Substrate effects on the corrosion performance of coated steels under immersed conditions

I. Costa
IPEN-CNEN/SP
Caixa Postal 11049
CEP 05422-970
São Paulo-SP-Brazil

S. E. Faidi
UMIST-Corrosion and Protection Centre
PO Box 88
Manchester

J.D. Scantlebury
UMIST-Corrosion and Protection Centre
PO Box 88
Manchester

Abstract

Little work has been reported in the literature concerning the influence of the substrate on the corrosion performance of coated metals under immersed conditions. In this study, effects of the substrate with minor compositional differences are specifically investigated.

Two mild steels and two low alloy steels, coated with a clear alkyd film, were studied under immersed conditions in a solution containing 3.5 % NaCl. The long term corrosion behaviour of these coated substrates was monitored by visual observation, potential-time measurements and electrochemical impedance spectroscopy. It was found that the observed trends in the corrosion performance were related to the inclusion content of the substrate and not to the small additions of alloying elements. Coated substrates which had the lowest inclusion content showed relatively longer times to failure.

The localised areas of corrosion attack, seen as black or brown spots, were associated with the distribution of the inclusions on the surface. A mechanism is proposed to account for the role of these inclusions on the overall performance of the paint.

Key terms: coated steels, substrate, inclusion content

Introduction

The work reported in the literature[1-6] concerning the influence of the substrate on the corrosion behaviour of coated systems compares metals of very different electrochemical properties. The general conclusion reached by the previous authors was that the corrosion performance of painted metals was dependent on the electrochemical nature of the substrate. Metal substrates with lower corrosion resistance produced faster rates of film deterioration[1,3,5].

When substrates of similar compositions were considered, some coating systems were observed to perform better on low-alloy steels as compared to carbon steels[7]. This would suggest that minor changes in the composition of the steel surface could have an important effect on the protective properties of organic coated systems when exposed to aggressive environments. This observation seems to be particularly true for atmospheric exposure of coated steels, since adherent and protective corrosion products which hinder further corrosion are formed on the defective areas of the coating. Nevertheless, for coated steels under immersed conditions very little work has been reported about the effect of the small addition of alloying elements on the corrosion behaviour of the steels.

Previous work carried out at UMIST [8] suggested that differences are found between two types of steels, mild steel and low-alloy steel type, when coated and fully immersed in chloride solution. However only visual observations were carried out with no attempt to explain the reasons for the differences. In order to investigate the relationship between the steel substrate characteristics and the corrosion behaviour of the steel when coated and immersed in sodium chloride solution this work was carried out.

Experimental

Two mild steels (MS 1 and MS 2) and two low alloy steels (LAS 1 and LAS 2), whose chemical composition is shown in Table 1, were tested electrochemically in a solution containing 3.5% wt NaCl and at ambient conditions.The surface of the steels was prepared by grinding with silicon carbide grit paper (up to grade 1200). The specimens were then degreased with trichloroethylene in an ultrasonic bath, hot air dried, and immediately stored in a desiccator over silica gel for at least three days before the coating was applied. A long oil alkyd was applied by flood spinning. The coated specimens were left overnight in a desiccator, before finally being cured in an oven at 40°C for four hours. The dry thickness of the coating was found to be in the range of 20 to 30 μm. The resulting coating was transparent making the observation of corrosion, blistering or delamination processes easier. The edges of the specimen were blanked off leaving an area of 10 cm^2 to be exposed to the test environment.

The alkyd coated specimens were subsequently fully immersed in aerated 3.5% wt sodium chloride solution and, in most cases, allowed to remain until the complete breakdown of the paint. During the immersion period the corrosion behaviour of the tested specimens was monitored by measuring the electrochemical corrosion potential, the electrochemical impedance characteristics and visual observations of the steels surfaces.

The electrochemical impedance measurements were performed in the frequency range of 65 kHz to 20 mHz, with 7 readings per decade over extended time periods of around 500 days. The measurements were carried out under potentiostatic control at the open circuit potential as a function of the exposure time. The amplitude of the exciting voltage applied varied according to

the resistance of the coating film. For coatings with resistances > $1x10^7\Omega.cm^2$, the amplitude applied was 50 mV, and for lower resistance coatings it corresponded to 20 mV. The experimental cell consisted mainly of a working electrode, a saturated calomel reference electrode, and a large graphite auxiliary electrode. The reproducibility of the data was established by using 4 specimens of each substrate. The maximum test duration was 500 days.

In order to check if the impedance data reflected the corrosion behaviour of coated steels, the extent of corrosion was assessed visually. The corrosion potential, E_{corr}, was also monitored during these prolonged tests in relation to a saturated calomel reference electrode (SCE). Some of the specimens tested were removed from the solution after a certain period of immersion since no corrosion could be detected from the impedance spectra even though corrosion could be seen on the surface. For this reason only three specimens corresponding to most substrates were compared.

Results and Discussion

The values of coating resistance, R_{pf}, were estimated from the Nyquist impedance diagrams as the chord AC of the arc that best fitted the impedance data, as illustrated in Figure 1. The development of the impedance response with immersion time is exemplified in Figure 2 for one of the specimens tested corresponding to the substrate LAS 2. Figures 3 to 6 show the variation in R_{pf} values with immersion time for the following substrates MS 1, LAS 1, MS 2, and LAS 2, respectively. Table 2 presents a summary of the development of the coating resistance, R_{pf}, with immersion time of the various specimens tested. A curve fitting procedure was used to find the semicircle that best fitted the experimental data in the Nyquist plot. At the beginning of the immersion period an arc running almost parallel to the Z" axis was produced for most coated specimens indicating an initial highly protective coating. This also indicated that the coating on the specimens used was not grossly defective, and there was no significant ionic transport through the coating.

From figures 1 to 4 and table 2 it can be deduced that the steel substrate seems to have an effect on the behaviour of the coated system. While the coating on the LAS 2 steel substrate remained very protective most of the time, relatively rapid deterioration of the protective properties of the coating occurred for most of the specimens corresponding to the substrate MS 1. The coating on one of the specimens of this latter substrate, (MS 1(4) table 2), however presented an exceptional resistance and it still showed a capacitive behaviour at the end of the test.

The performance of the coating-substrate system seemed to be ranked in the following order, LAS 2 >MS 2≈LAS 1>MS 1. The criteria used for comparing the performance of the coated substrates was the time for failure and the time for a decrease in R_{pf} to values $\leq 10^6\ \Omega.cm^2$. It can also be noted that two of the LAS 2 coated specimens did not fail during the period of the test, even though the R_{pf} corresponding to these specimens had dropped to values of the order of $10^6\ \Omega.cm^2$, after 200 and 300 days immersion, indicating that some deterioration of the system occurred. This supports the idea that even for cases when the coating is losing its protective characteristics, the lower corrosion of the LAS 2 substrate retarded the complete failure of the system.

For the coatings which maintained their protective characteristics during all the test, the substrate did not seem to have affected the performance of the system. This is expected since the coating in these cases works as an almost "perfect barrier" to the corrosive environment.

Despite the low coating thickness used, proper coating application after adequate surface preparation might have been the cause for the resulting outstanding coating characteristics obtained. The highly resistant coatings were evidenced by a capacitive behaviour at the end of the test period (500 days). Another possible reason for the excellent properties of some coatings, even after long periods of exposure, might have been their high cross-linking density resulting from a complete cure of the coating.

Unfortunately, "perfect coatings" do not occur in practice and defective coatings are usually found. Defects can also develop during the service lifetime of coatings. In these common cases, "non-perfect" coated systems, the substrate electrochemical properties is believed to affect the corrosion characteristics of the system. In the cases where R_{pf} decreased with time, it is considered that the corrosion process at the interface might have enhanced conduction through defects in the coating. Thus, substrates more susceptible to corrosion would result in lower times for failure of the coated system.

Differences in the general trend to resist corrosion failure however could not be related to the chemical composition. An attempt was then made to explain the reasons for the different behaviour exhibited by the various coated substrates based upon their microstructural characteristics. The inclusions present in the various steels used were analysed by Optical Microscopy and Energy Dispersive Microscopy. These were found to consist mainly of MnS in the case of the mild steel types and oxide or mixed (oxide-sulphide) in the case of the low alloy steels used. The average number of inclusions per cm^2, table 3, was also different for the various steels tested. For the steel MS 1 the average number of inclusions was 2 to 4 times larger than that of the other steels studied. The steel with the lowest number of inclusions was the LAS 2 and that was also the steel to resist the longest the corrosion failure of the coated system among the steels used.

The reasoning behind investigating the microstructure characteristics as a possible cause for the differences observed was that some of these features, which were later found to be related to the inclusions present in the steel, were easily revealed in the case of the steel substrate MS 1 after few days immersion. They were usually associated with small brown and black corroding spots, as illustrated in Figure 7 (a). In the case of the steel MS 1 the inclusions were aligned in the rolling direction as result of the production process being easily distinguished to the naked eye. Since sulphide inclusions are good electronic conductors and as such can take part in the electrochemical reactions they might contribute to the phenomenon of underfilm corrosion. They can also initiate pitting corrosion since they act as local cathodes for hydrogen evolution. Oxide particles on the other hand are poor electronic conductor and as such are not expected to be as effective as the sulphide types.

For most specimens tested localized corrosion was noted which was associated with small brown changing to black corrosion spots, Figure 7 (b) to (d). The localized corroding spots were most likely associated with "weak" areas of the coating which allowed localized attack of the substrate and production of alkali at the surrounding areas. These were either present initially or developed during exposure to the corrosive environment. Generally the corrosion of coated metals has its first step as the result of a galvanic effect with the anodic reaction being located at the bare metal exposed at a paint defect or "weak" area, and the cathodic reaction underneath the intact coating. The way the corrosion product acts subsequently is treated differently by three mechanisms. In one of the proposed mechanisms the corrosion product is considered to behave as inactive areas[9]. A second explanation assumes that the voluminous corrosion products affect mechanically the coating/metal bond, lifting the paint

and eventually causing the breakage of the interfacial bond[10]. A third hypothesis proposes that the corrosion products actively participate in the electrochemical reactions responsible for metal substrate corrosion and subsequent delamination[11].

It is believed that all the three proposed mechanisms might be operative depending on the characteristics of the coating and corrosion products formed. When the coating was highly protective during the whole test period, compact and not voluminous corrosion products consisting mainly of FeOOH (brown rust) were formed which might have blocked the access of corrosive species to the underlying metal without disturbing the bond metal oxide-coating. Since this type of rust is not a good electronic conductor it is unlikely to have taken part in the electrochemical reactions and the first mechanism is bound to have prevailed. This mechanism might have been operative in the case of the specimen MS 1(4) which showed small brown corrosion spots after few days immersion and was still unchanged when the test ended.

In some cases the corrosion black spot was surrounded by a delaminated area, Figure 7 (b), which was found to be related to the presence of sodium and hydroxide species detected by Auger and XPS analysis. Magnetite (Fe_3O_4), the black corrosion product, is an electronic conductor and thus might have participated actively in the electrochemical reaction eventually leading to delamination. The formation of voluminous corrosion products were only noticed in the late stages of corrosion of some of the specimens used and as such it is not believed to have played an important role in the cases studied.

The inclusions in the steels studied are believed to have an important effect on the initial stages of corrosion. The sulphide inclusions are cathodic to the ferrite matrix causing the creation of microgalvanic cells when an electrolyte is present. They work as nucleation sites for corrosion which might develop or not depending on the characteristics of the coating. Oxide inclusions although not metallic conductors might also affect the properties of coated steels by decreasing the adhesion of protective coatings[12]. Thus the areas associated to the oxide inclusions are areas where water could be easily accumulated leading to corrosion initiation.

What happens after corrosion has started however depends on the characteristics of the coating. For highly protective coatings the corrosion product is deposited on the initial local sites restricting the access of the corrosion species to the underlying metal. The corrosion of the substrate is stimulated as a result of the bare metal exposed locally at the coating defect but if the interfacial bond of the coating-metal oxide does not deteriorate at areas distant from the corroding spot, corrosion is restricted to the "weak" area leading to localized corrosion. The deposition of insoluble corrosion products around the void or localized corroding area follows. Corrosion products develop and rise over the corroding area and its surroundings forming a layer or incrustation which isolates the environment within the cavity from the bulk electrolyte. This subsequently retards the diffusion of corrosive species, and once the defective area has been blocked by insoluble corrosion product, corrosion can stop. This situation can be maintained for long times in the case of highly resistant coatings, until corrosion is allowed to start on other areas of the specimen.

For less resistant coatings with the presence of defects, pores, or "weak" areas corresponding to free volume regions however corrosive species will have easy access to the underlying metal. If due to the low coating resistance the bond at the coating-substrate interface is disturbed this can result in the loss of adhesion between the coating and the substrate. Since water can be replenished at these areas of the interface it forms a layer which can sustain corrosion. Once water has accumulated on large areas of the surface the corrosion characteristics of the substrate are supposed to have a significant effect on the anti-corrosion

properties of the system. The boundary regions between inclusions and metallic matrix are the likely regions for corrosion initiation due to a microgalvanic effect.

Inclusions can also affect the movement of water through a capillary or pore which is easier under the influence of a potential gradient, by electroendosmosis[12]. Consequently, galvanic couples at the interface may lead to a blister. In the blistered area, coating has lost its adherence and water may accumulate allowing generalized corrosion to start. Thus inclusions at the interface can act as additional corrosion promoters. Galvanic cells are set-up between the heterogeneity and the steel base. These cells are sufficient to activate the corrosion process as soon as the corrosive species reach the interface. MnS type inclusions which are cathodic relatively to bare metal can provide ideal nucleation sites for rusting. These when attacked by an acidic environment, produce HS^- and S^{2-} which in turn promote a faster dissolution rate of iron by decreasing its activation polarization[13]. Increasing acidity caused by hydrolysis reactions, leads to the reduction of hydrogen ions by electrons originating from the oxidation reactions. The evolution of hydrogen can occasionally cause the breaking of the crust of corrosion product. If this occurs, further corrosion is possible.

Conclusions

A correlation seemed to exist between the microstructural characteristics of the steel substrates used and their corrosion performance when coated and immersed in solution of 3.5% wt NaCl. The steel which had the largest average number of sulphide inclusions produced the lowest corrosion resistance. On the other hand, the longest times for failure of the coated systems tested were associated with the substrate of lowest inclusions content. It was proposed that the inclusions type and content of the various steels studied was the probable cause for the differences found in their corrosion performance under immersed conditions.

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Table 1 - Elemental composition of steels studied.

Steel	MS 1	LAS 1	MS 2	LAS 2
C	0.20	0.11	0.058	0.076
Si	0.04	0.47	0.012	0.36
Mn	0.67	0.78	0.24	0.36
S	0.028	0.010	0.012	0.009
P	0.011	0.013	0.011	0.093
Cr	n.d.	0.50	n.d.	0.88
Ni	0.016	0.02	0.02	0.013
Mo	n.d.	n.d.	0.01	n.d.
Co	0.005	0.007	0.006	0.006
Cu	0.01	0.32	0.03	0.28
Ti	0.003	0.03	0.003	n.d.
Al	0.002	0.03	0.046	0.035
Sn	0.004	0.006	0.013	0.007
Fe	balance	balance	balance	balance

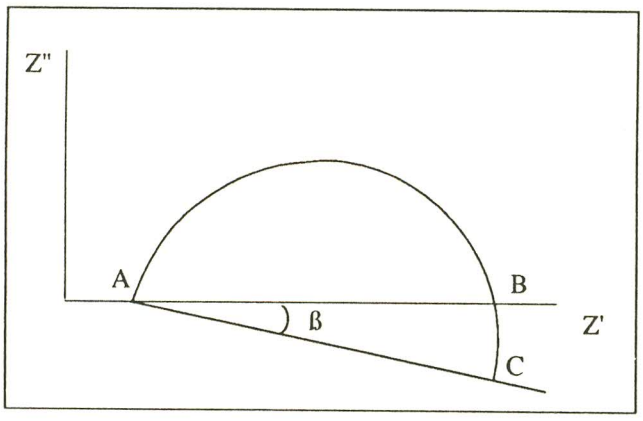
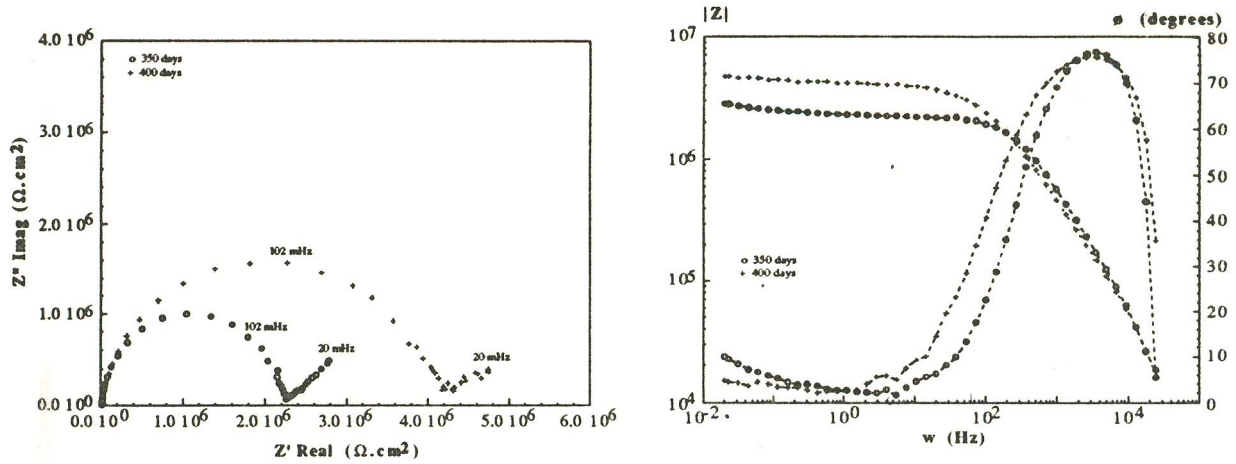
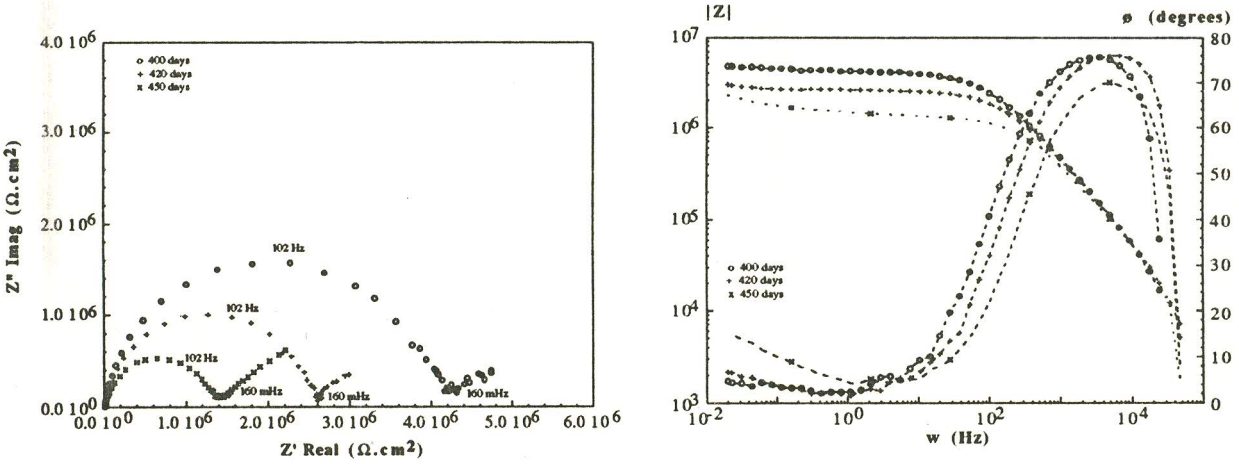


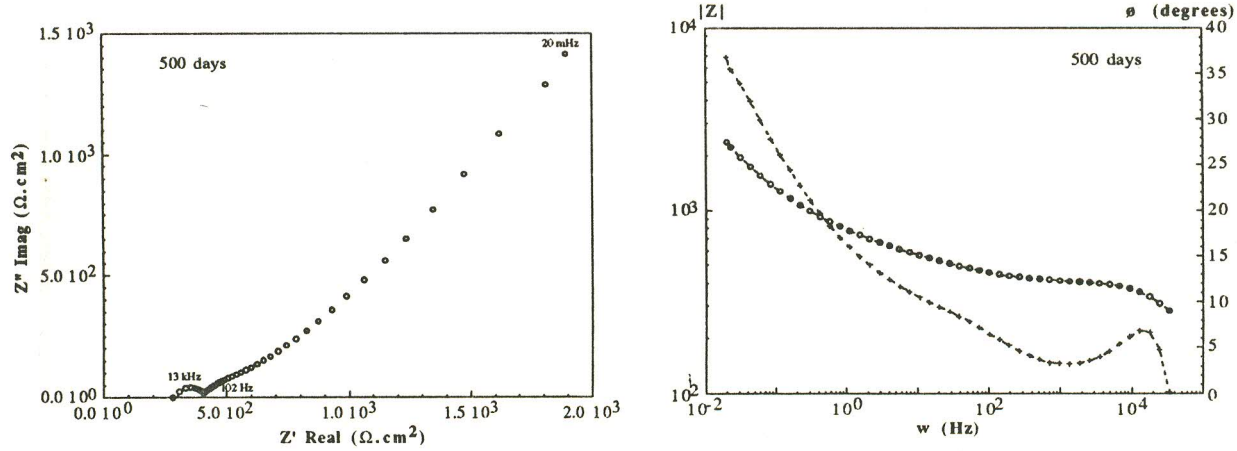
Figure 1 - Nyquist plot used for estimating R_{pf} from the chord AC (ß is the depression angle).



(a)



(b)



(c)

Figure 2 - Impedance response (Nyquist and Bode plots) of one of the specimens LAS 1 after (a) 350 and 400 days, b) 400, 420, and 450 days, and (c) 500 days immersion.

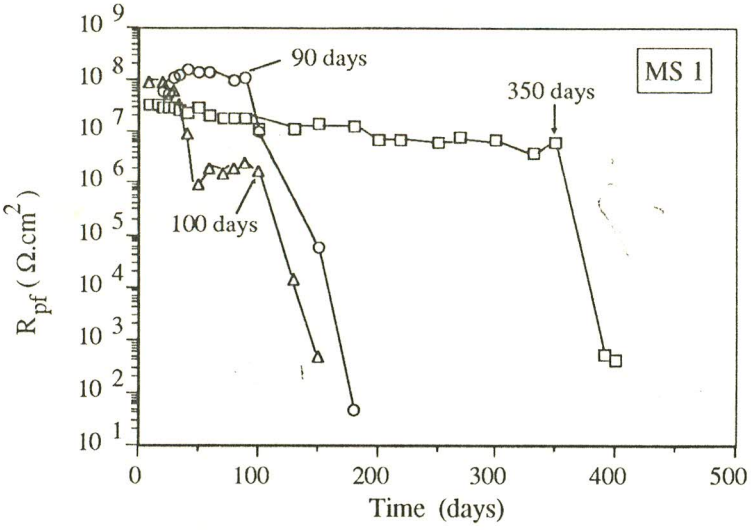


Figure 3 - Evolution of R_{pf} with immersion time for MS 1 specimens.

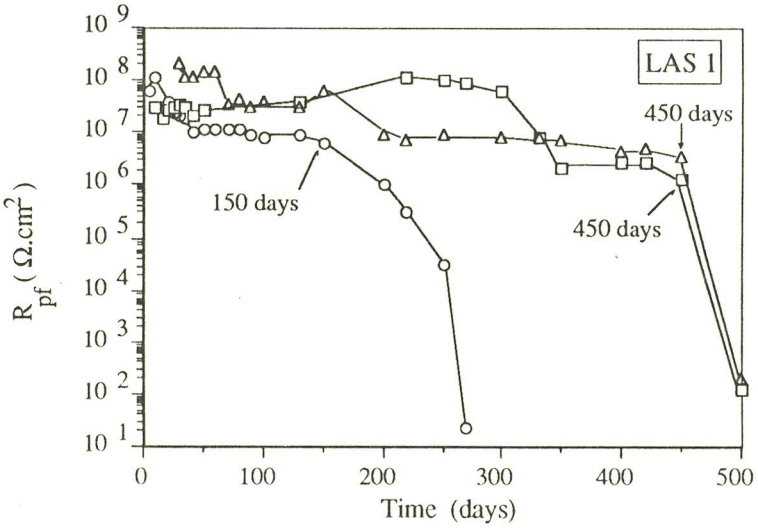


Figure 4 - Development of R_{pf} with immersion time for LAS 1 specimens.

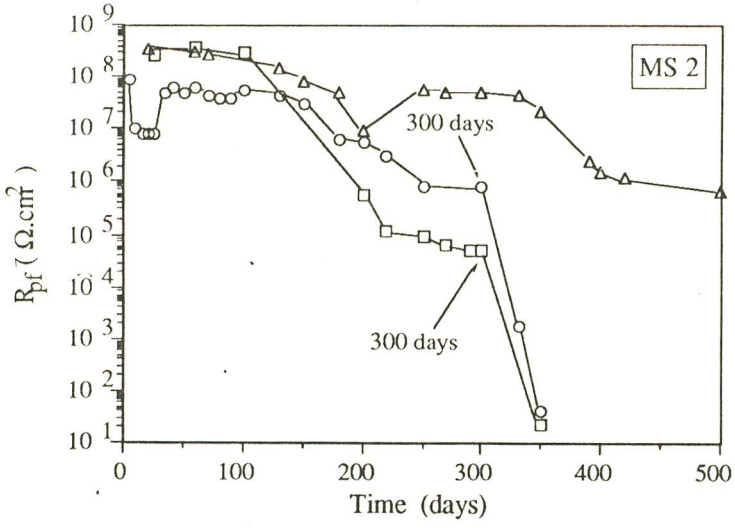


Figure 5 - Progress of R_{pf} with immersion time for MS 2 specimens.

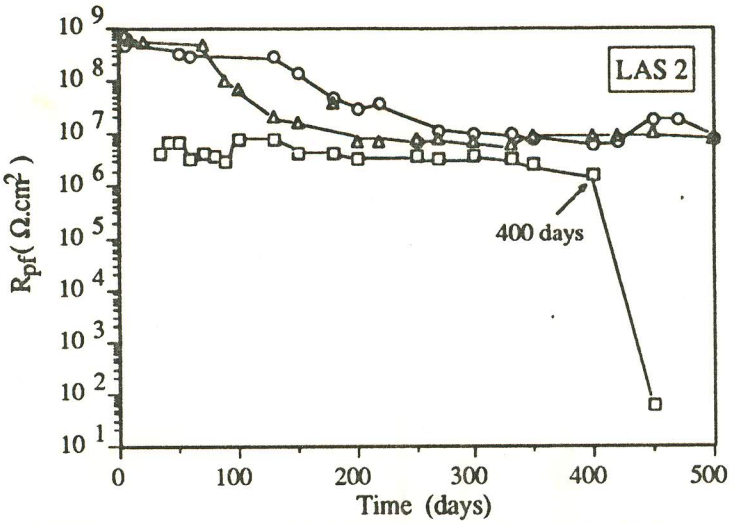


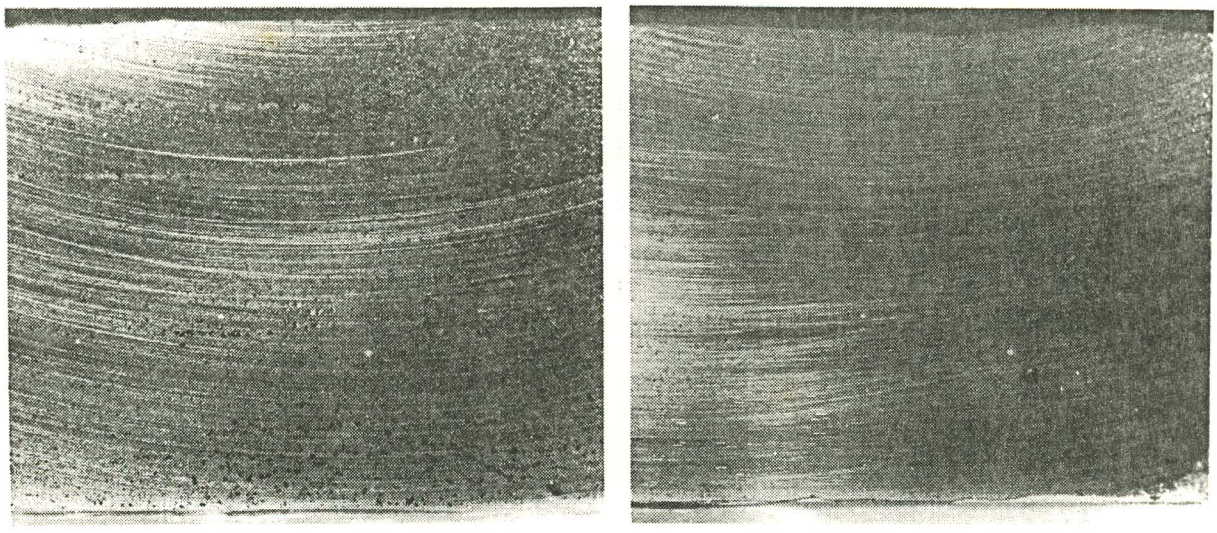
Figure 6 - Changes of R_{pf} with immersion time for LAS 2 specimens.

Table 2 - Time for coating failure and decay in resistance.

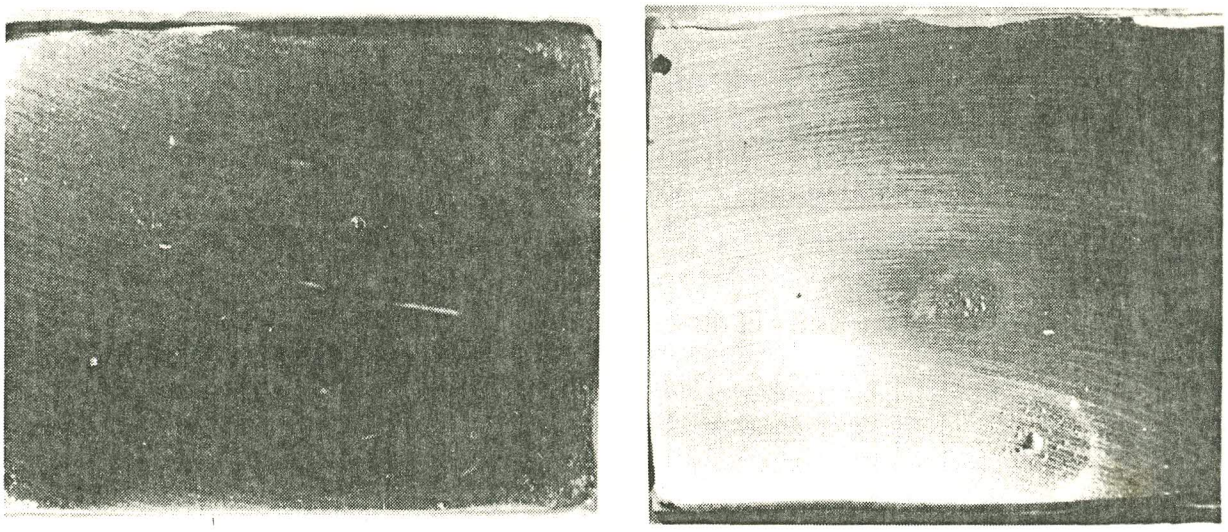
Substrate	time (days) for $R_{pf} \leq 10^6$ Ω.cm^2	time for failure (days)
MS 1 (1)	40	150
MS 1 (2)	100	180
MS 1 (3)	200	390
MS 1 (4)	always >10^6 Ω.cm^2	did not fail
LAS 1 (1)	90	250
LAS 1 (2)	330	500
LAS 1 (3)	200	500
MS 2 (1)	200	350
MS 2 (2)	390	did not fail
MS 2 (3)	180	350
LAS 2 (1)	35	450
LAS 2 (2)	200	did not fail
LAS 2 (3)	300	did not fail

Table 3 - Characteristics of most common inclusions in the steels used.

Steel	Average number of inclusions/cm^2	Most common types	Shape
MS 1	(6040±560)	mainly MnS Al_2O_3/SiO_2/MnO	elongated round
LAS 1	(3020±1600)	mainly SiO_2 Al_2O_3/MnS/Cu_2O TiO_2	round round round
MS 2	(2020±380)	mainly MnS Al_2O_3	lens round
LAS 2	(1440±100)	SiO_2 Al_2O_3 Al_2O_3/MnS	round round lens



(a) (b)



(c) (d)

Figure 7 - Coated steels after 30 days exposure to the chloride solution
(a) MS 1, (b) LAS 1, (c) MS 2, (d) LAS 2