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Weathering tests of photocatalytic facade paints containing ZnO and TiO_2

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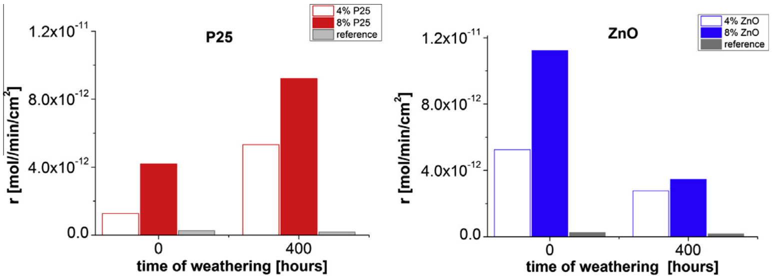
HIGHLIGHTS

- Paints containing photocatalyst TiO_2 or ZnO exposed to simulated weathering tests.
- Photocatalytic properties were studied using Acid Orange 7 as a model compound.
- Higher initial photoactivity of the unweathered paint with ZnO could be due to its significantly higher isoelectric point.
- Weathering of TiO_2 paints results in an increase of photoactivity.

GRAPHICAL ABSTRACT

Initial rates of dye Acid Orange 7 degradation as a function of weathering. (a) Paints containing TiO_2 (P25) and (b) paints containing ZnO.



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ABSTRACT

The photocatalytic properties of self-cleaning acrylic paint containing TiO_2 and ZnO were studied using Acid Orange 7 as a model compound. Paints were exposed to simulated weathering tests in a QUV panel. The initial photoactivity of the unweathered paints with ZnO was significantly higher. In the case of paints containing P25 the photocatalytic activity increases with weathering time, due to increasing destruction of the polymer resin and consequent exposure of the photocatalyst pigment to the Acid Orange 7 test solution. In contrast, in the case of paints containing ZnO, a decrease in photocatalytic activity is observed after weathering, due to the loss and/or photocorrosion of ZnO particles during the weathering process.

1. Introduction

In addition to the usual pigments and filler associated with regular paint, photocatalytic self-cleaning paints contain particles of a photocatalyst which exhibit a well-established light-driven self-cleaning action. The self-cleaning action of a photocatalytic paint is derived from a combination of photocatalytic activity and photoinduced superhydrophilicity. With both of these effects photons of light of energy greater than or equal to the band gap energy of the semiconductor photocatalyst generate electron hole pairs. In most cases these pairs recombine to generate heat but the photocatalyst phenomena is due to the photogenerated electrons and holes that reach the surface of the photocatalytic particle where they can participate in redox reactions. Thus, photoinduced holes exhibit a high oxidation potential and are able, either directly or indirectly, to decompose stable organic pollutants and the photogenerated electrons are able to reduce ambient oxygen. As a result,

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semiconductor photocatalysts can be used to clean organic deposits from its surface [1]. The underlying mechanism associated with the photo-induced superhydrohilic effect is the subject of significant controversy, but its features are that the surface of the photocatalyst becomes superhydrophilic, i.e. exhibits a water droplet contact angle $\ll 10^\circ$ upon irradiation with ultra-bandgap light [2,3].

The current commercial application of photocatalytic paints is mainly with regard to exterior, facade paints [4–9] which, via the photocatalytic process, are not susceptible, to soiling and so help to keep the surface of the building clean [10]. Recently, photocatalytic paints for use indoors have begun to be produced [11]. Apart from the usual household applications of such paints, e.g. degradation of pollutants and odours and maintenance of a superhydrophilic surface, self-cleaning paints are also being used to: (i) decompose ammonia in animal husbandry [12] (ii) remove VOCs and NO_x in underground garages [13] and (iii) maintain a photosterile surface, so that bacteria and fungi do not thrive [14,15].

The development of photocatalytically active paints is not easy, since a key part of stable paint development is the creation of better barriers to the photocatalytic mineralisation process, so that the polymer binder remains intact longer and the paint exhibits an appreciable lifetime as a coated film. Thus, in the preparation of a photocatalytic paint it is important to find a compromise between maintaining a reasonable degree of photocatalytic activity and still retaining a good paint stability. Clearly, a high level of photocatalytic activity in a paint will produce a low paint lifetime due to light-induced weathering and photo-chalking. On the other hand there must be sufficient photocatalyst so as to achieve a reasonable level of photo-induced self-cleaning.

Photocatalytic water-based facade acrylic paints contain typically three major components, namely: acrylic binder, pigment and photocatalyst [6–8]. For example the photocatalyst coating patented by Millenium Inorganic Chemical [8] consist of 5–40% (by volume) of photocatalyst, styrene acrylic copolymer binder, additional pigment (e. g. non-photocatalytic TiO_2), calcium carbonate, solvent thickeners, dispersants, coalescents and antifogging agents. The total amount of pigments (including photocatalytic TiO_2) is minimally 65% (by volume) [8]. This paper describes the results of an investigation into the parameters which influence the photocatalytic activity and stability of a water based paint with an acrylic binder containing either TiO_2 or ZnO as the photocatalyst and the results are relevant to those working in the area of photocatalyst paint development.

2. Experimental

A series of samples with various amount of photocatalyst were prepared. The titania photocatalyst used was P25 (Evonik-Degussa) which consists of 78% of anatase phase, 14% of rutile and 8% of amorphous phase [16] with specific surface area about 56 m^2/g and particle size 30 nm. The ZnO photocatalyst was provided by Umicore (Belgium) and consisted of a zincite phase with a specific surface area about 29 m^2/g and particle size ca 35 nm. The assessment of the photocatalytic activities of suspensions of these photocatalysts were carried out using a loading 0.2 g/dm^3.

In this work, the synthesized paints were based on an aqueous acrylic dispersion, with rutile titanium dioxide as the non-photocatalytically active pigment, and with fillers and special additives. Thus, the typical "photocatalytic" paint used here comprised: 4 g of photocatalyst, 11 g of rutile TiO_2 pigment (particle size 204 nm; surface area ca.10 m^2/g), 37 g of filler (calcium carbonate), 16 g of styrene acrylic copolymer, 0.5 g of dispersing agent, 1 g of special additive and 30.5 g of water. The special additive comprised: a wetting agent 67 Additive (Dow Corning) to ensure good wetting of the particles of fillers and pigments, anti-foaming agent Rhodoline 990 (Solvay) to prevent the formation of bubbles on the paint surface and a rheological agent ISCATHIX SR (ISCA).

Samples of the formulated paints were applied using a universal applicator ZUA 2000 (Zenther, Swiss) onto a glass substrate (soda lime glass 7.5 × 12 × 0.2 cm); the thickness of the wet paint was about 150 μm (thickness of dry paint was 90–100 μm). Samples were irradiated in a QUV panel (QUV-spray equipped with UVA-340 tubes, UV light intensity 1 mW/cm^2), Q-Lab, USA which simulated accelerated weathering effects such as sunlight, rain and marked temperature changes applicable to exterior paints. The whole cycle has four parts as follows: (i) UV irradiation, 1 W/m^2, 8 h, (ii) spraying with water, 7 dm^3/min, 4 min, (iii) condensation of steam, temperature 70 °C, 4 h and (iv) spraying with water, 7 dm^3/min, 4 min.

Contact angles of distilled water droplets on the surfaces were measured using drop shape analysis system (DSA30, Krüss, Germany) equipped with CCD camera (Stingray F046B, Allied Vision Technologies GmbH, Germany). Contact angles were calculated using appropriate software (DSA3, Krüss, Germany) by circle fitting. Surface analysis of paint surface was done using Philips ESEM 30 XL (Philips) equipped with with EDAX EDS detector.

In addition to contact angle measurement, experiments to assess the photocatalytic activity of the weathered samples were performed in a stirred batch photoreactor equipped with black light fluorescent tubes Sylvania BL-350 (11 W) with broad maximum at 365 nm. In this work, the photocatalytic activities of paint samples were determined using as a pollutant model the azo dye Acid Orange 7 (AO7) by placing the sample under test in 25 ml of an aqueous solution with an initial concentration of AO7 of 2.5×10^{-6} M; the irradiated area of each paint sample exposed to this solution was: 17.9 cm^2. The concentration of AO7 during each irradiation was measured by visible absorption spectroscopy ($\lambda_{max}(AO7) = 485$ nm; extinction coefficient 20,549 $dm^3\ mol^{-1}\ cm^{-1}$). Typically, in this work, the concentration of AO7, [AO7], decreases linearly with irradiation time, allowing the photocatalytic activity of the paint sample under test, as measured by the rate of disappearance of the AO7 dye (r, $mol\ dm^{-3}\ min^{-1}$), to be evaluated via the initial slope of the absorbance versus irradiation time plot of the data.

3. Results and discussion

First of all the photocatalytic activities of both materials in the form of aqueous suspensions were assessed via the photocatalysed induced bleaching of an aqueous AO7 solution, using a UVA irradiance of 2 mW/cm^2. The overall photocatalysed mineralisation of AO7 can be summarised as follows [17]:

$$C_{16}H_{11}N_2NaO_4S + 21O_2 \rightarrow 16CO_2 + 2HNO_3 + NaHSO_4 + 4H_2O \qquad (1)$$

The results of this initial study are shown in Fig. 1, from which it appears that the photocatalyst activities towards the photobleaching of AO7 for P25 and ZnO are rather similar, with ZnO appearing slightly better than TiO_2 (P25), although the latter is often taken as a standard (benchmark) photocatalyst material. Indeed, in our recent study [18], P25 was reported to be among the best photocatalyst for sensitising the bleaching of AO7 from about 10 commercial TiO_2 photocatalysts. The relevance of Fig. 1 is that in aqueous suspension both ZnO and TiO_2 photocatalysts appear to exhibit a similar activity with respect to the photobleaching of AO7.

The water droplet contact angles on different samples of paint were determined as a function of irradiation time in the QUV panel and the results are illustrated in Fig. 2a for samples containing