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Compatibility of photocatalytic TiO_2-based finishing for renders in architectural restoration: A preliminary study

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ABSTRACT

Self-cleaning finishing treatments based on the use of TiO_2 nanoparticles have been recently proposed for the protection of materials in cultural heritage, with the aim of increasing the durability of these materials in polluted environments. The results on stone seem encouraging, but the experimental tests on different porous materials, such as bricks and renders used in historical buildings, are still extremely limited.

In the present paper, the application of water dispersion of titania nanoparticles to the repair renders of the former *Del Corso* hotel (XVIII cent., Bologna, Italy) was evaluated. The building and its environment were first analysed for assessing the appropriateness of such finishing, then samples of painted renders identical to those provided for in the intervention work were manufactured and treated with the dispersion, both by brushing on the dry paint and by brushing on the wet paint (the latter procedure in order to enhance the particles retention by exploiting the mechanism of fresco paintings). The outcome of the different treatments was investigated mainly to evaluate its compatibility with the substrate and its durability, which could be of interest also for the application of photocatalytic finishing to renders in new constructions.

1. Introduction

Although TiO_2 (mainly in the rutile crystalline form) was introduced as white pigment in the painting industry since the early years of 20th century [1], its photocatalytic activity was highlighted in the Twenties and investigated more extensively starting from the Fifties, when the photochemical reactions occurring at the TiO_2 surface (mainly in the anatase form) started to be elucidated [2]. The progressive appraisal of these reactions disclosed a wide range of potential applications where anatase could be usefully employed and boosted its industrial exploitation. Under UV light exposure, TiO_2 experiences both redox reactions of absorbed substances and hydrophilic conversion [2], that can be jointly or singularly exploited for several functions, such as air purification of NO_x, SO_x, VOCs and other pollutants [1,3,4], self-cleaning and de-soiling [2], anti-fogging [2], anti-microbial [5] and anti-biofouling [6]. Hence, in recent years photocatalytic titania, mainly in the nano-sized form, has become an emerging material, gaining strong interest in different fields including the construction sector [7,8], where it is used mainly in coatings, paints and cement-based mortars/pavement blocks for air-purifying purposes [1,3], anti-microbial paints [5], anti-microbial tiles [3], and self-cleaning window glasses [4].

Despite the great potential acknowledged to photocatalytic titanium dioxide in the construction sector, there are still many open questions on its performance in real applications and on its health effect and environmental impact, hence a large amount of literature papers has been devoted to investigate these aspects. The concern about the environmental impact of titanium dioxide is quite logical, considering that its total demand in the world is about 3.7 Mt per year [4]. The generation of SO_x, sulphate waste and chloride waste during the production process was already pointed out in 1999, when the first Ecolabel Directive for indoor paints and varnishes fixed limits for these kinds of waste during the production of TiO_2-based pigments [9]. Recently, a study aimed at performing a LCA analysis of nano-TiO_2-coated window panes in comparison with

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uncoated ones highlighted that, at least for the process considered, photocatalytic panes involve lower acidification potential, eutrophication potential, air pollutants and smog formation potential, but higher global warming, fossil fuel depletion, water intake, human health impact and ecological toxicity [4]. However, the Authors conclude that, applying the multi-attribute decision analysis, the evaluation of nano-TiO_2 coated window panes is positive. The high embodied energy and emissions connected with TiO_2 manufacturing processes is highlighted also in Ref. [8]. However, titania can be also effectively used for replacing large amounts of cement in structural concrete (due to its positive effect on the degree of hydration) and for neutralizing gaseous pollutants, hence these aspects are suggested to improve concrete sustainability [10]. Moreover, according to ongoing research [11], alternative production processes may be used for manufacturing TiO_2 nanoparticles with lower embodied energy with respect to the current ones.

In terms of human health effects, literature shows extremely controversial opinions [12]. While some Authors define it 'not toxic' [1,13] or simply state that the one century long use of titanium dioxide is a guarantee of its safety for humans [2], IARC cautiously classified titanium dioxide in the Group "2B - possibly carcinogenic to humans" (as there is 'inadequate evidence in humans' and 'sufficient evidence in experimental animals'), pointing out the urgent need for research in this field. The concern about the risks associated to titania is quite widespread and many Authors underlined its toxicity [7,12], especially for workers involved in nanoparticles spraying and thus exposed to inhalation risks [7]. Nevertheless, the cytotoxic effect of TiO_2 was not evidenced in all the studies that were carried out and it was finally assessed that this effect depends on many factors, such as the crystalline polymorph and shape of TiO_2, its functional groups, and many others [5,12]. In terms of possible risks for aquatic life, results are controversial as well [14], but some Authors evidenced a significant release of TiO_2 nano- and micro-particles in aquatic environment from painted façades under the effect of rain runoff [14], hence this aspect is worth of deeper investigation.

Alongside the impact on health and environment, other aspects are currently actively investigated, such as new possible applications where titania might represent a promising solution for currently unsolved problems. Among these applications, photocatalytic TiO_2 nano-particles have been recently proposed also for the surface treatment of ancient materials in monumental buildings [13,15–21]. Given the sensitivity of stones, mortars and bricks to pollution-related decay, the application of titanium dioxide is intended to provide the materials with self-cleaning ability, drastically reducing their degradation. Photocatalytic titania is also expected to be active against bio-deterioration, which often threatens cultural heritage integrity [22]. Nevertheless, any application in the cultural heritage field must accomplish many additional requirements with respect to new buildings, such as compatibility (aesthetical, physic-mechanical, chemical, etc.), absolutely necessary for avoiding defects occurrence and for achieving a good durability also in aggressive environments (such as urban polluted areas).

Two main approaches were followed in proposing the application of TiO_2 to historical building surfaces. A first group of researchers suggested the dispersion of titania nanoparticles in (traditional) water repellent protective organic treatments (silane/siloxane [6], polyalkylsiloxane [15,17]) and organic coatings (aqueous suspension of an acrylic polymer [18]), while a second group suggested the direct application of self-cleaning dispersions of titania nanoparticles [13,16,19–21]. The two approaches appear antithetic, as in the first one materials surface is expected to become super-hydrophobic, while in the second one surface is expected to become super-hydrophilic.

In the papers pursuing the first route, TiO_2 nanoparticles were firstly added, along with other kinds of nanoparticles, to commercial poly-alkyl-siloxanes (water repellent coatings already widely used for surface protection of stone in cultural heritage) and applied to different sandstone [15]. The nanoparticles are here not photocatalytic, but they are meant to simply make the surface rougher and hence water repellent. The nanoparticles made the static contact angle slightly increase with respect to stone treated with plain poly-alkyl-siloxanes, while they caused an unacceptably high colour change. Conversely, in Refs. [18], titania nanoparticles were dispersed in an acrylic polymer matrix in order to achieve biocidal and hydrophobic features: the suspension was applied by brushing to marble and limestone substrates. Despite the positive outcome of the treatment in terms of biocidal and photodegradation efficiency, as well as in terms of colour variations, the possibly competing behaviour of titania nanoparticles and polymer matrix was highlighted: on the one hand the superhydrophilicity of the powder may interfere with the polymer, on the other hand titania may even catalyse the degradation of the organic binder [18].

Following to the second approach, an aqueous colloidal suspension of TiO_2 nanoparticles (1 wt%) was prepared by sol–gel and hydrothermal combined process and applied by spraying to a highly porous calcarenite [16], comparing its effect with a commercial suspension. Microcracked coatings were observed when titania concentration exceeds 2 wt% and/or for high amount of solutions sprayed (leading to film thickness greater than the critical one), but the 1% sol prepared led to no cracks formation. Negligible differences in colour and water sorptivity were registered between the treated and the untreated stones, while the methyl red decomposition test gave good results. Encouraging results were found also with aqueous suspensions, again obtained by sol–gel and hydrothermal method, used for spray-treating travertine [20]. Great lowering of the contact angle and a slight reduction of the initial absorption coefficient were found as a consequence of the treatment, but the long term water absorption by capillarity remained substantially the same. A purposely designed test, involving the spraying of water by a manual nebulizer onto 80° inclined samples (with and without UV exposure) was also performed in a further paper by the same Authors [21]: under UV exposure, a clear decrease in water absorption was surprisingly registered, which is in contrast with the decrease in contact angle and coefficient of water absorption. A commercial nanotitania suspension, with particle size around 40–50 nm and two different concentrations (0.5 and 1 wt%), was used for treating porous fired clay bricks [13]. Micro-cracked and not homogeneously thick coating was produced by spray application and a subsequent quite high colour change was registered, which however decreased after wetting–drying cycles. The titania presence produced a slight decrease in the contact angle (unaffected by UV exposure, differently from other findings on travertine [21], which was ascribed to different surface roughness of the material under testing), which however was surprisingly high in the untreated brick (about 112°), and again the final water absorption by water spraying of the treated samples was significantly reduced when exposed to UV. The application of wetting (by spraying) and drying cycles resulted in the removal of fragments of the microcracked coatings.

Although some good experimental results were reported on the application of titanium dioxide to cultural heritage, there are still many aspects to be fully elucidated, such as the performance of this material on different substrates [13], the long-term behaviour, the actual self-cleaning effect in real environments (self-cleaning ability is usually investigated by laboratory tests necessarily simplifying the exposure conditions) and many others.