

## TREATMENTS WITH SELF-CLEANING PRODUCTS FOR THE MAINTENANCE AND CONSERVATION OF STONE SURFACES

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### Abstract

*Cleaning stone surfaces is a crucial issue as irreversible and potentially harmful for the stone itself. Inadequate interventions might cause damage also visible over the time. Moreover they often have to be repeated, especially in urban areas, where the surfaces are more subjected to dusts deposition and pollution alterations. In order to reduce the need for cleaning, TiO<sub>2</sub>-based treatments have been proposed for their self-cleaning, depollution and antibacterial properties. These products are currently used to coat the outdoor surfaces of buildings but little experience has so far been made in the field of Cultural Heritage. This paper concerns the experiments carried out to evaluate efficiency, durability and harmfulness of three different TiO<sub>2</sub>-based products, either in form of nanoparticles or mixed with hydrophobic polymers, used to treat three carbonatic stones. A polydimethylsiloxane as reference polymer was used. Specimens of these stones were exposed to an urban polluted outdoor environment for eight months. The specimens were investigated by colorimetric measurements, surface observations and X-ray microanalyses by electron microscopy, contact angle measurements, Rhodamine tests, ion chromatography measurements and elemental analyses by X-ray fluorescence. The results showed that the photocatalytic products have a mild self-cleaning effect depending on the stone and tend to be easily washed away by the rain.*

**Keywords:** Photocatalytic product; TiO<sub>2</sub>-based product; Self-cleaning effect; Stone treatment; Maintenance

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### Introduction

In the framework of the activities related to the preventive conservation and maintenance of Cultural Heritage, the application of titanium dioxide (TiO<sub>2</sub>) based treatments on stone surfaces could greatly contribute in limiting cleaning interventions. Therefore, this point is noteworthy because the cleaning intervention is always irreversible and costly.

Nowadays several TiO<sub>2</sub> based products, such as mineral and organic coatings, are available for use in new buildings [1]. Because of its photo-catalytic properties, TiO<sub>2</sub> (in the allotropic form of anatase) is able to induce the photo-decomposition of inorganic (e.g. NO<sub>x</sub>) and organic pollutants (e.g. benzene and other aromatic compounds) adsorbed on its surface and has been proven to be very active in bacterial destruction [2, 3]. For this reason the TiO<sub>2</sub> photo-

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catalsis produces anti-polluting, self-cleaning and antibacterial effects [4-6]. TiO<sub>2</sub> based products have been scarcely tested on stone surfaces of artistic and historical interest [7]. The aim of this study is to test these innovative products for their use in the field of conservation of Cultural Heritage. In particular, the present research was carried out to verify the effectiveness of these products and the absence of damage on stone surfaces. It should be noted that TiO<sub>2</sub>, in the photocatalytic form of anatase, induces a superhydrophilicity of the surface, leaving the treated surfaces more exposed to the degradation agents such as acidic/alkaline rain water. This is, of course, a negative aspect in the case of stone surfaces of cultural interest because such surfaces are more vulnerable to deterioration due to pollutants dissolved in the rain. Concerning the possible side effects of the photo-catalytic reactions, particular attention should be focused on investigating the degradation mechanism of NO<sub>x</sub> [8, 9]. This molecule, in fact, under the catalytic action of TiO<sub>2</sub> can lead to the formation of NO<sub>3</sub><sup>-</sup>, having as cation the calcium ion in the presence of calcareous stone or mortar. Therefore, the soluble salt content of treated specimens could be an indicator of the potential damage that can be caused by the photocatalytic activity of TiO<sub>2</sub>.

The main purpose of this study was to evaluate the suitability of different TiO<sub>2</sub>-based treatments applied to three different types of stone in a polluted urban environment (city centre of Rome). In particular, we focused on efficiency, durability and harmfulness of the tested products.

## Experimental

The investigated TiO<sub>2</sub>-based products include a water dispersion of titanium dioxide in the form of nanoparticles and two different products where TiO<sub>2</sub> is mixed with silicon or fluoroacryl based polymers. In the latter products the combination with a water repellent is useful because it limits water penetration. Rhodorsil H 224 (polydimethylsiloxane) was taken into account as a reference water repellent material.

Stone specimens untreated and treated with the different products were exposed to a high level of traffic pollution for eight months.

Colorimetric measurements were used to evaluate aspects related to colour changes, as part of both the harmfulness of the treatment and its efficiency in reducing the soiling of the surface. Adhesion and durability of the treatments were studied with a focus of the surface morphology and the titanium concentration. These were investigated by scanning electron microscope coupled with an X-ray microanalysis (SEM-EDS) and X-ray fluorescence. The photocatalytic efficiency was evaluated by monitoring the discolouration of Rhodamine B, an organic dye applied on the stone surface [10]. Contact angle measurements were carried out to evaluate the hydrophilicity introduced by TiO<sub>2</sub>-based products and the treatment durability. Finally the analysis of the soluble salts present in the specimens treated with TiO<sub>2</sub>-based products was important to find evidence of possible decay factors.

### Materials

The three investigated stones are carbonatic rocks with different total integral open porosity (P<sup>o</sup>): white marble (~1.0P%); travertine from Tivoli (1.6÷9.0P%) and Lecce stone (~35P%), in form of specimens measuring 5cm × 10cm × 2cm. The treatment consisted in applying the following products containing TiO<sub>2</sub> and/or hydrophobic polymer: *Bioxy air* (CIR Ltd.), an aqueous microdispersion of silanes functionalized with photocatalytic TiO<sub>2</sub>; *Nama07* (Colorobbia Italy SpA), nanoparticles of titanium dioxide in aqueous dispersion (pH = 5.61); *two experimental products*, supplied by the Acep Ltd., applied in sequence and consisting of a primer, made of a *fluorinated acrylic polymer* and an *aqueous dispersion of alkyl silanes and photocatalytic TiO<sub>2</sub>* and *Rhodorsil H 224* (RH 224), a polydimethylsiloxane in aliphatic hydrocarbons, diluted 1:10.

Each treatment was applied until rejection on one face of the specimens (5cm × 10cm). The amount of product applied is given in Table 1 and varies depending on the porosity of the stone and the absorption of the product.

The untreated and treated specimens were exposed to a high level of traffic pollution with no rain shelter for eight months. They were placed on a rack 5m high on the ground with the treated faces having an angle of 45° with the horizontal plane.

**Table 1.** Volume of treatment applied for each stone specimen

Type of stone	Volume of applied product [mL <sup>3</sup> ]			
	Acep	Bioxy	Nama	RH 224
Marble	0.5 + 0.5	0.7	0.7	0.7
Travertine	1 + 1	1	1	1
Lecce stone*	5 + 5	5	5	5

\* The treatment was applied on specimens partially wet (10 mL<sup>3</sup> of water) to prevent the product containing TiO<sub>2</sub> penetrate too deeply

### Methods

**Colorimetric measurements** - Colorimetric analyses were carried out according to the European Standard EN 15886: 2010 [11] by a Spectrophotometer Konica Minolta CM 2600d in total reflectance (measurement area MAV 8mm). The colour changes ( $\Delta E$ ) were evaluated by the  $L^*a^*b^*$  system (CIE 1976). Thirty measurements were carried out on each stone specimen before and after the treatment and after the outdoor exposure [12-16].

**SEM-EDS analysis** – The morphology of the stone surfaces and the elemental maps were observed by an EVO 60 Zeiss scanning electron microscope, equipped with a lanthanum hexaboride filament cathode. The investigation was carried out at a variable pressure of 100Pa, without any pre-treatment of the samples, and the images were obtained in backscattered electrons mode.

**XRF analysis** - This technique was used because of its rapidity and non-destructiveness [17], which allows for the same specimen to be analysed as many times as necessary. The average surface amount of titanium was evaluated by a portable spectrometer equipped with an X-ray tube working at 60kV, 1.5mA and a 30mm<sup>2</sup> Si-drift detector [18]. The analysed spot is about 6mm in diameter and the measuring time 120s. In such conditions, detection limits range from a few tens to a few hundreds of mg/kg, depending on the element and the matrix. Given the relatively large size of the analyzed area only one measurement for each specimen was performed.

**Static contact angle measurements** - The static contact angle of the stone specimens was determined, according to the standard EN 15802: 2009 [19], by a Lorenz&Wettré instrument. For each specimen, the contact angle, expressed in degrees, was obtained by the average of 30 measurements carried out on each stone specimen before and after the treatment and after the outdoor exposure. Because of the strongly heterogeneous texture, it was not measured on the travertine.

**Soluble salt analysis** - Ion chromatography technique was used to monitor the presence of soluble salts produced by the photocatalytic activity of the TiO<sub>2</sub>. Stone specimens were cut to a size of 5cm × 3cm × 2cm and immersed in 30mL<sup>3</sup> of deionized water in closed plastic containers under stirring for 48h. After extraction of the soluble ions in water and consequent filtering, dissolved cations and anions were determined using a Dionex DX-100 ion chromatograph equipped with a 25μL sample loop.

**Photocatalytic activity assessment** – The rhodamine B-based colourimetric test was used to evaluate, before and after outdoor exposure, the photocatalytic activity of TiO<sub>2</sub>-based products applied on specimens. Specimens stained with rhodamine B (0.05% in ethanol) were exposed to xenon light using a Suntest CPS+ apparatus (Heraeus, Germany) irradiated with

30kJ/m<sup>2</sup> per minute. Discoloration of the rhodamine B was measured, by colourimetry, after 0.5, 2.0, 5.0 and 8.0h of irradiation, respectively.

## Results and discussions

### Colorimetric measurements

The average results of colorimetric measurements performed on all the different stone specimens before and after treatment and then exposed in a polluted urban environment are shown in Figures 1, 2 and 3. Colorimetric changes ( $\Delta E^*$ ) of the treated specimens were calculated with respect to the values of the colorimetric coordinates of the respective untreated stones and before ageing. The bars account three separate effects: ageing of the untreated stone, application of the treatment and application of the treatment plus ageing.

As regards the marble (Fig. 1), ageing produces relatively small changes, whereas the application of the treatments, in particular Nama, causes much larger ones. The colour changes in aged treated specimens show that the treatments have not introduced any beneficial effect.

Regarding the Lecce stone (Fig. 2), ageing alone produces strong changes in colour, however by far larger than those introduced by the application of the treatments. All of them reduced the colour changes after ageing, the best result being produced by Bioxy.

The results concerning travertine are shown in Fig. 3. Ageing produces modest effects, lower than the application of the treatment except for Bioxy. After ageing, the effect of the treatments is not significant except for RH 224 that produces a remarkably negative effect.

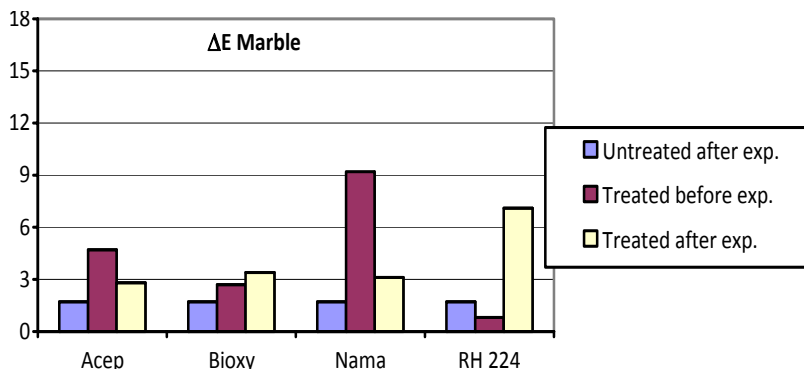


Fig. 1. Colour variation ( $\Delta E^*$ ) of marble specimens untreated and treated with different products before and after outdoor exposure

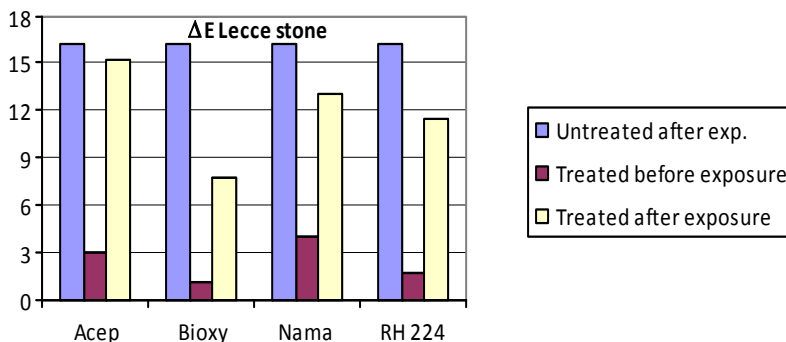


Fig. 2. Colour variation ( $\Delta E^*$ ) of Lecce stone specimens untreated and treated with different products before and after outdoor exposure

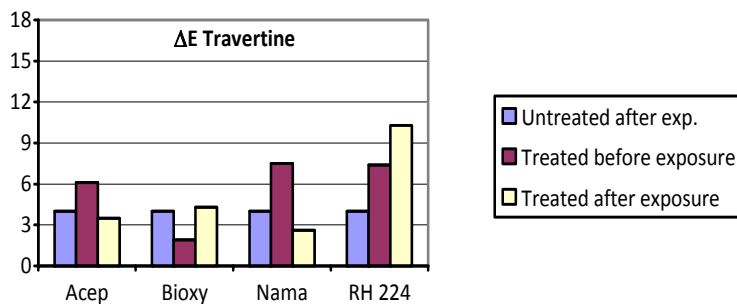


Fig. 3. Colour variation ( $\Delta E^*$ ) of Travertine specimens untreated and treated with different products before and after outdoor exposure

### SEM-EDS analysis

SEM studies (Figs. 4 and 5) were conducted to investigate the morphologies of the various products based on  $\text{TiO}_2$  applied to each lithotype. The morphologies of the treated surfaces depend on the stone porosity. On low porosity stones, such as marble and travertine, Nama and Bioxy produce a layer of flakes and a film with micro-cracks, respectively (Fig. 4 left and Fig. 5 left). The morphology of the surfaces treated with Acep (Fig. 5 right) is not evident and probably due to the low amount of product retained. Regarding the more porous Lecce stone, these morphologies are less visible because the products are easily absorbed; only in the case of Bioxy (Fig. 4 right) it is possible to observe the formation of a film with micro-cracks caused by shrinkage.

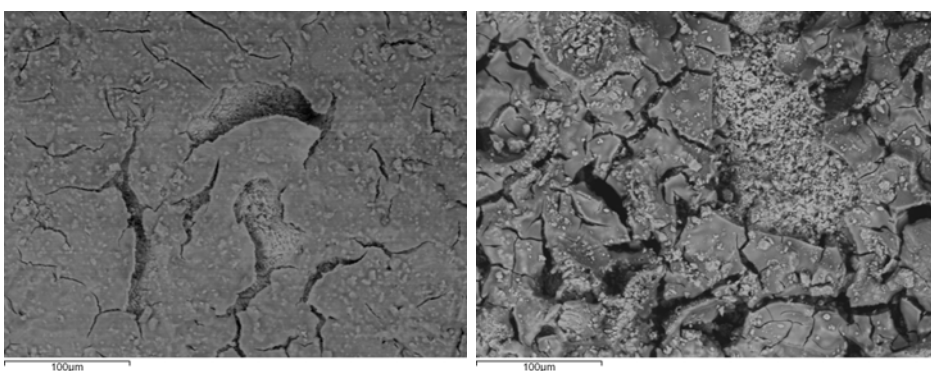


Fig. 4. SEM-BSE images of marble (left) and Lecce stone (right) before exposure; both samples are treated with Bioxy

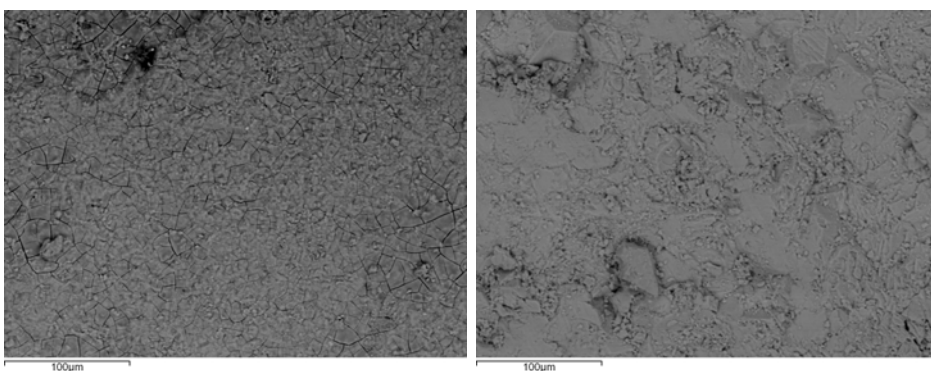


Fig. 5. SEM-BSE images of travertine treated with Nama (left) and marble treated with Acep (right) before exposure

The EDS elemental microanalysis shown in Table 2, allows to estimate, although with high uncertainty because of the small area of analysis (0.06mm<sup>2</sup>), the characteristic elements (titanium and silicon) of the products present on the treated surface. After 8 months exposure, there is a considerable decrease in the titanium content of the surfaces treated with Bioxy and also with Nama. This means that the adhesion of the treatment is modest and most of the product is removed by atmospheric agents. On the other hand, after outdoor exposure, the specimens treated with Acep maintain the low initial values of Ti and Si.

Also in all cases of specimens treated with Nama was detected the presence of chlorides and sodium ions on the surface; these elements after outdoor exposure are no present probably due they are washed away from the surface by the rain.

As regard these results, it should be taken into account that the areas to be analyzed were chosen by us and not at random as was the case with the XRF analysis.

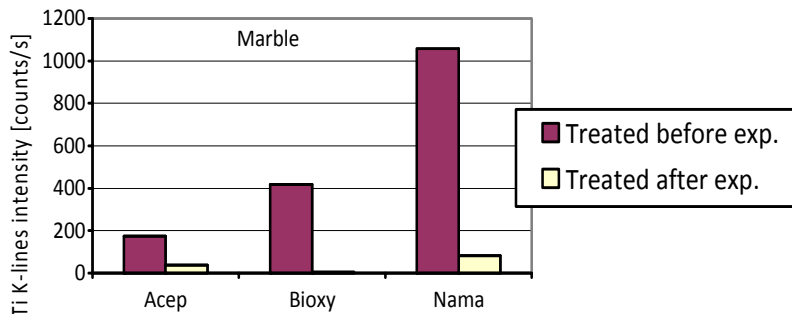
**Table 2.** EDS analysis of stone surfaces before and after outdoor exposure: the content of Ti and Si, with respect to the total of the elements, is reported in percentage by weight as minimum and maximum value

	Marble				Lecce stone				Travertine			
	Before exposure		After exposure		Before exposure		After exposure		Before exposure		After exposure	
	Ti	Si	Ti	Si	Ti	Si	Ti	Si	Ti	Si	Ti	Si
NT*	-	-	-	-	-	2÷3		4÷5	-	-	-	2
Acep	3÷4	2÷3	6÷3	2÷3	3÷5	2÷3	2÷5	7÷13	15÷16	9÷10	6	3
Bioxy	30÷40	15÷22	1÷3	1÷4	38÷56	16÷27	4÷6	3÷5	26÷28	16÷17	6	3
Nama	31÷35	-	10÷11	1	5÷10	1÷2	10÷15	3÷4	34÷49	1	21÷46	1÷3

\*NT= not treated specimens

**XRF analysis**

Figures 6-8 compare the Ti content on the specimen surface before and after exposure for each type of stone and each product. Given the uncertainty in identifying the analytical volume, such a comparison is performed by considering the Ti K-lines intensity (counts/s) [20]. Low porosity stones, such as marble and travertine, show similar behaviour. In particular, the Ti K-lines intensity of the Nama treatment is very high before outdoor exposure and is reduced after exposure, however maintaining the highest values among the treatments. In the case of the Acep treatment, although the initial amount of titanium is lower than for the Nama treatment, the loss after exposure is lower.



**Fig. 6.** Comparison of surface Ti contents for each product before and after the outdoor exposure for marble

The Bioxy treatment shows the lowest amount of surface Ti after exposure. A different behaviour is shown by the Lecce stone, due to its high porosity. Before exposure, as far as titanium content is concerned, it is reasonable to assume that Acep and Nama are easily absorbed by the Lecce stone whereas in the case of Bioxy it remains on the surface due to its polymeric features. After exposure, the amount of Ti is similar for all treatments, with the exception of Bioxy, which shows the highest relative decrease in the surface amount of Ti.

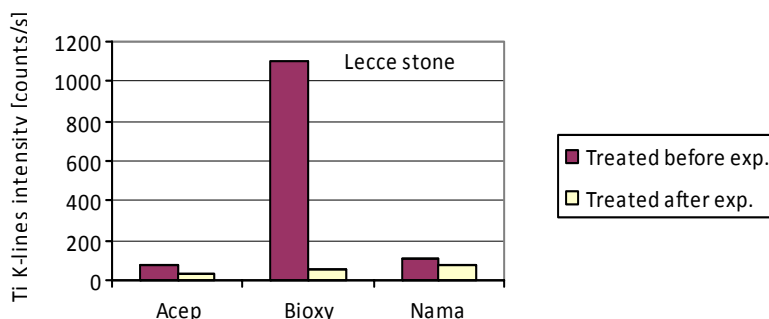


Fig. 7. Comparison of surface Ti contents for each product before and after the outdoor exposure for Lecce stone

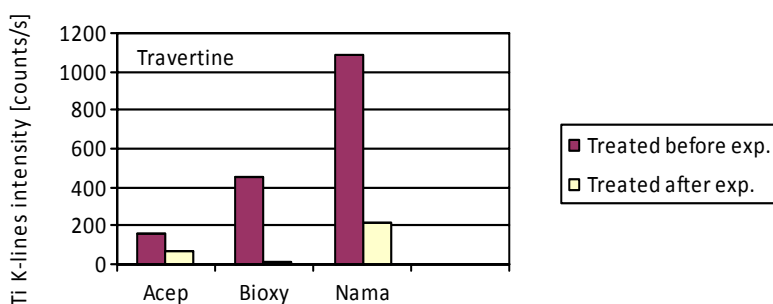


Fig. 8. Comparison of surface Ti content for each product before and after the outdoor exposure for travertine

**Static contact angle measurements**

In Table 3 are reported the average measurements of static contact angle of the marble and Lecce treated stones respect to the untreated specimens.

Table 3. Average measurements of contact angle on stone specimens untreated (NT) and treated before and after outdoor exposure

	Treatment	Before exposure	Outdoor exposure
Marble	NT	85 ± 4	119 ± 4
	Acep	79 ± 15	118 ± 5
	Bioxy	125 ± 4	93 ± 12
	Nama	Absorbed	108 ± 5
	RH 224	132 ± 8	129 ± 6
Lecce stone	NT	Absorbed	Absorbed
	Acep	137 ± 5	125 ± 3
	Bioxy	> 140	111 ± 14
	Nama	Absorbed	Absorbed
	RH 224	> 140	> 140

Before outdoor exposure, the marble specimens show that hydrorepellency is high in the case of treatment with Bioxy and RH and weak in the case of Acep and NT, in the case of Nama there is hydrophilicity. The low value of the contact angle of Acep is probably due both to the hydrophilic effect of the  $\text{TiO}_2$  and the poor presence of a water repellent component (as evident from SEM-EDX analysis). After ageing, the RH 224 treatment on the marble maintains the same degree of water repellency while the contact angle of Acep is similar to the values of NT because of the decrease of  $\text{TiO}_2$  on the surface. The Bioxy treatment reduces its hydrophobic properties showing a loss of hydrorepellent material which is also confirmed by the SEM-EDX/XRF analyses. The Nama specimens show a degree of hydrorepellency similar to that of NT as a result of the loss of titanium dioxide that was initially present. The increase in hydrophobicity of the untreated marble is probably due to the deposit on the surface of slightly apolar organic compounds from the environment.

The surface of the Lecce stone specimens treated with products containing water-repellent component (Bioxy and RH 224) maintain the hydrorepellency even after exposure to rain, with just a slight decrease in the case of Bioxy. The Nama treatment, due to the presence of the  $\text{TiO}_2$  nanoparticles, induces an increase of hydrophilicity compared to untreated specimens: the water drops deposited on Nama for the measurement are absorbed more quickly than on the untreated surface. A particular behaviour, on the Lecce stone, is shown by the Acep treatment. In this case probably the  $\text{TiO}_2$  is adsorbed while the hydrophobic component remains on the surface.

#### ***Soluble salts analysis***

The analysis of the soluble salts in the aged stone specimens shows insignificant variations in the ion content of the untreated specimens (NT) with respect to the specimens treated with the different  $\text{TiO}_2$  based products. Therefore, after eight months of outdoor exposure, the potential damage due to the photocatalytic activity of the  $\text{TiO}_2$ , in particular the oxidation of  $\text{NO}_x$  to  $\text{NO}_3^-$  is not evident. It can only be observed an increase in the content of soluble calcium in the case of treatment with the Nama and Bioxy that could be the result of an acid attack.

Here is reported (Table 4) the analysis results for the marble, expressed in milliequivalents of anion or cation per gram (meq/g) of dry mass of the sample. The results for the other stones follow a similar trend.

**Table 4.** Concentration of anions and cations in the supernatant liquid of the mixtures: stone after exposure/water

Marble	$\text{Cl}^- \times 10^{-5}$ (meq/g)	$\text{NO}_3^- \times 10^{-5}$ (meq/g)	$\text{SO}_4^{2-} \times 10^{-5}$ (meq/g)	$\text{K}^+ \times 10^{-5}$ (meq/g)	$\text{Na}^+ \times 10^{-5}$ (meq/g)	$\text{Ca}^{2+} \times 10^{-5}$ (meq/g)
NT* before exp.	2,1	1,0	4,4	0,8	6,0	39,6
NT*	6,5	1,6	4,8	0,8	7,8	33,7
ACEP	3,5	1,2	6,3	0,7	5,1	47,2
BIOXY	4,5	1,6	4,2	0,6	4,6	71,7
NAMA	4,1	2,0	6,0	1,2	4,2	111,0

\*= not treated (NT)

#### ***Photocatalytic activity assessment***

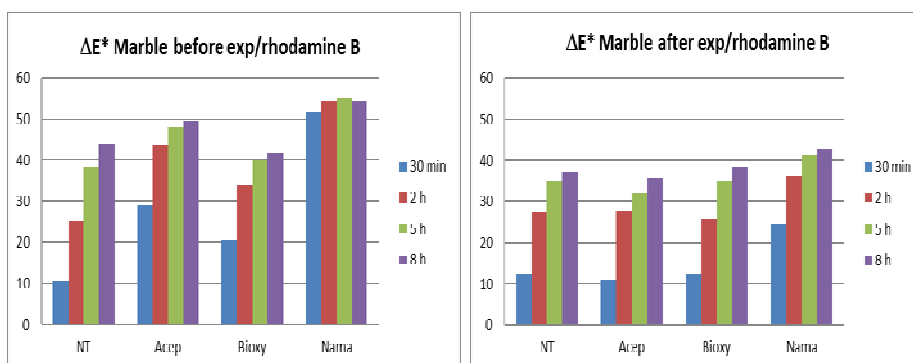
Rhodamine B discoloration tests highlight the different photoefficiency of the  $\text{TiO}_2$  based treatments also with respect to the exposed specimens in a polluted environment. Results



are shown as colour changes ( $\Delta E$ ) of specimens stained with Rhodamine B monitored after 30 min, 2, 5 and 8 h of irradiation.

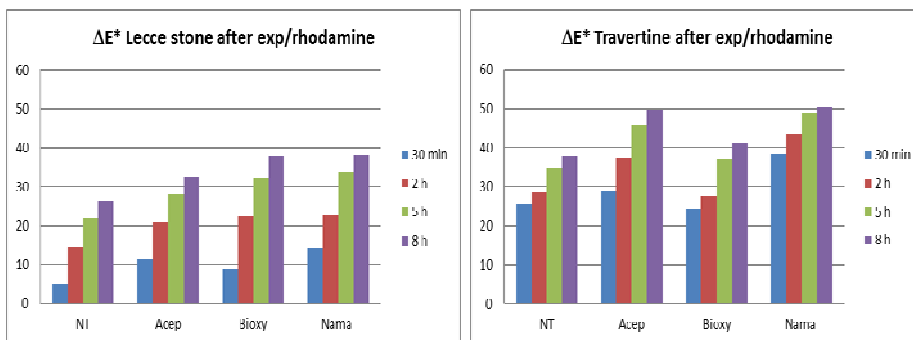
In Fig. 9 is reported the different behaviour of the marble specimens before and after outdoor exposure.

Nama treatment gives a discoloration more efficient than the other forms of treatment (Fig. 9 left) due to its higher specific surface area. The results indicate that photocatalysis is most effective within the first 30 min of irradiation, otherwise all treatments give  $\Delta E$  values higher with respect to the NT specimens.



**Fig. 9.** Colour difference ( $\Delta E$ ) with time of irradiation (30 min, 2, 5 and 8 h) of Rhodamine B applied on marble specimens before (left) and after (right) outdoor exposure

After ageing (Fig. 9 right), the  $\Delta E$  values of Acep, Bioxy and Nama are shown to decrease with respect to the not aged values due to the lower content of  $TiO_2$  remaining on the surface. However, Nama remains the most effective treatment for marble. Regarding exposed Lecce stone and Travertine specimens stained with Rhodamine B (Fig. 10), Bioxy and Nama in the case of the former lithotype while Acep and Nama in the latter case exhibit a higher discoloration than in the untreated stone.



**Fig. 10.** Colour difference ( $\Delta E$ ) with time of irradiation (30 min, 2, 5 and 8 h) of Rhodamine B applied on Lecce stone specimens (left) and Travertine (right) after outdoor exposure

These results show that the photocatalytic efficiency of the  $TiO_2$  based treatment is mainly influenced by the type of photocatalytic product and then by the porosity of the stone material. Photocatalysis is much more efficient in the case of the Nama treatment where  $TiO_2$  is

present as nanoparticles thereby offering the greatest surface exposure to the surrounding environment.

## Conclusions

Photocatalytic products examined in this research have shown a different behaviour among them and also with respect to the three stones.

The self-cleaning effect of the photocatalytic products tested was assessed by comparing the colour measurements before and after the outdoor exposure. It should be considered that also a treatment can induce a colour change.

In the marble, all treatments after outdoor exposure causes a slight increase of  $\Delta E$  with respect to the value of the stones not treated. We have to take into account that after outdoor exposure, the  $\text{TiO}_2$ -based products disappear from the surface losing their photocatalytic effectiveness. The water repellent treatment (RH 224) for its hydrophobic nature attracts nonpolar dust.

Concerning the travertine, RH 224 shows a behaviour similar to that in marble, while the photocatalytic treatments exhibit  $\Delta E$  similar or slightly lower than those of untreated surfaces. NAMA gives the best result and this is in agreement with the EDS and XRF analyses that detect the permanence of titanium after exposure.

Regarding the Lecce stone, all treatments after exposure show  $\Delta E$  lower than those of untreated stones in particular for Bioxy, RH 224 and Nama. Surfaces treated with Bioxy and Nama show a moderate photocatalytic activity but this is not in agreement with the low Ti contents measured by the EDS and XRF analyses. These investigations have measured only the titanium surface content while the  $\text{TiO}_2$  can be penetrated inside the porous Lecce stone, therefore, a greater developed surface could be accessible to UV rays to increase the photocatalytic activity respect to the low porosity stones.

As regards the potential harmfulness of treatments based on  $\text{TiO}_2$ , the results of ion chromatography not show an increase of  $\text{NO}_3^-$ , although we have to remember that nitrates are highly soluble and therefore they could be washed away by the rains.

In conclusion, all the treatments applied to the two low porosity stones show little or no self-cleaning effect, probably due to their poor adhesion to surfaces. For porous stone, such as stone of Lecce, the  $\text{TiO}_2$ -based treatments show a photocatalytic effectiveness slightly higher than that obtained in the other stones, as well as the self-cleaning effect, probably due to the fact that they penetrate deeper.

Respect to the treatments, the Nama product, containing only  $\text{TiO}_2$  nanoparticles, presents the most efficient photocatalytic activity due to the greatest surface exposure to the surrounding environment. However, this product is not sufficiently attached to the substrate and consequently after exposure only a little amount remains on the surface. Nama also makes the stone surface more hydrophilic. Both Bioxy and Acep present a lower photocatalytic activity, however Bioxy reduces soiling of porous Lecce stone more than the Nama treatment that is easily adsorbed in the porous matrix.

Acep and Bioxy contain both a hydrorepellent component useful to counteract the superhydrophilicity introduced by  $\text{TiO}_2$ . However after ageing, all forms of treatment disappear from the surface, in particular in the case of Bioxy and Nama and as result the self-cleaning effect is limited.

This study highlights the strong influence both of the porous structure of the stones, into which titanium dioxide is embedded, than of the nature of the product containing  $\text{TiO}_2$  on the photocatalytic properties of the resulting treatment.

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