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To cite this article: E Sassoni *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **949** 011005

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Restoration and preventive conservation of marble artworks: the HAP4MARBLE project

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The HAP4MARBLE project was funded by the European Commission within the call H2020-MSCA-IF-2014 of the Marie Skłodowska-Curie Actions (Grant Agreement n. 655239). The goal of the project was to develop an innovative conservation treatment for marble artworks exposed outdoors, which suffer from several deterioration processes predicted to be worsened by future climate change:

1) dissolution, owing to calcite solubility in rain and formation/dissolution of soluble salts originating from pollutant dry deposition, resulting in marble surface recession and loss of carved elements;

1) sugaring, i.e. granular disintegration caused by the anisotropic thermal behaviour of calcite grains, so that marble can be reduced to a sugar-like powder of isolated grains by just the pressure of a finger;

2) soiling, i.e. darkening induced by deposition and accumulation of atmospheric particulate matter;

4) bowing of thin slabs used as gravestones in historic cemeteries, commemorative stones or cladding in modern façades, induced by cyclic thermal excursions, which may lead to slab collapse.

To face these issues, the project was aimed at multi-functionalizing a recently proposed treatment [1], which is based on formation of hydroxyapatite (HAP, the main constituent of human teeth and bones), by reaction of marble with an aqueous solution of diammonium hydrogen phosphate [1].

Within the project, the HAP treatment was further developed [2] to achieve the following objectives:

1) Prevention of marble dissolution. By covering the marble surface with a continuous and dense layer of HAP (which is much less soluble than calcite), marble dissolution can be prevented. The influence of several parameters on the coating properties was investigated (e.g., concentration of the phosphate precursor, addition of organic solvents, reaction time, pH). The project results indicate that crack-free and pore-free coatings can be obtained by adding small amounts of alcohol to the ammonium phosphate solution [3]. So-formed coatings are able to significantly delay corrosion of marble, in a more effective way than commercial alternatives [3]. The feasibility of accelerating and promoting HAP formation by electrodeposition was also investigated [4]. By placing a metal electrode near the surface of the marble element and by applying an electric current, precipitation of HAP on the marble surface was found to be favoured, compared to standard chemical methods without current application [4]. This electrochemical route of HAP formation may be of interest to increase the resistance to dissolution in rain of marble elements such as historic and new slabs, as well as small movable sculptures.

2) Consolidation of sugaring marble. The ability of HAP formed inside intergranular fissures to re-establish cohesion among loose calcite grains, thus stopping material loss, was investigated. To this goal, a novel method to produce artificially decayed specimens with properties similar to those of naturally weathered marble (i.e., near-surface damage) was first developed [5]. Then, the consolidating effectiveness of the novel formulations of the HAP-treatment was evaluated, together with its aesthetic and microstructural compatibility [3]. The consolidating ability of the HAP-treatment was found to be comparable (if not superior) to that of available commercial treatments, with the



advantage of being effective in a much shorter time, being more compatible and/or more durable [3]. Considering that deteriorated marble in the field is often covered with a layer of gypsum, which can not always be removed before consolidation, a tailored formulation of the HAP treatment was specifically developed for gypsum-contaminated marble [6].

3) Arrest and prevention of marble bowing. The ability of newly formed HAP to mitigate thermal weathering of marble was also evaluated [7]. Initially bowed and initially fresh marble specimens, untreated and treated by various formulations of the HAP-treatment and by alternative consolidants, were subjected to heating-cooling cycles in dry and wet conditions. The project results indicate that, in the case of pre-bowed specimens, further bowing can be reduced, while pre-treatment by HAP of initially fresh marble can significantly delay the onset of bowing [7]. Notably, one of the commercial alternatives to HAP was found to significantly worsen the thermal behaviour of treated marble [7].

4) Development of self-cleaning ability. At present, architectural surfaces are often made self-cleaning by application of suspensions of photocatalytic nano-TiO₂. However, so-deposited TiO₂ nanoparticles are easily washed away by rain [8]. Therefore, to provide marble surfaces with durable self-cleaning ability, composite coatings were developed by embedding TiO₂ nanoparticles into insoluble HAP coatings. These composite coatings exhibited enhanced photocatalytic activity and durability, compared to currently available commercial products based on TiO₂ alone [8].

Finally, pilot applications of the HAP-treatment onto marble artworks were performed to derive a preliminary validation of the treatment's performance in the field. The most promising formulations were applied onto naturally weathered marble slabs that were then exposed in the Park of the Royal Palace in Versailles (France), where also a marble sculpture was treated with the HAP-treatment. The slabs and the sculpture have been periodically monitored for the last three years and in all cases a good conservation state has been registered.

For the implementation of the HAP4MARBLE project, Dr. Enrico Sassoni (the Marie Skłodowska-Curie Fellow) worked for 18 months with Prof. George W. Scherer at Princeton University (USA), for 6 months with Prof. Siegfried Siegesmund at Göttingen University (Germany) and for 12 months with Prof. Elisa Franzoni (Coordinator of the project) at the University of Bologna (Italy).

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 655239 (HAP4MARBLE project).

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