

# Influence of pigments on the photoactivity of TiO<sub>2</sub>-containing colored mortars compared with white mortars and sol-gel TiO<sub>2</sub> application route

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## ABSTRACT

In previous works, TiO<sub>2</sub>-containing commercial mortars were proved to show photoactivated properties due to the well-known semiconducting electronic structure of the anatase and rutile crystal forms of titanium dioxide. Photoactive mortars were provided by an industrial partner of the research project, Zecca Prefabbricati SpA, and intended as the surface layer of insulating panels for buildings exterior. These materials both allowed to degrade polluting compounds at the materials surface and decrease maintenance costs thanks to the self-cleaning attitude.

In this work, the possible interaction of TiO<sub>2</sub> with pigments which are usually added to the mix design in the production of colored mortars was investigated, with particular reference to synergetic or detrimental effects of this interaction on the photocatalytic activity, as well as on the self-cleaning attitude, of the studied materials.

**Keywords:** anatase, mortar, photocatalysis, self-cleaning, titanium dioxide

## 1 INTRODUCTION

Environmental pollution arising from industrial implants and urban factors is constantly increasing, causing aesthetical and durability concerns to urban structures exposed to the atmosphere. Every year, an energy almost equal to  $5 \times 10^{24}$  J is provided by the sun: this quantity is 10 thousands higher than the real energy consumption per year of the whole world. The need to find a way to take advantage of this huge resource, together with the need for an improved quality of the environment, is driving architects and planners to combine the use of solar energy and functionalized building materials in order to limit the energy consumption and reduce pollution, specially concerning urban environments.

TiO<sub>2</sub> photocatalytic activity, induced by the absorption of UV radiation, can be exploited to solve manifold purification issues arising from the use or production of harmful substances, not only due to industries but also to heating and traffic of urban centers. TiO<sub>2</sub> exhibits good efficiency in the degradation of organic pollutants [1] as well as inorganic compounds. Early works often focused on the removal of organic pollutants from wastewaters; however, in recent years also the aspect of removing gas phase organic compounds has attracted attention, since

volatile organic compounds (VOCs) emitted into the atmosphere in urban and industrial areas cause many environmental problems, specially concerning air quality degradation, and they are often responsible for malodorous air in buildings [2-4].

Photocatalysts are not especially useful for breaking down large volumes of soilage, but they are capable of destroying it as it accumulates, e.g., to prevent cigarette smoke residue stains. In addition, unpleasant odors are due to the presence of VOCs only in the order of 10 ppm by volume: at these concentrations, TiO<sub>2</sub> should be able to decompose such compounds even with scarce UV light. Alternatively, bright UV lamps are used in tunnels to reduce the pollution released by vehicles [5-8].

Construction materials represent an easily available medium to distribute photoactive substances over the widest surface area possible, gaining the maximum efficiency. Moreover, TiO<sub>2</sub> superhydrophilic properties can turn the negative effect of rain, which soils buildings due to atmosphere pollution conveyed by raindrops, into a positive action, thanks to the self-cleaning mechanism, which helps limiting surface color and composition alterations.

TiO<sub>2</sub> can be added to the mix design, or as a surface layer, by using TiO<sub>2</sub> containing paints or sol-gel deposition methods. Nevertheless, the use of TiO<sub>2</sub> in cement-based materials reduces its photocatalytic activity due to cement alkalinity, which is unfavorable to the adsorption of pollutants on the catalyst surface. Moreover, concrete undergoes carbonation in time, which decreases capillarity absorption and leads to the formation of a calcite layer on the surface, which obstructs TiO<sub>2</sub> active sites [9].

The simultaneous presence of other additives in the mix design can also have an influence on TiO<sub>2</sub> photoinduced properties: thus, this work focused on the evaluation of the photoactivity of TiO<sub>2</sub>-containing mortars and on the effect the addition of inorganic pigments can have on it.

## 2 EXPERIMENTAL

Tested materials were fiber-reinforced mortars containing anatase, which was added to the mix design in different percentages either in the form of nanometric powder, or as aqueous suspension, or as surface covering. Average diameter of TiO<sub>2</sub> particles was 88 nm for TiO<sub>2</sub> suspension, while TiO<sub>2</sub> powder had a particle size ranging from 150 to 400 nm, having purity higher than 92%. An

optimal anatase bulk admixture was chosen, as reported in previous work [10]; the influence of the addition of pigments to the mix design was investigated by preparing mortars having the same composition and containing three different types of iron-based pigments (Table 1).

The photocatalytic activity of colored specimens was compared to that of white specimens. Moreover, the possibility to add TiO<sub>2</sub> as a surface layer *via* sol-gel, instead of as bulk admixture, was considered: the aqueous solution was applied either by spraying or by dipping.

All tests were performed both on anatase-containing specimens and on a mortar which didn't contain any photoactive component, being the latter considered as reference. All mortars were characterized by the same mixture proportion, exception made for the anatase and pigment content; the chosen water-cement ratio was 0.56.

Samples photocatalytic activity was characterized in the mineralization of VOCs: 2-propanol was chosen as model reactant of organic compounds present in the atmosphere. The UV source was an Osram Vitalux lamp; the UV intensity was 2 mW/cm<sup>2</sup>. Samples were put in a quartz cell, whose atmosphere was saturated with 2-propanol. The cell was supplied with a seal plug that allowed to take air samples from the cell, which were in turn analyzed with gaschromatography (GC) to evaluate the 2-propanol quantity inside the cell and its variation in time; the presence of acetone and its increase in time was also detected, being acetone the reaction product of 2-propanol mineralization. GC analyses were performed after 0 h, 3 h, 6 h and 23 h of UV exposure.

Photocatalytic efficiency was further evaluated in the decomposition of organic dyes: rhodamine B was spread on specimens and dried, then its chromatic alterations due to photocatalytic degradation were investigated with color analyses, performed by means of a spectrophotometer (CM-2600d, Minolta), which gives the chromatic coordinates of the measured color in terms of the color space  $L^*$ ,  $a^*$ ,  $b^*$ . The color variation in time ( $\Delta E$ ) can be measured as spatial difference between two points, corresponding respectively to the color at the time  $t$  and to the initial color at  $t = 0$ :

$$\Delta E = \sqrt{(L_t^* - L_0^*)^2 + (a_t^* - a_0^*)^2 + (b_t^* - b_0^*)^2} \quad (1)$$

Mortars were also evaluated in atmospheric exposure tests. Specimens were placed on the roof of a building (15 m altitude, 45° slope) and exposed to the polluted urban atmosphere of Milan, facing South in order to maximize the exposure to sunlight. During exposure specimens could benefit of both sunlight (able to activate the photoinduced phenomena) and rain (necessary for the self-cleaning process to establish). Color was monitored as indicative parameter of the photoactivated self-cleaning attitude of samples, by using a spectrophotometer.

Finally, the materials wettability was studied through contact angle measurements.

Label	Anatase admixture		Pigment (by weight)
	Suspension	Powder	
R-2, R-4	-		Red (2% or 4%)
R-2-T, R-4-T	2%	3%	
Y-2, Y-4	-		Yellow (2% or 4%)
Y-2-T, Y-4-T	2%	3%	
G-2, G-4	-		Grey (2% or 4%)
G-2-T, G-4-T	2%	3%	
W	-		-
W-T	2%	3%	
W-T-S	Sol-gel coating		

Table 1: Composition of investigated photocatalytic mortars: anatase addition and pigments.

### 3 RESULTS AND DISCUSSION

#### 3.1 Photocatalytic activity

The results achieved in the study of 2-propanol degradation in the presence of white and colored mortars are reported in figure 1. Since GC revealed both the reactant and the reaction product, *i.e.*, 2-propanol and the acetone, it was possible to prove the actual mineralization of the VOC, while a decrease of 2-propanol concentration would have possibly been ascribed to a poor seal of the reactor cell. Moreover, the degradation could be calculated as the ratio between the areas of GC peaks of the reaction product and the reactant. Mortars photoactivity was proved to increase with irradiation time; multiple tests were performed on each mortar composition, since a dispersion of experimental data was noticed.

In all cases, white mortars led to an enhanced decomposition of 2-propanol, 50% in 23 h on average, with respect to colored ones (30%): the iron-based pigments added to the mix design inhibited the photocatalytic efficiency of TiO<sub>2</sub> of about 40%. This was ascribed to a more difficult adsorption of the VOC on the photocatalyst surface in the simultaneous presence of inorganic pigments.

Conversely, tests concerning the photocatalytic degradation of rhodamine B led to different conclusions. In this case, the tested specimens were those containing the yellow pigment and the white mortars. Red and grey specimens could not be investigated, since the test is based on covering the surface with the dye and measuring the variations of surface color due to its degradation; as rhodamine B displays a magenta color, the presence of a dark cementitious substrate would have markedly interfered with the measurements.

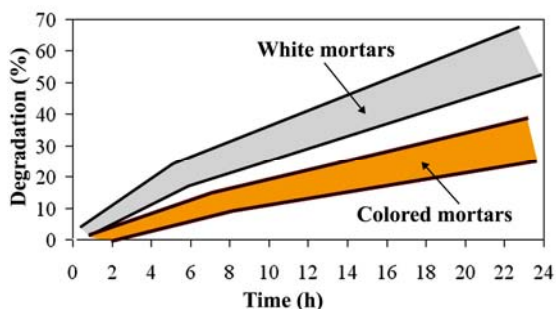


Figure 1: Photocatalytic degradation of 2-propanol.

Rhodamine B mineralization was calculated as the color difference between measurements performed at a given irradiation time and the initial color of the mortar soiled with the dye (Eq. 2).

$$\text{degradation (\%)} = \frac{a_t^* - a_0^*}{a_0^*} \times 100 \quad (2)$$

The total color difference,  $\Delta E$ , was considered as well as the sole difference in the  $a^*$  coordinate (red hue), which attests chromatic variations in the hue displayed by rhodamine. The last one was chosen as representative of rhodamine B decomposition, since  $\Delta E$  exhibited the same trend as  $\Delta a^*$  on white mortars, while different trends were observed on yellow mortars, due to the influence of the yellow pigment on the chromatic characterization of the specimen.

The behavior of specimens containing  $\text{TiO}_2$  as bulk addition was similar: a first fast decomposition of the organic molecule was observed, leading to a fast loss of color intensity, while after 1 h the reaction slowed down (Fig. 2). Conversely, the application of  $\text{TiO}_2$  sol-gel *via* spraying on mortars surfaces conferred to mortars a lower photoactivity.

On the basis of these results, new specimens were prepared by modifying both the composition of the applied sol-gel and the application method. Acidic ( $\text{pH} = 1.5$ ) and alkaline ( $\text{pH} = 13$ )  $\text{TiO}_2$  sol-gel was deposited on white mortars by 4 dipping steps alternated with heating at  $70^\circ\text{C}$  for 30 minutes. This procedure led to an increased photoactivity with respect to spray deposition; yet, the chosen dipping procedure still needs to be standardized.

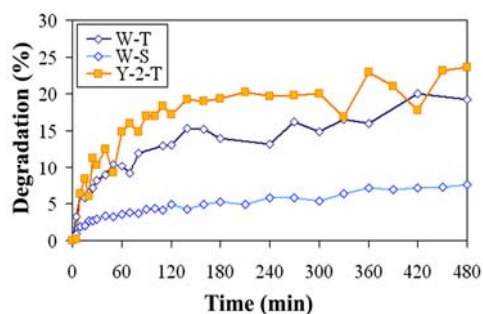


Figure 2: Photocatalytic degradation of rhodamine B.

### 3.2 Self-cleaning

To evaluate the self-cleaning attitude induced by the presence of a photoactive component, both standard mortars (table 1) were exposed to a polluted atmosphere for 10 months and their soiling, ascribed to the adsorption of dust and polluting agents, was monitored by spectrophotometry. Also in this case, more than a chromatic coordinate was considered: either total color variations were compared or brightness variations, since it was assumed that the main variations due to atmospheric soiling would cause a grey shift of the color. Therefore, it was possible to exclude the bulk coloring of the mortar from self-cleaning properties evaluation.

By comparing  $\Delta E$  and  $\Delta L^*$  results a strong influence of the original color on the chromatic alteration of the surfaces was observed. This behavior caused a more problematic elaboration of experimental results, since in previous works only white mortars were considered and no concern was found in employing  $\Delta E$ , which can give a more complete analysis. In the end, brightness variation was chosen as reference parameter in these investigations. Figures 3 to 5 present the brightness variations measured on red, grey and yellow specimens.

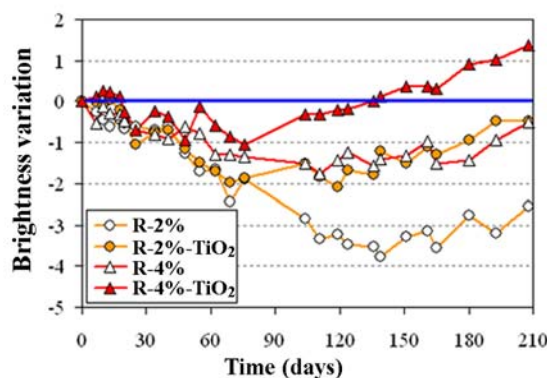


Figure 3: Brightness variations on red mortars exposed to the atmosphere.

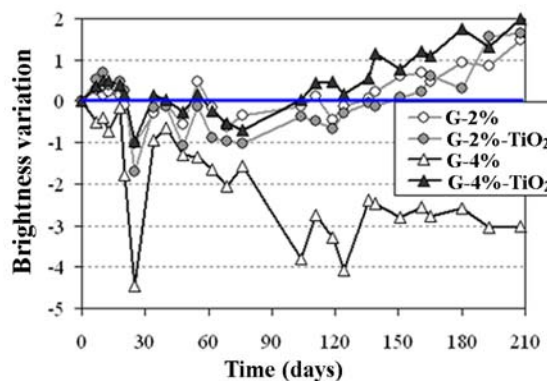


Figure 4: Brightness variations on grey mortars exposed to the atmosphere.

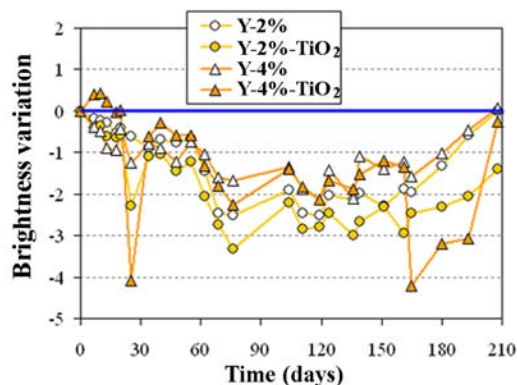


Figure 5: Brightness variations on yellow mortars exposed to the atmosphere.

On both red and grey specimens, either containing 2 % wt or 4% wt of iron pigments, the self-cleaning attitude was proved by a reduced brightness decrease, with respect to that observed on the corresponding specimens without  $\text{TiO}_2$ . Yet, the increase in the ability of specimens to maintain their original color was expected to be more pronounced. Conversely, mortars containing yellow pigments didn't exhibit any remarkable self-cleaning effect, and the soilage extent was comparable to that obtained on non-photocatalytic mortars. Though, yellow mortars actually proved to display a good photocatalytic efficiency, as demonstrated by rhodamine B degradation.

However, it must be noticed that self-cleaning doesn't involve the same mechanism as that required in photocatalytic performances: in fact, it is given by the action of the photocatalytic degradation of adsorbed agents and the photoinduced superhydrophilicity of  $\text{TiO}_2$  surface, which allows water to flow easily and remove particles, dust and other staining elements deposited on the surface, thus cleaning it. Therefore, an inhibition in the creation of the superhydrophilic state could be expected to explain the poor self-cleaning attitude of yellow mortars.

To support this hypothesis, contact angle measurements were performed during the following irradiation cycle: 8 days irradiation with UV light, 9 days storage in a dark room, 7 days UV irradiation and 21 days storage in a dark room. In fact, it was noticed that yellow mortars required more time to reach a superhydrophilic state: while on red, grey and white specimens the contact angle of water dropped to  $20^\circ$  after the first part of the irradiation cycle, yellow mortars maintained an elevated value of contact angle until the second UV irradiation step started.

The physical meaning of this behavior still needs further investigations, but can undoubtedly be ascribed to an interference between  $\text{TiO}_2$  photoactivation and iron-based pigments. In particular, two main mechanisms can be involved: either charge trapping effects on iron oxides, or a mix design effect, *i.e.*, yellow pigments more than the other colors can appear on the surface and thus shield  $\text{TiO}_2$  particles. By considering the technical data sheet of the three pigments, which are  $\text{Fe}_2\text{O}_3$  (red),  $\text{Fe}_3\text{O}_4$  (grey) and

$\text{FeOOH}$  (yellow), no difference in acidity was denoted, which could have led to the first interaction effect, while the latter pigment resulted to have the lowest density. Hence, as a first hypothesis a mix design effect was considered to be responsible for a lower self-cleaning performance of yellow mortars, since these pigments could have appeared on the mortar surface more massively than the other ones.

## 4 CONCLUSIONS

The photoinduced properties of commercial mortars, either white or colored, containing approximately 5% wt of titanium dioxide were investigated under different aspects: photocatalytic degradation of organic dyes and VOCs, self-cleaning attitude and wettability properties. The presence of  $\text{TiO}_2$  conferred to both white and colored mortars a good photocatalytic efficiency, though the presence of pigments partially inhibited the exploiting of this property. The self-cleaning attitude was exhibited by all tested photoactive specimens, exception made for mortars containing a yellow pigment. The application of a  $\text{TiO}_2$  sol-gel as a surface layer by dip coating was found to be more promising than the spraying application; this technique could avoid the problems due to interactions of  $\text{TiO}_2$  with pigments.

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