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VANESSA JOHNSON, JANE COLBOURNE, AND KATE NICHOLSON

A Digital Imaging Tool for Identifying Photoactive Zinc Oxide Watercolor Pigments

INTRODUCTION

Chinese white is a zinc oxide watercolor pigment made popular in the last half of the 19th century. Zinc oxide's photocatalytic properties and the resultant degradation on paper have only recently appeared in conservation literature (Hey 1987; Daniels 1990), and while zinc oxide–induced degradation in works of art on paper has been documented in various case studies (e.g., Kemp, Wise, and Hamilton 2004; Singer and Liddie 2005), some works of art on paper containing this photoactive pigment remain pristine more than a century after their creation. Variation in zinc oxide's photoactivity is tied to the variation in its UV-induced fluorescence, a well-established relationship in the literature (e.g., Winter and Whittem 1950; Klingshirn 2007; Clementi et al. 2012; Artesani et al. 2017, 2018) but one that is presently underutilized by paper conservators. Guides to pigment identification using UV-induced fluorescence typically only mention one fluorescent color for zinc oxide, and there is great disagreement between sources, with some describing fluorescence as yellow (Carden 1991; Cosentino 2014), blue (Isacco and Darrah 1993), and ranging from "orange-buff" to "bright apple green" (Nagle 1928, 307). This study aims to characterize the UV-induced visible fluorescence of zinc oxide watercolor pigments via fluorimetry and digital image analysis and tie these results to photoactivity in both mock-up and historic case study zinc oxide watercolor paints on paper. Digital image analysis of artworks illuminated by various wavelengths of light is a common practice among conservators and a low-cost method of identifying artists' materials, and while other methods are needed to verify the results of this preliminary identification, the method is promising for characterizing the photoactivity of zinc oxide pigments in artworks where its presence has been verified.

Zinc oxide watercolor paints were first introduced commercially by Winsor & Newton in 1834. Marketed as "Chinese white," the newly available white pigment led to a shift away from transparent watercolor painting in England in the latter half of the 19th century. Artists utilized Chinese white for highlights or mixed it with tints to create opaque body colors, which approximated the diffusely reflecting surfaces of oil paints (Avery 2002). This new style was promoted in many artists' manuals, which were publications meant to instruct the amateur artist in painting techniques. John Ruskin was an especially popular publisher of these manuals, and his writing influenced artists both in the UK and the United States to use the new zinc oxide pigment in their watercolors (Ruskin 1858).

ZINC OXIDE PRODUCTION METHODS

Chinese white was widely regarded as a chemically stable alternative to lead white in watercolors for more than a century; however, many watercolor paintings and pastels that contain these zinc oxide pigments have become visibly degraded in both the paint film and adjacent paper support. This degradation stems from zinc oxide's semiconducting properties, which are in turn dictated by the production method used.

Zinc oxide pigments have primarily been produced by one of two production methods: the *indirect* or French method and the *direct* or American method. The methods yield pigments with different crystallite sizes and morphologies, crystallinities, and electrical surface activity leading to reactions with surrounding materials. The *indirect* method was developed in France by Stanislas Sorel and E.C. Leclaire in 1840 and was the first method patented for mass-producing zinc oxide pigments (Remington and Francis 1954; Downs 1976). The method involves boiling zinc-containing ore, then igniting the zinc vapor in an oxygen-rich atmosphere and collecting the resultant pigment in a series of hoppers, which gather pigments of similar density and quality. These pigment crystallites range from 30 to 2000 nm in size, are nodular in

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shape, and have good crystallinity. The abundance of oxygen in the ignition chamber ensures a near-perfect 1:1 ratio of zinc-to-oxygen ions in the resultant pigment (Fleury 1912; Moezzi, McDonagh, and Cortie 2012). Although the pigments produced by this method in the 19th century could be made in abundance and with very high purity and bright white color, they remained too expensive for the American market.

The *direct* method of pigment production was developed in 1850 by the New Jersey Zinc Company to bypass the need to import zinc oxide pigments from France at great expense. They developed their production method by roasting zinc ores in a coal bed, resulting in zinc vapor and carbon monoxide. These were oxidized in an ignition chamber to produce zinc oxide and carbon dioxide. These pigments particles were needle-like and larger than *indirect* method particles, as well as lower in purity and less white but cheaper to produce. These pigments also had more surface defects, favoring an abundance of zinc ions as oxygen was only introduced at the end of the production process (Auer, Griebler, and Jahn 2005).

Both *indirect* method pigments and *direct* method pigments were sometimes annealed to remove impurities and improve their working properties. This annealing was often done in an anoxic chamber, which removed oxygen ions and volatile impurities from the polar surfaces (Auer, Griebler, and Jahn 2005). The literature suggests that the best pigments were annealed, with Arthur Hebert Church suggesting in his book *The Chemistry of Paints and Paintings* (1890) that the whitest, densest pigments were subjected to "powerful mechanical compression when red-hot" (135), whereas Winsor & Newton claims on their website that their 19th-century pigment was heated "to a very high temperature" that "produced the first real alternative white with good opacity" (Winsor & Newton 2011). The reason for annealing was primarily to improve working properties and opacity, although the process also ensured that pigments were not electrically active on their surfaces, a property of zinc oxide only understood in the 20th century after physicists began studying zinc oxide as a semiconductor.

PHOTOCATALYTIC PROPERTIES OF ZINC OXIDE

Zinc oxide is an *n-type* semiconductor, meaning it tends to maintain an abundance of electrons on its surface. These electrons are provided by the occupied valence orbitals of oxygen ions and comprise the valence band. When illuminated by a sufficiently energetic wavelength of light, these valence band electrons cross an energy gap into the unoccupied valence orbitals of the zinc ions where they become conductive, moving freely across the surface and filling what is known as the conductance band. After losing enough energy, they fall back to lower energy states.

When electrons are excited into the conductance band, they leave behind a "hole" (h^+) or positively charged space in the crystal lattice. Both excited electrons and holes are free to react with adsorbed oxygen and water. Initially, two reactions occur. An oxidation reaction occurs when holes prompt adsorbed water to dissociate (Dodd et al. 2006; Jacobs et al. 2017):

(1) Oxidation reaction: $H_2O + h^+ \rightarrow \bullet\, OH + H^+$

A reduction reaction involves the chemisorption of oxygen onto the particle surface via an excited electron (e^-), resulting in the creation of a superoxide (Dodd et al. 2006; Jacobs et al. 2017):

(2) Reduction reaction: $O_2 + e^- \rightarrow O^-_2$

Both reactions (1) and (2) create highly reactive products in hydroxyl radicals and superoxides, which can additionally combine with another surface electron to form hydrogen peroxide (Singh, Saha, and Pal 2015):

(3) $O^-_2 + 2H^+ + e^- \rightarrow H_2O_2$

Finally, another hydroxyl radical can form when hydrogen peroxide reacts with a proton formed in reaction (1) and another surface electron (Singh, Saha, and Pal 2015):

(4) $H_2O_2 + H^+ + e^- \rightarrow \bullet\, OH + H_2O$

Surface electrons and the holes they leave behind are the primary driver of reactions (1) through (4). Annealing zinc oxide pigments removes oxygen ions from the surface, decreasing overall electrical activity and increasing both oxygen defects and defects caused by shifting of surface zinc ions into the crystal lattice or out of the crystal entirely (Wang et al. 2005; Srinivasan et al. 2008) (note 1). These defects also create energetic traps for excited electrons to fall into. These trap states are within the band gap, meaning electrons spend less time on pigment particle surfaces before relaxing into these shallow trap states. In the absence of defects, Zhu et al. found that excited electrons could participate "in possible photocatalytic reactions rather than to recombine at the shallow energy levels of planar defects" (2014, 1).

DEGRADATION IN WATERCOLORS

Reactions (1) through (4) manifest in four distinct types of degradation in zinc oxide watercolors on paper: sulfate salt formation, screening of the paper support from UV damage, browning and embrittlement of the paper support, and cracking of the paint layer.

Sulfate Salt Formation

Sulfate salt formation occurs in the presence of sulfur dioxide or sulfuric acid, common industrial pollutants that, along with water, convert zinc oxide to zinc sulfide. The hydrogen peroxide formed in reaction (4) oxidizes zinc sulfide to form zinc sulfate mono or heptahydrate salts (Singer and Liddie 2005; Ebert, Singer, and Grimaldi 2012). These salts are deposited on the image surface in a process called *efflorescence* and can form pale halos if they are dissolved in high-humidity environments and migrate outward into the surrounding paper (Colbourne 2006) (fig. 1).

Paper Screening

Zinc oxide also screens paper from UV-induced photolysis by strongly absorbing wavelengths of light below ~390 nm (Stutz 1925; Bacci et al. 2007). This is the energy required for electrons to jump into the conductance band, meaning the more UV absorbent the pigment, the more reactive. UV screening manifests as distinct changes in paper tone from dark exposed paper to lighter paper where the pigment has been applied. At the pigment boundary, the paper can become brittle and strained due to varying rates of expansion and contraction due to moisture.

Paper Browning

Paper beneath and adjacent to zinc oxide pigments can become discolored via oxidation of cellulose hydroxide side groups (Daruwalla and Narsian 1966; Conte et al. 2012). First, as in the left side of reaction (4), hydrogen peroxide and an electron from zinc oxide's conductance band remove hydrogen from a hydroxide side group, leaving a carbonyl and creating a hydroxyl radical. These carbonyls increase the conjugated double bonds in cellulose, leading to greater absorption of visible light.

Cracking of the Paint Layer

Cracking and loss of paint layers containing zinc oxide are common and likely caused by a combination of two processes: (1) expansion and contraction of the paint layer with changes in humidity leading to a loss of film elasticity and (2) changes to intermolecular interactions between polysaccharides resulting from hydrolysis of glycosidic bonds in the gum medium. A combination of acids in the aged papers, UV light, repeated exposure to moisture and drying, and oxidative products described in reactions (1) through (4) likely work together to reduce elasticity in the paint layer. Monosaccharides themselves appear to be very stable and do not change composition or structure with age (Bonaduce et al. 2007; Riedo, Scalarone, and Chiantore 2013).

FLUORESCENT PROPERTIES OF ZINC OXIDE

The same process of excitation and relaxation of electrons that catalyze reactions (1) through (4) can also cause the emission of a photon in a process known as fluorescence.

Fig. 1. *Left*: Detail of *General View of St. Mary's Cathedral, Iona* with sulfate salt efflorescence visible as needle-like blooms on the painting's surface. *Right*: Zinc sulfate salts have formed and dissolved into the paper, slowing the rate of paper discoloration and creating a pale halo. From Singer and Liddie (2005).

The wavelength of the emitted photon is proportional to the energy gap crossed upon relaxation. This energy is either the energy of the gap between the conductance and valence bands, known simply as the band gap, or the energy of the gap between the conductance band and a trap state, which in zinc oxide tends to be a lower energy than the bandgap energy. Both types of relaxation are associated with a color of fluorescence, whereas the perceived overall fluorescence is a combination of these two fluorescent colors.

Near-band-edge (blue) fluorescence. Electrons relaxing across the bandgap emit a blue-colored light centered at between ~370 and 390 nm (Chen et al. 2011; Bandopadhyay and Mitra 2015; Artesani et al. 2018). Called the near-band-edge emission, this blue fluorescence is associated with pigments containing fewer defects, as it results from transitions between zinc and oxygen ions. Additionally, this fluorescence emits primarily from one polar surface, indicating that it is more prominent in pigments with shorter crystallite lengths (Fabbri et al. 2014). Both pigment crystals with fewer defects and smaller, shorter crystallite lengths are typical traits of pigments produced by the *indirect* method of production.

Green fluorescence. Additional "trap" states formed by crystal defects and impurities (Van Dijken et al. 2000) cause electrons to relax to energy levels closer to the conductance band, resulting in a longer emitted wavelength. These longer wavelengths are broad bands in zinc oxide that appear green in color. Oxygen vacancies and zinc interstitials, or zinc ions in positions they do not normally occupy, have been linked with this green fluorescence (Kröger and Vink 1954; Janotti and Van de Walle 2009) and with shorter excitation times (Zhu et al. 2014; Penfold et al. 2018). These defects are common in pigments produced by the *direct* method and occur along the long *c* axis of the crystallite, meaning the longer particles typical of this process increase the contribution of green fluorescence (Fabbri et al. 2014). Additionally, annealing both *direct* and *indirect* pigments tends to reduce the blue fluorescence by increasing defects, causing a greater green contribution to overall fluorescence.

DIGITAL IMAGING IN CONSERVATION

Establishing the relationship between fluorescence and photoactivity prompts the question of utility for conservators who wish to use this information to prevent photocatalysis in watercolors containing zinc oxide. A fluorimeter could allow a conservator to compare the intensity of the blue and green peaks quantitatively but is not readily available to those conservators working privately or in smaller institutions. Digital imaging methods present a promising alternative, as they are already widely used to characterize fluorescing materials in artworks illuminated by UV light. Zinc oxide watercolors present good candidates for fluorescence analysis, as they do not generally contain varnish layers and the minor fluorescence of polysaccharide binding media is typically far less intense than the pigment fluorescence.

Several factors complicate digital imaging methods of characterizing UV fluorescence. Variations in digital image capture standards can lead to miscommunication about a pigment's fluorescence, whereas different camera sensitivities can lead to variations in perceived color. Paper fluorescence can also interfere with characterization of pigment fluorescence, as watercolor paints are by their nature always semitransparent, even when heavily applied. Regardless, the error introduced by these complications may not be so great as to invalidate the utility of the method.

METHODOLOGY

The following methodology was carried out to assess the viability of a digital imaging method for determining whether a zinc oxide pigment is relatively inert or highly photocatalytic. It first aimed to link rates of photocatalysis with fluorescence, then determine how reliably fluorescence could be linked with photocatalysis, thus gauging the utility in this case of digital imaging as a predictive tool.

Creation of Mock-Ups

Mock-up samples were created using three types of paper substrates and eight pigments in gum arabic binding medium. Whatman #1 filter paper was chosen because it is free from fillers and additives and contains only cotton fibers. A naturally aged (~40 years) highly sized Fabriano NOT (cold-pressed) cotton rag watercolor paper was also selected because it contained a fluorescent calcium carbonate filler as well as cotton and linen fibers that would not themselves contribute additionally to fluorescence. Finally, a mid-19th-century wove, mixed-fibered handmade paper from a folio was used because it did not contain fluorescent fillers but rather wood pulp and discolored, acidic degradation products.

All pigments were added to a 1:4 w/v mixture of Cornelissen-supplied gum arabic in distilled water, a ratio suggested by Seymour (2007). In addition, 0.2 g of pigment were added for every 1.5 mL of gum water. This produced a pigment-rich paint that resisted cracking and flaking upon drying. This was applied to a 1 × 2 cm square area.

The eight pigments studied are listed in figure 2 and represent three analytical grade *indirect* method pigments, three analytical grade *direct* method pigments, and two commercially sourced artists' pigments. A contemporary Winsor & Newton Chinese white was initially included in this study but was abandoned because it contained titanium dioxide, making it difficult to compare with other pigments and historic case studies. A control sample was painted onto all papers consisting of the gum arabic water.

Production Method	Sample Number	Pigment
Indirect	1	Zinc oxide red seal from Norkem Limited
	3	Zinc oxide high purity from Norkem Limited
	4	Zinc oxide white seal, code 28170000 from Brüggemann Chemical, Ludwig, Germany
Direct	6	Zinc oxide American Process from Norkem Limited
	7	Zinc oxide 2011 from Grillo-Werke AG
	9	Zinc oxide spezial, code 28170000 from Brüggemann Chemical, Ludwig, Germany
Unknown	15	Kremer Pigments Zinc White 46300
	16	Cornelissen Zinc White

Fig. 2. Mock-up pigments and production methods.

Case Studies

Five watercolor paintings from the mid-19th to early 20th century were studied and compared with mock-ups. Three pieces were visibly degraded due to zinc oxide pigments, whereas two did not appear to be affected by the presence of the pigment. These case studies are listed in figure 3. All case studies were confirmed to contain zinc oxide via energy-dispersive x-ray analysis of zinc and sulfur ions. A high zinc-to-sulfur ratio verified that the pigments were oxides and not sulfides or sulfate salts.

Particle Size and Morphological Analysis for Determining the Production Method

Crystallites, or individual crystals making up zinc oxide pigment particles, were measured for all mock-up samples and for three case studies: *S.S. Buda,* the ruin drawing, and the watercolor by Thomas Harper. This was to provide a point of comparison between unknown case study and mock-up pigments and mock-up pigments produced by known methods. Given the extremely small size of zinc oxide crystallites, a TESCAN MIRA3 scanning electron microscope was utilized to collect images of powders and in situ pigments using the secondary electron detector. Crystal morphologies were also characterized using four characteristics: pyramidal ends, rod-like shape, nodular or round crystallites, and acicular or needle-like crystallites.

Crystallites were measured in ImageJ using its scale and measure functions. Lengths and diameters were measured for 100 crystallites from each pigment and calculations carried out assuming cylindrical geometry. Size values were obtained by calculating the cube root of volume. A similar method was carried out by Li and Haneda (2003), who measured 200 crystallites in the same way to obtain size ranges for zinc oxide pigments.

Inducing Photocatalysis in Mock-Ups

Samples were exposed to light in a Q-SUN Xenon Test Chamber Xe-1 light aging machine with a xenon arc lamp tungsten bulb (1800 W). The temperature inside the machine was moderated at 25°C. Two UV filters were used, a Daylight Q and Window Q filter, which approximate indoor conditions and restrict the UV light present. The machine was calibrated to 1.1 W/m^2 at 420 nm. Mock-ups were placed on top of a layer of Gore-Tex, which allowed gradual humidification from a triple layer of dampened Whatman #1 filter paper. All test samples were exposed to a total of 50 hours of light (note 2) in 5-hour increments, with rewetting of Whatman paper occurring between each exposure. Samples were dried overnight between increments. This was partly out of necessity because the light aging machine could not be run overnight but would also induce deterioration to the paint layer by expanding and contracting the paint layer and paper substrate.

Characterizing Degradation Visually and with Russell-Grams

After light exposure, any visible degradation in mock-ups was documented and compared with case studies. Additionally, peroxides were detected on samples after light exposure using Russell-grams, a technique first described by Russell (1908).

Date	Title	Artist	Type of Visible Degradation	Collection
Early 20th century (dates unknown)	*Bouquet of Flowers*	Irene Kendal (dates unknown)	Paint cracking and cupping, areas of paint loss	National Trust, UK
Dates unknown (late 19th century)	*General View of St. Mary's Cathedral, Iona*	Unknown	Sulfate salt conversion, paper browning	Historic Environment Scotland
1899	*S.S. Buda*	George Thompson (dates unknown)	Sulfate salt conversion, paint loss, paper masking, halos	Private
Mid-19th century	*View of the River Coquet*	Thomas Harper (1820–1889)	None	Laing Gallery, Newcastle Upon Tyne
Late 19th century	Ruin drawing (title unknown)	Unknown	None	Study collection at Burt Hall, Northumbria University

Fig. 3. List of case studies and visible degradation.

This technique involved sensitizing lithographic film with a 1.5% ammonium hydroxide solution, then placing the dry film emulsion-side down over the mock-ups in a Russell-box (fig. 4). Any peroxides formed on the zinc oxide surfaces reduced the silver nitrate in the film, resulting in a dark, exposed area corresponding to areas of degradation (Russell 1908; Daniels 1986). The film was exposed for 36 hours, then developed with a 1:1 mixture of Kodak Xtol with water, agitated for 6 minutes, then fixed in a 1:4 solution of Structurix fixative with water and finally rinsed for 15 minutes. The resulting image was high contrast and clearly mapped areas of peroxide formation.

Fluorimetry

Emission spectra were collected for mock-up samples on Whatman and folio paper using a Horiba FluoroMax 4 spectrofluorometer with excitation wavelength of 325 nm, slit opening of 2 nm, an output range of 335 to 640 nm, and a 60° angle of detection. Spectra were corrected for dark count by dividing the counts per second by microamps as measured by the reference detector. An average spectrum was created from the three spectra collected with highest return, as this represented the thickest painted regions. Minimum values were subtracted to correct the baseline, and area was normalized to 1 to facilitate peak area comparisons. The range of wavelengths was limited from 370 to 640 nm for *indirect* and commercial pigments and from 380 to 640 nm for *direct* method pigments, as this eliminated noise to either side of the main two peaks.

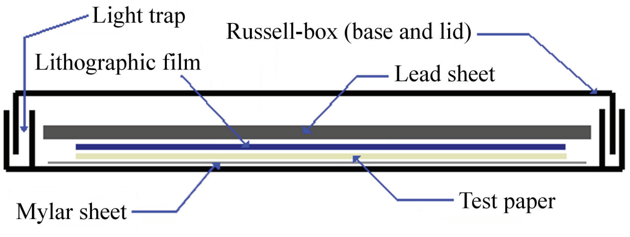

Fig. 4. Schematic for Russell-gram, following established method by William J. Russell (1908).

The processed spectra were analyzed using an Interactive Peak Fitter developed by Professor Tom O'Haver at the University of Maryland for use in MATLAB. Two Gaussian peak shapes were input and the peak fitter returned component peaks, as well as peak locations, heights, areas, R^2 values, and error percentages. These were compared among mock-ups to identify trends.

Digital Imaging

Mock-up samples. Mock-up samples were imaged in a blacked-out room using a Canon EOS 6D digital camera with a CMOS imaging chip with a built-in IR filter and fitted with a Kodak Wratten 2e UV-cut-off filter over the lens that cut out wavelengths below 400 nm. Two Narva LT 36W/073 black-light blue UV lamps supplied light at 365 nm and were set up at 45° angles to the sample at about a meter distance while

Case Study	Cropped Size (pixels)	Exposure (seconds)	f/stop	Camera Distance (m)	Camera	Light Source
Irene Kendal	67 x 104	1	8	2	Canon 6D	Narva UV
Thomas Harper	731 x 434	0.5	5	1	Canon 6D	Narva UV
S.S. Buda	17 x 18	15	8	2	Canon 6D	Narva UV
St. Mary's	JC4 – 435 x 477 JC7 – 238 x 230	NA	NA	0.1	Huawei cell phone camera	365-nm UV torch, fluorescent room light
Ruin drawing	57 x 72	8	8	2	Canon 6D	Narva UV

Fig. 5. Case study image acquisition parameters.

the camera was placed 23 cm from the sample. Exposure time was maintained at 0.5 seconds, white balance at 8000K, and ISO at 200. F-stop was adjusted for each paper type to avoid overexposure and was set to the following: 5.0 for Whatman paper, 6.3 for Fabriano paper, and 4.5 for Folio paper.

Images were cropped to 869 × 674 pixels and nonpigmented areas subtracted in ImageJ using a background subtraction methodology outlined in the appendix. RGB pixel intensity values were extracted, and both mean and median values for each channel were obtained in MATLAB. Normal distribution was assured by comparing the two values. Mean green intensity values were divided by mean blue intensity values from the same sample to characterize fluorescence from digital image data and determine if changes to these ratios occurred with light exposure or correlated to degradation.

Case studies. Imaging parameters for case studies varied, as they could not always be imaged in the photographic studio used for mock-up image acquisition. ISO was maintained at 200, but other parameters changed. These are shown in figure 5. Images were processed like mock-ups, although fluorescing areas were cropped to exclude paper, and therefore background subtraction was unnecessary.

RESULTS

Determination of the Production Method

Mean size values yielded a clear trend with all unknown pigments appearing most like analytical *indirect* method zinc oxides (fig. 6). This included both commercial artists' pigments and pigments from three of the five case studies. Two

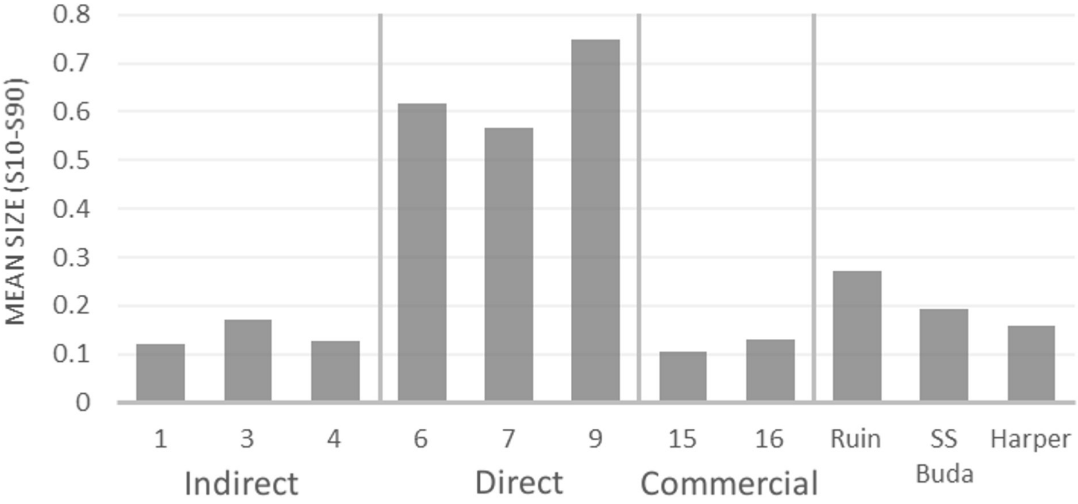

Fig. 6. Mean crystallite sizes for mock-up pigments and three case study pigments. Means exclude lowest and highest 10% of particles to eliminate skewing by outliers.

Sample	Pyramids	Rod-Like	Nodular	Acicular
1		●	●	
3		●	●	
4		●	●	
6	●	●		●
7	●	●		●
9	●	●		●
15		●	●	
16		●	●	
Ruin drawing		●	●	
Thomas Harper			●	
S.S. Buda			●	

Fig. 7. Morphologies of mock-up and case study crystallites.

case studies could not be analyzed, as the pigments were too embedded in the binding medium for clear analysis.

All unknown pigments were also morphologically like *indirect* method zinc oxides, shown in figure 7 as samples 1, 3, and 4. Nodular pigments are typical of *indirect* method paint pigments (Morley-Smith 1950, 1958) and were not found in any *direct* method samples, shown as 6, 7, and 9.

Russell-Grams

Only zinc oxides on Whatman paper imaged well using the Russell-gram technique, whereas other papers tended to image as black as the pigments. Two of each *indirect* and *direct* method analytical samples were imaged as well as both commercial artists' pigments. Developed images of these samples after 50 hours of light exposure showed very little to no peroxide formation on *direct* method pigments, whereas *indirect* method and commercial pigments both imaged darkly, indicating high levels of peroxide formation (fig. 8).

Visual Signs of Degradation

Two visible signs of degradation were observed in mock-ups after light exposure: paper browning and paint cracking. Browning was observed only on Whatman paper mock-ups, which all browned except *indirect* pigment 1. Browning on the verso was most severe for *indirect* samples 3 and 4. Paint cracking occurred in all samples on Fabriano and Folio papers except for commercial pigment 15 on Fabriano paper. Gum arabic control areas did not visibly change after light exposure.

Fluorimetry

Peak area ratios were calculated by dividing the areas of the green peaks by the blue peak areas. Doing so divided samples into two types: type 1 ratios were at or below 5 and included all but one *indirect* sample, including commercial pigments. Type 2 had ratios above 6, typically greater than 10, and included all *direct* method samples and *indirect* sample 1 (fig. 9). These ratios typically decreased in type 1 pigments and increased for type 2 pigments, except for *indirect* sample 3 on Whatman in the former case and *indirect* sample 1 on Whatman in the latter. *Direct* method sample 9 had a ratio in the hundreds due to the nearly complete absence of any blue peak.

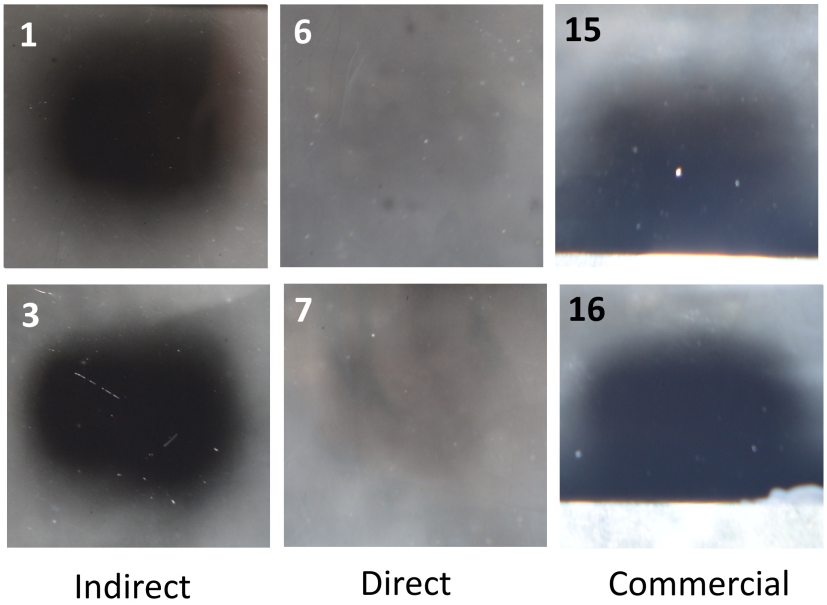

Fig. 8. Russell-grams of mock-up samples. Areas of peroxide formation image black.

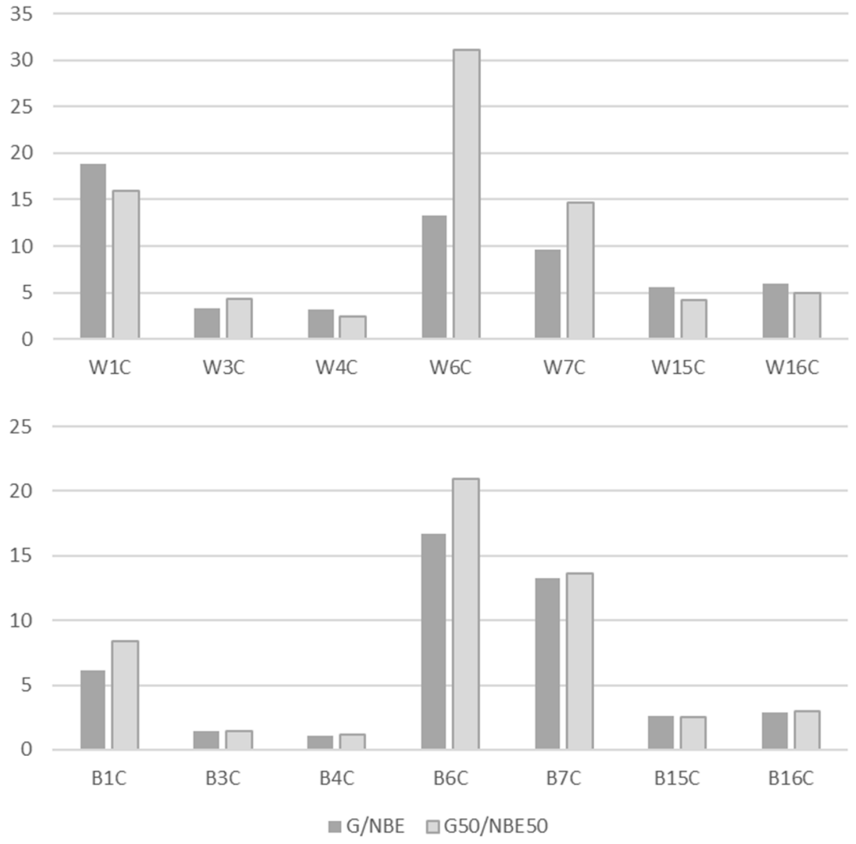

Fig. 9. Ratios of green-to-blue (near-band-edge or NBE) peak areas calculated using Tom O'Haver's Interactive Peak Fitter. W = Whatman #1 paper, B = Folio paper. Dark gray bars = unexposed samples, and light gray bars = after 50 hours of light and moisture exposure.

The two types were also distinguishable by peak shape. Type 1 contained a distinct blue peak of much higher intensity than the green peak, whereas type 2 contained a small blue peak and a strong green peak. Only *indirect* method pigments are represented by type 1, whereas type 2 contains all *direct* method pigments and one *indirect* method pigment (fig. 10).

Digital Image Analysis

Whatman paper mock-ups. Green/blue color channel ratios increased after light exposure for all pigments on Whatman paper except the control gum on paper, which decreased. This indicates that the increase was due to changes to the pigment and not the paper substrate. The green/blue ratios also grouped the pigments into the same two fluorescent types, as were observed using fluorimetry, apart from sample 9, which was grouped with type 1. This first type had a ratio below 1.7, whereas type 2 pigments had ratios over 1.7 (fig. 11).

Fabriano paper mock-ups. Changes in fluorescence on Fabriano paper after light exposure varied, and visible changes to pigment fluorescence were less obvious than the paints on Whatman paper. The two fluorescent types were still discernible, with type 1 maintaining ratios below 1.6 and type 2 above 1.6 (fig. 11)

Folio paper mock-ups. Green/blue ratios consistently decreased after light exposure for all pigments on Folio paper except *indirect* method sample 1. This trend was also seen in the control gum arabic painted onto Folio paper. This indicates that the decrease is likely due to the paper and not the pigments themselves in most cases. Green/blue ratios fell at or below 1.6 for type 1 pigments including sample 9, whereas Type 2 were above 1.6 (fig. 11).

Case studies. All green/blue ratios calculated from case studies were less than 1.6. The lowest ratios were from *General View of St. Mary's Cathedral, Iona*, followed by the Irene Kendal watercolor, then *S.S. Buda,* the ruin drawing, and finally the Thomas Harper piece with the highest ratio (fig. 12).

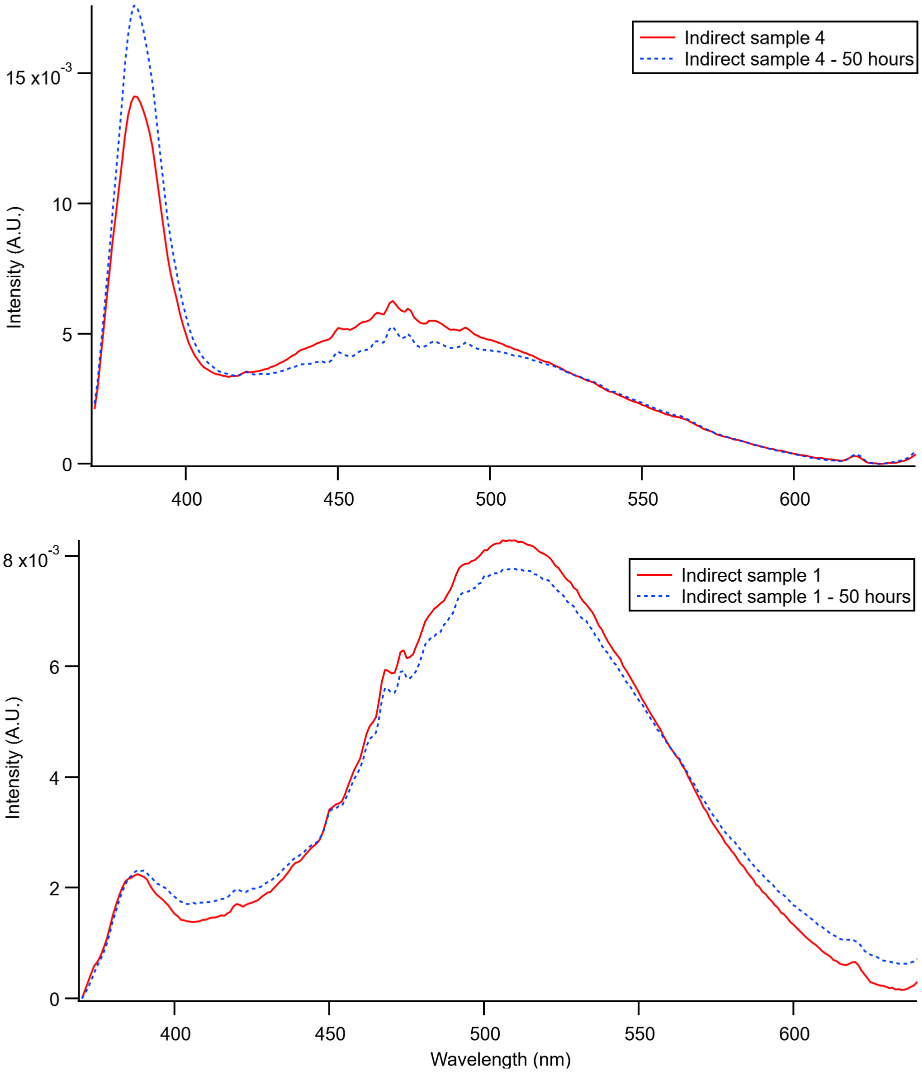

Fig. 10. Typical emission spectra for type 1 (top) and type 2 (bottom) pigments.

DISCUSSION

Relationship Between Fluorescent and Degradation Types

A strong negative correlation of -0.805 was found between the green/blue sRGB color channel ratios from Whatman paper and peroxide formation. Although the data set is small, this indicates that digital imaging may be a reliable indicator of photoactivity. Browning did not correlate well with green/blue sRGB color channel ratios, a trait that may be explained by the role of paper size in degradation type observed. Irradiated mock-ups on Whatman paper exhibited paper browning, whereas paints on Fabriano and Folio cracked after irradiation. This pattern of degradation is observable in those case studies in which the pigments have sunk into the page or appear to sit within the fibers. These pigments have, over time, caused browning of the paper, as in the case of *General View of St. Mary's Cathedral, Iona*. Irene Kendal's *Bouquet of Flowers* instead has severe paint cracking and loss. The type of degradation observed in photoactive pigments appears to be related to the degree of sizing in the paper sheet on which it has been painted. Where pigment sinks into paper fibers, these fibers interact more readily with peroxides forming on pigment surfaces and oxidize, eventually becoming brown. Sized papers are somewhat protected by the paint layer itself that sits primarily on top of the paper sheet and forms peroxides on the exposed surface of the paint film. These reactions, along with wet-dry cycles, cause cracking, cupping, and pigment loss.

Standardizing Acquisition Parameters and Processing Methods

Further development of an image processing tool requires standardization of image acquisition parameters. Dyer, Verri,

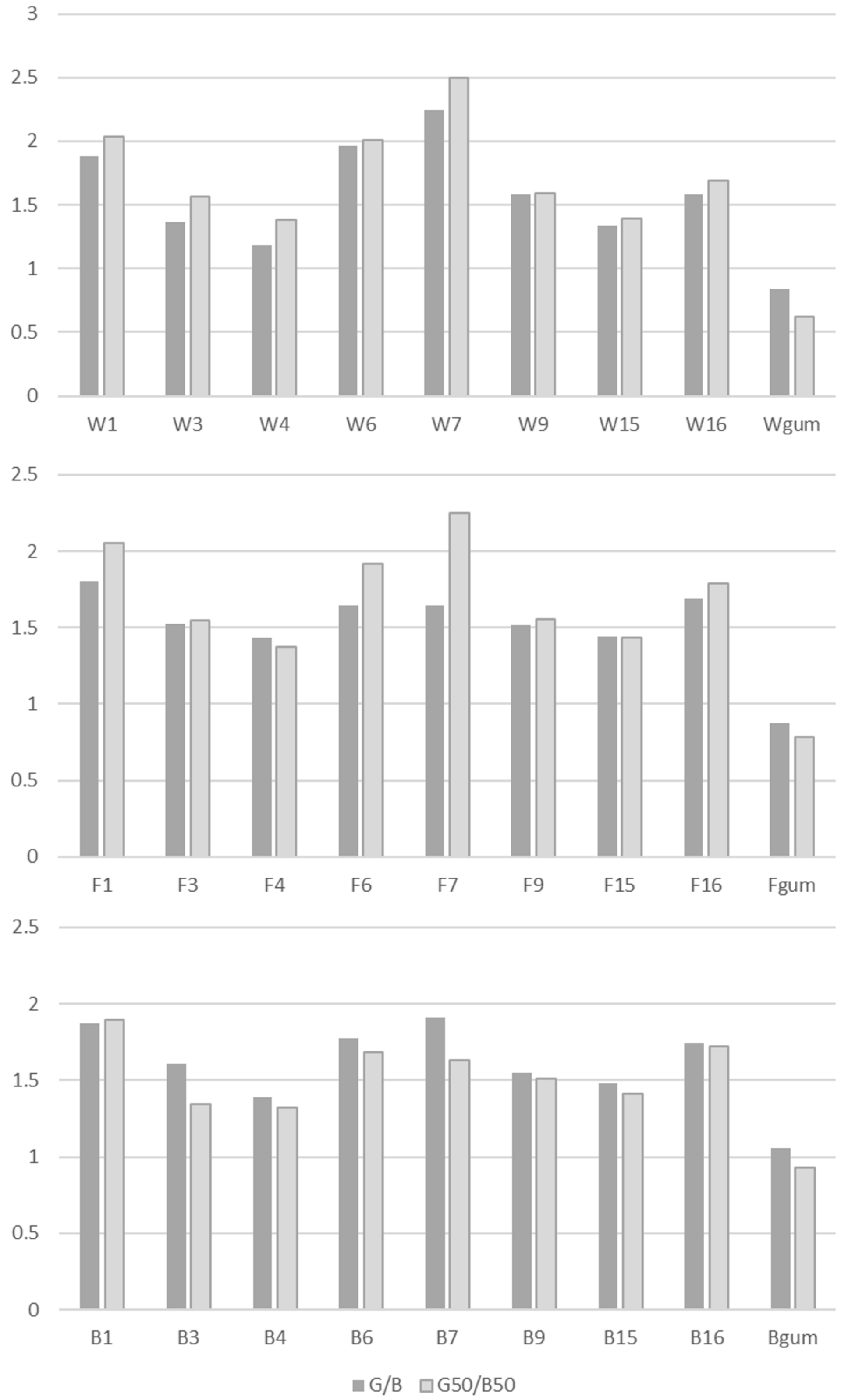

Fig. 11. Ratios of green-to-blue sRGB color channel ratios from digital images of mock-up samples. W = Whatman #1 paper, F = Fabriano paper, B = Folio paper. Dark gray bars = unexposed samples and light gray bars = after 50 hours of light and moisture exposure.

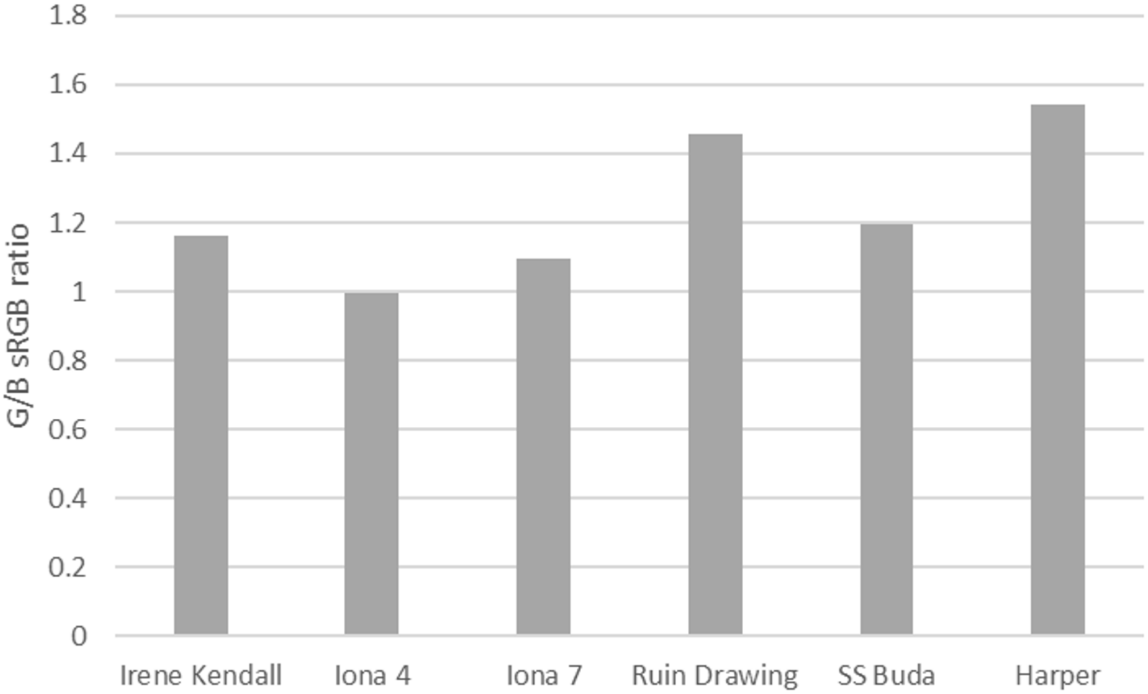

Fig. 12. Ratios of green-to-blue sRGB color channel ratios from digital images of case studies. Iona 4 and Iona 7 were both collected from *General View of St. Mary's Cathedral, Iona.*

and Cupitt (2013) outlined an ideal workflow for acquiring and processing UV-induced visible fluorescence digital images:

1. Image capture
2. Correction for uneven surface illumination
3. Correction for camera response using a Macbeth color chart in visible light
4. Correction for ambient light
5. Correction for changes to fluorescence due to pigment-binder interactions

Standardizing UV lighting and UV-cut-off filters is a simple first step, as is eliminating other light sources from the image acquisition area. Following procedures for steps 2 through 4 will eliminate most contributions to differences between imaging setups. Step 5 accounts for interfering fluorescence from binders and substrates. Inputs from UV reflectance grayscale references were input by Dyer, Verri, and Cupitt (2013) into a modified Kubelka-Munk equation to correct images pixel by pixel. This method was utilized effectively to obtain qualitative data for opaque paint layers but presents issues when applied to watercolors. In theory, the absorption coefficient in the Kubelka-Munk equation allows for image correction of semiopaque paint layers, but this coefficient cannot be determined for watercolors, as it requires a thickness value. Watercolor paints permeate the paper substrate and do not form cohesive layers that can be measured for thickness. A correction for fluorescing underlying paper may not be possible utilizing the Kubelka-Munk equation given this complication. Rather, an image processing method may require that paper substrates not be overly fluorescent in comparison to applied paints. Given that paper fluorescence appeared to reduce significantly with light exposure, and that historic case study papers were not very fluorescent, historic artworks may not in fact suffer from the complication presented by a highly fluorescent substrate. Even if a zinc oxide watercolor wash were semitransparent, the intensity of its fluorescence compared with the substrate may in fact allow for image processing using green/blue sRGB color ratios.

Current Pigment Manufacturing Trends

All commercial artists' pigments in this study and analyzed case study pigments proved to be produced by the *indirect* method of production. Although it has been established that these pigments tend to be photoactive and that annealing can in fact reduce the photoactivity of zinc oxide, the commercial pigments studied do not appear to be annealed. Additionally, the permanence rating for watercolors is still based on the tendency to fade, a metric that cannot be applied to a white pigment. Winsor & Newton give zinc oxide a permanence rating of AA, or Extremely Permanent. No mention is made of its photoactivity, which is somewhat understandable, although as mentioned earlier, the site does reveal the company's practice of heating zinc oxide pigments "to a very high temperature" in the 19th century (Winsor & Newton 2011). Golden similarly strives for quality in their paints, assigning permanence ratings to their watercolors based on the ASTM light-fastness scale, but again this scale only accounts for fading (Golden Artist Colors 2016). The idea of permanence in watercolors may need to be re-evaluated for photoactive white pigments such as zinc oxide.

Although tempting, replacing *indirect* pigments with *direct* method pigments in watercolors is not entirely preferable due to the latter's greenish hue. Instead, an annealed *indirect* method pigment may present the best option for watercolor paint manufacturers. *Indirect* method sample 1 was the only pigment that did not cause browning on Whatman paper, although it did show signs of peroxide formation. It is a lower-purity grade *indirect* method pigment with a similar fluorescence to *direct* method pigments, being the only pigment in the type 2 fluorescence grouping. Importantly, it had excellent whiteness and dispersed well in gum arabic. Such a pigment could present a model for paint manufacturers wishing to produce less photoactive pigment. Although this pigment did crack on highly sized papers, this may be due to the absence of a humectant in the mock-up paints. Watercolors often include glycerine or honey, which can mitigate the issue of paint cracking, although these were excluded from test paints to simplify paint mixtures and reduce interference from fluorescing or UV-absorbing media.

Implications for Storage and Display

Dark storage is standard for paper artworks, as is maintaining relative humidity levels around 50%. Unfortunately for conservators, reoxygenation of zinc oxide surfaces has been documented in the dark, occurring as atmospheric oxygen takes up the position of surface oxygen vacancies. This replenishes valence band electrons and reduces trap states, increasing conductivity (Bao et al. 2011; Gurwitz, Cohen, and Shalish 2014). The extent of this effect is not known, although it has not been reported that the crystal is completely reoxygenated, nor that it converts pigments with an excess of defects into highly photoactive pigments with strong blue fluorescence. As such and given light's role as the main energy for degradation reactions (1) through (4), dark storage is mostly advantageous for watercolors with zinc oxide pigments.

It is tempting to recommend anoxic storage and display to mitigate this reoxygenation, although studies indicate that by removing adsorbed water and oxygen from pigment surfaces, anoxia increases surface electron accumulation (Brown 1957; Gurwitz, Cohen, and Shalish 2014). Townsend et al. (2008) reported an increased rate of yellowing and embrittlement of paper in the presence of conductive pigments, whereas pigments such as Prussian blue, vermilion, purple madder, and sepia have been reported to fade in anoxia (Townsend et al. 2008; Thomas 2012; Ford 2014; Lerwill et al. 2015). The risk of reoxygenation in dark storage is not so great as the risk to paper and other pigments in anoxia, and therefore the latter is not recommended for zinc oxide regardless of its level of photoactivity.

Display conditions must primarily reduce exposure to intense levels of light, as intense lighting may result in prolonged peroxide formation. The process of obtaining materials for Russell-grams meant that six months elapsed between light exposure and collection of data, and yet peroxide formation was still easily detected on the more photoactive *indirect* method pigments. Low or intermittent moderate lighting is therefore recommended for the display of zinc oxide–containing watercolors.

Although UV light is the primary catalyst for zinc oxide's photoactivity, conductivity is still measurable on the pigment surfaces when illuminated by visible wavelengths of light as demonstrated by Gurwitz, Cohen, and Shalish (2014) (fig. 13). Overall reduction of light intensity and exposure is vital to reduce this conductivity and the persistent peroxide formation associated with it.

Additional complications are presented by museum lighting recommendations that utilize the lux or foot-candle unit, one which only accounts for the intensity of visible wavelengths of light. The shift to LED lighting simplifies lighting concerns, as they do not contain the UV and IR components present in incandescent or fluorescent lighting. They are also tunable, allowing for the reduction of blue wavelengths if desired. Implementation guidelines

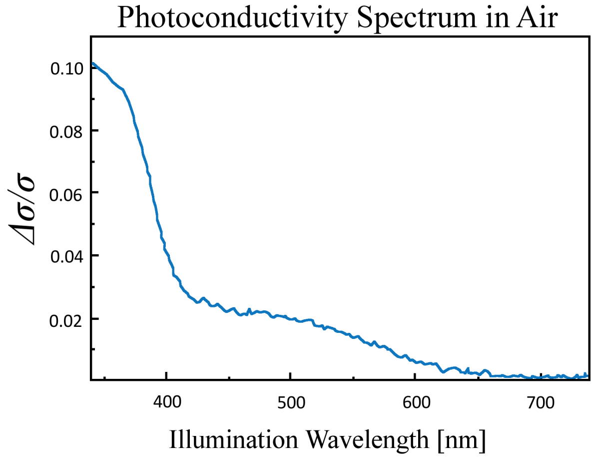

Fig. 13. Measured conductance on zinc oxide surfaces when illuminated by various wavelengths of light. Conductivity is reduced but maintained when illuminated by visible wavelengths. Figure credit: Gurwitz, Cohen and Shalish 2014.

for LED lighting are readily available (e.g., Weintraub 2010; Druzik and Michalski 2012; Perrin, Druzik, and Miller 2014), as are methods for replicating original illumination conditions if a museum wishes to display a piece in similar lighting to the time period in which it was produced (Cuttle 2000; Schanda, Csuti, and Szabó 2015). Historic lighting has the added benefit of tending to have a lower blue contribution. As demonstrated by Gurwitz, Cohen, and Shalish (2014), lower intensity lighting tending toward yellow and red wavelengths will reduce surface conductivity and photocatalytic reactions on zinc oxide pigment surfaces.

CONCLUSIONS

This study has connected the varied fluorescence of zinc oxide pigments in watercolors with their variable photoactivity and resulting degradation of paint films and paper substrates. The relationship between production method and photoactivity was explained, with *indirect* method pigments dominating in historic examples but suffering from higher rates of photoactivity due to their low defect concentration. Evidence in the literature suggested that pigment manufacturer Winsor & Newton likely annealed their pigments to improve working properties, unknowingly increasing defect concentrations in the process and reducing photoactivity.

Distinct size differences between production methods allowed for the production method of unknown study pigments to be identified via crystallite size analysis. Modern commercial pigments compared well with *indirect* method analytical zinc oxides (commercial pigments at 0.105–0.131 μm and *indirect* analytical pigments at 0.121–0.170 μm). Sizes measured from three case studies also indicated an *indirect* production method (Harper at 0.159 μm, *S.S. Buda* at 0.193 μm, and the ruin drawing at 0.271 μm). Contemporary and case study pigments were also morphologically similar to analytical *indirect* zinc oxides, being short and nodular in shape rather than needle-like as is typical of *direct* method zinc oxides.

Visible signs of degradation took two forms in mock-up samples after exposure to light and moisture for 50 hours. Browning of the paper substrate behind and adjacent to pigments was observed for all samples on Whatman #1 filter paper, whereas all samples except commercial pigment 15 cracked on sized Fabriano and Folio papers. Zinc oxide pigments generally caused browning of the paper when the paint had sunk into the paper fibers, as seen in unsized Whatman #1 filter paper samples and *General View of St. Mary's Cathedral, Iona.* Paints on highly sized papers such as Fabriano and Folio mock-up papers experienced cracking and loss of media, also observed in Irene Kendall's *Bouquet of Flowers*. Although all mock-up pigments experienced browning on Whatman paper and cracking on sized Fabriano and Folio papers, these effects were most severe for *indirect* samples 3 and 4, both high-purity analytical-grade zinc oxides.

Both fluorimetry and digital image analysis grouped pigments into two types. Type 1 pigments included *indirect* pigments 3 and 4 and the commercial artists' pigments. They were characterized by low green/blue ratios and a green peak centered at 460 to 485 nm (Zhu et al. 2014), a peak location associated with low defect concentrations and high photoactivity (Zhu et al. 2014). Type 2 pigments included *indirect* pigment 1 and all *direct* method pigments except in digital image analysis when sample 9 was grouped with type 1 pigments. Type 2 contained a green peak at 500 to 515 nm, a location associated with high defect concentrations and low photoactivity. Type 1 pigments tended to be those that degraded most severely in mock-ups, whereas type 2 did not. Additionally, Russell-grams for type 1 pigments imaged darkly while type 2 did not, apart from *indirect* sample 1, which still produced surface peroxides but did not cause paper browning. Case studies followed the trend established by mock-ups. Paintings without visible signs of degradation had high green/blue sRGB color ratios, whereas those with degradation due to zinc oxide pigments had lower ratios.

Green/blue sRGB color ratios were relative within data sets and not consistent across paper types. Some consistency can be achieved with further refinement and standardization of image acquisition and processing methods, although methods for correcting for substrate fluorescence suffer from limitations presented by the nature of watercolor paints to permeate the paper substrate. Given that paper fluorescence appears to diminish with degradation, historic samples may not suffer from too much interference by the substrate when characterizing fluorescence. Additionally, green/blue sRGB color channels were consistently higher for type 2 pigments than type 1, indicating that these color channel ratios may provide a valuable tool for characterizing photoactivity if interfering fluorescence and quenching can be accounted for.

Low green/blue sRGB color channel ratios for case studies indicate that these have not obtained a defect concentration high enough to be in the type 2 class, indicating that even after 100 years they are still photoactive. Along with theories that zinc oxides may reoxygenate in dark storage, this finding indicates both that surface defect concentration increases very slowly and that a reaction endpoint may not be reached by photoactive type 1 pigments.

Storage for all paintings containing zinc oxide should follow general recommendations for paper. Of greatest concern are display conditions given the persistence of peroxide formation in dark storage. The literature suggests that conductance on zinc oxide surfaces is maintained even when UV and infrared wavelengths are removed from lighting. LED lighting naturally eliminates these harmful wavelengths and is tuneable, meaning the blue contribution can be reduced, which will in turn reduce photoactivity. Reduction in lighting intensity and duration is similarly possible using contemporary museum lighting and is best practice for zinc oxides.

Although anoxic display and storage removes oxygen and moisture that would eliminate peroxide formation, anoxia should be avoided for zinc oxide–containing watercolors, as surface conductivity is increased in vacuum.

Pigment manufacturers presently do not account for photoactivity when classifying pigments for permanence, relying only on fading that does not account for white pigments. Additionally, commercial pigments in this study were *indirect* method pigments of the first, reactive fluorescent type. Perhaps future pigment suppliers could produce watercolor paints with annealed *indirect* pigments, reducing photoactivity while maintaining the brilliant whiteness valued in Chinese white. Permanence scales could be expanded or modified for photoactive pigments to account for variation in surface conductivity.

APPENDIX: BACKGROUND SUBTRACTION METHOD IN IMAGEJ

Background subtraction was carried out in ImageJ of UV fluorescence images taken with the Canon EOS 6D digital camera. A duplicate image was created, then the Subtract Background process was opened. With “create background” selected, the rolling ball radius was set to 20. This smoothed the intensity curve of the image and removed shadows and surface texture. The image was then converted to luminance and an auto threshold applied. Selecting a dark background when thresholding blackened the fluorescent area. Remaining holes in the dark area were filled with Process → Binary → Fill holes. Finally, the luminance image was subtracted from the original color image using Process → Image Calculator. The remaining image consisted of only fluorescing areas on a black background.

NOTES

1. Although the absence of oxygen ions has been detected in zinc oxides in a gradient along the *c* axis (Fabbri et al. 2014; Johnson 2020) and is likely the cause of the conversion of blue fluorescence to green with age, the formation of oxygen vacancies is energetically unfavorable in zinc oxide lattices produced by the *indirect* and *direct* methods. Rather, replacement by hydrogen is a more likely mechanism for the removal of oxygen ions. For clarity, this study will refer to the defect as an oxygen vacancy even though it is more likely a hydrogen substitution. This is not yet verified, however, although a stoichiometry favoring zinc ions is well documented (Janotti and Van De Walle 2007; Oba, Togo, and Tanaka 2008; Ellmer and Bikowski 2016).

2. Based on experiments by Singh, Saha, and Pal (2015). By replicating the author’s exposure levels in the presence of moisture, peroxide formation was assured in the time allotted.

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