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Application of a polymer-based photocatalytic coating for the protection of limestone stones substrates: an exposure study

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***Abstract* – In the last decades there have been several studies on cultural heritage regarding the performance of protective and consolidating coatings for the prevention of decay. A coating must have several characteristics such as: efficiency, breathability, and must be durable and reversible. In this research work we tried to verify the performance of a commercial protective product such as Fosbuild FBLE 200, which is composed of a TiO_2 nanopowder dispersed in an aqueous solution of an acrylic polymer. This product, which exhibits depolluting, antimicrobial, water-repellent and self-cleaning characteristics, has been applied on different lithotypes such as: Carrara marble, Noto and Comiso stone and exhibited in two different outdoor environments such as Catania and Palermo. These two cities are mostly affected by pollution produced by vehicular traffic; moreover, Catania is also affected by pollution produced by the activity of Mount Etna.**

I. INTRODUCTION

In the field of cultural heritage, protective coatings play a key role in the preservation of monuments, statues and many other works of historic and artistic interest. These treatments are necessary [1-6] in order to prevent the development of numerous possible degradation phenomena, such as the formation of black crusts, chromatic alterations, detachment of the substrate, erosion and many other effects [7-10]. The main factors which give rise to these processes are: the interaction between the substrate and air pollutants (sulphur dioxide, particulate matter and nitrous oxides), the crystallization of soluble salts and biodeterioration [1]. Stone materials are amongst the substrates, which mostly suffer from the aforementioned degradation phenomena and for this reason they have been, and still are, at the centre of attention in this field [11].

Today nanotechnologies play a key-role in technical-scientific progress thanks to their strong potentiality and multiple applications in different research fields. Introducing such products in Cultural Heritage appears to be a new frontier that could lead to the solution of some problems, according to the needs of a correct conservation of the monuments. In fact, many products now used in conservation, such as composite based polymeric materials, were studied and tested in various research areas and then readapted to the need of the Cultural Heritage sector. So, applying them to Cultural Heritage requires extensive analytical research useful to assess their potentialities and possible risks [1-6].

The aim of the present work is to evaluate the performance of a commercial protective polymeric coating, namely Fosbuild FBLE 200, which is composed of a TiO_2 nanopowder dispersed in an aqueous solution of an acrylic polymer. Laboratory tests have highlighted disinfectant, antimicrobial, water-repellent and self-cleaning properties of the product, along with potent biocidal effects [12], which make this product very promising for specific applications in the cultural heritage field. Fosbuild FBLE 200 was tested through an outdoor exposure study carried out in two Italian cities, Palermo and Catania, which are characterized by different environmental conditions and sources of air pollution. Three different stone substrates of carbonate nature were examined: Carrara marble, Noto stone and Comiso stone. The first is one of the most widespread stone materials in

Italian statuary and monumental architecture, whilst the following two are calcarenites characteristic of Sicilian architecture. Both treated and untreated samples were exposed for a 2-year period in both sites and analyses were carried out at the end of the first and the second year to evaluate the performance of the coating. The specimens were exposed and monitored for a 2-year experimental campaign (from July 2011 to July 2013). The results obtained from the exposure of untreated specimens have already been published in a previous work [13].

II. MATERIALS AND METHODS

In the present research work on the three stone types object of the experimental study, a photo-catalytic formulation based on TiO_2 nanoparticles (titanium dioxide), known as Fosbuild (FBLE 200), was tested. The research was aimed at evaluating the inhibitory capacity, in an outdoor environment, of this product, and therefore its effectiveness as a depolluting, antimicrobial, water-repellent and self-cleaning agent of surfaces treated.

The product is distributed by the company Steikos srl (Italy) and is composed of a titanium dioxide nano-powder (anatase crystalline phase with mean particle diameter of 20 nm) dispersed in an aqueous suspension of an acrylic polymer (polymer 4 wt%, TiO_2 0.3 wt%). The product was applied with the aid of a brush for each lithotype using two different quantities: 1 mg cm^{-2} (high quantity) and 0.5 mg cm^{-2} (low quantity) [14].

Three different stone substrates of carbonatic nature have been treated and exposed. Carrara marble and Noto and Comiso stone. These were then exposed outdoors in two Italian sites, Catania and Palermo, which are characterized by different environmental conditions and pollution. Both cities are influenced by pollution produced by high vehicular traffic [15-16] rather than by industry or domestic heating. Precisely, Catania is located on the Sicilian east coast overlooking the Ionian Sea, at the foot of Etna, which is the largest active volcano in Europe that releases gaseous and ash emissions (plumes) that hit the city several times a year. Instead, Palermo is located in a large gulf of the north-western Tyrrhenian coast of Sicily. The most important natural contribution to the total aerosol particulate matter in the city of Palermo derives from the erosion of outcropping rocks, as well as from soils and sea spray [17-18].

Samples were then characterized by using a multi-analytical approach. In order to evaluate the suitability of the product applied to the treated specimens, measurements were carried out for the determination of the contact angle (to evaluate the impermeability to liquid water) and colorimetric tests (to estimate the chromatic alteration of the stone material after application), according to the regulations in force (Uni NorMal 20/85). In particular, the contact angle determines the wettability of the treated surfaces (NorMal 33/89). The measurement was performed first on the specimens as they are and then on the treated ones.

After the exposure period, respectively after the first and second year, the samples were characterized by means of: stereomicroscope observations, colorimetric analyzes, ion chromatography and infrared spectroscopy.

- Colorimetric analyses were carried out by means of a Konica Minolta CM 2600d portable spectrophotometer, referring to the CIE L* a* b* chromaticity diagram and the NorMal 43/93. L* is luminosity or lightness, which varies from black (value = 0) to white (value = 100); a* ranges from +a*(red) to –a*(green) and b* varies from +b* (yellow) to -b* (blue).
- Ion chromatography was carried out with a Dionex 4000i instrument, equipped with a gradient pump, a conductivity detector (CDM-1), and eluent gas module (EDM-2), with accuracy of 1.5%. SO_4^{2-}, NO_3^- and Cl^- were quantified. The separation columns used for the anions were a Dionex AS4A or AS5A-5 mm (AMMS-1 micromembrane suppressor) [45]. For the preparation of test solution, reference was made to UNI 11087 (2003).
- FT-IR investigation was used to identify the main mineralogical phases constituting the particulate deposited on stone surfaces. The spectrophotometer used was a Perkin Elmer Spectrum 100, equipped with an attenuated total reflectance (ATR) accessory. Infrared spectra were recorded in ATR mode, in the range of 500–4000 cm^{-1} at a resolution of 4 cm^{-1}.

III. RESULTS

A. Pre-exposure

Treated samples were analyzed prior to exposure using colorimetry and contact angle measurements in order to assess the suitability of the coating following the Uni NorMal 20/85 technical standard. Chromatic variation with respect to the untreated specimen is expressed in terms of ΔE*, according to the following equation:

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

All samples displayed values of ΔE* below the threshold value of 5, under which the colour variation is imperceptible to the human eye [12], proving the suitability of the product. With regards to the contact angle, all treated samples displayed values above 90°, highlighting the hydrophobic behaviour of the coating, hence it’s suitability.

B. Post-exposure

The preliminary analysis of the samples exposed at the two sites and examined by stereomicroscope showed that, between the first and second year of exposure, the surfaces of the samples showed an increase in the amount of deposited particulate, which is greater in the untreated samples. An example is shown in figure 1.

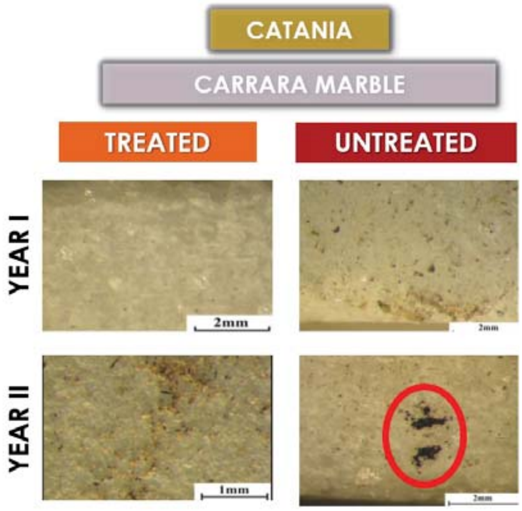

Fig. 1. Observation under stereomicroscope of the surfaces of the samples (treated and untreated) of Carrara marble taken in the first and second year of exposure in Catania.

The largest deposition concerned the Noto stone samples (Fig.2). This is probably due to the greater intrinsic roughness and porosity [13] of the material which allows the deposited particulate to be captured and retained more easily. In particular, in the specimens exhibited in Catania, a greater abundance of black particles was highlighted, most likely attributable to the explosive activity of Etna (greater deposition of volcanic ash) unlike the Palermo site.

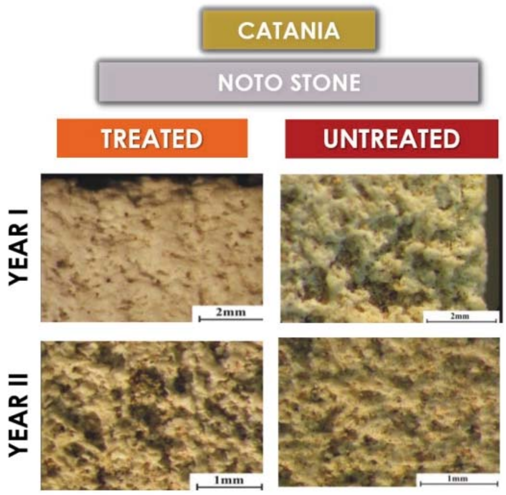

Fig. 2. Observation under stereomicroscope of the surfaces of the samples (treated and untreated) of Noto stone taken in the first and second year of exposure in Catania.

The Carrara marble samples show, in both sites, a slight blackening and yellowing of the surfaces during the two years of exposure. The samples that showed a good capacity for self-cleaning power (with values of variation of the luminosity ΔL * lower than a sample of untreated marble and exposed to the same conditions) are those taken at the end of the first year (Fig.3).

BRIGHTNESS VARIATION (ΔL*) after Year I

CATANIA – CARRARA MARBLE

Treated	Untreated
-1.35	-2.84

CATANIA – NOTO STONE

Treated	Untreated
-4.39	-4.38

CATANIA – COMISO STONE

Treated	Untreated
-3.65	-3.72

*Fig. 3. Brightness variation (ΔL *= = L * value after exposure - the L * value before exposure) values obtained after the I year of exposure, of the samples of Carrara marble and Noto and Comiso stone.*

With regards to the Noto and Comiso stone, almost all the specimens exposed in Catania and Palermo show a moderate blackening (greater for the Noto stone, Fig. 3) and yellowing compared to the specimens as they are exposed to the same conditions.

As for the specimens treated with titanium dioxide, the results obtained from the chromatographic analysis show that in the Carrara marble samples the formulation seems to show excellent effectiveness only in the first exposure year, in both sites. In fact, the concentrations of the three ionic species considered are low when compared with the data obtained from the specimens as they are and exposed to the same conditions (Fig. 4). Conversely, the data obtained at the end of the second year shows that the formulation no longer performs its self-cleaning function, probably aiding the deposition processes. The latter result is greater for specimens treated with a greater quantity of product.

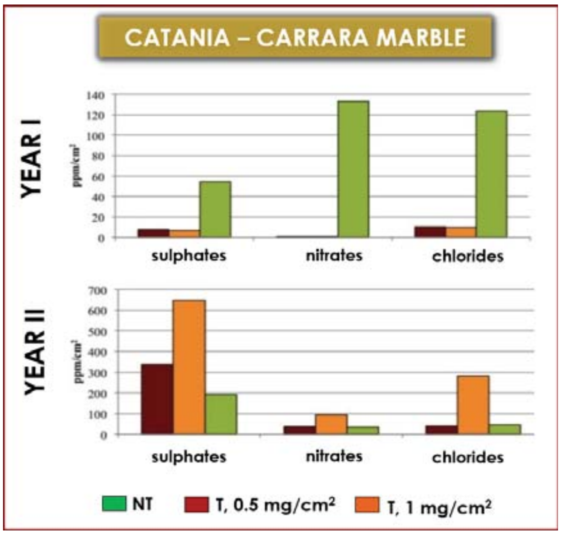

Fig. 4. Bar graphs displaying the concentration of sulphates, nitrates and chlorides of both treated (T, 0.5 mg / cm²; T, 1 mg/cm²) and untreated specimen (NT) determined with ionic chromatography. The graphs show the concentration after one year of exposure and after two years of exposure, of the Carrara marble samples in Catania.

Instead, the data relating to the treated specimens of Noto and Comiso stone (Fig. 5) shows a negative response already from the first year and, subsequently, also in the second exposure year, in both sites.

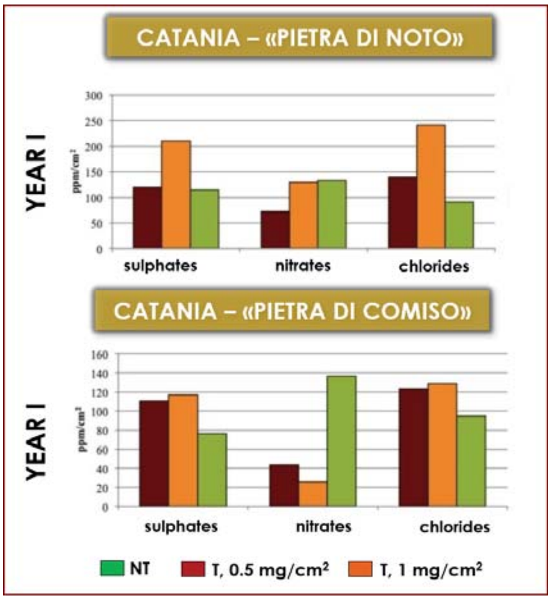

Fig. 5. Bar graphs displaying the concentration of sulphates, nitrates and chlorides of both treated (T, 0.5 mg / cm²; T, 1 mg/cm²) and untreated specimen (NT) determined with ionic chromatography. The graphs shows the concentration after one year of exposure, of the Noto and Comiso stone in Catania.

In fact, the concentrations of sulphates, nitrates and chlorides are very high if compared with those of the untreated specimens exposed to the same conditions.

The FT-IR analysis was conducted in order to identify the mineralogical phases constituting the powders taken from the surfaces of the specimens, both as they are and treated, exposed in both sites. The results obtained showed a marked compositional homogeneity of all the samples taken at the end of the first exposure year. In fact, the acquired spectra revealed the exclusive presence of the bands in them characteristics of calcite at 1410-20, 871 and 710 cm^{-1}. In the second year of exposure, in addition to the calcite bands, a weak peak centered at 1100 cm^{-1} was also observed in all the samples (Fig. 6) indicating the presence of gypsum. This result shows the initial formation of the sulphation process on the surface of the samples, which over time can lead to the formation of black crusts.

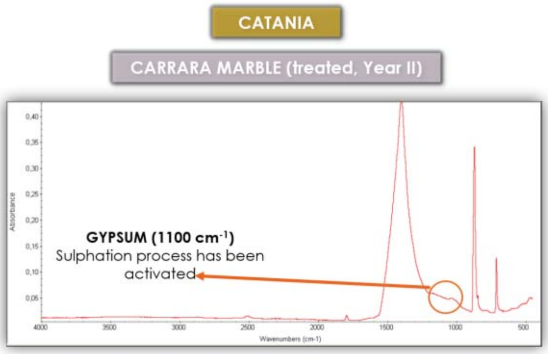

Fig. 6. Representative IR spectrum of treated samples after two years of exposure. Alongside the characteristic peaks of calcite, it is possible to observe a weak band at 1100 cm^{-1} which is typical of gypsum.

IV. DISCUSSION

Probably due to the higher porosity which led to the penetration of the product in the bulk of the substrates, Fosbuild FBLE 200 proved to be not so efficient in protecting the calcarenites from degradation. A high concentration of inorganic salts, along with widespread deposition of particulate matter on the surface and darkening detected thanks to colorimetric measurements, are indices of the low performances of the tested product when applied to “Pietra di Noto” and “Pietra di Comiso”. In fact, no significant differences were found with respect to the untreated samples.

Differently, results obtained from the Carrara marble samples revealed to be more promising. After one year of exposure, when compared to untreated samples, the concentration of sulphates, nitrates and chlorides is significantly lower in the treated specimen, highlighting the ability of the coating in blocking the interaction of the surface with airborne pollutants. Moreover, colorimetric analysis showed only a slight yellowing of the surface after one year, and no significant differences in terms of brightness, confirming the stability of the product. The same conclusions are further supported by the microscopic images, in which a clear difference between the treated and untreated samples can be seen. However, results have also shown that after two years of exposure, the performance of the product decreases. In fact, the concentration of sulphates, nitrates and chlorides increases, indicating the penetration of atmospheric pollutants. Also, microscopic images and colorimetric measurements showed darkening and yellowing of the surface; where the latter could be also due to partial degradation of the polymer itself. Finally, the IR spectra show a weak peak around 1100 cm-1 which, in accordance with the high sulphate concentration detected via ionic chromatography, underlines the activation of the sulphation process.

Different application techniques and methods can be tested in the future in order to overcome the problem of pore penetration of the coating. In this regard, only tested two different amounts of polymeric coating were tested in this work, whereas a more thorough study needs to be conducted in order to determine the ideal quantity to be applied. Therefore, further developments include the optimization of the system employed, especially in terms of amount of product used per unit area of substrate. Instead, if the problem resides in the nature of the polymer itself, regardless of the amount used, new coatings will need to be tested and their performances compared to Fosbuild FBLE 200.

V. CONCLUSIONS

The results of this study revealed that the performances of polymeric coatings to be used in the field of cultural heritage depend on a variety of parameters, such as the nature of the coating itself, the intrinsic characteristics of the substrate and also the environmental conditions surrounding the exposure site. Moreover, this study shows that, in order to evaluate the performance of a specific coating, it is crucial to perform outdoor exposure studies and not limit the evaluation to laboratory tests, which may be misleading. With regards to Fosbuild FBLE 200, this polymeric coating revealed to have possible applications for Carrara marble, whereas the performances on calcarenites is less promising.

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