Self-cleaning products' Performance on ETICS

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Abstract: External thermal insulation composite systems (ETICS) have been used to improve the energetic efficiency of the buildings. However, its finishing layer is exposed to the weathering, which can lead to several physical-mechanical and aesthetical anomalies. Protection products with hydrophobic, biocide and self-cleaning properties are often used to minimize this problem. In fact, some of these products have a photo-induced self-cleaning ability.

This study aims at studying the behavior of three self-cleaning products when applied on ETICS. The photo-catalysis is induced by the addition of titanium dioxide nanoparticles in these paints. Characterization tests, such as ultrasonic pulse velocity, surface hardness, gloss, color, roughness, and wettability by contact angle, were carried to evaluate the alterations that these products possibly induce on the finishing render of the treated ETICS. A self-cleaning test was also carried out to determine the efficiency of these products. This test relies on the degradation of three different stains, rhodamine B (RhB), methylene blue (MB) and graffiti, when exposed for 360 hours to monochromatic (ultraviolet source) or polychromatic (solar radiation) radiation. The self-cleaning effectiveness was evaluated based on the comparison of the colorimetric coordinates prior and after the exposure. It was thus possible to understand the degradation of the stains during the two exposures and to observe the self-cleaning performance of the three products when applied on ETICS.

According to the results, the application of the three products in the ETICS caused an increase on the ultrasonic propagation speed and the surface hardness. The products also contributed to an increase in the gloss of the ETICS surface and significantly reduced its roughness. It was concluded that the protection products enhance the self-cleaning capacity and, ultimately, improve the hydrophobic and aesthetical properties of the ETICS.

Keywords: ETICS; Protection products; Self-cleaning; Titanium dioxide; Photo-catalysis

1.Introduction

External thermal insulation composite system (ETICS) has been used to improve the energetic efficiency of the buildings [1], by reducing the thermal losses throughout the external walls [2]. This system has three different layers in its constitution: the thermal insulation layer, a base coat reinforced with glass fiber and a topcoat often named as paint. The external layer of ETICS is however exposed to the environment and thus to weathering. The most frequent decay forms in this system are generally aesthetic anomalies (e.g. stains, discoloration) [1,3,4]. In order to minimize this problem, the application of products with self-cleaning properties can form a useful protection layer.

In recent years, self-cleaning products have been standing out for its various applications such as glazed facades, self-cleaning coatings, self-cleaning tiles, car mirrors and decoration materials [5]. As a matter of a fact, a self-cleaning product can prevent the aesthetic degradation of the facade, due to the photocatalytic effect induced by specific additives. Materials with self-cleaning characteristics generally contain titanium dioxide, TiO_2, a semiconductor that has been proving its importance on removing organic pollutants and dyes [6,7].

The self-cleaning characteristics of titanium dioxide is caused by photocatalysis, a physical-chemical process that occurs in semiconductor materials when they absorb ultraviolet (UV) photons with energy greater than the material band gap. When the photon is absorbed by the material, the electrons move from the valence band (BV) to the conduction band (BC) [8-11], which causes a charge imbalance, originating a reactive hole (h+) and an electron (e-). Thus, the reactive hole and the electron, which are on the surface of the material, can participate in the photocatalytic process by chemical reactions with water molecules (H_2O) and oxygen (O_2), present in the environment. The photocatalytic reactions is graphically presented in Figure 1 [12].

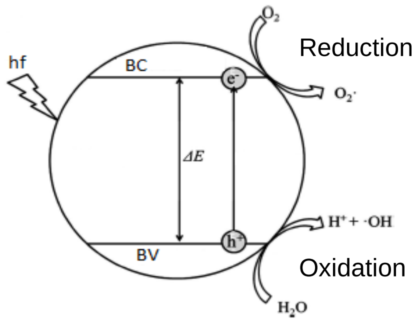

Figure 1 - Representative diagram of the photocatalytic reactions that occur in the semiconductor, where BC is the conduction band, BV the valence band and ΔE a *band gap* (adapted from Xu [12]).

The free radicals, •OH, which result from the oxidation reactions involved in this process, can react with some molecules of the pollutants, converting them in another species which are water soluble. These compounds can then be washed by rainwater [9].

In the construction field, nanoparticles of titanium dioxide, TiO_2, are applied on building materials, such as cement and paint, to improve its characteristics. It is important to note that photoinduced hydrophilicity is a consequence of self-cleaning. This feature can thus increase the wettability of the façade surface, and thus a complete physical-chemical compatibility among the self-cleaning products and the existing layer is necessary [13].

Several authors studied the photocatalytic effect throughout dyes degradation [7,14-18]. The most used dye was rhodamine B (RhB), which is also used in the current study.

This study aims at evaluating the behavior of three protection products with self-cleaning characteristics.

2.Materials and methods

2.1 Materials

The materials used in the experimental setup of this study consist of a ETICS solution (P0) and three protection products (P1, P2 and P3). The products are described in detail below, in accordance with their data sheets. Given that P2 is an experimental product, no description is currently available. It should be noted that the three products contain titanium dioxide, TiO_2 in their composition and the percentage of incorporation of the products is among 10 to 25% in mass.

The ETICS solution (P0) used in this study has a thermal insulation layer of expanded polystyrene (EPS) and a base layer composed of a cement-based binder, sand, fillers, additives and it is reinforced with a glass fiber network. The finishing layer is composed of acrylic copolymers in aqueous solution, pigments and additives.

Finishing paint **P1** is based on a 100% acrylic aqueous dispersion, with rutile titanium dioxide and inert loads. Paint **P3** is based on a 100% acrylic aqueous dispersion, pigmented with rutile titanium dioxide.

Two layers of each protection product were applied on ETICS. After drying (≈24h), the sample were cut in 150 x 150 mm specimens (Fig. 2).

2.2 Characterization of the products

With the aim of understanding the behavior of each product when applied to ETICS, several tests, which aims at determining **ultrasound propagation speed**, **surface hardness**, **gloss**. **roughness** and **contact angle** were carried out.

The ultrasonic propagation speed was determined with an ultrasonic equipment, Steinkamp Ultrasonic Tester BP-7, and was performed according to FE Pa 43 [19]. Surface hardness was defined using a durometer, Shore A, and according to ASTM D2240 [20]. The gloss of the surfaces was assessed by means of a Rhopoint Novo-Gloss Lite glossmeter and in accordance with ASTM D6578 [21]. Roughness was measured with a Elcometer 223 roughness meter. Finally, the contact angle were measured by sessile drop technique (Axisymmetric Drop Shape Analysis) and determined by applying a microdrop of water to the surface of the specimen. The contact angle was measured by image analysis using MATLAB using equation (1).

$$\theta = 2 \arctan \left(\frac{2 \times \mathrm{hm}}{\mathrm{am}}\right) \qquad (1)$$

Where, *hm* is the height e *am* the diameter of the microdrop, respectively. The final result is obtained by calculating the mean value of several static contact angle measurements.

All tests were repeated three times and the mean and standard deviation were calculated over the performed measurements.

2.3 Self-cleaning test

This assay aimed to analyze the degradation of the three stains (rhodamine B, methylene blue, graffiti) (Figure 2) applied on the surface of the specimens, with the aim of analyzing the self-cleaning capacity of the three products.

Rhodamine B and methylene blue were applied 0.5ml by pipette on the surface of the specimens, in accordance with the Italian standard UNI 11259 [22], which refers to specimens with a dimension of 160x140mm and to a rhodamine B concentration of 0.05g/l. The *graffiti* was applied using a silver spray *paint.*

The samples were exposed either to sun or to an ultraviolet radiator for 30 days, with an average period of 12h of radiation per day.

A Minolta CR-410 chromameter was used to evaluate the color of the specimens before and after the exposures. The CIELAB color system was used to measure three color coordinates (L*, a*, b*). The value L* corresponds to the brightness, which ranges from 0 (black) to 100 (white). The values a* and b* characterize the chromatic coordinates of red-green (+a* indicates red and -a* green) and yellow-blue (+b* corresponds to yellow and -b* to blue), respectively. The two metrics *a* and b** allow to calculate the chroma or color saturation, according to Equation (2).

$$C = \sqrt{a^2 + b^2} \qquad (2)$$

The total color variation, ΔE*, was also obtained by the expression represented in Equation (3).

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad (3)$$

Where ΔL^* represents the difference between the L^* at the end and beginning of the test; Δa^* represents the difference between a* at the end and beginning of the test; Δb^* is equivalent to the difference between b^* at the end and beginning of the test.

Figure 2– Example of a sample with 2 RhB stains, 2 MB stains and graffiti.

3. Results and discussion

3.1 Product characterization results

Table 1 shows the results obtained from the initial characterization of the products, with the values of ultrasonic propagation speed (S_p), surface hardness, contact angle, gloss, and roughness.

Table 1– Mean values (Avg.) and standard deviation (Sd) of the characterization tests of the samples under study: P0, corresponds to the ETICS solution, and P1 to P3 to the three studied products.

Samples	S_p (m/s)		Surface hardness		Contact angle (°)		Gloss (GU)		Roughness (mm)	
	Avg.	Sd	Avg.	Sd	Avg.	Sd	Avg.	Sd	Avg.	Sd
P0	2016,0	32,5	79,00	6,33	56,30	5,40	1,30	0,06	0,774	0,142
P1	2126,1	78,7	80,70	4,86	36,65	1,69	1,75	0,06	0,690	0,038
P2	2111,1	23,1	84,07	1,00	31,71	4,66	1,69	0,09	0,573	0,038
P3	2096,4	31,0	83,11	2,78	62,75	1,92	1,68	0,03	0,657	0,018

The speed of sound propagation was 5.5% higher in P1 when compared with the reference sample, P0. In P2 and P3, this variation is slightly less pronounced, corresponding to 4.7% and 4%, respectively. These results indicate that any of these products contribute positively to increase the compactness and reduce the tendency to microcracking of the treated ETICS.

Regarding the surface hardness, the application of the products results into an overall increase in the hardness of the ETICS. Treatment P1 increased its hardness by 2.2%, if compared to the untreated specimen P0, whereas 6.4% and 5.2% increase was observed for P2 e P3, respectively. Therefore, it can be concluded that the application of the products slightly increases the surface resistance of the ETICS solution, being this effect more pronounced in P2 and P3. Analyzing the values of the contact angle, P3 stands out with the highest value, presenting an increase of 11.4% compared to P0, indicating a reduction of the wettability of the treated substrate. On the other hand, the contact angle was much lower for P1 and P2 (decrease of 34.9% and 43.7%, respectively).

The gloss increased with the application of the products, when compared to the reference value, P0. Treatments P2 and P3, have very similar gloss values, whereas P1 was the product which stand out the most, with a gloss value that represents a variation of 34.8%.

The three products induce also a decrease of the roughness, if compared to the reference P0. In addition, the high standard deviation associated with this measurement emphasizes the heterogeneity of its surface. When compared with the standard sample, the roughness of P1 decreased by 10.8%, while in P2 there was a reduction of 26% and in P3 there was a reduction of 15.1%.

3.2 Self-cleaning test

This section presents the results of the samples exposed to solar and UV radiation analyzed using the colorimeter. This test is essential for assessing the degradation of color of the three spots (rhodamine B, RhB, methylene blue, MB, and graffiti, G) in the initial state and after exposure to solar and UV radiation.

It is important to highlight that, after 14 days of sun exposure, there was a total degradation of the RhB and MB stains, as shown in Figure 3. Conversely, after 360 h of UV radiation exposure, there were no noticeable changes in any stain.

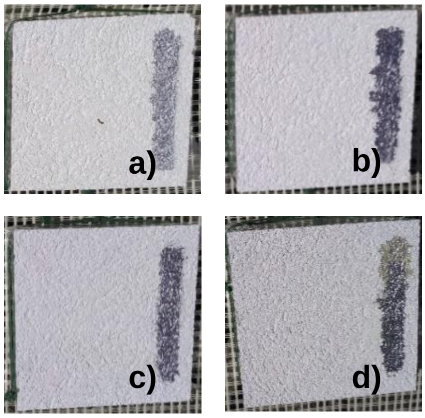

Figure 3– Samples after 14 days of sun exposure, without stains, where a) P0, b) P1, c) P2 and d) P3.

3.2.1 Stains colorimeter results in P1

Figure 4 shows the obtained values of luminosity, L*, and chroma, C*, in P1 for all stains (rhodamine B, RhB, methylene blue, MB, and graffiti, G).

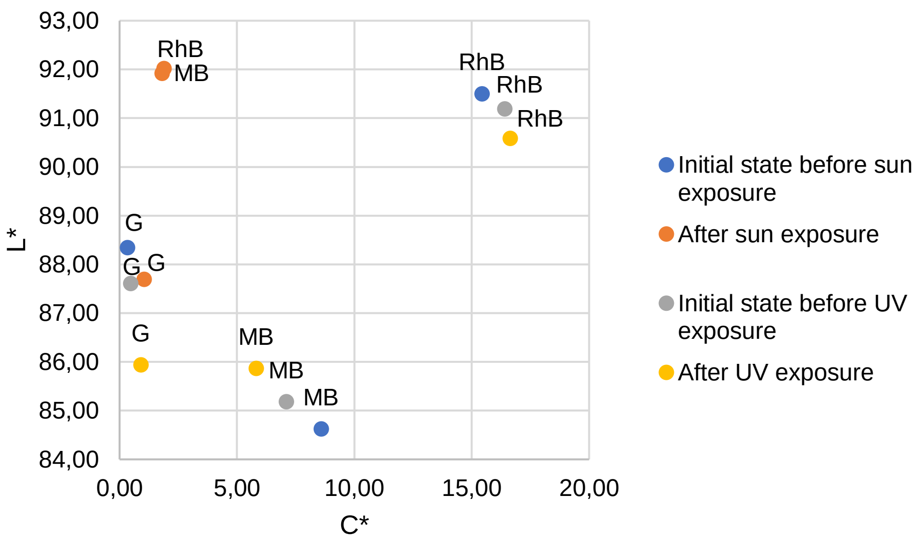

Figure 4 – Average values of luminosity, L*, and saturation, C*, of stains in the initial state, after sun and UV exposure in P1, where RhB corresponds to rhodamine B, MB to methylene blue and G to graffiti.

According to Figure 4, the MB and RhB samples had an equivalent behavior after sun exposure. They both showed a significant increase in the value of luminosity and a decrease in the chroma value. Regarding L*, the RhB dye had an increase of 0.6%, while MB had an increase of 8.6%. This indicates that the luminosity values are similar to those in their initial state without spots. In another hand, the chroma parameter C* considerably changed. The parameter C* of RhB stain, after the exposure to sun, exhibited a reduction of 87.7%. This variation is due to the decrease of the chromatic coordinate a* to a value very close to zero (-0.08 ± 0.02), which corresponds to an almost perfect white. This means that the surface has returned to its original chromatic coordinates. The chroma in the MB stain reduced 78.9% after sun exposure. This variation is due to chromatic coordinate b*, which at the beginning is negative (-8.37 ± 0.31) and after sun exposure becomes positive (1.79 ± 0.10). This means that its tonality has changed from a slight tone of blue to yellowish. In this way, these significant changes confirm the effectiveness of self-cleaning, due to the nanoparticles titanium dioxide in the composition of the product. The graffiti, after sun exposure, presented an increase in the value of C*, because the value of the chromatic coordinate b* has increased. The photocatalytic paints can not remove this stain.

After the exposure to UV radiation, there were no significant variations in the L* and C* parameters in the three applied stains, RhB, MB and G. It can be concluded that no self-cleaning capacity was observed when using this wavelength of the UV radiation.

3.2.2 Stains colorimeter results in P2

Figure 5 shows the obtained values of luminosity, L*, and chroma, C*, in the three stains (rhodamine B, RhB, methylene blue, MB, and graffiti, G) applied in P2, in the initial and final state of two exposures.

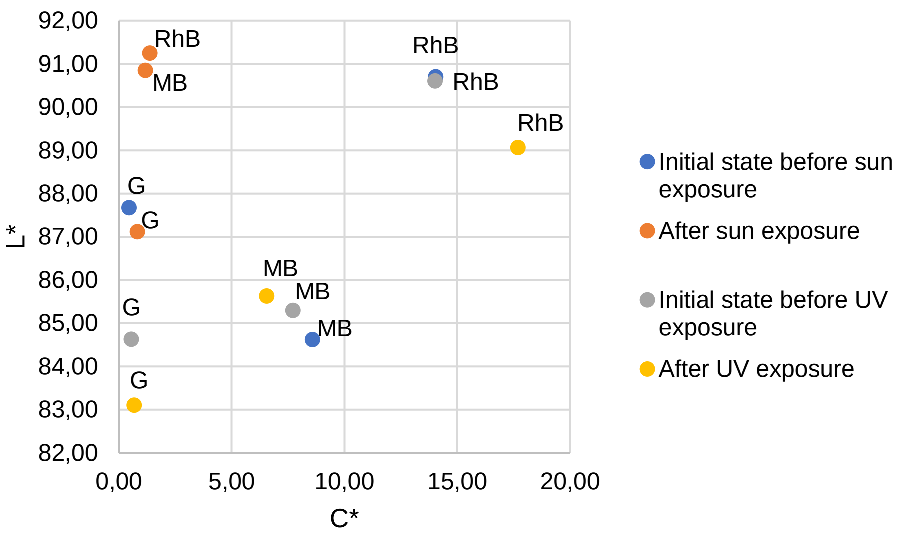

Figure 5 – Average values of luminosity, L*, and chroma, C*, of stains in the initial and final state of the two exposures in product 2, P2, where RhB corresponds to rhodamine B, MB to methylene and G to graffiti.

After sun exposure, the spot luminosity value increased of 0.6% in RhB and 7.4% in MB. For chroma, C*, the value decreased 90.2% and 86.3% in the cases of RhB and MB, respectively. RhB's C* variation is a consequence of the reduction of the value of the chromatic coordinate a* to -0.07 ± 0.06, when at the beginning this coordinate has a value of 14.04 ± 0.54. This stain almost disappeared, obtaining an almost perfect white. The change in the MB chroma value is due to the chromatic coordinate b*, which changed from the bluish (-8.32 ± 0.15) to slightly yellow color (1.14 ± 0.19). Regarding the graffiti, similarly to what happened in the sample P1, the chroma value increased due to the chromatic coordinate b*. The changes in RhB and MB confirm the self-cleaning effect, being the stains almost eliminated. However, graffiti stain was not eliminated in specimenP2, similarly to P1.

After exposure to UV radiation, no significant color variations in the three stains were observed, and it was not possible to understand the self-cleaning capacity of this product in this exposure. This behavior can be attributed to the inadequate UV radiation for activation of the photocatalytic effect and/or the lack of proper experimental conditions (e.g. adequate relative humidity) that would help in the process, as also mentioned in P1.

3.2.3 Stains colorimeter results in P3

Figure 6 shows the obtained values of luminosity, L*, and chroma, C*, in P3 for all stains (rhodamine B, RhB, methylene blue, MB, and graffiti, G).

Similarly, to what happened in the two previous products, RhB and MB stains exposed to solar radiation show a similar behavior, almost disappearing.

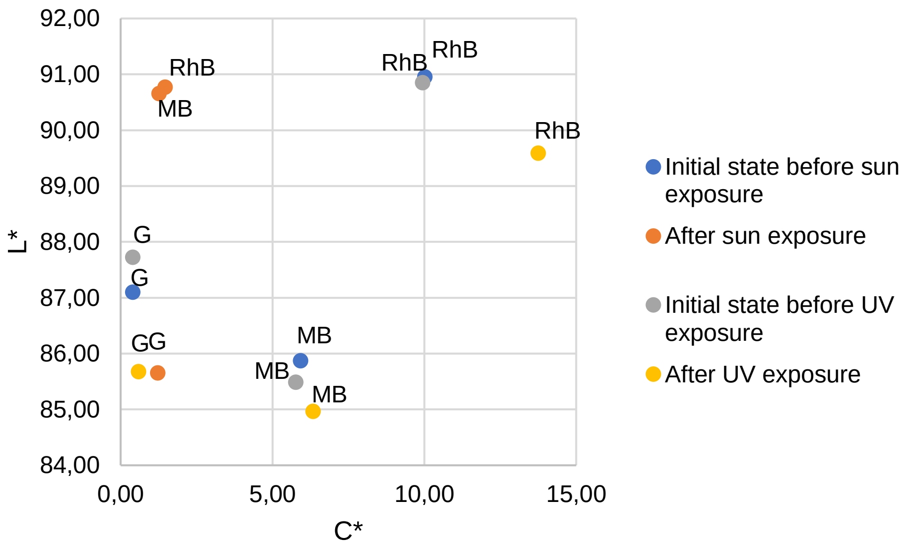

Figure 6 – Average values of luminosity, L*, and chroma, C*, of stains in the initial *state,* after sun exposure and UV radiation of product 3, P3, where RhB represents rhodamine B, MB methylene blue and G graffiti.

In fact, both stains significantly decreased the chroma value, 85.4% in RhB and 78.8% in MB. In the case of RhB, this change was due to the decrement of the chromatic coordinate a*, from 10.00 ± 1.14 to -0.13 ± 0.03. The variation of MB chroma is a consequence of the variation of the value of the chromatic coordinate b*, since at the beginning the value is -5.89 ± 0.63, which represents the blue tint, and at the end is 1.23 ± 0.13, which indicates slight yellow coordinate. Regarding the behavior of *graffiti,* similarly to the other products, this stain was not removed.

The behavior of this product after UV exposure is again similar to the products P1 and P2, since there are no significant changes in the samples.

3.2.4 Comparison between the results obtained from RhB stain

There are several factors among the three products under analysis that must be considered, regarding the results obtained in the color's evaluation test. The changes in the color of the stains are evident, with special emphasis on the RhB and MB dyes, being the first to register the greater variations in C* parameter. Thus, Figure 7 is presented to access the self-cleaning performance of each test piece. The figure depicts the variations of the average values of luminosity, L *, and chroma, C *, obtained with the colorimeter for the RhB stain, since this is where the most significant changes were found.

By direct analysis of the Figure 7, the variation in component C *, when compared with the reference P0, is higher in all products. However, it is in P2 and P1 that this difference got in evidence, respectively $\Delta_{C^*_{P1}} = 13{,}54$ and $\Delta_{C^*_{P2}} = 12{,}67$. In absolute terms, it should be noted that in all products the chroma value at the end of the sun exposure is similar to each other and close to zero. Thus, with this analysis it is concluded that any of the three products adds to the ETICS (P0) surface the self-cleaning characteristic, since the three can degrade the stain. However, P1 and P2 demonstrate the greatest difference between the initial and final state, which may indicate a better performance of these products when compared to P3.

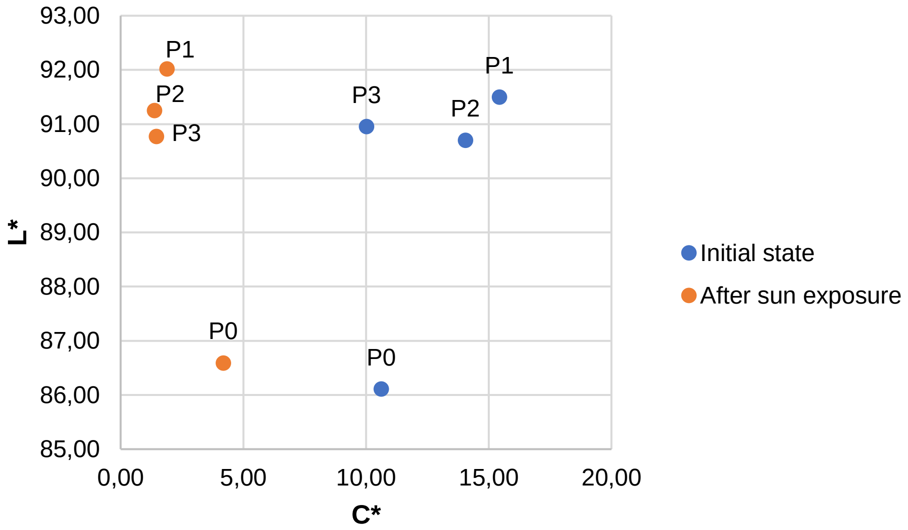

Figure 7 - Average values of luminosity, L *, and chroma, C *, of the RhB spot in the initial state and after sun exposure, where P0 represents the reference, P0, and P1 to P3 the three products.

3.2.5 Stains color variation

Table 2 shows the color variation, ΔE*, determined using equation 2 for each spot for sun exposure and UV radiation. It was verified that the values of sun exposure are considerably different from those of UV radiation, except for graffiti that in both exposure, with variation visible at naked eye (ΔE* < 5). Thus, it can be concluded that the products are not suitable for this type of stains, which incorporates also a polymeric-based adhesive binder.

According to the values obtained in the sun exposure, it was concluded that the three products provide efficient self-cleaning properties, with elimination of RhB and MB stains. P1 and P2 demonstrated to be the most promising paints, with the most significant color variation in these stains. In addition, it was verified that also P0 can eliminate these two stains, which suggests that the surface itself has self-cleaning characteristics, due to the incorporation of titanium dioxide in the ETICS finish layer.

In the UV radiation exposure test, it was not possible to perceive the self-cleaning effect. The variations that occurred were minimal, and the color variation was again not macroscopically noticeable (ΔE* < 5) [23].

Table 2– Values of color variation, ΔE*, of the three spots, RhB, MB and *graffiti,* after each exposure, solar and UV, in samples P0 to P3 (the greyish spots indicate the higher ΔE* among the three products).

Samples	After solar exposure			After UV exposure		
	ΔE* of RhB	**ΔE* of MB**	***ΔE** * **of Graffiti**	**ΔE* of RhB**	**ΔE* of MB**	***ΔE** * **of Graffiti**
P0	10,36	10,86	1,43	4,95	1,6	1,21
P1	15,49	12,62	1,42	0,99	1,56	1,73
P2	14,15	11,48	1,29	3,99	1,35	1,82
P3	10,17	8,58	2,04	4,02	1,4	2,19

3.3 Discussion

The propagation speed of sound and surface hardness both have increased after the application of the products. Thus, it is concluded that the three products confer a further resistance to microcracking and higher compactness to the surface of the ETICS topcoat. Through the application of the products, it was possible to partially fill the existing voids and pores.

The application of the products increased the gloss values, with a slight improvement of the aesthetic features of the ETICS surface.

All products reduce the ETICS roughness. This effect is more evident in P2. It is worth noting that that roughness decrease can also reduce the accumulation of atmospheric particulate matter.

Regarding the contact angle, the behavior of P3 differs from that of P1 and P2. Product P3, when applied to a surface, reduced its wetting capacity, thus increasing the contact angle [13]. On the other hand, P1 and P2 showed an inverse behavior, contributing to a more noticeable hydrophilicity of the treated surfaces. The presence of TiO_2 nanoparticles might have contributed to this increase. According to Saini *et al* [11], the higher the surface wetting, the most significant the self-cleaning efficacy. Products P1 and P2 show a higher self-cleaning effect, when compared to P3, being more adequate for this purpose, however, showing lower hydrophobic properties.

Based on the results obtained in the self-cleaning assay, it is concluded that the self-cleaning of the three products worked properly outdoor with direct solar radiation, eliminating all the stains. Conversely, ultraviolet radiation was not able remove the stains under study. It might have been useful to adopt a higher wavelength of the UV radiation (approximately 400 nm) to activate the photocatalytic effect of titanium dioxide [18]. According to IPMA weather data [24], the UV component of the solar spectrum is in the range of 290 nm and 400 nm, and a wider wavelength may also justify a more efficient self-cleaning outdoor. In addition, the exposure time was only 360h, which may have been insufficient to obtain macroscopically visible changes. It should also be noted that the absence of certain experimental conditions, such as humidity, may also be a further factor of the inactivation of the photocatalytic effect. In fact, a high relative humidity (70-100%) is generally registered outdoor in the area of Lisbon, even during summer time.

4.Conclusions

It is possible to conclude that the three products add new positive characteristics to the surface of ETICS. These products improved surface resistance and reduced the porosity on the surface. The products have also decreased roughness, which prevents the accumulation of undesired particles. Furthermore, the products also increased the surface gloss, and provide a whiter surface, improving the aesthetic features of the system. These factors can contribute to increase durability of ETICS. Regarding self-cleaning, it was observed, through sun exposure, that the three products added self-cleaning characteristics to the surface. Based on the results of the color variation, P1 and P2 had the most significant variations and thus the most efficient self-cleaning effect.

It can be concluded that products which incorporates titanium dioxide nanoparticles can effectively induce photo-activated self-cleaning properties, with effective removal of the (rhodamine or methylene blue) stains within 14 days of sun exposure. The three products are suitable for application in ETICS and can contribute to a long-term performance of these systems.

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