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# Preliminary investigations of the action of nanostructured materials for the conservation of fresco paintings in high-humid environments

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***Abstract* – A preliminary study on the protective effect of nanostructured materials developed for the conservation of fresco paintings sited in high humidity environments is here reported. The study has been performed on mock-up samples prepared on the base of a non-invasive investigation performed on the frescos of the complex St. Mary of the Cave in Marsala (Trapani, Italy). The mock-up samples simulate both the stone support and the mortar preparation as well as the fresco painted with the same kind of pigments found in two of fresco paintings. Some nanostructured materials such as nano-sized fluorosilanes in water, nanosilica in water, nanolime and their mixtures have been tested evaluating the effect on the colour appearance and on surface properties.**

## I. INTRODUCTION

In the last two decades, several nanostructured materials have been developed for the restoration and conservation of stone artefacts [1-5]. Their particular properties make this class of compounds very interesting and useful, mainly in all the circumstances where the size of the materials needs to be controlled to achieve the best results and where the environmental parameters are crucial for the maintenance of a good conservation state. On the other hand, there are some specific contexts such as hypogea or environments with high humidity where there are several unsolved problems of conservation. In many cases, the interests around them is high due to their historical artistic and religious impacts and to the presence of wall paintings. However, the high humidity, the strong thermal inertia and the dark light make the conservation of the fresco paintings not easy. One of the cause of degradation is the salt crystallisation [6,7] which is also the consequence of a very bad conservation state of the frescos. In this case, the restoration requires specific solutions for each step of the work, including an appropriate choice of the materials for the consolidation and protection. In the last years, some nanostructured materials have been proposed such as nanolime, taking in the mind the compatibility with the original substrates and the pigments and their stability at high humidity conditions [8,9]. However, some advantages can occur like the developing of different form of calcium carbonate [10,11]. Other studies are reported recently in literature but it is still a challenge [12]. Here, a preliminary study on nanostructured materials developed for the conservation of fresco paintings sited in high humidity environments is reported. The study, with the goal to compare the performance of some of the nanostructured materials, is organized in three part: 1. non-invasive investigation of a fresco located in a cave with high humidity; 2) preparation and aging of mock-up samples simulating the fresco; 3) application of nanostructured dispersions developed as protectives and consolidants and evaluation of their performance. The complex St. Mary of the Cave in Marsala (Trapani, Italy) [13,14] was chosen as case study for the simulating of the mock-up samples. The frescoes in fact are in a very poor conservation state. A diffuse inconsistent and coherent surface deposit is present together with a chromatic alteration mainly due to a whitening of the surface. The causes of the degradation can be related primarily to the presence of water in various forms: capillary rise, infiltration, and condensation.

## II. EXPERIMENTAL SECTION

Several mock-up samples, of size 5x5x2 cm and specimens of size 5x5x1 cm, were obtained, according to the UNI EN 10921 standard. The mock-up samples were cleaned and washed with running water, immersed in deionized water for 30 minutes and dried in an oven at a temperature of 60 ± 2 °C until constant weight was reached. The mock-up samples were used as references for the preparation of the mock-up painted samples, which have been used to perform the aging and the application of nanostructured materials. The mock-up painted samples were prepared applying three layers. The first is simulating the so-called *arriccio*, the second so-called *tonachino* and the third is the pictorial layer where the chosen pigments, such as yellow ochre and cinnabar, are some of the ones identified in the frescos of the complex St. Mary of the Cave. Each mock-up was tripled to evaluate the repeatability of the tests.

*Fig. 1. Example of mock-up painted samples simulating the fresco.*

Three nanostructured dispersions such as nano-sized fluorosilanes in water, nanosilica in water, nanolime in hydroalchoolic medium and their mixtures have been tested. The efficacy of formulations is performed through the following techniques: colorimetry to evaluate the color changing. Water absorption by capillarity and Water vapour permeability to evaluate the Water repellence and the Breathability, respectively. The wettability was evaluating by slowly adding a drop (25μL) of distilled water on the mock-up surface.

## III. PRELIMINARY RESULTS

Here the preliminary results about the wettability show the differences between the tested formulations.

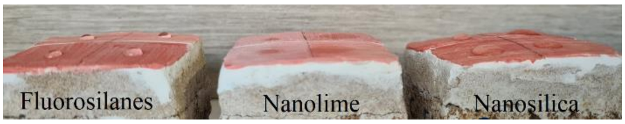


*Fig. 2. Example of wettability of formulations applied on mock-up samples prepared with the fresco techniques.*

The best wettability performances were observed for the nano-sized fluorosilanes with a well defined drop on the surface while in the case of nanolime the drop is totally adsorbed with an angle contact close to zero. The nanosilica show an intermeddled behaviour with favourable wettability.

The stone total colour difference was evaluated, for each protective, on painted mock-up specimens of size 5 × 5 × 2 cm. An Ocean Optics reflectance spectrophotometer equipped with a DH-mini light source and a USB 2000 + XR1 detector, operating in the spectral range 190–1100 nm, was used. Data were acquired by setting a CIE D65 standard illuminant, and a CIE 10◦ standard colorimetric observer. The CIE L*a*b* colour space was used as a reference system where each colour is defined by three colorimetric coordinates: L* is the coordinate of lightness; a* is the red/green coordinate and b* is the yellow/blue coordinate. For each specimen five regions, few mm$^2$ in size each, were examined and averaged. The total colour difference, $\Delta E^*_{21}$, was calculated in the CIE L*a* b* colour space by using the following equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where $\Delta L^* = L_{*2} - L_{*1}$ is the lightness difference; $\Delta a^* = a_{*2} - a_{*1}$ is the red/green difference and $\Delta b^* = b_{*2} - b_{*1}$ is the yellow/blue difference. The obtained values (Table I) suggest that the application of fluorosilanes does not substantially alter the surface color, as evidenced by a total $\Delta E^*_{21}$ of less than 5 (limit suggested by Istituto Superiore per la Conservazione ed il Restauro).

*Table I. Averaged colour parameter difference of treated mock-ups.*

| | ΔL* | Δa* | Δb* | ΔE*$_{12}$ |
|---|---|---|---|---|
| ***Fluorosilanes*** | -2,8 | -1,0 | 0,4 | 3,1 |
| ***Nanolime*** | 30,2 | 1,1 | 2,7 | 30,3 |
| ***Nanosilica*** | -32,6 | -2,0 | 15,5 | 42,1 |

Applying nanolime significantly enhances ΔL* due to surface bleaching. Conversely, when nanosilica is applied, it results in negative values for lightness difference, leading to darkening.

The amount of water absorbed by capillarity is evaluated according to the UNI EN 15801. The averaged water absorption curves for capillarity obtained by plotting the average values of the amount of water absorbed per unit area, Qi, as a function of the time for the stone and the mock-up with mortar is reported in Fig. 3.

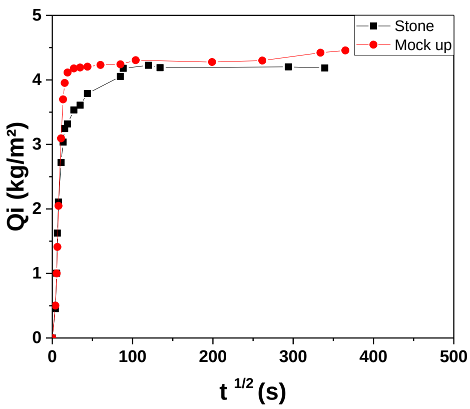


*Fig. 3. Amount of water absorbed per unit area, Qi, as a function of the time, for three different mock-up samples.*

The initial linear trend of the untreated specimens is followed by a plateau whose value indicates that the stone is characterized by a high aptitude for the absorption of water by capillarity. The presence of mortar doesn't affect the water absorption according with a similar interaction of the mortar with water such as for the stone. The tests of the treated sample are still in progress.

The water vapour permeability is determined according to the UNI EN 15803 standard. Measures are still in progress. The preliminary results show some differences between the tested nanostructured materials, the difference in the color is not a critical parameter while the wettability clearly show the difference between the systems, with the best performances of nano-sized fluorosilanes. The water repellency and the Breathability is still under evaluation.

The research work will evaluate the performances of the tested formulations and the aging of the mock-up samples under the environmental conditions of the thermo-hygrometric conditions of the complex St. Mary of the Cave in order to simulate their real applicability.


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