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Mechanical and laser cleaning of spray graffiti paints on a granite subjected to a SO_2-rich atmosphere

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HIGHLIGHTS

- Red, blue, black and silver graffiti paints on granite were subjected to SO_2.
- SO_2 influences on the mechanical and laser cleaning performance.
- Aged samples were more difficult to clean, suffering higher global colour changes.
- Hydrogommage® with silica abrasive achieved the best results.

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ABSTRACT

Cleaning effectiveness of four graffiti spray paints artificially aged by SO_2 exposure on granite was evaluated. Two different removal procedures were applied: i) mechanical methods with different micro abrasives (Hydrogommage® – combining action of air, water and micro abrasive-silica or aluminium silicate and IBIX® – combining action of air and micro abrasive-silica or calcium carbonate), and ii) a ns Nd:YVO_4 laser working at 355 nm.

It was concluded that the cleaning with mechanical procedures and laser was influenced by the SO_2 exposure. Aged samples were more difficult to clean, suffering higher global colour changes. Hydrogommage® with silica abrasive achieved the best results, due to a combination of a satisfactory paint extraction and low morphological damages induced to the granite.

1. Introduction

Graffiti paints as form of vandalism are spread across the cities and can be found covering cultural heritage monuments and statues. However, graffiti is not just an aesthetical problem because they may interact with the stone and the environment leading to physical and chemical alterations of the stone. Despite important amounts of money are spent in cleaning campaigns and European Commission has started to invest in urban environment policies to prevent and eliminate graffiti [1], the ageing of the graffiti and its subsequently influence on the cleaning procedures were only evaluated in two recent works [2,3].

The traditional cleaning methods of graffiti paints are: i) the application of chemical products generally alkalis and acids, which react with the paint and dissolve it [4–8] and ii) mechanical procedures based on the removal of the paint by abrading the surfaces through low pressure projection of abrasives in dry or wet via [9–11]. Since the late 80s, the application of laser has experimented an important development in cultural heritage cleaning due to a better understanding of the physical processes involved in laser technology [10,12]. The cleaning with laser is based on the ablation of layers according to the different absorption levels among the undesired layers and the substrate to be safeguarded [12]. The laser ablation is a non-linear process that happens when

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the irradiation fluence (energy deposited per unit area) is higher than the threshold of the material to be extracted which is an intrinsic property [12]. Only short duration pulses lasers are used for cleaning of cultural heritage objects through a complex phenomenon depending on the laser parameters (i.e., pulse duration, wavelength, repetition rate, etc.) and the material to be preserved [12,13]. Pulse duration will be responsible of the ablation mechanism by photothermal, photochemical and mechanical effects for short-pulse lasers, i.e., nanosecond lasers, and with minor photothermal effects for ultrashort-pulse lasers, i.e., picosecond and femtosecond lasers [14–20]. Currently, despite ultrashort-pulse lasers could develop less harmful effects than nanosecond lasers, the most commonly used lasers to clean cultural heritage objects are nanosecond lasers, because ultrashort-pulse lasers consisted on complex and voluminous systems [13,21–25].

The mechanical methods are often associated with inhomogeneous cleaning and damages induced to the substrate such as mineral grain extraction or formation of fissures and cracks [9,26], since they act by abrasion through pressurized projection of abrasives. Although these methods have not been investigated sufficiently before, low pressure methods and soft abrasives seem to be a suitable alternative for cultural heritage to minimize the referred problems [26]. The micro blasting technology Sponge-Jet® (a dry soft-abrasive blasting media with a sponge-like urethane involving calcium carbonate particles) and Exastrip® (calcium carbonate particles) were successfully tested by Carvalhão & Dionísio in susceptible carbonate substrates [8] to remove Motip Home & Hobbylacquer® graffiti paints comparatively to the also tested KOH alkaline cleaner. These micro blasting methods induced less morphological changes. The low-pressure system Hydrogommage® (a circular projection of air, water and microabrasive composed by silica) was tested by Pozo-Antonio et al. to remove Montana Colours® graffiti paints on two granites with different composition and texture with satisfactory results. The drawback of the former method was the increase of the average roughness (Ra) around 10 μm for both granites [10]. The suitability of Hydrogommage® as a cleaning method of graffiti paints on granite substrate was later confirmed by hyperspectral imaging technique [27].

Lasers applied to cleaning of cultural heritage are preferred to extract graffiti paints on highly valuable and more fragile substrates since they allow a precise and localized cleaning with selective action adjusted in real time [13]. The different harmonics-wavelengths of nanosecond neodymium-based systems Nd:YAG [22,28–31] or Nd:YVO_4 [10,24,27,32,33] are the most commonly used lasers in stone cleaning. There are many published papers about the optimization of the laser cleaning of graffiti paints, in both substrates: carbonate [28,31,34] and granitic stone [10,32,33]. Regarding granite, different fluences of the Nd:YVO_4 laser working at 355 nm were studied by Fiorucci et al. for cleaning blue, red, black and silver graffiti [32]. More recently, a detailed study was carried out with the same laser in order to detect the optimal fluences to clean different colour graffiti paints on the main granite-forming minerals (quartz, plagioclase, potassium feldspar and biotite) on a calco-alkaline granite [24]. The cleaning performance by laser is influenced by the behaviour of the different granite-forming minerals and the textural characteristics of the granite, such as the cleavage and fissural system [24]. In addition, Rivas et al. confirmed that the cleaning effectiveness of graffiti paints by a Nd:YVO_4 laser at 355 nm depends also on the composition of the paint; while for red, blue and black Montana Colors® paints, satisfactory results were obtained, for silver paint a translucid carbon film rich in aluminium particles easily visible under naked eye remained on the stone surface [33]. Later, these cleaning effectiveness levels achieved by the laser were confirmed by means of hyperspectral imaging technique [27].

The previously cited works focused on mechanical and laser cleanings mainly considered fresh or unaged graffiti, i.e., the effectiveness evaluation of graffiti cleanings were performed using graffiti paints under laboratory conditions without interaction with the environmental agents (e.g., rain and/or atmospheric pollutants) as it happens in the real practice [2,3]. Nevertheless, a work regarding the influence of the SO_2 ageing on the graffiti cleaning effectiveness with chemical procedures on a granite substrate must be mentioned [3]. It was verified that the composition of the graffiti paints influenced their resistance under SO_2 rich environments and that after ageing, the paints became more difficult to clean with chemical procedures. Moreover, Sanmartín & Cappitelli [2] evaluated the interaction of metallic and non-metallic graffiti paints with two types of igneous stones and a fossiliferous limestone under different accelerated ageing tests (involving exposure to humidity, freeze-thawing cycles and NaCl and Na_2SO_4 salts).

Therefore, this research intends to study the influence of the graffiti ageing (exposure to a SO_2 rich environment) on the cleaning effectiveness with mechanical and laser techniques on a granite. Granite is indeed the most common ornamental and cultural heritage stone in the NW Iberian Peninsula [10,24,32,33]. The practical applicability of this study should also be highlighted since it intends to cover the graffiti cleaning of large areas of graffiti on facades by mechanical methods and small areas of more fragile and delicate stone pieces of art by means of laser ablation.

2. Materials and methods

2.1. Granite

Rosa Porriño, a two-mica calco-alkaline coarse-grained granite with a panallotriomorphic heterogranular texture was selected for this study. This granite is composed of 40% quartz (grain sizes from 3.8 to 0.8 mm), 27% K-feldspar (microcline, grain sizes reaching 10 mm), 14% plagioclase (grain sizes smaller than 1.8 mm), 8% biotite (1–2 mm in grain size), 2% muscovite and 5% accessory minerals [35]. A total of 180 stone parallelepipeds of 5 cm $\times$ 5 cm $\times$ 1.5 cm were prepared from disc-cutting finished-slabs.

2.2. Spray paints

Montana Colours® graffiti spray paints were selected based on previous researches [32,33,36,37]: devil red (R-3027), ultramarine blue (R-5002), graphite black (R-9011) and silver chrome (RAL-7001). These paints are basically alkyd spray paints with exception of silver spray, a polyethylene-based graffiti paint. A detailed chemical and mineralogical characterization of these graffiti paints can be consulted in Ref. [33]. A distance of 30 cm and an angle of 45° were maintained when the paints were sprayed over the stones during 30 s. Afterwards the samples were left seven days to air-dry in the laboratory (18 ± 5 °C; 60 ± 10% HR).

A total of 36 samples of each colour were painted, making a total of 144 samples. Also, 36 samples of granite were left without paint to serve as unaged reference.

2.3. Ageing process

Half of the painted samples (hereinafter referred as "unaged") were maintained during two months in the laboratory controlled conditions (18 ± 5 °C; 60 ± 10% RH) and the other half was placed in a FITOCLIMA 300EDTU climatic chamber (25 °C; 98% RH) with SO_2 exposure (hereinafter referred as "aged") also during two months. Unpainted granite samples (18 samples) were also placed