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Extended summary

Smart surfaces for Architectural Heritage: self-cleaning titanium dioxide nano-coatings on travertine

Curriculum: Architettura, Costruzioni e Strutture

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Abstract. The development and application of self-cleaning treatments on historical and architectural stone surfaces could lead to significant improvements in conservation, protection and maintenance of Architectural Heritage.

Titanium dioxide (TiO_2) can be used to realize transparent self-cleaning coatings on stone surfaces as an active and preventive protection system, limiting cleaning and maintenance actions, decreasing the onset of degradation processes and reducing maintenance costs.

The self-cleaning ability of titanium dioxide is due to its two photo-induced properties activated by ultraviolet irradiation of solar light: photocatalysis and superhydrophilicity. The aim of this research is to analyse this effect. Two different titania-based products, obtained by two different processes, were deposited on travertine (a porous limestone often used in historical and monumental buildings) by spray coating in two different ways, obtaining a single-layer and a three-layers treatment for each product. The effects of deposited amount of titania on the characteristics of treated surfaces were evaluated in following analyses.

In order to verify the potential use of titania in the field of Cultural Heritage, the maintenance of appearance properties of the treated travertine surfaces was monitored by colour and gloss analyses.

The potential harmful effects of photo-induced hydrophilicity and eventual greater water ab-

sorption by treated stone was evaluated through water absorption by capillarity, static contact angle and surface water absorption analyses before and after the TiO_2 deposition.
De-pollution and soiling removal tests were carried out under UV-light exposure to evaluate photo-induced effects and self-cleaning efficiency.
Results seem to allow the use of TiO_2-based treatments on historical and architectural surfaces made up by travertine. Further analyses are necessary to evaluate the multidisciplinary features of TiO_2 nano-coatings.

Keywords. Architectural Heritage, nano-coating, self-cleaning, titanium dioxide, stone.

1 Problem statement and objectives

1.1 Nanotechnology and building surfaces

Technological research affected several traditional fields over the past decades searching for better performing materials, products, systems and methods, involving different sectors all over the world. New technologies can meet some of the requirements that usual techniques can not satisfy, integrating unexpected features even in existing elements. The application of surface treatments on architectural and historical surfaces could bring to significant improvements in different applications in building and conservation, protection and maintenance of Cultural Heritage.

Among new technologies, nanotechnology is a very promising tool to turn simple materials into smart, efficient, functionalized materials [1]. It can be applied in building industry, thus improving both the properties of construction materials and the quality of the whole building and surrounding area and it can be used even in the field of Architectural Heritage as a restoration treatment in order to realize new smart surfaces over ancient traditional materials. Nanotechnological treatments are able to convert historical surfaces into new tools to exploit renewable resources, reduce pollution and develop new functions similarly to new materials.

1.2 Titanium dioxide nano-coatings as a self-cleaning treatment in the field of Architectural Heritage

Titanium dioxide (titania or TiO_2) nano-particles can be used to realize transparent self-cleaning coatings on several surfaces, including stones, thus limiting cleaning and maintenance actions [2-8]. The self-cleaning ability of titanium dioxide depends on the synergy of its own photo-induced properties activated by solar light: superhydrophilicity and photocatalysis. Under ultraviolet exposure TiO_2 becomes superhydrophilic and so creates a uniform water film on treated surfaces, preventing contact between external dirt and the substrate itself and making removal of soiling agents easier. The ultraviolet irradiation can also activate the photocatalytic property of TiO_2 [2]. This characteristic allows the photo-decomposition of polluting substances absorbed or deposited on TiO_2 coatings by redox reactions induced by solar light. Titanium dioxide is one of the most used photocatalytic material, because of its outstanding efficiency, inexpensiveness and compatibility with a large number of building materials [3].

2 Research planning and activities

2.1 The prerequisites for the application of nano-coatings on stone surfaces

The application of titania on stone surfaces, both for new buildings and even more for the preservation of Architectural Heritage, is subject to the fulfillment of several prerequisites [9]:

- the preservation of original aspect of treated substrates after deposition of the coating;
- the absence of adverse effects due to physical and chemical changes induced by TiO_2;
- the real efficiency of photocatalysis to degrade stain and polluting substances;

- the durability of the coatings and of its features over time;
- the compatibility with other restoration techniques (as regards the application on historic elements);
- the advantage in its use, considering the costs of the application of these products on stone surfaces;
- the evaluation of impacts on environment and human health associated with all the stages of production and use of these nanostructured materials.

In this investigation the first three requirements were deeply evaluated. Furthermore, the analysis of the microstructure of deposited coatings was carried out.

2.2 Materials: nano-structured titania and stone substrate

Two different TiO_2-based products, obtained by two distinct processes, were analyzed in this investigation: an experimental solution, developed by Salentec s.r.l. [4, 5], and a commercial suspension (made by Colorobbia s.p.a.). Both products were applied through spray coating in two different ways, thus obtaining a single-layer (S1, C1 respectively) and a three-layers (S2, C2) treatments to compare with untreated case (UT).

Travertine, a porous carbonatic limestone often used in building and monuments since ancient times, has been selected as the reference substrate.

2.3 Experimental phases

2.3.1 Microstructure analysis

The morphology of the coating deposited on travertine was observed by the use of several microanalyses.

The nature and the size of titania nanoparticles were established through X-ray diffraction (XRD), transmission electron microscopy (TEM) and dynamic light scattering (DLS) analysis. The surface of TiO_2-based coatings after deposition on stone substrates was observed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

2.3.2 Aesthetic aspect

The aesthetical properties of treated substrate were monitored by the use of color [4-10] and gloss [9, 11, 12] analyses.

The chromatic variation was evaluated in the CIELAB color space through a portable colorimeter [10]. The CIELAB method defines a color through three different parameters, thus obtaining a three-dimensional color space: L^* (lightness from 0, black, to 100, diffuse white), a^* (red-green axis, positive values towards red and negative values towards green), b^* (yellow-blue axis, yellow values are positive and blue values are negative). The CIELAB color space includes all the colors perceivable by naked eyes. The difference ΔE^* between two different colors is defined by the following equation:

$$\Delta E = \sqrt{\left(L*_1 - L*_2\right)^2 + \left(a*_1 - a*_2\right)^2 + \left(b*_1 - b*_2\right)^2} \tag{1}$$

where the each coordinate is referred to two different colors taken into account. In this case, the chromatic values are referred to the travertine surfaces before and after the treatment.

The gloss defines the specular reflection level of a surface and it is measured in Gloss Units, usually from 0 (perfectly matte surfaces) to 100 (glossy surface) [12].

2.3.3 Treated substrate and photo-induced hydrophilicity

The photo-induced hydrophilic effect of TiO_2 on stone surfaces could bring to higher water absorption and, consequently, to harmful contact with the agents of decay carried by water (as for example soluble salts, acidic/basic compounds, microorganisms).

The consequences of high wettability induced by titania were evaluated by the use of three different tests: capillary water absorption [4, 13], static water contact angle [5-9, 14] and a specific surface water absorption test. Because of the test methods, it was not possible to perform the capillary water absorption [13] test under UV irradiation. On the other hand, static contact angle analysis [14] and the surface water absorption test were carried out both without and in the presence of UV light.

2.3.4 Self-cleaning effect

To evaluate the self-cleaning efficiency of titania coatings on travertine, the photoactivity of both products was evaluated by the use of de-pollution [4, 5, 15-19] and stain decoloration [4-9, 20, 21] tests.

The de-polluting effect of TiO_2 was assessed monitoring the degradation of nitrogen oxide (NO) by a continuous flow test method in a reaction chamber under UV illumination [19].

The de-coloration of stain was evaluated through chromatic measurements of photodegradation of rhodamine B [21], an organic dye used to simulate soiling processes because of its resistance to UV-A irradiation [22], applied over both untreated and treated surfaces then exposed to ultraviolet light.

2.3.5 Outdoor experience

In order to evaluate both feasibility of use and efficiency of titania treatments on stone surfaces, a case study was performed in a real urban environment [23, 24]. The façade of Sant'Andrea Apostolo, a former church in the centre of the city of Ascoli Piceno (Central Italy, Marche), made up by travertine, was covered by the four different treatments previously analyzed in the indoor experimental phase.

The self-cleaning effect was assessed monitoring the chromatic values of stone surfaces during time up to a total of about 18 months.

3 Analysis and discussion of main results

3.1 Microstructure analysis

The presence of anatase nanoparticles, the crystalline form of titanium dioxide having the highest photocatalytic activity, was clearly showed by XRD analysis of Salentec solution. A partial aggregation of anatase crystallites was noticed: the final average crystal size ranges from 10-20 nm observed through TEM to 40-50 nm according to DLS analysis. On the other hand, the mean size of Colorobbia suspension, about 18 nm, was directly provided by the manufacturer. The dimension of TiO_2 nanoparticles could play a very important role in the photocatalytic process, since usually smaller crystals show better photoactivity.

As regards the coating morphology, Salentec solution showed an irregular aggregation of titania nanoparticles, while Colorobbia coatings were more homogeneous and uniformly deposited on treated stones. Both coatings are far below 1 μm thickness. The lack of homogeneity can be mostly due to the deposition procedure (spray coating).

The presence of titanium on stone surfaces was confirmed by EDS analysis in a very evident way.

3.2 Preservation of original aspect of treated surfaces

The transparency of all analyzed coatings was well evident. Obtained results are shown in Table 1.

Table 1. Aesthetical changes on treated substrates: color and gloss variations (standard deviations in parentheses).

	Salentec surfaces			Colorobbia surfaces		
	UT	S1	S2	UT	C1	C2
*L**	78.6 (1.7)	79.5 (1.8)	79.3 (1.2)	84.4 (0.8)	84.4 (0.3)	84.2 (0.3)
*a**	3.5 (0.4)	3.2 (0.3)	3.2 (0.3)	2.2 (0.1)	2.2 (0.1)	2.4 (0.0)
*b**	9.8 (1.0)	8.7 (1.0)	8.0 (1.3)	8.7 (0.2)	9.1 (0.3)	9.1 (0.2)
ΔE^*	---	1.4	1.9	---	0.4	0.6
GU	3.1 (0.6)	3.6 (0.7)	2.8 (0.6)	1.5 (0.5)	2.0 (0.7)	2.7 (0.6)
ΔGUs	---	+0.5	-0.3	---	+0.5	+1.2

Chromatic changes ranging between 2 and 3 can be considered negligible in several applications [25]. In the field of Architectural Heritage, even greater color changes are usually considered acceptable, up to $\Delta E^* = 5$ [26] and $\Delta E^* = 10$ [9]. As regards specular reflection, gloss variations below 2 GUs are usually considered not appreciable by naked eye [9]. In conclusion, titania treatments do not affect the aesthetic properties of treated stones.

The aesthetical changes induced on treated substrates are not strictly related to different amounts of TiO_2 applied on stone.

3.3 Treated stones and photo-induced hydrophilicity

Both Salentec and Colorobbia treatments do not seem to alter water absorption of treated stone surfaces in an evident and harmful way, but they showed very different behaviors under UV light.

Photo-induced hydrophilicity was well evident in Salentec case, since static water contact angle clearly decreased under UV irradiation, but it did not caused higher water absorption. In fact, surface water absorption under ultraviolet light was inferior and more uniform in comparison with untreated case, apart from the irregular features of stone substrates.

As regards Colorobbia, the water absorption was barely influenced by the presence of TiO_2 and, because of the chemical composition of the product, there was no evidence of hydrophilic effect of titanium dioxide under ultraviolet illumination.

The static contact angle values and water uptakes were not clearly influenced by the different contents (single-layer and three-layers) of titanium dioxide deposited on the travertine.

3.4 Self-cleaning efficiency

The photocatalysis of analyzed TiO_2-based coatings was well evident for both de-polluting and self-cleaning purposes.

The photo-degradation of NO under ultraviolet light was well evident and it ranged from 25% to 50% of the initial concentration of nitrogen oxide. The decomposition of NO ended as soon as the UV light turned off.

Both treatments showed de-coloration of artificial stain applied on travertine surfaces, degrading up to 90% of original color due to rhodamine B after 26 hours-long exposure to UV rays. Colorbbia product showed better efficiency than Salentec treatment (at the end of the test, three-layers Salentec coating S2 degraded hardly above 80% of the dye). Anyway part of the photo-degradation of the organic dye was induced directly by ultraviolet irradiation, as shown by the results of untreated surfaces.

Both photocatalytic tests demonstrated that higher titania amount did not necessary lead to a proportionally higher photoactivity.

3.5 Outdoor analysis

The color changes due to exposure to polluted urban atmosphere were under the human eye possibility of detection in all analyzed cases, both treated and untreated. In conclusion, the deposition of stain caused by urban pollution was too slow and it altered the aspect of travertine in a negligible way during a period of 18 months.

Obtained results were not useful to ensure neither the self-cleaning ability of titania nor its durability in outdoor environment.

4 Conclusions

The nature of nano-TiO_2-based coatings applied on travertine surfaces was deeply analyzed to establish both efficiency and compatibility of titania self-cleaning coatings on building stones. Travertine, a natural porous limestone often used in building, was chosen as representative for both modern and historical stone surfaces.

Two different products based on anatase nanometric crystals of TiO_2 were considered: an experimental solution, Salentec, and a commercial suspension, Colorobbia. Both treatments were applied by spraying, each one in two different amounts, thus obtaining a single-layer and a three-layer coating, up to a total of four different treatment cases to analyze. Two respective untreated cases were used to assess the behavior of original stones used for both studies.

The results depended barely on the amount of TiO_2 applied on travertine. The application of titanium dioxide to obtain self-cleaning stone surfaces has met the prerequisites designated at the beginning of the experimental:

- aesthetical changes induced by treatments are hardly noticeable and fully compatible with their use in the field of restoration;
- the photo-induced hydrophilicity of titania did not seem to necessary lead to higher water absorption, a potential harmful consequence for stone substrates;
- both de-polluting and self-cleaning effects were clearly evident, the latter especially in short-term exposure to ultraviolet light (in comparison with untreated surfaces).

The use and study of TiO_2 over stone surfaces include several future scenarios. To analyze part of these factors, it is necessary to develop a multidisciplinary life-cycle assessment on titanium dioxide.

Titania coatings can prevent the formation of pathogens on treated surfaces, acting as a biocidal. The sterilizing potential of TiO_2 products on stone surfaces could be an interesting field for both research and large-scale applications.

Durability tests can be useful to monitor the microstructure and the nano-properties of the thin film during real long-term use and to determine the ability of the coatings to maintain their performances over time.

Finally, it is important to evaluate the potential risks from nanotechnology and nanomaterials to human health early in product development in order to safely manage it.

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