

Article

# Artificial Ageing of Photocatalytic Nanocomposites for the Protection of Natural Stones

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**Abstract:** During the last ten years, photocatalytic nanocomposites combining titania nanoparticles with silicon-based matrices have received increasing attention in the stone conservation research field, because they offer an effective multifunctional approach to the issue of stone protection. However, much work still has to be done in studying the behaviour of these nanocomposites in real environmental conditions and understanding to what extent they are able to retain their effectiveness and compatibility once applied on outdoor surfaces. The latter is a key information that should lie at the basis of any successful conservation and maintenance campaign. The present study provides insight into this relevant topic through laboratory testing by assessing the artificial ageing of two silane-based photocatalytic nanocomposites, previously selected through an accurate testing on different natural stones. Three accelerated ageing procedures, based on artificial solar irradiation, heating and rain wash-out, allowed simulating about two years of outdoor exposure to some of the weathering factors to which stones are normally subjected. The results provided quite accurate information about the long-term behaviour of the products and on the role that the stone properties play therein. It was shown that, when the products are able to penetrate deeply enough inside the stone pores, they retain much of their hydrophobising and photocatalytic properties and maintain a good compatibility with the stone substrates, even after partial chemical degradation of the alkyl-silica matrices has occurred on the very stone surface.

**Keywords:** natural stones; protective coatings; titania nanoparticles; photocatalysis; silane; durability; artificial ageing; solar irradiation; thermal ageing; rain wash-out

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## 1. Introduction

The protection of natural stones used in historical buildings has been traditionally fulfilled through the application of suitable water-repellent polymers, which are known to modify the interface between the stone and the outer environment and, thus, limit the capillary absorption of condensed water (with atmospheric pollutants and salts dissolved therein) into the porous stone network [1,2].

During the last ten years, a significant advance in the field of stone protection has been made through the development of nanocomposite treatments, which rely on the combination of traditional polymer matrices (mostly polyacrylates or siloxanes) with inorganic nanoparticles. On the one hand, blends of nanoparticles and polymers or organo-modified silica nanoparticles alone showed the property of enhancing the water-repellent features of traditional polymeric treatments [3–6]. On the other hand, nanomaterials such as ZnO and TiO<sub>2</sub>, which proved to be effective in the photocatalytic oxidation and removal of particulate deposit or in the prevention of biofilm growth on stone artefacts [6–9], were combined with polymer matrices to obtain multifunctional treatments with

hydrophobising and photocatalytic/antifouling properties [10–14]. Lately, this kind of treatments have received increasing attention from the part of both conservators and industrial manufacturers, as important European research initiatives such as the H2020 Nano-Cathedral project stand to witness [15].

One issue of great relevance to the evaluation of these multifunctional treatments is their durability [16]. This is true, in a general sense, for any kind of protective treatments because the planning of sustainable conservation campaigns on historical buildings and monuments requires that a reasonable prediction should be made as to how long the protective effect of the treatments will endure after their application and exposure in outdoor conditions. For various reasons, this is not an easily attainable goal, not least because of the persistent gap between academic research and conservation practice. Besides that, there are inherent difficulties (and, to the present day, a lack of established guidelines) in the set-up of appropriate laboratory conditions and protocols to mimic the effects of some of the weathering factors found in the natural environment and of their synergistic combination. Accelerated ageing procedures, performed on laboratory scale, have been part of many studies concerning the use of polymers such as acrylics for the purpose of stone conservation. These studies addressed e.g., the resistance towards photo-oxidative degradation [17–21] and salt-induced damage [21,22].

As regards the durability of TiO<sub>2</sub> nanoparticles as protective agents, the retention on the stone surface and photocatalytic efficacy upon rain wash-out [23–28] and exposure to UV light [24–32] have been considered. A widely accepted conclusion is that, even though results may also depend on the characteristics of the stone substrates chosen for the application, nanoparticles alone suffer from poor mechanic stability [33]. At the same time, the durability of TiO<sub>2</sub>-based polymeric treatments, one of whose aims is to improve the retention of nanoparticles on the treated stone surfaces, poses additional specific questions. Whilst it is demonstrated that polymeric matrices enhance the mechanic stability of nanoparticles [34,35], the implication of nano-TiO<sub>2</sub> in the photo-oxidative degradation of the matrices [36,37] needs to be circumstantiated, as regards to both the effects that this degradation may have on the general protective performance and compatibility of the treatments and the influence that the stone-treatment interaction exerts on the timescale of the process. Both of these questions, together with the set-up of reliable ageing protocols, deserve attention from a research perspective that aims to improve the current knowledge about photocatalytic protective treatments in the field of built heritage conservation.

In a previous publication [37], which discussed the results of the addition of TiO<sub>2</sub> nanoparticles on the chemical–physical properties and the protective performance of two different alkyl-alkoxysilane matrices, an initial assessment was carried out regarding the durability of the resulting nanocomposites by focusing on the TiO<sub>2</sub>-induced chemical degradation of the alkyl-silica gel networks and on its effect on the water absorption of two different porous stone substrates after a time-limited exposure (600 h) to artificial sunlight. The encouraging conclusion was that, even though TiO<sub>2</sub> nanoparticles are seen to accelerate the photo-oxidative degradation of the matrices, this only affects the performance of the treatments on the very stone surface, having quite limited effects on the reduction of water absorption by capillarity.

In the present research, the ageing behaviour of the same two photocatalytic nanocomposites, applied to four different stone substrates having very different microstructural and mineralogical characteristics, is studied through a comprehensive investigation protocol that considers three main ageing factors, namely heat, solar irradiation and meteoric precipitation. Compared to other protocols available in the literature [23,27], the one proposed here is marked by a systematic investigation of the effects of different stress agents, considered both separately and additively, on the protective effectiveness and compatibility of the treatments and by a consideration of the role that the stone properties play therein. Based on the results of a previous evaluation of the protective performance that assessed the best stone/treatment combination [37,38], each of the two treatments under study was applied on two appropriate stone substrates and its response towards accelerated long-term ageing was evaluated with respect to changes in the surface wettability, capillary

absorption, weight, surface morphology, photocatalytic activity, surface colour and water vapour permeability of stone specimens.

## 2. Materials and Methods

### 2.1. Stones

Four rocks, characterised by different microstructural (Table 1) and mineralogical properties [39,40], were selected for this study. All of them have a place in the history of European architecture as building materials. Lumaquela de Ajarte (from Treviño, Castile and León, Spain) is a biomicrite stone with creamy greyish colour, composed of shell fragments in a highly porous carbonate matrix consisting of recrystallised fossils (>99% calcite). Apuan marble (from Carrara, Tuscany, Italy) is a compact metamorphic rock composed of calcite (>99%). Obernkirchen sandstone (from Bückeberge, Lower Saxony, Germany) is a fine to medium-grained, porous quartz-arenite (90% quartz and 8% kaolinite) with colour ranging from white-grey to light orange. Schlaitdorf sandstone (from Schlaitdorf, Baden-Württemberg, Germany) is a whitish to yellowish coarse-grained quartz-arenite, characterised by a clastic fraction (~75% quartz) dispersed in a kaolinite (~12%) and dolomite (~9%) matrix.

**Table 1.** Properties of the selected stones: open porosity (%vol.) and median pore diameter ( $\mu\text{m}$ ), obtained from Mercury Intrusion Porosimetry (MIP) measurements [39].

Property	Ajarte	Obernkirchen	Apuan Marble	Schlaitdorf
Open porosity	23.5 $\pm$ 0.4	24.1 $\pm$ 0.1	0.7 <sup>a</sup>	16 $\pm$ 1
Median pore diameter	1.96 $\pm$ 0.04	11.1 $\pm$ 0.6	1.3 <sup>a</sup>	8 $\pm$ 4

<sup>a</sup> In the case of Apuan marble, measurements were performed on one specimen instead of two.

### 2.2. Protective Treatments

WNC and ANC (Chem Spec srl, Peschiera Borromeo, Italy) are protective formulations developed in the framework of the Nano-Cathedral Project and consist of alkylalkoxysilane reactive sols with small amounts of TiO<sub>2</sub> nanoparticles. Specifically, WNC is a water-based emulsion of silane oligomers (15% *w/w*) and TiO<sub>2</sub> nanoparticles (0.96% *w/w*), while ANC is composed of silane monomers (40% *w/w*) in 2-propanol and only contains a tiny fraction of TiO<sub>2</sub> (0.12% *w/w*) [38]. The alkyl-silica gel produced upon hydrolysis and condensation of the silane units imparts water-repellent features to the coatings, while TiO<sub>2</sub> nanoparticles add photocatalytic and self-cleaning properties.

In the preparatory stage of this study, these formulations were applied onto the four selected stones and their protective performance was evaluated through an accurate laboratory testing (see §2.4) in comparison with the commercial TiO<sub>2</sub>-free siloxane treatment SILRES BS290 (Wacker Chemie GmbH, Munich, Germany). The application was done by capillary absorption for 6 h. Prior to the treatment, stone specimens were dried in oven at 50 °C overnight and then cooled down in a silica gel desiccator. The amount of treatment absorbed was determined by weighing each specimen before the application and a minimum of 30 days after it, which is enough to allow a complete evaporation of the solvents and an advanced sol-gel transition. Based on the results of laboratory tests [37–39], one treatment per stone was selected to undergo the subsequent artificial ageing. The respective amounts of dry matter absorbed are reported in Table 2.

**Table 2.** Amounts (mg/cm<sup>2</sup>) of the treatments WNC and ANC absorbed by Ajarte, Apuan marble, Obernkirchen and Schlaitdorf stones, measured after drying and curing.

Product	Ajarte	Obernk.	Apuan m.	Schlait.
WNC	9 $\pm$ 4	9 $\pm$ 2	–	–
ANC	–	–	0.51 $\pm$ 0.07	16 $\pm$ 5

### 2.3. Ageing of Treatments

A complex ageing procedure was conceived in order to assess how the performance of the treatments is modified upon exposure of treated stone specimens to different chemical, physical and mechanical stress agents. First, to evaluate the response of the treatments to solar irradiation, a first set of specimens were aged in a sunlight simulator and, to isolate the contribution of solar light from that of heating, a thermal ageing procedure was conducted on a second set. Then, to evaluate the stability, particularly of TiO<sub>2</sub> nanoparticles, under the mechanic stress of meteoric water, a third set of specimens were subjected to a simulated neutral pH rain. Moreover, to evaluate the combined effects of sunlight and rain, the first set of specimens, after the solar ageing, were subjected to the simulated rain. On the whole, three ageing procedures were conducted in parallel and two of these were also conducted sequentially. All procedures were designed by drawing on the experimental set-ups found in recent literature. The main difference is that, while other set-ups involve multiple cycles of short-time UV irradiation and rain wash-out steps [27], the proposed scheme is characterised by a sequential application of only two long-time steps of solar and rain ageing.

Overall, 21 specimens per stone and treatment (including equal subsets of  $5 \times 5 \times 2$  and  $5 \times 5 \times 1$  cm<sup>3</sup> specimens and a larger subset of  $5 \times 2.5 \times 1$  cm<sup>3</sup> specimens for the different tests) underwent the three ageing procedures. The testing of the performance after ageing relied on at least two replicas.

#### 2.3.1. Solar Irradiation Ageing

The solar ageing was conducted for 1500 h (in two steps of 750 h) in a solar box (Suntest XLS+, Ametek, Inc., Berwyn, PA, USA) equipped with a Xenon arc lamp (NXE 1700) simulating daylight (cut-off filter for wavelengths  $\lambda < 295$  nm), which is an experimental set-up similar to others reported in the literature [18,24,27]. The irradiance of the lamp was set to 765 W/m<sup>2</sup> in the 300–800 nm range, with a reported emission of about 65 W/m<sup>2</sup> in the range from 300–400 nm, which is close to the hypothetical upper limit of UV irradiation of natural daylight (70 W/m<sup>2</sup>) [24,41]. The surface temperature of the specimens, measured through a black body reference, was kept at  $65 \pm 5$  °C. Considering irradiance and exposure time, the radiant energy provided to the specimens in the 300–400 nm range was 351 MJ/m<sup>2</sup>, corresponding to about 27 months [24,42] of natural UV (UVA + UVB) exposure for horizontal surfaces in Southern England (Reading, 51°27' N, 0°58' W) and 22 months [24,43] in Southern Mediterranean Europe (Cyprus, Athalassa, 35°15' N, 33°40' E). For non-horizontal surfaces, where the natural incident radiation is reduced by inclination and orientation, the real exposure time corresponding to the total UV irradiance of the test is clearly much longer than estimated. However, these values can be assumed as upper limits for the exposure conditions of Northern- and Southern-European buildings, respectively.

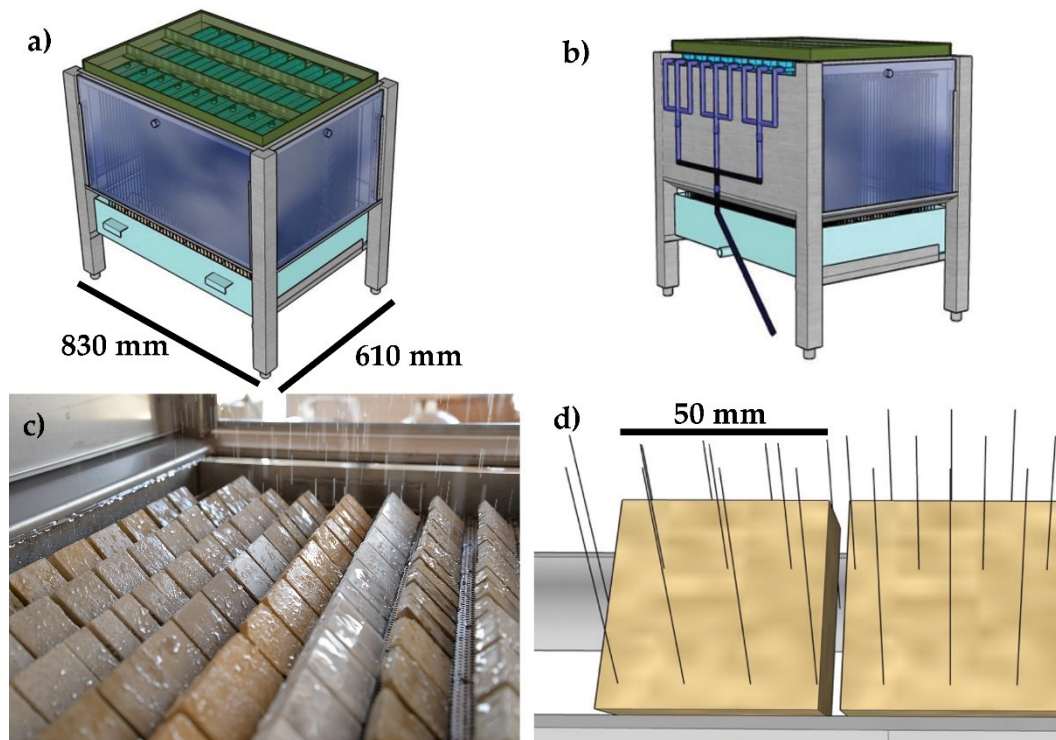
#### 2.3.2. Thermal Ageing

As in previous experiments simulating the stability of acrylic polymers in real outdoor conditions [19], a thermal ageing of stone specimens was conducted for 1500 h in two steps of 750 h each, at  $65 \pm 5$  °C in a non-ventilated oven. The temperature and exposure time were set to be the same as for the solar ageing, so that a comparison between the effect of heat alone (thermal ageing) and the combined effects of UV light and heat (solar ageing) was possible.

#### 2.3.3. Rain Wash-Out Ageing

The resistance to rain wash-out was assessed in a purposely designed rain chamber (Figure 1) equipped with a peristaltic pump (Behr Labor-Technik GmbH, Düsseldorf, Germany) and a set of medical needles ( $d = 0.2$  mm) that provide constant dripping of distilled water (pH 7) at a rate of about 82 mm/h. Based on one similar experiment reported in the literature [23], the stone specimens were placed on a rack and tilted by 45° with respect to the horizontal plane. Each of them was hit by drops according to the scheme shown in Figure 1d, thus causing water to flow on most of the surface. Furthermore, to achieve a more homogeneous wash-out, all specimens were displaced by 0.5 cm along the needle axis and rotated by 180° for half of the testing time. The test was conducted in 4

steps of 24 h, with 7 h of wetting followed by 17 h of drying at room temperature. This made up 2300 mm rain, which corresponds to about 3 years of outdoor exposure according to a rough estimation of the average yearly rainfall across Europe (750 mm [44]).



**Figure 1.** Rain chamber: front (a) and rear (b) view, with display of the hydraulic system to ensure a controlled dripping of water; (c) stone specimens placed inside the chamber and tilted by 45°; (d) scheme of the controlled dripping of water.

#### 2.4. Testing of Specimens

The capillary water absorption test was carried out on  $5 \times 5 \times 2$  cm<sup>3</sup> specimens according to the gravimetric method (standard protocol EN15801 [45]). The specimens were weighed at the following time intervals: 10 min, 20 min, 30 min, 60 min, 4 h, 6 h, 24 h, 48 h, 72 h and 96 h. The amount of water absorbed per unit area after 96 h ( $Q_i$ , mg/cm<sup>2</sup>) and the relative capillary index ( $CI_{rel}$ ), i.e., the ratio of the integrals from 0 to 96 h of the absorption curves of treated (t) and untreated (nt) specimens ( $\int_0^{96} [Q(t)]_t dt / \int_0^{96} [Q(t)]_{nt} dt$ ), were used to describe the long-term absorption behaviour, while the relative absorption coefficient ( $AC_t/AC_{nt}$ ), which represents the ratio of the absorption coefficients of treated ( $AC_t$ ) and untreated specimens ( $AC_{nt}$ ) during the first 30 min of the test, was used to describe the short-term absorption behavior.

Static contact angle ( $\theta$ ) measurements were performed on  $5 \times 5 \times 1$  cm<sup>3</sup> specimens according to the standard protocol EN15802 [46], using an OCA 20 PLUS (DataPhysics Instruments, Filderstadt, Germany). The analysis was conducted 10 s after drop deposition, with a drop volume of 5  $\mu$ L, on 15 spots per specimen. Drop profiles were processed according to Laplace-Young theory. Distilled water was used as liquid. Measurements were performed from few hours to few days after the end of the respective ageing procedures, and were also repeated several months later, after the specimens had been kept in the dark, to check for the possibility that reversible light-induced superhydrophilicity of titania, particularly after artificial solar irradiation, may affect the wetting behaviour of surfaces. No difference, i.e., no reversible change in contact angle values, was observed between the two measurements. This is probably due to the low TiO<sub>2</sub> content in the two nanocomposites, whose wetting behaviour is dominated by the hydrophobic properties of alkyl-silica matrices.

Water vapour permeability tests were performed on  $5 \times 5 \times 1$  cm<sup>3</sup> specimens according to the standard protocol EN15803 [47], using the “wet cup” system. The cups were filled with 5 mL of a

saturated aqueous solution of  $\text{KNO}_3$  (0.32 g/mL) and placed in a climatic chamber (Bresciani srl, Milan, Italy) at  $23 \pm 1$  °C and  $50 \pm 3\%$  RH. Then, after a dead time of about 60 h, they were weighed at intervals of 24 h for 5 days. The mass change ( $\Delta m$ ) was plotted against time ( $t$ ) and the slope of the linear section of the curve ( $G$ , in kg/s) was used to calculate the water vapour permeability ( $\delta$ ,  $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ ). The relative permeability  $\delta_t/\delta_{nt}$  is defined as the ratio of the vapour permeabilities of treated specimens ( $\delta_t$ ) and their untreated counterparts ( $\delta_{nt}$ ).

The aesthetic compatibility of the treatments upon ageing was assessed on  $5 \times 5 \times 2$  cm<sup>3</sup> specimens through diffuse reflectance Vis-light spectroscopy (Konica Minolta, Tokyo, Japan) CM-600D Vis spectrophotometer with a D65 illuminant at 8°, 360–740 nm wavelength range) according to the standard protocol EN15886 [48]. Measurements were carried out on 25 spots per specimen. The results were expressed in the CIE  $L^*a^*b^*$  colour space and the average values of  $L^*$ ,  $a^*$  and  $b^*$  were used to calculate the colour change  $\Delta E^*$  with respect to the untreated specimens, which should not exceed the threshold value of 5 in order to meet the aesthetic requirements in the cultural heritage field [49].

The photocatalytic activity of the treatments was assessed on  $5 \times 2.5 \times 1$  cm<sup>3</sup> specimens (3 replicas) by means of the Rhodamine discolouration test, as previously described [37]. The extent of discolouration ( $D^*$ ) was calculated by considering the  $a^*$  colour coordinate, which represents the red component in the CIE Lab space. Since the test relies on the deposition of a liquid solution and the latter is influenced by the water-repellent properties of the coatings, specimens treated with the commercial treatment SILRES BS290 (Wacker Chemie GmbH) were used as blank. In order to discriminate the actual photocatalytic process from the photolytic and thermal degradation of the colourant,  $D^*$  values at 150 min for specimens treated with the photocatalytic products ( $D^*_t$ ) were divided by those relative to SILRES BS290 ( $D^*_{\text{SILRES}}$ ). Values of the  $D^*_t/D^*_{\text{SILRES}}$  ratio higher than 1 indicate the presence of photocatalytic activity.

The morphology of untreated, treated and aged specimens was observed through Environmental Scanning Electron Microscopy in BSE mode (low vacuum) by an EVO 50 EP ESEM (Zeiss GmbH, Oberkochen, Germany) on  $5 \times 2.5 \times 1$  cm<sup>3</sup> specimens.

The weight loss of stone specimens upon ageing was measured and reported as product loss (%wt.), that is, percentage weight loss over the amount of product applied.

### 3. Results and Discussion

In a previous article [37], which discussed some aspects of the chemical degradation of WNC and ANC when applied on glass slides and subjected to solar irradiation for 600 h, it was shown that, while silane matrices alone do not undergo a degradation of the organic functional groups, the addition of  $\text{TiO}_2$  accelerates the process quite clearly. The rate of this degradation showed a dependence on the amount of nanoparticles present in the two protective formulations: when nanoparticles are present in very low concentration (as in the product ANC), the kinetics of the process turns out to be slow enough not to have remarkable effects on the chemical stability of the product, whereas these effects become quite relevant in the presence of a higher  $\text{TiO}_2$  content (as in the product WNC). However, once the two products were applied on stones and subjected to the same solar irradiation, the result was that their effectiveness in preventing the absorption of water into stones was retained to a very good extent. The proposed explanation of this fact was that, insofar as the products were able to penetrate deep into the stone pores, they were protected from incoming radiation and did not suffer from strong photo-oxidative stress. Ajarte and Obernkirchen stones, which were the substrates chosen for the tests, are actually highly porous stones.

One of the aims of the present study was to investigate the role of the stone properties in the retention of the protective effectiveness upon ageing. Four stones with remarkable differences in porosity and mineralogical composition were selected to this purpose: alongside the above mentioned Ajarte and Obernkirchen stones, Schlaitdorf and Apuan marble are mid- and low-porosity stones, respectively. From the mineralogical point of view, Ajarte and Apuan marble are mostly composed of calcite, while Obernkirchen and Schlaitdorf are quartz-arenites.

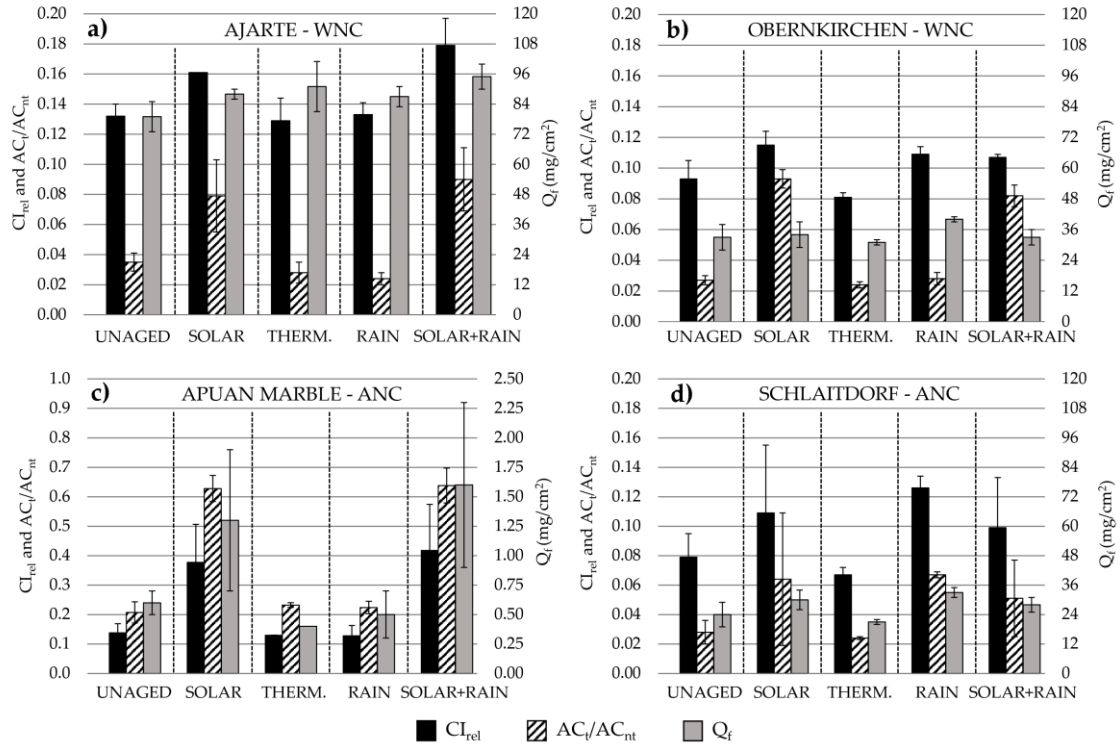
According to the results of contact angle (Table 3) and capillary absorption (Figure 2) measurements, solar irradiation is the only ageing procedure that induces significant effects on the protective behaviour of WNC and ANC. A decrease in static contact angle, ascribable to the solar-induced degradation of the alkyl-silica matrices [37], is indeed observed regardless of the product applied, whereas rain ageing is only responsible for a very moderate decrease and thermal ageing has substantially no effects in terms of water-repellency (Table 3). This demonstrates that the degradative effect of solar ageing is essentially a light-induced one, while the contribution of moderate heating, common to both solar and thermal ageing, is in all respects irrelevant. The effects of solar ageing on the wetting behaviour of treated stones range from a total loss of water-repellency on Ajarte, Obernkirchen and Apuan marble, which revert to their original contact angle values as untreated materials, to a significant reduction in the case of Schlaitdorf stone treated with ANC. The latter is partly due to the lower TiO<sub>2</sub> content of the product, but a role of the stone properties can also be claimed. A comparison between Apuan marble and Schlaitdorf stone, where the same product ANC is applied, proves instructive in this sense. In the case of marble, where most of the product concentrates on the surface, which is also quite smooth, the loss of water-repellency is complete, whereas on a stone like Schlaitdorf, characterised by an open porosity of about 15% and a high macroscopic surface roughness, not only is the product less exposed to incoming radiation even on the very surface, but its penetration provides for an extensive coverage of the inner pore surface, resulting in a lower degradation and a lower decrease in contact angle.

The importance of product penetration in commanding a greater or lower retention of the protective effectiveness comes across quite clearly by observing the results of water absorption measurements by capillarity (Figure 2). Since some degradation of the products was shown to occur on the stone surface, it is not unexpected that an increase in the short-term water penetration rate ( $AC_i/AC_{nt}$ ) by two to three times is observed on all stones after solar ageing. However, if the long-term absorption behaviour is considered, the difference between Ajarte, Obernkirchen and Schlaitdorf stones on the one hand and Apuan marble on the other prove that the degradative effects do not extend far below the stone surface. In the former case, both the capillary index ( $CI_{rel}$ ) and the total amount of water absorbed at 96 h ( $Q_f$ ) remain satisfactory even after 1500 h of irradiation, whilst a substantial increase occurs in the case of Apuan marble, pointing out that product penetration is critical for the durability of the protective performance.

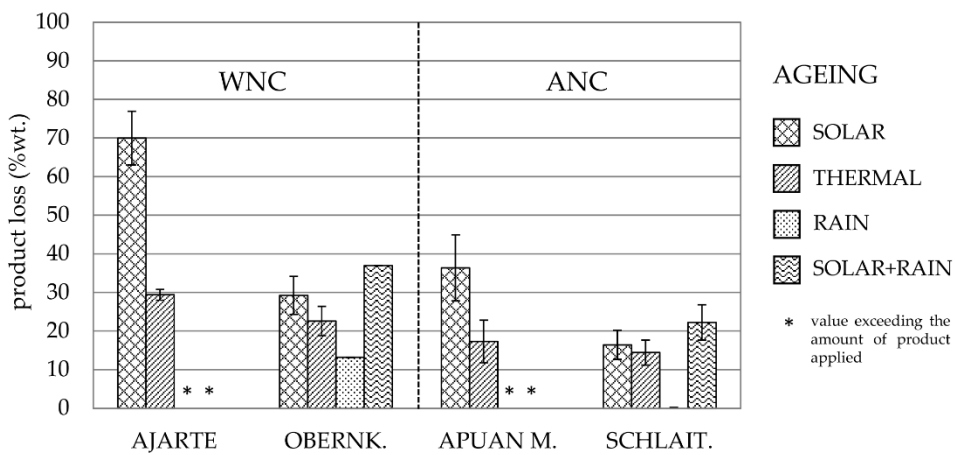
**Table 3.** Static contact angle ( $\theta$ ) of Ajarte, Obernkirchen, Apuan marble and Schlaitdorf specimens treated with WNC/ANC before ageing (UNAGED) and after solar, thermal, rain and sequential solar-rain ageing, with standard deviation ( $\sigma$ ).

Ageing	WNC				ANC			
	Ajarte		Obernk.		Apuan m.		Schlait.	
	mean	$\sigma$	mean	$\sigma$	mean	$\sigma$	mean	$\sigma$
Unaged	122	7	136	3	140	10	137	3
Solar	<10	–	<10	–	58	5	110	0
Thermal	122	8	138	2	130	4	134	4
Rain	126	2	128	4	122	7	130	3
Solar+Rain	<10	–	<10	–	45	2	106	5

In order to investigate whether the chemical degradation of the treatments is accompanied by a removal or a morphological alteration in the surface coatings, the weight decrease of the stone specimens after the three ageing procedures was measured (Figure 3) and their surface morphology was analysed by SEM (Figures 4 and 5).



**Figure 2.** Water absorption behaviour of (a) AjarTE; (b) Obernkirchen; (c) Apuan marble and (d) Schlaitdorf specimens treated with WNC/ANC before ageing (UNAGED) and after solar, thermal, rain and sequential solar-rain ageing; relative capillary index ( $CI_{rel}$ ), relative absorption coefficient ( $AC_i/AC_{nt}$ ) and amount of water absorbed at 96 h ( $Q_i$ ,  $mg/cm^2$ ).



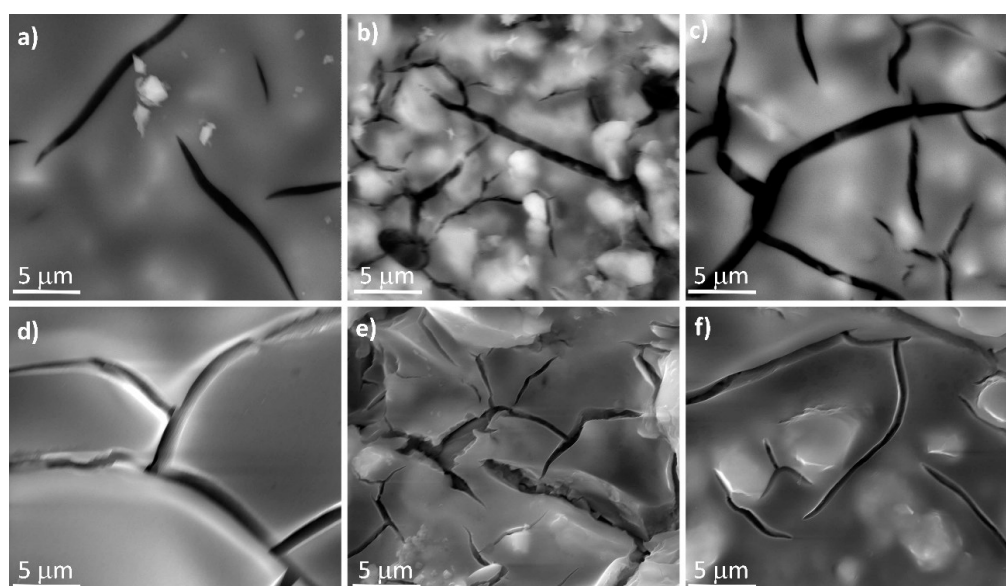
**Figure 3.** Product loss (%wt.) from AjarTE, Obernkirchen, Apuan marble and Schlaitdorf specimens treated with WNC/ANC upon solar, thermal, rain and sequential solar-rain ageing. In the case of AjarTE stone and Apuan marble, whose calcite matrix is prone to dissolution under rain wash-out (rain ageing and solar-rain ageing), asterisks are placed instead of product loss values, since losses due to the dissolution of the calcite matrix exceed the amount of product applied (for AjarTE stone: by +31% and +45%, respectively; for Apuan marble: by +141% and +326%, respectively).

The values of product loss upon ageing reported in Figure 3 show that a decrease of about 25% and 15% of the amount of product applied occurs after thermal ageing for WNC and ANC, respectively. Such decrease is comparable in magnitude on AjarTE and Obernkirchen and on Apuan marble and Schlaitdorf, respectively, so it turns out to be independent from stone properties such as porosity and mineralogical composition. Its cause probably lies in the slow and steady evaporation



of residual water and alcohol which result from the ongoing curing of the alkyl-silica gel network and tend to remain trapped in the gel deep inside the stone matrix. The aqueous product WNC is characterised by a slower evaporation and curing, which explains its greater weight loss upon heating. In turn, solar irradiation is responsible for an excess product loss, which can be ascribed to the chemical degradation of alkyl-silica, marked by the disappearance of alkyl groups [37]. The magnitude of this loss is higher for the product that contains a greater amount of titania (WNC), but it also varies strongly from stone to stone. On the two calcite stones, Ajarte and Apuan marble, the loss is indeed much higher than on the quartz-arenites Obernkirchen and Schlaitdorf. This may stem from the fact that chemical degradation compromises the adhesion of the products to calcite crystals more than it does in the case of silicate minerals.

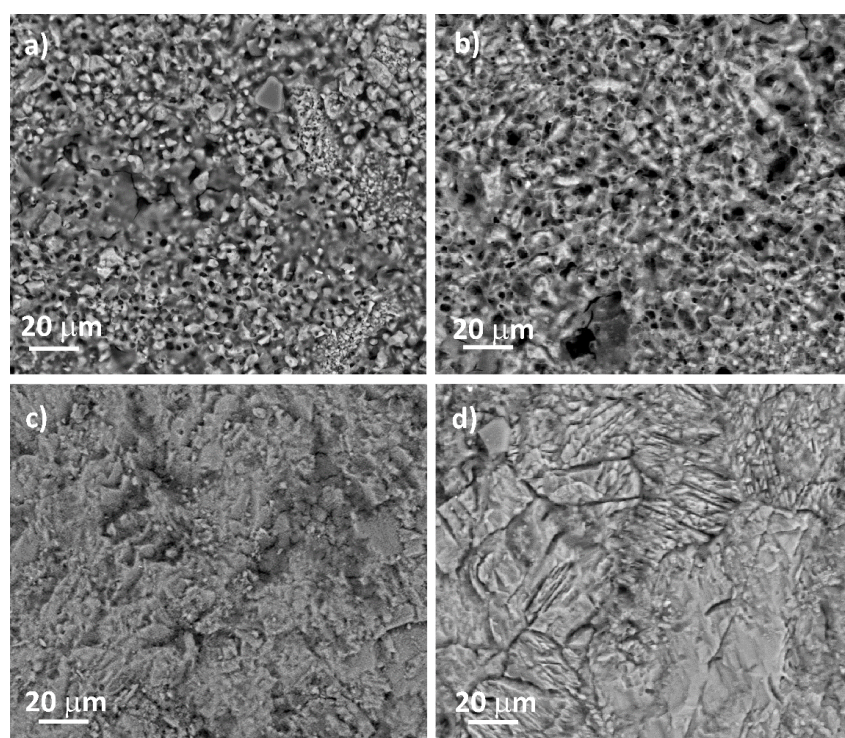
The effects of the solar-induced degradation are not so well discernible from a visual point of view. Where the morphology of the treatments is neatly visible on the stone surface with their characteristic network of shrinkage cracks, as is the case of Ajarte and Obernkirchen stones, both solar and thermal ageing induce further breaking of the coating layer, increasing the frequency of cracks and reducing the coverage of the mineral surface (Figure 4). Only in the case of Ajarte, where solar irradiation determines a considerable excess product loss, there is evidence of a greater morphological alteration induced by solar irradiation as compared to thermal ageing, with the appearance of bright clusters due to the surface mineral roughness, from an initially continuous and smooth coating layer (Figure 4b).



**Figure 4.** SEM micrographs of Ajarte (a,b,c) and Obernkirchen (d,e,f) stone specimens treated with WNC/ANC in BSE mode: before ageing (a,d); after solar ageing (b,e); after thermal ageing (c,f).

Rain wash-out, alone and in combination with solar ageing, is another case where the outcome of an ageing procedure is strongly influenced by the stone properties, mainly surface roughness and porosity. As shown in Figure 3, whilst on the quartz-arenites Obernkirchen and Schlaitdorf the weight loss upon solar and thermal ageing is lower than seen on calcite-based stones, the partial run-off and dissolution of the calcite crystals causes a weight loss that even exceeds the amount of treatment applied. However, as the values of contact angle in Table 3 and the SEM images in Figure 5 stand to witness, upon rain ageing the coatings and their protective efficacy are preserved on Ajarte stone, although the details of the mineral surface are less well defined and the coating layer appears perforated by a greater number of apertures and their width is perceivably larger (Figure 5b). In the case of Apuan marble, where the coating layer is less visible, a deterioration of the crystalline matrix can be perceived, with a clear detachment of the grain boundaries and the appearance of new transversal grain micro-fractures (Figure 5d). Finally, an additional weight loss can be traced back to the sequential application of solar irradiation and rain ageing. Again, this loss is not negligible on

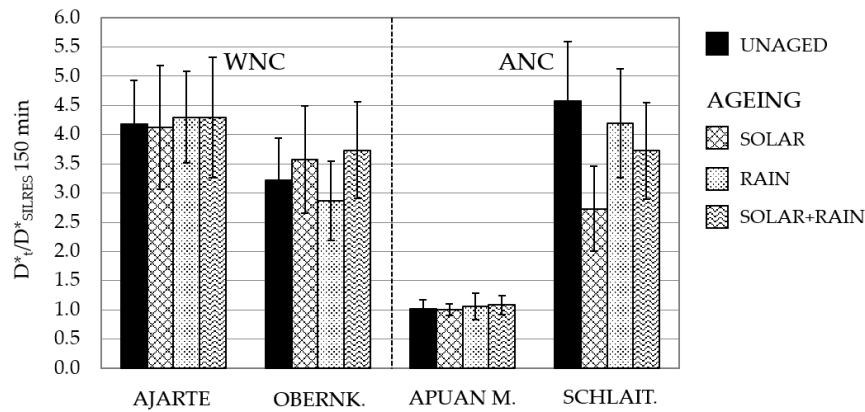
Ajarte and is especially high on Apuan marble, which suggests the fact that the chemical degradation of the coatings also reduces to some extent their mechanic stability on substrates where the stone-coating interaction is inherently less strong.



**Figure 5.** SEM micrographs of Ajarte (a,b) and Apuan marble (c,d) specimens treated with WNC/ANC in BSE mode: before ageing (a,c); after rain ageing (b,d).

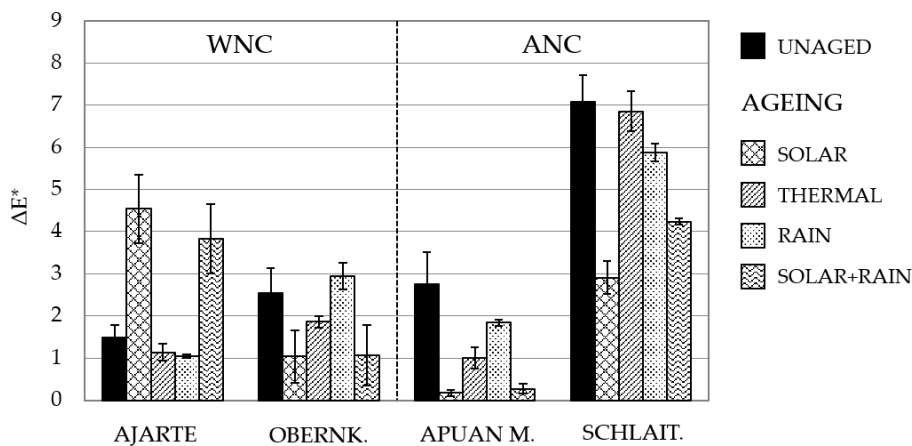
Since it has been shown how the different ageing procedures, notably solar irradiation, modify the surface properties of treated stones, among which water-repellency has the greatest relevance, it is of interest to assess which changes affect the second most relevant of these properties, namely photocatalytic activity.

By a previous spectroscopic study of the two formulations WNC and ANC [37], it was demonstrated that TiO<sub>2</sub> nanoparticles show a detectable chemical interaction with the embedding alkyl-silica matrix of WNC. In the present study, one further step ahead was made by investigating whether the chemical degradation of the matrices upon solar ageing goes so far as to compromise the mechanic stability of nanoparticles and their photocatalytic activity. In Figure 6, it can be observed that results are quite promising in this regard. In the cases of Ajarte and Obernkirchen stones, photocatalytic activity is almost unchanged after irradiation in the solar box and rain ageing carried out alone, and it remains almost unaltered when rain ageing is performed on the specimens already aged by irradiation. This is a strong evidence of the fact that the interaction between nanoparticles and the silica gel resists the degradation of the alkyl functional groups and continues to ensure an effective anchoring of nanoparticles to the substrate. In the cases of Apuan marble and Schlaitdorf stones, the results are less satisfactory but still point at a good retention of titania. In fact, as regards Apuan marble, the low amount of treatment applied and the low concentration of nanoparticles present therein proved to be insufficient for achieving any photocatalytic activity even before the ageing. On Schlaitdorf stone, the treatment ANC displays quite good photocatalytic properties, which are reduced upon ageing, although there is not a clear indication as to the reason of this reduction and the different trend of photocatalytic activity upon solar ageing and sequential solar-rain ageing cannot be readily explained. For this solvent-based product, spectroscopic analysis did not allow to detect a chemical interaction between the silica matrix and the titania nanoparticles [37], hence a less stable anchoring of nanoparticles to the embedding matrix and to the stone surface might explain these somewhat fluctuating values of photocatalytic activity.



**Figure 6.** Photocatalytic activity ( $D^*_t/D^*_{SILRES}$ ) at 150 min of Ajarte, Obernkirchen, Apuan marble and Schlaitdorf specimens treated with WNC/ANC: before ageing (UNAGED); after solar, rain and sequential solar-rain ageing.

The last issue considered in this research is whether the compatibility of the treatments, represented by the colorimetric characteristics (Figure 7) and the water vapour permeability (Table 4), is significantly modified upon ageing.



**Figure 7.** Colour change ( $\Delta E^*$ ) of Ajarte, Obernkirchen, Apuan marble and Schlaitdorf specimens.

Regarding the colour change ( $\Delta E^*$ ), it ought to be considered that both formulations have darkening and yellowing effects. When applied to three of the four stones (Figure 7), they induce a chromatic change lower than the eye perception threshold of 5. In the case of WNC, the darkening and yellowing effects are very mild from start and tend to wear off with the slow drying of the gel. More problematic is the compatibility of ANC in the case of Schlaitdorf stone, where a colour change higher than the threshold is obtained, most probably due to the absorption of a rather high amount of product and to its inherently high saturating power. Among the three ageing procedures, solar irradiation is the only one having a significant impact on surface colour, as it can be observed in Figure 7. In the case of WNC, the colour change after irradiation increases on Ajarte stone, though remaining below the threshold value of 5, and it even decreases in the case of Obernkirchen stone. As regards the alcohol-based treatment ANC, whose darkening effects are more pronounced at the beginning, solar ageing highly improves the aesthetic compatibility, notably in the case of Schlaitdorf stone, by brightening the surface colour and bringing the value of  $\Delta E^*$  well below the threshold of acceptance.

**Table 4.** Water vapour permeability of Ajarte, Obernkirchen, Apuan marble and Schlaitdorf specimens treated with WNC/ANC before ageing (UNAGED) and after solar, thermal and rain ageing, with standard deviation ( $\sigma$ ): absolute permeability ( $\delta_t$ ,  $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ ) and relative permeability with respect to the untreated stone ( $\delta_t/\delta_{nt}$ ).

Product	Stone	Ageing	$\delta_t$ ( $/10^{-11}$ )		$\delta_t/\delta_{nt}$	
			mean	$\sigma$	mean	$\sigma$
WNC	Ajarte	Unaged	1.65	0.32	0.68	0.08
		Solar	1.03	0.11	0.47	0.02
		Thermal	1.04	0.00	0.43	0.02
		Rain	1.25	0.26	0.45	0.04
	Obernk.	Unaged	1.09	0.09	0.77	0.21
		Solar	0.72	0.05	0.42	0.07
		Thermal	0.69	0.02	0.46	0.00
		Rain	0.77	0.03	0.66	0.01
ANC	Apuan m.	Unaged	0.10	0.03	0.90	0.08
		Solar	0.12	–	1.00	–
		Thermal	0.14	–	0.93	–
		Rain	0.01	0.00	0.19	0.04
	Schlait.	Unaged	0.88	0.17	0.99	0.20
		Solar	0.58	0.18	0.58	0.11
		Thermal	0.64	0.04	0.69	0.05
		Rain	0.57	0.05	0.73	0.07

Finally, as regards the water-vapour permeability (Table 4), it can be observed that treated stones undergo a reduction which is totally negligible in the case of Apuan marble and Schlaitdorf stone and does not exceed 30% in the case of Ajarte and Obernkirchen stones. In all cases, the permeability of the porous medium is not impaired. The ageing of treated stones leads to a reduction in permeability by another 20–40%, somewhat irrespective of which ageing procedure is applied. An exception is represented by Apuan marble, where an inordinate reduction by as much as 70% occurs after rain ageing. However, further research would be needed to confirm this result, for the methodology employed to measure the vapour permeability (see §2.4) turned out to be less reliable on stones with extremely low porosity such as Apuan marble. On the other three stones, the values of relative permeability after ageing are steadily higher than 0.4, which can still be regarded as an acceptable result [50].

#### 4. Conclusions

This article presented the results of a comprehensive investigation of the ageing behaviour of  $\text{TiO}_2$ -based photocatalytic nanocomposites for the protection of natural stones. Key point of the study was an accurate understanding of the effects that three different long-term artificial ageing procedures, performed on laboratory scale and based on heat, solar light irradiation and rain wash-out, have on the protective performance of the treatments. A special attention was paid to clarify, from a technological perspective, whether  $\text{TiO}_2$  nanoparticles compromise the protective performance and compatibility of the treatments and whether they retain their photocatalytic activity after long-term ageing. Moreover, the implication of stone properties such as porosity in the durability of the treatments was discussed.

Two different nanocomposite formulations, both consisting of silane matrices with the addition of small amounts of  $\text{TiO}_2$  nanoparticles (less than 1%  $w/w$ ), were applied on four different natural stones. After a laboratory assessment of the protective performance that selected the best stone-treatment combinations, each of the two formulations was applied on two stones and their ageing was conducted in the laboratory. The ageing procedures were set up to simulate a period of at least 24 months of outdoor exposure to solar irradiation in dry conditions, and about 36 months of rain

wash-out. This duration should be regarded as the minimum time required for a sustainable conservation treatment.

The main results of the investigation can be summarised as follows:

- a. The ageing procedures do not seriously compromise the protective efficacy of the treatments. Indeed, even though solar ageing expectably induces a certain photochemical degradation of the alkyl-silica matrices, this only involves the very stone surface, while the treatment that penetrated into the stone microstructure and settled on the inner pore surface retains its integrity, ensuring a rather stable protection of the pores towards water penetration. Moreover, both treatments retain a good aesthetic compatibility after ageing and do not end up compromising the stone vapour permeability.
- b. The alkyl-silica matrices are able to ensure a good mechanical stability of TiO<sub>2</sub> nanoparticles on the stone surface, as it can be argued from the retention of photocatalytic activity upon rain wash-out. Furthermore, as the sequential application of solar and rain ageing seems to prove, this stability is retained even after the organic functional groups of the embedding alkyl-silica matrices have undergone photochemical degradation, which is probably due to the retention of the silica backbone molecular structure.
- c. The stone properties were shown to have a strong influence on the ageing behaviour of the treatments. Indeed, treatments tend to have a higher durability when applied to stones with higher porosity and higher surface roughness, because the former grants a deeper penetration and the latter contributes to protecting the treatments from the effects of photochemical degradation.

These results represent a first, laboratory-based answer to some of the questions raised by the development of hydrophobising and photocatalytic treatments for the protection of stones. A desired outcome of research in this field is that knowledge of the ageing behaviour of materials, which should always be evaluated in their interaction with stones, may be generally recognised as fundamental information to improve the design of new conservation treatments and to assist in their laboratory validation.

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