

## Thinning of oxalate patina with Er:YAG laser stand-alone and in combination with Agar and Carbogel systems

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In this work, the removal tests of the oxalate patina present on the 15th century mural painting are described. The thinning of oxalate patina is of utmost importance due to its widespread presence on natural and artificial stone substrates. The removal tests were performed either by the laser cleaning or by the combined chemical followed by laser approach. The output of these tests, monitored with optical coherence tomography, profilometry and colorimetric measurements, is discussed and compared.

The laser cleaning tests were accomplished with a short-free running Er:YAG laser (El.En.spa) emitting at 2.94 microns with variable pulse duration. The pigment transformation due to the thermal or photo-oxidation processes under the laser beam is a well-known phenomenon. For this reason, the resistance of red ochre pigment, present also in the fresco, was verified through a series of irradiation tests on laboratory prepared specimens. A very good resistance towards the laser radiation was ascertained under all the tested fluences (3.8-9.4 J/cm<sup>2</sup>).

As a further step, it was verified that the Er:YAG laser does not allow for the non-contact oxalate expulsion. However, the mechanical disruption of the oxalate patina was achieved. Consequently, the disrupted patina was removed with cotton swab soaked with water or isopropanol. The phenomenon of photomechanical disintegration was enhanced when laser irradiation was performed in presence of isopropylalcohol as a wetting agent. This is due to the efficient coupling of the 2.94 microns laser radiation into the vibrational modes of –OH groups of alcohols. The etch rate, which in this context means the depth of the disrupted layer, was calculated as a function of the applied fluence. The 7.0 and 7.6 J/cm<sup>2</sup> fluences proved as the most efficient and time-wise reasonable operation conditions to diminish the 40 microns thick oxalate layer.

The combination of chemical followed by physical cleaning was tested as well. To this aim, two commonly used gels (Agar and Carbogel) were charged with EDTA chelate (5% tetrasodium ethylenediaminetetraacetate) and left to act for 30 minutes. The preliminary action of poultice charged with chelate agent allowed to diminish the laser fluence and to operate at 5.0 J/cm<sup>2</sup> with the results comparable to those achieved by standalone laser irradiation.

In conclusion, the preliminary chemical cleaning followed by mild laser ablation appears as beneficial. Moreover, Agar poultice ascertains better adhesion and therefore more homogeneous cleaning results.

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