ASSESSING THE SELF-CLEANING BEHAVIOUR OF INORGANIC TREATMENTS FOR STONE

L. Sermasi[1]*, A. Fregni[2], R. Fabris[3] and E. Franzoni[4]

Abstract

The increasing amounts of particulate matter and gaseous nitrogen oxides in polluted urban areas affects a variety of materials in heritage buildings and sculptures exposed outdoor, by causing soiling deposition and deterioration. To fight this problem, the use of nanoparticles of photocatalytic titanium dioxide (TiO_2) was proposed several years ago as a strategy to provide architectural surfaces with self-cleaning behaviour. Very promising results were obtained in many laboratory studies, where nano-TiO_2 applied over different substrates was found to successfully reduce nitrogen oxides concentration in air and to deteriorate dyes of different organic compounds applied over the substrates. However, many studies remained at a laboratory stage, as some limitations were highlighted for these treatments, such as the short-term retention of TiO_2 over the substrates, with limited effectiveness and possible release of harmful titania nanoparticles in the environment due to rain washout. Moreover, the onsite self-cleaning performance of these treatments in real heritage buildings, which involve different materials, roughness, exposure, and climatic conditions, is far from being assessed.

In this study, the performance of an inorganic treatment based on the combination of ethyl silicate and titania nanoparticles applied to porous limestone was investigated. This combination is expected to guarantee long-term adhesion of the nanoparticles over the substrate without significantly affecting the photocatalytic ability of TiO_2. After assessing the compatibility of treatments in terms of colour and physical properties, their self-cleaning performance was assessed in realistic conditions that aim at overcoming the limitations of current tests. First, a purposely developed artificial soiling was applied over the treated and untreated substrates, then the self-cleaning behaviour was investigated, by spraying artificial rain also reproducing the impact pressure of real one over vertical façade. The results contribute to a better understanding of the behaviour of TiO_2 as a protective treatment and may help in developing durable and effective surface treatments.

Keywords: TEOS, TiO2, artificial soiling, artificial rain, colour measurement.

1. Introduction

Air pollution in urban areas is a threat also to heritage buildings. Many architectural materials are prone to weathering and darkening, due to soiling accumulation in urban areas. Studies on atmospheric particulate matter in cultural heritage have been conducted mainly on limestone, marble, lime mortars and carbonate stones (Doehne and Price 2010), however soiling is a problem also for heritage concrete characterized by a texturized and rough surface (Franzoni *et al.,* 2024).

Soiling is the deposit affecting building surfaces and is constituted by small particles, dust and greasy deposits from the atmospheric aerosol pollutants, which adhere to the surface by organic compounds such as hydrocarbons and fatty acids (Franzoni and Bignozzi 2021). The main agent responsible for the dark colour of soiling is carbon black, usually coming from incomplete combustion of petroleum products, including diesel and fuel oil, from burning of firewood and other combustion processes (Grossi *et al.,* 2003). Hence, black soiling accumulation on buildings and monuments is more intense in urban areas and gives both a negative aesthetic effect and stone decay, i.e. generation of gypsum and other soluble salts due to deposition of particles that accelerate the oxidation rate of SO_2 (Grossi *et al.,* 2003).

---

[1] *Linda Sermasi, PhD student, Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, Bologna, Italy, linda.sermasi2@unibo.it

[2] Alberto Fregni, Professor, Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, Bologna, Italy, a.fregni@unibo.it

[3] Riccardo Fabris, PhD, Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, Bologna, Italy, riccardo.fabris2@unibo.it

[4] Elisa Franzoni, Professor, Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, Bologna, Italy, elisa.franzoni@unibo.it

*Corresponding author

In this paper, a preventative inorganic surface treatment is presented as a possible innovative solution to help the removal of soiling by rain and avoid the growth of biofilm. The treatment was developed starting from that presented in a previous study (Franzoni *et al.,* 2024), given the potential shown in combining the benefits of inorganic protection with those of anti-soiling action.

The treatment was obtained by the incorporation of photocatalytic nano-TiO_2 into a tetraethylortosilicate inorganic matrix (TEOS). Thus, it is expected to combine the beneficial effects of TEOS (consolidating effect, stability to outdoor environment) (Zárraga *et al.,* 2010) and the self-cleaning ability of photocatalytic nano-TiO_2 in the anatase form. TEOS is also expected to improve the adhesion of titania nanoparticles to the substrates and to prevent their removal by rain washout.

The self-cleaning effect provided by the presence of TiO_2 nanoparticles over the stone surface is due to two simultaneous actions. The redox reactions of adsorbed substances promoted by UV light, which allow the decomposition of organic matter. The photoinduced hydrophilicity, which is expected to help the removal of dirt and deposits by rain (Franzoni and Bignozzi 2021).

The treatment's self-cleaning effectiveness was investigated with a new experimental procedure designed by the authors. After the samples' treatment, artificial soiling was applied, then the samples were exposed to artificial rain. At each step, the colour of the samples was qualitatively and quantitatively assessed.

2. Materials and methods

2.1 Materials

The substrate used in the tests is Lecce stone, a porous limestone composed mainly of calcium carbonate and particularly vulnerable to deterioration problems (Calia *et al.,* 2014). The samples (Figure 1-A), having size 50 × 50 × 15 mm^3, were cut by sawing from a single slab.

The self-cleaning treatment was prepared by mixing:

- A commercial TiO_2 fine-particulate (Aeroxide TiO_2 P25, Evonik) composed of crystalline titania predominantly in the anatase form
- Ethyl silicate (Estell 1000, CTS, Italy) composed of TEOS 25 wt% in white spirit.

The nano titania powder was added to TEOS in a concentration of 0.5 wt%. The TiO_2 concentration was lowered compared to the previous study (Franzoni *et al.,* 2024) because the aim was to obtain a compromise between self-cleaning effect and colour compatibility.

The suspension obtained was stirred and sonicated, to facilitate the dispersion of the nano particles. Right after the sonication the samples were treated by brushing (4 brushstrokes on each sample). The samples were weighed before and immediately after the treatment. The samples were left in laboratory conditions for 3 weeks for curing. A total of 11 samples were treated (Figure 1-B), while an equal number of samples was left untreated for comparison.

2.2 Methods

2.2.1 Artificial soiling deposition

The treated and untreated samples were exposed to artificial soiling deposition, to simulate what happens on the surfaces of stone monuments exposed to soiling accumulation. Two different artificial soiling mixtures were prepared, starting from the composition suggested in ASTM D7897-18:2023 (Standard practice for laboratory soiling and weathering of roofing materials to simulate effects of natural exposure on solar reflectance and thermal emittance). This standard was taken as a reference, even though the application field is different, because, to the authors' best knowledge, no studies on artificial soiling for cultural heritage exist so far. The two mixtures were obtained by combining 4 different mixes in various amounts:

- Dust, namely 20 g/L montmorillonite added in 1 L of deionized water
- Salts, namely 3 g/L NaCl, 3 g/L $NaNO3$, 4 g/L $CaSO4\cdot 2H2O$ dissolved in 1 L of deionized water
- Soot, namely 13.7 g/L commercial carbon black, Aqua-Black 001, Tokai Carbon Co. Ltd, diluted in 1 L of deionized water
- Particulate Organic Matter (POM), namely 14 g/L humic acid dissolved in 1L of deionized water.
- The two artificial soiling mixtures prepared were:
- "Soiling 1", aiming to simulate soiling in hot and humid climates: 61 wt% of dust, 31 wt% of salts, 8 wt% of soot.

- "Soiling 2", aiming to simulate soiling in moderate summer and cold winter climates: 16 wt% of dust, 7 wt% of salts, 8 wt% of soot, 69 wt% POM.

Samples were placed horizontally and the soiling mixture was applied perpendicularly over their surfaces using an airbrush (pressure 1.4 bar, distance airbrush-sample's surface 27 cm), assuming uniform deposition of the mixture over the sample's surface. The amount of soiling mixture deposited over each sample was 0.86 g ± 0.5 g. This quantity was visually assessed aiming at recreating high soiling accumulation, as the one visible in some parts of exposed stone monuments. This amount of soiling is different from what is indicated in the previously cited Standard, because the latter is designed for smooth and non-porous substrates, whereas the stone samples used in the present study are rough and porous. Following the directions of ASTM D7897-18:2023 (Standard practice for laboratory soiling and weathering of roofing materials to simulate effects of natural exposure on solar reflectance and thermal emittance), the amount of soiling applied on the samples could theoretically correspond to about 200 years of soiling accumulation, but the exact number of years in this specific case in unknown. After the soiling application each sample was heated for 5 minutes under an infrared lamp (70°C) to evaporate the water. Then, samples were left for 10 days in laboratory conditions (in the dark, to prevent photoactivation) for drying.

Eight samples (4 treated "A" and 4 untreated "UA") were exposed to soiling 1 (Figure 1-C) and eight samples (4 treated "B" and 4 untreated "UB") were exposed to soiling 2 (Figure 1-D). All the samples' labels are described in Table 1.

Table 1: Description of all the samples used.

Condition	Samples' labels	Soiling application
Untreated	UA1-UA4	Soiling 1
Treated	A1-A4	
Untreated	UB1-UB4	Soiling 2
Treated	B1-B4	
Untreated	UC1-UC3	For characterization (without soiling)
Treated	C1-C3	

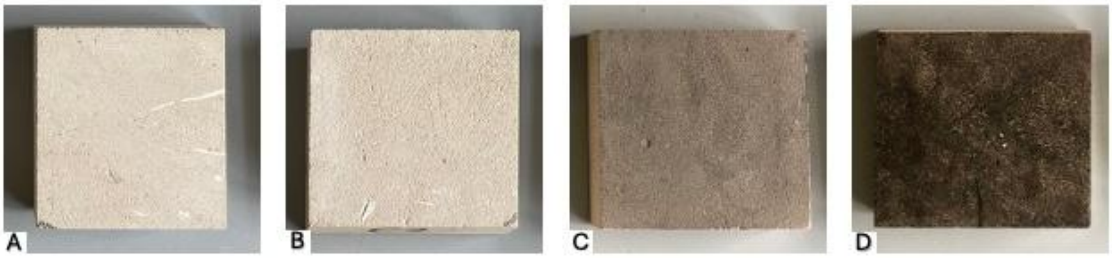

Figure 1: Lecce Stone samples: A) untreated sample; B) treated sample; C) sample after the application of soiling 1; D) sample after the application of soiling 2.

2.2.2 Artificial rain exposure

After soiling application, samples were exposed to artificial rain, to evaluate the treatment's behaviour after rain washout. The experimental setup is shown in Figure 2. Samples were placed 90° tilted, to simulate a vertical façade. Deionized water having pH = 5.1, similar to natural rain pH (Sivalingam *et al.,* 2024), was sprayed on each sample from a fixed distance (35 cm). The water spray reached the sample with a pressure of 25 Pa, which was considered a realistic but gentle pressure compared to values found in literature on the force of impact of waterdrops falling on a rigid surface, which were collected in soil erosion studies (Nearing *et al.,* 1986) (Nearing and Bradford 1987).

Each sample was subjected to 3 artificial rain cycles. A rain cycle consisted in spraying 200 ml of water (in 20 seconds) on the sample's surface and letting the sample dry for 2 days in laboratory conditions. Before the rain exposure, the samples were left under UV radiation for 1 hour, for photoactivation. Both treated and untreated samples were subjected to this exposure, to eliminate the possible colour variation caused by photodegradation of soiling. A rain cycle simulates a rain intensity of 30 mm/h, which corresponds to heavy rain (Bosio *et al.,* 2023).

Figure 2: Experimental setup for the application of artificial rain.

2.2.3 Samples characterizations

The water capillary absorption rate of the treated and untreated samples was measured according to EN 15801:2010 (Conservation of cultural property - test methods - Determination of water absorption by capillarity). The water absorption by immersion of the treated and untreated samples was measured, according to EN 13755:2008 (Natural stone test methods - Determination of water absorption at atmospheric pressure).

The evaporation rate of the treated and untreated samples was measured by a procedure in which the samples were immersed in deionized water until saturation and then they were wrapped with tape leaving only the treated face uncovered. Samples were left in room conditions (T=23 ± 1°C, UR=40.6 ± 8%) and weighed every 24 hours. This test allowed to investigate if the treatment inhibits water evaporation.

The chromatic characterization of the samples was carried out by measuring the colour with a 3nh NH310 colorimeter (8 mm measuring aperture). The measurements were performed on 5 points for each sample and were expressed in the CIELAB colour space through the coordinates L*, a*, b*, where L* measures the brightness, a* measures the green-red variation and b* measures the blue-yellow variation. The colorimetric difference (ΔE^*) of the samples in relation to the original stone colour was calculated by the formula:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

To evaluate the treatment's self-cleaning effect, the colorimetric difference was calculated at different stages of the test: after the treatment ($\Delta E^*_{0,1}$), after the soiling application and drying ($\Delta E^*_{0,2}$) and after each artificial rain cycle, in dry conditions ($\Delta E^*_{0,3}$, $\Delta E^*_{0,4}$, $\Delta E^*_{0,5}$).

3. Results and discussion

The rates of water capillary absorption of the treated and untreated samples are reported in Table 2. In general, all treated samples showed a slight decrease in the rate of water absorption compared with untreated samples. Thus, the treatment was effective in decreasing the speed at which water entered the substrate. This might increase the durability of the stone, as most of the degradation processes, i.e. freeze-thaw cycles, are worsened by water ingress in the material. Moreover, as the coefficient's decrease from treated samples to untreated ones was minor, it was possible to infer that the treatment does not have a pore-blocking effect and is compatible with the substrate.

The water absorption values of the treated and untreated samples are reported in Table 2. The results showed that the water absorption of treated and untreated samples was basically unchanged. Hence, the treatment does not influence significantly the overall porosity of the samples and, therefore, it can be considered compatible with the substrate also form this point of view.

Table 2: Water capillarity absorption rate (CA) and water absorption values (WA) of treated (A, B and C) and untreated (UA, UB and UC) samples.

	Samples										
	UA1	UA2	UA3	UA4	UB1	UB2	UB3	UB4	UC1	UC2	UC3
CA ($kg/m^2s^{1/2}$)	0.071	0.066	0.066	0.065	0.069	0.071	0.066	0.065	0.079	0.073	0.070
WA (%)	9.67	11.25	11.24	10.97	11.64	11.25	11.31	11.23	13.32	11.38	12.53
	A1	A2	A3	A4	B1	B2	B3	B4	C1	C2	C3
CA ($kg/m^2s^{1/2}$)	0.058	0.056	0.059	0.061	0.059	0.055	0.056	0.058	0.055	0.056	0.063
WA (%)	11.52	11.27	11.19	11.25	11.66	11.11	11.48	11.87	10.82	11.48	12.11

The results of the water evaporation test are reported in Table 3. Treated specimens showed a slightly smaller water evaporation speed, compared to the untreated specimens. Evaporation rate depends on the difference between the saturation of the material and the relative humidity of the environment and on the type and size of pores of the material (Perez-Ema *et al.,* 2024). Hence, the fact that the evaporation capacity of stone was minimally affected by the treatment is consistent with the results previously described for the absorption coefficient.

Table 3: Water evaporation of untreated and treated samples.

	Untreated Samples		**Treated Samples**	
Time (h)	**Incremental mass loss due to evaporation (g)**	**Std. Dev.**	**Incremental mass loss due to evaporation (g)**	**Std. Dev.**
24	6.288	0.089	5.723	0.583
48	1.079	0.191	0.920	0.120
72	0.321	0.023	0.314	0.109
120	0.004	0.000	0.007	0.008
144	0.022	0.001	0.018	0.003

The aesthetic compatibility of the treatment was assessed through the calculation of the colorimetric differences before and after the treatment ($\Delta E^*_{0,1}$), which are reported in Table 4. The colorimetric differences between the treated and untreated samples are very low and they are lower than that generally considered acceptable ($\Delta E^* \leq 5$) (Franzoni *et al.,* 2014). Even with visual observation, the difference is barely noticeable ($\Delta E^* < 2$). This confirms that the treatment does not significantly alter the colour of the treated surface, hence, it is aesthetically compatible. This result is not obvious, as the white colour of titania might induce unacceptable colour changes. In fact, the amount of titania nanoparticles contained in the treatment, and thus deposited on the surface, was kept sufficiently limited.

The self-cleaning effect of the treatment was assessed through the removal of artificial soiling by artificial rain. The results are shown in Table 4 in terms of colorimetric differences after each rain cycle ($\Delta E^*_{0,3}$, $\Delta E^*_{0,4}$, $\Delta E^*_{0,5}$). The values show that:

- in the untreated samples, a lower amount of soiling was removed by artificial rain (reduction of colour change due to soiling: 18%)

- in the treated samples, the amount of soiling removed by rain was higher. Soiling 1 was removed slightly more easily than soiling 2, in fact samples with soiling 1 obtained a reduction of colour change due to soiling of 23%, instead samples with soiling 2 of 22%. However, in no case the treatment was able to clean completely the sample's surface from soil. The reason for this could be double. Firstly, as the stone is highly porous, a fraction of soiling could have been absorbed and therefore, it was not washed out by rain. The second reason is that the amount of soiling deposited on each sample was very high, preventing in some way the photoactivation of the titania underneath, and, instead, the number of rain cycles was limited. Moreover, the samples were sprayed with an amount of soiling corresponding to approximately 200 years all at once, and intermediate rainfall events that could have occurred during this period were not considered. Thus, 3 rain cycles (with an intensity equivalent to 3 intense events) were not sufficient to remove that amount of soiling. Better results in terms of surface's self-cleaning ability could be obtained by increasing the number of rain cycles at which the samples are exposed and by interposing the application of soiling with intermediate rainfall events.

Table 4: Colorimetric difference (mean and standard deviation) for treated (A-B) and untreated (UA-UB) samples.

	$\Delta E^*_{0,1}$ (after treatment)		**$\Delta E^*_{0,2}$ (after soiling)**		**$\Delta E^*_{0,3}$ (after 1st rain cycle)**		**$\Delta E^*_{0,4}$ (after 2nd rain cycle)**		**$\Delta E^*_{0,5}$ (after 3rd rain cycle)**	
	Mean	**Std.Dev.**	**Mean**	**Std.Dev.**	**Mean**	**Std.Dev.**	**Mean**	**Std.Dev.**	**Mean**	**Std.Dev.**
Samples A	1.31	0.37	29.59	2.15	24.19	2.31	23.31	2.36	22.76	1.97
Samples B	1.23	0.30	46.07	4.03	38.33	3.13	36.78	2.33	36.04	2.01
Samples UA	-	-	29.38	1.53	26.52	2.00	25.10	2.25	24.01	1.94
Samples UB	-	-	46.02	1.94	39.74	1.57	38.01	0.85	37.60	0.89

4. Conclusions

Lecce stone samples were treated with an inorganic treatment made of TEOS mixed with titania nanoparticles (0.5 wt%), which was applied by brushing. This treatment was applied with the aim of evaluating its compatibility with heritage substrates and its self-cleaning performance. For the latter, the procedure adopted was developed by the authors and consisted of the application of artificial soiling on the samples and the subsequent washing with artificial rain.

The treatment resulted compatible, hence adequate for heritage stone. In fact, the application of the treatment caused: (i) no alterations in the porosity of the substrates; (ii) a very slight lowering in the water absorption rate; (iii) a very slight decrease in the evaporation rate. Moreover, the treatment did not cause a visible alteration in the surfaces' colour, resulting also aesthetically compatible.

The treatment improved the soiling removal with respect to untreated samples, but it did not allow the complete removal of soiling. More rain cycles should probably be applied to obtain a better cleaning of the surfaces. It was observed that the treatment's self-cleaning performance was unaffected by the exposure to artificial rain, as it keeps its performance at each rain cycle. Further studies on the artificial soiling formulations are necessary to make it more representative of real conditions. In fact, artificial soiling should remain on the surface rather than being absorbed by the porous substrate.

References

Bosio, R., Cagninei, A. and Poggi, D., 2023, Large laboratory simulator of natural rainfall: from drizzle to storms, Water, 15, 2205

Calia, A., Laurenzi Tabasso, M., Maria Mecchi, A. and Quarta, G., 2014, The study of stone for conservation purposes: Lecce stone (southern Italy), Geological Society London Special Publications, 391, 139–156

Doehne, E. and Price, C., 2010, Stone Conservation: An Overview of Current Research, in Journal of the American Institute for Conservation, Getty Conservation Institute, ISBN 978-1-60606-046-9

Franzoni, E. and Bignozzi, M.C., 2021, 15- TiO_2 in the building sector, in Metal Oxides, Titanium Dioxide (TiO_2) and its applications, Parrino and Palmisano (eds.), Elsevier, ISBN 978012819960, 449-479

Franzoni, E., Pigino, B., Leemann, A. and Lura, P., 2014, Use of TEIS for fired-clay bricks consolidation, Materials and Structures, 47, 7, 1175-1184

Franzoni, E., Pizzigatti, C. and Fabris, r., 2024, Developing inorganic coatings with nano TiO_2 for heritage concrete and assessing their self-cleaning performance by a new laboratory test, Construction and building materials, 449

Grossi, C.M., Esbert, R.M., Díaz-Pache, F. and Alonso, F.J., 2003, Soiling of building stones in urban environments, Building and Environment, 38, 147-159

Nearing, M.A., Bradford, J.M. and Holtz, R.D., 1986, Measurement of force vs. time relations for waterdrop impact, Soil Science Society of America Journal, 50, 1532-1536

Nearing, M.A. and Bradford, J.M., 1987, Relationships between waterdrop properties and forces of impact, Soil Science Society of America Journal, 51, 425-430

Perez-Ema, N., Alvarez de Burgo, M., Gomez-Heras, M., 2024, Monitoring changes in hydric properties of treated stone material with conservation products by time-sequential IR thermography, Archaeological and Anthropological Sciences, 16, 91

Sivalingam, S., Vishal, G. and Anush, B., 2024, Environmental and health effects of acid rain, in Health and environmental effects of ambient air pollution: Volume 1: Air pollution, human health and the environment, Mohammad Hadi Dehghani, Rama Rao Karri, Teresa Vera, Salwa Kamal Mohamed Hassan (eds.), Elsevier, 9780443160882, 91-107

Standard C.E.N. EN 15801:2010, Conservation of cultural property - test methods - Determination of water absorption by capillarity

Standard C.E.N. EN 13755:2008, Natural stone test methods - Determination of water absorption at atmospheric pressure

Standard ASTM D7897-18:2023, Standard practice for laboratory soiling and weathering of roofing materials to simulate effects of natural exposure on solar reflectance and thermal emittance

Zárraga, R., Cervantes, J., Salazar-Hernandez, C. and Wheeler, G., 2010, Effect of the addition of hydroxyl-terminated polydimethylsiloxane to TEOS-based stone consolidants, Journal of Cultural Heritage,11, 138–44