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Surface characterization and effectiveness evaluation of anti-graffiti coatings on highly porous stone materials

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ABSTRACT

In this study, two commercial sacrificial anti-graffiti systems, provided as water emulsion, were applied on a highly porous stone. The behavior of the anti-graffiti treatments was investigated by means of differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy in attenuated total reflectance mode (ATR-FTIR), colorimetric tests, and water static contact angle measurements.

The presence of a protective coating enhanced the removal of paint sprayed on the stone. However, penetration of the staining agent below the surface, due to the high porosity of the substrate, caused difficulties in eliminating the paint. In fact, repeated cleaning procedures, involving hot water, mechanical action, and chemical removers, did not allow a complete removal of the paint.

The examined systems behaved against graffiti in different ways. No affinity between the wax-based product and the paint was observed; nevertheless, this behavior did not result in good anti-graffiti performances. On the contrary, the penetration of the paint into the fluorine-based coating yielded a good anti-graffiti effectiveness, since the stain was easily eliminated from the surfaces.

The anti-graffiti coatings survived in limited areas after the cleaning processes, although the studied compounds are suggested as sacrificial products. Such behavior may affect the maintenance activities, when the surface is no longer protected and the coating need to be renewed, since compatibility problems, as well as harmful accumulation, could occur because of further treatments on these surfaces.

1. Introduction

The term "graffiti" means any unwanted painting, drawing, lettering or scribble painted, written or carved on a surface. In recent years, graffiti, especially spray paintings, have been regarded as a form of art and they are becoming increasingly frequent. However, when graffiti are performed on cultural heritage buildings, they still remain a vandalism. The impact of graffiti on artifacts of historical and artistic relevance is heavy in social and economic terms, because of degradation and devaluation of the affected areas, as well as of high cleaning costs.

Graffiti removal is usually carried out by cleaning methods based on abrasive mechanical action or chemical substances [1–3]. These procedures may cause severe damage, therefore they should be avoided on historic surfaces. In such cases, preventive actions are to be preferred.

Anti-graffiti measures consist in applying protective coatings on the surfaces to preserve. The final topcoat should prevent the contact between the staining agents and the substrate and reduce the adhesion of dirt. To this aim, products with a low surface free energy, thus a reduced surface wettability, are generally chosen [4–8].

The production of such products is fast developing and sacrificial or permanent anti-graffiti systems are tailored. The sacrificial products are removed during the cleaning process and they need to be renewed; the permanent systems, on the other hand, can withstand repeated cleaning cycles. Formulations for application to stone materials have been based on waxes [9], polysaccharides [9], polyurethanes [10,11], silicon resins [9,12,13], and fluorinated polymers [5,9,12,14–16]; recently, also organic–inorganic hybrid materials have been proposed as anti-graffiti systems [17–19].

As requested to any other protective treatment for stone materials, the anti-graffiti products should not alter the appearance of the treated surfaces or hinder water vapor exchanges between the substrate and the environment, at least. They should impart water-repellency and oleophobicity to the treated surfaces, to avoid or limit penetration of the stain, and, in addition, they should not deteriorate under environmental conditions [20]. Finally, the employment of environment-friendly products, safe for both users and the environment, is increasingly encouraged.

The effects of anti-graffiti systems have been sufficiently investigated on compact stone substrates [3,21–28], whereas only few studies in literature are devoted to stone materials with a high

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porosity [24,29–31]. In addition, most of the published papers deal with products' properties and procedures for stain removal [4,22,32–37], while the anti-graffiti efficacy is not discussed in depth.

Porous stone surfaces affected by graffiti may be very difficult to clean, because these substrates can absorb the staining agents, sometimes even in large amounts [31]. Moreover, an incomplete elimination of the protective coating – especially in the case of sacrificial products – may affect the surface's properties and the maintenance arrangements. Although such aspects can be particularly significant for porous substrates, once again, little attention has been paid to these materials.

Starting from these issues, an experimental work aimed at improving knowledge about performances and behavior of anti-graffiti systems on highly porous stone materials, was undertaken.

Two commercial sacrificial anti-graffiti systems were selected. The first is based on polymer waxes to use directly on stone surfaces; the second is composed of waxes and acrylic-fluorinated resins to apply on surfaces previously treated with a proper primer (based on acrylic-fluorinated copolymers). These anti-graffiti systems were chosen on account of the limited impact on both the environment and the stone materials expected from their use. All the products analyzed in this work are provided, in fact, as water emulsion. Furthermore, graffiti removal by means of hot water is suggested in the technical sheets, while chemical removers are recommended only to enhance unsatisfactory results of the cleaning process.

In an early study [38] these anti-graffiti products were investigated to evaluate harmlessness on "Lecce stone", a calcarenite characterized by a very high porosity (above 30%). Negligible variations in esthetic properties, tolerable reductions in water vapor permeability and improved superficial hydrophobicity of the treated samples, were found. The studied products were, consequently, assumed as good candidates for anti-graffiti treatments of this highly porous stone.

The present paper focuses on the effects of a staining action, performed with a dye spray paint, and the outcome of the subsequent cleaning process. Firstly, both the anti-graffiti products and the paint were subjected to a thermal and spectroscopic characterization by means of differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy in attenuated total reflectance mode (ATR-FTIR), respectively. In a second stage of the study, the stone surfaces were investigated before and after the anti-graffiti treatments; to this aim, ATR-FTIR analyses, colorimetric tests, and water static contact angle measurements, were performed. The same investigations were repeated after both the staining and the cleaning processes. To simulate graffiti, an aerosol spray paint was applied, because this is the most used staining agent in real practice. The appearance of the surfaces was also inspected with a stereomicroscope.

2. Experimental

2.1. Materials

Two commercial anti-graffiti systems were studied. Both are suggested for reversible protection of porous and non-porous stone materials against spray-painted graffiti. However, the manufacturers strongly recommend preliminary examinations to test the products for each specific application. The following are the details of composition and information about all the used products.

AG1 product (Mapei S.p.A., Italy) is a ready-to-use water emulsion of polymer waxes. It can be directly applied on clean and dry stone surfaces in quantities ranging from 30 to 150 g/m^2, depending on the porosity of the substrate. As reported in the technical sheet, the removal of graffiti drawings from surfaces treated with AG1 can be performed using hot water (at about 80 °C); a commercial remover, hereinafter called R1, may help to eliminate residual stains.

R1 product (Mapei S.p.A., Italy) is a glycol ether-based solution for the cleaning of graffiti-damaged surfaces. It is a ready-to-use gelatinous product that can be applied by brush. It acts within 10 min, then, it can be easily removed with water.

AG2a product (GEAL – Bel Chimica Srl, Italy) is based on acrylic-fluorinated copolymers in water emulsion. It can be used, as supplied, on natural and artificial stone materials, employing from 125 to 170 ml/m^2. Its application as a primer is strongly recommended in order to facilitate the adhesion of the anti-graffiti product (AG2b, described below) to the surface.

AG2b product (GEAL – Bel Chimica Srl, Italy) is based on polymer waxes added to acrylic-fluorinated resins in water emulsion. Application of 65–125 ml/m^2, without any dilution, on stone surfaces previously treated with the AG2a product, is suggested. The suppliers advise to clean the surfaces protected with the AG2 system (that is, the AG2a primer and the AG2b protective) using hot water at about 80 °C and a stiff-bristled brush first. In case of inadequate cleaning results, they recommend a special commercial remover (R2), illustrated in the next point.

R2 product (GEAL – Bel Chimica Srl, Italy) is a mixture of surfactants and solvents specifically tailored for the cleaning of stained surfaces protected with the AG2 system. This remover is ready-to-use 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.

The staining agent used in this study is a commercial aerosol spray paint (Briolux Spray by CP Italia), orange-colored, provided in a pressurized can. A preliminary selection was performed and the chosen paint was preferred because it was easily detected by infrared spectroscopy; additionally, it was clearly distinguishable from both the stone support and the anti-graffiti products.

For commercial reasons, additional details on the chemical composition and the structure of both the anti-graffiti systems and the spray paint are not available.

The anti-graffiti systems were tested on a highly porous calcarenite, named "Lecce stone". This stone is widely employed since long time as construction material in the southeastern Italy and it is typical of the baroque monuments and buildings of the region. In addition, it can be considered as representative of the porous materials used for historic and civil buildings in many countries of the Mediterranean basin. Calcite is its principal constituent, along with very small quantities of clay and other non-carbonate minerals [39–41]. "Lecce stone" exhibits a very high porosity, usually ranging from 30 to 45% [29,42–45] and a unimodal porosity distribution with a radius mainly between 0.5 and 4 μm [39,46].

2.2. Preparation of samples

The anti-graffiti products were separately applied by casting on glass slides, acting as an inert substrate, in order to characterize the materials. Similarly, two coats of paint were sprayed on the glass support.

Prismatic stone specimens with dimensions of 5 cm × 5 cm × 1 cm were cut from a quarry block. Prior to use, the samples were smoothed with abrasive paper (180-grit silicon carbide), cleaned with a soft brush and washed with deionized water in order to remove dust deposits, according to UNI10921 standard protocol [47]. The stone specimens were completely dried by a cyclical procedure: 22 h in oven at 60 °C, followed by 2 h in a desiccator with silica gel (relative humidity R.H. = 10 ± 5%) at room temperature. The samples were weighted at the end of