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The Corrosion Behavior of Anti-Graffiti Polyurethane Powder Coatings

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Anti-graffiti coatings have become more important. These layers must guarantee excellent corrosion protection properties, and graffiti must be easily removable, without reducing protection and aesthetic properties. In this study, anti-graffiti and corrosion behavior of two anti-graffiti polyurethane powder coatings were studied. These layers were deposited on aluminum substrate, with two different surface finishes, smooth, and wrinkled. The action of four different removers are investigated. Graffiti were drawn on coatings by means of red acrylic spray paint. Methyl-ethyl-ketone (MEK) and a "commercial" remover were the most effective solvents, in terms of graffiti removal capability, producing limited change in aesthetical surface aspect for smooth finishing. The wrinkled surface was less resistant. Corrosion protection properties, after removal action and contact with the remover, were evaluate by electrochemical impedance spectroscopy. After approximately 5 hours, coatings were no longer protective due to formation of defects. To simulate the weathering effect, UV-B cyclic test (4 hours of UV exposure followed by 4 hours of saturated humidity at 50 °C) were performed for 2000 hours. Gloss and color changes were measured, and electrochemical impedance spectroscopy measurements were performed after aging and graffiti removal.

Keywords: *Organic coatings, Anti-graffiti layer, Powder coatings, Electrochemical impedance spectroscopy*

1. Introduction

For painted metal structure, the graffiti removal results a big problem because of the protective coatings and graffiti are of the same chemical nature (polymeric matter) and, therefore, a good adhesion between the two materials is expected. In addition the main graffiti removal method is the use of solvents, which may also affect the protective paint by changing both aesthetic and protection properties. The development of specific anti-graffiti coatings showed a relevant growth only in recent years. The phenomenon has prompted the coatings industry to individuate new solutions to limit the high costs related to the removal of graffiti.

There are two strategies to limit the graffiti problems. The first is the use of non-permanent coating that is scarified during removal of the graffiti [1-4]. This solution is practical and relatively cheap, but there is the necessity to re-deposit the protective layer at each cleaning cycles. The second possibility is the individuation of permanent coatings, which are able to resist to numerous cleanings actions. With this approach, the main strategy is the use of fluorinated and silicone composites in paint formulations reducing the wettability of the surface, preventing the adhesion of graffiti and facilitating removal [5-7]. However, the cost of this type of coatings is high and in some cases, the presence of anti-wetting agents could reduce the adhesion between the coating and the substrate. The use of polyurethane-based coatings could be a reliable solution to obtain good properties and to reduce costs. In fact, polyurethane layers show very good thermal stability, resistance to frost, abrasion, high outdoor durability and weatherability. They are therefore suitable for aggressive application in aggressive environment. In addition, their aesthetic properties are excellent. These coatings have excellent chemical resistance thus providing the necessary properties anti-graffiti coating [5-11].

The objective of this study was to evaluate the properties of two anti-graffiti polyurethane coatings with different cross-linking degree, as a function of different artificial accelerated aging. A more crosslinked coating, and hence more rigid, should present higher anti-graffiti properties but, in the same time, reduced mechanical properties and corrosion resistance.

Two different surface finishing's (shiny and wrinkled) were also considered both for aesthetic reasons (modified gloss) both to evaluate the influence of the surface roughness on graffiti removal action.

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Table 1 Studied samples with surface finishing and polymeric matrix characteristics

Samples name	Surface finishing	Matrix resin
1S	smooth	hydroxylated polyester with a high number of hydroxyl (approx. 300)
1W	wrinkled	hydroxylated polyester with a high number of hydroxyl (approx. 300)
2S	smooth	hydroxylated polyester with a medium number of hydroxyl (approx. 200)
2W	wrinkled	hydroxylated polyester with a medium number of hydroxyl (approx. 200)

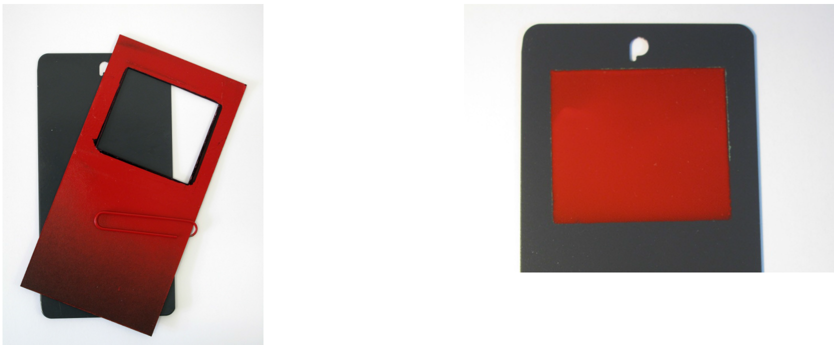

Fig. 1 Used mask to define the test area for the graffiti simulation.

2. Experimental Procedure

Two different anti-graffiti polyurethane powder coatings with different degrees of cross-linking were deposited on aluminium alloy AA1050 panels (AkzoNobel Coatings SpA - Como, Italy). The coating/substrate adhesion results higher than 10 MPa, typical values of this kind of paint. Table 1 shows the samples under investigation: surface finishing and cross-linking degrees are described.

The two formulations differ mainly by the number of hydroxyl groups present in the chain. The samples of the series 2 have a minor amount of hydroxyl groups to obtain a coating with higher mechanical flexibility. Each type of sample presents two surface finishes, smooth and wrinkled, obtained by the addition of a wrinkling wax. The thicknesses of all the samples are approximately 60 μm. As graffiti simulating agent a red acrylic spray paint (Dupli-Color, RAL 3002) was used, according to ASTM D6578. A mask (Fig. 1) was employed to define the test area.

4 different remove agents were studied: 5%wt Na_3PO_4 solution phosphate, a commercial turpentine (Ecoidea Fidea), Methyl-ethyl-ketone MEC (JT Baker) and a specific commercial graffiti remover (X-Graf produced Lu & MI). The composition of last mean is confidential but it is based on 5-15% aliphatic and 5% aromatic compounds. The anti-graffiti properties of the coatings were evaluated measuring the variation of gloss, colour and roughness. The gloss difference was measured at 60° with a glossmeter NL3A. The colour change was investigated by means of a colorimeter Minolta CM 2600d considering ΔEa^*b^* according to the CIELab method [12,13], while the surface Ra roughness was obtained with a profilometer MarSurf PS1.

The graffiti removal was performed according to ASTM D6578 with a detergent soaked white cotton cloth. The maximum variations allowed by the standard to consider acceptable coatings are the following: 10% in gloss (60°) and 2 points of colour according to the CIELab scale. Maximum 10 removal cycles are carried out.

To simulate the weathering effect, UV-B cyclic exposure tests (4 hours of UV exposure followed by 4 hours in saturated humidity at 50 °C), following ASTM D6578 method A, were the carried out for a total time of 2000 hours. Gloss and colour changes were measured after aging and after the graffiti removal considering multiples of 250 hours. In these last tests were considered only the removing agents than have shown in the previous tests the best behaviour (MEK and commercial remover). The graffiti were deposited on the samples after UV-B aging; then the removal action was performed.

Electrochemical impedance measurements (EIS) were carried out to check the evolution of the corrosion protection properties of the coatings in function of the extent

Table 2 Number of cycles of graffiti removal effectiveness of the different studied removers

Remover\ samples	1S	1W	2S	2W
5%wt Na_3PO_4	0	0	0	0
turpentine	0	0	0	0
MEK	4	0	5	0
Commercial remover	4	4	10	4

of aging (UV-B exposure and graffiti removal actions). A two electrodes configuration (Pt wire as CE and sample as WE) was considered using a Solartron 1296 potentiostat and a Solartron 1255 FRA in a $(NH_4)_2SO_4$ 3.5%wt and 0.5%wt NaCl solution in the frequency range 105Hz - 10-2 Hz using a 20mV signal amplitude.

In addition, to simulate the behaviour of the coatings after frequent contacts with the commercial remover, EIS measurements were carried out after each hour of contact with the removing agent for a maximum time of 10 hours. The electrochemical impedance data were fitted using ZSimpWin software considering two electrochemical equivalent circuits (e.e.c.) made of 1 or 2 time constants (capacitance and resistance in series), depending on the impedance response of the system.

3. Resutls and Discussion

3.1 Removal cycles

First of all the effectiveness of different removers has been studied. Table 2 shows the cleaning cycles considering different samples and removers. 10 cycles were chosen as an upper limit, above which anti-graffiti properties of the sample are considered excellent. Graffiti was considered completely removed only of limited changes of the surface in terms of colour and gloss before and after the cleaning action. In particular, following the guidelines of the standard, the acceptance criteria for the effectiveness the graffiti removal action was: (1) maximum 10% for gloss difference measured at 60° (before and after cleaning) and (2) maximum two points difference in the CIELab scale for the colour.

The sodium phosphate solution and turpentine did not shows positive results. These solvents seem to be unable to remove completely the graffiti probably to their low aggressiveness.

MEK and commercial remover resulted more effective in removing graffiti for several times with colour and gloss changes lower than the threshold values. In addition, it is possible to observe an increase of the gloss caused by residual traces of the graffiti. No significant differences between the types of paints are observed. The surface finishing seems to affect much more the ease of cleaning of the coatings surface compared to the chemistry of the coatings.

In fact, the surface finishing appears to be determinant to facilitate the removal of the coloured pigment. The removal of the graffiti on the wrinkled surface results extremely more difficult in comparison to the case of glossy surface.

MEK is able to remove completely all traces of the spray. This solvent is however very aggressive on the polymeric material, in particular for the sample with wrinkled finishing. There are no substantial variations in terms of colour, but a progressive modification of roughness is observed. At the same time, a decrease of gloss values under the threshold limit is measured, as shown, for example, in Fig. 2. Commercial remover results effective for cleaning the surface of the coatings, even on wrinkled surfaces. The removal is very quick and easy and, for the first few cycles, there were no substantial damages of the coatings. With the progress of the cleaning action test, however, on both types of polymers, it is possible to note the formation of lighter spots (Fig. 3). Probably the remover interacts with the dark pigments of the paint

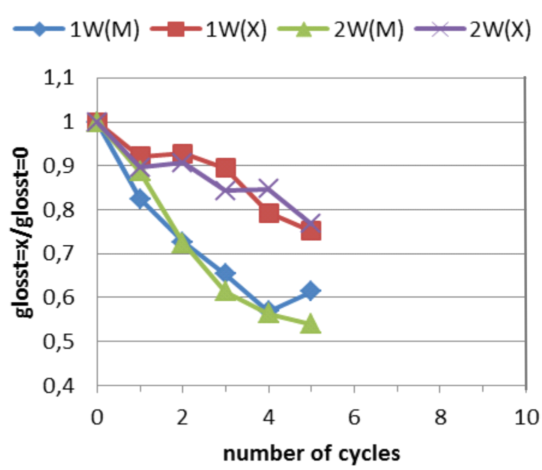

Fig. 2 Gloss change after removal cycles using MEK (M) and commercial remover (X) means for the wrinkled surface samples.

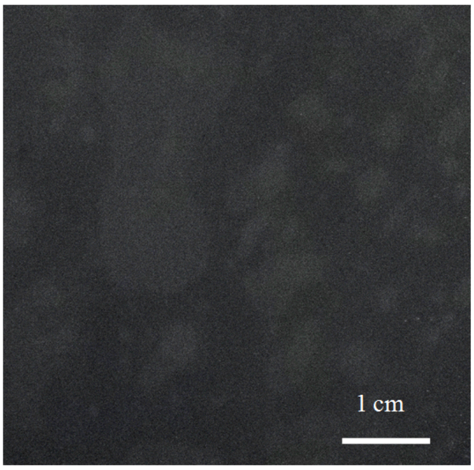

Fig. 3 1W sample after 8 removal cycles using commercial remover.

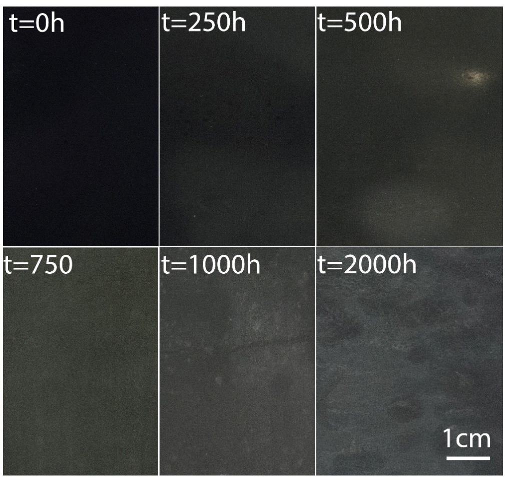

Fig. 4 Surface of sample 1S after different UV-B exposure time.

leading to not homogeneous colour changes. With the increase of the removal cycles number the quantity and the extent of lighter areas rose more and more and became no acceptable in terms of anti-graffiti properties.

The aging cycle was intentionally chosen to produce a very heavy damage of the surface, simulating a very long natural aging in a reasonable time. After the UV-B exposure, the damage level and the protection properties of the coatings were tested. The graffiti deposition and their removal were evaluated. Fig. 4 shows the sample 1S after different exposure times. One can observe that the damage is clearly visible and it increases with the exposure time. The UV-B resistance resulted to be strongly dependant on the surface finishing. Fig.s 5 and 6 highlight the noticeably gloss and colour changes for the wrinkled surfaces compared to the glossy samples.

Wrinkled samples show a more noticeable degradation of the aesthetic properties compared to the glossy samples, with a loss of gloss already in the first 250 hours. Even the colour change is greater for this surface finish. The general performance of all samples leads to an increase of the L (brightness) component values of the colour, probably due to the chalking phenomenon of the coatings surface. No remarkable differences in behaviour could be observed in terms of polymer matrix after low exposure time. Despite a lower crosslinking, also the series 2 shows a good behaviour. Only after very long exposure, time the series 2 shows colour changes more evident than series 1. Then, the anti-graffiti properties of the weathered surface are considered. Considering the ease of removal on the aged surface, it is possible to affirm that there are no particular difficulties. Only for very long aging time, it is relatively difficult to remove the graffiti. From a visual observation the cleaning seems to be complete using

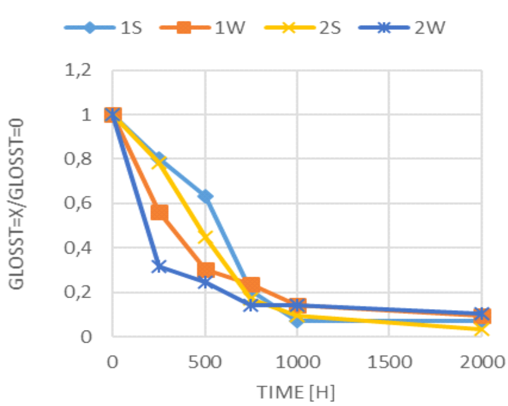

Fig. 5 Gloss change during UV-B exposure time for the studied samples.

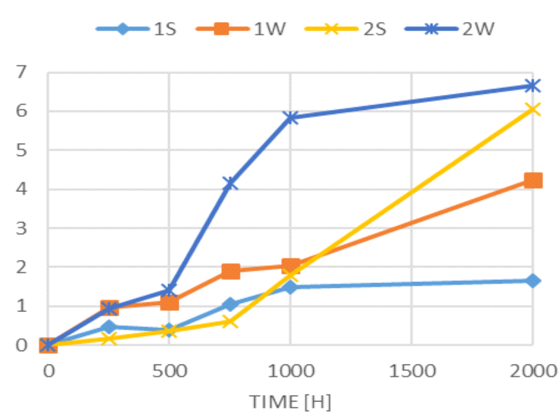

Fig. 6 Colour change during UV-B exposure time for the studied samples.

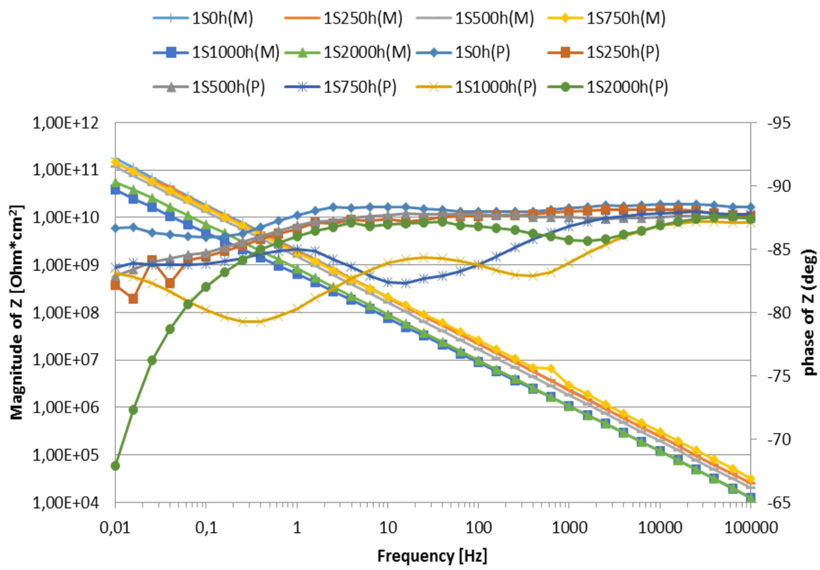

Fig. 7 Impedance diagrams (modulus and phase) of 1S sample at different UV-B exposure time.

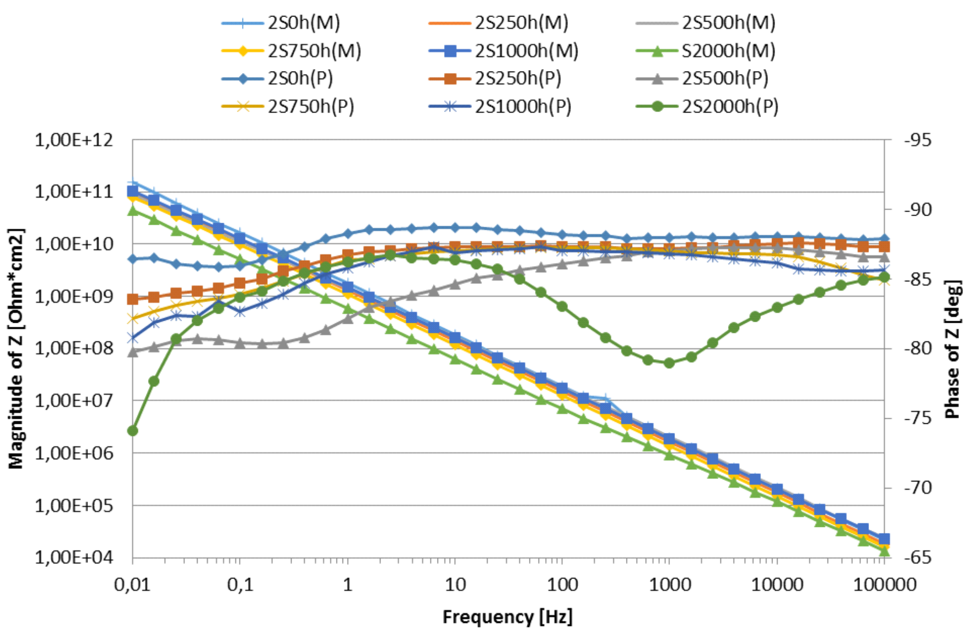

Fig. 8 Impedance diagrams (modulus and phase) of 2S sample at different UV-B exposure time.

both removers. The coatings resulted capable of withstanding cleaning even after long UV-B exposure periods. It is inevitable that some of the highly damaged surface layers could be partially removed during the cleaning action. This action produces a slight recovery of the aesthetic properties (gloss and colour) in comparison with the not aged surfaces. This phenomenon is more evident with the MEK (in particular after several exposure hours) because this solvent resulted to be very aggressive for the surface. On the contrary, commercial remover easily eliminates the graffiti producing a uniform action, avoiding the formation of darker areas.

3.2 Electrochemical impedance spectroscopy

The effects of the UV-B exposure, the cleaning action and the contact with removers on the protection properties were also investigated. Fig.s 7 and 8 show, respectively, for samples 1S and 2S, the impedance diagrams after dif-

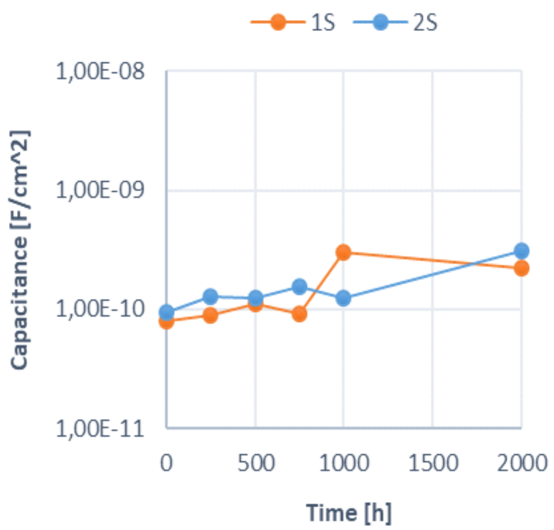

Fig. 9 Coating capacitance obtained from the fitting of EIS data at different UV-B exposure time for samples 1S and 2S.

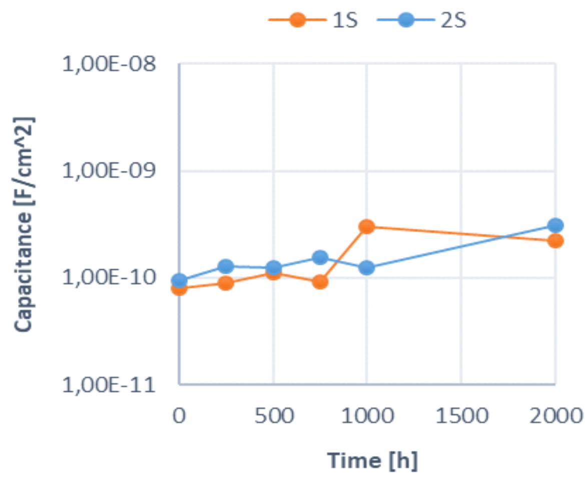

Fig. 10 Pore resistance obtained from the fitting of EIS data at different UV-B exposure time for samples 1S and 2S.

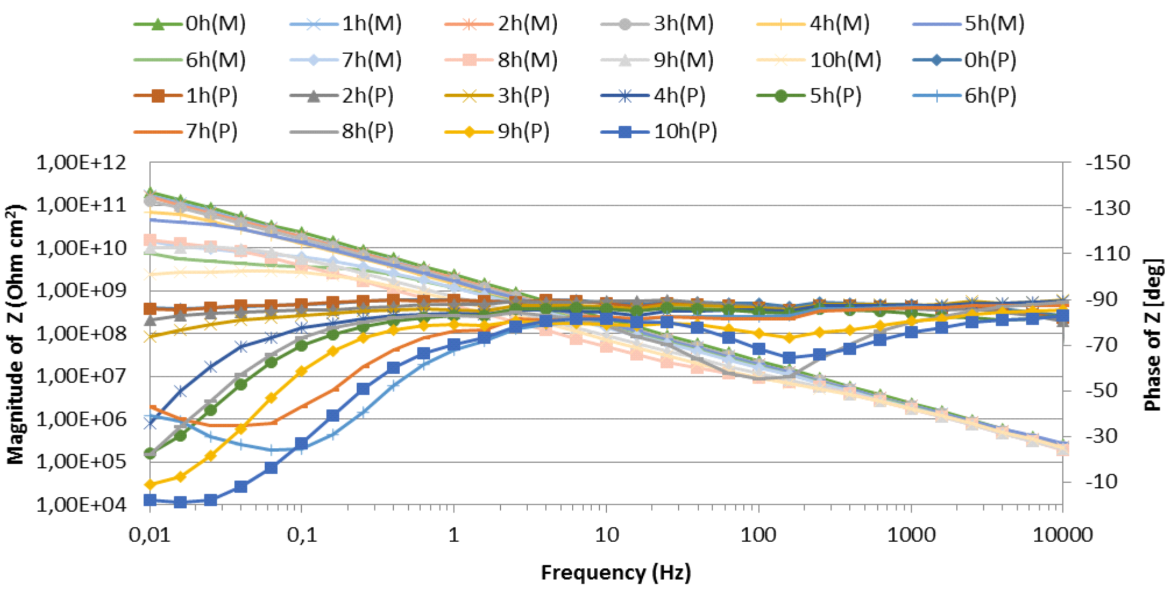

Fig. 11 EIS Modulus and phase of sample 1S in function of contact time with commercial remover.

ferent UV-B exposure times.

The impedances values for both types of samples remain very high, even after 2000 hours of aging. These values (always higher than 10^{10} Ohm cm^2 considering the impedance modulus in the low frequency range) confirm the high protective properties of these coatings. Considering more in detail the sample 1S, a slightly decrease of the impedance modulus after the 750 hours can be observed; however the paint remains protective without the formation defects. The EIS data were than fitted using an e.e.c. made of a single time constant before 750 hours and with two time constants for longer immersion time. The parameters related to the diagram at high frequencies are connected with the characteristics of the coating; the second time constant is related to the reactions on the substrate. Similarly, the impedance values of sample 2S are very high. Comparing with the previous sample a higher impedance modulus for long exposure time is detected. The changes in phase, however, suggest that the deterioration of coating is present. Probably after long exposure

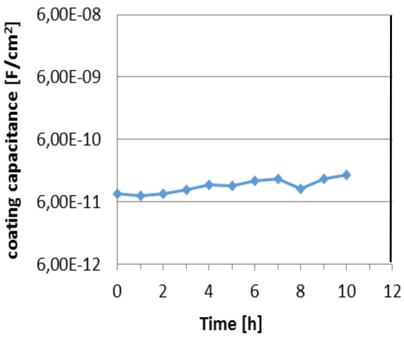

Fig. 12. Coating capacitance obtained by fitting EIS data for sample 1S after different time in contact with commercial remover.

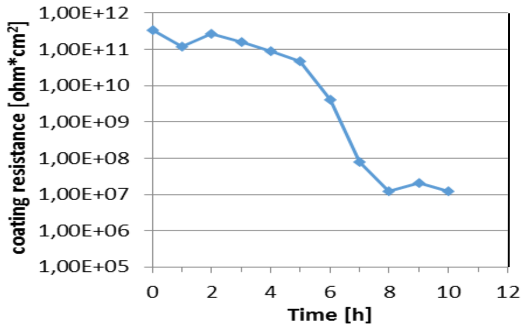

Fig. 13 Coating resistance obtained by fitting EIS data for sample 1S after different time in contact with commercial remover.

time the formation of critical defects is likely to take place thus affecting the protective properties. Considering the values obtained from fitting process shown in Fig.s 9 and 10 it is possible to observe that both type of samples show a very similar behaviour.

Considering the high pore resistance values, the protective properties are maintained during whole immersion time. Probably the impedance measurements are not able to evaluate the UV-B aging, which could be very heavy, but limited to the upper coating layers. The external surface layers are likely to be remarkably damaged but the depth of the degradation of the polymer is limited thus maintaining unchanged the protection properties [14]. Such coatings are therefore able to offer high protection properties even after very heavy aging. This fact is confirmed by the presence of high change in gloss and colour, directly connected with the coating surface, and limited change in the electrochemical parameters connected with the properties of the whole thickness of the paint. Considering the effect on the protective properties of the contact with the removers Fig. 11 shows the impedance diagrams for the sample 1S in function of time of contact with the commercial remover.

After a few hours of contact with the solvent it is possible to observe an important decrease of the total impedance, which becomes more sensitive increasing immersion time. However, the modulus values remain very high due to the protection capability of the coating. At 6 hours of immersion, a sudden decrease of the module in the middle-low frequency range is observed. This aspect indicates a collapse of protection offered by the coating. The impedance data were fitted up to 5 immersion hours with a simple RC circuit. After this time an e.e.c. with two time constants is used, where the parameters at higher frequencies are related to the coating while those at lower frequencies to the reactions occurring on the substrate.

Fig.s 12 and 13 show the coating capacitance and resistance as a function of immersion time for sample 1A in contact with commercial remover.

Considering the coating capacitance values, a trend towards slightly higher values is present. This beahviour is normally correlated to water uptake. However in this case the situation is more complex. The samples are in contiuous contact with the solvent whereas the water is present only for the time necessary to perform the impedance measurement. More interesting is the trend related to the coating resistance. Immediately after short immersion time a trend towards lower values is clearly observed. After 5 hours rapid decrese to very low values is observed. The impedance measurements were repeated to corroborate the experimental results. It was observed that in the 4 - 6 hours range at list one relevant defect

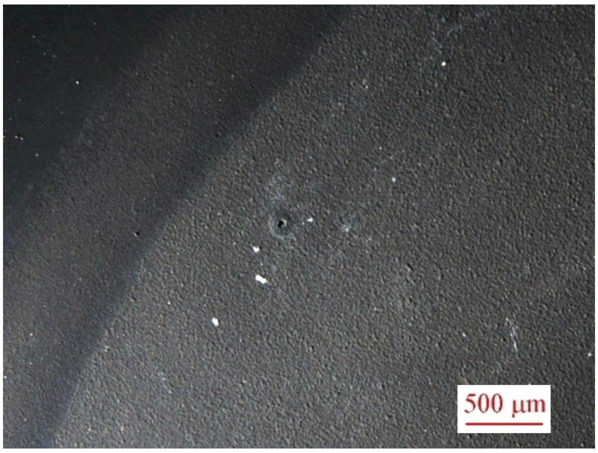

Fig. 14 surface of sample 1S after 10 hours of contact with commercial remover.

in the coating is very likely to occur. This aspect allows to affirm that in few hours the coating loss its protective properties for the formation of defects that allow the electrolyte to come in contact with the substrate. Corrosion phenomana take place at the interface between the substrate and the coating.

Fig. 14 shows the 1S sample surface after 10 hours of contact with commercial remover observed by optical microscope. Already after the first hours of contact significant defects appeared. In addition, colour and surface appearance changes are observed. Probably the remover interact with the coating causing the formation of blisters, which then tend to burst. With the increase of immersion time, the number of these type of defects increases. In addition, the surface appearance change becomes more and more evident. The colour and appearance change looks similar to that found during the test of graffiti removal through cleaning cycles.

4. Conclusions

The use of mild removal solutions as sodium phosphate solution and turpentine showed poor results for graffiti removal.

Increasing the action strength of the solvent the results were improved; however, in the same time the removers interact with the pigments base and polymeric matrix of the coating, leading to the surface appearance changes. The simulation of the cleaning cycles evidenced no significant differences between the two formulations of paints. In terms of anti-graffiti properties, it is possible to conclude that a coating less cross-linked, as the samples of series 2, shows the same characteristics of the series 1, with the advantage of presenting better mechanical properties.

On the contrary, the surface finishing shows a significant influence on the behaviour of the coatings. The smooth finish gives the best performance of cleaning then the wrinkled one.

After artificial accelerated aging by means of UV-B exposure both systems maintained the protection properties.

On the contrary, the prolonged contact with the remover leads to the formation of defects in the coating with a loss of protection properties.

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