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Discoloration of White Concrete Containing Photoactive TiO₂



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ABSTRACT

Photoactive titania is able to activate chemical reactions in the presence of UV radiation by producing a free electron and an electron hole. These can activate e.g. decomposition of organic compounds and oxidation. This phenomena has inspired the development of new products that possess so called photoactive functional surface properties. Being a fine powder, titania needs to be bound with some kind of adhesive material. Organic binders have the disadvantage of becoming potentially decomposed in the course of the photoactive reactions, whereas inorganic binders remain intact. Cement (OPC) as the most widely used binder would be one obvious choice. White mortar samples containing titania (TiO₂) were found to turn yellow during the exposure to UV-light both in outdoor and laboratory conditions. The discoloration could harm the visual appearance of high quality concrete surfaces if not taken into consideration while selecting the titania type. Key words: Photoactivity, UV exposure, titania, concrete, discoloration

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1. INTRODUCTION AND OBJECTIVES

Photoactive titania is able to activate chemical reactions in the presence of UV radiation by producing a free electron and an electron hole. Those can activate e.g. decomposition of organic compounds and oxidation of NO_x. This phenomenon has inspired development of new products that possess so called photoactive functional surface properties. Being a fine powder, titania needs to be bound with some kind of adhesive material to the product. Organic binders have the disadvantage of becoming potentially decomposed in the course of the photoactive reactions whereas inorganic binders remain intact. Cement (OPC) as the most widely used binder would be one obvious choice. White mortar samples containing titania (TiO₂) were found to turn yellow under the exposure of UV-light both in outdoor and laboratory conditions. The discoloration could harm the visual appearance of high quality concrete surfaces if not taken into consideration while selecting the titania type. The objectives of the present study were to investigate white mortar surface discoloration in outdoor conditions, to verify the discoloration lab conditions and to identify the conditions and components required to produce the discoloration.

2. MATERIALS AND EXPERIMENTAL SET UP

Tables 1 and 2 give information on the titanias and mortar mixes used. According to the XRD analysis both titanias were well crystallized anatase. The peaks of titania B were clearly wider, indicating smaller crystallite size. DTG measurement revealed about 3 times larger weight loss of titania B within both of the temperature ranges, 25 – 173 °C (8.45 w %) and 173 – 700°C (3.87 w %), compared to titania A (2.39 and 1.16 wt %). The first weight loss was attributed to free moisture and the second one bound water or hydroxides (Mettler TGA 851e). In the filtered specimens the reference material to white cement was pure precipitated calcium carbonate (PCC, product name "Calofort U") produced by Specialty Minerals. Iron oxide was Fe₂O₃, a fine powder produced by Merk Chemicals by the product code 3924. All colorimetric measurements were with a Minolta spectrophotometer CM -525i.

Table 1. Titanium dioxides used in the tests. The batches as well as their chemical composition were delivered by Sachtleben Pigments.

Property	Titania A	Titania B
Crystal Form	Anatase	Anatase + Ti hydroxide
Crystal size [nm]	10 – 30	6
Specific surface area [m ² /g]	70 – 120	250 – 350
Particle size (d50) [μm]	1 – 3	1 – 2
pH-value (approx.)	4 – 7	5 – 7
TiO ₂ content (approx.) [%]	99	> 85
S content [%]	< 0.4	< 0.3
Fe [mg/kg]	< 70	< 70
Na [mg/kg]	< 250	< 1000

Table 2. Mortars.

Component	Content
White OPC (Aalborg White)	600 - 700 kg/m ³
Water	240 – 280 kg/m ³
Aggregate (White limestone R22 0-2 mm by Finnsementti)	1300 – 1500 kg/m ³
Superplasticizer (Glenium 51 by BASF, 17.5 %)	6 kg/m ³
Titania 0-12 w% (of cement) *)	0 - 84 kg/m ³

**) Part of the water, superplasticizer and TiO₂ were mixed to produce a "milky" suspension prior to adding to the mix*

2.1 UV exposure of mortars

The mortar specimens were cured in the dark at T 20 ± 2 °C, RH 40 % until the age of 14 months. In the outdoor conditions the specimens were at a 45 degrees inclination, tested surface on top, facing south, close to a motorway in Espoo (Helsinki area), Finland. The outdoor storage started in August 2006 and ended in February in 2009. In lab conditions the mortar specimens were subjected to cyclic treatment consisting of UV radiation, rain and darkness. The filter combination was selected to simulate the UV radiation of a cloudy summer afternoon in the Helsinki area. The duration of 5.5 cycles corresponded to the UV and rain of one summer month.

2.2 Preparation and UV exposure of filtered specimens

The filtered specimens were prepared by filtering the tested material combinations on a glass fiber from a dilute water suspensions. No aggregate was used in the filtered specimens. This technique allowed the preparation of samples also without OPC. The thickness of the cake was approximately 3 mm. In the first stage UV exposure the filtered specimens were placed between two acryl plates (thickness 3 mm) into a UV chamber that enabled uniform radiation. Each sample was followed by one reference sample covered by aluminum foil in order to block the UV-light (Figure 1). The chamber test was cyclic, with each cycle consisting of 8 h of UV radiation in a dry atmosphere followed by 4 h of condensation in vapor. After the first stage, the specimens were exposed to the second stage UV radiation in outdoor conditions in a horizontal position on the roof of VTT research facility for 66 days starting in June 2009.

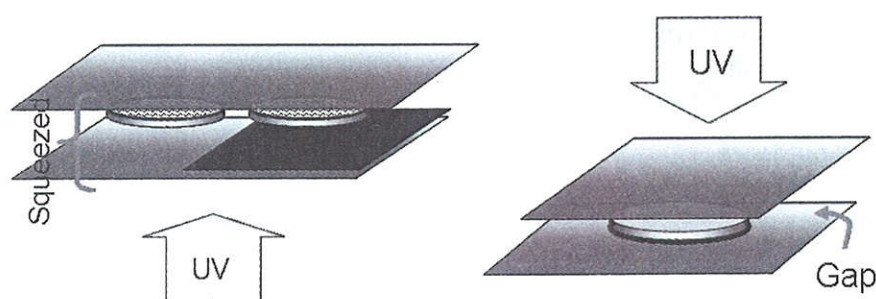


Figure 1. Schematic presentation of the 1st stage UV exposure of the filtered specimens on the left and second stage on the right. In the first stage the total duration of cyclic test was 800 hours: 533 h in UV and 267 in dark. The acryl plates and sample holder were squeezed together, which limited the access of H₂O, CO₂ as well as other environmental gasses to the specimens. In the 2nd stage the samples on VTT roof top in the Helsinki area for 66 days in summer 2009.

3. RESULTS

During the first seven month period which fell to the dark seasons the color of all mortars changed. The specimens darkened slightly (dL) and their increased chromaticity was mainly caused by the yellow component. Over the whole measuring period the marked color change of the titania A containing samples could be divided into stepwise increase of the yellow shade during the strong UV exposure of the summer period (Figure 2) and continuous but diminishing darkening regardless of UV-exposure. The darkening in the traffic area is mainly caused by the accumulation of soot particles. Over the same period the darkening of titania B containing samples was rather diminishing than increasing and chromaticity due to yellowing stayed at a constant level. The results in lab conditions showed that the yellowing was caused by titania (Figure 3). The results of the filtered specimens can be given here only as a condensed conclusions (below), but will be published elsewhere.

4. CONCLUSIONS

- White cement mortars made with photoactive titania A showed a clear yellow discoloration tendency in outdoor and lab conditions when exposed UV radiation.

- In outdoor conditions the yellow shade of the mortars made with titania A increased in a stepwise manner, with summer season being more effective than winter.
- The mortars made with titania B clearly showed less yellowing tendency, being very close to that of the references.
- The discoloration was related to the presence of cement because calcite titania A suspension filtered on a glass fiber filter did not turn yellow in similar conditions.
- Without titania, white cement faded when exposed to UV radiation.
- The superplasticizer tested (Glenium 51) did not cause discoloration. It rather faded than turned increasingly yellow in UV-exposure.
- The presence of iron oxide diminished the effect of UV radiation.

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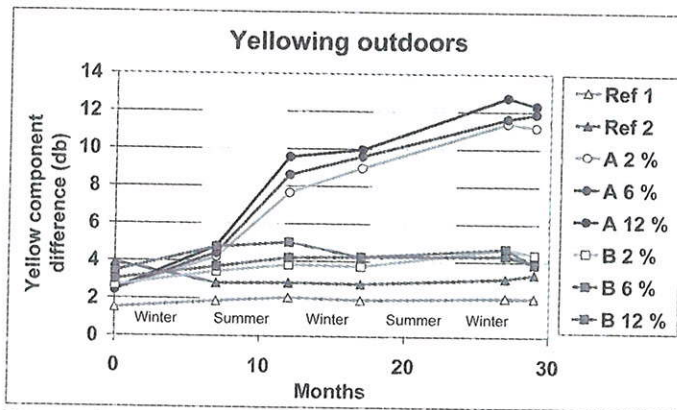


Figure 2. The yellow component difference db of mortar surfaces compared to absolute white in outdoor conditions starting in August 2006 and ending in February 2009.

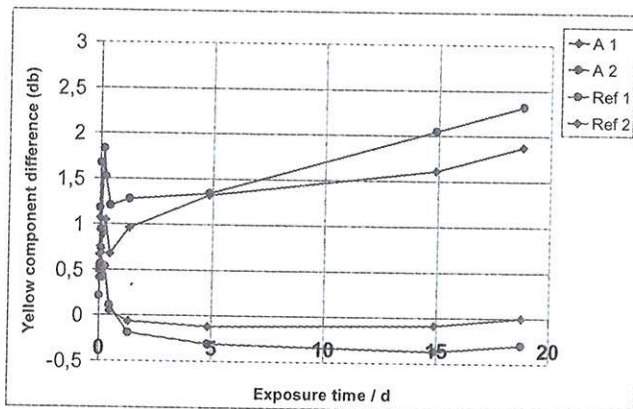


Figure 3. The yellow component difference db of mortar surfaces compared to absolute white in laboratory UV climate chamber experiments. Climate chamber environment was according ISO4892-2. Ref 2 and sample A 2 contained 2% (by weight of cement) zinc stearate.