EVALUATION OF THE EFFECTIVENESS OF TITANIUM DIOXIDE (TiO_2) SELF-CLEANING COATING FOR INCREASED PROTECTION AGAINST CBRN INCIDENTS IN CRITICAL INFRASTRUCTURES

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ABSTRACT

Self-cleaning building materials is a form of passive safety technology that is used to provide increased resistance against chemical, biological, radiological and nuclear (CBRN) incidents. This paper is aimed at evaluating the effectiveness of a self-cleaning coating based on a dispersion in ethanol of titanium dioxide (TiO_2) powder at 0.5 gr/L distributed directly on stone materials. The parameters analysed in this study were stealthiness, performance against a toxic industrial chemical (TIC) and durability. It was found that the TiO_2 coating has low visibility, is able to partly remove TIC from the air and has high durability.

Keywords: *Titanium dioxide (TiO_2) self-cleaning coating; stone materials; stealthiness; toxic industrial chemical (TIC); durability.*

1. INTRODUCTION

The management of chemical, biological, radiological and nuclear (CBRN) safety of critical infrastructures requires a complex mixture of technologies and capabilities (Malizia *et al.*, 2010, 2011; 2012; Gallo *et al.*, 2012; Cenciarelli *et al.*, 2013a, b). In order to have an efficient CBRN emergency response system, it is necessary to arrange for the realisation and tuning of prediction models before the CBRN incident to be effective during and after the incident. In addition, the following decontamination procedures, and stand-on and stand-off detectors for chemical, biological and radiological agents are required (Bellecci *et al.*, 2010; Gaudio et *al.*, 2011; Pazienza *et al.*, 2013, 2014; Gaudio *et al.*, 2013a, b).

Our work highlights areas that we define as passive safety technologies, which can inherently provide increased resistance against a CBRN incident or speed up the return to full efficiency after the incident. When the protected infrastructures are not strictly of military use, such as offices and ministries, the level of decontamination that is needed is much higher than that of barracks or other facilities that can rely on the protection and training of personnel (Raber *et al.*, 2001). This paper focuses on one such passive safety technology; self-cleaning building materials.

The working principle of self-cleaning building materials is semiconductor photocatalysis, which increases the effectiveness of a photoreaction where a semiconductor acts as a catalyst and photon can originate from the sun or from a light source. The absorption of a photon of energy higher than the band gap of semiconductor activates these reactions. This results in the promotion of an electron from the valence band to the conduction band, with the concomitant generation of a hole in the valence band. In order to achieve an efficient catalysis, a new process involving electrons and holes at the semiconductor surface must be more efficient of the major deactivation process, which is the recombination between them (Figure 1). If the photocatalysis reaction is conducted in the presence of oxygen, it results in a semiconductor-sensitised photo-mineralisation from organic compounds present in the environment (Chen & Mao, 2007):

$$\textbf{Organic pollutant} + O_2 \xrightarrow[h\nu \geq E_{bg}]{\text{Semiconductor}} H_2O + CO_2 + \textbf{mineral acids} \tag{1}$$

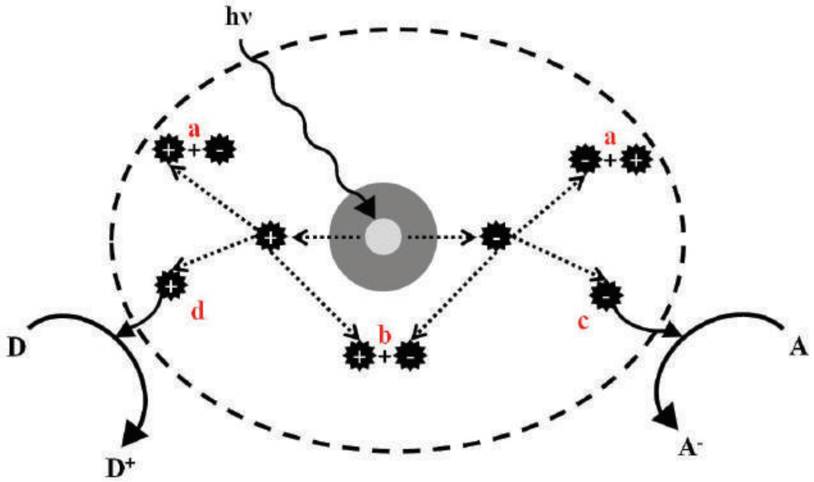

Figure 1: Formation and deactivation process of holes and electrons in the semiconductor particle. The dashed circle indicates the surface of the semiconductor. Reactions (a) and (b) are the electron-hole recombination at the surface and bulk respectively. Reactions (c) and (d) occur at the surface of the semiconductor particle. A indicates acceptor; A^-, reduced acceptor; D, donor; and D^+, oxidised donor. (Redrawn and adapted from Mills & Le Hunte (1997))

The use of photocatalyst materials in CBRN compounds is well documented, with many papers discussing the mineralisation of chemical warfare agents, and disinfection in water or on surfaces (Vorontosov *et al.*, 2004, 2005; Ming-Show *et al.*, 2006). Although the self-cleaning properties of photocatalyst materials were known since the 1960s, it is only in recent years they have begun to be used in a wide manner. The first application of self-cleaning concrete in Italy was in the *Dives in Misericordia* Church in Rome which was officially opened in 2003 (Pacheco-Torgal & Jalali, 2011). A number of experimental evidences have confirmed the ability of these coatings to oxidise organic molecules (Cassar *et al.*, 2004). It has also been demonstrated that these coatings have anti-microbial properties. Even if the mechanism is not completely clarified, according to several studies, it is believed that the metal oxides carry the positive charge while the microorganisms carry negative charge, causing electromagnetic attraction between microorganisms and the metal oxides, which leads to oxidisation and finally the death of microorganisms, such as algae (Linkous *et al.*, 2002) and bacteria (Zhang & Chen, 2009; Gupta *et al.*, 2013; Sikong *et al.*, 2010; Haghi *et al.*, 2012; Jain *et al.*, 2012). Generally, these materials are used in mortar or plaster. Many semiconductors have been tested as self-cleaning materials, but the most largely used is titanium dioxide (TiO_2) because of its efficiency, and low toxicity and cost.

There is another important mechanism that works well for TiO_2 self-cleaning coating, which is super-hydrophilicity. When a TiO_2 film is exposed to an ultraviolet (UV) irradiation, a very strong interaction develops between the photocatalytic surface and the water that is present in environment, which tends to spread on it in a flat manner rather than as a sphere. This effect can be explained by considering the high surface density of hydroxyl groups formed by UV light after the interaction between TiO_2 and water (Eshaghi et al., 2011). When the surface is rinsed with water, the contamination, such as oil, is washed away. Combining this effect with the degradation of organic matter, due to the photocatalysis process previously mentioned, it is possible to obtain a self-cleaning surface.

This paper is aimed at evaluating the effectiveness of a self-cleaning coating based on a dispersion in ethanol of micrometer size Degussa P25 TiO_2 powder at 0.5 gr/L distributed directly on stone materials. The parameters analysed were stealthiness, performance against a toxic industrial chemical (TIC) and durability.

2. METHODOLOGY

2.1 Stealthiness

In order to maintain stealthiness during the application, it is better that the coating is as less visible as possible. In our work, in order to evaluate this aspect, we made colorimetric measurements with a UV-Vis spectrophotometer (Jasco Inc.; the analysis was conducted according to the manufacturer's protocol) on some frequently used stone materials, such as travertine and brick, before and after the TiO_2 coating was applied. The variation of colour allowed for the evaluation of the visibility of the treatment.

2.2 Performance Against a TIC

The effectiveness of TiO_2 coating was evaluated by testing it against hydrogen sulphide, which is a TIC. This class of chemical compound can be considered as even more dangerous than chemical warfare agents due to its availability, as reported by DOL (2014).

The TiO_2 coating was spread on the travertine surface according to the following procedure:

1. A layer of TiO_2 was laid on a travertine plate, then cut with a microtome. The travertine plate was then transferred into a cuvette equipped with a cap that allows the passage of a teflon tube.
2. The bottom of the tube was inserted into the stopper of a flask containing an aqueous solution of thioacetamide (CH_3CSCH_3) acidified with hydrochloric acid (HCl). After sealing the flask, the mixture was heated at 60 °C in a thermostat. Thioacetamide is unstable under these conditions and reacts with water, resulting in the release of hydrogen sulphide.
3. The cuvette was radiated with UV from a xenon lamp for at least 8 h to simulate sunlight exposure.
4. At the end of the UV irradiation phase, a small sample of the exposed portion of the lamina was taken and analysed via Fourier transform infrared (FTIR) spectroscopy and ion chromatography techniques.

The whole procedure was repeated with a non-treated plate as a reference. Figure 2 shows the experimental setup.

2.3 Durability

In order to assess the durability of the coating, the effect of rain falling on TiO_2 treated stone materials with area of 2 cm^2 for two years was simulated in Rome, Italy (780 mm/year). It was calculated that 150 cm^3 of water would fall the plate from a height of 30 cm using a peristaltic pump (Figure 3). The persistence of the coatings of the stone material was evaluated by analysing the reflectance UV spectra.

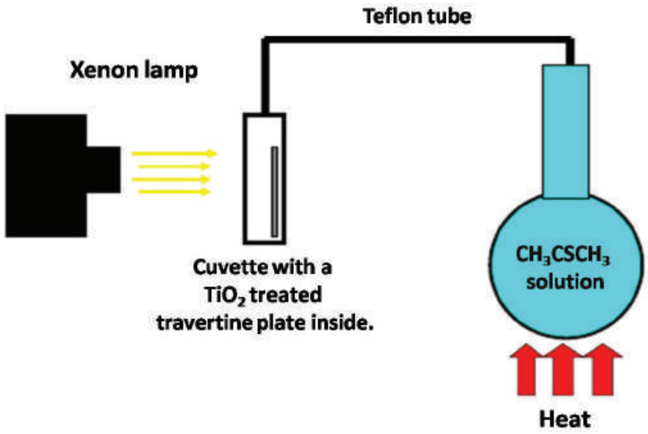

Figure 2: Experimental setup for evaluating the performance of TiO_2 coating against hydrogen sulphide.

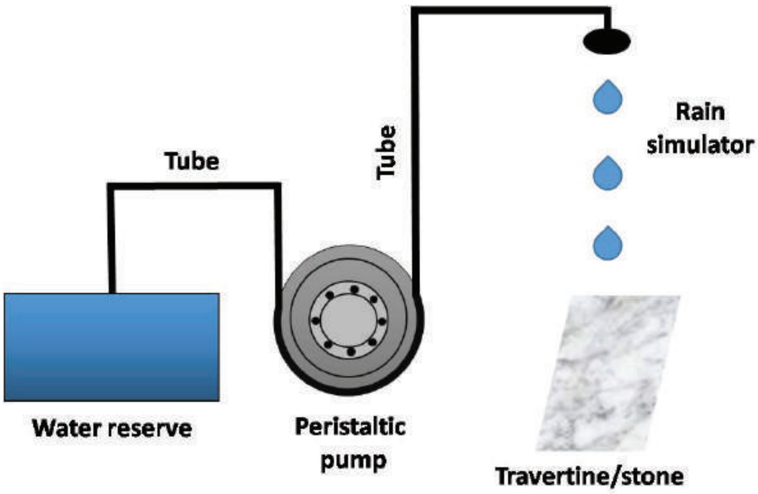

Figure 3: Experimental setup of the rain simulator.

3. RESULTS & DISCUSSION

3.1 Stealthiness

From the reflectance UV-Vis spectra, a quantitative measure of colour can be obtained. It is expressed as a point in a limited three-dimensional space, which are called chromatic coordinates. While translation of chromatic coordinates can be done in several ways, we choose the CIE*Lab* (CIE, International Commission on Illumination; *L*, lightness of colour; *a*, position between red / magenta and green; and *b*, position between yellow and blue) approach with coordinates *L.a.b*. This method, developed by the CIE in 1976, allows unambiguous encoding of the entire visible spectrum independently of any graphics technology. It is not important in this particular case how these values are defined, but it is important that the evaluation of the variation of colour correspond to the measurement of distance between the points representing the colour, which is known as the Pythagorean distance ΔE (CIE, 2014).

A value of $\Delta E = 2$ is considered as the limit of sensitivity of the human eye. This value is reported in Figure 4, which also shows the measures of variation of colour on 25 TiO_2 treated travertine plates, where these variations are averaging on the same order of magnitude. Similar results were obtained for bricks (data not shown). If the goal is to ensure complete invisibility of the coating, there is a large amount of literature about the possibility to synthesise nano-sized particles of titanium (for example, Peng *et al.* (2005)). This particle size causes the absence of scattering of visible light and this coupled with the absence in TiO_2 bands absorbing visible light make negligible the hiding power opacity of the coating, without affecting the photocatalytic effectiveness of the coating itself, at least for the initial phase after the treatment.

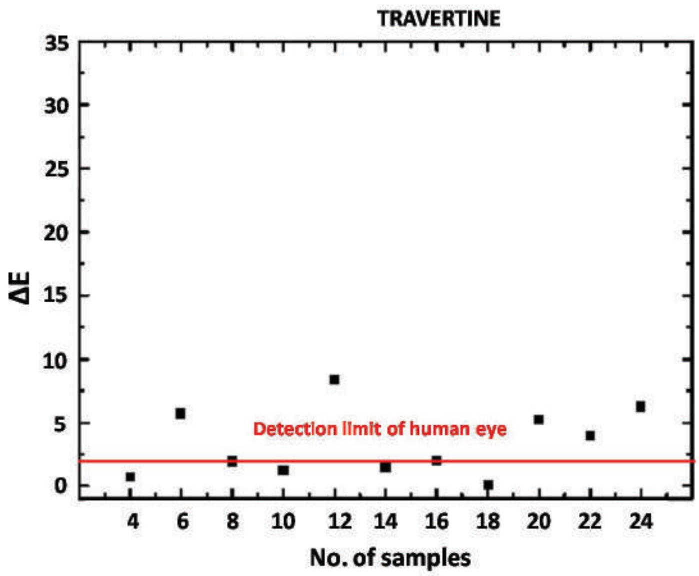

Figure 4: Variation *ΔE* for 25 TiO_2 treated travertine plates. The red bar is the human eye sensitivity.

3.2 Performance Against a TIC

Figure 5 shows the comparison between the FTIR spectra obtained from the TiO_2 treated and untreated plates after UV irradiation. There are intense bands assigned to carbonate, which is the most important component of travertine that is clearly identifiable and present in both spectra. There are also some identifiable bands, as reported in Table 1, that can be assigned to sulphate ions, which are not present in the reference sample of travertine without titanium. This corresponds to the expected reaction:

$$\mathbf{H_2S + O_2 + Photocatalyst \longrightarrow H_2SO_4} \quad (2)$$

where H_2S is hydrogen sulphide, O_2 is oxygen and H_2SO_4 is the reaction product, sulphuric acid. This finding infers that the TiO_2 coating is able to oxidise hydrogen sulphide by turning it into sulphur oxide and then removing it from the atmosphere.

3.3 Durability

Due to its strong 320 nm absorbance band (Table 1), TiO_2 was easily detected on carbonate (as shown by the difference between the black and red lines in Figure 6). It is observed that there is no difference between the UV spectra obtained before (red line) and after (green line) simulated rainfall. This indicates that even without any binder for the bonds to support, the photocatalyst has remarkable persistence on stone.

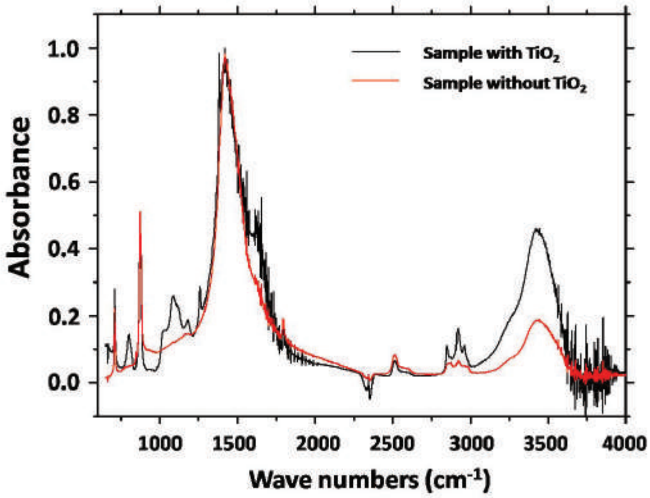

Figure 5: FTIR spectrum of travertine with and without TiO_2 after exposure to hydrogen sulphide acid and 8 ours of UV light.

Table 1: Intensities and attributions of absorption of the spectroscopic bands.

Band (cm^{-1})	Intensity of absorption	Attribution
1,090	Medium	Sulphate
1,117	Shoulder	
1,184	Weak	
1,470	Strong	Carbonate
3,500	Wide	Hydroxyl

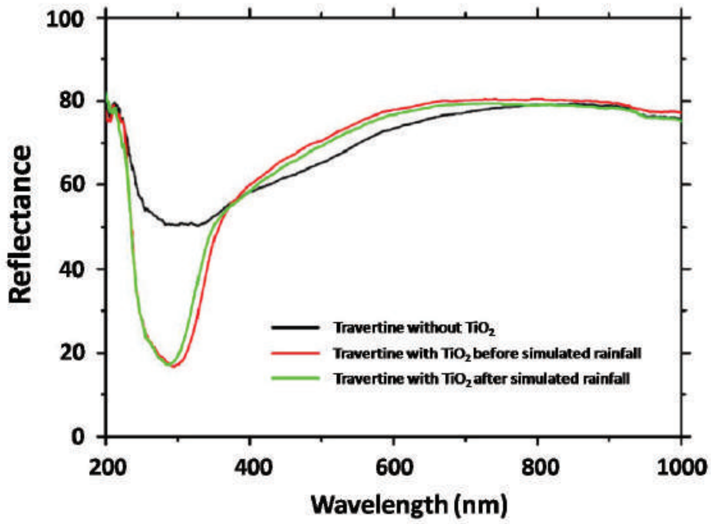

Figure 6: Reflectance UV spectra for travertine.

4. CONCLUSION

The effectiveness of TiO_2 self-cleaning protection to provide increased resistance against CBRN incidents was evaluated in this paper. It was found that the coating applied on common stone materials has low visibility, is able to partly remove TIC from the air and has high durability. It is necessary to underline that additional studies are required to properly evaluate the performance of self-cleaning coatings. While, in this study, the performance was evaluated for a maximum of several days after the treatment, for this kind of application, tests for over a number of years are necessary for more precise evaluation

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