STONES AND MORTARS PROTECTION: THE NEW FRONTIER OF HYBRID COATINGS

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The environmental conditions can seriously affect the monumental stones and for this reason conservation of historical buildings is nowadays an important issue. Atmospheric pollution is the main responsible for stones deterioration and its impact on buildings has been studied in a systematic and scientific manner [Price, 1996]. Some of the major pollutants that seriously affect stoneworks are carbon, sulphur and nitrogen oxides together with aerosol particulate matter such as smoke, the main responsible of surface soiling. Lastly, the presence and movement of moisture within a material, facilitated by high porosity, can enhance and alter the concentration of weathering agents and aid their damaging activity.
In the last few years, hybrid coatings based on the synergic interaction between nanomaterials (nano-oxides) and tradition hydrophobic resins have been applied for restoration and conservation of works of art.

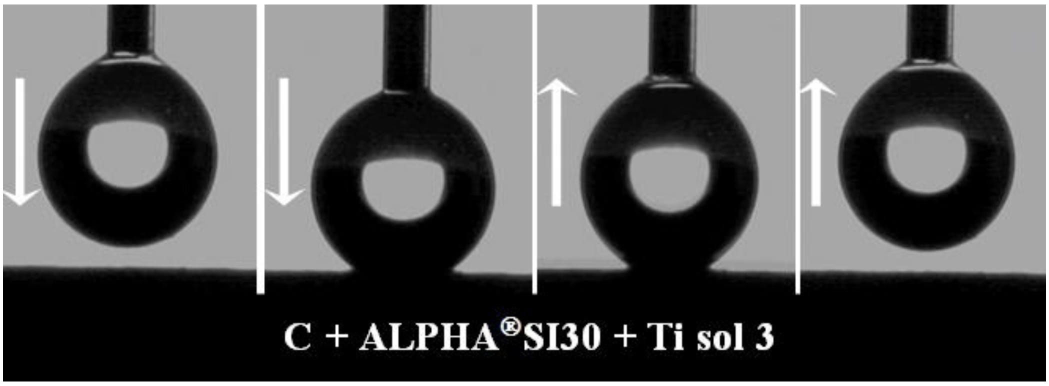
In this work a commercially available Si-based resins have been applied as protective agents on both stone materials (Carrara, Botticino, Candoglia marbles and Angera stone) and mortars made using both hydraulic binder NHL 3.5 and lime putty. Furthermore, since it is well known that the mix of resins with nanoparticles allowed to obtain complete buoyancy and self-cleaning properties, hybrid coatings containing home-made TiO_2 nanoparticles mixed with the commercial silane polymers ware applied to the stones and mortars.

The results concerning the physico-chemical characteristics of the bare stones compared with those of the treated samples will be presented and discussed. In order to evaluate the stability of the applied coatings towards degradation induced by solar radiation and interaction with the atmospheric pollution, accelerated ageing tests under UV irradiation and exposure to a typical polluted urban environment for some months (during the autumn-winter period) have been carried out. For this purpose the following analyses have been performed: contact angle measurements, SEM-EDS (Scanning Electron Microscopy with X-ray microanalysis), IC (Ion Chromatography), colorimetric tests by DRS (Diffuse Reflectance Spectroscopy) followed by CIELab elaboration, porosity measurements, water absorption by capillarity and water vapor permeability.
Static contact angle (θ) measurements on the stone surfaces were performed in order to know their wetting properties. The application of AlphaSI30 coating leads to hydrophobic materials ($90° < \theta < 100°$) [Fermo et al., 2013]. In order to improve the water repellence of the coatings, nanoparticles (TiO_2) deposition techniques [Soliveri et al., 2012] was used to induce superhydrophobicity ($\theta > 150°$). In this latter case, due to the enhanced water repellency of the resin-TiO_2 film, the water drops bounced and rolled off the treated layer: the images sequence in Figure 1,

taken by rising very slowly the support up to the contact with the pendant drop, until the drop stuck onto the TiO_2 hybrid surface, well evidences the superhydrophobic behaviour.

In order to investigate the stability of the coatings, accelerated aging tests by UV irradiation were carried out. Colorimetric measurements (CIELab) were performed to verify the color modification (yellowing) of the protective film due to solar exposition.

Fig. 1. Evidence of the superhydrophobic behaviour of the hybrid layer (Alpha®SI30+ Ti sol 3) on C marble by water contact angle images. The images sequence, taken by rising very slowly the support up to the contact with the pendant drop, until the drop stuck onto the TiO_2 hybrid surface, well evidences the superhydrophobic character of the composite layer (the first two images are relative to the drop before and when it touches the surface and the second two after this event: the drop stays unmodified)



Color and static contact angle measurements were carried out for hydrophobic and superhydrophobic systems before and after 10h of UV exposure (Table 1). The treated samples did not show both a visible colour and contact angle variations even after UV irradiation (always $\Delta E^* \leq 4$, $\Delta\theta^* \leq 3$).

Tab. 1. Variation of CIELAb parameters (DE) and contact angles before and after UV ageing for hydrophobic (stone+AlphaSI30) and superhydrophobic (stone+AlphaSI30+titania sol) systems

Stone/treatment	**ΔE**	**Δθ**
A+AlphaSI30	4.0	–
A+AlphaSI30+titania sol	2.0	-2
B+AlphaSI30	1.9	–
B+AlphaSI30+titania sol	0.9	+3
C+AlphaSI30	3.1	–
C+AlphaSI30+titania sol	3.0	-3

The effect of exposure in an typical urban polluted environment has been evaluated and a reduction of salts growth process has been obtained for both the surface treatments (pure resin and hybrid coating).

References

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