Applied Surface Science 433 (2018) 312–320

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Efficiency and durability of a self-cleaning coating on concrete and stones under both natural and artificial ageing trials

P.M. Carmona-Quiroga[a,*], S. Martínez-Ramírez[b], H.A. Viles[a]

[a] School of Geography and the Environment, University of Oxford, South Parks Road, OX1 3QY, Oxford, United Kingdom
[b] Instituto de Estructura de la Materia (CSIC), C/Serrano 121, 28006 Madrid, Spain

ARTICLE INFO

Article history:
Received 2 June 2017
Received in revised form
14 September 2017
Accepted 8 October 2017
Available online 9 October 2017

Keywords:
Self-cleaning coating
Photocatalytic TiO_2
Stone
Concrete
Durability
Outdoor exposure

ABSTRACT

This study aimed to test the performance under long-term working conditions of a commercial self-cleaning coating, a water-based TiO_2 sol, on three building materials important in recent and older European heritage; Portland limestone, Woodkirk sandstone and concrete. First, the compatibility of the coating (effect on petrophysical properties) with the substrates was demonstrated by examining aesthetic properties and water vapour permeability of the building materials and secondly, the self-cleaning ability of the TiO_2 nanoparticles in degrading artificial stain (rhodamine B) under UV light was evaluated. Finally, the durability (lasting performance) of photocatalytic activity was assessed during one year of outdoor exposure trial and 2000 h of accelerated ageing in a chamber with UV radiation and condensation cycles. Results showed that photocatalytic activity was unaltered on concrete, whereas on sandstone, particularly after artificial ageing, it was reduced due to the removal of nanoparticles from the surface. On limestone, a decrease of TiO_2 content was observed but photodegradation efficiency (ability to perform as self-cleaner) seemed not to be affected.

1. Introduction

Airborne contaminants derived from natural and human sources are an important cause of deterioration and degradation of buildings and monuments. Since the mid-1990s, the ability of TiO_2 to oxidize and decompose organic and inorganic materials or pollutants has been used in a broad range of photocatalytic products (fabrics, purification systems, etc.) including coatings [1]. Self-cleaning coatings can keep the surfaces of the materials cleaned by the action of sunlight (under UV radiation TiO_2 generates electron pairs that in redox reactions decompose airborne particulate matter attached to the surface such as smoke or soot from burnt fossil fuels, dust from Earth's crust materials or industries, etc). In addition to this photocatalytic effect, there is also photo-induced hydrophilicity that prevents the adhesion of these organic contaminants and dust by flattening water droplets on the surface of the materials [1].

On historic surfaces, however, application of these coatings is still limited [2] and mainly confined to scientific research [2,3–7]. Taking into account that repeated cleaning methods (washing; brushing; micro sand-blasting; chemical treatments; etc.) can cost more than self-cleaning coating application and may themselves cause further damage to deteriorated materials, self-cleaning coatings might offer an effective way to reduce the impact of pollutants on cultural assets by reducing aesthetic damage (soiling) and associated deterioration of building materials.

On concrete, nowadays the building material par excellence on civil engineering and already part of our more recent built heritage, they have been used more extensively, mainly as non-reactive cement fillers to cement mixes that accelerate cement hydration rates [8–10]. The adhesion of nanoparticles in cement mixes is more effective than with coatings [9]. However, studies have also shown that nanoparticles embedded in the cement matrix may lose their efficiency (ability to degrade pollutants) [11] since cement hydration products can precipitate on the surface of nanoparticles [12]. Regardless of the method of incorporation of TiO_2 nanoparticles, the results so far have shown their potential in preserving heritage aesthetics (self-cleaning effect), and also on reducing environmental air pollution (depollutant effect) [2,8]. However, research to date on the durability (lasting performance) of self-cleaning coatings on stones and cementitious materials in the long term, under real working conditions (outdoor exposure), is still limited [13]. Conversely, their performance under accelerated weathering conditions has been better explored since these tests produce fast useful results by simulating and combining different environmen-

---

[*] Corresponding author. Present address: Instituto de Ciencias de la Construcción Eduardo Torroja (CSIC), C/Serrano Galvache 4, 28033 Madrid, Spain

E-mail address: paulacq@ietcc.csic.es (P.M. Carmona-Quiroga).

https://doi.org/10.1016/j.apsusc.2017.10.052
0169-4332/© 2017 Elsevier B.V. All rights reserved.

tal conditions. So, the adhesion and wearing resistance of these coatings have been evaluated through pull-off, tape adhesion and impact tests with mixed results [14,15]. Tests designed to simulate outdoor conditions with UV light alone or combined with water flow [5,11,16–19] have found loss of their photocatalytic activity due to the loss of efficiency of the nanoparticles caused by the adsorption of pollutants or reaction by-products or due to their loss of adhesion. Water flow (rain) can improve the photocatalytic activity of the nanoparticles by removing the adsorbed species if there are not strongly adhered [19,20]; however it can also wash the nanoparticles away [6,18].

Since accelerated ageing tests cannot accurately reproduce all environmental factors [13] and can produce anomalous effects, testing under natural environmental conditions is of crucial importance. In fact, it is recommended to run both accelerated and natural ageing tests in parallel to evaluate materials durability [21]. Up to date, however, there is limited knowledge on the performance in the long-term of self-cleaning coatings on different type of stones whose intrinsic properties may result in different durability issues [13,15].

This study aims to assess how durable is the self-cleaning activity of commercial water-based sol of TiO_2 nanoparticles sprayed on stones and concrete in the long-term during not only an artificial weathering test but also an outdoor exposure trial. To do this, samples were either kept for up to 2000 h in a chamber with UVB radiation or exposed outdoors in the South of England for one year. Test conditions were not designed to be equivalent because as mentioned before environmental factors cannot be accurately replicated in a chamber. This approach is intended to correlate the results of both ageing tests and evaluate possible similarities in the degradation of the coating, self-cleaning efficiency included.

2. Experimental

2.1. Self-cleaning coating application on the substrates

A commercial and ready to use nano nitrogen-doped anatase TiO_2 aqueous sol (2.4 %wt of anatase nanoparticles of 10–40 nm of diameter; water-based) was sprayed at room temperature onto the upper faces of Portland limestone, Woodkirk sandstone (APS Masonry, Oxford, UK) and paving concrete slabs (Grey Superpave from Rogers Gardenstone, Faringdon, UK). Two coats were applied over successive days on specimens of different sizes (each in triplicate), 150 × 75 × 10 mm; 85 × 65 × 10 mm and 75 × 35 × 10 mm, with a HVLP (High Volume Low Pressure) spray, recommended by the product manufacturer, to reproduce the easiest application method on real walls. To avoid coating runs samples were brushed afterwards with a roller. The average product uptake (dry weight) was $11 \pm 0.5\,g/m^2$ for limestone, $44 \pm 2\,g/m^2$ for sandstone and $129 \pm 16\,g/m^2$ for concrete. However due to the concrete hydraulicity, this value cannot be exclusively accounted for by the uptake of nanoparticles but also for cement hydration products.

Portland limestone (Jurassic, UK) is a white oolitic limestone quarried in the Island of Portland (Dorset, UK) and commonly used in English and European built heritage. The variety used here, Jordan's whit bed, is constituted of oolites (0.1–0.5 mm in diameter), scattered shell fragments (around 5 mm in diameter) and a low proportion of micritic matrix. Its water accessible porosity, determined following EN 1936:2006 standard [22], is 14%.

Woodkirk sandstone (Carboniferous, UK), quarried in Leeds (UK) has been used since the 18th century in many buildings and pavings in the UK [23]. It is a light brownish-buff, fine grained sandstone mainly composed of quartz. Other constituents are feldspars, mica crystals and opaque minerals (iron oxides). Its water accessible porosity is around 8%.

Grey concrete paving slabs (Grey Superpave from Rogers Gardenstone, Faringdon, UK) with a water accessible porosity of 11% and characterized for their smooth finish was the last substrate selected as a representative material of current civil engineering works.

2.2. Ageing tests

Slabs with and without the self-cleaning coating were exposed to two different ageing trials. In a UV chamber (QUV, Q-Lab Corporation) triplicate samples of dimensions 150 × 75 × 10 mm (area irradiated of 95 × 63 mm) and 75 × 35 × 10 mm were exposed for 2000 h to cycles consisted of 4 h of UVB radiation ($0.45\,W/m^2$ at 313 nm) at 60 °C and 4 h of condensation without radiation at 50 °C [24].

The outdoor weathering test was carried out in a non-polluted field site in Wytham Woods near Oxford (UK) where uncoated and coated samples (150 × 75 × 10 mm and 75 × 35 × 10 mm) were left tilted at 45° in a rack facing South for 1 year (April 2015 to May 2016; time intervals in which samples were brought to the lab to be analysed are included in this period). Climatic conditions were recorded at the nearby Radcliffe Meteorological Station (University of Oxford) (Table 1) and average solar radiation from the PVGIS Solar Radiation database [25] calculated as $3070\,Wh/m^2$ day. UV radiation, as 3% of solar radiation, was $92.1\,Wh/m^2$ day of which a 5% was UVB ($4.6\,Wh/m^2$ day). For the total outdoor exposure period, samples were subjected to $6\,MJ/m^2$ of UVB radiation, 740 mm of rain and temperatures ranging from 0 to 25 °C whereas for the accelerated ageing test slabs were subjected to $1.6\,MJ/m^2$ of UVB radiation, no rain but 1000 h of condensation without radiation and temperatures ranging from 50 to 60 °C.

Table 1 summarizes the environmental conditions over this period.

Every 500 h for the accelerated ageing test, or every 3 months for the outdoor exposure trials, samples were brought to the lab to characterize changes in the colour of the surfaces and to assess their photocatalytic activity.

2.3. Analysis of physical properties

Colour, gloss and water vapour permeability were characterized before and after application of the self-cleaning coating, each on triplicate samples.

Colour coordinates, $L^*a^*b^*$ were determined with a Minolta CM-700d spectrophotometer; L^* for lightness; a^* for the red (+)/green(−)hue and b^* for the yellow (+)/blue (−) hue. Five (on 85 × 65 × 10 mm slabs) and three measurements (on 75 × 35 × 10 mm slabs) per sample were taken for natural and accelerated aged samples using a stencil. Overall colour variations (ΔE^*) were evaluated by the following equation, $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$. Gloss, at a specular reflection angle of 85° was measured with a TQC glossmeter using three (85 × 65 × 10 mm) and two (75 × 35 × 10 mm) measurements per slab for the natural and artificial weathered samples respectively. Finally, water vapour permeability (δ) was studied to EN 1015-19:1999 standard [26] on the 75 × 35 × 10 mm specimens.

2.4. Durability and photocatalytic activity studies

Durability of the self-cleaning coating was tested by examining changes in the chromatic properties of the surface and by evaluating their photocatalytic activity. Before and at the end of each exposure period (every 500 h or 3 months) colour coordinates and ΔE^* were determined as mentioned before.

Photocatalytic activity of the untreated and coated slabs, the latter before and after each natural or artificial exposure periods