Study of the effectiveness of *graffiti* removal techniques and anti-*graffiti* coatings in porous materials

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1 Introduction and objectives

The presence of *graffiti* in buildings facades is a problem that affects many buildings in urban areas and needs some attention. This type of manifestation is found in several buildings such as schools, private residences, train building stations, train wagons and street furniture including traffic lights and garbage bins. However, illegal *graffiti* that is not considered art by the general public can disfigure and devalue the image of the buildings [1, 2, 3].

Graffiti removal is an expensive process that sometimes is not particularly effective. Cleaning *graffiti* from porous materials such as mortar and natural porous stone is very difficult since the penetration of the pigments is usually deep [2]. Additionally, the use of inadequate cleaning methods may damage the coatings materials. The high costs associated with *graffiti* removal and their great aesthetic impacts on building facades justify that new preventive and curative methods are developed to solve this problem [4].

The use of anti-*graffiti* products can work very well, since it facilitates cleaning the *graffiti,* assuming an important role in the maintenance of buildings and contributing to an increased durability of the materials [2, 4, 5]. These anti-*graffiti* products form a protective barrier against the *graffiti* and facilitate their removal by generating a water- and oil-repellent surface that prevents the intrusion of paint in porous surfaces of coating materials. Commonly there are two main groups of anti-*graffiti* products in the market: sacrificial and permanent [4, 5]. The sacrificial are eliminated during the cleaning process together with the *graffiti* paint, and have to be reapplied after the removal process [4, 6]. Permanent anti-*graffiti* are not dissolved with the products used to clean the *graffiti* and therefore can withstand the repeated cleaning cycles [4]. The majority of the studied products are based on waxes, polyurethanes, fluorinated polymers, silicone resins and, recently, fluoroalkylsiloxane [2, 4, 6]. Since the waxes and polyurethanes have a limited durability and may induce substantial decrease in water vapour permeability, other products have been studied such as fluoroalkylsiloxane and organic-inorganic hybrid products. These products have demonstrated a good performance in porous materials due to their capacity to generate a low surface energy preventing the absorption of water and paint and because they allow diffusion of water vapour [4, 7].

The majority of studies performed have investigated the application of these products on dense stones, whereas only few studies in literature are devoted to porous materials more used in Portugal, such as mortar, painted mortar and porous stone [6, 7, 8]. According to the latest Census 2011, 84% of buildings in Portugal are coated with traditional render or crushed marble mortar and 11.6% with stone [8].

This study intends to evaluate the effect produced by the application of three/four commercial anti-*graffiti* products (two sacrificial and one permanent) on three substrates (stone, mortar and painted mortar), in order to determine their suitability for the protection of these porous materials. Firstly, the effectiveness of the four anti-graffiti products (two permanent and two sacrificial) on the cleaning process was evaluated. In a second stage of the study, modifications induced by three of these products in the physical properties of the substrates (water repellence, water vapour permeability, porosity and colour) were assessed.

2 Experimental program

2.1 Materials

2.1.1 Anti-*graffiti* products

In this experimental work, four commercial anti-*graffiti* were studied: two sacrificial products and two permanent products. The chemical characteristics of the products are shown in the Table 1. According to the technical sheets, three of these products can be applied on porous materials (S_{silox}; S_{nano} and P_{fluor}).

Table 1 - Studied anti-*graffiti* products and their chemical characteristics

Anti-*graffiti*	**Type**	**Chemical characteristics**
S_{silox}	Sacrificial	Water-based organosiloxane emulsion with special additives
S_{nano}	Sacrificial	Coating with SiO_2 nanoparticles
P_{fluor}	Permanent	Water-based fluoroalkylsiloxane
P_{silic}	Permanent	Aqueous nanostructured emulsion of silicon-based molecules.

2.1.2 Substrates

Four anti-*graffiti* products were applied on three substrates: Portuguese calcareous stone (*Moleanos* limestone), lime mortar and lime mortar with silicate-based paint.

The *Moleanos* is a beige limestone characterized by, approximately 8.3% at 9.4% of open porosity. The mortar studied consists of a pre-dosed lime-based mortar characterized by a very high open porosity (between 38% and 45%) and a low bulk density (between 1000 kg/m^3 and 1200 kg/m^3). These values were determined through laboratory tests. The paint used was a silicate-based paint. According the technical sheet, this is a mineral paint based on an inorganic binder (potassium silicate) pigmented with rutile titanium dioxide and inert fillers.

For the first phase of the experimental campaign rectangular specimens (100× 100×20 mm for mortar and 200× 200× 20 mm for stone) were used. In the second phase prismatic (80× 40× 40 mm), circular (D = 160 mm and e = 20mm) and rectangular specimens (200 × 200×20 mm) and samples of mortar applied on bricks (300× 200× 20 mm) were used.

2.1.3 *Graffiti* paints

The *graffiti* paints used in this study were two commercial aerosol spray paints (blue and grey) and a blue felt marker with a 15 mm tip from Mtn (Montana Colours, Inc.). The spray paints are alkyd resins aerosol with different pigments.

2.1.4 *Graffiti* removal products

Two commercial *graffiti* removers were used in the cleaning procedures. R_{decap} is a paint stripper indicated for removing *graffiti* form substrates protected with sacrificial anti-*graffiti* (S_{silox} and S_{nano}) or unprotected surfaces. It is a gelatinous product that can be applied by brush and acts within 5 minutes. R_{solv} is a commercial product provided in a pressurized can. This remover consists of an organic solvent and is indicated for slight painted surfaces. R_{solv} was used to remove *graffiti* from substrates protected with permanent anti-*graffiti* coatings.

2.2 Sample preparation

Before the application of the anti-*graffiti* products, the specimens were cleaned with a moist cloth to remove any dirt and then were kept in laboratory conditions until constant weight (25.5 $\pm$ 0.5 ºC and 44.6 $\pm$ 7.8% R.H.).

The products were applied according the recommendations reported in technical sheets. The application of anti-*graffiti* products S_{silox}, P_{fluor} and P_{silic} was performed with brush, while the S_{nano} product was applied by spraying. In the specimens used on the porosity test, the anti-*graffiti* products were applied on all sides of the specimens. In the others specimens, the anti-*graffiti* products were applied only in one of the sides. The number of anti-*graffiti* layers and the drying time between layers adopted were the recommended on the technical sheets. Then the specimens were kept in laboratory conditions for two weeks (23.6 $\pm$ 0.9 ºC and 60.5 $\pm$ 8.5% R.H.).

The *graffiti* paints were applied according to ASTM D7089 [9]. The spray paints were pulverized at a constant speed and pressure, maintaining a distance of 15 cm from the specimen and with on a 45 degree tilt. The marker paint was applied with a constant speed and pressure too. In order to apply the *graffiti* paints in parallel lines, it was used a stencil with the lines designed (Figure 1). Then the specimens were kept in laboratory conditions for two months

2.3 Evaluation tests

2.3.1 Cleaning efficiency assessment

The cleaning procedure was based on an adaptation of ASTM D7089 [9]. After the follow-up of some *graffiti* removal works, and review of the recommendations of the anti-*graffiti* technical sheets, it was decided to adopt the cleaning levels indicated in Table 2. In this study, a high-pressure water jet at 100 bar and 60 to 70 ºC of temperature was used.

Since the high-pressure water could damage the lime-mortar specimens, the cleaning of these samples was performed using running tap water and a brush (Table 2).

The cleaning efficiency of each level was appraised according to an evaluation scale (Table 3) based on different "classification numbers" elaborated by Garcia & Malaga (2012) [10]. The classification number is defined on the basis of the amount of paint remaining on the surface after the cleaning level performed.

The cleaning procedure was performed on specimens treated with the four anti-*graffiti* products and on untreated specimens to use as control samples for comparison purposes.

To assess the effects of *graffiti* removal after the last cleaning level, the colour variation was measured by using a colorimeter, according to ASTM D2244 (2002). Twenty-five and nine readings were performed at the stone and mortar specimens, respectively. The colour variation (ΔE) was calculated using the CIELAB values (L, a and b), and the following equation:

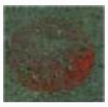
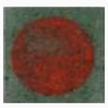
$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

Where L is the luminosity coordinate; a is the red/green coordinate and b the yellow/blue coordinate.

Table 2 - Cleaning levels adopted

Substrate	Cleaning levels	*Graffiti* completely removed with
Stone	**level 1**	high-pressure cold water wash
	level 2	high-pressure hot water wash
	level 3	commercial based *graffiti* remover and high-pressure hot water wash
Mortar with or without silicate paint	**level 1**	brushing with cold water
	level 2	brushing with hot water
	level 3	brushing with commercial *graffiti* remover and water wash (1st cycle)
	level 4	brushing with commercial *graffiti* remover and water wash (2nd cycle)

Table 3 - Evaluation scale for the assessment of the cleaning results (Garcia & Malaga, 2012)

	**CN 0**	**Complete removal of colour (100%)**
	CN 0,5	Isolated smalll punctiform residues of colour
	**CN 1**	**Punctiform residues of colour; in the case of felt-tip markers, palish shadows are observed**
	CN 1,5	Single laminar residues of colour (cleaning effect >90%)
	**CN 2**	**Laminar residues of colour; in the case of felt-tip pens contour shadows are observed.**
	**CN 3**	**Clear recognition of colour; coloured contours clearly noticeable (cleaning effect 30-75%)**
	**CN 4**	**Surface is only slightly affected by the cleaning process (cleaning effect <30%)**
	**CN 5**	**No cleaning effect**

2.3.2 Physical and hydric characterization tests

Table 4 indicates the experimental tests performed on the three substrates treated with the three selected anti-*graffiti* products (S_{silox}, P_{fluor}, S_{nano}). The selection of these three products was based on the amount of information available in the technical sheets.
The test procedures indicated in Table 4 were performed on untreated specimens to use as control samples for comparison purposes.
The colour changes caused on the substrates' surface by the application of anti-*graffiti* products were measured with a colorimeter.

Table 4 - Tests performed and procedures used

Test procedures	Standard procedure
Capillary water absorption	EN 1015 - 18 (2002)
Drying behaviour	Test No. II.5 - RILEM (1980)
Apparent porosity and bulk density tests	Test No. I. 1 - RILEM (1980)
Water vapour permeability	NP EN 1015 - 19 (2008)
Water absorption under low pressure	Test No II 4 - RILEM (1980)
Colour	ASTM D2244 (2002b),

3 Results and discussion

3.1 Cleaning results

The use of the Table 3 [10] has allowed evaluating the results of cleaning corresponding to each level. Thus, for each substrate, it was possible to understand up to which level of cleanliness most of the paints were removed.

The visual inspection of the results revealed that is more difficult to remove *graffiti* from unprotected surfaces and, in fact, the anti-*graffiti* protection facilitated the removal.

In the stone specimens protected with the anti-*graffiti* products, it was found that more than 90% of the grey paint was removed only with high-pressure cold water wash (level 1). It appears also that both blue paints were removed from the protected surfaces using the high-pressure hot water (level 2). The results are considered satisfactory in comparison with those obtained on the unprotected stone samples. In these, the high-pressure cold water was totally ineffective at cleaning any of the paints. The blue spray paint was removed only by using a remover product (level 3). In addition, after the last level, residual stains (or *graffiti* "ghosts") were observed on the unprotected stone samples.

The evaluation of the colour modifications with a colorimeter allowed identifying the variations that are not detectable by the human eye. The colour parameters shown in Table 5 reveal that the highest colour variation (ΔE) was detected in samples without anti-*graffiti* protection.

Table 5 - Results of the measurements of colour after cleaning the *graffiti*

Colour changes after cleaning the *graffiti* (ΔE)						
Substrate	*Graffiti* paints	S_{silox}	P_{fluor}	S_{nano}	P_{silic}	Without anti-*graffiti*
Moleanos limestone	Blue spray	5.29	7.61	6.69	5.07	8.75
	Blue felt-tip	5.21	6.93	6.70	6.58	10.31
	Grey spray	5.69	6.79	7.29	7.44	10.90
Lime-base mortar	Blue spray	5.00	4.47	3.84	5.63	14.93
	Blue felt-tip	6.22	5.21	4.54	11.14	15.30
	Grey spray	4.70	5.19	5.64	10.25	28.21
Lime-based mortar painted	Blue spray	3.48	1.13	1.44	1.23	5.87
	Blue felt-tip	3.28	2.35	2.90	7.69	38.42
	Grey spray	1.34	5.77	9.21	15.41	25.08

Following a classification reported by other authors [4, 5], for ΔE values lower than 5 units, the colour variations cannot be perceived by a human eye; ΔE values between 5 and 10 units, the colour variations can be seen by the human eye but are considered tolerable; finally, the ΔE values higher than 10 units produce clearly visible colour changes that are considered unacceptable.

Analysing the colour variations shown in Table 5 it is possible to conclude that all the variations obtained on stone are detected by the human eye. It is also concluded that cleaning was more successful on the stone samples treated with the sacrificial anti-*graffiti* based on organosiloxane (S_{silox}), since they present smaller colour variations.

Regarding the lime-based mortar specimens painted and unpainted, it was found that, in the protected samples, most of the grey paint was removed by brushing with hot water, while the blue paints were only removed by brushing with remover and wash. The results show that the cleaning procedures were wholly ineffective on the unprotected samples, since the paint colours are clearly recognized on the surfaces ($5.87 \leq \Delta E \leq 38.42$). In both substrates, cleaning of grey paint was more successful on samples treated with the sacrificial anti-*graffiti* S_{silox} (1.34 and 5.00 for painted and unpainted mortar, respectively), while the cleaning of blue paints was more effective on samples treated with the anti-*graffiti* products S_{nano} and P_{fluor} ($1.13 \leq \Delta E \leq 5.21$).

In general, the grey paint was easier to remove than the blue paints. However, it was found that the grey paint left yellowish stains on the painted and unpainted mortar samples treated with the anti-*graffiti* products S_{nano}, P_{fluor} and P_{silic}.

Comparing the substrates, it is clear that the mortar showed higher amount of paint residue after cleaning than stone. This difference is directly related to the higher porosity of mortar. As reported by other researchers, the paint pigments easily penetrate the pores of mortar hindering their complete removal.

3.2 Physical performance results

Table 6 presents the results obtained in the various test performed to evaluate the water behaviour and physical properties of the treated and untreated substrates.

Through a first analysis it is possible to conclude that the anti-*graffiti* products introduce changes on the physical performance of substrates. There were changes in the values of all physical characteristics, except in open porosity.

The results of the capillary suction indicate that the anti-*graffiti* products reduce the initial water absorption of the substrates. However, this reduction depends on the type of anti-*graffiti* product and the substrate.

The results allow concluding that all anti-*graffiti* products showed a good performance since they caused significant reductions in the capillary water absorption of the stone (88% to 96%) and unpainted mortar (87% to 90%). In the painted mortar substrate it is concluded that the capillary water absorption and under low pressure was significantly reduced by the silicate based paint (reductions of 90% and 98%, respectively), and, therefore, the effectiveness of the anti-*graffiti* products was not so obvious. On this substrate the permanent anti-graffiti based on fluoroalkylsiloxanes showed the best performance because it caused a reduction at 75% of the capillary water absorption.

Table 6 - Results of the physical characterization tests

Parameter	**Substrate**	S_{silox}	P_{fluor}	S_{nano}	**Without anti-*graffiti***
Apparent porosity (%)	*Moleanos* limestone	8.39	8.62	9.36	8.74
	Lime-based mortar	39.47	43.42	44.65	42.28
	Lime-based mortar painted	40.17	36.01	n.a.	37.02
Capillary water absorption coefficient ($kg/m^2.min^{0.5}$)	*Moleanos* limestone	0.0034	0.0013	0.0094	0.0782
	Lime-based mortar	0.022	0.098	0.088	0.894
	Lime-based mortar painted	0.170	0.022	0.038	0.087
Water absorption under low pressure ($kg/m^2.min^{0.5}$)	*Moleanos* limestone	0.008	0.008	0.000	0.019
	Lime-based mortar	0.99	4.52	0.19	5.66
	Lime-based mortar painted	0.128	0.000	0.005	0.096
Water vapour diffusion resistance factor, μ	*Moleanos* limestone	263.85	231.73	231.73	204.62
	Lime-based mortar	17.24	14.67	14.55	13.12
	Lime-based mortar painted	14.77	17.44	13.90	14.89
Drying index, I_s	*Moleanos* limestone	0.251	0.230	0.160	0.143
	Lime-based mortar	0.400	0.281	0.262	0.194
	Lime-based mortar painted	0.269	0.388	0.188	0.254
Velocity of drying ($kg/m^2.min^{0.5}$)	*Moleanos* limestone	0.0031	0.0040	0.0061	0.0082
	Lime-based mortar	0.0084	0.0073	0.0093	0.0110
	Lime-based mortar painted	0.0146	0.0093	0.0137	0.0130

*n.a. - not measured

Regarding the water absorption under low pressure, it is found that the sacrificial anti-*graffiti* with SiO_2 nanoparticles, S_{nano}, presents the best performance because it causes significant reductions on all the substrates (between 94% and 100%). The excellent performance shown by S_{nano} may be related to the pores filling capacity characteristic of nanoparticles present in its composition. The anti-*graffiti* S_{silox}

presents reduction of 60% and 83% for stone and unpainted mortar, respectively, but on the painted mortar it does not cause any reduction. Finally, the permanent anti-*graffiti* based on fluoroalkylsiloxane leads to reductions of 60%, 20% and 100% for stone, unpainted mortar and painted mortar. Thus, it is concluded that the anti-*graffiti* P_{fluor} presents the best results for painted mortar (reduction of 100%). In summary, it can be said that the results of water absorption under low pressure are very variable on the various substrates.

The influence of the application of these products on the water vapour permeability of the substrates was also evaluated. It is possible to conclude that all products increased the coefficient of resistance to the diffusion of water vapour in stone and unpainted mortar. The most significant increases found on these substrates were achieved by the application of the sacrificial anti-*graffiti* based on organosiloxanes (S_{silox}) (29% and 30% respectively), while the other products revealed minor increases (between 11% and 16%). This trend of values was confirmed in the drying test, since the product S_{silox} also showed the worst results having registered increases of the drying rate between 76% and 106% for stone and unpainted mortar, respectively. The other products, P_{fluor} and S_{nano}, caused increases on the drying rate between 13% and 61%. For the painted mortar, it is concluded that the silicate based paint does not reduce, significantly, the water vapour permeability, since the values showed in Table 6 are close to the unpainted mortar values. On this substrate, only the products P_{fluor} and S_{silox} caused a slightly increase of the coefficient of resistance to the diffusion of water vapour (17% and 6%), respectively.

The water vapour permeability and the drying rate are considered to be the most important proprieties that should be evaluated to determine the suitability of the anti-*graffiti* products for application on the support materials [4, 5]. In addition to these properties, the initial drying velocity should be evaluated too. The results showed that the drying velocity also shows reductions after the anti-*graffiti* application. The S_{silox} and P_{fluor} products caused major reductions in the drying velocity of the stone and unpainted mortar samples (24% to 61%), while S_{nano} registered very slight reductions on all substrates (0 to 16%). On the painted mortar samples, it is found that only the product P_{fluor} caused a reduction of 29% of the drying velocity.

Finally, comparing the values shown in Table 6, it is possible to confirm the following trend: the highest drying rate is registered for the product (S_{silox}) that has the greatest coefficient of resistance to water vapour diffusion, while the lowest drying rate is registered for the product (S_{nano}) that has the lowest coefficient of resistance to water vapour diffusion.

Besides the evaluation of the hydric properties being very important to determine the suitability of the anti-*graffiti* products for porous substrates, the appearance of the surfaces should be also evaluated [10]. Table 7 presents the colour variations induced by the application of the four anti-*graffiti* products.

The results indicate that stone was the substrate most affected by the application of the anti-*graffiti* products since it presents the highest values of total colour variation ($1.6 \leq \Delta E \leq 6.8$). However, it appears that the most significant variations are considered acceptable according to various authors [4, 5, 6].

Table 7 - Results of the measurements of colour determined after the application of anti-*graffiti* products

Substrate	Colour changes, ΔE			
	S_{silox}	P_{fluor}	S_{nano}	P_{silic}
Moleanos limestone	1.60	5.04	5.68	6.80
Lime-based mortar	3.09	3.18	0.29	4.09
Lime-based mortar painted	1.87	2.94	0.49	4.60

Analysing the values shown in Table 7, it is possible to conclude that the sacrificial product based on organosiloxane, S_{silox}, produced the smaller changes of colour on stone, while the permanent product based on silicone, P_{silic}, caused the highest colour variation.

In the painted and unpainted mortar, the sacrificial product with SiO_2 nanoparticles presented the best results, since the colour variations are insignificant (0.49 and 0.29, respectively). On the other hand, the permanent product based on silicone presented the highest colour changes (4.09 and 4.60 for unpainted and painted mortar, respectively), as verified on stone.

4. Conclusions

This study shows that the use of anti-*graffiti* products facilitates *graffiti* removal, especially on painted and unpainted mortar. In fact, on the samples of these substrates without anti-*graffiti* treatments, the cleaning procedures were unsuccessful.

The sacrificial product based on organosiloxane, S_{silox} presented the best performance in cleaning all paints of *graffiti* on stone substrate. On painted and unpainted mortar, this product showed the best results in cleaning the grey paint, since it does not leave yellowish stains on the surface as the other products. However, the blue paints were more successfully cleaned on the samples treated with the permanent anti-*graffiti* based on fluoroalkylsiloxanes and the sacrificial anti-*graffiti* with SiO_2 nanoparticles. Finally, the permanent product based on silicone, P_{silic} showed an unsatisfactory performance at cleaning, since it presented the highest colour variations after *graffiti* removal.

Among all the tested anti-*graffiti* products, the sacrificial product, S_{nano}, with SiO_2 nanoparticles, presented the best physical performance since it significantly reduced the water absorption, it did not significantly influence the drying behaviour and water vapour permeability and it did not change the colour of the painted and unpainted mortar samples. The permanent product based on fluoroalkylsiloxanes, P_{fluor}, has shown a good performance too in terms of drying behaviour and water absorption. For these reasons and based on the cleaning results, it is considered that S_{nano} and P_{fluor} are the products more suitable for unpainted mortar, since this substrate has high open porosity.

On the other hand, the product based on organosiloxane demonstrated to be more indicated to painted mortar, due to the excellent cleaning performance ($\Delta E < 3.5$ for all paints), water vapour permeability and drying behaviour.

Finally, despite the slight changes induced in the permeability to water vapour and drying behaviour, the sacrificial product based on organosiloxane, S_{silox}, was the most efficient in cleaning.

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