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Study of the cleaning effectiveness of limestone and lime-based mortar substrates protected with anti-*graffiti* products

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ABSTRACT

Graffiti are a current happening that affects many monuments and buildings in urban areas. Additionally, *graffiti* removal involves high costs. To protect the surface of materials, anti-*graffiti* products have been developed to prevent the penetration of *graffiti* paint into the pore system of the substrates, facilitating its subsequent cleaning. This paper presents a comparative study of four commercial anti-*graffiti* products (two sacrificial and two permanent) applied on three types of substrates (limestone and lime-based mortar with or without a finishing paint layer), in order to evaluate the effectiveness of anti-*graffiti* protected surfaces cleaning with various *graffiti* paints (two alkyl resin spray paints and one felt-tip marker). To evaluate the facility of *graffiti* products was investigated by visual inspection (with a scale of evaluation), colorimetric tests and by FTIR analysis. The results showed that, indeed, the anti-*graffiti* products facilitate cleaning the *graffiti*, especially those on the more porous substrate (mortar). However, the cleaning effectiveness protected with anti-*graffiti* products greatly depends on the type of *graffiti* paint applied (its colour and application by spray or marker). In general, grey paint was easier to remove than blue paints. However, it was found that the grey paint left yellowish stains.

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1. Introduction and research aim

Graffiti are a current trend that affects many monuments and buildings in urban contexts. The term *graffiti* is derived from the Italian *graffiare* that corresponds to the plural of *graffito*, which means "inscribe in a hard surface". *Graffiti*, as a form of artistic or revolutionary expression, have existed for thousands of years. However, *graffiti* have undergone several changes throughout its history, not only in their visual appearance and types of inks used but also the type of motivation to make them [1].

Even though some are true works of art, *graffiti* are mostly considered a form of vandalism [1-3]. In addition to contributing to the devaluation and visual defacing of buildings, *graffiti* are sometimes associated with social decline and insecurity [2,4]. In monuments and historic buildings, this phenomenon is a problem, since it

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http://dx.doi.org/10.1016/j.culher.2016.04.004 1296-2074/© 2016 Published by Elsevier Masson SAS. affects the architectural heritage and, consequently, the tourism. On the other hand, *graffiti* removal is very expensive [3]. Only in 2010, the Portuguese railway company, CP, spent 304,000 euros to clean *graffiti* from train wagons [5].

There are several cleaning methods, such as those involving water jet, grit-blasting, chemical removal, laser technology and atmospheric plasma. Nevertheless, mechanical and chemical methods are the most often used [1,3,4,6]. However, when *graffiti* are executed on porous substrates, the former methods are not fully effective and may cause irreversible damage, leading to the need of preventive actions [3,4,7].

Anti-*graffiti* protection coatings can work very well, since they facilitate *graffiti* removal, assuming an important role in the maintenance of buildings and contributing to the increase of the durability of the materials. These anti-*graffiti* products form a protective barrier against the *graffiti*, preventing penetration of the paint into the pore system of the substrates, thus facilitating its subsequent cleaning [2,4,6,8].

These anti-*graffiti* products can be classified in three categories: sacrificial, semi-permanent and permanent [2,4,6]. The sacrificial products are eliminated during the cleaning process together with

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the *graffiti* paint, and have to be reapplied after the removal [4,9]. Semi-permanent products can be applied in several layers, but are also eliminated after a few (two or three) cleaning cycles [4,9]. Permanent anti-*graffiti* are not dissolved with the products used to clean the *graffiti* and therefore can withstand repeated cleaning cycles. The use of anti-*graffiti* products facilitates the cleaning process since *graffiti* removal from protected surfaces is usually performed with chemicals or with hot water jet only [4].

The majority of the studied products are based on waxes, polyurethanes, fluorinated polymers, silicone resins and, recently, fluoroalkylsiloxane [2,4,9,10]. However, polyurethanes change the colour of material surfaces and create a barrier to the passage of water vapour [4,9,11]. The reduction of the substrate water vapour permeability can lead to the accumulation of liquid water contributing to its deterioration. Additionally, there are some quite porous stones (e.g. limestones such as travertine and moleanos) or rendering mortars that present higher porosity and, therefore, the application of some anti-graffiti coatings such as polyurethanes that can block the passage of water vapour through pores is not recommended for these claddings regardless of their in-service performance and durability. For this reason, polyurethane-based anti-graffiti are not suitable for porous materials, since they have a relatively low durability and, in some cases, may even damage the substrate. Another disadvantage is their low resistance to UV light, because long sun exposure causes the coating to yellow, changing its colour. Despite these disadvantages, polyurethanes allow multiple cleaning cycles [12–15].

On the other hand, it appears that the use of products based on waxes or silicones (sacrificial products), although with a limited life-time, does not reduce the permeability to water vapour as much as the polyurethanes products, and for that reason, they are more suitable for porous substrates [4,6,11] and continue to be more often used. However, when exposed to UV radiation, the anti-graffiti products based on waxes have a limited durability and the antigraffiti products based on silicones lose their hydrophobic capacity [6,11].

Recently, newer products have been synthesized based on fluorinated compounds as reported in several studies related to their effectiveness as anti-graffiti protection [4,10,16–18]. The presence of fluorine in anti-graffiti products has been studied because it works both as a water-repellent and an oil-repellent. Fluorinated polymers provide anti-graffiti protection because of their low surface energy, high resistance to solar and UV radiation, permeability to water vapour, and an increased durability provided to the coatings. Thus, it is possible to obtain permanent antigraffiti protection with high resistance to several cleaning cycles [4,18]. Additionally, according to some studies, the anti-graffiti products with fluorinated polymers and fluoralkylsiloxanes reveal good results in terms of graffiti cleaning [4,16].

The organic-inorganic hybrid products and the inclusion of nanoparticles in anti-graffiti products have also been investigated [4,15,19]. Many aspects can be improved with this technology, including: corrosion preventive coatings, self-cleaning capacity, antibacterial coatings, development of anti-glare glasses, resistance of paints, and anti-graffiti coatings [19]. Nanosilica, for example, has been included in products based on organic polymers. Its inclusion improves some of the properties of the coatings in particular the hardness, chemical and thermal stability, UV resistance, and transparency [4,15].

The majority of the studies performed have investigated the application of these products on compact stones, since the buildings with historical value are mostly made of or clad in stone. In this sense granite, marble, limestone and sandstone are the stones most often studied [4,6,10,16,20,21]. Only few studies in the literature are dedicated to less compact materials, such as rendering mortar and some porous natural stones [9,10,20].

Moreover, there are many buildings coated with painted renders. According to the latest Census 2011, 84% of the buildings in Portugal are coated with traditional render or crushed marble mortar and 11.6% with stone cladding [22]. *Graffiti* removal from this substrate is quite difficult because the chemical products used to remove the *graffiti* paint also remove the original paint of the mortar substrate [3]. In this case, the cleaning process is usually replaced by the application of a layer of paint over the walls to hide the *graffiti*. However, the repeated application of this layer can reduce the water vapour permeability of the render and cause a great aesthetic impact since its colour is not usually the same as that of the original paint of the wall [3]. For these reasons, it is important to study the effects of the anti-*graffiti* products on the cleaning efficiency of the *graffiti* on painted mortar.

This experimental work intends to evaluate the effectiveness of four commercial anti-graffiti products to facilitate the cleaning of three porous substrates (limestone and lime-based mortar with and without a paint finishing layer), in order to determine their suitability for protection against graffiti.

2. Experimental work

2.1. Materials

2.1.1. Substrates

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

Moleanos is a beige limestone characterized by, approximately, 8.3% to 9.4% of open porosity, frequently used to clad buildings facades in Portugal [23]. The mortar studied consists of a pre-dosed lime-based mortar characterized by high open porosity (38–45%) and low bulk density (1000–1200 kg/m³) [24,25]. The selection of a lime-based mortar had to do with its high porosity and use as a coating in many old buildings in Lisbon.

To paint the mortar samples, a silicate-based paint was used. According to the technical sheet, this is a mineral paint based on an inorganic binder (potassium silicate) pigmented with rutile titanium dioxide and inert fillers and suitable for mineral substrates such as lime-based mortar.

2.1.2. Anti-graffiti products

Four commercial anti-graffiti products were studied: two sacrificial products and two permanent products. The chemical characteristics of the products are shown in Table 1. According to the technical sheets, the anti-graffiti products $S_{silox} S_{nano}$ and P_{fluor} can be applied on porous materials. The technical sheet of anti-graffiti product P_{silic} does not have any information about which materials it is suitable for. Based on exhaustive research, it was concluded that these anti-graffiti products were the most innovative in the market and it was decided to evaluate their performance.

2.1.3. Graffiti paints

The *graffiti* paints used in this study were two commercial aerosol spray paints, FLUOR blue (Mtn 94, serial number: 14R71067 and code bar: 8 427744 145511) and grey (Mtn 94, RV–121/Icarus Grey, serial number: 11R15908) and a blue felt marker with a 15-mm tip from Montana Colours (Mtn, code bar: 8 427744 107536). The spray paints are alkyd resins aerosol with various pigments. According to ASTM D7089 [26], blue is one of the more difficult colours to remove. On the other hand, according to the experience of some *graffiti* remover companies, grey paint is easier to remove than blue paint.

good results in terms of *graffiti* cleaning [4,16]. The organic-inorganic hybrid products and the inclusion of materials it is suitable for B

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