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Published in:
Microchemical Journal

DOI:
10.1016/j.microc.2015.11.048

Link to publication

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A quick assessment of the photocatalytic activity of TiO₂ pigments — From lab to conservation studio!

B.A. van Driel a,b,c,⁎, P.J. Kooyman d,1, K.J. van den Berg b, A. Schmidt-Ott e, J. Dik c

Keywords:
- Acid blue 9
- Titanium white
- Paint
- Dye degradation
- Photocatalytic activity

1. Introduction

In 1921, when Pablo Picasso was forty years old, a method to produce titanium pigment on an industrial scale was developed and introduced soon after [1]. Since then he has been using titanium white in his work: a photocatalyst [2], which may cause major damage to his legacy. And he was not the only one [1].

Not only is titanium white used in paintings [3–6], it has also found its way into plastic art objects and photographic paper (resin coated prints), leading to degradation problems [7,8].

1.1. Photocatalysis

Titanium dioxide is a known photocatalyst. The photocatalytic degradation cycle is shown in Scheme 1. When titanium dioxide absorbs UV light (step 1) a chain of events possibly leading to the production of radicals (step 2b) is initiated. These radicals can attack the surroundings of the pigment and that can cause a breakdown of the organic medium resulting in embrittlement, loss of gloss or chalking (step 3). When colorants, pigments or dyestuffs are involved, the color can also be affected (step 3) [9–11].

If one of the steps leading to radical formation is prevented, the catalytic degradation cycle is stopped. This happens, for instance, when a pigment with an inorganic surface coating is used. In this paper the term coating or surface coating indicates a coating on the surface of the pigment grains. This treatment is performed during the production of the pigment, prior to the addition of the pigment to the paint. The coating on the pigment particles, often alumina and/or silica, functions as a barrier between charge carriers and surface adsorbents, and prevents radical formation (step 2a). In this case, the pigment has a protective effect on the organic matrix by acting as a UV absorber [12,13].

The ratio between recombination (step 2a) and radical formation (step 2b) determines for a large part the photocatalytic activity of a titanium dioxide powder. This ratio is affected by a number of characteristics (section 1.2 and 2.1), one of which is the titanium dioxide crystal structure. Two crystal structures of titanium dioxide are used in the pigment industry: anatase and rutile. Unfortun-
such as differences in bandgap, recombination rate, charge carrier mobility and mobility of the hydroxyl radical. However, to date no consensus has been reached [14–17]. Several methods exist to assess photocatalytic activity of photocatalytic semiconductors such as titanium dioxide. Test reactions such as the conversion of isopropanol to acetone [18] and dye degradation reactions [19,20] are commonly described to characterize catalyst powders. However, they require a certain level of expertise and equipment. The same limitation holds for other methods that have been proposed such as photoconductivity measurements [21], the evaluation of CO2 from an enclosed paint film [22], ESR analysis [23] and full characterization of the pigment. Finally, accelerated aging tests are a valuable tool in the field of paint development. These tests can assess the stability of a paint over time, which, in a paint containing titanium dioxide, can be related to the photocatalytic activity of the pigment. However, these test are time consuming and cannot be performed on original material [24]. Thus, there are currently no routine methodologies to determine the photocatalytic activity of TiO2 pigments prior to their use by artists or conservators. The main goal of this paper is the introduction, description and validation of such a method.

2.1. Titanium dioxide powders

Ten titanium dioxide powders were collected to evaluate the photocatalytic activity test. The powders have different applications such as catalysts, industrial pigments and artist pigments, and cover a wide range of characteristics (Table 1). The TiO2 powders were acquired from different sources and used without any treatment. Due to confidentiality issues the source of the powders cannot always be disclosed. Some titanium dioxide powders were accompanied by characterization data from the supplier (Table 1). Others were analyzed in our laboratories to determine the most important properties that can influence the photocatalytic activity. Such as crystal structure, specific surface area, particle size and surface coating (bold in Table 1). Titanium dioxide powders with an unknown crystal structure were characterized using X-ray diffraction (XRD). The diffractometer used during this study is a Bruker D8 Advance with a Cu Kα X-ray source. The crystal structure was determined using the search and match application of the EVA software. The specific surface area (BET area) was determined via nitrogen sorption isotherms at 77 K using a Quantachrome Autosorb-6B or a Micromeritics TriStar II 3020. The powders were degassed for 16 h at 200 °C to prevent the structural transformation from anatase to rutile which has been reported to happen in a wide temperature range between 400 and 1200 °C [35]. The BET area was calculated via the multipoint BET method over a linear range of relative pressures between 0.05 and 0.26 using 20 to 21 data points.

Transmission electron microscopy (TEM) images were obtained using an FEI Tecnai F20 electron microscope, equipped with a FEG and operated at 200 kV. Particle size distributions were determined by hand from the micrographs. Scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDX) with a JSM9100VL SEM and a ThermoScientific SDD detector or TEM-EDX using the previously described TEM and an Oxford Instruments EDX system were used to investigate inorganic coatings. The copper signal in the TEM-EDX spectra is due to background radiation hitting the copper sample holder grid.

Organic coatings on the TiO2 powders were investigated by pyrolysis-gas chromatography-mass spectroscopy (Py-GC-MS) using a ThermoScientific Focus GC coupled to an ISQ LT MS using the Xcalibur software and a multi-shot pyrolyzer EPA/Py-3030D. 1 μl tetramethylammonium hydroxide (TMAH) is added to the samples before injection of the cup.

2.2. UV box

A UV box was constructed at Delft University of Technology [2] (Fig. 1). The UV box has ten spots where beakers can be placed with a magnetic stir unit, of which the 6 central spots ensure similar UV

![Scheme 1. Photocatalytic degradation cycle.](image-url)
exposure. The UV box was equipped with 8 UV lamps of 18 W providing an intensity of 100 ± 20 μW/cm², with a wavelength maximum at 365 nm. The temperature in the UV box was kept below 40 °C with a water-cooling system.

At full intensity, the amount of UV radiation within the UV box is about 27 times as high as in an “office environment” (Table 2), 200 times as high as in a “low UV office environment”, 270 times as high as in a “high UV dimmed light environment” and 2000 as high as in a “low UV dimmed light environment” [36]. It is assumed that the degradation time of the dye in the test scales accordingly.

2.3. Photocatalytic activity test

The test developed in this study, further referred to as the ‘developed test’ or the ‘standard test’, is a dye degradation test. Similar experimental setups have been reported in literature [19,38–40]. Each test is optimized for a specific purpose but all these tests have a similar approach. An organic dye is dissolved in a liquid to which the active powder, in this case titanium dioxide, is added. The dispersion is properly mixed and irradiated by, in this case UVA, light. At time intervals samples are taken from the beaker and the dye solution is separated from the powder and subsequently analyzed by UV–Vis spectrophotometry.

The developed test is based on a method, further referred to as the ‘base test’, designed to determine the photocatalytic activity of titanium dioxide catalyst powders [2]. Several problems occurred with the base test, which required adjustments and thus the development of a new test for a new purpose: determining the photocatalytic activity of titanium dioxide pigment powders.

Table 3 describes the parameters that were adjusted during the development of the test and indicates the reason for the adjustment. This section further describes the developed test and the development process in detail.

2.3.1. Adjustments during test development

The methylene blue used in the base test [2] absorbs on the silica coating of some titanium white pigments which disturbs the result of the test [41]. It was substituted with acid blue 9 (Erioglaucine disodium salt, referred to as AB9, used as received from Sigma-Aldrich) [42].

Titanium dioxide pigment powders, when coated, are difficult to disperse in water and a dispersing agent needs to be added. The dispersion agent was chosen based on a tradeoff between quality of dispersion and effect on the photocatalytic degradation process. The chosen dispersion agent is a sodium polyphosphate solution [100 g/L] (further referred to as Calgon) used as received from Tronox. Two batches were used; one received in 2012 and one received in 2015. When Calgon is used, the ultrasonic bath has a negligible benefit on the dispersion and therefore on the final AB9 degradation rate. However, it is important to employ constant stirring to avoid the titanium dioxide powder to settle on the bottom of the beaker.

When performing the test with the dispersion agent, the previously used filters [2] to separate the dye solution from the TiO₂ prior to UV–Vis analysis did not function. Furthermore, the filters clogged due to the larger particle size of the pigment powders. The new separation method is sedimentation of the titanium dioxide powder using an Eppendorf centrifuge for 2 runs of 5 min at 5000 rpm.

2.3.2. Developed/standard test

50 mg of TiO₂ powder was dispersed in a 100 ml 0.03 mM acid blue 9, 1% v/v Calgon solution. The dispersion was stirred with a spatula for initial mixing. A magnetic stirrer was added to the dispersion and the beaker was covered with a watch glass. The beaker was put on a stirring plate in the UV box (section 2.2). At time intervals samples (4 ml) were taken from the beaker and centrifuged twice for 5 min at 5000 rpm in a Savant Speedfuge HSC10 AC. Between the two runs, the supernatant was transferred to a clean Eppendorf centrifuge tube to separate it from the titanium dioxide. The solution was analyzed with a UV–Vis spectrophotometer, Unicam UV 500, at 630 nm and the concentration of acid blue 9 was evaluated with Vision software according to a calibration line (Eq. 1).

\[
C(AB9) = 0.012 + 0.0001: \quad R^2 = 0.99
\] (1)

Degradation curves were fitted by a first order exponential decay (Eq. 2), which yields a value for the reaction rate coefficient k. For the
degradation curves that do not reach \( C(t) = 0 \) mM, this fit has an error due to extrapolation.

\[
C(t) = C_0 e^{-kt} \quad \text{with} \quad C_0 = 0.03 \, \text{mM}
\]

\[ (2) \]

2.3.3. Effect of operational parameters

Operational parameters such as temperature, stirring speed, UV intensity, initial concentration of dye and titanium dioxide loading can have an effect on the results [43]. If the test is performed in a comparative manner and these parameters are kept constant, the categorizing of pigment grades is accurate. Nevertheless, these parameters were investigated in order to obtain insight into the order of magnitude of these variations and to investigate the feasibility of downscaling.

2.3.3.1. Effect of UV intensity, temperature and stirring speed.

The effect of UV intensity on the degradation time is investigated by performing the test at full and half UV intensity. Experiments were performed with eight lamps (standard) and with four lamps on. Turning four lamps off (positions 1, 4, 5, 8) reduces the UV intensity by approximately 50% (Fig. 1).

The stirring speed was investigated by performing the experiments at different stirrer settings on the magnetic stirring plate (setting 2–5). The effect of temperature was investigated in the range between 29 and 39 °C. The temperature was monitored using a thermometer connected to the UV box and adjusted with the water-cooling system.

2.3.3.2. Scale down.

The possibility of scaling down the test is considered in case only small amounts of pigment powders are available. Two different downscaling strategies were considered. First, reducing the absolute amount of powder. This changes the \( \text{TiO}_2/\text{AB9} \) solution ratio or pigment loading (category 1). Second, scaling down the total experiment while keeping the \( \text{TiO}_2/\text{AB9} \) solution ratio constant (category 2).

The experiments were carried out with titanium dioxide powders C2, I3 and O1 (Table 1). Because of the smaller volume of the experiments, smaller aliquots (1 ml) were removed at time intervals. Consequently 1 ml cuvettes were used. Furthermore, influencing effects were investigated such as liquid surface to volume ratio (category 3), type of glassware (extension B) and Calgon age (extension N). Finally, fragments of the paint reconstructions (section 2.4.4) of titanium dioxide powders I3 and O1 were scraped off their support and tested without further treatment. In this case the available amount of scraping was used. With knowledge of the pigment volume concentration (PVC), this amount is calculated back to an approximate mass of \( \text{TiO}_2 \) in the acid blue 9 solution, which is not necessarily equal to 50 mg. The specifications of the experiments are summarized in Table 4.

2.3.4. Further test development

To use the test in conservation practice as a qualitative evaluation, the use of lab equipment should be limited. The UV box may be replaced by any UVA source available, as the degradation time scales directly with the UV intensity (section 3.2.1). The separation step, which is necessary to do UV–Vis spectrophotometry, can be skipped for qualitative evaluation because a visual evaluation of the dye degradation can be done with a color scale or with reference dispersions. For the production of this color scale, a range of \( \text{TiO}_2/\text{AB9} \) dispersions with different acid blue 9 concentrations has been produced and photographed (section 3.3.1, Fig. 7).

2.4. Paint reconstructions

Paint reconstructions were prepared as a preliminary assessment of the predictive character of this test. The reconstructions were evaluated with respect to chalking after UV exposure (qualitative visual assessment). Degradation of the binder material causes the pigment to appear unbound at the surface, this phenomenon is called chalking.

Paint reconstructions were prepared of all ten titanium dioxide powders (Table 5). All reconstructions, with the exception of samples I3 and O2, were prepared and investigated in 2012 at Tronox and Delft University respectively. The samples were prepared by mixing pigment with hot-pressed linseed oil with an added dryer. The dryer, provided by Tronox and used without any treatment, was a mix of industrial dryers with 0.15% w/w calcium drier, 0.20% w/w zirconium drier and 0.05% w/w cobalt drier with respect to the oil.

Reconstructions of I3 and O2 were prepared and investigated at the RCE in 2014. Again pigment was mixed with, in this case, cold-pressed linseed oil obtained from van Beek. Talens Siccatief de Courtai was used as a dryer, one drop was added to approximately three grams of paint.

The paints were mixed with a pigment volume concentration ranging between 15 and 40% and ground on an automatic muller. At Tronox a Mimex type 2000 was used and at the RCE a similar model was used. The muller was operated 3 times 25 rotations employing a weight of 5 kg. A pallet knife was used to handle the paint during the grinding of pigments and the paint application. The paints were then

---

Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base test [2]</th>
<th>Developed test</th>
<th>Reason for adjustment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye</td>
<td>Methylene blue</td>
<td>Acid Blue 9</td>
<td>Methylened blue adsors on surface coating of pigments</td>
</tr>
<tr>
<td>Volume dye solution</td>
<td>100 ml</td>
<td>10–100 ml</td>
<td>Scale down</td>
</tr>
<tr>
<td>Mass TiO2</td>
<td>50 mg</td>
<td>50 mg</td>
<td>Scale down</td>
</tr>
<tr>
<td>Separation for analysis</td>
<td>Millipore membrane filter</td>
<td>Sedimentation by centrifugal force</td>
<td>PTFE filter malfunctions with dispersion agent and clogs with large TiO2 particles</td>
</tr>
<tr>
<td>Dispersion aid</td>
<td>Ultrasonic bath</td>
<td>1% v/v Calgon</td>
<td>Pigments with a surface coating do not disperse properly</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base test [2]</th>
<th>Developed test</th>
<th>Reason for adjustment</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Methylene blue</td>
<td>Acid Blue 9</td>
<td>Methylened blue adsors on surface coating of pigments</td>
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<td>Scale down</td>
</tr>
<tr>
<td>Mass TiO2</td>
<td>50 mg</td>
<td>50 mg</td>
<td>Scale down</td>
</tr>
<tr>
<td>Separation for analysis</td>
<td>Millipore membrane filter</td>
<td>Sedimentation by centrifugal force</td>
<td>PTFE filter malfunctions with dispersion agent and clogs with large TiO2 particles</td>
</tr>
<tr>
<td>Dispersion aid</td>
<td>Ultrasonic bath</td>
<td>1% v/v Calgon</td>
<td>Pigments with a surface coating do not disperse properly</td>
</tr>
</tbody>
</table>
spread on Leneta cards at Tronox or on a piece of Melinex at RCE, using
an applicator with a layer thickness of 200 µm.

The paint reconstructions were irradiated by UVA lamps in the UV box described previously or in a similar UV box at RCE and visually evaluated for chalking. Further investigation of the surface was done by imaging the surface using SEM. To this end, the paint reconstructions were gold-coated for 15 s with a JEOL JFC-1200 fine coater using a vacuum of 45 Pa at a working distance of approximately 5 cm. The SEM was operated in high vacuum mode.

3. Results and discussion

3.1. Test evaluation

The developed test was evaluated with respect to feasibility, the effect of the dispersing agent and the reproducibility. Furthermore, we aim to relate the developed test to surface degradation of reconstructed paints, which is discussed in this section as well.

3.1.1. Feasibility

Fig. 2A demonstrates that acid blue 9 without TiO₂ does not degrade under UV irradiation and that acid blue 9 with TiO₂ without UV irradiation also does not degrade. We can thus conclude photocatalysis is the degradation mechanism.

Fig. 2 and Table 6 illustrate the initial results of the ten titanium dioxide powders measured with the developed test. Based on the results, the titanium dioxide powders were divided into four different categories: stable pigments (Fig. 2A) and fast (Fig. 2B), intermediate (Fig. 2C) and slow (Fig. 2D) degradation. We defined the categories in terms of reaction rate coefficients (Table 7).

Categories fast and intermediate degradation (Fig. 2B and C) correspond to anatase and rutile without inorganic coating. All the anatase powders without inorganic coating (Fig. 2B), with different characteristics, degrade the dye faster than the rutile powder without inorganic coating (Fig. 2C). This confirms that rutile is less active than anatase. The ‘fast degradation’ category has two subsections (Table 7). The two less active anatase powders O1 and O2 (Fig. 2B) correspond to the powders with a polyol coating. It seems that the organic surface treatment has an influence on the photocatalytic activity, possibly by occupying surface absorption sites. Within the group of anatase powders (see Fig. 2B) powder I3 is interesting. This product, Hombitan LW from Sachtleben Chemie, is advised for use in interior paints as discussed in the introduction. Remarkably, it is illustrated here that it has a similar photocatalytic activity as Hombikat UV-100 (C2) from the same company, which is produced to be a highly active catalyst.

The differences between the rutile powders with an inorganic coating (Fig. 2A vs. 2D) are possibly due to the different qualities of the pigment powders. For example, the rutile powders with an inorganic coating (Fig. 2A) are powder I3, which is produced to be a highly active catalyst.

Table 4

List of downscaling experiments. The code name consists of TiO₂ code-mass TiO₂/Volume AB 9 solution — extension explained in the remark column. n represents the number of times the test was performed.

<table>
<thead>
<tr>
<th>Experiment code</th>
<th>Volume of AB 9 solution (0.03 mM) [ml]a</th>
<th>Mass of TiO₂ [mg]</th>
<th>Category</th>
<th>Remark</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>I3-25/50</td>
<td>50</td>
<td>25</td>
<td>2</td>
<td>Experiment in 250 ml beaker</td>
<td>6</td>
</tr>
<tr>
<td>I3-10/20</td>
<td>20</td>
<td>10</td>
<td>2</td>
<td>Experiment in 50 ml small neck bottle</td>
<td>4</td>
</tr>
<tr>
<td>I3-10/20</td>
<td>20</td>
<td>10</td>
<td>2</td>
<td>Experiment in 50 ml beaker</td>
<td>2</td>
</tr>
<tr>
<td>I3-5/100</td>
<td>10</td>
<td>5</td>
<td>2</td>
<td>Experiment in 50 ml small neck bottle</td>
<td>2</td>
</tr>
<tr>
<td>I3-5/108</td>
<td>10</td>
<td>5</td>
<td>2</td>
<td>Experiment in 50 ml beaker</td>
<td>1</td>
</tr>
<tr>
<td>I3-25/100</td>
<td>100</td>
<td>25</td>
<td>1</td>
<td>Experiment in 250 ml beaker</td>
<td>4</td>
</tr>
<tr>
<td>I3-10/100</td>
<td>100</td>
<td>10</td>
<td>1</td>
<td>Experiment in 250 ml beaker</td>
<td>2</td>
</tr>
<tr>
<td>I3-5/100</td>
<td>100</td>
<td>5</td>
<td>1</td>
<td>Experiment in 250 ml beaker</td>
<td>3</td>
</tr>
<tr>
<td>I3-50/100</td>
<td>100</td>
<td>50</td>
<td>Standard and 3</td>
<td>Experiment in 250 ml beaker</td>
<td>3</td>
</tr>
<tr>
<td>I3-50/100 N</td>
<td>100</td>
<td>50</td>
<td>Standard</td>
<td>Experiment in 250 ml beaker</td>
<td>1</td>
</tr>
<tr>
<td>I3-100/200</td>
<td>200</td>
<td>100</td>
<td>3</td>
<td>New batch of Calgon</td>
<td>1</td>
</tr>
<tr>
<td>I3-75/150</td>
<td>150</td>
<td>75</td>
<td>3</td>
<td>New batch of Calgon</td>
<td>1</td>
</tr>
<tr>
<td>I3-25/50</td>
<td>50</td>
<td>25</td>
<td>3</td>
<td>New batch of Calgon</td>
<td>1</td>
</tr>
<tr>
<td>I3-12.5/25</td>
<td>25</td>
<td>12.5</td>
<td>3</td>
<td>New batch of Calgon</td>
<td>1</td>
</tr>
<tr>
<td>I3-paint-1</td>
<td>100</td>
<td>53a</td>
<td>Paint</td>
<td>119 mg paint, dried approximately 2 months</td>
<td>1</td>
</tr>
<tr>
<td>I3-paint-2</td>
<td>100</td>
<td>65–100b</td>
<td>Paint</td>
<td>156 mg paint, dried approximately 6–8 months</td>
<td>1</td>
</tr>
</tbody>
</table>

a The AB9 solution contains 1 vol.% of Calgon solution, except if stated otherwise in remark column.
b TiO₂ mass in paint fragments is an estimate based on mass of the paint film and initial pigment volume concentration.

Table 5

Preparation of paint reconstructions.

<table>
<thead>
<tr>
<th>Paints</th>
<th>Oil</th>
<th>Dryer</th>
<th>Muller</th>
<th>Support</th>
<th>Layer thickness</th>
<th>Location</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1, C2, A1, O1, 11, 12, 14, 15</td>
<td>Hot-pressed linseed oila</td>
<td>Industrial dryer provided by Tronox (Ca, Zr, Co)</td>
<td>Mimex type 2000</td>
<td>Leneta card</td>
<td>200 µm</td>
<td>Tronox &amp; TU Delft</td>
<td>2012</td>
</tr>
<tr>
<td>I3, O2</td>
<td>Cold-pressed linseed oil, van Beek</td>
<td>Siccatief de Courtrai, Talens</td>
<td>Similar model</td>
<td>Melinex</td>
<td>200 µm</td>
<td>RCE</td>
<td>2014</td>
</tr>
</tbody>
</table>

a Unknown brand, purchased at a paint store.
dispersion with stable titanium dioxide (I5) of 60 days (UV Box) to 300 years (dimmed light, low UV environment, 50 lx@10 μW/lm). In comparison, for the dye in a dispersion with an unstable pigment (C2) this range is 200 min (UV box) to 280 days (dimmed light, low UV environment). For the dye in a dispersion with an intermediate pigment (A1) this is 13 days (UV box) to 60 years (dimmed light, low UV environment). Since this test deals with a well-mixed system, these times will be much higher for real paints systems. Nevertheless, the time frame for anatase-mediated degradation is alarming!

3.1.1. Dispersion agent. The dispersion agent has an effect on the degradation rate (Fig. 4): the reaction rate coefficient is 1.6 times smaller with the addition of the dispersion agent. This can have several reasons. Firstly, the Calgon acts on the surface of the pigment where it may block some of the radical formation by occupying surface sites. This is similar to the effect of an organic coating on the photocatalytic activity which was described in section 3.1.1. Secondly, the addition of an excess of Calgon can change the pH of the solution and supply ions (sodium and phosphate) to the dispersion. A change in pH can alter the surface charge of titanium dioxide and therefore affect the dye adsorption to the surface [19]. Furthermore, ions present can interact with the radicals further influencing the degradation rate [19]. The effect of Calgon is assumed to be the same for each experiment, therefore the relative photocatalytic activities evaluated with the test are not affected. In fact, adding two or ten times more Calgon had no effect on the degradation rate. This suggests that it is in fact the Calgon surface monolayer which is rate-determining.

3.1.2. Reproducibility

For the envisioned application, the test should classify the pigments in terms of their photocatalytic activity (pigment grade). Since many parameters can influence the test results [43], the test should be performed in a comparative way by including a known stable and a known catalytic powder as references.

Fig. 3 illustrates two types of variation of test results, first the variation per team of researchers (within a group) and second the variation between the different teams (between the groups). Each group, indicated by a different color, represents a different team of two researchers performing the experiments. To investigate reproducibility, the experiments with titanium dioxide I3 under standard conditions (50 mg TiO2, 100 ml AB9 dye solution, 1%vol/vol Calgon) are compared. In group 1 temperature (range 29–33 °C) and stirring speed (setting 2–5) were varied to investigate operational parameters. However, no clear trends

Table 6

<table>
<thead>
<tr>
<th>Code</th>
<th>k [min⁻¹]</th>
<th>Category</th>
<th>Chalking [yes/no]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.001</td>
<td>Intermediate</td>
<td>No</td>
</tr>
<tr>
<td>C2</td>
<td>0.018</td>
<td>Fast</td>
<td>Yes</td>
</tr>
<tr>
<td>I1</td>
<td>5.9E-5</td>
<td>Stable</td>
<td>No</td>
</tr>
<tr>
<td>I2</td>
<td>0.00025</td>
<td>Slow</td>
<td>No</td>
</tr>
<tr>
<td>I3</td>
<td>0.016</td>
<td>Fast</td>
<td>Yes</td>
</tr>
<tr>
<td>I4</td>
<td>3.2E-5</td>
<td>Stable</td>
<td>No</td>
</tr>
<tr>
<td>I5</td>
<td>3.8E-5</td>
<td>Stable</td>
<td>No</td>
</tr>
<tr>
<td>A1</td>
<td>0.00018</td>
<td>Slow</td>
<td>No</td>
</tr>
<tr>
<td>O1</td>
<td>0.005</td>
<td>Fast</td>
<td>Partially*</td>
</tr>
<tr>
<td>O2</td>
<td>0.007</td>
<td>Fast</td>
<td>Yes</td>
</tr>
</tbody>
</table>

* The edges of the paint film, which are thinner than the rest of the film, show chalking.

Table 7

Degradation categories in terms of reaction rate coefficients.

<table>
<thead>
<tr>
<th>Category</th>
<th>k range [min⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>k &gt; 0.0025</td>
</tr>
<tr>
<td>Sub-categories:</td>
<td>k &gt; 0.015</td>
</tr>
<tr>
<td></td>
<td>0.0025 &lt; k &lt; 0.015</td>
</tr>
<tr>
<td>Intermediate</td>
<td>0.0005 &lt; k &lt; 0.0025</td>
</tr>
<tr>
<td>Slow</td>
<td>0.0001 &lt; k &lt; 0.0005</td>
</tr>
<tr>
<td>Stable</td>
<td>k &lt; 0.0001</td>
</tr>
</tbody>
</table>
Fig. 3. Degradation of acid blue 9 — Indication of reproducibility. Degradation curves of I3 experiments under standard conditions. The different groups indicate different researchers performing the test at different moments between 2012 and 2015.

Fig. 4. Influence of Calgon on the degradation of acid blue 9 — Group 5: Degradation curves of I3 experiments under standard conditions without Calgon. Average Group 1: Average of degradation curves (Group 1) shown in Fig. 3, experiments with Calgon.

were observed, therefore these experiments can be added to this comparison.

The variation within each group is understandable and is attributed to the experimental error because the experiment consists of many steps, there is a slight variation of UV intensity per beaker spot, there is a warm-up time for the lamps to reach full intensity which is not always taken into account and the ambient temperature of the lab can fluctuate.

The variations between the different groups are not well understood. However, the effect on each TiO2 powder is similar and therefore classification can still be done accurately. Some equipment change took place, however this does not explain the differences in the results. Fig. 4 shows the variation of results within one group of experiments performed without the addition of the dispersion agent Calgon. This indicates that it is not the presence of Calgon which causes the variation in results.

It is clear from these results that it is important to perform the test in a comparative fashion (by one team of researchers) with a known catalytic and a known stable standard in order to perform proper classification.

3.1.3. Paint degradation

Fig. 5 shows the clear difference in morphology of the paint surface of a chalked (A) and a non-chalked (B) paint film after artificial UV aging. The chalked paint is clearly rough compared to the non-chalked paint, caused by the free pigment particles on the paint film surface.

Table 6 shows that all the paints with titanium dioxide powders from the category 'fast degradation' exhibited chalking within 2 months of artificial aging by UV radiation, whereas all the other paints did not. It is therefore concluded that the measured photocatalytic activity is a good indication for the stability of a simple (pigment + binder) paint system.

It is assumed, for simplicity, that the 200 min exposure that leads to dye degradation in the photocatalytic activity test of powder I3 and C2 (Fig. 2A) directly correlates to the two months exposure leading to chalking of the paint-out. Within this assumption, the degradation of a reconstructed paint film with pigment from the category “fast degradation” would lead to damage in a dimmed light low UV environment (50 lx@10 μW/lm) within 340 years. This time decreases in environments with higher light intensity and UV content to 32 years (500 lx@10 μW/lm) and 5 years (500 lx@75 μW/lm). On the other hand, a pigment of the category “stable” will not affect its binder for thousands of years. It is therefore essential for risk assessment and preventive conservation to have an indication of the photocatalytic activity of the pigment.

3.2. Effect of operational parameters

The effect of temperature within the range of 29–39 °C and stirring speed (setting 2–5) did not have a clear effect on degradation speed (Fig. 3, group 1).
3.2.1. The effect of UV intensity

Table 8 shows the effect of UV intensity on the reaction rate coefficient. Reducing the UV intensity by approximately half caused a decrease in reaction rate coefficient of 1.6 times for powder I3 and of 2.3 times for powder O1. Taking into account the variation in the photocatalytic activity test shown in Fig. 3 and the fact that 4 lamps yield approximately half the UV intensity including some slight variations inside the UV box (Fig. 1), this suggests that the decrease in UV intensity is directly correlated to the decrease in reaction rate coefficient.

These results are in agreement with the review by Zangeneh et al. [43] who describe different relationships between degradation rate and UV intensity at low, intermediate and high UV intensities. The threshold intensity between low and intermediate intensity is a factor 200 higher than the intensities used in this experiment meaning that we operate at low intensity according to this scale. The results also correspond to the results obtained by Egerton et al. [10] who observe a direct correlation of isopropanol to acetone conversion rate to UV intensity at low UV intensities. The threshold intensity between low and intermediate intensity is a factor 10 to 20 higher than the intensities used in this experiment.

<table>
<thead>
<tr>
<th>Code</th>
<th>kz temp [min⁻¹]</th>
<th>k8 temp [min⁻¹]</th>
<th>k8/k4</th>
</tr>
</thead>
<tbody>
<tr>
<td>I3</td>
<td>0.010</td>
<td>0.016</td>
<td>1.6</td>
</tr>
<tr>
<td>O1</td>
<td>0.002</td>
<td>0.005</td>
<td>2.3</td>
</tr>
</tbody>
</table>

3.2.2. Scale down

Fig. 6 provides an overview of the downscaling results. The main experiments were performed with titanium dioxide powder I3. Fig. 6A shows the effect of decreasing the total size of the experiment while keeping the TiO₂:AB9 solution ratio constant. The plot demonstrates that decreasing the scale in this fashion decreases the remaining acid blue 9 concentration after 5 h of exposure, thus the degradation proceeds faster. No change in degradation rate was expected. This result is explained by the investigation of the effect of liquid surface to volume ratio in the beaker. The investigation shows that higher surface to volume ratio systems degrade faster. The 100 ml and 50 ml experiments were both carried out in a 250 ml beaker, and since the amount is fairly large, taking a sample does not influence the surface to volume ratio significantly. However, 20 ml and 10 ml experiments were carried out in a 50 ml beaker and taking out a 1 ml sample strongly influences the volume of the experiment, causing an increase of the surface to volume ratio and thus an increase of degradation rate.

This is also confirmed by the degradation plots as a whole. The first data points of the experiments follow the same trend, however, when the surface to volume ratio starts to be significantly affected, these trends start to differentiate. A higher surface to volume ratio causing a
higher degradation rate may be explained by a higher oxygen content per volume (entering the dispersion through the liquid surface) and a higher UV irradiation per volume (reaching the beaker mostly from above). Both effects are expected to increase the degradation rate.

Fig. 6B and D illustrate the results of the same experiments that do not show the rate-increasing trend. This is due to the glassware. The small volume experiments illustrated in Fig. 6B and D (10 and 20 ml) were carried out in a narrow-necked bottle instead of a beaker (Table 4). This influences the liquid surface and thus the surface to volume ratio with the above-described consequences. Furthermore, the glass was rather thick which could result in some UV filtering thereby decreasing the UV-intensity. The rate-increasing trend shown in Fig. 6A is compensated by the rate-decreasing trends caused by doing the experiment in the bottle.

Finally, Fig. 6C shows that decreasing only the absolute amount of titanium dioxide decreases the degradation rate as was expected.

In general, the results demonstrate that scaling down the test is feasible. However, going below 5 mg of TiO₂ leads to practical problems. Furthermore, new effects, such as surface to volume ratio, cannot be neglected.

3.3. Further development

3.3.1. Color scale

Fig. 7 illustrates the color scale and the reference dispersions used to make the scale. The usability of the reference dispersions was assessed by asking researchers to estimate the acid blue 9 concentration. The concentration was subsequently evaluated by UV-Vis spectrophotometry. All researchers were successful in the estimation of the acid blue 9 concentration based on the reference dispersions attesting to the power of this visual method.

3.3.2. Testing reconstructed paint fragments

Fig. 8 shows the results of the degradation test performed on paint fragments of reconstructed paints. This is a test for real object applicability and it gives an indication that separation of pigment and binding media is not necessarily required. Degradation of acid blue 9 happens five to ten times slower than for the same pigment as a loose powder. This is expected because the pigment surface, where radicals are formed, is not easily accessible for the organic dye. Some binder may need to be degraded before the radicals reach the dye and start the degradation mechanism. Nevertheless, this result is promising for further development in the applicability of this test for the field of conservation. Paint 1 degrades slower than paint 2 due to the lower pigment loading (Table 4).

4. Conclusions

A test was developed to assess the photocatalytic activity of titanium dioxide pigments in a comparative manner. Several parameters influencing the test have been investigated. The proposed test is based on existing dye degradation tests commonly used in the field of catalysis engineering. The base test proved to be inadequate for direct use in our application. The main problem of the existing methodology was the absorption of the methylene blue dye to the pigment surface and dispersion of the pigment powders into the dye solution. This prevents proper assessment of the photocatalytic activity of pigment powders.

In this study, we have shown that these limitations can be overcome using acid blue 9 as an alternative for methylene blue and by adding a dispersion agent. The new test distinguishes between four categories of stability and relates well to chalking of artificially aged reconstructed paint-outs. Our main innovative contribution is therefore that a quick and easy test is now available for quantitative and qualitative assessment of titanium dioxide pigment photocatalytic activity. This was previously not possible without expertise, complex equipment or very time-consuming accelerated aging procedures. The test is especially suitable for powder material. We are currently considering the assembly of a toolkit which could be made available to potential users. Furthermore, the first steps have been taken to design a test suitable for real object samples. It has been demonstrated that the test is not chemically limited in sample size, which means that only the practical aspects need to be tackled for further developments of the test.

Acknowledgments

This work is facilitated by the Rijksmuseum Amsterdam and financially supported by AkzoNobel, who also provided some of the tested TiO₂ powders. Further materials were provided by Tronox (TiO₂, dryers and dispersing agents), Sachtleben Chemie (TiO₂) the van Gogh museum (TiO₂) and the RCE reference collection (TiO₂). The automatic muller used at RCE is on permanent loan from Old Holland. The authors are thankful for these contributions. Several experiments have been carried out by students Molecular Science and Technology (D. van den Berg, I. du Fossé, R. Verheijen F. van Dockum, E. Remmelts and S. Pahud de Mortange) from Delft University of Technology and by high school students Max Koster and Michel Pan. Willy Rook and Ben Norder have contributed to BET and XRD analysis performed at Delft University of Technology. Bart van der Linden has been a great help during the laboratory work. Furthermore, the authors would like to acknowledge Henk van Keulen and Ineke Joosten at the Netherlands cultural heritage agency (RCE) for their help with Py-GC-MS and SEM imaging.

References


