

Article

Weathering of Two Anti-Graffiti Protective Coatings on Concrete Paving Slabs

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Abstract: The durability of anti-graffiti coatings is of special relevance since, unlike other protective treatments, they are not only affected by environmental factors, but also by often aggressive cleaning procedures. However, little is known about the long-term performance of either permanent or sacrificial coatings. This study explores the durability of two commercial coatings on concrete paving slabs under both natural and artificial ageing tests. The results of this research show that a fluorinated polyurethane and a crystalline micro wax weathered in less than 2000 h in a chamber with UVB radiation and after one year of outdoor exposure in the south of England. The former weathered by getting yellow and dark, and eventually, only under the accelerated ageing test, by losing its adhesion to the concrete slabs, and the latter weathered by getting dark, cracked and by reducing its water repellency under natural conditions. Cleaning efficiency of the protected surfaces from graffiti paints was therefore diminished, particularly when pressurized water spray was used on the polyurethane coated surfaces, since the treatment was partially removed and the concrete surface eroded.

Keywords: anti-graffiti; wax; fluorinated polyurethane; concrete; QUV; weathering; durability; coating; outdoor exposure; accelerated ageing

1. Introduction

The development of anti-graffiti coatings is a growing challenge, since the problem of graffiti, which has social and economic impacts, needs to be counteracted. In fact, in New York where this phenomenon started in the 1960s, despite anti-graffiti initiatives (including the application of these coatings) graffiti has not yet been got rid of [1]. Anti-graffiti coatings can help to attenuate this problem by minimizing cleaning efforts and discouraging graffiti writers, through hindering the adhesion of paints to the surface of the materials and so making graffiti easier to remove, but their durability can be an issue. Several different factors affect their integrity (thickness, gloss, adhesion) and therefore their protective ability: including cleaning procedures (solvents, pressure water, etc.) and environmental conditions (temperature, UV radiation, etc.). However, new formulations available in the market are expected to be more long-lasting.

On concrete—the building material par excellence in civil engineering works and a target for graffiti writers—a new factor can affect both the effectiveness and durability of the protective treatments and substrates. Portland cement, as a hydraulic binder of concrete, can chemically interact with anti-graffiti products, giving rise to modified hydration products [2].

Various studies have dealt with the performance of anti-graffiti coatings on concrete. Neto et al. [3] revealed that a permanent protective coating (fluorinated polymer), which is able to withstand

more than one graffiti cleaning cycle, was more effective than a sacrificial coating made of wax. Sacrificial coatings only withstand one cleaning cycle since they are removed along with the graffiti and they therefore need to be reapplied after a cleaning procedure. However, neither of the treatments prevented the penetration of the paints in the pore systems of the materials, and thus it was impossible to remove all the paints without damaging the substrate. In contrast, Malaga and Mueller [4] found out that on their concrete slabs, a sacrificial product was more effective than a permanent one, and Carmona-Quiroga et al. [5] showed that two permanent coatings were not sufficient to facilitate graffiti removal. These differences in efficiency of anti-graffiti coatings on concrete and cement-based materials are the result of various factors: porosity and roughness of the substrates, type and durability of the anti-graffiti product and cleaning procedures to remove graffiti paints [6,7].

As the expected longevity of coatings has increased, the importance of durability studies has risen in parallel [8]. However, up to date, the very few papers that have assessed the resistance of anti-graffiti coatings to ageing [9–11] have basically found that the coatings became deteriorated. Durability studies of anti-graffiti coatings in particular and coatings in general are normally performed under accelerated laboratory conditions to produce fast results in reasonable time [12]. However, correlation between these results and the ones obtained in natural exposure trials can be controversial since accelerated tests are a simplification of real environmental conditions [12]. Therefore, the results that they produce should be taken carefully. Even correlations between outdoor weathering trials are difficult because of the differences in solar radiation, temperature, humidity, pollution, etc. in different locations or even in the same location over time. A desirable solution is the combination of outdoor and accelerated tests. This study aims to fill the gap of durability studies of anti-graffiti coatings by assessing whether a permanent and a sacrificial product are durable enough on concrete using both natural and artificial ageing trials.

The performance and durability of two current commercial formulations, a fluorinated polyurethane (permanent coating) and a micro wax (sacrificial coating), were evaluated on smooth concrete slabs before and after a range of weathering times: 3, 6, 9 and 12 months of outdoor exposure in the south of England and after 500, 1000, 1500 and 2000 h in a chamber with UVB radiation.

2. Materials and Methods

2.1. Application of Anti-Graffiti Coatings

Paving concrete slabs (225 mm × 225 mm × 35 mm, Grey Superpave from Rogers Gardenstone, Faringdon, UK) with a smooth finish were cut to different sizes for easy handling following test requirements and space constraints in the chamber: 150 mm × 75 mm × 10 mm; 85 mm × 65 mm × 10 mm; 75 mm × 35 mm × 10 mm and 30 mm × 25 mm × 10 mm.

Then, cut specimens were coated with two commercial anti-graffiti coatings, a permanent and sacrificial one. The permanent product (P) is an aqueous dispersion (ca. 75% of water) of a fluorinated polyether-urethane anionomer (ca. 25%) based on PFPE (perfluoropolyether) and the sacrificial coating (S) is a water-based crystalline micro-wax (emulsion with pH 7). Two coats of both products were applied on consecutive days at room temperature by HVLP (High Volume Low Pressure) spray on the upper smooth surface of the samples in triplicate and the excess was brushed with a roller. Samples were left to dry to constant weight and then the residue of the coatings was determined; 169 ± 17 g/m² for the permanent treated surfaces and 104 ± 18 g/m² for the sacrificial treated ones.

2.2. Ageing Trials

Samples of dimensions 150 mm × 75 mm × 10 mm and 75 mm × 35 mm × 10 mm (both treated and untreated) were artificially weathered in a QUV chamber (Q-Lab Corporation, Westlake, OH, USA) for up to 2000 h. (For the bigger samples, the area irradiated was 95 mm × 63 mm). During each 500-h period, the samples were removed from the chamber to characterize the surfaces and perform

graffiti painting and cleaning episodes (Figure 1). The chamber was fitted with a UVB lamp (0.45 W/m^2 at 313 nm) which is known to give fast results in photo degradation studies. Each 500 h, the samples were exposed to 250 h of UV exposure at 60° and 250 h of condensation without radiation at 50°C (a cycle consisted of four h of UV radiation followed by four h of condensation [13]).

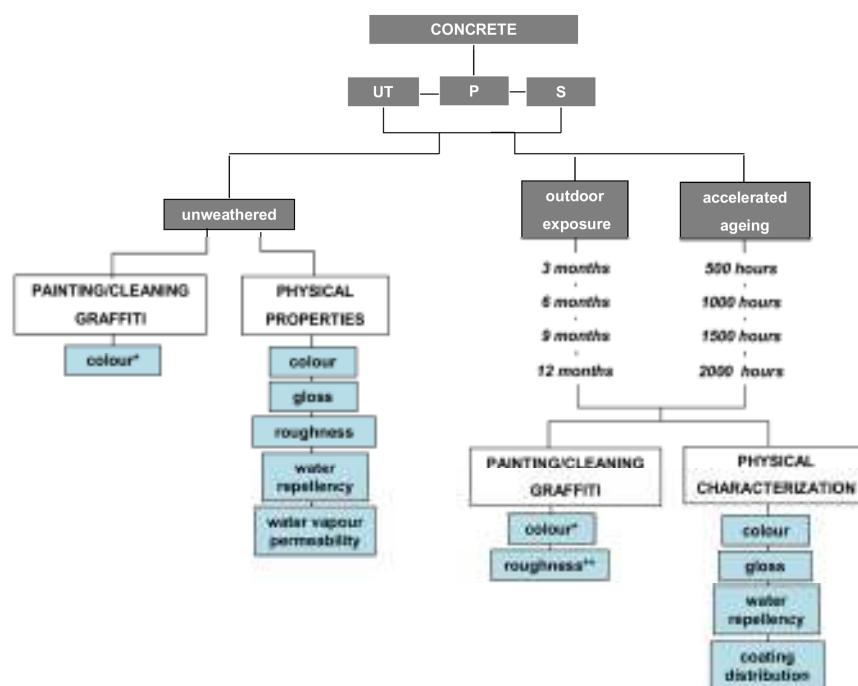


Figure 1. Flow chart of the experimental procedure on untreated concrete (UT) and treated with the permanent (P) and sacrificial (S) anti-graffiti coatings. * For the untreated samples, there was only one painting-cleaning cycle before weathering; for the ones coated with the sacrificial coating, there was one cycle before weathering and another cycle at the end of both ageing trials; and for the samples coated with the permanent product, there were four cleaning cycles before weathering and four cycles during the ageing trials. ** At the end of both ageing trials on the coated samples.

A different set of samples ($150 \text{ mm} \times 75 \text{ mm} \times 10 \text{ mm}$, $85 \text{ mm} \times 65 \text{ mm} \times 10 \text{ mm}$ and $30 \text{ mm} \times 25 \text{ mm} \times 10 \text{ mm}$) was naturally aged for 1 year (April 2015 to May 2016) in the south of England (Wytham Woods, outskirts of Oxford) in a wooden rack facing south (samples tilted 45°). Every 3 months, samples were removed from the field site to carry out the surface analysis and graffiti painting and removal episodes (Figure 1). Table 1 summarizes the climatic conditions in this temperate maritime region over the exposure period provided by the nearby Radcliffe Meteorological Station of the University of Oxford. According to the PVGIS (Photovoltaic Geographical Information System) - Solar Radiation database [14], the average solar radiation in Oxford is 3070 Wh/m^2 day. UV radiation is 92.1 Wh/m^2 day (3% of solar radiation) and UVB radiation is 4.6 Wh/m^2 day (5% of UV radiation).

Table 1. Environmental conditions in central Oxford (Radcliffe Meteorological Station; latitude: 51.7614, longitude: -1.2636) near the field site (Wytham Woods, UK; latitude: 51.7759, longitude: -1.3379) for the four exposure periods in the duration of one year.

weather conditions	Apr.–July 2015	Aug.–Nov. 2015	Nov.2015–Feb. 2016	Feb.–May 2016	Total
Sun (h)	653	305	178	490	1626
Rain (mm)	105	160	215	196	676
Warmest daily mean air temperature ($^\circ \text{C}$)	24.7	22.05	13.7	18.25	24.7
Coolest daily mean	6.2	7.25	-0.25	2	-0.25

 air temperature (°C)

2.3. Painting and Cleaning Graffiti

Samples periodically removed from the chamber and field site were submitted to graffiti painting and cleaning episodes as follows. Four to five solvent-based alkyd spray paints (Madrid red, pistachio green, electric blue, black and on the artificial aged samples also divinity white), an acrylic silver spray paint and a black marker (water-based tempera), all from Montana Colors, were applied in a cross stripe pattern on the anti-graffiti coated specimens as well as on untreated control samples of 150 x 75 x 10 mm before and after natural and artificial weathering. Sprays were applied in a double layer from a distance of approximately 10 cm, and the marker pen was also traced twice. Long stripes were painted first (black marker, silver and black spray) and one hour later short stripes were painted with the remaining colours. One day after applying the paints, cleaning of graffiti was attempted using different procedures. For the untreated samples and the ones coated with the permanent product, half of the samples were cleaned with paint remover (Dupli-Color Graffiti-Ex spray, MOTIP DUPLI GmbH, Hassmersheim, Germany) and brush with nylon bristles, and the other half with the remover and high pressurized water spray (80 bars, Kärcher K2 pressure washer, Winnenden, Germany) afterwards. Both cleaning methods were carried out twice (which represented a cycle), each time the remover was left on the surface for 15 minutes. On the untreated samples only one painting and cleaning episode was carried out whereas on the ones coated with the permanent product four cycles took place. The sacrificial coated samples were cleaned with high pressurized hot water spray (110°C and 90 bars) following the coating manufacturer's guidelines (one single episode).

On the aged samples four painting and cleaning episodes were carried out on concrete specimens coated with the permanent coating: after 3, 6, 9 and 12 months of outdoor exposure and after 500, 1000, 1500 and 2000 h in the chamber. However, on the artificially aged samples only the cleaning procedure with paint remover and brush was used, since the size of the irradiated area was just 95 x 63 mm. On the samples treated with the sacrificial coating, only one episode was carried out after 2000 h of artificial weathering and 12 months of outdoor exposure.

2.4. Characterization of the Physical Properties

Surface properties of the concrete such as colour, gloss and contact angle were characterized before and after application of the coatings and during the ageing trials (Figure 1). Colour was also measured after the graffiti application and cleaning cycles. Water vapour permeability and roughness were determined before and after the application of the coatings, and the latter also after performing the last cleaning episode.

$L^*a^*b^*$ colour coordinates were measured with a Minolta CM-700d portable spectrophotometer (Konica Minolta, Tokyo, Japan) and total colour changes determined (ΔE^*) using the following equation $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$ (L^* , lightness; $+a^*$ red, $-a^*$ green; $+b^*$ yellow, $-b^*$ blue). Five (85 mm x 65 mm x 10 mm) and three measurements (75 mm x 35 mm x 10 mm) per slab were taken on naturally and artificially weathered samples respectively, and ten measurements for the evaluation of the efficiency of the graffiti removal (150 mm x 75 mm x 10 mm specimens) all with the help of a stencil to relocate the same measurements points.

Gloss was determined at specular reflection angle of 85 °C with a TQC glossmeter (TQC B.V., Capelle aan den IJssel, The Netherlands). Three (85 mm x 65 mm x 10 mm) and two (75 mm x 35 mm x 10 mm) measurements were taken per slab for the naturally and artificially weathered samples, respectively.

Water repellency of the concrete surfaces was determined by measuring the water contact angle with an IT Concept Tracker (IT Concepts, Lyon, France). Three drops of five microlitres of Millipore MilliQ water were manually deposited onto the surfaces and the Laplace-Young equation was used to fit the drop profile.

Water vapour permeability (δ) was studied using the EN 1015–19 standard [15] (75 mm \times 35 mm \times 10 mm), and the roughness parameter R_z (average distance between the tallest peak and the lowest valley in five sampling cut-offs [16]) was measured with a Surftronic S128 (Taylor Hobson, Leicester, United Kingdom) roughness tester (5 measurements per area of interest) on the 150 mm \times 75 mm \times 10 mm slabs.

The surface of aged concrete slabs was examined with a Leica MZ10 F stereomicroscope (Leica Microsystems, Wetzlar, Germany).

Statistical analysis (one way ANOVA; pairwise multiple comparison), when relevant, was performed with SigmaPlot 13.

3. Results and Discussion

3.1. Characterization of the Surface Properties of Concrete

Prior to exploring the durability of both anti-graffiti coatings, how they affect the physical properties of concrete was studied (Table 2). Neither of the treatments induced perceptible colour variations ($\Delta E^* < 3$), nor significant changes in roughness or in the low water vapour permeability of concrete (respectively $P = 0.141$ and $P = 0.654$; one way ANOVA, $\alpha = 0.05$). The latter parameter, one of the most relevant in assessing the suitability of protective coatings, has been found to be the main drawback of polyurethane and wax anti-graffiti coatings in research studies [17–19].

Table 2. Surface properties of concrete: untreated (UT), treated with a permanent (P) and a sacrificial anti-graffiti coating (S). Standard deviation in parentheses, $n = 3$.

surface parameters	UT	P	S
L^*	68.54 (1.68)	67.06 (0.38)	70.21 (0.32)
a^*	0.13 (0.08)	0.17 (0.11)	0.27 (0.02)
b^*	7.71 (0.40)	8.31 (0.44)	9.26 (0.45)
ΔE^*	-	1.78 (0.33)	1.91 (0.36)
Gloss at 85°	4.02 (1.53)	8.28 (3.83)	17.46 (2.57)
R_z (μm)	23 (4)	21 (4)	18 (3)
contact angle (°)	18.3 (7.6)	104 (3.5)	87.6 (0.7)
$\delta \cdot 10^{-12}$ (kg/ m s Pa)	2.62 (0.21)	2.65 (0.79)	3.12 (0.94)

Changes in surface gloss by the two coatings were visible following Garcia and Malaga [20] who established a 2 unit threshold to perceive variation in gloss. However, only results from the permanent coating are acceptable according to the technical instruction from the German Federal Highway Research Institute [21] for testing anti-graffiti coatings on concrete, which defines a gloss threshold of 10 units.

Water contact angles on the uncoated and coated surfaces were determined since these measurements are related with the surface energy of the substrates that controls the adhesion of graffiti paints. Both treatments made the surface of concrete water repellent, but the permanent anti-graffiti coating (P) was the only one that provided sufficient hydrophobicity (contact angle $> 90^\circ$). With wax (S), the contact angle measurements hardly reached 90° (Table 2). In the literature, it has also been reported [3,4] that permanent anti-graffiti coatings are more hydrophobic than wax-based sacrificial products.

3.2. Ageing of the Anti-Graffiti Coatings

Immediately after the first 500 h of accelerated weathering, the polyurethane coating on the surface of the concrete specimens started to deteriorate. The treatment became dark, slightly patchy, and sticky to the touch. Measurements of the colour coordinates on those surfaces showed that

luminosity (L^*) not only decreased by around 12 units but b^* (yellow hue content) slightly increased (Figure 2,a1). The overall colour variations, ΔE^* , after this first episode were higher than 10 units (Figure 2,a2). With increasing time of exposure to UVB radiation, the progressive removal of the darkened (aged) polyurethane coating was observed (Figure 3,P, unweathered and aged for 1500 and 2000 h), therefore luminosity of the samples rose gradually and ΔE^* decreased accordingly, the latter by an average value of 6 units. As a result of the loss of adhesion of the coating (particularly after 1000 h), gloss caused by the treatment was lost (Figure 4,a). Yang et al. [22] reported the importance of UV radiation and high temperatures (50–60 °C) in the degradation of a fluoro polyurethane topcoat (among other coatings) exposed in a QUV chamber with blistering being the initial ageing sign. Deflorian et al. [12] also pointed out loss of adhesion as a common phenomenon of degradation of coatings in accelerated ageing trials.

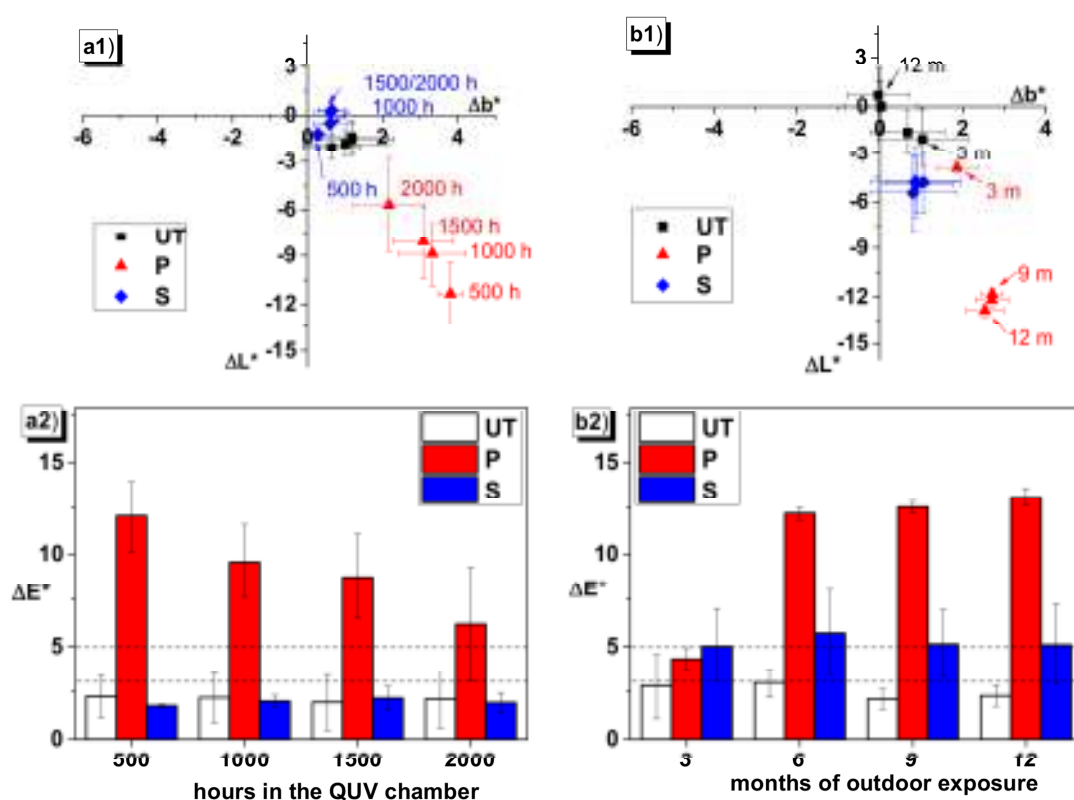


Figure 2. Variation of chromatic coordinates, L^* (luminosity) and b^* (yellow hue) (1), and overall total colour, ΔE^* (2) of surfaces of concrete: untreated (UT), treated with a permanent (P) and a sacrificial anti-graffiti coating (S) after artificial (a) and natural weathering (b).

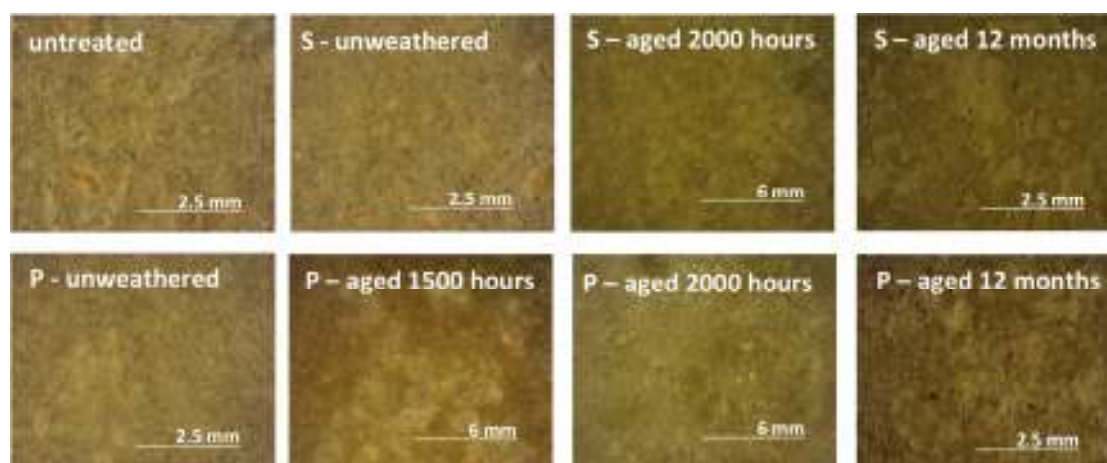


Figure 3. Stereo-microscope images of the surface of concrete: untreated and treated with the permanent (P) and sacrificial (S) anti-graffiti coatings before and after artificial and natural ageing; respectively after 1500 and 2000 h in a QUV chamber and after 12 months of outdoor exposure.

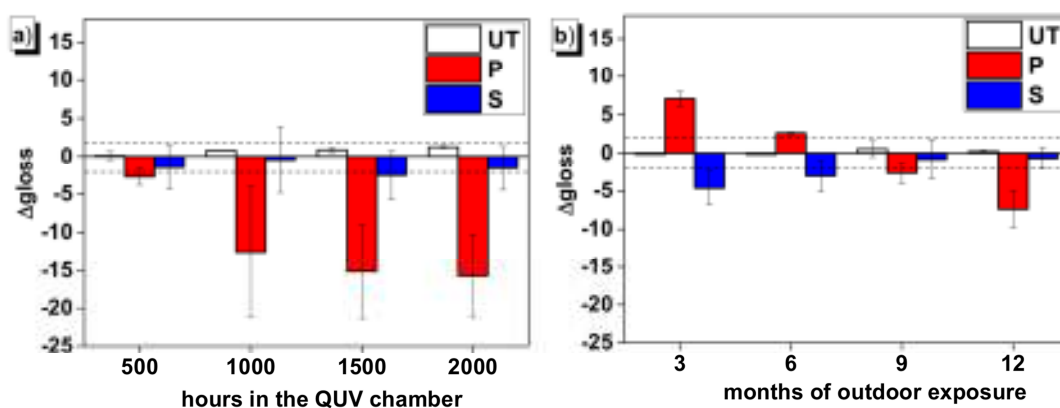


Figure 4. Variation of gloss on the surfaces of concrete: uncoated (UT) and coated with a permanent (P) and a sacrificial (S) anti-graffiti treatment after accelerated (a) and natural (b) weathering.

After only six months of outdoor exposure, the polyurethane also deteriorated by becoming dark and yellow (Figure 2,b1) and experienced the same total colour variations that 500 h of artificial weathering caused (Figure 2,b2; $\Delta E^* = 12$). From 6 to 12 months of outdoor exposure, colour changes were steady and unlike on the artificially aged substrates the already weathered coating kept adhere to concrete (Figure 2,b2 and Figure 3,P aged for 12 months). After an initial rise in gloss over the first 6 months of outdoor exposure, this decreased but to a lower extent than recorded on artificially weathered samples (7 vs 15 gloss units) (Figure 4,b). Therefore, accelerated ageing trial has a more damaging effect than outdoor exposure on the permanent anti-graffiti coating.

Unlike the fluorinated polyurethane coating, the micro wax one did not seem to be affected by intense UVB radiation and condensation cycles between 60 and 50°C (Figure 3,S, unweathered and aged for 2000 h). Changes in colour and gloss were not noticeable to the naked eye; $\Delta E^* < 3$ (Figure 2,a2) and $\Delta \text{gloss} < 2$ (Figure 4,a) after 2000 h of exposure in the chamber. García [23] reported similar good durability results of an aqueous emulsion of polymeric waxes under UV/condensation cycles on a clay brick and a few stones. However under natural conditions, the sacrificial coating got slightly yellow and darker with visible but acceptable overall colour changes (ΔE^* around 5 units) that were stable during the whole year trial (Figure 2,b2). The adhesion of dirt and pollutants could be one reason why the coating became slightly darker [18].

After three months of exposure, a decline in gloss was also recorded ($\Delta \text{gloss} = -4.6$, Figure 4,b); however, with time samples recovered their original gloss. These changes could be the result of the textural changes of the film on top of the concrete that showed some cracks after 9 and 12 months of outdoor exposure (Figure 3,S, aged for 12 months). In fact, Urquhart [24] has reported that wax-based anti-graffiti coatings can develop gloss when rubbed. Since only the natural weathered samples were in direct contact with (rain) water, this may responsible for both textural and gloss changes of the wax.

The surfaces coated with the polyurethane were still water repellent even when the treatment was removed from the surfaces after artificial weathering, since the treatment penetrated into concrete (Figure 5). Hydrophobicity of the sacrificial coated samples after ageing tends to fluctuate around the 90° threshold, as on the unweathered surfaces. However, lower contact angle values were measured after one year of outdoor exposure (average value of 75°), when cracks were observed on the micro wax coating (Figure 5; Figure 3,S, aged for 12 months).

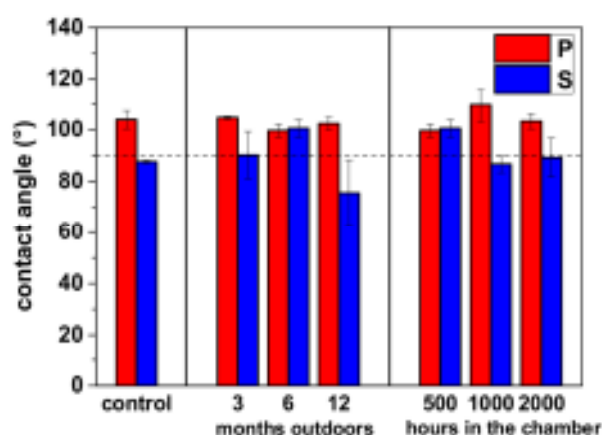


Figure 5. Water contact angle measured on the surface of anti-graffiti coated concrete after artificial and natural weathering. P = permanent treatment, S = Sacrificial treatment, control = unweathered coated surfaces.

3.3 Graffiti Removal

The efficiency of the coatings in facilitating graffiti removal with different cleaning procedures was evaluated before, during and after the ageing trials. Following visual inspection of the samples (Figure 6) and determination of the overall colour variations of the surfaces (ΔE^*) (Figure 7), it can be pointed out that both unweathered anti-graffiti coatings made it easier to clean graffiti on the concrete surface. The sacrificial coating was particularly effective because spray paints and pen were completely removed, despite having measured lower contact angles on the concrete surfaces treated with this product. However, the hot pressure water used to remove both the wax and the graffiti paints eroded the surface of the material as revealed by the increase in the value of the roughness parameter, R_z (Figure 8). Malaga and Muller [4] also reported better cleaning efficiency on concrete and stones coated with a microcrystalline wax than with a permanent coating (fluorinated silane) and attributed these results to the different distribution of the protective products. Even distribution of the wax prevented graffiti from penetrating into the pores of the building materials, unlike the fluorinated coating that left pores less covered with the protective coating.

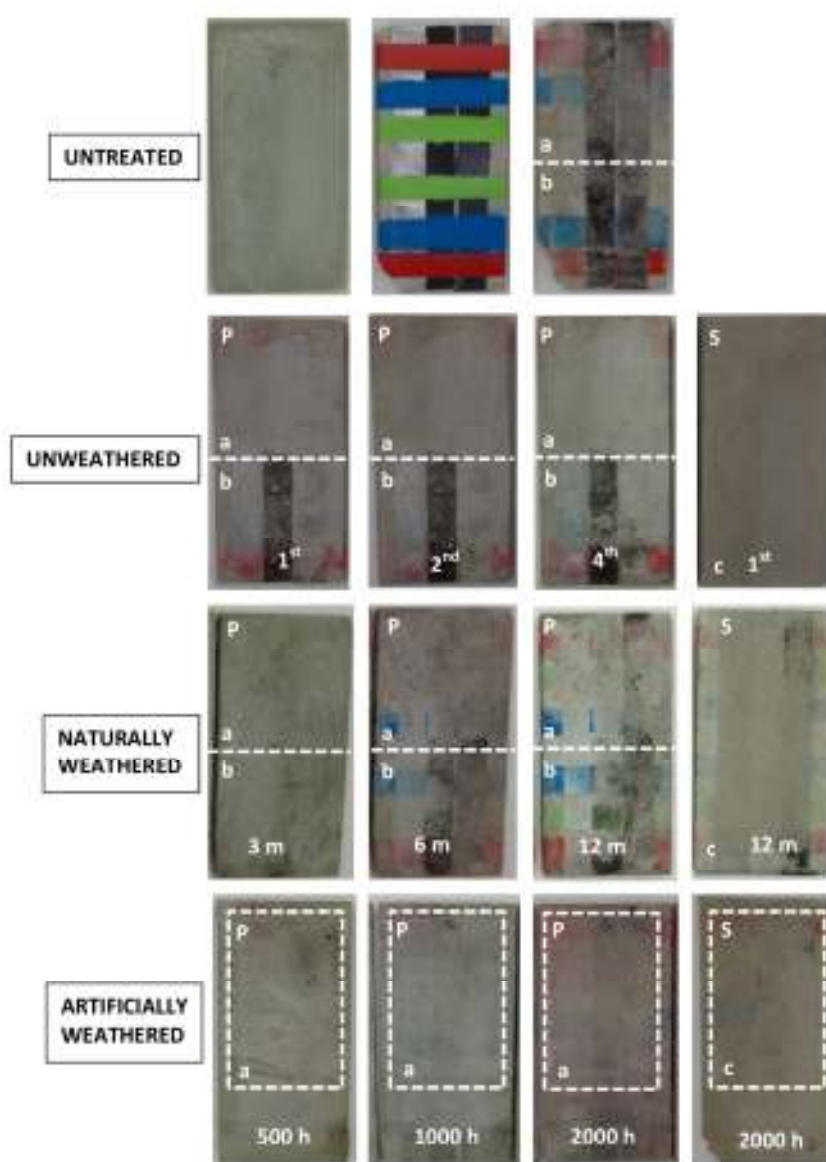


Figure 6. Graffiti removal on untreated concrete, treated with the permanent (P) and sacrificial (S) anti-graffiti coatings before ageing (1st, 2nd and 4th cycles) and after natural (3, 6 and 12 months) and artificial weathering (500, 1000 and 2000 h). Cleaning methods: (a) detergent and brush; (b) detergent and high pressurized water spray; (c) high pressurized hot water spray.

On the surfaces treated with the permanent coating, the results of graffiti removal were satisfactory when cleaned with detergent and brush. Small residues of paint were observed after consecutive painting-cleaning cycles (Figure 6), but most of the paint was removed (ΔE^* around five units are visible but acceptable, Figure 7,a) without damaging the substrate (no changes in roughness) (Figure 8). On the contrary, detergent and pressure water not only were less effective to erase graffiti paints, as silver, red and black (pen) stripes were clearly visible right after the first cleaning episode (Figure 6). Moreover, this cleaning procedure damaged both the anti-graffiti protection and the concrete specimens by removing partially the former and by increasing the roughness of the surfaces (Figure 8) leaving them more vulnerable to successive painting and cleaning cycles as shown by the increase in ΔE^* (Figure 7).

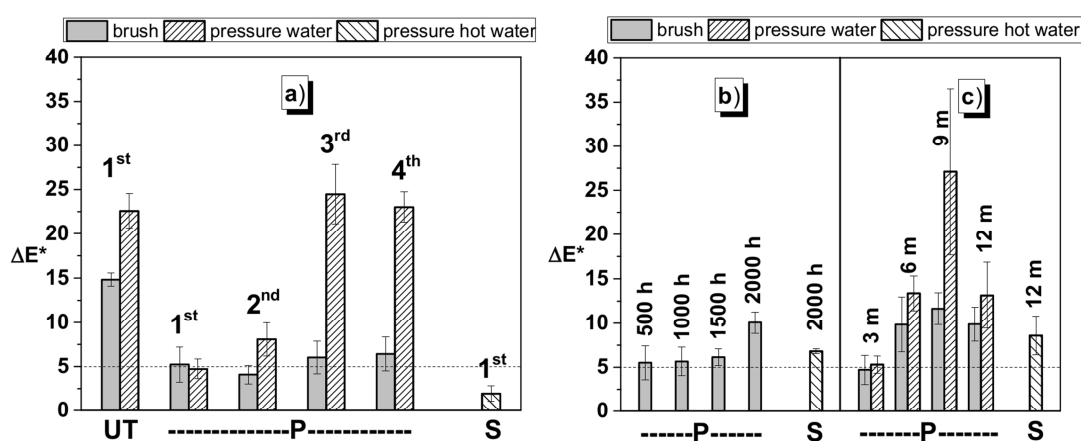


Figure 7. Colour changes on the surface of anti-graffiti-coated concrete after graffiti removal on the originally painted areas: (a) before weathering, (b) after artificial and (c) after natural weathering. P = permanent anti-graffiti coating, S = sacrificial coating, UT = without anti-graffiti.

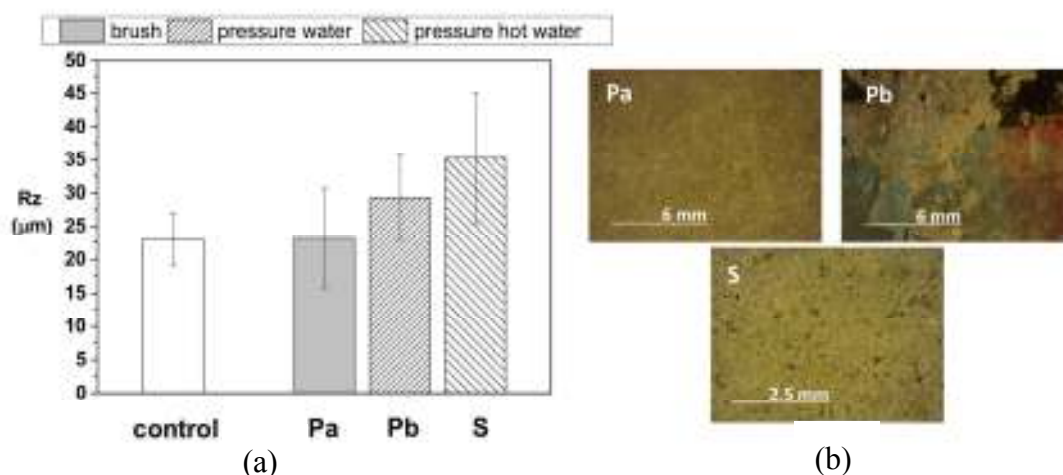


Figure 8. (a) Roughness (R_z , μm) of the anti-graffiti coated samples (P = permanent coating and S = sacrificial coating) after different cleaning graffiti procedures with (Pa) detergent and brush, (Pb) detergent and pressure water and (S) hot pressure water. Four painting-cleaning cycles on Pa and Pb and one on S coated samples. Control = untreated and unpainted concrete. (b) Stereomicroscope images of the anti-graffiti coated surfaces on which R_z was measured after removal of graffiti.

After weathering, the sacrificial coating lost some of its cleaning efficiency. Colour residues were slightly more visible (Figure 6) on the naturally weathered than on the artificially aged slabs ($\Delta E^* = 7$ vs. $\Delta E^* = 8.5$, Figure 7) in agreement with the degradation (cracking) of the wax after one year of outdoor exposure.

In contrast, the permanent coating that weathered heavily under both weathering tests largely retains its cleaning efficiency during the first three months of outdoor exposure and 1500 h in the chamber (ΔE^* ranged between 5 and 6, Figure 7). As pointed out above, even when the treatment is weathered and removed from the surfaces, concrete was still water-repellent (Figure 5). However, after the completion of both tests, the cleaning efficiency is reduced when compared with the unweathered coatings. Paint became smudged on the artificially weathered samples, whereas remains of solid colour were observed on the naturally aged slabs, particularly when cleaned with pressure water where the stripes are more noticeable (Figure 6).

4. Conclusions

The ability of two commercial anti-graffiti products in facilitating graffiti removal on concrete slabs diminished after being naturally and artificially aged.

The fluorinated polyurethane (permanent coating) became weathered after 500 h in a chamber with UVB radiation and after six months of outdoor exposure in the south of England. The coating yellowed and darkened and eventually lost its adhesion under accelerated conditions, while surfaces still remained water repellent. Cleaning with pressurized water spray also partially removed this anti-graffiti protection.

The sacrificial coating also deteriorated under natural environmental conditions by initially getting slightly dark and finally by losing part of its water repellency due to cracking. It seemed that artificial ageing with UVB radiation did not affect its integrity; however, in the end graffiti removal was also less efficient on both types of weathered surfaces than on the unweathered ones.

The different responses of both anti-graffiti products to accelerated and natural ageing trials reveal the necessity of running both types of tests when assessing the weathering resistance of anti-graffiti coatings.

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Conflicts of Interest: The authors declare no conflict of interest.

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