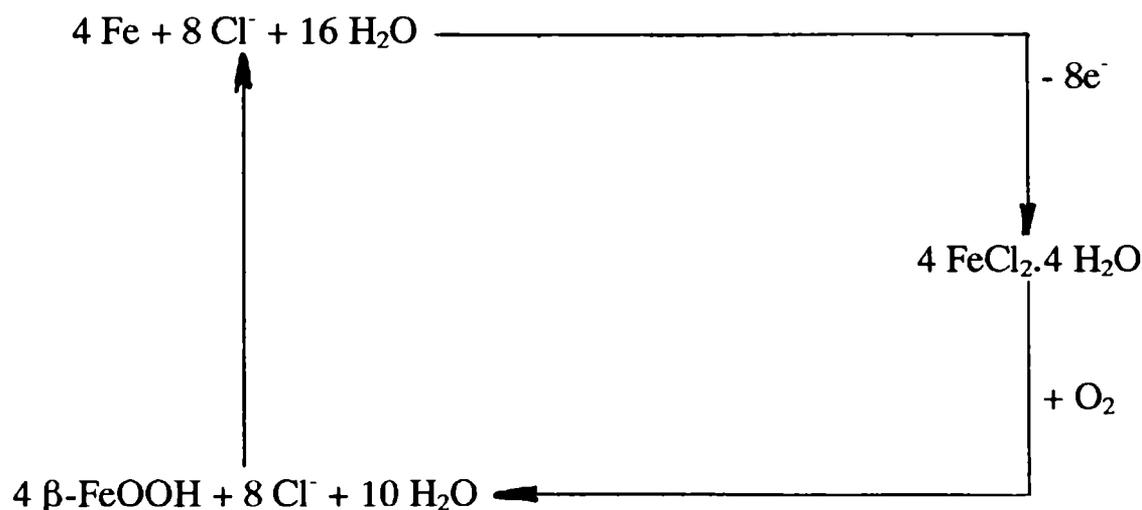
### Salt spray cabinet and adhesion tests

**Fig. 7** shows the dry adhesion values as a function of the film application method, brushing samples have the highest adhesion strength (> 30 kgcm<sup>-2</sup>) and the rolling ones the lowest (about 24 kgcm<sup>-2</sup>); the others (spinning and spraying) do not greatly differ since they have an average value of 28 and 26 kgcm<sup>-2</sup>, respectively.

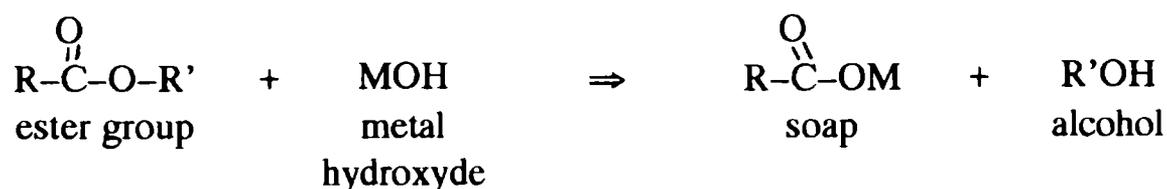
The amount of adhesion loss is dependent on the severity of the exposure and the strength of the specific paint/metal interactions. Thus, different studies have shown an adhesion loss coincident with the presence of water at the metal/coating interface [19-23]. The pull-off and the cross cut tape tests applied on the exposed areas immediately after withdrawing the samples from the salt spray chamber produce the results shown in Fig. 7 and Tables 3 - 4. These indicate that the major shift in adhesive strength occurs in the order  $S_n > S_y > R > B$  for non-scratched samples and  $B > R \approx S_n > S_y$  for the scratched ones.

As it was quoted before, the adhesion values are reduced on exposure to aqueous solution. However, the interesting fact is not this reduction but the finite level of adhesion remaining after immersion. The adhesion loss is thought as molecules of water reaching the metal/paint coating interface and the hydrogen bonding with the available hydrophilic groups of the polymer. It might be surprising that this water does not cause rapid underfilm corrosion. Taking into account the water permeability data given in Table 2, and assuming that the water vapour could be still lower, the possible explanation is that where the paint film remained intact the amount of water necessary to cause interfacial disbonding is substantially less than the amount required to form a discrete aqueous phase, therefore, it would not be able to support the charge transfer process associated with corrosion nor to avoid that adhesion settles to an acceptable and consistent value. Besides, this fact is also supported by the above mentioned restriction of the  $Cl^-$  diffusion through the paint film.

On the other hand, for cross scribed samples all tests have shown a direct relationship between adhesion loss and corrosion attack neighbor to the scratch. In this region, the cross scribe becomes an anode where Fe dissolves as  $Fe^{+2}$ , in principle, according to the following reaction mechanism [24].



and the metal under the paint film becomes the cathode. An electric circuit is formed throughout the paint film. At the cathode,  $OH^-$  ions are formed by the oxygen reduction reaction; the alkaline medium, created as the steel corrosion progress, rapidly attack the oil base of the alkyd film, saponifying it, according to:



where R and R' are alkyl groups. As a result of this coating degradation, paint adhesion weakens facilitating the metal/coating disbonding and, consequently, the lateral access of electrolyte to the paint/steel interface which feedbacks the process.

## CONCLUSIONS

- AC together with DC and standardized procedures have considerable value in assessing the protective ability of a paint film from scientific and methodic studies of anticorrosion problems. Knowledge about the changes in permeability, conductivity and adhesion properties of coatings when exposed to aggressive environments is important, not only because it indicates how the coating may behave in practice, but also because it gives an insight into its protective properties in prevention of corrosion of the metal substrate.
- From the values of corrosion potencial, ionic and charge transfer resistance on immersion time, the alkyd paint applied by means of four different methods showed relatively good protective properties in the order  $S_y > R \approx S_n$  but very poor ones for sample B. On the other hand, when submitted to the salt spray cabinet test, all the steel sheets coated with intact alkyd films have shown high resistance to the strongly aggressive medium (5% NaCl). Likewise, the cross scribed samples only shown corrosion at and close to the cross.

Taking into account the overall results, the more effective application method was spraying followed by rollering, spinning and, in last term brushing, also further work needs to be done to confirm some of the assumptions made here.

## ACKNOWLEDGEMENTS

The authors would like to thank the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC) and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for their financial support of this research work.

## REFERENCES

- [1] J.E.O. Mayne, *Official DIGEST*, **24**(235), 127 (1952).
- [2] J.E.O. Mayne, "Corrosion", L.L. Shreir de., Butterworth (Boston), vol.2, 15:24 (1976).
- [3] H. Leidheiser, Jr., *Prog. Org. Coat.*, **7**, 79 (1979).
- [4] W. Funke, U. Zorll & B.G.K. Murth, *J. Paint Technol.*, **41**(530), 210 (1969).
- [5] W. Funke & H. Haagen, *Ind. Eng. Chem. Prod. Res. Dev.*, **17**, 50 (1978).
- [6] W. Funke, *J. Coat. Technol.*, **55**(705), 31 (1983).
- [7] W. Funke, *J. Oil Col. Chem. Assoc.*, **68**, 229 (1985).
- [8] B.A. Boukamp, *Report CT88/265/128, CT89/214/128*, University of Twente, The Netherlands (1989).
- [9] E.E. Schwiderke & A.R. Di Sarli, *Prog. Org. Coat.*, **14**, 279 (1980).
- [10] C.I. Elsner, R.A. Armas & A.R. Di Sarli, *Portugalæ Electrochim. Acta*, **13**, 5 (1995).
- [11] D:M: Brasher & A.H. Kingsbury, *J. Appl. Chem.*, **4**, 62 (1954).
- [12] J.J. Ritter & J. Kruger, *Corrosion Control by Organic Coating*, H. Leidheiser, Jr. ed., NACE, Houston, Tx, 28 (1981).

- [13] T. Szauer & A. Brandt, *J. Oil Col. Chem. Assoc.*, **67**, 13 (1981).
- [14] D.J. Frydrych, G.C. Farrington & H.E. Townsend, *Corrosion Protection by Organic Coatings*, M.W. Kendig & H. Leidheiser, Jr. eds., vol. 87-2, p. 240, The Electrochem. Soc., Pennington, NJ, (1987).
- [15] L.M. Callow & J.D. Scantlebury, *J. Oil Col. Chem. Assoc.*, **64**, 119 (1981).
- [16] C.I. Elsner, R.A. Armas & A.R. Di Sarli. In press.
- [17] A.L. Glass and J. Smith, *J. Paint Technol.*, **39**, 490 (1967).
- [18] H. Corti, R. Fernandes Prini and D. Gómez, *Prog. Org. Coat.*, **10**, 5 (1982).
- [19] J.W. Watt & J.E. Castle, *J. Materials Sci.*, **18**, 2987 (1983).
- [20] H. Leidheiser, Jr. & W. Funke, *J. Oil Col. Chem. Assoc.*, **70**(5), 121 (1987).
- [21] H. Hansman, *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 252 (1982).
- [22] W. Schwenk, *Corrosion Control by Organic Coatings*, H. Leidheiser, Jr. de., NACE, Houston, Tx, 103, (1981).
- [23] P. Walter, *Off. Digest*, **37**, 1561 (1965).
- [24] W. Funke, *J. Oil Col. Chem. Assoc.*, **62**, 63 (1979).