Corrosion Study Of Industrial Painting Cycles For Garden Furniture

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Abstract

Different cycles of industrial painting of steel and galvanised steel for making garden furniture were studied in order to overcome problems in covering tips, edges, sharp corners, commonly found in practice. Painting cycles, including cataphoresis or a Brugal® treatment, were used. The following characterisation was carried out: (a) measurement of the film thickness of the coating; (b) evaluation of the defects in the organic coating; (c) corrosion resistance in a Salt Fog Chamber according to ASTM standard B 117 and (d) electrochemical impedance measurements.

In general terms, test have yielded good results in assessing the best performance with different industrial cycles of painting. Good performance of every cycle has been shown in geometrically simple samples (tubes externally coated), while the corrosion behaviour of geometrically complex shapes (stretched net, round-drilled and stamped sheets) strictly depends on the selected painting cycle. The experimental results showed the effectiveness of the cataphoretic primer in increasing metal substrate coverage, so increasing corrosion resistance. The same was not obtained by using a Brugal® pre-treatment. Galvanised steel performed better than not galvanised one in the Salt Fog Chamber Test, but this result was not confirmed by Electrochemical Impedance Spectroscopy (EIS) data. This electrochemical technique confirmed to be really a useful tool to clarify the behaviour of protected samples under accelerated corrosion conditions.

Keywords: Cataphoresis, powder painting, corrosion resistance, surface pre-treatments, conformal coating.

Introduction

The garden furniture market is continuously growing together with the welfare of industrial countries, and different materials can be used to produce such artefacts. Wood and plastic are frequently used but some disadvantages have to be considered such as UV degradation and discoloration as well as poor mechanical properties in the case of plastic artefacts, while mainly high production costs and high maintenance cost as far as wood artefacts are concerned. Metallic substrates such as aluminium or steel can be preferred mainly for mechanical reasons (lightness together with mechanical resistance and therefore stability). However, garden furniture is usually exposed to medium aggressive environments (formed by cycles of humidity-dry, rain, temperature gradients, UV radiation, and, depending on the atmosphere, chlorides and other contaminants), resulting in a surface damage which must be avoided mainly for aesthetic reasons.

It is well known that the use of coatings to protect metallic substrates against aggressive environments is the most widely used anticorrosive technology [1], and many of the coating deposition technologies can be utilised in garden furniture production too.

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As far as industrial painting of steel garden furniture is concerned, the up-to-date technology involves the use of a phosphate pre-treatment followed by a sprayed powder coating. However, the aesthetical needs of chairs and tables for garden make the geometry of these artefacts particularly unsuitable for a good and defect-free application of the organic coating. In fact, welds between tubes, tubes and plates, corners and the very numerous sharp edges as well as crevice areas, are critical zones where non-uniform coating thickness as well as holidays could be present. The current products do not really offer a good and long lasting protection of metallic garden furniture, particularly if these artefacts are exposed to very humid or marine atmospheres.
Nowadays the demand of this industry for improved performances forces to the use of new high performance technologies or to the use of well established technologies already applied in other production fields, where pre-treatments, metallic coatings as well as different coating deposition technologies could be considered. However, application of new technologies must consider also the economical aspects of the production which do not allow noticeable increase of costs.

Actually, the possibility of selection among metallic, organic and inorganic coatings opens a wide spectra in protection systems. Some metallic coatings are able to provide to the substrate electrochemical protection too; this is the case of zinc on steel [2]. Then galvanised steel instead of bare steel could be used in garden furniture production, and this process can be considered an innovation. The cathodic protection provided by zinc can drastically reduce anaesthetic red rust spots, however, this metallic coating implies a lower adhesion at the metal/paint interface and then could involve the selection of a more suitable substrate pre-treatment.
Among pre-treatments, Brugal® instead of phosphatization on steel could be proposed. In fact, such a pre-treatment, other than an organic layer acting as a primer, can offer the protection deriving from the presence of chromates in it.

Nevertheless, the organic coating remains the low cost protective barrier which provides also aesthetic properties to the substrate. Barrier properties mainly depends on the nature of the binder of the coating and of the thickness of the dry film, if this is free of defects [3]. The presence of defects in an organic coating mainly comes from the paint application technologies, where substrate treatments and coating deposition can be the critical steps. A poor or inadequate application procedure is the most common source of premature failure caused by pinholes, pores presence or by an unexpected thinning of the coating thickness. At the same time a not-proper surface preparation or cleaning could result in defects through the coating and premature coating detachments. The presence of defects on the surface is as larger as more complex is the geometry of the metallic substrate to be covered.
In the production of garden furniture, powder paints have proved to be easily applicable; however, this technology showed to be not able to eliminate the presence of defects in the coating.

To this aim, cataphoretic paint, which has been widely used in the automotive industry, could be the best solution to really protect the metal substrate in the most critical zones and its use for garden furniture is completely innovative. As well known, cataphoresis is a process of deposition of a protective film on a conductive surface from a colloidal dispersion of polymeric particles in water. It has some advantages like the excellent coverage of complex surfaces and the almost absolute absence of organic solvents. On the other hand, disadvantages are related with the high cost of the industrial plant, formulation of resins able to be applied with, and difficulty to obtain high thickness [4].

The aim of this study is to evaluate different cycles of industrial painting of steel and galvanised steel to produce garden furniture, where the main problems to be solved can be resumed as follows: (a) a better coverage of complex shapes of the garden furniture seats, (b) maintenance of the

aesthetic properties, and (c) long lasting resistance to aggressive environments, particularly marine or highly humid.
In order to evaluate corrosion resistance of the new protective procedures, accelerated tests together with electrochemical ones were carried out.

Experimental
All the samples analysed in this work were provided by an industrial manufacturer. The industrial painting cycle is schematically shown in Fig.1. The traditional production process is marked with a bold arrow, where the steel substrate is usually pre-treated producing a crystalline tricathionic phosphate layer and then, a powder polyester topcoat is applied.

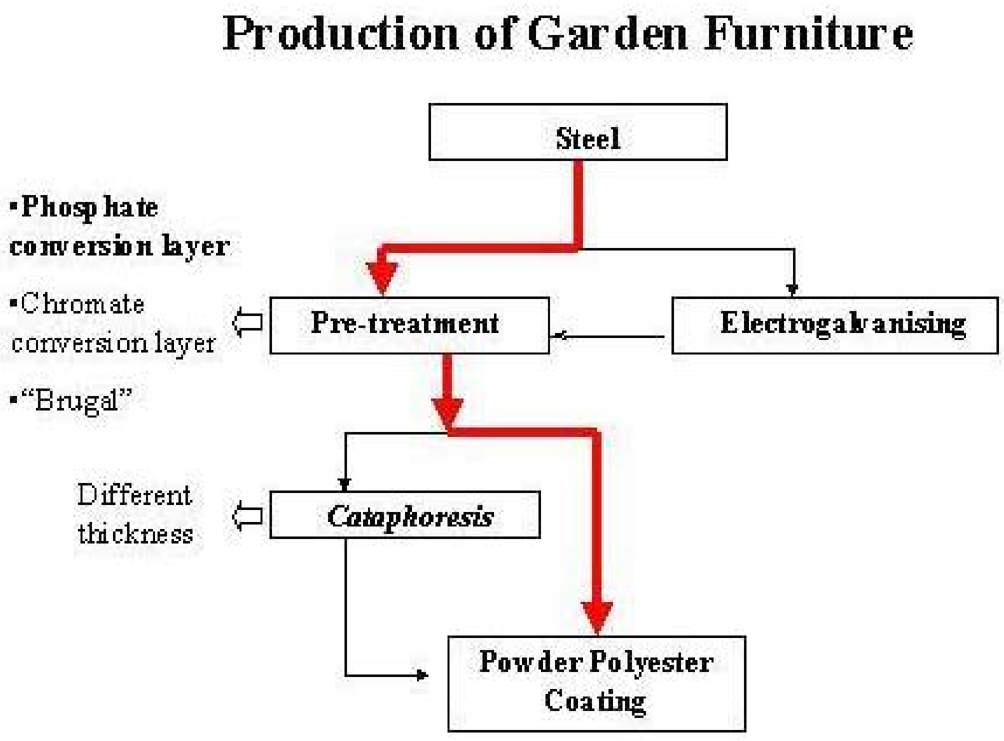


Fig.1. Flow chart of the industrial painting cycle. In bold the traditional process.

Some samples were produced following innovative procedures, in particular:

- Brugal® instead of phosphatising on steel was used,
- electro-galvanised steel with zinc coating thickness of about 7 µm was used as substrate, followed by different pre-treatments including phosphatising or chromatising (both, yellow or colourless),
- a cataphoretic epoxy type primer was applied before powder paint deposition. The thickness of this primer was varied by using different application voltages or multiple deposition steps. An usual thickness in the plain regions was of about 18 µm.

The combination of parameters leads to the experimental matrix shown in Table I. In the following, some symbols have been used for the designation of different painting cycles, namely: 3T is phosphatized steel coated with powder resins; 4T is steel with a Brugal® primer and coated with powder resins; 1T, 6P and D are three different kind of samples where over the phosphatized steel a cataphoretic primer was applied followed by the powder coating. These last samples were produced by different factories and in particular sample D was obtained using higher voltages in order to obtain a high primer thickness.

Tab. 1. Different cycles used to produce experimental samples

Samples		3T	1T/6P	D	4T	-	-	-
Zinc (Electro-galvanising)						X	X	X
Chemical Conversion Pre-treatment	Phosphatising	X	X	X		X	X	
	Chromatising							X
	Brugal ®				X			
Primer (Cataphoresis)	Normal thickness		X				X	X
	High thickness			X				
Powder Polyester Topcoat		X	X	X	X	X	X	X

In order to study the effect of geometry of seats and backs on the efficiency of the proposed innovative protection procedures, three different design solutions were selected: stretched, round-drilled, and net-stamped sheet (Fig.2). These geometry could differ mainly as far as the presence of edges and sharp corners is concerned, which could result in coating defects and, as a consequence, in a diminished durability of garden seats. As a non-critical geometry, cylindrical tubes were analysed as well.

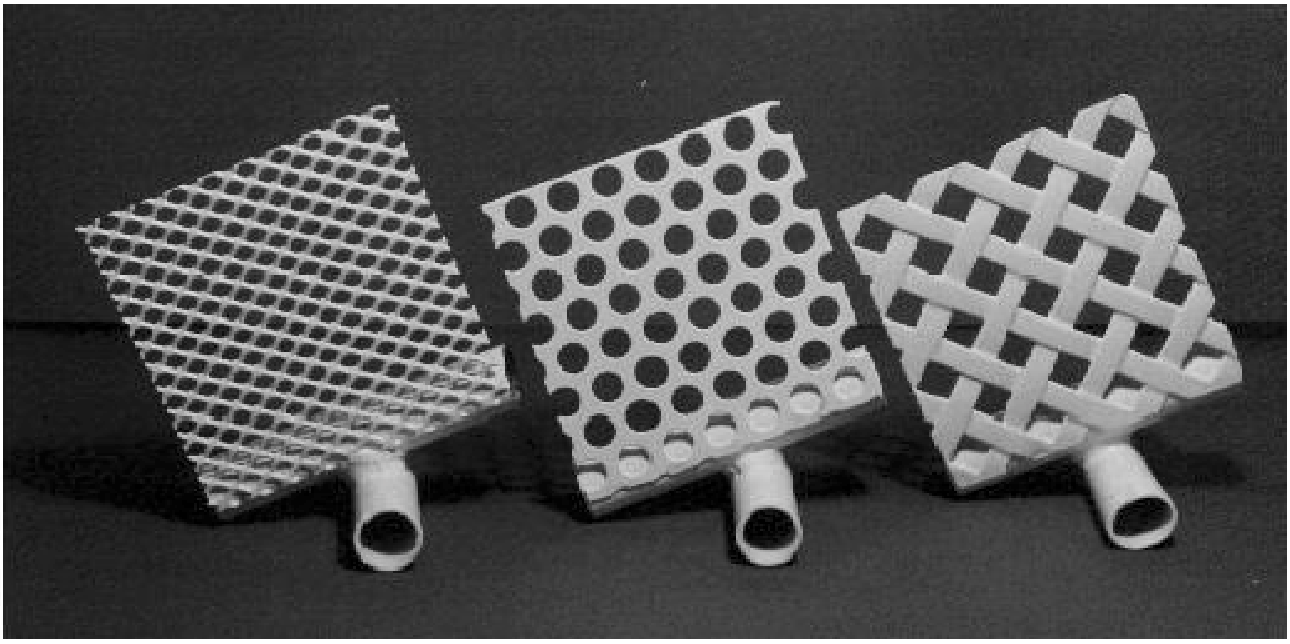


Fig.2. Geometry of samples. From the left, stretched, round-drilled and net-stamped sheets for seats and backs.

In order to evaluate the efficiency of the proposed innovative industrial painting cycles, microstructural and corrosion characterisation was carried out, namely:

- measurement of the thickness of the protective coating by a magnetic device (Karl Deutsch Lektoscope) (measuring the whole coating system), and by metallographic observation of cross section with an optic microscope with image analysis (Leica Qwin) (measuring just the topcoat thickness);

- evaluation of the defects at the organic coating/substrate interface by metallographic observation with an optic microscope;
- corrosion resistance test in Salt Fog Chamber according to ASTM standard B 117, up to 30 days;
- electrochemical impedance spectroscopy (EIS) carried out in a 3.5% NaCl solution, both on the tube part of the sample and on the flat part. The area of the tube samples was of about 40 cm^2, whereas the flat specimens, even if the apparent immersed area was the same, had a different real immersed area due to the different geometry and it was of about 80 cm^2 (net stamped and round drilled samples) and of about 100 cm^2 (stretched samples). Electrochemical impedance measurements were carried out using a PAR 273 potentiostat connected to a 1255 Solartron FRA in a three electrode electrochemical cell where the counter electrode was a platinum net and the reference electrode was Ag/AgCl (207 vs SHE). The selected frequencies range was $10^{-3} – 10^5$ Hz.

Results and discussion

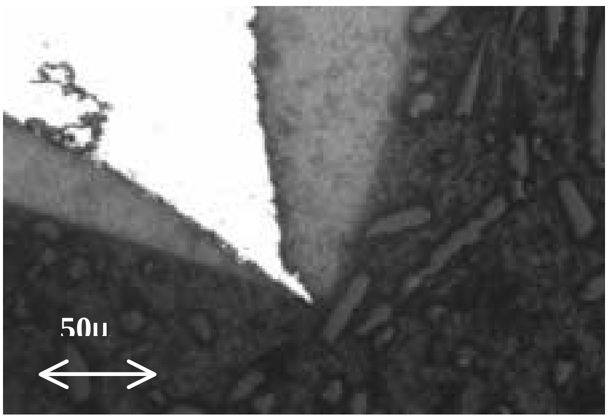
Microstructural characterization

These data were discussed in a previous paper of our [5] and they will be presented here shortly. Thickness of organic topcoat was evaluated on tubes, by cutting a metallographic section perpendicular to the tube axis and polishing it. Thickness was measured on the whole circumference by using an optic microscope (method A). On the other hand, the use of a magnetic device (method B) permitted the determination of the total thickness, including cataphoretic when present, measured along the tube axis at four points of the circumference. Some representative results are shown in Table 2.

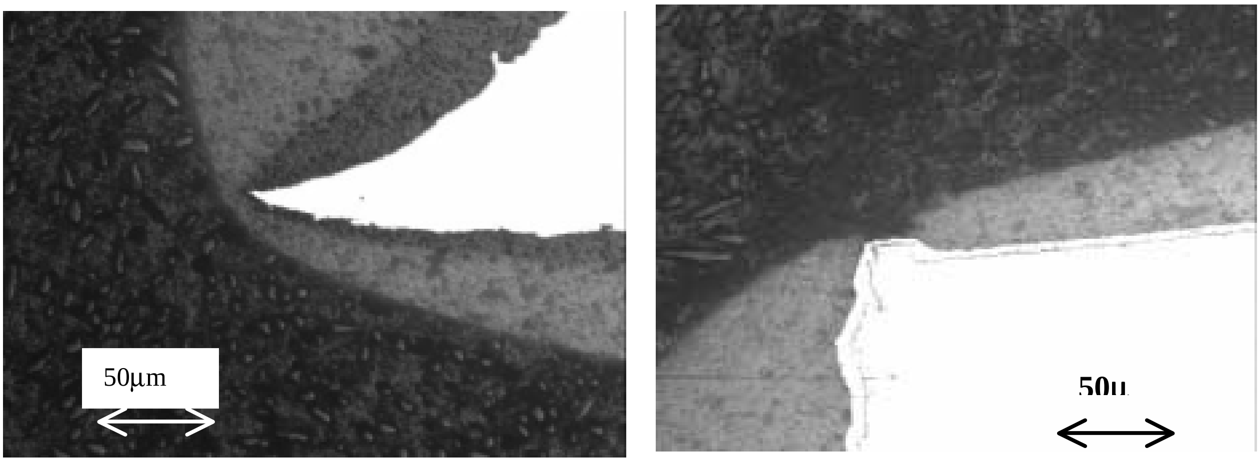
Tab. 2. Thickness measurement on painted tubes. A: made with microscope at a metallographic section (just the topcoat); and B: made with a magnetic detector (whole paint system).

Sample		**Average thickness (µm)**	**Maximum thickness (µm)**	**Minimum thickness (µm)**	**Standard deviation (µm)**
Steel	A	158	181	139	13
	B	188	237	124	38
Steel + Cataphoresis	A	206	306	159	37
	B	316	365	285	23
Steel + Brugal®	A	165	305	107	40
	B	163	224	108	38
Galvanised steel	A	115	147	88	20
	B	191	222	161	18
Galvanised steel + Cataphoresis	A	203	235	159	26
	B	277	342	233	37

It is possible to see the dispersion (large standard deviation) of values, both those obtained with method A or those coming from method B. This is not really unusual in the industrial application of a powder coating. The average value of film thickness is different between the two measurement methods because of the different methodologies and techniques used as discussed elsewhere [6], nevertheless, the coating thickness ranking appears to be the same using the two different methods.
From these results, it doesn’t seem to exist a correlation between the thickness of the topcoat and the metallic substrate, as can be seen by comparing the thickness of the topcoat between steel and galvanised steel in Table 2. The only effect that can be observed is that the thickness of the powder polyester topcoat is higher when applied after the cataphoretic primer. The same is not observed when Brugal® was used as primer. Probably the cataphoretic layer is able to favour the deposition of the sprayed polyester powder and then, the efficiency of this treatment. However, research is in progress to confirm such a statement.
The thickness measured on the tubes area seems to be high enough in order to give good barrier properties against corrosion. However, a similar thickness must be present also at the corners or at sharp edges, where the cataphoretic primer could improve the coverage of the metal substrate. A microscopical observation was then carried out to control the defects at the organic coatings/substrate interface.
Defects due to low thickness or pinholes are absent in the cylindrical part or in the plane areas of the samples. Opposite to cylindrical areas, the coating thickness changes greatly at the machined metal sheets, consequently coverage decreases at welds and at sharp edges.
Fig.3 shows how critical can be the situation at the machined part of the seats due to the complex geometry of these artefacts. The edges to cover can be very sharp and in these areas the coating thickness decreases drastically and tips often remain uncoated. This typical condition is represented in Fig.3 a and b for steel and galvanised steel substrates respectively. It is interesting to observe that the galvanised steel shows an uncovered area even if the edge is not as sharp as that present in the case of the steel substrate. Such a situation was observed frequently on our samples, suggesting that for some wettability reasons covering of sharp zones is more critical for galvanized substrates with respect to steel substrates.



(a)



(c) (b)

Fig.3. Geometrically critical zones: (a) sharp edge without cataphoretic film, (b) uncovered corner on galvanised steel without cataphoretic film, (c) sharp edge covered with cataphoretic film and topcoat.

Fig.3c shows how the cataphoretic primer is able to cover also the tip of a very sharp edge with a thin organic layer. This layer, rounding the tip of the edge favours also the deposition of powder paint forming a film able to completely cover the sharp edges. However even when a cataphoretic primer is present, the thickness of the organic layer at the edges remains thin.
Even the cataphoretic film can become not continuous due to a Faraday's cage effect as an example at the contact angle between substrate and metal drop due to welding, however, in this case the topcoat is able to protect the zone resulting in a smooth surface [7].

Corrosion resistance

Salt Fog Chamber Test

The samples were first exposed for 30 days in a Salt Fog Chamber in order to develop red rust corrosion of the substrate, i.e. uncovered zones (defects, pores, holidays) in geometrically critical areas.
As expected, corrosion on tube surfaces was never found at the end of the test. Such behaviour agrees with the microscopical observation previously discussed; so we can conclude that defects in the coatings are almost absent on the tube surfaces. So, the main interest was focused on machined part of the samples, where the different employed geometry (stretched, round-drilled and net-stamped) could induce coating discontinuities and then, corrosion development.
Actually, the samples introduced in the Salt Fog Chamber have developed rust spots in the geometrically critical zones: weld, machined sheets, etc. By visual observation after the test it seemed that the stretched samples had a higher number of red rust spots independently on the kind of coating procedures that was adopted. In the tested area, this design exhibits many potential defect points because of the presence of a high number of sharp corners, then geometry of the chair seat seemed to be a critical parameter. However we must remember that, due to the particular geometry, the area of the stretched samples exposed to the aggressive environment is higher with respect to the others geometry tested, then the defects density could be almost the same in the three considered

cases. Probably, in order to have a more precise information we need to use a quantitative measuring technique, as for example impedance (EIS).

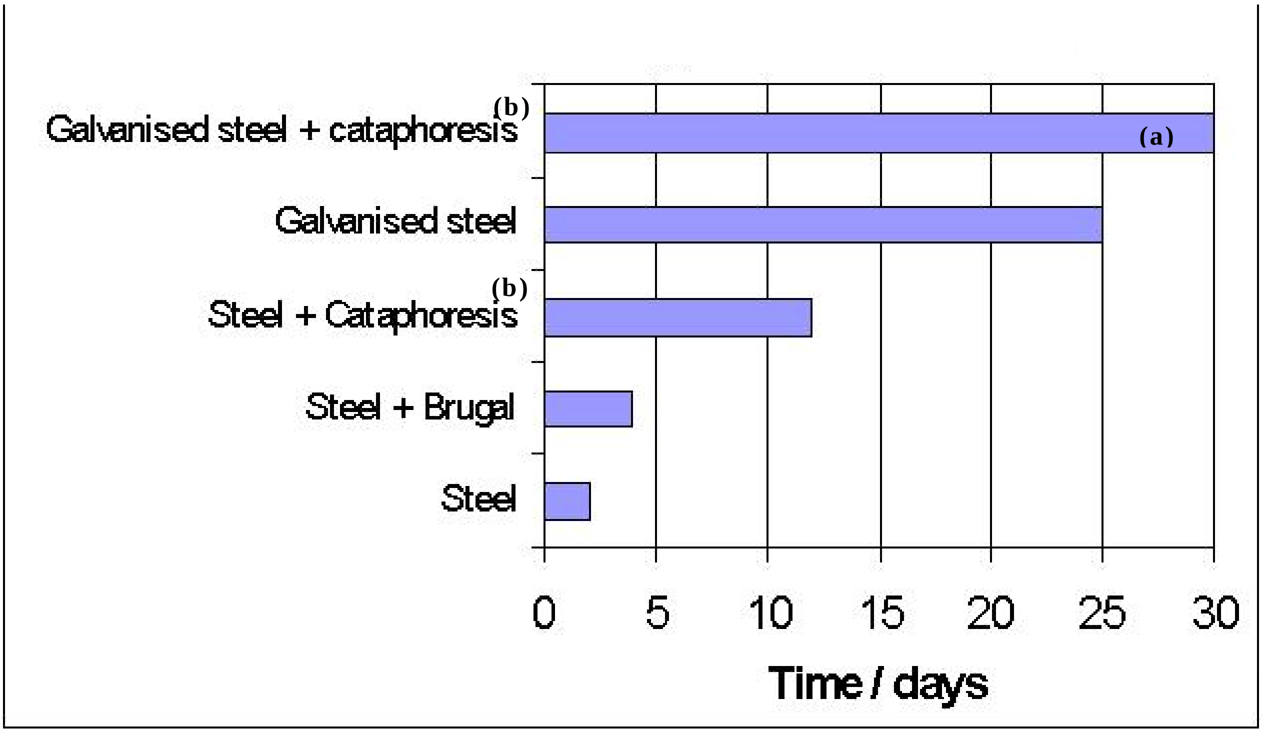


Fig.4. Results of Salt Fog Chamber test, reported as days for reaching a rust degree 5 according with ASTM D 610 (corresponding with 3% of total area covered with rust). All samples are covered with a polyester topcoat. (a) No rust was detected after 30 days; (b) samples with a normal thickness of cataphoretic paint.

Representative results of corrosion resistance are shown in Fig.4. This figure shows the result of Salt Fog Chamber for stretched sheet samples, however the other geometry showed the same ranking. Evaluation of rust degree was made according to ASTM standard D 610. In this figure, it is represented the time to reach the rust degree number 5 in the standard, which corresponds to 3% of the total painted surface covered with rust spots.

As expected, steel substrate protected only by the polyester powder paint has shown the poorest performance. The corrosion tests confirm that in this case edges and corners are poorly protected as highlighted by microscopical observation. Spots of red rust are diffusely present all over the stretched sheets and time of appearance as well as total number of attack points seems to be related to the geometrical complexity of the sheets.

Brugal® pre-treatment didn't improve the corrosion resistance of the paint system and the samples reach the fixed rust degree just after 4 days. In fact, the organic matrix of Brugal® undergoes the same problems at the edges presented by the other organic products and the total thickness in these zones decreases drastically. Moreover, the chromate amount in this type of treatment seems to be too low to be really protective under the selected test conditions.

On the contrary, cataphoretic primer on phosphatised steel results in better performances, due to a sufficiently good covering of tips, edges and corners. The time to reach the rust degree number 5 is multiplied at least by a factor three, going from four to twelve days. Nevertheless, it was really difficult to detected differences in protection related to the use of different deposition procedures of the cataphoretic films.

By observing the behaviour of galvanised samples it is possible to notice a large increase of the corrosion resistance, even when cataphoretic layer was not applied. In this case, the time to reach 3% of red rust increases up to 25 days. When the two protective systems, zinc and cataphoresis,

work together the improvement is even better and no red rust was detected during the testing time. The use of a chromate conversion layer as pre-treatment instead of a phosphate conversion one, has not shown any particular improvement of the corrosion resistance. Moreover, differences between the two chromatation layers (yellow and colourless) were not revealed by this test [7].
Although salt fog chamber test gives a rank of studied samples, the disadvantage of this assessing is that reports just the presence of red rust coming out through the organic film, but underfilm corrosion as well as white corrosion (very difficult to evaluate since the topcoat is white) are not evaluated. The estimation is only qualitative and red rust spots evaluation is really uncertain because of the geometrical complexity of the testing area, which increases the subjectivity of the test.

Electrochemical Impedance Measurements

Electrochemical measurements were performed separately on the tube areas of the samples which represent an almost perfect coating, and on the plain areas which as well visible in Fig.2 represent areas with a probable high density of defects on the coating. As explained in the experimental part, the selected testing area is quite large (in the range of 100 cm^2) then the results obtained by the electrochemical test can be considered as highly representative of the behaviour of the studied samples.

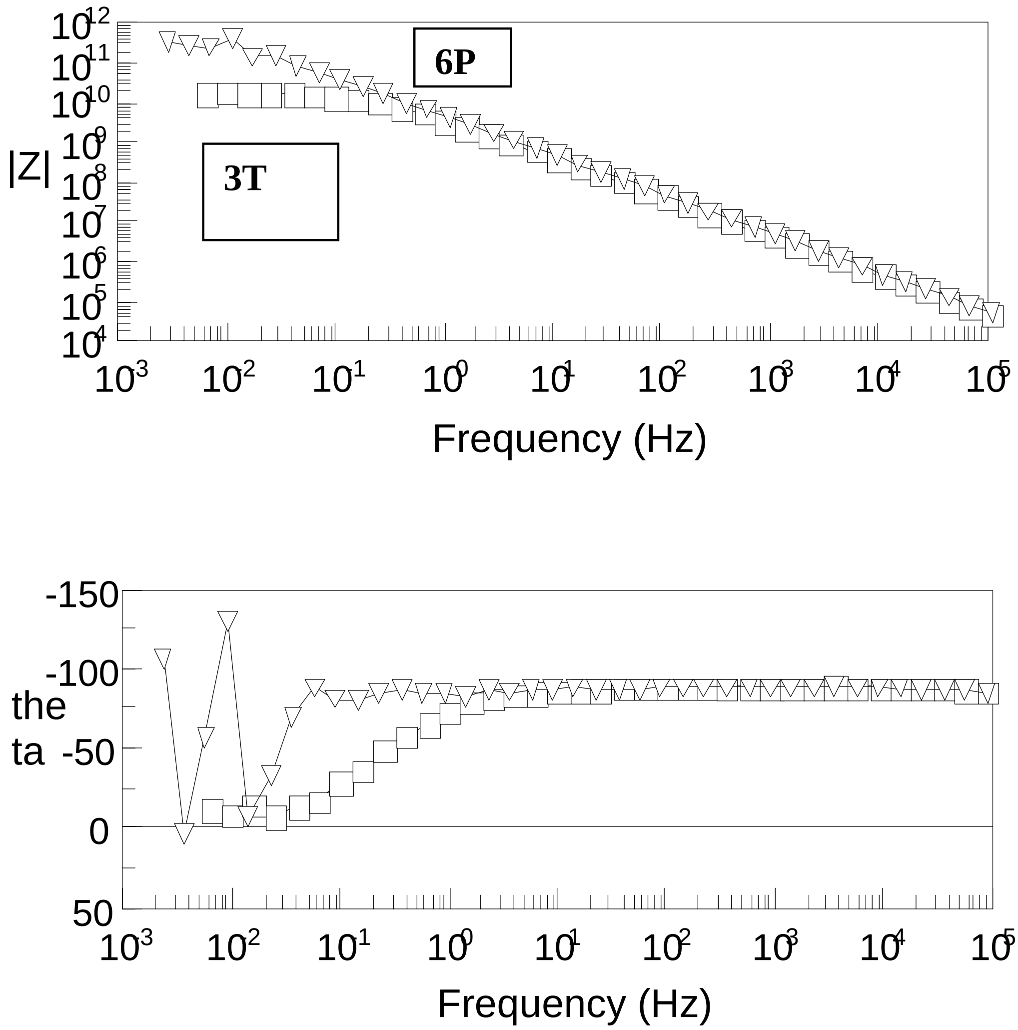


Fig.5. Impedance data of samples 3T (without cataphoretic primer) and 6P (with cataphoretic primer) after 26 days of immersion in 3.5% NaCl solution. Impedance modulus is expressed in Ohm*cm^2.

Fig.5 shows the impedance data obtained in a sodium chloride solution using the tube type samples. The Bode representation of two selected samples (3T without cataphoretic primer and 6P with a cataphoretic primer) obtained after 26 days of immersion clearly shows that the barrier properties of the two samples are still good after the long testing time. Impedance modulus of sample 6P at the lowest measured frequency is almost one order of magnitude higher with respect to that of sample 3T, however, both values are very good confirming the good protection of the powder resin coating when the coated area does not present geometrically critical zones. All the other tested samples behave in a similar way showing that no one of the selected innovative treatments (galvanizing, Brugal®, or cataphoretic primer) give some remarkable improvements on the traditional treatment which does not present defects through the coating.

The corrosion behaviour appears to be quite different when impedance measurements are performed on the plain parts of the samples. As an example, Figs. 6 and 7 show impedance data, in Bode representations, of samples 1T and 4T respectively, after different time of immersion in the testing solution. Looking at Fig.6 it appears evident a large decrease of the impedance modulus at the lowest frequencies with respect to the data observed in Fig. 5 since the beginning. Obviously, the barrier properties of the organic coating are drastically reduced, because of the thickness decrease which can be of about one order of magnitude at the sharp edges and corners of the sample. Moreover, as a function of time it is possible to observe a slight decrease of the impedance. However, corrosion protection can be considered just enough for sample 1T, where the presence of the cataphoretic primer allows the impedance modulus, measured at the lowest frequency, to remain, also at the end of test (26 days,) in the range of 10^7 ohm·cm^2.

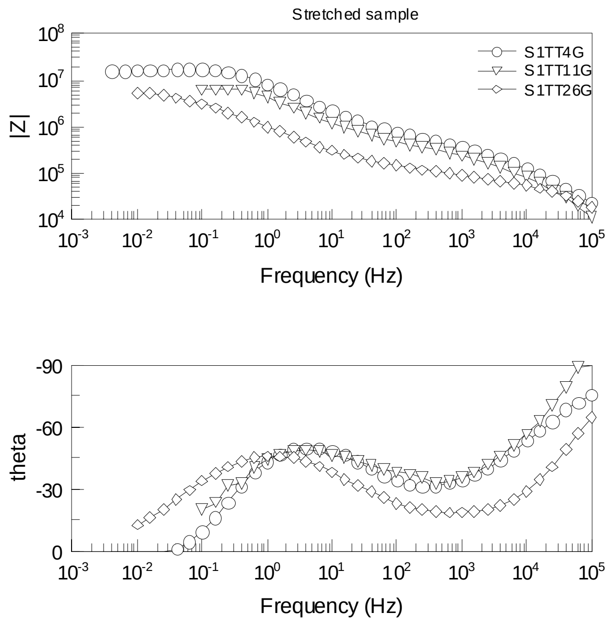


Fig.6. Impedance data, in Bode representations, of sample 1T after different days of immersion in the testing solution (4G = 4 days, 11G = 11days, 26G = 26 days).

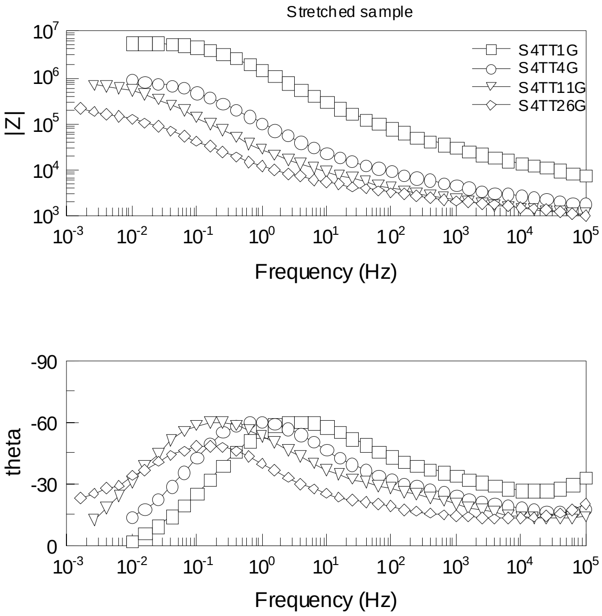
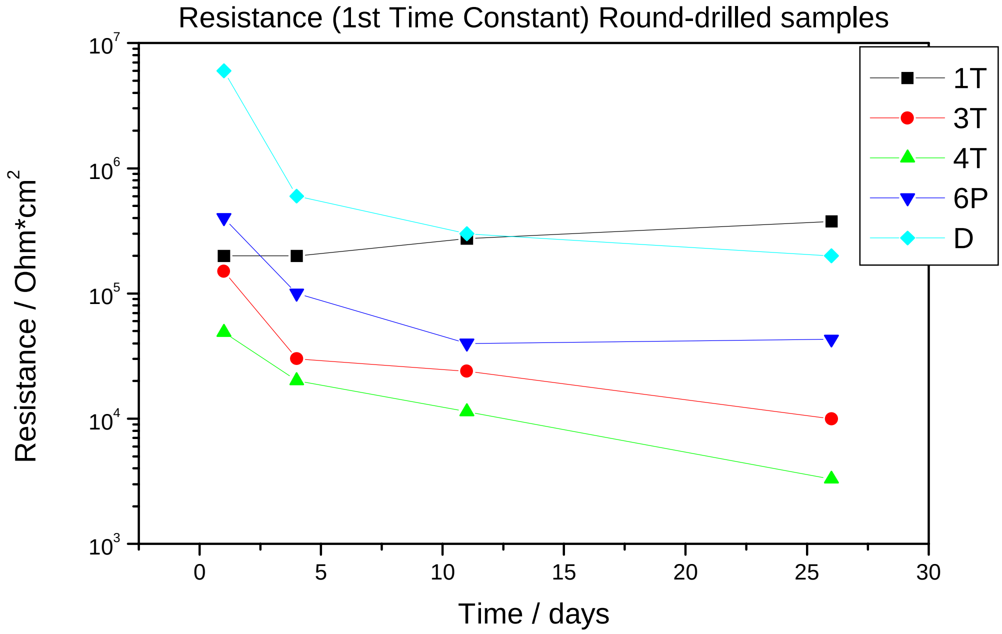


Fig.7. Impedance data, in Bode representations, of sample 4T after different days of immersion in the testing solution (1G = 1 day, 4G = 4 days, 11G = 11days, 26G = 26 days).

The behaviour of sample 4T (with the Brugal® primer, Fig.7) appears to be different. Only at the beginning of testing is comparable with that of sample 1T, but as a function of time it is possible to observe a remarkable decrease which reaches about 10^5 ohm·cm^2. Such a decrease is related to the presence of a large number of defects in the organic coating which allow the electrolyte to reach the substrate, corroding it. As previously observed in the Salt Fog Chamber test, the Brugal® primer is not able to protect the sharp edges of the samples, whereas a cataphoretic primer can do it and impedance measurements allow to better quantify differences between samples.
In order to characterise the protective system, impedance data were analysed by Boukamp fitting procedure [8], using a well known equivalent electrical model, where two RC nets are proposed, the second one in series with the first resistance and representing respectively the coating electric properties (coating capacitance and pores resistance) and the faradic reactions (double layer capacitance and charge transfer resistance). As usual, capacitances have been represented by Constant Phase Elements (CPE) but in our discussion only resistances elements will be considered. This two time constant model is well known and very frequently utilised to represent organic coatings with defects and pores [9,10]. Under our experimental conditions, only after very long testing time the impedance can be affected by the presence of diffusional components related to the growth of corrosion products inside the coating defects, but our analysis do not appear to be affected at all.
Resistances values are represented in Fig.8 a and b for some samples in the round drilled geometry, having steel as a substrate and where the resistance related to the first time constant (pores resistance) and that one related to the faradic reactions (charge transfer resistance) are represented respectively. The two parameters have a similar trend with time, showing a more or less pronounced general decrease. Apart from the anomalous trend of sample 1T, all the samples maintained the same rank during immersion. In particular, all samples produced with the cataphoretic primer show higher values both of the first and of the second time constant resistances with respect to the traditional process (sample 3T) or to the Brugal® primer (sample 4T). Among the group of samples with the cataphoretic primer, those obtained with the higher applying voltage (sample D) showed an initial higher resistances value which after few days of immersion becomes

very similar to the values of sample 1T. On the contrary sample 6P has the worst behaviour compared to the other samples, suggesting that application accuracy (good process control in the industry) can be a determining factor as far as barrier properties and corrosion resistance are concerned.



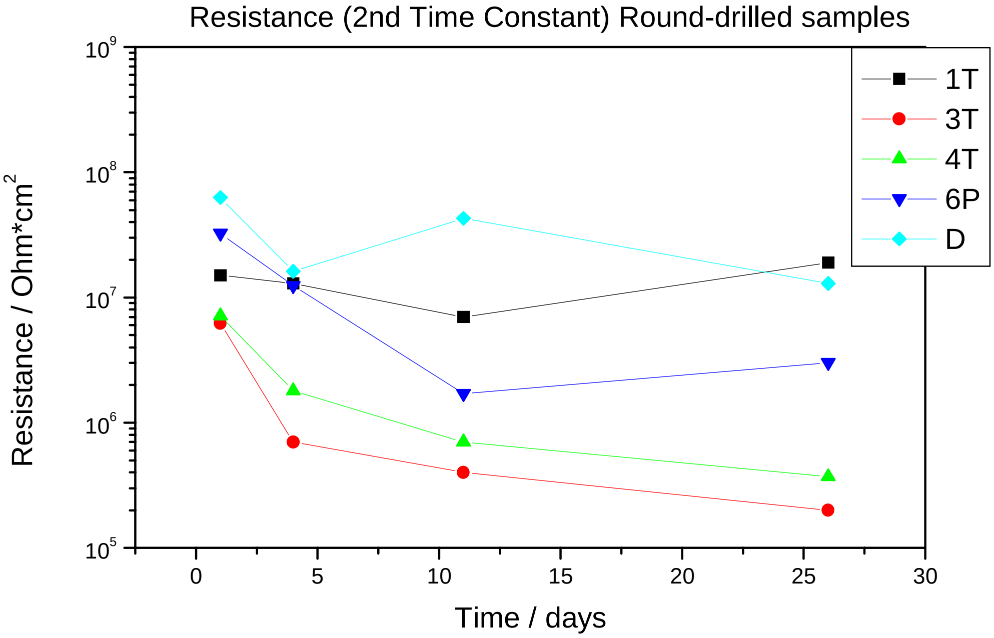


Fig.8. Resistances values of samples in the round drilled geometry and with steel as substrate: (A) first time constant (pores resistance), (B) second time constant (charge transfer resistance).

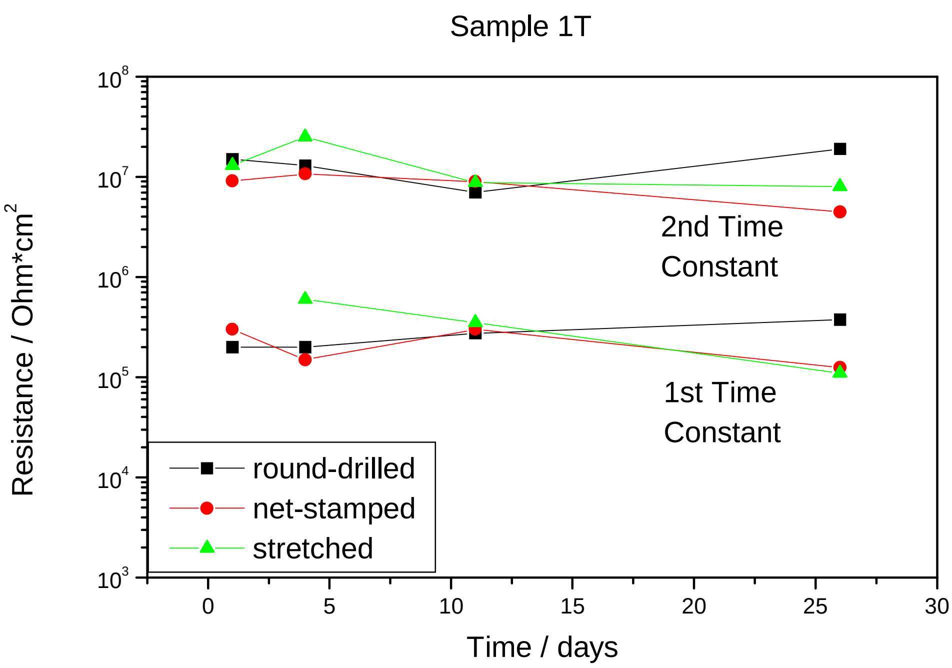
As far as the sample protected with the Brugal® primer is concerned, no improvement in barrier properties was observed. In fact, the resistance of the first time constant (pore resistance in Fig.8 a) is even lower than that of sample 3T produced in the traditional way. However, looking to the faradic resistance (second time constant in Fig. 8 b) it is possible to observe an unexpected reversal of the rank with a higher resistance of sample 4T with respect to sample 3T. This result can probably be explained by considering that the corrosion rate of the steel substrate in sample 4T could be decreased due to the presence of the chromates inhibitors.

The two parameters considered in our work seems to give very similar information about protection properties of the different coating systems, suggesting that corrosion occurs in the pores at the bottom of the defects and that a wet area increase (decrease of the faradic resistance [11,12]) is related to the formation of new low resistance areas in the coating (increase of the pores area). Such a consideration is also confirmed by the increase, sometimes observed, of the two resistance parameters at the end of the test after 26 days because of some pores closure effects due to the growth of corrosion products.

Better than Salt Fog Chamber test, impedance measurements allow a clear discrimination of the behaviour of the various specimens, where differences between samples with or without cataphoretic primer are quite evident, but where it is also possible to clearly differentiate among samples presenting the cataphoretic primer obtained under different production condition. Both pore resistance (first time constant) or the resistance related to faradic reaction (second time constant) are able to give quantitative information concerning the protective properties of the studied coating systems.

It is now interesting to observe if impedance analysis can confirm the indications coming from the Salt Fog Chamber test concerning the effect of geometry on the corrosion behaviour of the protected samples. The observation of samples after that test, in fact, suggested that the metal working of the plain part of the sample by stretching (stretched samples) induced a higher number of defects in the organic coating due to a higher presence of corners and sharp edges.

Fig.9 a and b shows, as an example, resistance values of sample 1T (representing coatings with the cataphoretic primer) and sample 3T (representing coatings without cataphoretic primer) respectively. In this figure both resistances related to the first and the second time constant are represented. As expected, the trend of the two parameters of sample 1T is almost constant with time, whereas a clear decrease is observed in sample 3T. Some differences concerning the geometry effect can be observed in sample 3T just after one day of the immersion, but these differences do not agree with the observation of the accelerated test in the salt fog. On the contrary, almost no any difference can be observed between the various geometry after eleven days of immersion nor for sample 3T nor for sample 1T, and also at the end of test the behaviour of geometrically different samples can be considered very similar. Hence the pore resistance (first time constant) which is related to the presence of defects passing through the coating and which, as observed microscopically, is mainly associated to the defects due to the geometrical criticality, do not allow to highlight a different influence of the various geometry taken in account in this experimental work. This apparent contradiction with the observations made at the end of the Salt Fog Chamber test can be explained by considering that the higher number of rust spots observed in the stretched samples after the accelerated test were present on a surface area which was almost 20% wider with respect to those of net stamped and round drilled samples, giving an idea of a higher damage. This data confirms how difficult is the evaluation of a rusting percentage made only by visual observations. During electrochemical measurements impedance is considered as a function of the testing area (100 cm^2 for stretched samples and only 80 cm^2 for the two other types), then we can conclude that the defect density is quite similar for all the considered geometry and that the differences observed during the test in salt fog are only apparent.



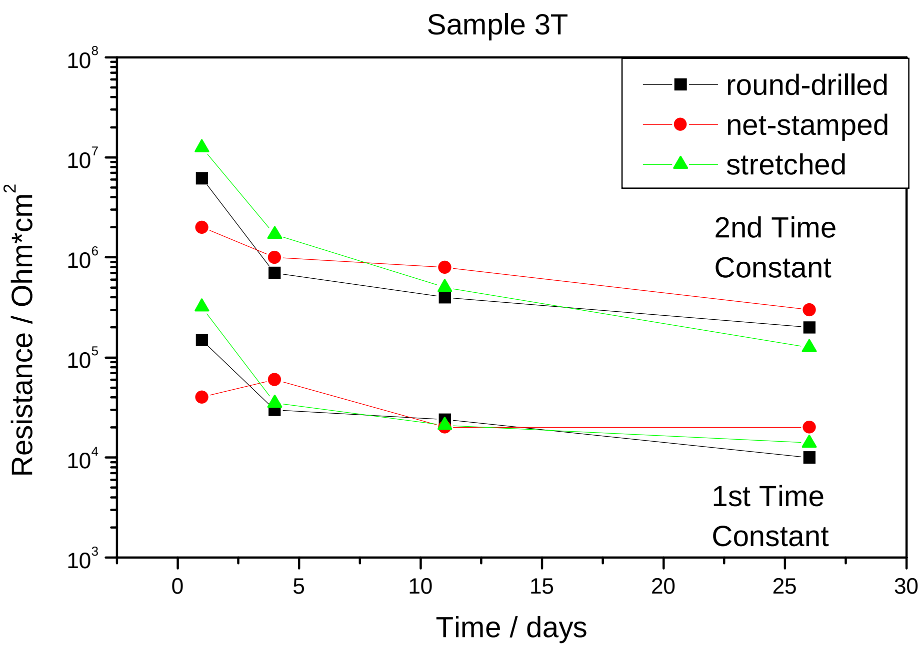


Fig.9. Resistance values of sample 1T representing coatings with the cataphoretic primer (A) and of sample 3T representing coatings without cataphoretic primer (B). In this figure both resistances related to the first and the second time constant are represented.

By observing the trend of the two resistance related to the two time constants observed in the impedance diagrams in Fig.5 it was supposed that corrosion phenomena occur in the pores at the substrate interface. However, it was not clear if samples degradation was only due to the metal corrosion or if a coating delamination also occurred around the main defects, depending on the kind of pre-treatment or primer used.

It is well known that resistances of the two time constants of the equivalent electrical circuit can be related to various degradation phenomena at the metal coating interface [12], then it is possible to analyse the trend of these two parameters during immersion in order to obtain more information concerning the corrosion protection offered by the studied systems.

The ratio between the resistances (faradic resistance/coating resistance) related to the two time constants can be written as:

$$R_{faradic}/R_{coating} = R_{cto}/\rho d \qquad (1)$$

where R_{cto} represents the charge transfer resistance of the bare steel (which can be considered a constant when the corrosion mechanism remains constant), ρ is the resistivity of the electrolyte in the coating, d is the thickness of the coating (which can also be considered a constant if swelling of the coating does not occur). Then this ratio remains constant if no delamination occurs and if the resistivity in the coating remains constant. The resistivity in the coating could vary during immersion depending on the structure of the coating, the chemical composition of the electrolyte and the evolution of defects and porosity in the coating. However, under our experimental conditions it is possible to suppose that it remains constant or that it decreases slowly during immersion leading to an increase of the ratio $R_{faradic}/R_{coating}$.

The experimental trend of this ratio is shown, as an example in the case of net stamped samples, in Fig.10. The behaviour of the studied samples is not homogeneous and in general there is no a clear and continuous trend with time. In some cases, as samples 1T and 3T, it is possible to affirm that the ratio $R_{faradic}/R_{coating}$ is almost constant, then excluding possible delamination at the metal interface. Delamination in fact induces an increase of the wet area where faradic reactions can occur, resulting in a decrease of $R_{faradic}$ and consequently in a decrease of the ratio $R_{faradic}/R_{coating}$ [13,14]. Such a behaviour is only slightly shown by some specimens as 4T and 6P; nevertheless, it is difficult to state that for these samples there was degradation related to a delamination process, because there were no evidences of coating delamination after the Salt Fog Chamber test.

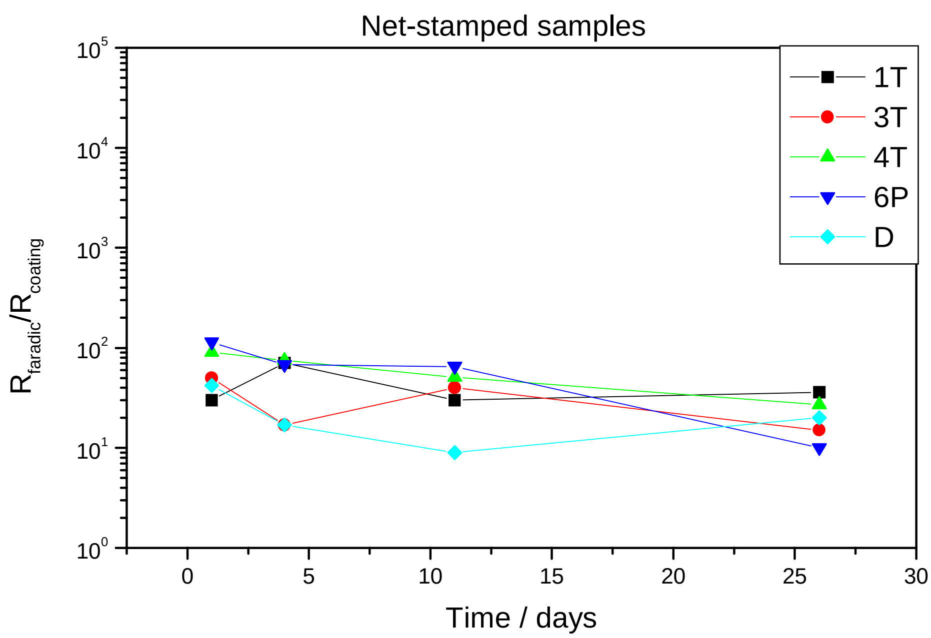
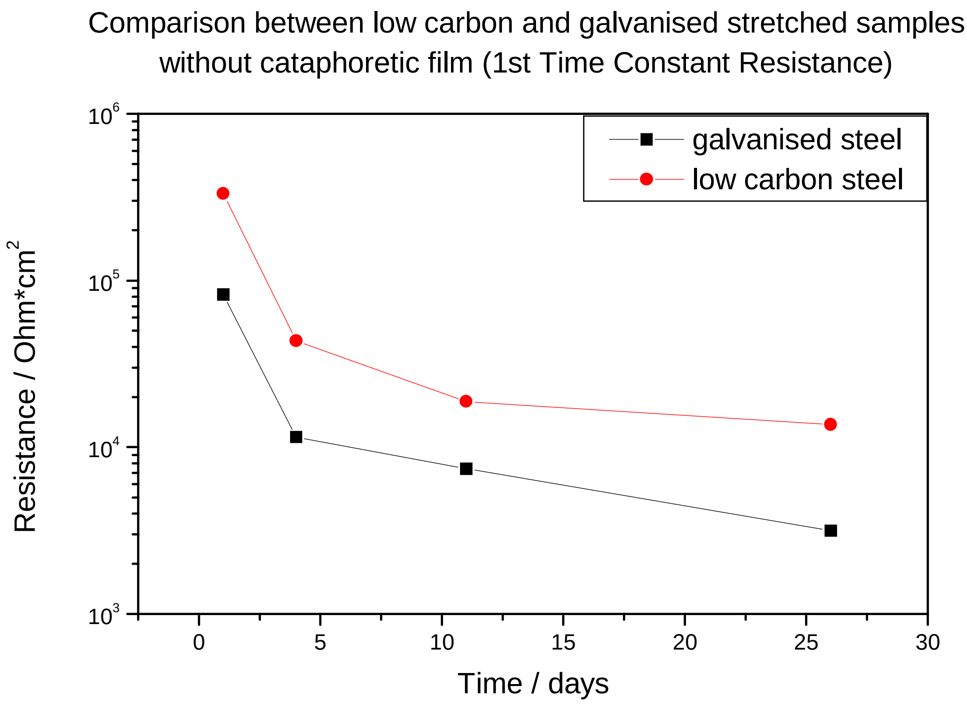


Fig.10. Trend with time of the ratio $R_{faradic}/R_{coating}$ for net stamped samples.

Impedance data on galvanised steel are now discussed. Fig.11 a and b show the coating resistance, related to the first time constant, of steel and galvanised steel samples without and with the cataphoretic primer respectively. All the samples presented a decrease of the values with time and in particular, values obtained on the steel substrate appeared to be three times higher than those obtained on the galvanised steel when the cataphoretic primer is absent (Fig.11a), and such a difference is even wider when the cataphoretic primer is present (Fig.11b). It seems that the use of cataphoresis noticeably improves the barrier properties when applied on the steel substrate, but such improvement is really very poor when the cataphoretic layer is applied on the galvanised substrate. Such a result does not agree with the results of the Salt Fog Chamber test, where galvanised steels behaved always better than steel substrates. Probably the corrosion behaviour of galvanised steel appeared to be better with respect to the steel substrate also because the white zinc corrosion products were hardly detectable on the white organic coating and on sodium chlorides deposits. On the contrary, impedance data reveal that the organic coating on the galvanised steel is even more defective than that obtained on the not galvanised steel.



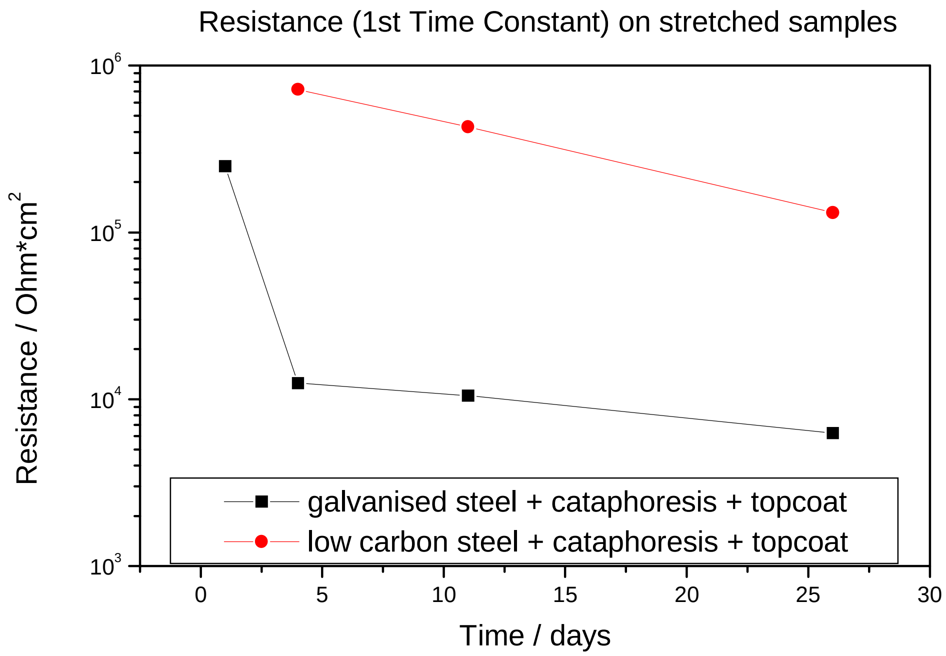


Fig.11. Trend with time of pores resistance, related to the first time constant, of steel and galvanised steel samples without (A) and with (B) the cataphoretic primer.

In Fig.12 it is compared the trend of the resistances relevant to the second time constant of steel and galvanised steel substrates protected with the cataphoretic primer using, as an example, the stretched geometry. The remarkable difference of the two values can not only be justified by supposing a lower corrosion rate of the steel substrate with respect to of the galvanised one. This parameter too, reveals the better behaviour of the steel substrate which is mainly related to the presence of a higher defect density on the galvanised steel substrate. Moreover, the slope of the curve relevant to the galvanised sample, between 4 and 26 days of immersion, seems to be steeper than that observed for the same sample in Fig.11b. Such a trend, where $R_{faradic}$ is decreasing much more rapidly than $R_{coating}$ could suggest that contrarily to steel substrate, the wet area of the substrate is increasing not only because of a certain increase of defects through the coating but also because of delamination phenomena around the defects.

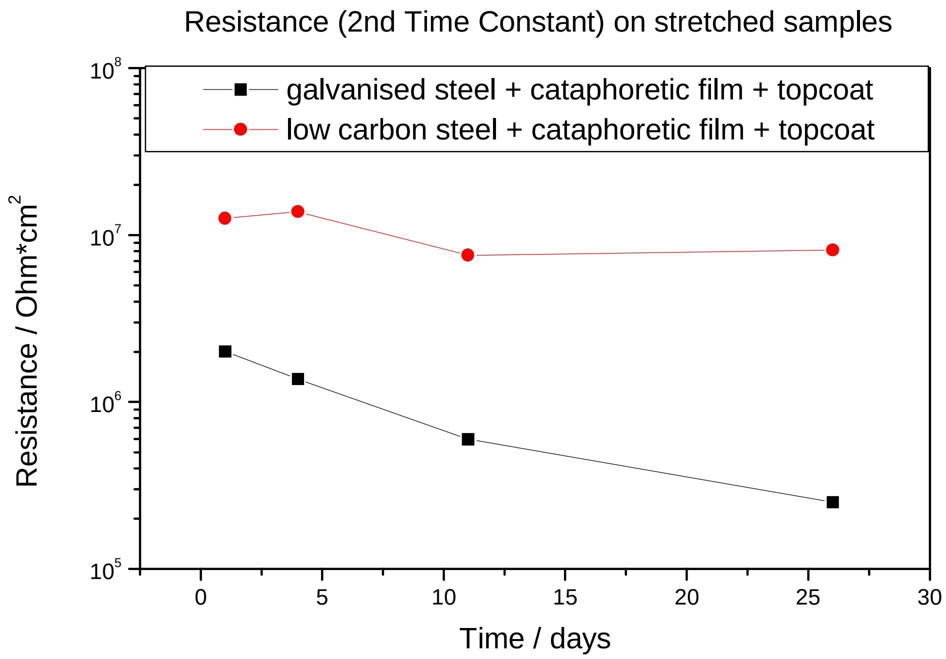


Fig.12. The trend with time of the resistances relevant to the second time constant of steel and galvanised steel substrates protected with the cataphoretic primer, in the stretched geometry.

Conclusions

The presence of a cataphoretic film seems to promote the deposition of a thicker layer of powder polyester paint, and is able to produce a good covering of all the geometrically critical parts of the components used in the production of garden furniture. These artefacts are characterised for a particularly complex geometry of seats and backs then the results of this work suggest to introduce cataphoresis in the industrial painting cycles.

The complementary action of zinc and cataphoresis in the industrial painting cycles appear to be controversial. The cataphoretic layer itself improves notably the performance of the system, and the use of galvanised steel would be conditioned by a possible coating delamination, besides, defectiveness in the powder polyester coating seems to increase.

It is important to remark that blistering of the coatings was not directly observed in all the tested samples, then coating delamination phenomena seem not to be really critical in our systems, however it is important to remind that the zinc/paint interface could suffer easier coating detachments and anodic undermining under field working conditions and that impedance data suggested the possibility for this phenomenon to occur.

Brugal® pre-treatment has not shown real improvement of anticorrosive properties of the protection system, because its low content of chromate is not able to protect adequately the surface. In addition, organic vehicle suffers the same problems as topcoat in covering the critical zones.

Electrochemical impedance measurements revealed to be a quite useful tool to correctly interpret the corrosion behaviour of the studied samples, giving more quantitative information and helping to solve doubts coming from accelerated test performed in the salt fog chamber.

Finally, it is remarkable the fact that the technologies analysed are not innovative themselves, but it is innovative the application of them on garden furniture.

Acknowledgements

Authors are grateful to EMU GROUP for the technical support in samples production, to Pierluca Del Buono for microscopical observations and to Prof PierLuigi Bonora all the time body and soul of the research.

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