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Case study

Evaluation of mechanical soft-abrasive blasting and chemical cleaning methods on alkyd-paint graffiti made on calcareous stones

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ABSTRACT

This study focuses on the assessment of three graffiti cleaning systems on alkyd-paint graffiti aerosols made on two Portuguese calcareous stones, a marble, *Branco*, and a limestone, *Lioz*. These calcareous stones are commonly used in Portugal as building materials and ornamental stones. Two non-conventional commercial dry soft-abrasive blasting media (MC1 and MC2), specifically developed to clean the sensitive and delicate surfaces were tested: MC1 uses a sponge-like urethane polymer involving spherical calcium carbonate particles and in MC2 pure spherical calcium carbonate particles are used. An alkaline cleaner based on a solution of potassium hydroxide was also tested. The criteria for assessing the effectiveness and potential risks included changes in the chromatic parameters, static contact angle and surface roughness of the stones, identification of deleterious products and modification of the morphology and the composition of the surfaces. The methods were effective in the removal of the paint layers, although surfaces became slightly lighter. Adapting the classification proposed by Garcia and Malaga, 2012, the mechanical soft-abrasive cleaning methods were classified for both stones as Class C, i.e., with ΔE_{ab} near 12. The chemical cleaning was classified as Class A for the marble ($\Delta E_{ab} < 5$) and as Class B for the limestone ($5 < \Delta E_{ab} < 10$). No subproducts were identified. With the chemical cleaning, distinct removal of crystals or dissolution of grain boundaries in addition to surface dissolution was observed. The cleaning methods presented a slight low damage potential to these stone materials, i.e., the impact of the cleaning methods on the topography of the surfaces was much reduced. These methods also altered the water repellence of the stone surfaces. An increase in the static contact angles was observed and could be related with changes in the roughness of the surfaces and also to unremoved polymers absorbed in some of the pores of the surfaces.

1. Research aims

Graffiti can severely damage materials and lead to important materials losses and even to loss of value. Graffiti is an ongoing and increasing problem in various regions across the world and a general threat to cultural heritage.

This study focuses on the evaluation of mechanical soft-abrasive blasting and chemical cleaning methods on alkyd-paint graffiti made on Portuguese calcareous stones. These stones, a marble, *Branco*, and a limestone, *Lioz* are commonly used as building materials and ornamental stones. Changes in the chromatic parameters, static contact angle and surface roughness of the stones, identification of deleterious products (i.e. salts) and modification of the morphology and the composition of the surface, were the criteria for assessing the effectiveness and potential risks of the three graffiti cleaning systems.

An increased knowledge of this interaction provides valuable insight and greater understanding of the vulnerability of stone to graffiti removal systems, namely to some Portuguese stones.

2. Introduction

Graffiti is an engraving, scratching, cutting or application of paint, ink or similar matter on the stone surface [1]. Graffiti is generally the result of an act of vandalism although some may have historical, aesthetical or cultural values and should be conserved. Graffiti media includes a wide range of materials such as paints applied by brushes (oils and synthetic resins) or aerosols (polyurethanes, lacquers and enamels), dyes, felt-tip markers,

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ball-point pens, wax and oil crayons and lipsticks, chalks, adhesive labels and posters and the physical scratching of surfaces [2,3].

Graffiti, as an act of vandalism, is undoubtedly a major danger to stone cultural heritage and a risk for the preservation of the historical and cultural legacy for future generations. Graffiti can severely damage stone, accelerating its decay and lead to important materials losses and even to loss in value and significance [2,3]. Moreover, graffiti has also inevitable negative economic impacts to stone cultural heritage due to the impossibility to enjoy it adequately, and also to the necessity of adoption corrective measures, such as application of graffiti cleaning methods and preventive protection by using anti-graffiti coatings.

Graffiti cleaning is an essential part of conservation treatments, necessary for aesthetical reasons but also to ensure better preservation of stone materials. Although graffiti cleaning methods are potentially effective they present, in some cases, the potential for excessive material removal or other changes to the surfaces and, consequently, superficial, or even structural damage. Some graffiti cleaning methods can also accelerate stone decay through interaction with stone substrata or generation of by-products which, remaining within the material, may affect the future preservation [3–5]. The chemical, physical and mineralogical structure and physical condition of the stone material, type of preexisting soiling or patina present and type of graffiti marker should also be taken into consideration [5,6].

Different techniques and methods have been studied and used to remove graffiti such as those involving water jet, grit-blasting, chemical removal, laser technology and atmospheric plasma [6–22]. The development of anti-graffiti protection/barrier coatings intended to facilitate the removal of graffiti from the surfaces is also a subject of interest [23–40].

An understanding of the principles, effectiveness, harmfulness and nocivity of each cleaning method and its comparison is thought to be essential for its conscientious use. Therefore, this study focuses on the assessment of the effects of mechanical soft-abrasive blasting and chemical-cleaning methods on alkyd-paint graffiti made on calcareous stones. In previous works, were assessed the effects of these alkyd-paint sprays in these stones subjected to simulated graffiti situations [41,42].

3. Materials and methods

3.1. Materials description and characterization

Two Portuguese calcareous stones commonly used in Portugal as building materials were chosen: a Cretacic limestone – *Lioz* and a Cambrian to Upper Silurian white marble – *Branco* (Fig. 1a and b). These materials have been widely used in monuments and are still used in the construction of modern buildings and sculptures.

Lioz is a coarse cream microcrystalline limestone, bioclastic and calciclastic, whereas *Branco* is crystalline calcite marble (~98% calcite), with a granoblastic texture with medium-grained zones. A detailed petrographical, chemical, physical and mechanical characterization of this limestone and marble is presented by [43] and [44], respectively. In spite of their different geological and petrographical characteristics, both lithotypes present very low porosity (< 0.40%) and water absorption capacity (< 0.15%); their uniaxial compressive and flexural strength can be considered medium to high (> 1000 $kg.cm^{-2}$ and >200 $kg.cm^{-2}$, respectively).

The alkyd spray paints used in this work (Fig. 1c) correspond to trademarks MOTIP HOME & HOBBYLACQUER® [45]. The colors selected were gentian blue (RAL code R-5010), carmine red (R-3002) and jet black (R-9005). These sprays were chosen based on their low price and availability in non-specialized stores and their probable different interactions with stone substrata due to the use of different pigments, dyes or fillers. Details of the particular paint formulations are proprietary of the manufacturer and not available.

A set of 24 parallelepiped test cupons (7 × 5 × 1.5 cm) with smooth and homogeneous surfaces (cuted using a circular diamond saw, finished using carborundum 180 and without any other surface finish) were previously prepared for each lithotype. The cupons were uniformly sprayed with the alkyd-paints (at an average angle of 45° and from a distance of 30 cm, at 18–25 °C air temperature and 60–70% relative humidity) in order to simulate the graffiti action [41]. The paints created a smooth, uniform and dense overcoat and filling in surface irregularities in both lithotypes [41]. A second set of samples was left unpainted and considered as reference.

The cleaning tests were performed 24 months after the application of alkyd spray paints.

3.2. Tested graffiti cleaning methods

Two non-conventional commercial dry soft-abrasive blasting media, specifically developed to clean the sensitive and delicate surfaces (Fig. 1d and e), were used in this study: MC1 (Sponge-Jet ™) and MC2 (Exastrip ™). MC1 uses a sponge-like urethane polymer involving the abrasive composite (spherical calcium carbonate) whose function is to reduce dust levels and minimize abrasion of the substrate. In MC2 pure spherical calcium carbonate particles are used. The abrasive used in MC1 and MC2 was White SPOCC Sponge Media™ and EXAHDO® media, respectively. Besides the similar chemical composition, the particles dimension is different: in MC1 particle's range varied between 27 μm–100 μm whereas with MC2 between 70 μm–200 μm, as confirmed by FESEM (Fig. 2). Both technologies use low effective adjustable compressed air (0.5–2.5 bar), to propel the particles. In these experiments a maximum pressure of 2 bar was used, being the media amount and velocity tightly controlled to obtain the specified paint-removal and surface-profile results.

Several aspects regarding health and safety issues and waste production must be mentioned when dealing with these soft-abrasive blasting cleaning methods. It is mandatory to encase the site carefully and the operators must be protected from inhaling dust particles. Moreover, they must use eye protection and also auricular protectors due to noise produced by the compressed air systems. The abrasive used in MC1 has the advantage of being able to be reused several times.

Both blasting techniques have already been applied in the masonry cleaning of historical buildings such as the Wisconsin and Idaho state capitols, Washington Square Arch in New York, Mission San José y San Miguel de Aguayo in Texas, Notre Dame and Bercy Bridge in Paris [46–50].

A chemical method (CC1) based on a solution of potassium hydroxide (10–30% wt%) and surfactants (1–2% wt%, 2-aminoethanol) was also used (AGS 60™, Trion Tensid AB, Sweden). Potassium hydroxide is a suitable alkaline cleaner for acid sensitive historic masonry materials. This product was applied in two steps by soft brush on the stone wet surfaces and was leave to act for 30 minutes (1st step) + 15 minutes (2nd step) until paint graffiti was dissolved, followed by hot pressure tap water rinse (50 °C) to increase the effectiveness of the alkaline cleaner for removing the graffiti spray paint. These samples were, then, dried and stored for 15 days in the laboratory environment (at 20 ± 2 °C air temperature and 60 ± 5% relative humidity). Also several aspects regarding health and safety issues must be mentioned when dealing with graffiti chemical removals, since they are potentially toxic and are often primary irritants of the skin, eyes and mucous membranes. So, it is recommend having good ventilation and the operators must use eye, airways and skin protections.