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A proof of principle

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Determining The Presence of Photocatalytic Titanium White Pigments via Embedded Paint Sample Staining: A Proof of Principle

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ABSTRACT

Twentieth century paints often contain titanium dioxide and zinc oxide based white pigments that can range from photostable to highly photocatalytic. Photocatalytic pigments can cause the degradation of paint upon UV exposure, whereas photostable pigments may be benign or can protect paintings from degradation. Hence, knowing whether or not a pigment is photocatalytic is of high importance for risk assessment and the subsequent decision making process concerning storage and exposure conditions of objects. Here we present a proof of principle, focused on titanium white paints, for an easy-to-use and low-tech application of a commercial photocatalytic activity indicator ink (PAII) on embedded paint samples or cross sections. This test determines, qualitatively, if a photocatalytic pigment is present in a white paint sample. The PAII paint sample staining application shows an obvious color change, within five minutes of UV irradiation, for paint samples containing photocatalytic pigments. A microscope with a camera and a UV source are the only necessary equipment for the application of this method. A quantitative image processing protocol is also proposed as an extension of the staining method by applying open source software analysis to measure the color change using photographs. The test was evaluated on reference paints with well-characterized pigments and applied on samples from modern paintings by Piet Mondriaan, Robert Ryman, and Lucebert, indicating the presence of harmful photocatalytic pigments in these cases. The novel application of a commercial ink on paint samples offers a simple test, not just for assessment of photocatalytic activity of titanium white pigments, but which may in future be applied for the detection of photoactive forms of zinc white and other potentially harmful semiconductor pigments in art objects.

Introduction

Many pigments commonly found in works of art can be classified as semiconductors. The molecules of these materials have a bandgap between the valence band and the conduction band that can be bridged by photons of an energy exceeding the bandgap. Semiconductor pigments include vermilion, cadmium red and yellow, chrome green, zinc white, and titanium white (Anaf et al. 2014). Several semiconductor pigments, such as titanium white and zinc white, may also function as photocatalysts (Kobayashi and Kalriess 1997; Laver 1997; Benedix et al. 2000; Yang et al. 2010; Gunnarsson 2011; Smijs and Pavel 2011; Baudys et al. 2015; van Driel et al. 2016, 2017b; Morsch et al. 2017). When such a pigment is irradiated with photons that have a larger than bandgap energy, an electron from the valence band is excited to the conduction band, forming a photogenerated electron and a positive hole. The electron and hole can migrate to the pigment surface, where they react with water and oxygen forming highly reactive radicals. The radicals can participate in several (photo-oxidative) reactions such as the breakdown of surrounding organic material, like the binding medium of a paint or pollutants (Mills and Le Hunte 1997; Umar and Aziz 2013; Zangeneh et al. 2015; Morsch et al. 2017; van Driel et al. 2017b). Photocatalytic activity is influenced, among other factors, by modification of the crystal structure (Sclafani and Herrmann 1996; Ohno, Sarukawa, and Matsumura 2002), the use of dopants (Luo and Gao 1992; Dozzi et al. 2013), or the application of (inorganic) surface coatings (Werner 1969; Johansson 1991; Braun, Baidins, and Marganski 1992; Laver 1997; Schiller, Müller, and Damm 2002; van Driel et al. 2016).

Titanium white, the most abundantly used pigment of the twentieth century, has been produced in a range of photocatalytic activities ranging from highly photocatalytic to photostable (Laver 1997; van Driel et al. 2016). Presently, most artists' pigments are photostable rutile pigments with inorganic surface coatings, classified as type IV pigments following D476-84

ASTM 1988. However, this is a relatively recent development. Photocatalytic, uncoated anatase pigments have been on the market and have been found in works of art (Laver 1997; van Driel et al. 2017a). Furthermore, zinc white, another potential photocatalyst, was also commonly used in oil paints and is often mixed with titanium white to obtain the required paint properties (Kuhn 1986). Both these pigments are potentially detrimental to works of art, and thus knowledge about their photocatalytic activity in a painting is of high importance.

Different methods have been proposed for the assessment of photocatalytic activity (mostly of TiO_2). Most methods monitor an alternative photocatalyzed reaction to categorize photocatalytic activity, by evaluating, for instance, chemical conversion or color change. These are referred to as 'dummy' reactions (Irick 1972; Xu et al. 1999; Mills et al. 2005; Daneshvar et al. 2006; Rauf and Ashraf 2009; Mills, Hill, and Robertson 2012; van Driel et al. 2016). Other proposed approaches are photoconductivity measurements (Irick 1972), monitoring radical formation by electron spin resonance spectroscopy (Ceresa, Burlamacchi, and Visca 1983) or artificial aging of paint films (Morsch et al. 2017; van Driel et al. 2017b), for instance by measuring the evolution of CO_2 from a confined paint film under irradiation (Christensen et al. 1999, 2000). All of these methods have limitations in that they are time consuming and require professionals and specific equipment to carry out, or they cannot be performed on art objects or samples from art objects.

The most promising methods for use by conservators (accustomed to visual assessments and without ready access to analytic equipment) are based on color change, such as monitoring the change of a dye in an aqueous solution under ultraviolet (UV) irradiation (van Driel et al. 2016). The aim to develop a test usable on samples from objects was initially envisioned to be an adaptation of such a dye system. However, its development was considered redundant in light of the work of Mills and co-workers on an indicator ink available as a commercial product (Mills et al. 2005, 2013, 2014a, 2014b, 2016; Mills and McGrady 2008; Mills, O'Rourke, and Wells 2014; Mills, Wells, and O'Rourke 2014, 2016, 2017; Mills and Wells 2015; Baudys, Krýsa, and Mills 2017; van Driel et al. 2018b). This product, developed over the past decade, is called a photocatalytic activity indicator ink (PAII) and was developed and validated to determine photocatalytic activity of TiO_2-containing self-cleaning tiles and windows. The concept of the inks is that they irreversibly change color, upon UV irradiation, in the presence of a photocatalyst (through photo-reduction). The ink consists of a mixture of a dye, a polymer solution (hydroxyl ethyl cellulose, HEC), a surfactant, and a sacrificial electron donor (commonly glycerol). The sacrificial electron donor reacts with the photogenerated hole, while the photogenerated electron reduces

the dye causing color change. The reaction of the sacrificial electron donor (glycerol to glyceric acid) prevents the recombination of electron and hole, thus facilitating the reaction of electrons with the ink. It has been demonstrated that the inks, in the absence of glycerol, show no color change.

$$TiO_2 + h\,\nu(E > E_{bg}) \rightarrow TiO_2(h^+) + TiO_2(e^-) \qquad \text{excitation by UV light}$$

$$Glycerol + TiO_2(h^+) \rightarrow Glyceric\ acid \qquad \text{hole scavenging}$$

$$TiO_2(e^-) + O_2/H_2O \rightarrow reducing\ species/radicals \qquad \text{photocatalytic cycle}$$

$$Dye + TiO_2(e^-)\ or\ reducing\ species/radicals \rightarrow reduced\ dye \qquad \text{color change}$$
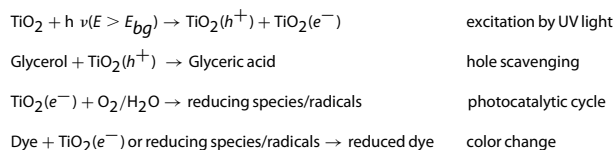
PAII color change curves have been demonstrated, on multiple occasions, to relate directly to the photocatalyzed oxidation of several pollutants (Mills et al., 2005–2017), proving its reliability as a method to assess photocatalytic activity. Even though the inks are a good indicator for real degradation processes, the test is based on the alternative reactions of photo-reduction and hole scavenging and may therefore be influenced differently by environmental factors.

Furthermore, several methods of monitoring color change such as change of absorbance (UV-VIS), diffuse reflectance spectroscopy, and digital photography (RGB (ΔR) or Lab (Δa) color space) have also been shown to have good correlation. Recent work in the field of PAII (Mills and Wells 2015; Mills, Wells, and O'Rourke 2017) is concerned with the development of PAII labels and the application of PAII on powdered materials and semiconductors other than titanium dioxide.

Staining techniques have been employed since the mid-twentieth century for the characterization of organic components in paint samples (Sandu et al. 2012). While the techniques lost popularity with the introduction of new, non-invasive techniques, microscopy analysis remains the first step of micro-invasive analysis. Hence, it is in this scope that we propose the application of PAII, developed by Mills et al. (2005–2017), by staining paint samples from modern paintings.

In this study we present a practical method indicated as 'PAII staining' to identify if a (titanium) white paint contains harmful photocatalytic pigment. This information is critical for risk assessment and subsequent decisions about exposure conditions of twentieth century art objects. The presented proof of principle is primarily focussed on titanium white. However, zinc white, as a common pigment used alone or in mixture with titanium white, and also known for its photocatalytic properties, is taken into consideration as well. The application is investigated by testing reference paint samples of accurately known composition and photocatalytic activity, based on earlier testing, as well as one commercial tube paint and three samples previously collected from modern paintings by Piet Mondriaan, Robert Ryman, and Lucebert.

Experimental

Sample set

 Table 1 describes the investigated samples presented in this paper. All samples are analysed as embedded paint samples, prepared either from fragments or as layered cross sections. All samples were embedded using Technovit® 2000LC (a polymer based on methyl methacrylate, produced by Heraeus Kulzer) and subsequently ground and polished using standard methods to create a flat and smooth surface. Between experiments on the same sample, the surface was re-polished to remove the blue ink. While sample polishing is not critical for the reduction process of the ink, it is important for the quality of the results. Especially for quantitative assessment, it is important to prepare the sample carefully and following a standardized protocol. Different embedding resins can be used, after ensuring that the resin does not react with the ink, which can be easily done by running a blank test.

Reference samples

The reference samples were selected, based on prior research (van Driel et al. 2018a, 2018b), to represent a range of extreme properties (photocatalytic versus photostable and inert) and common compositions found in modern oil paints (primarily those based on TiO_2, in a range of pigment volume concentrations, with some also containing $BaSO_4$, ZnO, and aluminium stearate). A tube paint was added to the selection, chosen because of its similarity in composition to one of the tested reference mixtures, and because it is a commercially available artist's paint. The tube is dated between 1982 and 1986, based on the tube design.

The reference samples consist of 13 dried paints compounded in the laboratory for a previous study and a tube paint, applied in single or multiple layers (Table 1). In the one case of a layered structure, each layer is designated as a different sample (R5a and R6b). The paint samples are all prepared by mixing dry pigments and additives with bleached linseed oil (Van Beek) containing a drier (Co/Zr drier of an unknown brand, donated by Pieter Keune, added as 0.1% v/v to the oil). The pigments and additives are uncoated anatase (Hombitan LW, Sachtleben Chemie), organically coated anatsase (A-HRF, Hunstman), coated rutile (CR-826, Tronox), zinc oxide (46300, Kremer Pigmente), barium sulfate (58700, Kremer Pigmente), and aluminium stearate (58960, Kremer Pigmente). The prepared paints are applied either with a brush on a primed canvas (Lefranc & Bourgeois, CB1015, Canvas board for oil, acryl, and alkyd) or with a drawdown bar on 250 µm thick Melinex® (Mylar/Polyester/Biaxially-oriented polyethylene terephthalate, purchased from Labshop). The tube paint (Titanium white oil paint: Talens Amsterdam oil colors) was painted onto the support using a brush.

Samples from paintings

Three modern oil paintings were selected based on the confirmed presence of anatase and the availability of paint samples obtained in the scope of other research projects (listed in Table 1).

Instrumental analysis

The reference pigments had been tested for photocatalytic activity by a dye degradation test and by artificial aging under UV in previous studies (van Driel et al. 2016, 2018b). The Talens tube paint (R5) and the canvas board were analysed by X-ray diffraction (XRD).

Instrumental analysis was done on the three samples from paintings to determine the pigments and additives present. Samples P1 and P2 were analysed by the authors with a variety of methods such as X-ray fluorescence spectrometry (XRF), XRD, and scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDX). In addition to previously reported information (van den Berg et al. 2012), sample P3 was analysed by STEM-EDX.

XRF was performed using a Bruker tracer III-SD. For P1, the XRF was operated at 40 kV and 10 µA without a filter. For P2, the XRF was operated under the same conditions with the additional use of an Al/Ti filter. The crystalline phases were analyzed by XRD using a Discover D8 microdiffractometer with a general area detection diffraction system (GADDS) two dimensional detector (Bruker AXS, Karlsruhe, Germany). The samples were measured without preparation on a concave microscope slide. Diffractograms were acquired in reflection mode with CuKα radiation (40 kV, 30 mA). The GADDS software was used for integration and the Bruker AXS Eva software for phase identification using the ICDD PDF database.

All STEM-EDX analysis was performed at AkzoNobel. Paint fragments were glued with a cyanoacrylate glue to an Al pin, and after 30 minutes curing time sectioned with a Leica UC6 cryo-ultramicrotome using a diamond knife (cryo 35 degrees). Thin sections of ∼100 nm thickness were collected dry on C coated Cu TEM grids. The prepared samples were analyzed in a JEOL 2010F field emission gun TEM (200 kV) equipped with a STEM unit. The STEM-EDX mappings were acquired using a ThermoFisher 30 mm^2 Ultradry silicon drift EDX detector.

PAII staining method

A range of PAI-inks are commercially available but the Basic Blue 66 PAII (the 'Visualizer', BB66, purchased from Ink Intelligent) is most suitable for low activity

Table 1. Investigated samples.

Code[a]	Description
Pure anatase-based reference paint samples	
R1a-RMA	Uncoated anatase (UA) on canvas, PVC[b] = 22%
R1b-RMA	Uncoated anatase (UA) on Melinex, PVC = 25%
R1b-RCE	Uncoated anatase (UA) on Melinex, PVC = 25%
R1c-RMA	Uncoated anatase (UA) on Melinex, PVC = 15%
R2-RMA	Organically coated anatase (CA(org)) on Melinex, PVC = 15%
Mixed anatase-based reference paint samples	
R3-RMA	Uncoated anatase (UA) + ZnO on Melinex (1:1, v/v) PVC: 10% UA + 10% ZnO
R4-RMA	Uncoated anatase (UA) + $BaSO_4$ on Melinex (1:1, v/v) PVC: 14% UA + 14% $BaSO_4$
R5a-RMA	Tube (Anatase + ZnO) layer on top of coated rutile on canvas (2 layers on canvas)
R5a-RCE	Tube (Anatase + ZnO) layer on top of coated rutile on canvas (2 layers on canvas)
R5b-RMA	Tube (Anatase + ZnO) on canvas
Rutile-based reference paint samples	
R6a-RMA[c]	Coated rutile (CR) on canvas, PVC = 37%
R6b-RMA	Coated rutile (CR) layer between canvas and tube paint (2 layers on canvas) PVC: 37%
R6b-RCE	Coated rutile (CR) layer between canvas and tube paint (2 layers on canvas) PVC: 37%
R7-RMA	Coated rutile (CR) + aluminum stearate on Melinex (2% vol Al stearate) PVC: 20%
Other reference paint samples	
R8-RMA	ZnO on Melinex, PVC: 13%
R9a-RMA	$BaSO_4$ on Melinex, PVC: Unknown
R9b-RMA	$BaSO_4$ on canvas, PVC: 44%
Samples from paintings	
P1-RMA	Untitled, Robert Ryman, 1960, Stedelijk Museum Amsterdam Sample 'C', received from L. Steyn and K.J. van den Berg[d]
P2-RMA	Alle schatten komen uit Afrika, Lucebert, 1985, Bouwfonds kunstcollectie[e].
P3-RMA	Victory Boogie Woogie, Piet Mondriaan, 1944, Gemeentemuseum, Den Haag Sample 2207/05, received from the Cultural Heritage Agency of the Netherlands (K.J. van den Berg)[f].

[a]'RMA' or 'RCE' refer to the microscope that was used. More details are reported in section 2.3.
[b]Pigment volume concentration.
[c]Sample R6a-RMA was erroneously irradiated with a magnification of 25x, affecting the UV intensity reaching the sample through the microscope. Nevertheless, in view of the known stability of the pigment and the long total analysis time (90 min), the sample was not repeated at the correct magnification.
[d]Sample from the JPI-CH CMOP project, from a case study painting supplied by the Stedelijk Museum (Steyn forthcoming).
[e]Sample acquired (from painting at the Bouwfonds Kunstcollectie) during the Ph.D. project of the author in the scope of 'The white of the 20th century – An explorative survey into Dutch modern art collections' (van Driel et al. 2018b).
[f]Sample was part of the investigation performed by the Cultural heritage agency of the Netherlands and the Gemeentemuseum in The Hague (van den Berg et al. 2012).

surfaces and offers the most intuitive color change (from blue to colorless). Based on the dry application of the pen, compared to the wet application of the brush (Figure 1), the pen was the applicator of choice in this study. Because of its temperature sensitivity, the pen was kept in the refrigerator when not in use.

The cross section without ink is examined and photographed with a microscope under visible light (Dark field microscopy, DF) and UV light (no color correction equipped with filterset 02 EX G 365, BS FT 395, EM LP 420). After the initial examination, the ink is applied onto the cross section until the entire sample is covered by the blue color. Subsequently, the sample is again examined and photographed under visible light (DF, $t = 0$). In this study two different Zeiss microscopes were used, designated as 'RCE' and 'RMA' (Table 1). Microscope 'RMA' (Rijksmuseum, Amsterdam) is equipped with a LED light and an in-house color calibration software (Smelt and Erdmann 2017), whereas microscope 'RCE' (Rijksdienst voor het Cultureel Erfgoed, i.e. Cultural Heritage Agency of the Netherlands) is equipped with a halogen lamp (100W) and does not have color calibration. After the

Figure 1. Photograph of the visualizer pen and brush (top) and their application on paper (bottom). The pen was chosen in this study for its dry and therefore more reproducible application.

examination of the blue color on the sample, the cross section is exposed to a UV source. In the case of microscope 'RMA' this was done in situ using the Calibri UV LED (365 nm, equipped with filterset 02 EX G 365, BS FT 395, EM LP 420) on the microscope, set at 10% UV intensity and using a 50x magnification (UV intensity $= 2.29$ mW/cm^2). If UV irradiation is performed through the microscope, it is important to keep the optics, including the magnification, constant. Varying the microscope setting can alter the UV-intensity reaching the sample. When using microscope 'RCE' irradiation was performed on an external UV source (Spectroline SB100/F, UV intensity $= 1.4$ mW/cm^2). This difference was used to explore the effect of UV intensity on the rate of color change.

At the following time points: 5, 10, 15, 20, 25, 30, 60, and 90 min; the sample was examined and photographed under visible light (DF, fixed exposure time). Subsequently color correction was carried out for the photographs taken on the 'RMA' microscope.

The photographs are evaluated both visually and quantitatively by extracting color values and calculating the normalized color change. In this study the open source software ImageJ with the MBF imageJ for Microscopy plugin bundle (Collins 2007) was used to extract RGB values from the photographs (see Appendix). However, other image softwares such as Adobe Photoshop, or different color spaces (such as Lab, monitor Δa), could also be used. For BB66 the largest change occurs in the 'R' value from blue (RGB $\approx 0, 0, 255$) to white (RGB $\approx 255, 255, 255$). The final value of interest is the change in normalized red value as described in equation 1.

$$\Delta RGB_r = (R/(R + G + B))_{t=0} - ((R/(R + G + B))_{t=t} \quad (1)$$

Results and Discussion

Both methods of analysis – visual, and by quantitative monitoring of color change in a color space of choice – will be discussed, followed by an evaluation of the measurement set-up and a preliminary repeatability test.

Visual assessment of color change

Reference paint samples

Figure 2 shows the results from a set of four reference samples tested on the 'RMA' microscope: highly photocatalytic (uncoated anatase, R1a), medium photocatalytic (organically coated anatase, R2), photostable (coated rutile mixed with aluminium stearate, R7), and inert (barium sulfate, R9b). Per sample, three pictures of the initial situation are presented: a UV photograph and two dark field photographs before and after application of the ink. Additionally, two photographs after 15 and 90 min of UV irradiation are shown. This sample set provides the proof of principle that color change is observed in the samples containing photocatalytic pigments (R1a, R2). On the other hand, color change is not observed for the photostable (R7) or inert pigments (R9b), or in the priming layer on the canvas board (R1a and R9b), which contained rutile and calcium carbonate (XRD). Evidently, the aluminium stearate additive in sample R7 does not contribute to any color change. Additionally, the different behavior of layers is visible: in the photographs of sample R1a, uncoated anatase on primed canvas, it is clear that the top layer changes color whilst the bottom layer, the priming, remains blue. Thus, this serves as a proof of concept that the method is also spatially resolved and therefore suitable to investigate layered structures. Both samples R2 and R7 show what seems to be a layer
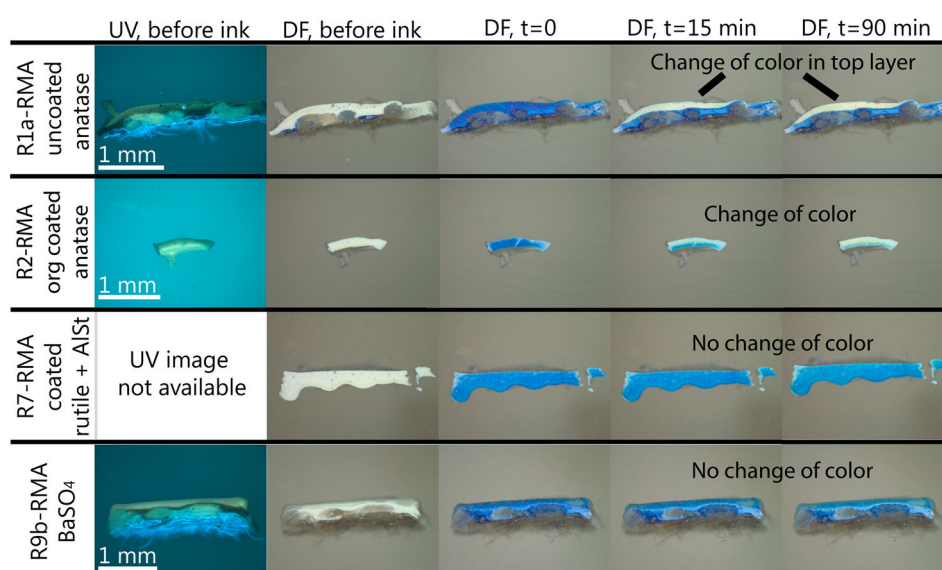

Figure 2. Photographs of a subset of reference samples (uncoated anatase, organically coated anatase, coated rutile, and barium sulfate) before the ink is applied, shown in ultraviolet (UV) and dark field (DF), when the ink is applied ($t = 0$) and after 15 and 90 min of UV irradiation. Both anatase samples show color change.
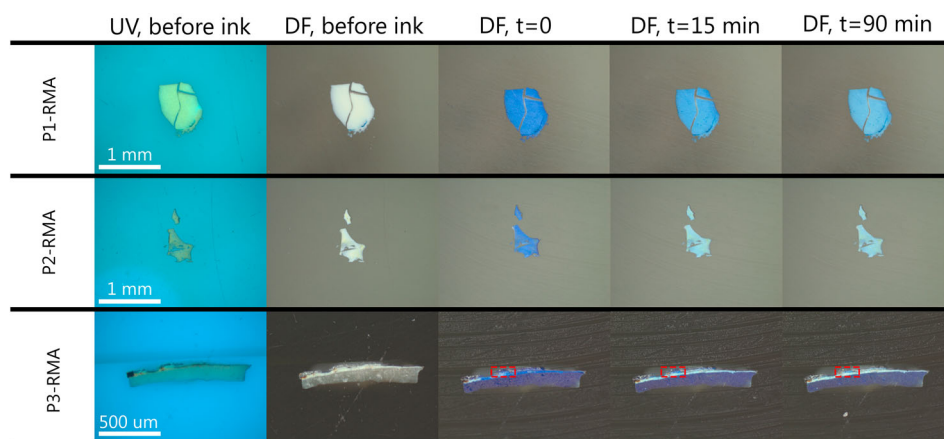
Figure 3. Photographs of samples from paintings under investigation before the ink is applied, shown in ultraviolet (UV) and dark field (DF), when the ink is applied ($t = 0$) and after 15 and 90 min of UV irradiation.

structure with different rate of color change. However, these samples were cast as a single layer and this phenomenon is likely related to differences in pigment volume concentration due to phase separation upon horizontal drying.

Samples from paintings

Figure 3 shows the photographic results for the three samples from paintings that were investigated with the 'RMA' microscope. Samples P1 and P2 were fragments mounted flat, and P3 was an existing cross section. All samples show a degree of color change, indicating that they contain photocatalytic material.

Table 2 provides an overview of the supporting analysis for the paint samples. This shows that in the Robert Ryman (P1) and Lucebert paintings (P2), ZnO and anatase are present, both possibly photocatalytic and thus causing the ink's color change. The PAII test successfully confirms the presence of photocatalytic material in the paintings. It also indicates the importance of such testing because, based on their date (1960 and 1985 respectively), one might expect the use of more recently developed pigments present on the market such as a coated rutile.

STEM-EDX on the P3 flake suggests an association between titanium dioxide and calcium carbonate,

possibly indicating a composite pigment. Whatever the exact type of pigment, it is clear from PAII staining that the middle layer of the sample contains severely photocatalytic material which, based on the instrumental analysis and earlier data, is likely an uncoated anatase pigment. Because the paint layer is located between two other layers and is not reached by UV light, the risk of photocatalytic degradation of the material in this layer is minimal. Based on the earlier scanning electron microscopy (SEM) EDX data one of the other layers also contains titanium dioxide. If we examine the PAII results in Figure 3 carefully (P3, red boxes), the top layer (likely layer 3 in the previous SEM-EDX data) does also show color change but at a slower rate. This could be related to the fact that this layer contains a different type of TiO_2 and also to the fact that this layer contains other white pigments and fillers diluting the color change effect (Table 2). The PAII staining method provides an unambiguous and spatially resolved indication of the presence of photocatalytic material.

Practically, the test will often be assessed visually using photographs such as those presented in Figures 2 and 3. Initial set-up of the test requires an evaluation of the time to discoloration and the visual extent of the change, highly dependent on the UV

Table 2. Supporting analysis on samples from paintings.

Painting	XRF[a]	XRD	STEM-EDX[b]	Other
P1	(S), (Ca), Ti, Ba, Zn, Sr	ZnO, Anatase, BaSO₄, SrSO₄	BaSO (Sr associated), TiO_2, ZnO, Zn-organic (soap? Needle like structure), Al (0.3at%) and Si(0-0.1at%) associated with TiO_2	n/a[c]
P2	(Ca), Ti, Ba, Zn, (Pb), (Sr), (Nb), (Zr)	Anatase, ZnO	n/a	n/a
P3[d]	n/a	Anatase and rutile (data from 2012).	Zn (omnipresent, does not look like particles), Ca, Ti uncoated (Ti/Ca possibly composite), Ba, clay, Al (omnipresent).	SEM-EDX (data from 2012): 3 layers containing Ca (1), Ti + (Ca) (2), Ti + Ba + Zn + S (3)

[a]Elements reported in brackets indicate low elemental peaks in XRF.
[b]at% = atomic percentage.
[c]n/a = not applicable; the specific analysis was not performed on that sample.
[d]The exact location of sample P3 is unknown; it is suggested to be from the frame due to the presence of wood fibers identified by FTIR. Since analysis was performed on several samples in different campaigns of research, the precise correlation of the data summarized in the table to the layers observed in cross section P3 is not known with certainty.

source. This time and extent of color change can be assessed in relation to a standard pigment known to be photocatalytic. However, further visual PAII testing does not require simultaneous analysis of a reference sample. The qualitative method is completely valid but less applicable for comparison of a set of samples. For comparison, quantitative analysis is more accurate.

Quantitative and comparative assessment of color change

 Figure 4 displays the complete dataset collected under standard conditions ('RMA' microscope; UV 10%; magnification 50x, excluding R6a for which 25x was used). In this figure we show the ΔRGB_r for each time point (0–90 min). An accurate classification of photocatalytic materials can be made after five minutes of irradiation. This result confirms the speed benefit of this test as reported by Mills et al. (2005–2017) on a microscopic system such as a paint sample. Generally, the rate of color change can be empirically divided into four categories after five minutes: the paints causing no change or a negative change (A); the paints causing an immediate but minor visually perceptible change (B); the paints causing a well noticeable change (C); and the paints causing a major change (D). All samples reach a correct 'yes' or 'no' classification based on prior testing of the pigment's photocatalytic activities and aging behavior, under the criterion *color change = photocatalytic material present*. However, two samples do not exactly follow the expected behavior (van Driel et al. 2018b). The one sample which was based solely on ZnO (R8) shows much less photocatalytic discoloration than expected, based on previous artificial aging studies under UV, where it showed similar oil degradation rates to uncoated anatase. This unexpected behavior may be caused by the difference between irradiation under a broad or narrow UV source (Kobayashi and Kalriess 1997; Sakthivel et al. 2003; ;van Driel et al. 2018b); by inhibiting the reaction of the photogenerated election with atmospheric oxygen (Mills, Wells, and O'Rourke 2017); or by the electronic structure of ZnO, which dictates the recombination processes (Artesani et al. 2016). On the other hand, organically coated anatase (CA(org), R2) was expected to display less discoloration than uncoated anatase (van Driel et al. 2018b) but it falls into the same category. This may be due to the fact that the pigment is coated with a soft organic coating, possibly removed during sample preparation (polishing).

As expected for a proof of principle stage, the method (sample preparation and testing) is not accurate enough to investigate minor changes such as those corresponding to a range of different pigment volume concentrations of uncoated anatase (samples within category D, R1a, R1b, and R1c). Variability can be related to several factors such as the amount of active material present at the polished surface, the paint porosity (related to composition, binding medium, and age), and the exact amount of ink applied.

In category A (photostable and inert pigments), a small negative ΔRGB_r is presented (0–30 min), followed by a positive ΔRGB_r (60–90 min). The negative ΔRGB_r is not visually noticeable in the photographs (Figure 2). This change is not completely understood but could be due to the process of extraction of the RGB values, to the absorption or drying process of the ink in the support, and/or to the measurement error induced by the low hiding power of barium sulfate. The positive ΔRGB_r at longer time scales (60–90 min), on the other hand, is visible in the microscopic photographs and is suggested to be caused by processes other than photocatalytic dye reduction. These could be photolysis or dye sensitization processes causing direct photodegradation of the ink at longer irradiation times (Mills, Wells, and O'Rourke 2017). These processes do not compromise successful 'yes' or 'no' classification at shorter times.

While classification in this study was straightforward, it is possible that a minor amount of photocatalytic material or a low photocatalytic activity material remains unnoticed (false negative). However, these circumstances are also less likely to cause damage to the paint.

Measurement set-up & repeatability

In this study the main sample set was evaluated with a microscope ('RMA') equipped with a stable LED light (aging magnification: 50x) and equipped with in-house color calibration software. To evaluate if this high quality set-up is required, we compared the qualitative classification when performed with a standard microscope, equipped with a halogen lamp and without color correction ('RCE'). This comparison was performed on a subset of three reference samples: photostable (coated rutile R6b), photocatalytic (uncoated anatase R1b) and, based on the PAII staining, moderately photoactive (mixed tube paint R5a). These samples were chosen because they represent different speeds of degradation (no change (A)/mid (C)/high change (D)). Figure 5 indicates that the same order of photocatalytic activity is obtained with both set-ups. The samples investigated on the 'RCE' microscope did show slower color change: this is due to a difference in irradiation conditions. The samples on the 'RMA' microscope are irradiated with a UV source connected to the microscope that has an intensity of 2.29 mW/cm^2, while the samples on the 'RCE' microscope were irradiated with an external UV source with an intensity of 1.4 mW/cm^2. For photosensitive pigments, the higher intensity of UV consistently gave a higher speed of color change. When performing the test
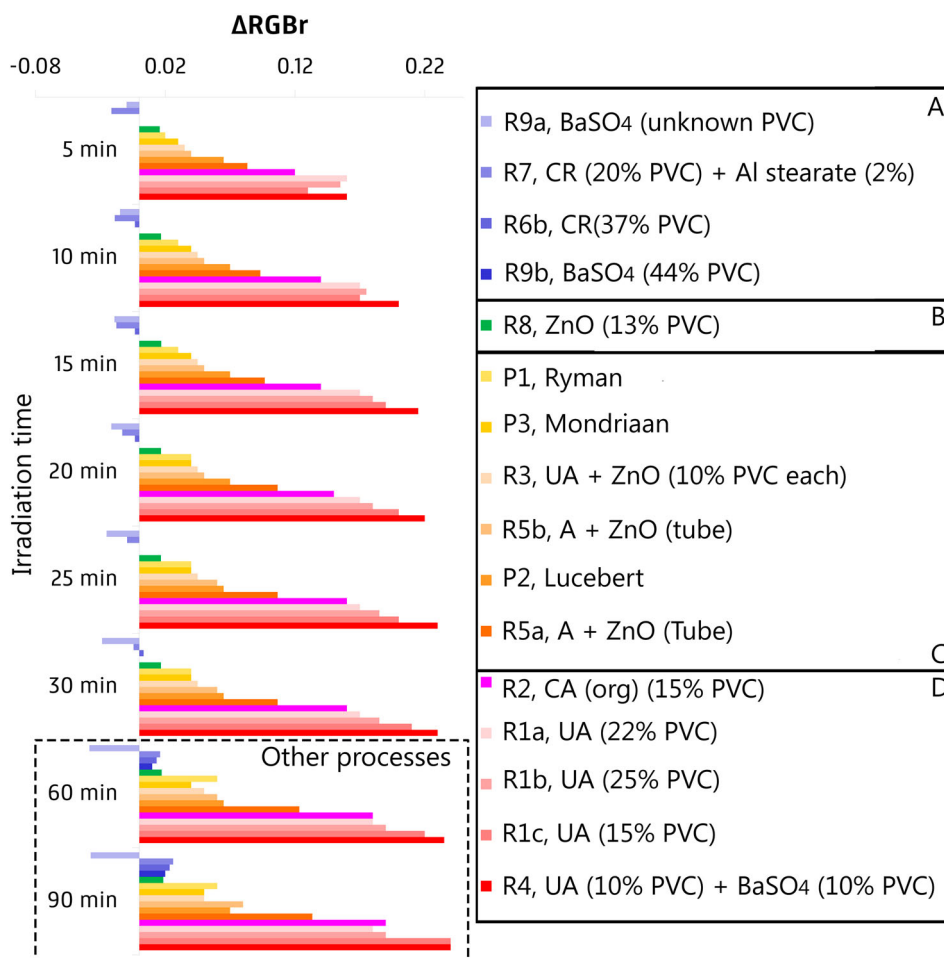
Figure 4. Complete dataset acquired via standard procedure (ΔRGB_r at all the different time intervals: 5, 10, 15, 20, 25, 30, 60, 90 min). If the sample was repeated, the average is shown. Four categories were discerned: A, stable; B, minor change; C, medium change; D, major change. At longer irradiation times (60, 90 min) other processes start to play a role (see text).

with a different UV source, or under other different conditions, the expected time to notice color change should be evaluated using references of known photocatalytic activity.

Figure 6 shows the repeatability of the measurements on both set-ups. Again, we present a subset of the data, in this case only looking at samples containing active pigments. The samples were polished between measurements. Depending on the amount of active material present at the polished surface, the consistency of the measurement conditions, and the exact amount of ink applied, variability will be introduced. Despite these variable factors the repeatability of the test is as good as can realistically be expected for both microscopes.

Outlook

In an effort to work towards a more quantitative method, further research on characterized reference samples is required. This research should involve investigations into the polished surface, the porosity of the ink support, the presence of different binding media, the influence of the environment (including pH), the influence of other components in the paint (additives, driers) and the interaction with other semiconductor pigments. Concrete questions that came up during this study also need to be investigated. These included photolysis processes that play a role at longer time scales as well as the predictive power of the test for organically coated titanium dioxide or zinc oxide containing samples. To confirm whether the organic coating of CA(org) is polished away, possibly giving a false positive PAII result, the test could be performed on an unmounted paint fragment for comparison. Furthermore, to understand more fully the behavior of ZnO, different well-characterized ZnO pigments with known photocatalytic behavior should be investigated at different irradiation conditions, with and without access to atmospheric oxygen.

Other improvements could include automated color extraction, or the use of photocatalytic indicator labels (currently under development by Mills et al.), which would address issues of unstandardized data processing and unrepeatable application. If these labels were small and easy to remove, one could even envision applicability on the actual paint surface without taking a sample, rendering the method non-invasive.
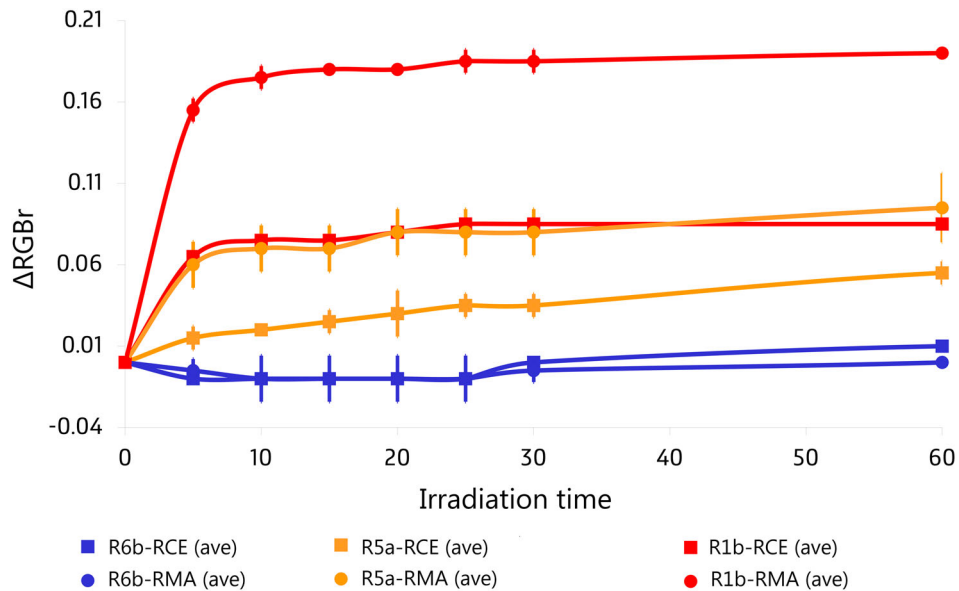
Figure 5. ΔRGB_r for stable, medium photocatalytic and high photocatalytic samples on both microscopes (RMA/RCE) indicating no color change, mid-range color change, and high color change, respectively. The classified order is identical for both measurement set-ups.
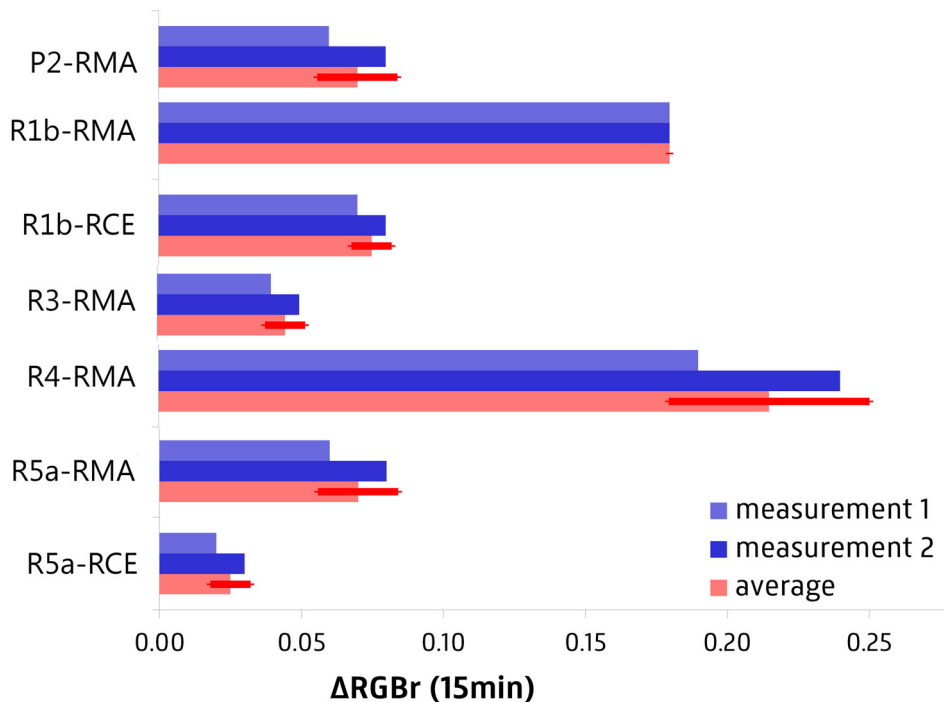

Figure 6. Repeatability of measurements on samples containing photocatalytic pigments. ΔRGB_r(15 min) is presented for measurements 1, 2, and the average, including standard deviation.

Conclusion

In this study we demonstrated the proof of principle for the use of BB66 PAII staining for the determination of the presence of photocatalytic material in embedded paint and cross section samples. The method shows a good qualitative classification within five minutes and can spatially resolve different layers. The quantitative assessment indicates promising repeatability, for two measurement set-ups tested (differing in the type of microscope and UV source).

At this stage, the test has several limitations related to the quantitative assessment of the results. Firstly, the test cannot distinguish differences in amount of photo-catalytic material (pigment volume concentration). Secondly, the limited test results for zinc oxide paints and organically coated anatase paints are not consistent with known degradation behavior. Thirdly, paints with admixed colored pigments may not be amenable to the test. Despite these limitations, the qualitative test can be used successfully by conservators with a microscope routinely used for the study of paint cross

sections. However, quantitative interpretation will be challenged by the fact that each sample from an object will be unknown and inhomogeneous. Further development of the quantitative application of the test, to rank photocatalytic activity on a continuous scale rather than with a discrete 'yes' or 'no', should be performed on well characterized and self-made references.

This paper is the first step towards implementation of the qualitative interpretation of PAII staining in conservation practice and the further development of the quantitative interpretation of the test. Samples from paintings are widely available in studios and laboratories across the world. Applying this method on these samples, in a standardized manner, would reveal valuable and immediately applicable information about the risk of degradation of those paintings.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Appendix

RGB extraction

Using the open source software Image J (https://imagej.nih.gov/ij/, 1997–2016) the following steps can be followed for RGB extraction:

- Convert a set of photographs to a stack (Image/Stacks/Image_to_stack)
- Split the single photograph or stack in separate color images for red, green, and blue
    o Open ROI manager (Analyze/Tools/ROI manager)
    o Click Rectangular Tool and select the region to be measured
    o Add to ROI manager
    o Copy ROI to other photographs (each photograph has its own ROI manager window)
    o Click RGB/Merge Split Tool
- Measure R: ROI manager → Measure
- Measure G: ROI manager → Measure
- Measure B: ROI manager → Measure

Because the region of interest (ROI) is duplicated for each photograph, slight movement of the photograph can result in a shifted region of interest, which may affect the extracted RGB values. This is particularly significant when analysing small regions (for example in thin paint layers). To account for this variability RGB values over several (large and small) regions of interest are averaged. In the future automated RGB extraction may address this variability.