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Nd:YVO_4 laser removal of graffiti from granite. Influence of paint and rock properties on cleaning efficacy

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ABSTRACT

This paper presents the cleaning efficiency results for four differently coloured graffiti paints applied to two types of granitic stone by Nd:YVO_4 laser at 355 nm. The paints were characterized in terms of mineralogy and chemistry using x-ray fluorescence, X-ray diffraction, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscope (SEM); paint absorbance in the ultraviolet–visible–infrared range (200–2000 nm) was also assessed. The studied granites had different mineralogy, texture and porosity properties. Cleaning efficiency was evaluated by polarized microscopy, SEM, FTIR spectroscopy and spectrophotometer colour measurements. The results indicate differences in the effectiveness of surface cleaning for the blue, red and black paints as opposed to the silver paint, mainly attributed to chemical composition. No evidence was found that the granite properties had a bearing on laser effectiveness, although the degree, type and spatial distribution of transgranular fissures in the stone affected the overall assessment of cleaning effectiveness. Polarized light microscopy observations and colour measurements showed that the intensity and distribution of fissures affect the depth of paint penetration, ultimately affecting the cleaning efficiency for both granites.

1. Introduction

Graffiti on monuments and historic buildings is not just an aesthetic problem; it also represents a threat to conservation efforts. Conventional methods for removing graffiti paint can have undesirable side effects as they are often difficult to control. They are typically based on the application of chemicals or mechanical abrasion, each method with its drawbacks: in the former, the possibility of chemical contamination with consequences for future conservation, and in the latter, the risk of removing the natural or artistic surface patina (see [1,2] and references therein).

These circumstances have resulted in the need for effective approaches to cleaning stone and removing graffiti that also preserve historical and artistic values. Laser cleaning is considered to be a well established alternative cleaning technique (see, e.g., [3,4]) in the cultural heritage field, with advantages as follows: there is no mechanical contact or abrasion, it allows precision removal of thin layers of material (contamination, paint, corrosion, etc.), the method is automated and self-controlled and the technique is environmentally friendly.

The use of laser to remove graffiti has been reported by several authors who mostly use different harmonics of the Nd:YAG laser (the 1604 nm, 532 nm and 355 nm wavelengths). In one study [5], the first and second harmonics (1064 nm and 532 nm, respectively) were used to remove graffiti from neolithic sandstone; however, paint removal was not uniform and a treatment based on organic solvents was necessary prior to use of the laser. Another study [6] compared the effectiveness of the second (532 nm) and third (355 nm) harmonics for removing different coloured spray paints from standard construction substrates (glass, steel, timber, marble and concrete); it was concluded that better results were obtained with the third harmonic, as it fully removed the pigment and polymer base of the paints without damaging the substrate, whereas the second harmonic left traces of the polymer base. Yet another study [7] compared the cleaning results obtained using laser radiation at 308 nm (XeCl excimer laser) and at 1064 nm (Nd:YAG laser), finding that the XeCl ultraviolet radiation fully removed the paint, whereas the infrared Nd:YAG removed the pigment but frequently left traces of the polymer base and also damaged the substrate. The same authors, in the case of the 1064 nm laser, also observed differences in ablation thresholds and absorbance for the same paint applied to different substrates, suggesting, as possible explanations, different surface absorbance rates or substrate–paint interactions. Other authors [4] have recently reported satisfactory results for graffiti removal using the second harmonic, but point to problems with metallic paints.

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Further studies [8] have described strategies for removing graffiti from limestone using the three Nd:YAG laser harmonics and both the N-mode and Q-switching mode, concluding that the results depend both on the nature of the graffiti and the lithotypes. The nature of the substrate was found to clearly influence cleaning efficacy. Two studies–one that evaluated the impact of the microstructure (roughness and porosity) and moisture content on graffiti removal from mortars using the Nd:YAG fundamental wavelength [9] and another that analysed the influence of rock microstructure on the removal of dark encrustations from marble [10] – highlighted the crucially important issue of adjusting laser exposure conditions to the microstructure characteristics of each stone type when considering which laser cleaning method to apply.

We present a study on the effectiveness of removing different colour graffiti from two different granites using the third harmonic (355 nm) of an Nd:YVO_4 laser with a high repetition rate. This kind of laser emits very low energy pulses (0.1 mJ) with a repetition rate that can be set in the kHz range; these features allow better control of the layer-by-layer ablation process and more uniform treatment over the whole surface than with the Nd: YAG laser.

Described in previous works [11–15] was the use of this kind of laser to remove different coating layers from granites, along with the associated problems. In the research described in this article we evaluated different responses to laser cleaning by different coloured spray paints and assessed whether the granite properties conditioned the cleaning process. Granite, which has been widely used in the construction of historical buildings and monuments in Spain, especially in the northwest, is a lithotype whose textural peculiarities condition its response to different kinds of conservation interventions [16–20]. For the purpose of the study we selected two internationally known commercial quality granites, Vilachán and Rosa Porriño, similar in terms of roughness but different in terms of porosity, grain size and mineralogy. To our knowledge, no studies exist that analyse laser cleaning of graffiti from different granites. To achieve our objectives, prior to cleaning, the paints and granites were characterized and the laser irradiation parameters for the ablation process were determined.

2. Materials and methods

2.1. Graffiti characterization

We selected four commercial colours – Montana Mtn® Classic brand [21] – identified by their RAL codes [22] as ultramarine blue (R-5002), devil red (R-3027), graphite black (R-9011) and silver chrome. These colours were recommended by cultural heritage professionals due to their different responses to conventional cleaning procedures. The paints were characterized using the following equipment:

(1) An X-ray fluorescence spectrometer (Siemens SRS 3000), to determine the chemical composition of the major and trace elements. For this analysis, the paint was applied to nitrocellulose supports and measurement was made directly, with the results expressed as a percentage of the element (expressed as oxide) after subtraction of the signal from the nitrocellulose support.
(2) A Fisons EA-1108 elemental analyser, to analyse the elemental composition (CHNS) of residue scraped from the paints applied to an aluminium support.
(3) An X-ray diffractor (SIEMENS D-5000), to characterize mineralogical composition using the random powder (grazing incidence) method.
(4) A Fourier transform infrared (FTIR) spectroscope (Thermo Nicolet® 6700), to characterize the functional groups for each paint. The paints applied to aluminium supports were analysed (i.e., whole samples) and also the soluble fraction in universal organic solvent (acetone). The references provided in Socrates [23] were used to identify the functional groups.
(5) A UV–vis/NIR spectrometer (PerkinElmer Lambda 900) with an integrating sphere (Spectralon® of 150 mm), to measure the diffuse reflectance of the paints in the range 200–2000 nm. Paint absorbance was calculated from diffuse reflectance as ABSORBANCE = 1 − REFLECTANCE. The technique was applied to dried paint on different surfaces (granite and metal).

2.2. Granite selection and paint application

Two commercial quality ornamental granites from quarries in northwest Spain were selected, called Vilachán and Rosa Porriño. Vilachán is a fine-grained panallotriomorphic heterogranular adamellite [24], composed of quartz (47%), potassium feldspar (10%), plagioclase (15%), biotite (7%), muscovite (18%) and zircon and other mineral accessories (3%). The grain sizes of the different minerals range between 2 mm and 0.3 mm. Open porosity (accessibility to water following [25]) is 2.82%. Rosa Porriño is a two-mica calc-alkaline coarse-grained granite with a panallotriomorphic heterogranular texture, composed of quartz (40%), potassium feldspar (27%), plagioclase (14%), biotite (8%), muscovite (2%) and chlorite and opaques as accessories (5%). Open porosity (following [25]) is 0.84%. Grain sizes range through 10 mm (potassium feldspar grains), 3.8–1.2 mm (quartz grains) and 2.0–0.3 mm (biotite grains).

Samples measuring 4 cm × 4 cm were prepared from 2 cm thick honed slabs of the two granites. Mean roughness measured with a Wyko NT1100 in PSI mode was 3.20 μm for Vilachán granite and 4.29 μm for Rosa Porriño granite. The samples were painted with the four colours. Painting was performed in two phases separated by an interval of 24 h. The graffiti was sprayed onto the stone for 3 s at an angle of 45° and from a distance of 30 cm. After painting, samples were left to air-dry in the laboratory during seven days.

In order to characterize the morphology, continuity, thickness and penetration depth of the paints, cross-sections of the granite surfaces painted with the four colours were viewed using petrographic microscopy (NIKON Eclipse LV100 POL) and scanning electron microscopy (SEM) (JEOL JSM-6700F) with energy dispersive X-ray spectrometry (EDS) (Oxford Inca Energy 300 SEM).

2.3. Laser cleaning

Samples underwent laser irradiation with the aim of fully removing the spray paint while causing minimal damage to the stone surface. The laser used was an Nd:YVO_4 (Coherent AVIA Ultra 355–2000) at the 355 nm wavelength and with 25 ns pulse duration. The intensity profile at laser output was Gaussian TEM00 and beam diameter at the $1/e^2$ intensity level was about 2.2 mm. The pulse repetition rate could be selected from single-shot to 100 kHz with energy per pulse of around 0.1 mJ.

The beam impinged perpendicularly onto the target surface of the specimen placed on a motorized XYZ-translation stage (Newport ILS-CC), with a controller (Newport MM4006) to manage movement of the stage and to start/stop the laser using digital transistor–transistor logic output. The specimen surface was precisely positioned at the beam waist of the focused beam using the *Z*-direction stage. Customized software was used to program the controller in any arbitrary trajectory and to synchronize the laser with specimen displacement.

Homogeneous irradiation of the target within 10 mm × 10 mm was achieved by scanning the sample along a grid of linear trajectories. Owing to the number of parameters involved in laser treatments, decisions regarding the most suitable values for graffiti cleaning purposes were based on previous studies of granites