





Influence of the Distribution of a Spray Paint on the Efficacy of Anti-Graffiti Coatings on a Highly Porous Natural Stone Material

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Abstract: Graffiti on facades often has a heavy impact in social and economic terms, particularly when historical and artistic artefacts are affected. To limit the damages to the surfaces, preventive plans are implemented and anti-graffiti coatings are used as a protective measure. In this study, the distribution of a spray paint inside a highly porous stone, with and without anti-graffiti protection, was investigated. Two commercial sacrificial anti-graffiti systems were used and an acrylic-based paint was applied as staining agent. Environmental scanning electron microscopy and energy-dispersive X-ray spectroscopy (EDS) microanalysis were performed to characterise, from the morphological and chemical point of view, the anti-graffiti coatings and the paint. Maps of the main elements were acquired to locate the different products inside the stone. Chemical removers were used to clean the stained surfaces, then the effectiveness of the cleaning was assessed by visual observations and colour measurements, as well as on the basis of percentage of residual stain. The obtained results highlighted that the anti-graffiti efficacy strongly depended on the characteristics of the applied coating. This latter usually acted as a barrier, but good results were obtained only where the stain did not remain as a separate layer, but penetrated the protective coating. Microcracks in the anti-graffiti coating were action.

Keywords: stone protection; anti-graffiti efficacy; coating characterisation; ESEM-EDS; colour measurements; chemical cleaning; Lecce stone; acrylic-based paint

1. Introduction

In recent years, graffiti is an ever-growing phenomenon; writings and drawings are found on many different surfaces, especially in urban contexts. Although these writings are sometimes regarded as a form of art (the so-called "street art") [1], they always have great aesthetic impacts on buildings. In particular, negative effects are undoubtedly observed on monuments and historic buildings. Besides damages from the aesthetic point of view, high maintenance costs and additional threats, both due to removal interventions, have to be expected. The application of anti-graffiti coatings on the surfaces is used as a preventive measure to try to contain these problems.

Many tools, such as spray cans, felt-tip markers, ballpoint pens, chalk, crayons, and lipstick are used to draw the graffiti. Spray paints are the most widely applied because they can be quickly and easily applied to any type of substrate [2]. Their chemical composition can be highly varied, but they always contain [2,3]: Pigments, that give the colour; binders, as a matrix, to provide the adhesion to the painted surface; and solvents, to promote the spreading. Other substances can be present in the formulation—usually, plasticizing agents, to improve the adherence, and propellants, to produce the jet of the paint mixture [4].

The anti-graffiti coatings, by generating a repellent surface, act as a barrier that prevent the contact between paints/inks and the substrate and facilitate its ready cleaning. Two major kinds of products are usually used for protecting surfaces against graffiti: Sacrificial or permanent systems. The sacrificial products are removed together with the paint and they need to be reapplied; the permanent systems are not taken away during the cleaning process and they can withstand several cleaning cycles. Products used to provide an anti-graffiti barrier to stone surfaces are based on waxes [5], polyurethane [6–8], polysaccharides [5], silicon-based resins [5,9–13], and fluorinated polymers [5,8,14–17]; recently, organic–inorganic hybrids [18–21], nanocomposite materials [22–24], and fluorosurfactants [25] have been also proposed as anti-graffiti systems.

Usually, the synthesis process, chemical characterisation, and properties after application on inert substrates, such as glass or Teflon, are firstly assessed. However, in order to use the anti-graffiti products for different applications in the field, the performances and durability of these materials as a coating have been investigated on several stone substrates (natural stone, cement, mortar, brick, concrete) [26–34] or on metallic surfaces [14,35,36]. Nevertheless, studies dealing with the effects on highly porous stone materials are still limited in the current literature, although in these materials the penetration of the staining agent can be deeper and a good cleaning can be hampered. In addition, the effects of the anti-graffiti products on the substrate's properties have been investigated, while the interactions between the protective coatings and dirt have been scarcely examined, although this latter aspect could help in tuning the anti-graffiti formulations and the cleaning procedures as well.

This work aims to analyse the distribution of a spray paint inside a highly porous natural stone material with and without anti-graffiti protection. The distribution of the paint was examined in terms of accumulation as a superficial layer, penetration into the protective coating, and staining of the internal parts of the stone. The influence of the paint penetration on the removal of the dirt was investigated. Two commercial sacrificial anti-graffiti systems were tested on "Lecce stone", a calcarenite having open porosity of 42%; an orange acrylic-based paint was used as staining agent. The morphological features of the anti-graffiti coating and the chemical characterisation of the different layers covering the stone surface were carried out. Commercial chemical removers were used to clean the stained surfaces, then the effectiveness of the cleaning was assessed by colour measurements and visual inspection. A method to assess the effectiveness of the cleaning procedures, on the basis of residual stain found on the surfaces after the removal of the paint, was also proposed.

The anti-graffiti coatings prevented the penetration of the paint into the porous substrate, thus facilitating its cleaning. The efficacy strongly depended on the characteristics of the coating, which acted as a barrier. Better results were obtained only where the coating incorporated the stain, while microcracks in the anti-graffiti coating were able to nullify the protective action.

2. Materials and Methods

2.1. Stone Material, Anti-Graffiti Systems, and Spray Paint

The anti-graffiti systems were tested on "Lecce stone", a highly porous calcarenite widely employed as construction material for monuments and buildings in southeastern Italy. This stone mainly contains calcite, along with very small quantities of clay and other non-carbonate minerals [37]; the porosity ranges from 30% to 45% [37–40]. The stone material used in this study exhibited a porosity of 42%, with pore-size distribution mainly between 0.3 and 10 μ m, as analysed by mercury-intrusion porosimetry [41]. "Lecce stone", because of these characteristics, can be considered as representative of the porous materials used for historic and civil buildings in the Mediterranean basin.

Two commercial systems, suggested for reversible protection of porous and nonporous stone materials against spray-painted graffiti, were investigated.

The first product, AG1 (supplied by Mapei S.p.A., Milan, Italy), was a water emulsion of polymer waxes. According to the information detailed in the technical sheet, quantities ranging from 30 to 150 g/m^2 can be directly applied on clean and dry stone surfaces.

The second anti-graffiti system, AG2 (by GEAL-Bel Chimica Srl, Agliana (PT), Italy), was based on polymer waxes and acrylic-fluorinated resins. Preliminary application (from 125 to 170 mL per m²) of a primer (AG2a), consisting of acrylic-fluorinated copolymers in water emulsion, is suggested to enhance the adhesion of the anti-graffiti coating to the stone surface. The subsequent treatment is performed with a water emulsion of polymer waxes added to acrylic-fluorinated resins (AG2b), employing 65–125 mL per m², without any dilution.

In all the previous cases, the appropriate amount of product to be used depends on the porosity of the substrate.

The suppliers suggest the cleaning by means of hot water at about 80 °C and a stiff-bristled brush first. To eliminate residual stains, they recommend commercial removers specifically tailored for the cleaning of stained surfaces protected with the anti-graffiti systems. A ready-to-use gelatinous product, which consists of a glycol ether-based solution (R1), is suggested as graffiti remover for surfaces treated with AG1. This remover can be applied by brush, it acts within 10 min, and it can be easily removed with water. The R2 remover, ready-to-use, is a mixture of surfactants and solvents and it can be applied by either brush or spraying. A few minutes after the application, the remover has to be emulsified with water; then, it can be removed with a stiff-bristled brush, rinsing with water.

A commercial aerosol spray paint (Briolux Spray, CP Italia, Bari, Italy), orange-coloured (RAL code 2005) and provided in a pressurised can, was selected as the staining agent. A methyl-methacrylate resin is the main component of the applied paint, as found by Fourier-transform infrared spectroscopy (FTIR) in a previous study [42]. In fact, acrylic resins are often used as binders in commercial spray paint [2].

Information about the anti-graffiti systems, the removers, and the spray paint are listed in Table 1. For commercial reasons, additional details on the chemical composition of these products are not available.

Product	Chemical Composition ¹	Density ¹ (g/m ³)	pH ¹	T_g^2 (°C)	T_m^2 (°C)
AG1	Water emulsion of polymer waxes	0.980	9–10.5	41 ± 2	65 ± 4
AG2a	Acrylic-fluorinated copolymers in water emulsion	1.008	5	53 ± 2	72 ± 2
AG2b	Water emulsion of polymer waxes added to acrylic-fluorinated resins	1.002	7	35 ± 1	58 ± 1
R1	Dipropyleneglycol methyl ether (>90%)	0.050	6–8	Not applicable	Not applicable
R2	Mixture of surfactants and solvents	0.980	7	Not applicable	Not applicable
Paint	Methyl-methacrylate resin and pigments	_	_	> 100	_

Table 1. Chemical composition and main details of the used products.

¹ Data from technical sheets; ² Glass transition temperature (T_g) and melting temperature (T_m) measured by DSC (differential scanning calorimetry) scans from 10 °C to 100 °C [42].

2.2. Preparation of the Stone Samples and Treatments

Prismatic stone specimens, with dimensions of $5 \times 5 \times 1$ cm³, were cut from a quarry block. According to UNI10921 standard protocol [43], the samples were smoothed with abrasive paper (180-grit silicon carbide), cleaned with a soft brush, and washed with deionised water in order to remove dust deposits. The stone specimens were completely dried in oven at 60 °C, until the dry weight was achieved, and stored in a desiccator with silica gel (relative humidity (RH) 15%) at 23 ± 2 °C.

Sets of 5 stone samples were subjected to the procedures detailed below and summarised in Table 2.

Before the application of the anti-graffiti products, the stone specimens were kept for 24 h in laboratory conditions (at 23 ± 2 °C and $50 \pm 5\%$ RH).

Samples	Protection	Staining	Cleaning
AG1	100 g/m ² AG1 anti-graffiti (by brush)	Orange acrylic paint (2 coats by spraying)	R1 remover 15 min + brushing under running tap water at 60 °C (repeated twice)
AG0-1	_	Orange acrylic paint (2 coats by spraying)	R1 remover 15 min + brushing under running tap water at 60 °C (repeated twice)
AG2	140 g/m ² AG2a primer (by brush) +24 h in laboratory +80 g/m ² AG2b anti-graffiti (by brush)	Orange acrylic paint (2 coats by spraying)	R2 remover 15 min + brushing under running tap water at 60 °C (repeated twice)
AG0-2	_	Orange acrylic paint (2 coats by spraying)	R2 remover 15 min + brushing under running tap water at 60 °C (repeated twice)

Table 2. Procedures performed on the stone samples.

Taking into account the porosity of the stone material and the recommendations reported in the technical sheets, the following amounts of products were applied by brush: 100 g/m^2 of the AG1 anti-graffiti; 140 g/m² of the AG2a primer, then, after 24 h, 80 g/m² of the AG2b product. Both the anti-graffiti systems were applied on 5 samples. Only one $5 \times 5 \text{ cm}^2$ side of each specimen was treated and the quantity of anti-graffiti product to apply was controlled by weight measurements, using an analytical balance (model BP 2215, Sartorius AG, Göttingen, Germany) with an accuracy of $\pm 0.1 \text{ mg}$.

The brushing procedure was preferred to simulate the methodology of application more commonly used in field conditions.

At the end of the treatments, all the samples were kept in the laboratory for 8 months. During this stage, the average values of temperature and humidity were 25 ± 2 °C and $45 \pm 5\%$ RH, respectively.

After this period, the staining with the spray paint was carried out on the protected stone samples. Two coats of paint were sprayed on specimens placed on a 45° tilted surface. The distance between the sample surface and the nebulizer was about 15 cm. Paint deposition on the lateral sides of the specimens was avoided by protecting these areas with a polyethylene terephthalate (PET) film. The same staining procedure was performed also on 10 untreated stone specimens (AG0) to compare the properties of the stained stone in the absence of protective coatings. After the application of the paint, the samples were stored for 3 days in the laboratory at 23 ± 2 °C and 50 ± 5 % RH.

Finally, the removal of the sprayed paint was performed 15 days after its application using the recommended chemical removers. The cleaning under hot water, suggested by the manufacturers as the first cleaning action, was not carried out, because a previous study [43] highlighted that this procedure was ineffective on the "Lecce stone" surfaces protected with either AG1 or AG2 system.

The AG1 samples were cleaned with the R1 remover, while the R2 remover was employed to clean the AG2 samples. Both the chemical removers were tested also on the stained unprotected surfaces (5 samples treated with AG0-1 were cleaned with R1, and 5 samples treated with AG0-2 were cleaned with R2). The removers were applied by brush and rinsed after 15 min using running tap water at 60 °C and a brush. This procedure was repeated twice; the samples were then dried and stored for 10 days in the laboratory at 23 ± 2 °C and $50 \pm 5\%$ RH.

The environmental conditions during both the treatments and the storing were monitored by means of a thermo-hygrometer (mod. EMR812HGN, Oregon Scientific, Kowloon, Hong Kong), that can collect temperature data in a range from -50 °C to 70 °C (with an accuracy of ± 0.1 °C) and relative humidity data in a range from 2% to 98% (with a precision of $\pm 1\%$).

2.3. Analytical Investigations

Morphological observations by environmental scanning electron microscopy (ESEM, mod. Philips XL30, FEI Company, Eindhoven, The Netherlands) were performed in order to study the distribution of the products. Fresh fractured surfaces of specimens, without metallisation, were investigated. The observations were carried out in low-vacuum mode (0.6–3.2 Torr, 25 kV); the pressure values inside the ESEM sample chamber were set in order to optimise the observation of each sample. Both secondary (GSE) and backscattered (BSE) electron detectors were used. Energy-dispersive X-ray spectroscopy (EDS), coupled to the ESEM microscope, was applied to perform elemental analyses. Qualitative spectra on spots (live time 30 s) were collected on the surfaces of the specimens; the paint alone was sprayed on an aluminium stub and analysed after solvent evaporation. Distribution maps of the elements (matrix 256×220 , dwell 200 ms, 25 kV) were acquired on the same fractured surfaces observed through the ESEM. The EDS spectra and maps were processed using the software Genesis Spectrum (version 6.2, EDAX Inc., Mahwah, NJ, USA).

Colour measurements [44] were performed with a tristimulus colorimeter (mod. Chroma Meter CR300 Konica Minolta Inc., Tokyo, Japan), using CIE standard illuminant C, in order to evaluate the colour variations due to the staining and to the subsequent cleaning. Sets of 5 samples for each treatment were investigated. Ten measurements were performed on each specimen and the colorimeter was recalibrated to a calibration plate at the start of the measurement session. The colour changes (ΔE^*_{ab}) were calculated through the $L^*a^*b^*$ (CIE 1976) [45] system, using Equation (1):

$$\Delta E^*_{ab} = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2} \tag{1}$$

where L^* is the lightness/darkness coordinate, a^* the red/green coordinate (+ a^* indicating red and $-a^*$ green), and b^* the yellow/blue coordinate (+ b^* indicating yellow and $-b^*$ blue).

All the colour variations were evaluated by comparison with the untreated surfaces, using the averaged values of L^* , a^* , and b^* for each sample.

In addition, the residual stain (RS) after the cleaning procedure was evaluated as a percentage by Equation (2):

$$RS = [(\Delta E^*_{ab})c/\Delta E^*_{ab})s] \times 100$$
⁽²⁾

where (ΔE^*_{ab}) c is the colour variation of the cleaned surfaces and (ΔE^*_{ab}) s is the colour variation of the stained surfaces.

3. Results and Discussion

3.1. Morphological Characteristics and Elemental Microanalysis of the Coatings

The morphological appearance of the surfaces by ESEM observation is shown in Figure 1.

The AG1 coating produced a thick film and the morphological features of the stone were completely hidden. It is of note that some small cracks (highlighted in Figure 1b) were observed in the coating. This result was unexpected, since cracks are seldom seen in wax-based coatings. However, some studies described defects in the films where waxes as water emulsions were applied [3,46,47]. The AG2a product yielded a very thin coating; in fact, high magnifications were necessary to perceive this layer. The application of AG2b gave, as a whole, a thicker coating, even if the morphological features of the stone support were still easily recognised.

The EDS spectra acquired on the untreated and treated stone surfaces are reported in Figure 2.

The application of AG1 caused a strong increase of the carbon content on the surface (Figure 2b). At the same time, a noticeable reduction of the signal due to the calcium, which can be related only to the calcite of the stone material (Figure 2a), was measured. Both these results confirmed the presence of a thick wax-based coating on the investigated surface. The EDS spectra acquired in several points of the AG1 samples were always comparable, even where cracks were observed through the ESEM. This behaviour suggested that the stone surface was uniformly covered, in spite of the defects in the AG1 coating.



Figure 1. Environmental scanning electron microscopy (ESEM) images: (**a**) untreated stone surface; (**b**) stone surface treated with AG1 (crack in the coating is highlighted); (**c**) stone surface treated with AG2a; (**d**) stone surface treated with AG2(a + b).

The microanalysis performed on the stone samples treated with AG2a revealed the presence of fluorine (Figure 2c), as expected, because of the fluorinated nature of the anti-graffiti primer. In this case, the signal of Ca was reduced just to a limited extent, as a consequence of a very thin coating on the surface. After the subsequent treatment with AG2b, the peak due to the Ca decreased further (Figure 2d), giving evidence of a thicker film on the stone. However, the Ca peak was high enough to indicate that the anti-graffiti products did not accumulate on the surface. In comparing these surfaces to the previous ones (i.e., the AG2a samples), the content in C increased, while the amount of F decreased. In fact, the AG2b product mainly contained waxes, with limited quantities of fluorinated polymers.

The EDS spectra acquired on the paint sprayed on an aluminium stub revealed a very high content of C (Figure 3), in accordance with the presence of the methyl-methacrylate binder as the main component. Bismuth, along with traces of titanium and vanadium, was also found; these elements can be ascribed to pigments and/or to additives in the paint formulation, but further identification of the ingredients in the paint was not possible.



Figure 2. Energy-dispersive X-ray spectroscopy (EDS) spectra: (**a**) untreated stone surface; (**b**) stone surface treated with AG1; (**c**) stone surface treated with AG2a; (**d**) stone surface treated with AG2(a + b).



Figure 3. EDS spectrum acquired on the paint sprayed on aluminium stub.

Additionally, the EDS microanalysis allowed identification of the typifying elements of each coating (listed in Table 3, along with the energy values of the related peaks). All these elements were subsequently used as markers to recognise the presence of both the anti-graffiti products and the paint in the stained samples. Therefore, the stone was identified through the calcium; AG1 and AG2b were found by searching for high contents of carbon; the fluorine was used to recognise AG2a; the bismuth allowed distinguishing of the paint.

Coating	Marker Elements ¹	Characteristic X-ray Line Energies (keV)
_ 2	Ca	3.69; 4.01
AG1	С	0.28
AG2a	F	0.67
AG2b	С	0.28
Paint	Bi	2.42

Table 3. Typifying elements used as marker elements of the coatings on stone and the energy values of the related peaks in the EDS spectra.

¹ Results from the EDS spectra; ² Spectra acquired on the untreated stone.

3.2. Distribution of the Paint

The distribution of the paint was examined in terms of accumulation as a superficial layer, penetration into the protective coating, and staining of the internal parts of the stone. The observations of the fractured surfaces of the stained samples revealed different behaviours, depending on the surface's treatment performed before the application of the spray paint.

In the samples treated with AG1, after the staining, three separate layers were observed (Figure 4a). The most superficial level can be ascribed to the paint because the numerous bright points in this layer matched the Bi in the elemental maps (Figure 4c). Under the paint, a homogeneous coating only made of C accounted for the presence of a separate layer: that is, the AG1 coating. The average thickness of this film was around 5 μ m and no clear evidence of the penetration of the anti-graffiti product into the stone was observed. In fact, in examining the distribution maps (Figure 4c), high contents in C were not found where Ca was detected. The anti-graffiti product mainly remained on the surface in spite of the high porosity of the substrate, which usually enhances the penetration of both the protective product and the paint [28,32]. However, it is worth mentioning that, in some points, the brighter components, due to the Bi in the paint, were found also below the surface (Figure 4b). Near these areas, the protective coating seemed lacking and, as a consequence, the staining agent easily penetrated into the stone. It is likely that this latter phenomenon took place where the anti-graffiti coating was fissured (Figure 1b).



Figure 4. Fresh fractured surface of sample treated with AG1 after the staining: (**a**,**b**) ESEM images; (**c**) distribution maps of the elements acquired in the area showed in (**a**).

In the stained samples previously treated with AG2, a uniform superficial layer coated the stone substrate (Figure 5a). In this case, it was difficult to distinguish the different products (i.e., AG2a, AG2b, and the paint) in separate layers. Only the presence of a very thin level of F (Figure 5b) revealed where the AG2a coating was located. The obtained results can support the hypothesis, made in a previous study [42], that the paint penetrated the AG2b coating, as a consequence of the high free volume fraction of this polymer film.

Finally, the stained untreated specimens were investigated. In these samples, since no barrier was applied on the stone surface, the paint easily permeated the substrate (Figure 6a). The Bi, and consequently the paint, was found not only on the superficial layer, but also inside the stone (Figure 6b). The penetration depth was not uniform, but the paint was often detected over 20 µm below the surface.



Figure 5. Fresh fractured surface of sample treated with AG2 after the staining: (**a**) ESEM image; (**b**) distribution maps of the elements.



Figure 6. Fresh fractured surface of untreated sample (AG0) after the staining: (**a**) ESEM image; (**b**) distribution maps of the elements.

3.3. Efficacy of the Removal Procedure

Negligible changes in the aspect of the stone surfaces were obtained after the anti-graffiti treatments, as discussed in our previous studies [42,48]. The colour variations measured after the application of the protective coatings were very low. A $\Delta E^*_{ab} = 1.08$ was calculated for the AG1 samples, while $\Delta E^*_{ab} = 0.28$ for the AG2 specimens. In both cases, the colour differences were imperceptible by the naked eye.

After the paint application, naturally, the aspect of the stained surfaces dramatically changed (Figure 7e–h). This outcome was further corroborated by colour measurements since extremely high ΔE^*_{ab} values were calculated. Dissimilar colour variations were measured in the protected samples (Figure 7e,g), suggesting a different interaction between the protective coatings and the paint.



Figure 7. The stone samples before the treatments (**a**–**d**); after both the anti-graffiti treatment and the staining (**e**–**h**); and after the cleaning procedure (**i**–**l**). The colour variations by comparison with the untreated surfaces are reported.

The cleaning procedure yielded an incomplete removal of the paint from the surfaces previously treated with AG1. The unsuccessful result, already clear to the visual inspection by the naked eye (Figure 7i–l), left the ΔE^*_{ab} values very high. Although the non-impregnating anti-graffiti products usually show a better efficacy [26], in the samples treated with AG1, the presence of the applied product only on the surface did not guarantee satisfactory results, as already found in other highly porous materials [28]. The paint was the only component in the most external layer, while the chemical remover was likely formulated to affect just the protective coating. In fact, the same chemical remover was ineffective on the paint alone (Figure 7j). Additionally, the paint penetrated into the stone (Figure 4b), through the cracks in the coating. Both these factors negatively influenced the stain removal.

On the contrary, the removal of the paint from the AG2 samples was quite successful (Figure 7k). In this case, the incorporation of the stain into the protective coating probably enhanced the anti-graffiti

effectiveness. The application of a primer coating (i.e., the AG2a coating) avoided the penetration of the stain within the porous structure of the stone, making possible a more effective cleaning.

The removal of the paint from the unprotected samples completely failed. Similar and very high ΔE^*_{ab} values were obtained for the two sets of specimens. Actually, the fact that most of the paint still remained on the surfaces was already obvious by visual inspection (Figure 7j,l). In the unprotected samples, the presence of paint deep inside the surface undoubtedly restricted the efficacy of the cleaning. On the other hand, other studies showed that the unprotected stone surfaces frequently retained paint residues even when the cleaning achieved satisfactory results to the macroscopic observation [49].

A residual stain (RS) of 45.20% was calculated for the AG1 samples, while RS was 9.77% for the AG2 specimens (Figure 8a). RS around 70% were found in the unprotected samples.

For each set of samples, the RS values were also reported as a function of the related ΔE^*_{ab} (Figure 8b), and a trend line was drawn. According to a classification followed by other researchers [27,49,50], when the ΔE^*_{ab} values are lower than 5, the colour changes, and the cleaning as well, are adequate; as the ΔE^*_{ab} values increase up to 10, the colour variations can be seen but they are still tolerable; ΔE^*_{ab} values higher than 10 produce clearly visible colour changes that cannot be accepted. Taking into account the results and the previous considerations, RS values below 10% can be judged acceptable; RS between 10% and 20% are not optimal, but tolerable; RS of 20% is the upper threshold. Above this latter value, the cleaning procedure does not give suitable results.



Figure 8. Residual stain (as defined in Equation (2)) on the surfaces after the cleaning procedures: (a) with respect to the previous treatment; (b) as a function of ΔE^*_{ab} (the standard deviations are indicated). In (b), the green lines define the optimal cleaning, the red lines indicate the threshold limit for suitable cleaning).

4. Conclusions

In this study, two commercial sacrificial anti-graffiti systems were applied on a highly porous stone with an open porosity of 42%. The protective products, both provided as a water emulsion, were chosen to try to fulfil the requirement of low environmental impact of the treatments and to apply safety and health practices. The distribution of an acrylic spray paint in protected and untreated stone was investigated, as well as the cleaning of these surfaces.

The obtained results highlighted that the distribution of the paint, examined in terms of accumulation as a superficial layer, penetration into the protective coating, and/or infiltration inside the stone, strongly influenced the removal efficacy.

As expected, the paint dramatically changed the aspect of the stained surfaces, but dissimilar, even if extremely high, ΔE^*_{ab} values for the protected samples suggested different interactions between the two protective coatings and the stain. Where the applied coatings, working as a barrier, isolated the

stone material from the spray paint, effectiveness against graffiti damages was observed. Conversely, the stained unprotected surfaces still exhibited high ΔE^*_{ab} and significant residual stain (about 70%) after the cleaning. The penetration of the paint into the substrate, as a consequence of the high porosity of the stone, strongly influenced the cleaning efficacy, because the stain inside the pores was very difficult to remove. Also, microcracks affecting the anti-graffiti coating caused the penetration of the stain into the stone, thus its cleaning was unsuccessful. The presence of a thick protective barrier, which covers and completely hides the stone, as found by the ESEM observation and the EDS elemental analysis, did not guarantee anti-graffiti protection. In fact, better results were obtained where a thinner polymer coating, which incorporated the stain, was found on the surface. In this case, after the cleaning procedure, the ΔE^*_{ab} (around 5) was tolerable and the percentage of residual stain (10%) was low.

The knowledge of both the treatment performances and the distribution of the staining agent can give important feedback for the tuning and/or the correction of products aimed at ensuring optimal and cost-effective anti-graffiti protection.

In addition, the proposed method for estimation of the residual stain can be helpful in the assessment of the graffiti cleaning efficacy on the basis of percent of paint/marker removed, as indicated in the current standards and in many studies in the literature. The evaluation of the colour changes also allowed to indicate threshold values for the residual stain after the cleaning. A rate below 10% can be indicative of acceptable cleaning actions, while residues over 20% give evidence of unsuccessful results.

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