

UvA-DARE (Digital Academic Repository)

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

van Driel, B.A.; Kooyman, P.J.; van den Berg, K.J.; Schmidt-Ott, A.; Dik, J.

DOI

[10.1016/j.microc.2015.11.048](https://doi.org/10.1016/j.microc.2015.11.048)

Publication date

2016

Document Version

Final published version

Published in

Microchemical Journal

License

CC BY-NC-ND

[Link to publication](#)

Citation for published version (APA):

van Driel, B. A., Kooyman, P. J., van den Berg, K. J., Schmidt-Ott, A., & Dik, J. (2016). A quick assessment of the photocatalytic activity of TiO₂ pigments - From lab to conservation studio! *Microchemical Journal*, 126, 162-171. <https://doi.org/10.1016/j.microc.2015.11.048>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)



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

^a Conservation Department, Rijksmuseum Amsterdam, Hobbemastraat 22, 1071 ZC Amsterdam, Netherlands

^b Cultural Heritage Agency of the Netherlands, Hobbemastraat 22, 1071 ZC Amsterdam, Netherlands

^c Materials for Arts and Archeology, 3ME, Delft University of Technology, Mekelweg 2, 2628 CD Delft, Netherlands

^d Catalysis Engineering, ChemE, Delft University of Technology, Julianalaan 136, 2628 BL Delft, Netherlands

^e Materials for Energy Conversion & Storage, ChemE, Delft University of Technology, Julianalaan 136, 2628 BL Delft, Netherlands

ARTICLE INFO

Article history:

Received 12 July 2015

Received in revised form 25 November 2015

Accepted 25 November 2015

Available online 4 December 2015

Keywords:

TiO₂

Photocatalytic activity

Dye degradation

Paint

Titanium white

Acid blue 9

ABSTRACT

Titanium dioxide is the most abundantly used white pigment of the 20th century. The pigment is still in use, both in the production of contemporary art and for the conservation of older artwork as a retouching pigment. Unfortunately, next to its positive characteristics, the pigment has one major potential drawback: its photocatalytic activity that can cause degradation of artworks in which it is used. In this paper, we report on a new method to test the photocatalytic activity of different quality grades of titanium dioxide white pigments. This can be done quantitatively in a chemical lab or qualitatively in a quick and easy way, in a museum or artists' studio, with limited use of lab equipment. The photocatalytic degradation of an organic dye, acid blue 9, in an aqueous solution containing titanium dioxide, is followed over time by means of UV–Vis spectrophotometry. Dye solutions containing pigments with high photocatalytic activity lose their color within several hours of UVA exposure. On the other hand, dye solutions containing UV-stable titanium dioxide do not degrade within 24 h of UVA exposure. Insight in the photocatalytic activity of titanium white pigments, which can be obtained with this novel test, is of great importance for preventive conservation of modern art.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

In 1921, when Pablo Picasso was forty years old, a method to produce titanium white 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].

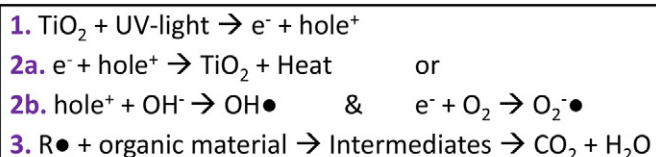
If one of the steps leading to radical formation is prevented, the catalytic degradation cycle is stopped. This happens, for instance, when a pigment with an inorganic surface coating is used. In this paper the term coating or surface coating indicates a coating on the surface of the pigment grains. 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. In general, literature shows that anatase has the highest photocatalytic activity of the two polymorphs [14, 15]. Several explanations have been proposed for this phenomenon,

* Corresponding author at: Conservation Department, Rijksmuseum Amsterdam, Hobbemastraat 22, 1071 ZC Amsterdam, Netherlands. Tel.: + 31 624167438.

E-mail addresses: b.van.driel@rijksmuseum.nl (B.A. van Driel), p.j.kooyman@tudelft.nl, patricia.kooyman@uct.ac.za (P.J. Kooyman), k.van.den.berg@cultureelerfgoed.nl (K.J. van den Berg), a.schmidt-ott@tudelft.nl (A. Schmidt-Ott), j.dik@tudelft.nl (J. Dik).

¹ Current address: Department of Chemical Engineering, University of Cape Town, Private Bag X3, Rondebosch 7701, South Africa.



Scheme 1. Photocatalytic degradation cycle.

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 CO_2 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 tests are time consuming and cannot be performed on original material [24]. Thus, there are currently no routine methodologies to determine the photocatalytic activity of TiO_2 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.

1.2. Pigments

Titanium white is a group name for titanium dioxide based white pigments, known in the pigment industry as pigment white 6 (PW6). During the development of titanium white, many pigments with different characteristics have been on the market. First, composite pigments were developed, followed by pure anatase pigments and pure rutile pigments, produced by either the chloride or the sulfate process. The different processes yield pigments with different characteristics and containing different trace elements [1,6,25]. A wide variety of inorganic and organic coatings have been employed to decrease the photocatalytic activity or to improve other properties, such as wettability of the pigment [1,6,26].

Titanium white pigments used in art before 1940 consist of either composite pigments or pure anatase [1]. After the discovery of rutile, the pigment industry continued the production and supply of anatase for some applications such as artist pigments. Artist paint manufacturer Talens, for instance, switched to rutile for oil paints only in the 1990's and still uses anatase for gouache today [27]. The motivation for the switch in oil paints was partly based on artists complaining about discoloration of mixtures of titanium white and alizarin lake [28,29].

Currently, pigments of a very high stability grade [30–32] are available. However, industrial pigments with high photocatalytic activity are also still readily available. Hombitan LW by Sachtleben Chemie GmbH, an anatase grade pigment, is among others recommended for “road marking paints, lime paints and interior emulsion paints” [33]. Because anatase is the cheaper grade of TiO_2 , there is an economic benefit to using it [34].

The above-mentioned facts demonstrate that photocatalytically active titanium dioxide pigments have been, and still are, widely present on the pigment market. It has thus been finding its way into artist paints, restoration materials and industrial paints (which are also used in works of art), posing a serious threat to 20th century restoration works and 20th century art objects.

1.3. Motivation and objective

In general, it is wise to do a quick screening of the photocatalytic activity of TiO_2 pigments before using them. When considering putting a work of art on display, one should investigate what type of pigment is present. Insight in the photocatalytic activity of different titanium dioxide pigments, and how this relates to their effect in artworks, is essential to protect our cultural heritage.

Currently, no method is available to do a screening of TiO_2 pigments in a quick and easy way (section 1.1). Therefore, the main objective of this study is to develop a quick test to distinguish the different grades of titanium white pigments based on their photocatalytic activity. The test should be simple, reliable, robust, fast, cheap, easy to use and it should provide quantitative or qualitative results depending on the users' objective.

2. Material and methods

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 TiO_2 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 $\text{Cu K}\alpha$ 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 degasser and 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 JSM5910LV 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 TiO_2 powders were investigated by pyrolysis-gas chromatography-mass spectroscopy (Py-GC-MS) using a ThermoScientific Focus GC coupled to a ISQ LT MS using the Xcalibur software and a multi-shot pyrolyzer EGA/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

Table 1
Titanium dioxide powder properties^a. In the text, the titanium dioxide powders are indicated using the code listed in the first column. C indicates a catalyst, I indicates an industrial pigment, A indicates an artist pigment and O indicates an unknown type of pigment ('other').

Code	Structure	Particle Size [nm]	BET [m ² /g]	Coating	Type
C1	Rutile	100	12	Uncoated	Catalyst
C2	Anatase	10	250	Uncoated	Catalyst
I1	Rutile	190	15	SiO ₂ [10–20%], Al(OH) ₃ [0–10%], ZrO ₂ [0–2%]	Industrial pigment
I2	Rutile	30	60	Al, Si, Zr, polyacohol	Industrial pigment
I3	Anatase	100	11	Uncoated	Industrial pigment
I4	Rutile	40	40–60	Al(OH) ₃ [5–10%], ZrO ₂ [0–2%]	Industrial pigment
I5	Rutile	300	18	Al, Si, Zr	Industrial pigment
A1	Rutile	175	19	Al, Si	Artist pigment
O1	Anatase	140	8	Polyol coated	Reference collection RCE
O2	Anatase	80	12	Polyol coated	Hobby pigment (meant to paint textile)

^a Differences in precision are due to information obtained from the manufacturer vs. obtained by our own analysis. The latter are indicated in bold.

exposure. The UV box was equipped with 8 UV lamps of 18 W providing an intensity of $100 \pm 20 \mu\text{W}/\text{cm}^2$, 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).

$$C(\text{AB9}) = 0.012 + 0.0001; \quad R^2 = 0.99 \quad (1)$$

Degradation curves were fitted by a first order exponential decay (Eq. 2), which yields a value for the reaction rate coefficient k . For the

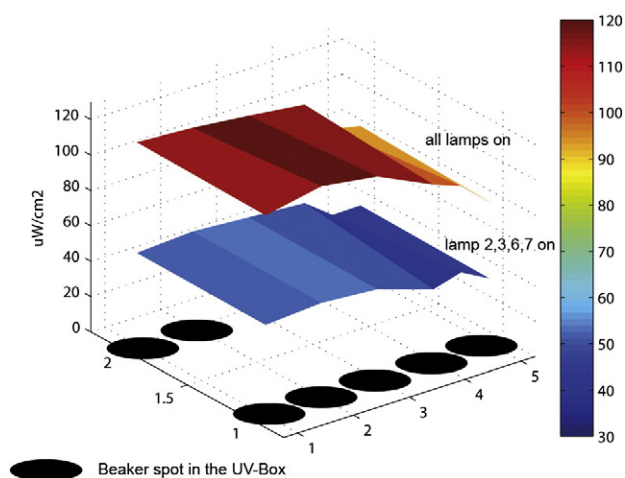


Fig. 1. UV box with UV intensities measured with all lamps on and with lamps 2, 3, 6 and 7 on. The distance between the stirring plate and the lamps is approximately 25 cm.

Table 2Ratio of UV in the UV box to real indoor situations (beaker area = 36.3 cm², luv box = 100 μW/cm²).

	Illuminance [lm/m ²] [36]	Illuminance [lm/beaker area]	UV-content [μW/lm] [37]	UV-light per beaker [μW]	Ratio
UV-box	–		–	3630	
Office environment	500	1.82	75	135	27
Low UV office environment	500	1.82	10	18	202
High UV dimmed light environment	50	0.18	75	13.5	269
Low UV dimmed light environment	50	0.18	10	1.8	2017

degradation curves that do not reach $C(t) = 0$ mM, this fit has an error due to extrapolation.

$$C(t) = C_0 e^{-kt} \text{ with } C_0 = 0.03 \text{ mM} \quad (2)$$

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 on (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 effect of 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 TiO₂:AB9 solution ratio or pigment loading (category 1). Second, scaling down the total experiment while keeping the TiO₂: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) 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 TiO₂ 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 TiO₂/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 3

Adjustments made for test development.

Parameter	Base test [2]	Developed test	Reason for adjustment
Dye	Methylene blue	Acid Blue 9	Methylene blue adsorbs on surface coating of pigments
Volume dye solution	100 ml	10–100 ml	Scale down
Mass TiO ₂	50 mg	5–50 mg	Scale down
Separation for analysis	PTFE Millipore membrane filter	Sedimentation by centrifugal force	PTFE filter malfunctions with dispersion agent and clogs with large TiO ₂ particles
Dispersion aid	Ultrasonic bath	1% v/v Calgon	Pigments with a surface coating do not disperse properly

Table 4
List of downscaling experiments. The code name consists of TiO₂ code-mass TiO₂/Volume AB9 solution^a – extension explained in the remark column. n represents the number of times the test was performed.

Experiment code	Volume of AB9 solution (0.03 mM) [ml] ^a	Mass of TiO ₂ [mg]	Category	Remark	n
I3-25/50	50	25	2	Experiment in 250 ml beaker	6
I3-10/20	20	10	2	Experiment in 50 ml, small neck bottle	4
I3-10-20B	20	10	2	Experiment in 50 ml beaker	2
I3-5/10	10	5	2	Experiment in 50 ml, small neck bottle	2
I3-5/10B	10	5	2	Experiment in 50 ml beaker	1
I3-25/100	100	25	1	Experiment in 250 ml beaker	4
I3-10/100	100	10	1	Experiment in 250 ml beaker	2
I3-5/100	100	5	1	Experiment in 250 ml beaker	3
I3-50/100	100	50	Standard and 3	Experiment in 250 ml beaker	3
I3-50/100 N	100	50	Standard	Experiment in 250 ml beaker New batch of Calgon	1
O1-25/50	50	25	2	Experiment in 250 ml beaker	2
O1-10/20	20	10	2	Experiment in 50 ml, small neck bottle	2
O1-5/10	10	5	2	Experiment in 50 ml, small neck bottle	2
C2-50/100Z	100	50	Standard	Experiment in 250 ml beaker No Calgon added	1
C2-50/100 N	100	50	Standard	Experiment in 250 ml beaker New batch of Calgon	1
I3-100/200	200	100	3	Experiment in 250 ml beaker	1
I3-75/150	150	75	3	Experiment in 250 ml beaker	1
I3-25/50	50	25	3	Experiment in 250 ml beaker	1
I3-12.5/25	25	12.5	3	Experiment in 250 ml beaker	1
I3-paint-1	100	53 ^b	Paint	119 mg paint, dried approximately 2 months	1
I3-paint-2	100	65–100 ^b	Paint	156 mg paint, dried approximately 6–8 months	1

^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.

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 coatings: an incomplete coating can offer active sites for photocatalysis.

These results would not have been obtained with previously described degradation tests, due to the problems described in section 2.3.1 thus the test proves its feasibility and worth.

If the UV ratios described in section 2.2 are assumed (Table 2), as well as the direct relation between degradation rate and UV intensity; extrapolation of the results yields a degradation time of the dye in a

Table 5
Preparation of paint reconstructions.

Paints	Oil	Dryer	Muller	Support	Layer thickness	Location	Year
C1, C2, A1, O1, I1, I2, I4, I5	Hot-pressed linseed oil ^a	Industrial dryer provided by Tronox (Ca, Zr, Co)	Mimex type 2000	Leneta card	200 µm	Tronox & TU Delft	2012
I3, O2	Cold-pressed linseed oil, van Beek	Siccatief de Courtrai, Talens	Similar model	Melinex	200 µm	RCE	2014

^a Unknown brand, purchased at a paint store.

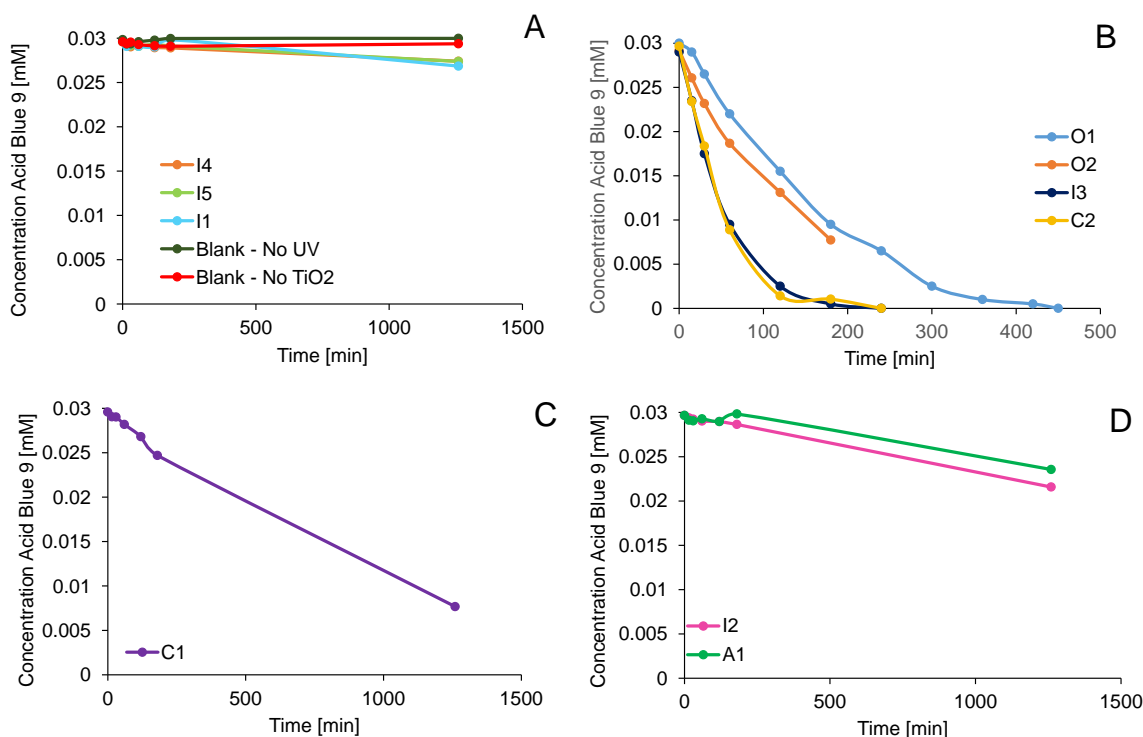


Fig. 2. Feasibility of the photocatalytic activity test – Degradation of acid blue 9 over time. The results are categorized in four categories: (A): Blanks and stable pigments, (B): Fast degradation which has two subcategories, (C): Intermediate degradation and (D): Slow degradation.

dispersion with stable titanium dioxide (I5) of 60 days (UV Box) to 300 years (dimmed light, low UV environment, 50 lx@10 $\mu\text{W}/\text{lm}$). 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!

3.1.1.1. 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 group of two researchers performing the experiments. To investigate reproducibility, the experiments with titanium dioxide I3 under standard conditions (50 mg TiO_2 , 100 ml AB9 dye solution, 1%vol/vol Calgon) are compared. In group 1 temperature (range 29–33 $^{\circ}\text{C}$) and stirring speed (setting 2–5) were varied to investigate operational parameters. However, no clear trends

Table 6

Reaction rate coefficients calculated based on a first order exponential decay fit and evaluation of chalking of paint reconstruction after artificial UV aging two months.

Code	k [min^{-1}]	Category	Chalking [yes/no]
C1	0.001	Intermediate	No
C2	0.018	Fast	Yes
I1	5.9E-5	Stable	No
I2	0.00025	Slow	No
I3	0.016	Fast	Yes
I4	3.2E-5	Stable	No
I5	3.8E-5	Stable	No
A1	0.00018	Slow	No
O1	0.005	Fast	Partially ^a
O2	0.007	Fast	Yes

^a 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.

Category	k range [min^{-1}]
Fast	$k > 0.0025$
Intermediate	$0.0005 < k < 0.0025$
Slow	$0.0001 < k < 0.0005$
Stable	$k < 0.0001$

Sub-categories:
 $k > 0.015$
 $0.0025 < k < 0.015$

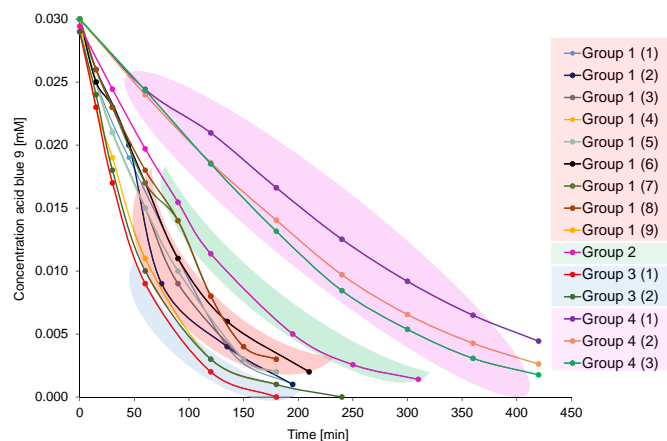


Fig. 3. Degradation of acid blue 9 – Indication of reproducibility. Degradation curves of I3 experiments under standard conditions. The different groups indicate different researchers performing the test at different moments between 2012 and 2015.

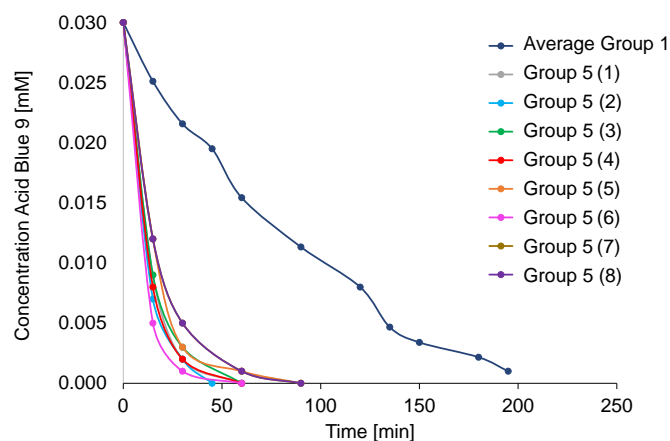


Fig. 4. Influence of Calgon on the degradation of acid blue 9 – Group 5: Degradation curves of I3 experiments under standard conditions without Calgon. Average Group 1: Average of degradation curves (Group 1) shown in Fig. 3, experiments with Calgon.

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).

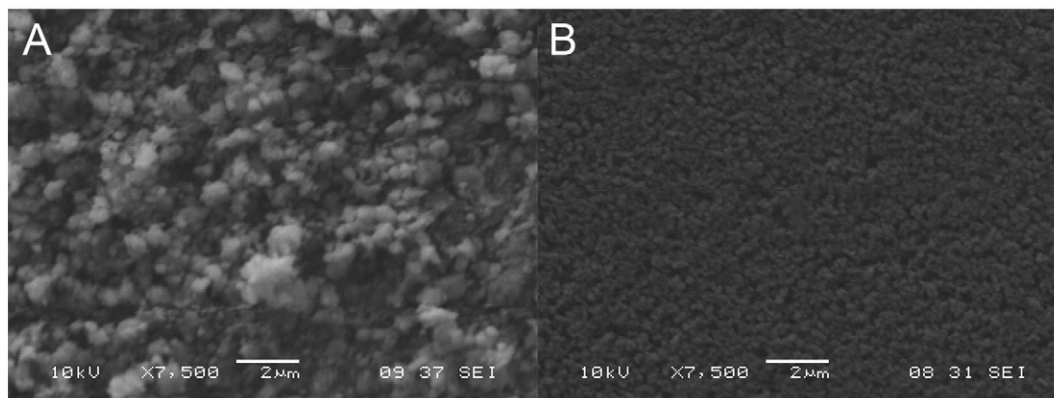


Fig. 5. SEM picture of a chalked paint surface, C2 (A) and a non-chalked paint surface, I1 (B) after 2 months of accelerated aging.

Table 8

Reaction rate coefficients for the developed test with powders I3 and O1 at different exposure conditions, calculated based on a first order exponential decay fit.

Code	k_4 lamps [min^{-1}]	k_8 lamps [min^{-1}]	k_8/k_4
I3	0.010	0.016	1.6
O1	0.002	0.005	2.3

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 corresponds 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.

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 TiO_2 :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

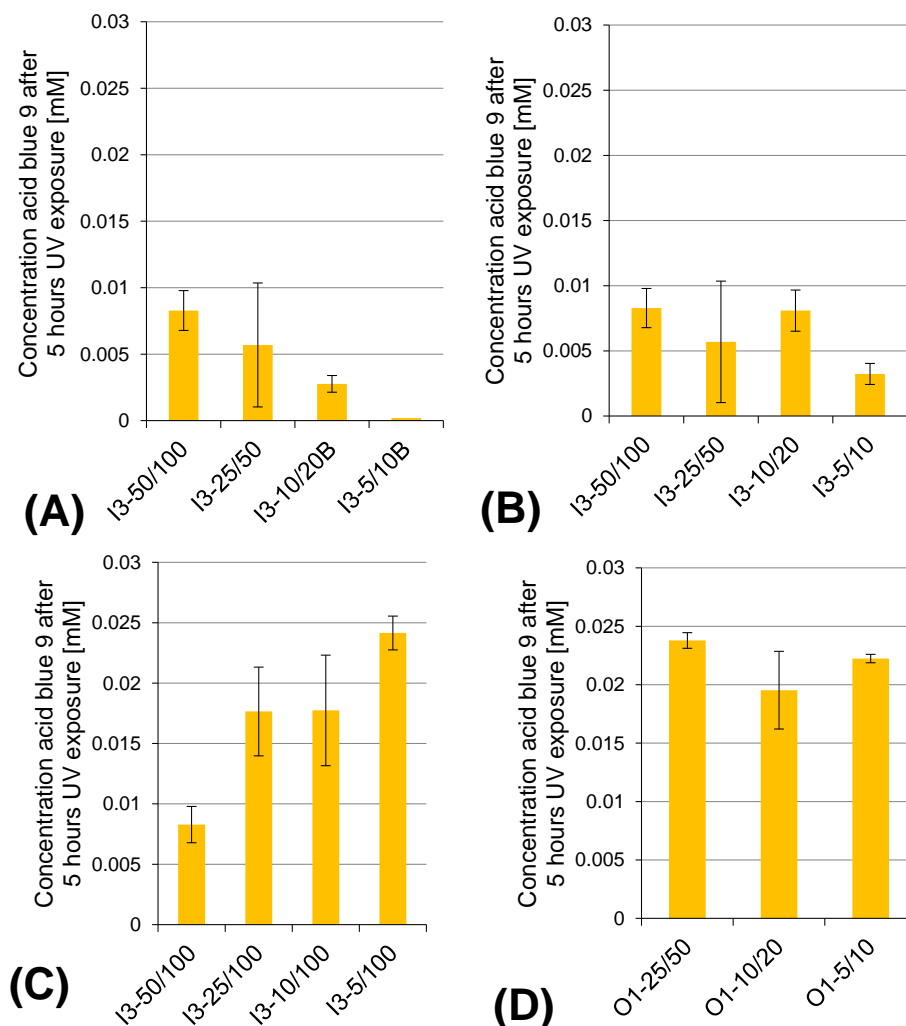


Fig. 6. Results of downscaling. Concentration of acid blue 9 after 5 h of UV exposure. A) Powder I3, category 2, B) Powder I3, category 2, using a 50 ml small neck bottle for the 20 ml and 10 ml experiments, C) Powder I3, category 1, D) Powder O1, category 2, using a 50 ml narrow-necked bottle for the 20 ml and 10 ml experiments. Experiments are summarized Table 4.

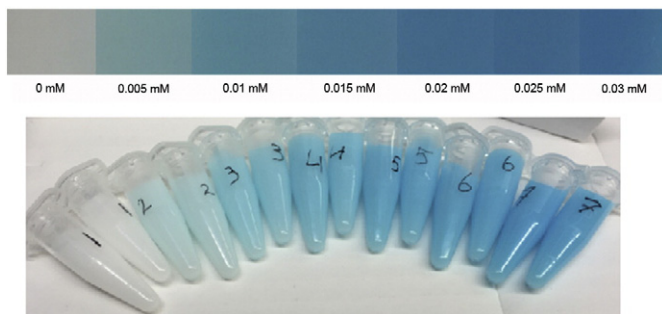


Fig. 7. Color scale and reference dispersions. The reference dispersions contain TiO_2 powders and a known concentration of AB9 dye.

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 TiO_2 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.

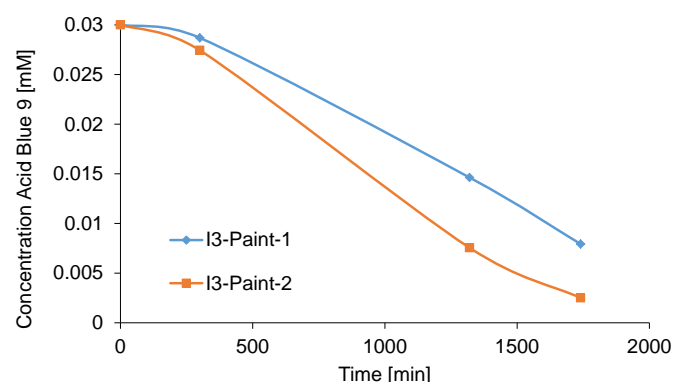


Fig. 8. Acid blue 9 degradation of paint fragments in suspension.

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 TiO_2 powders. Further materials were provided by Tronox (TiO_2 , dryers and dispersing agents), Sachtleben Chemie (TiO_2) the van Gogh museum (TiO_2) and the RCE reference collection (TiO_2). 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

- [1] M. Laver, Chapter 10: titanium white, in: E.W. Fitzhugh (Ed.), *Artists' Pigments: Volume 3: A Handbook of their History and Characteristics* (pp. 295–355), National Gallery of Art, 1997 <http://dx.doi.org/10.2307/1506685>.
- [2] P. Du, A. Bueno-López, M. Verbaas, A.R. Almeida, M. Makkee, J.A. Moulijn, G. Mul, The effect of surface OH-population on the photocatalytic activity of rare earth-

- doped P25-TiO₂ in methylene blue degradation, *J. Catal.* 260 (2008) 75–80, <http://dx.doi.org/10.1016/j.jcat.2008.09.005>.
- [3] de Keijzer, M., de Groot, S., Megens, L., & Van Keulen, H. (2008). Schildertehchnisch onderzoek aan Mondriaans Compositie met rood, zwart, geel en grijs uit 1920. *Unpublished results*. Instituut Collectie Nederland
- [4] M. de Keijzer, The colourful twentieth century, in: S. Fairbrass, J. Hermans (Eds.), *Modern Art: The Restoration and Techniques of Modern Paper and Paints*, United Kingdom institute of Conservation, ISBN: 1871656044 1989, pp. 13–20.
- [5] K.J. van den Berg, C. Miliani, A. Aldrovandi, B.G. Brunetti, S. de Groot, K. Kahrim, M. de Keijzer, H. van Keulen, L. Megens, A. Sgamellotti, M.R. van Bommel, Chapter 7: the chemistry of Mondrian's paints in victory boogie woogie, in: M.R. van Bommel, H. Janssen, R. Spronk (Eds.), *Inside Out Victory Boogie Woogie*, Amsterdam University Press, Amsterdam, ISBN: 9789089643735, 2012.
- [6] M. de Keijzer, The history of modern synthetic inorganic and organic artists' pigments, in: J.A. Mosk, N.H. Tennent (Eds.), *Contributions to Conservation: Research in Conservation at the Netherlands Institute for Cultural Heritage*, James & James (Science Publishers) Ltd, ISBN: 1-902916-09-3, 2002.
- [7] T.B. van Oosten, I. Fundeanu, C. Bollard, CastroC. d., A. Lagana, Lights out! The conservation of polypropylene wall tapestries, in: B. Keneghan, L. Egan (Eds.), *Plastics. Looking to the Future and Learning From the Past*, Archetype Books, ISBN: 1904982433, 2008.
- [8] T.F. Parsons, G.G. Gray, I.H. Crawford, To RC or not to RC, *J. Appl. Photogr. Eng.* 5 (2) (1979) 110–117.
- [9] G. Völz Hans, G. Kaempf, G. Fitzky Hans, A. Klaeren, The chemical nature of chalking in the presence of titanium dioxide pigments, in: F.H. Winslow (Ed.), *Photodegradation and Photostabilization of Coatings*, ACS Symposium Series, American Chemical Society, 151 1981, pp. 163–182.
- [10] T.A. Egerton, C.J. King, The influence of light intensity on photoactivity in TiO₂ pigmented systems, *J. Oil Col. Chem. Assoc.* 62 (1979) 386–391.
- [11] N.S. Allen, M. Edge, A. Ortega, G. Sandoval, C.M. Liauw, J. Verran, J. Stratton, R.B. McIntyre, 927–946, Degradation and stabilisation of polymers and coatings: nano versus pigmentary titania particles, *Polym. Degrad. and Stabil.* 85 (3) (2004) 927–946, <http://dx.doi.org/10.1016/j.polymdegradstab.2003.09.024>.
- [12] R.R. Blakey, The role of titanium dioxide in the protection of paint media, *Tioxide Technical Service Report D 9104 GC*, 1980.
- [13] C.H. Hare, The degradation of coatings by ultraviolet light and electromagnetic radiation, *JPCL* (1992).
- [14] W. Kim, T. Tachikawa, Moon, G.-h., Majima, T., & Choi, W., Molecular-level understanding of the photocatalytic activity difference between anatase and rutile nanoparticles, *Angew. Chem. Int. Ed.* 53 (51) (2014) 14036–14041, <http://dx.doi.org/10.1002/anie.201406625>.
- [15] A. Sclafani, J.M. Herrmann, Comparison of the photoelectronic and photocatalytic activities of various anatase and rutile forms of titania in pure liquid organic phases and in aqueous solutions, *J. Phys. Chem.* 100 (32) (1996) 13655–13661, <http://dx.doi.org/10.1021/jp9533584>.
- [16] A.L. Linsebigler, G. Lu, J.T. Yates, Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results, *Chem. Rev.* 95 (3) (1995) 735–758, <http://dx.doi.org/10.1021/cr00035a013>.
- [17] P.A. Christensen, A. Dilks, T.A. Egerton, J. Temperley, Infrared spectroscopic evaluation of the photodegradation of paint Part II: the effect of UV intensity & wavelength on the degradation of acrylic films pigmented with titanium dioxide, *J. Mater. Sci.* 35 (21) (2000) 5353–5358, <http://dx.doi.org/10.1023/A:1004898913140>.
- [18] G. Irick, Determination of the photocatalytic activities of titanium dioxides and other white pigments, *J. Appl. Polym. Sci.* 16 (9) (1972) 2387–2395, <http://dx.doi.org/10.1002/app.1972.070160917>.
- [19] M.A. Rauf, S.S. Ashraf, Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution, *Chem. Eng. J.* 151 (1–3) (2009) 10–18, <http://dx.doi.org/10.1016/j.cej.2009.02.026>.
- [20] K. Doushita, T. Kawahara, Evaluation of photocatalytic activity by dye decomposition, *J. Sol-Gel Sci. Technol.* 22 (1–2) (2001) 91–98, <http://dx.doi.org/10.1023/A:1011220505116>.
- [21] J. Chin, S. Scierka, T. Kim, A. Forster, Photoconductivity technique for the assessment of pigment photoreactivity, *Proceedings of the 81st annual meeting of the FSCT*, 2003 (November 2003).
- [22] C. Jin, P.A. Christensen, T.A. Egerton, E.J. Lawson, J.R. White, Rapid measurement of polymer photo-degradation by FTIR spectrometry of evolved carbon dioxide, *Polym. Degrad. Stab.* 91 (5) (2006) 1086–1096, <http://dx.doi.org/10.1016/j.polymdegradstab.2005.07.011>.
- [23] E. Ceresa, L. Burlamacchi, M. Visca, An ESR study on the photoreactivity of TiO₂ pigments, *J. Mater. Sci.* 18 (1) (1983) 289–294, <http://dx.doi.org/10.1007/BF00543837>.
- [24] R.L. Feller, Accelerated aging: photochemical and thermal aspects, in: D. Berland (Ed.) *Getty conservation institute*, 1994 (ISBN: 0-89236-125-5). 1).
- [25] J.H. Braun, A. Baidins, R.E. Marganski, TiO₂ pigment technology: a review, *Prog. Org. Coat.* 20 (2) (1992) 105–138, [http://dx.doi.org/10.1016/0033-0655\(92\)80001-D](http://dx.doi.org/10.1016/0033-0655(92)80001-D).
- [26] D.N. Furlong, Surface chemistry of silica coatings of titania, in: H.E. Bergna (Ed.), *The Colloid Chemistry of Silica*, American Chemical Society, 234 1994, pp. 535–559.
- [27] B. Klein-Ovink, Personal Communication. Apeldoorn2014.
- [28] P. Keune, Personal communication. Amsterdam2015.
- [29] R. Johnston-Feller, R.L. Feller, C.W. Bailie, Curran, M. (1984). The Kinetics of Fading, Opaque paint films pigmented with alizarin lake and titanium dioxide, *JAIC* 23 (2) (1984) 114–129, <http://dx.doi.org/10.1179/019713684806028269>.
- [30] Kronos®, TiO₂ – Grades and Applications, Kronos information 2.1, <http://kronosio2.com/data-sheets-and-literature/brochures/finish/7/812015> (Retrieved 26-05-2015, from).
- [31] DuPont™, Titanium Dioxide for coatings, Ti-Pure® titanium dioxide, http://www2.dupont.com/Titanium_Technologies/en_US/tech_info/literature/Coatings/CO_B_H_65969_Coatings_Brochure.pdf (Retrieved 26-05-2015, from).
- [32] R. de Bondt, TiO₂, the technical and the rational, <http://sv.slf.cc/dokument/Robin%20De%20Bont,%20Tronox,%20TiO2,%20the%20technical%20and%20the%20rational.pdf> (Retrieved 26-05-2015, from).
- [33] Sachtleben Chemie GmbH, Product information 04.001.03.14.e, http://www.sachtleben.de/fileadmin/pdf_dateien/titandioxid/HOMBITAN_LW.pdf (Retrieved 26-05-2015, from).
- [34] L.M. Sherman, Stretch TiO₂, <http://www.ptonline.com/articles/stretch-tio21999> (Retrieved 18–11-2014, 2014, from).
- [35] D.H. Hanaor, C. Sorrell, Review of the anatase to rutile phase transformation, *J. Mater. Sci.* 46 (4) (2011) 855–874, <http://dx.doi.org/10.1007/s10853-010-5113-0>.
- [36] The engineering toolbox, http://www.engineeringtoolbox.com/light-level-rooms-d_708.html (Retrieved 10-03-2015, from).
- [37] K.P.M. Guire, SoLux Ultraviolet Radiation primer, <http://www.solux.net/cgi-bin/tlistore/infopages/uv.html> (Retrieved 19–11-2014, from).
- [38] M. Dias, E. Azevedo, Photocatalytic decolorization of commercial acid dyes using solar irradiation, *Water Air Soil Poll.* 204 (1–4) (2009) 79–87, <http://dx.doi.org/10.1007/s11270-009-0028-6>.
- [39] A. Bianco Prevot, C. Baiocchi, M.C. Brussino, E. Pramauro, P. Savarino, V. Augugliaro, G. Marci, L. Palmisano, Photocatalytic degradation of acid blue 80 in aqueous solutions containing TiO₂ suspensions, *Environ. Sci. Technol.* 35 (5) (2001) 971–976, <http://dx.doi.org/10.1021/es000162v>.
- [40] M. Jank, H. Köser, F. Lücking, M. Martienssen, S. Wittchen, Decolorization and degradation of erioglaucine (Acid Blue 9) dye in wastewater, *Environ. Technol.* 19 (7) (1998) 741–747.
- [41] K. Gude, Gun'koV.M., J.P. Blitz, Adsorption and photocatalytic decomposition of methylene blue on surface modified silica and silica-titania, *Colloids Surf., A.* 325 (1–2) (2008) 17–20, <http://dx.doi.org/10.1016/j.colsurfa.2008.04.035>.
- [42] N. Daneshvar, D. Salari, A. Niaei, A.R. Khataee, Photocatalytic degradation of the herbicide erioglaucine in the presence of nanosized titanium dioxide: comparison and modeling of reaction kinetics, *J. Environ. Sci. Health., B.* 41 (8) (2006) 1273–1290, <http://dx.doi.org/10.1080/03601230600962302>.
- [43] H. Zangeneh, A.A.L. Zinatizadeh, M. Habibi, M. Akia, M. Hasnain Isa, Photocatalytic oxidation of organic dyes and pollutants in wastewater using different modified titanium dioxides: a comparative review, *J. Ind. Eng. Chem.* 26 (0) (2015) 1–36, <http://dx.doi.org/10.1016/j.jiec.2014.10.043>.