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# Effectiveness of commercial anti-graffiti treatments in two granites of different texture and mineralogy

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ABSTRACT

This paper presents a study of the efficiency of two chemically different anti-graffiti coatings (sacrificial and permanent anti-graffiti products) on two different compositional and textural granitic stones, Rosa Porriño and Albero.

First, both uncoated and coated surfaces of the granites were characterized using stereomicroscopy and scanning electron microscopy, static contact angle measurements, colour spectrophotometry and gloss measurements. Results showed that both anti-graffiti products increased the static contact angle of the surfaces. The permanent anti-graffiti made them water-repellent without causing notable colour changes.

Second, effectiveness of the anti-graffiti products was evaluated by means of the removal of two different spray graffiti paints (blue and silver colours) on both granites protected with the above-mentioned anti-graffiti products. The cleaning procedures were those recommended by the manufacturers. Fourier Transform Infrared spectroscopy and the previously mentioned techniques were used to assess the cleaning efficiency of the coated surfaces by detecting or not the presence of graffiti remains. As a result, textural differences in the granites, chemical composition of the graffiti paints and removal time were found to be the key parameters controlling the effectiveness of graffiti removal. On Albero granite, more residues of paint were found in its fissure system. Blue graffiti based on alkyd and polyester resins was more readily removed than silver paint. In general terms, graffiti extraction was more effective 30 days after painting than 3 days after.

## 1. Introduction

Graffiti, perceived as vandalism, is a persistent problem around the world, especially in urban areas where it can be found on public transportation, civil infrastructure, monuments and buildings. Among the different graffiti cleaning procedures the most popular ones that involve the use of detergents or solvents (chemical procedures) and/or pressure water (mechanical procedures) are not always satisfactory [1] and can be quite expensive (e.g. the estimated cost of cleaning graffiti in UK is over £1 billion a year [2]). Moreover, sometimes they may even be counter-productive, especially on porous materials such as concrete and natural stone [3–7]. On the one hand, chemicals can be retained in their pore systems (even after washing with pressure water) and this contamination can result in the precipitation of salts [3–5]. On the other hand, mechanical procedures can open or create fissures or cracks which would favour water absorption and the adhesion of future graffiti paints [4–7]. For all those reasons and not only for aesthetic impact, graffiti is a major threat particularly on built heritage materials. Even the less aggressive cleaning methods with low pressure water (100–200 psi), which are less efficient in cleaning graffiti, have associated hazards since excess of water can favour salt migration as well as freeze-thaw deterioration [8].

Laser cleaning of graffiti, despite being expensive and time-consuming and still under refinement, is the method recommended in situations where traditional procedures can be harmful to the stone [[10],[9]]. This technique also has certain limitations; as occurs with traditional cleaning methods, laser efficiency depends on the type of paint to be extracted [10]. The higher the absorbance of the paints to laser radiation, the more efficient is their removal. This fact explains the highest difficulty to remove metallic colours (gold, silver and bronze) that contain high reflectance Al-rich particles [10,11]. Occasionally, laser cleaning can cause colour variations on the substrates because of migration of organic compounds from the graffiti into their pores [12], the own interaction of the laser beam with the minerals of carbonate

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stones causing the yellowing [13], the fading of the K-feldspar in pinkish granite [14] or changes in the oxidation state of ferrous oxide compounds [9]. Even fusion of different granite forming minerals and the appearance of fractures have been reported [15,16].

Despite granite being one of the most common building stone worldwide, research on the cleaning effectiveness of graffiti on granitic samples is scarcer than for carbonate stones [17–19]. Recent studies have compared the effectiveness of different (chemical, physical and laser) methods of graffiti removal on granites showing unsatisfactory results in spite of the low open porosity of the substrates examined (around 1%) [5,15,20]. All of the evaluated procedures produced harmful effects on the stones (chemical contamination, opening of fissures and alteration of rock-forming minerals) and even when graffiti was removed from the surfaces, graffiti still remained in fissures inaccessible to all the cleaning methods; e.g. after laser cleaning [10].

Considering the main drawbacks of laser and traditional cleaning procedures (chemicals retained in the pore systems, fusion of minerals and fractures), anti-graffiti coatings could be an alternative solution to optimize graffiti removal. These treatments hinder the adhesion of paint to the surface of the materials and so, make graffiti easier to remove with solvents and/or water with low pressure. In general, anti-graffiti products can be divided into two main groups. On the one hand, products based on waxes, polysaccharides and acrylates belong to the group of sacrificial anti-graffiti coatings which are removed together with graffiti. On the other hand, polyurethanes, siloxanes and epoxy resins are part of the permanent coatings group which can withstand various cleaning cycles without needing reapplication [21].

However, there have been published a few previous studies on such innovative treatments and their potential for use on built heritage where they provided an efficient protection with minimal modification of the historic substrate. Such studies have been mainly focussed on limestones and sandstones [6,21–25] with uneven results. The effectiveness of these products on granites has been even less well explored. In two earlier works, Carmona-Quiroga et al. [26,27] found that the performance of two different permanent anti-graffiti coatings was more satisfactory (less global colour changes after graffiti removal) in a limestone than in a granite due to their different finishes: smoother limestone was easier to clean than the rougher granite.

To fill the knowledge gap on the cleaning effectiveness of graffiti on granitic stones, the evaluation of the application of permanent or sacrificial anti-graffiti coatings on granite could be an effective solution for graffiti removal, as opposed to traditional cleaning methods.

As it is well known that textural peculiarities influence the response to different kinds of conservation interventions [28,29], two renowned commercial quality granites with different porosities, mineralogy and texture (Rosa Porriño and Albero) were used in the current paper. Both granites were coated with a permanent and a sacrificial anti-graffiti products in order to test their effectiveness in the removing of two graffiti paint of different easiness of removal following a previous study [10]: an easier graffiti to be extracted (blue graffiti) and a more difficult one (silver graffiti). Their cleaning effectiveness was evaluated by means of microscopic and spectroscopic techniques. Prior to this evaluation, the surface properties of the granites were characterized after the application of both anti-graffiti coatings.

## 2. Materials and methods

### 2.1. Granitic samples, anti-graffiti coatings and graffiti paints

#### 2.1.1. Granitic samples

Two commercially valuable granites from NW Iberian Peninsula, Rosa Porriño and Albero, were selected. Rosa Porriño is a post-Hercynian two-mica granite [30] with a panallotriomorphic heterogranular texture, composed of quartz (40%), potassium feldspar (27%), plagioclase (14%), biotite (8%), muscovite (2%) and chlorite and opaques as accessories minerals (5%). It is a coarse grained granite with crystals up to 10 mm (microcline) grains. Considering the physical properties, accessible porosity (AP) following [31] is 0.96% (v/v), total porosity (TP, mercury injection, AutoporeIV9500 porosimeter of Micrometrics) is 1.45% (v/v), water absorption coefficient (under pressure) is 0.48% (w/w) [32], water absorption coefficient (by capillarity) is 0.37% (w/w) [32] and apparent bulk density is 2605.00 $kg\ m^{-3}$ [33].

Albero is a pre-Hercynian equigranular medium grained granite [30] and it is composed by quartz (22%), K-feldspar (43%), plagioclase (23%), muscovite (4%), biotite (7%) and apatite, zircon, rutile, chlorite and sillimanite as accessories minerals. It is a coarse grained granite with an average grain size of 5 mm. Therefore, Albero has a finer grain-size than Rosa Porriño. Regarding the physical properties, accessible porosity (AP) following [31] is 3.87% (v/v), total porosity (TP, mercury injection, AutoporeIV9500 porosimeter of Micrometrics) is 4.08% (v/v), water absorption coefficient (under pressure) following [31] is 1.52% (w/w), water absorption coefficient (by capillarity) following [34] is 1.32% (w/w) and apparent bulk density is 2541.47 $kg\ m^{-3}$ [35].

Albero is slightly more porous than Rosa Porriño, both in terms of accessible porosity and total mercury intrusion porosity. Comparing accessible porosity and total porosity by mercury injection (AP/TP), Rosa Porriño shows a lower percentage of accessible voids to mercury that are also accessible to water. However, Albero shows a higher level of communication among voids. Both granites have a pore size distribution characterized by the presence of typical trans-granular, inter-granular and intra-granular fissures [28]. 11 saw cutting-finished slabs of 6 cm × 6 cm × 2 cm for each granite were used.

#### 2.1.2. Anti-graffiti products

Both granites were coated with two commercial anti-graffiti products: a permanent water based fluoralkyl siloxane (AGr1) and a sacrificial water based crystalline micro wax (AGr2). Two coats of each product were sprayed onto the surface of the materials on consecutive days. In total for both types of granite, 10 slabs were coated (5 with AGr1 and 5 with AGr2) and 1 slab per granite was left uncoated as a reference sample. Coated samples were dried at room temperature (18 ± 5 °C, 50 ± 10% RH) until constant mass. The flow of the current research can be consulted in Fig. 1.

#### 2.1.3. Graffiti paints

Two spray paints, Blue Ultramarine and Silver Chrome from Montana Colors S.L. (http://www.montanacolors.com) were selected. Following a previous study [10], these graffiti paints showed different behaviour during cleaning, being blue graffiti the easiest to remove. As reported in [10] Blue Ultramarine is composed of alkyd and polyester resins, while Silver Chrome showed a predominance of polyethylene-type polymers. In Table 1, the composition of these two graffiti paints by X-ray Fluorescence (XRF, Siemens SRS 300) and Elemental analyser (CHNS, Fisons EA-1108) is shown. XRF was used 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 oxide after subtraction of the signal from the nitrocellulose support. An elemental analysis (CHNS determination) was made of the residue scraped from the paints on an aluminium support.

For each granite, four slabs coated with the same anti-graffiti product were covered with each graffiti paint (Fig. 1). A sample coated with each anti-graffiti was left unpainted for use it as a reference. The graffiti paints were sprayed once on half of each specimen from a distance of 10 cm during 10 s.

### 2.2. Cleaning procedure

The removal of the graffiti was performed at two different moments: after 3 days of drying at laboratory conditions (18 ± 5 °C, 50 ± 10% RH) and after 30 days of drying under laboratory conditions, in order to simulate immediate or delayed cleaning procedures respectively