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Assessment of the Activity of Photocatalytic Paint Using a Simple Smart Ink Designed for High Activity Surfaces

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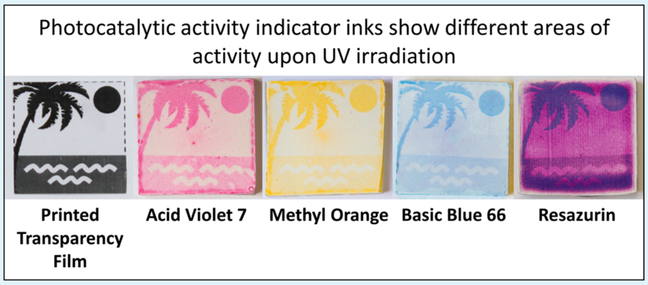

ABSTRACT: The use of an acid violet 7 (AV7) smart ink to assess the activity of photocatalytic paint is demonstrated. A linear correlation is established between the change in oxidized dye concentration, as measured by diffuse reflectance, and the change in the green component of the RGB color values, obtained using a portable hand-held scanner, suggesting that such tests can be monitored easily using an inexpensive piece of hand-held office equipment, as opposed to an expensive lab-based instrument, such as a diffuse reflectance UV/vis spectrophotometer. The bleaching of the AV7 follows first order kinetics, at a rate that is linearly dependent upon the UVA irradiance (0.30−3.26 mW cm^{-2}). A comparison of relative rate of bleaching of the AV7 ink with the relative rate of removal of NO_x, as determined using the ISO test (ISO 22197-1:2007), established a linear relationship between the two sets of results and the relevance of this correlation is discussed briefly.

KEYWORDS: *photocatalysis, ink, acid violet 7, photocatalytic paint, titania, digital scanner, printed filter*

INTRODUCTION

The self-cleaning film industry is large and expanding and the range of commercial self-cleaning building materials currently available include; glass (e.g., Pilkington glass),[1] concrete (e.g., Italcementi),[2] ceramic tiles (e.g., TOTO),[3] and paint (e.g., STO).[4]

As such commercial photocatalytic products have emerged, so have ISO standards been developed. Among other things, current ISO standards involve the photocatalytic destruction of volatiles (for air purification applications) and organic-pollutants in solution (for water purification applications). In all current ISO tests, analysis can be fairly labor intensive, requiring the necessary analysis of model pollutants, trained technicians, and expensive analytical equipment, such as a NO_x analyzer (in the removal of nitric oxide[5]), a UV/vis spectrophotometer (in the degradation methylene blue[6]), and ion chromatography (for DMSO degradation[7]), to name but a few.

A recent review by Mills et al.[8] describes a wide range of ISO tests used for the assessment of the activity of photocatalyst films. A complement to these slow but effective technical tests is the use of photocatalyst activity indicator inks,[8] one of which uses the dye resazurin (Rz).[9] Figure 1 illustrates how the resazurin ink works on a photocatalyst surface. Briefly, upon irradiation of the photocatalyst with light, of energy greater or equal to the band gap of the semiconductor, electron−hole pairs are created. The photogenerated holes are effectively "mopped" up by an electron donor, for example, glycerol, present in the ink film, preventing recombination of the photogenerated electron−hole pairs, thus allowing the photogenerated electrons to reduce subsequently and irreversibly the resazurin dye (blue) to resorufin (pink). Such an ink can be used not only to reveal the presence of a photocatalytic coating, but also to provide a measure of the photocatalytic activity of a surface by monitoring the color change over time, under controlled irradiation conditions.[10] This method has the general advantages over the other, more conventional methods used to assess photocatalytic activity in terms of low cost, simplicity, and speed. The color change can be easily monitored by eye, for qualitative work, by UV/vis spectrophotometry (e.g., for transparent glass samples), or by diffuse reflectance spectrophotometry (for nontransparent surfaces such as ceramics or concrete) for quantitative studies.

Although a number of studies using a photocatalytic activity indicator ink have been reported on self-cleaning glass, there have been none on photocatalytic paints.[11−14] This work focuses on the use of photocatalytic activity indicator inks for use on high activity surfaces, such as a photocatalytic paint, and, for comparison, a high activity TiO_2 sol−gel coating.

EXPERIMENTAL SECTION

Unless otherwise stated, all chemicals used in this project were purchased from Sigma-Aldrich and were used as supplied. The photocatalytic paint (STOClimasan Color) was purchased directly from STO.[15]

Photocatalyst Activity Indicator Ink Preparation. As we have seen, a typical photocatalyst activity indicator ink comprises redox dye, Dox, which can be readily reduced irreversibly by conductance band electrons in the semiconductor photocatalyst. The ink also contains an

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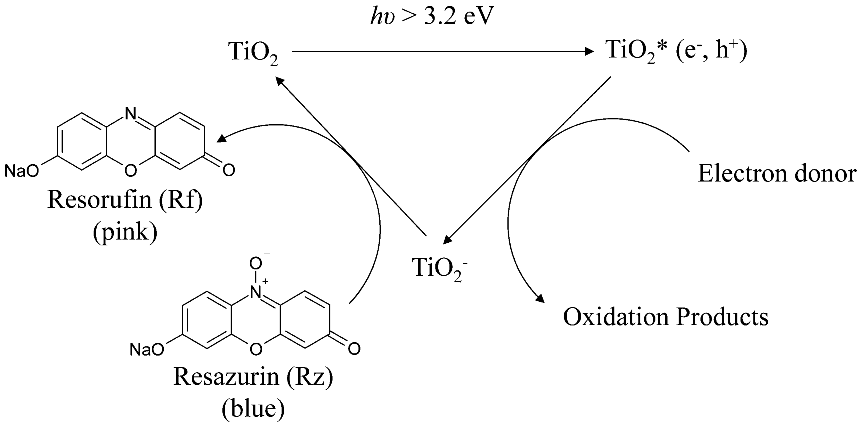


Figure 1. Mechanism of photocatalytically sensitized reduction of resazurin ink (blue) to resorufin (pink).

electron donor, typically glycerol, and a resin to contain the above components. All of the above are dissolved in water to form the overall ink. Typically the redox dye is Rz, but in this work four different dyes were tested, namely, acid violet 7 (AV7), methyl orange (MO), basic blue 66 (BB66), and resazurin (Rz). Each of the inks were prepared according to the following generic formulation: 20 g (1.5 wt %) of hydroxyethyl cellulose, 2 g of glycerol, and 20 mg of polysorbate 20, to which the dye was added, that is, 50 mg of AV7, 25 mg of MO, 50 mg of BB66, or 20 mg of Rz. Each prepared ink was left stirring overnight on a magnetic stirring plate to ensure all the dye was dissolved. A small amount of surfactant, polysorbate 20, was added to each ink to reduce the surface tension of the ink and allow an even coating to be applied on a variety of different photocatalytic surfaces, such as paint and glass.

High Activity, Sol−Gel Titania Coated Glass Slides. A paste of titania nanoparticles was prepared using the sol−gel method described elsewhere by Mills et al.,[16] and coated onto 25 × 25 mm^2 cut microscope slides using a doctor blade technique. Briefly, 3 M Scotch tape was applied to either side of the glass, to create a casting trough ca. 2 cm wide, to which a few drops of the sol−gel titania paste were pipetted at the top and then the paste was drawn down the length of the trough to create a uniform 120 μm thick coat of the paste using a glass rod. Once dry, the Scotch tape was removed and the sol−gel film was annealed at 450 °C for 30 min with a ramp rate of 10 °C min^{-1}. The film was then left overnight to cool slowly inside the furnace to create a final robust, clear coating of anatase titania approximately 2 μm thick.[16] These films have proven to be much more active than commercial self-cleaning glass films, such as Activ.[17]

Photocatalytic Paint Coated Glass Slides. Pieces of 25 × 25 mm^2 and 50 × 100 mm^2 of 4 mm thick glass were cut and coated with STOClimasan Color photocatalytic paint using a K-bar 4 (RK PrintCoat Instruments Ltd.) to provide a 40 μm thick wet film of the paint. Thus, briefly, a few drops (0.2 mL) of the paint were deposited onto the top of the glass coupon and the K-bar placed above and drawn firmly through it to create the film. The K-bar was subsequently cleaned with water and acetone. The coated glass slides were then left to dry overnight in the dark (thickness of dried film = ca. 30 μm).

Ink Coating. The ink was applied to either the sol−gel-coated glass samples or the paint-coated glass samples using the same drawdown method used for the application of the paint. Thus, a K-bar 3 was used to produce a ca. 24 μm thick wet film of the ink, which was dried for 10 min in an oven at 70 °C prior to irradiation, to produce an ink film typically ca. 4 μm thick.

Irradiation Setup. All irradiations were performed using a Blak-Ray XX-15BLB UV bench lamp fitted with 2 15 W UVA bulbs (λ_{max} (emission) 368 nm). In one set of experiments the adjustable shelf height was altered to generate a range of irradiances (3.26 − 0.75 mW cm^{-2}) although, in most cases, the self-was fixed so as to provide a UV irradiance of ca. 1.65 mW cm^{-2}. UV irradiance were measured using a hand-held UVX Digital UV Intensity Meter fitted with a 365 nm sensor. All irradiations were performed in air.

The photocatalytic bleaching of each of the inks were monitored using both diffuse reflectance (CM-2500D spectrophotometer, Konica Minolta) and a portable hand-held scanner (N90HT, EasyScan). RGB color values can be extracted from digital images by most image editing software packages with an eyedropper/color picker tool; Adobe Photoshop and Microsoft Paint are two common image editor software packages capable of doing this. However, such programs do not lend themselves to the easy recording of multiple RGB values from a collection of images, as required in this work, nor do they easily allow their subsequent copying and pasting into a plotting program, such as Excel, to create the necessary plots of R, G, and B values versus irradiation time. As a consequence, an in-house macro was written in Excel that allows the RGB values of any digital image to be determined, and placed automatically in the spreadsheet, ready for plotting as a function of irradiation time, using a custom color extractor tool. A downloadable copy of this macro (RGB Extractor) with guide can be obtained from ref 18.

NO_x Test: Removal of Nitric Oxide. The photocatalytic ability of the STOClimasan Color photocatalytic paint was assessed by measuring its NO_x removal capability over a range of different UV irradiances, otherwise determined in accordance with ISO 22197-1:2007. Thus, all samples were pretreated in order to decompose any residual organic matter by irradiating with an ultraviolet lamp (1 mW cm^2) for 960 min, under a flow of zero-calibration gas at 3 L min^{-1}. The test piece under study was placed in the photoreactor with the space between the test piece and the window a constant of 5.0 ± 0.5 mm. The test gas supply was adjusted so as to supply 1 ± 0.05 μL L^{-1} of NO and 1.56% ± 0.08% of volume fraction of water vapor at 25.0 ± 2.5 °C, that is, a relative humidity of 50% at 25 °C. The test gas was allowed to flow into the photoreactor, without photoirradiation, with a flow rate of 3 ± 0.15 L min^{-1}, for 30 min while the change in the volume fractions of NO and NO_2 were monitored using an Enviro Technology Service plc NO_x analyzer model T200. After 30 min, the gas flow was maintained and irradiation of the sample commenced. The variation in the NO and NO_2 volume fractions during the photoirradiation process were recorded for 300 min. After this 300 min period, irradiation was halted, but the test gas flow maintained for a further 30 min, during which time the NO fraction was seen to return to its original level. Using the NO_x data recorded during the 300 min photoirradiation, the amounts of NO_x removed, NO_2 generated, and therefore net amount of NO_x removed by the test piece were calculated.

RESULTS AND DISCUSSION

The commercially available paint chosen for this work was STOClimasan Color photocatalytic paint which is designed for interior use, and utilizes visible, as well as UV light, to degrade pollutants and odors which can accumulate indoors using a carbon-modified TiO_2 photocatalyst, manufactured by Kronos.[19] The carbon is incorporated onto the titania by

Scheme 1. Photocatalytic Reduction of Methyl Orange Producing the Hydrazine Derivate

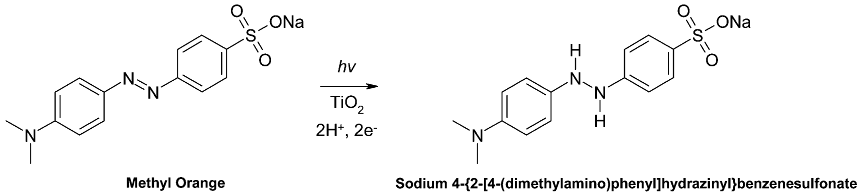
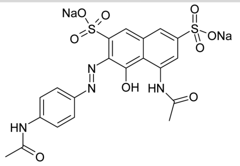
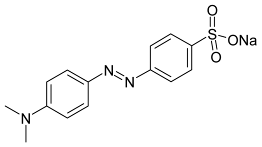
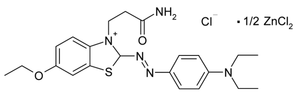
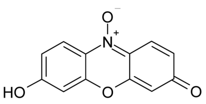


Table 1. Structures of the Four Dyes Assessed and the Time Taken to Fully Bleach on Sol−Gel Titania Paste, STOClimasan Color Paint, and Activ Glass

Ink	SC Surface	Irradiance/ mW cm^{-2}	Time to bleach/ min	Optimum RGB Component^{a}
Acid Violet 7				
	Paste	1.65	0.3	green
	STO Paint	1.65	60	green
	Activ$^{\text{TM}}$	1.65	∞^{c}	green
Methyl Orange				
	Paste	1.65	0.4	green
	STO Paint	1.65	60	green
	Activ$^{\text{TM}}$	1.65	∞^{c}	green
Basic Blue 66				
	Paste	0.15	0.3	red
	STO Paint	0.15	2	red
	Activ$^{\text{TM}}$	1.65	10	red
Resazurin				
	Paste	0.15	0.8^{b}	red
	STO Paint	0.15	8^{b}	red
	Activ$^{\text{TM}}$	1.65	30^{b}	red

[a] The RGB color component (obtained from digital scans) that gives the biggest change over the course of the bleaching of the dye. [b] "Bleaching" in this case means the change from blue to pink. [c] No color change was observed over a 120 min irradiation period.

introducing a carbon containing compound, such as pentaerythritol,[20,21] to titania with subsequent thermal treatment at temperatures up to 400 °C to produce a yellow powder.[21] Work by Zabek et al.[21] has demonstrated that the yellow visible light organic, conjugated, carboxylate photosensitizer can be easily extracted from Kronos vlp 7000 by heating a suspension in alkaline solution (pH 12.5). After centrifuging, a white powder is produced (titania) with a yellow/brown supernatant (a solution of the organic photosensitizer). In this work, a similar extraction was performed on the STOClimasan Color photocatalytic paint. Analysis by FTIR-ATR of the dried brown solid from the supernatant, yielded similar peaks to those obtained from the Kronos vlp 7000 extract, at 1576 and 1415 cm^{-1}, which can be attributed to asymmetric and symmetric stretching vibrations of a conjugated organic carboxylate group.[21] UV/vis analysis of the extracted photosensitizer from both the Kronos vlp 7000 and the STOClimasan Color paint also appeared very similar.

An initial assessment of the STOClimasan Color paint using a standard resazurin ink (Rz) proved the ink to be inappropriate for use with such a high activity paint. Thus, the color change of the Rz ink film on the paint film (blue to pink) occurred in less than 1 s under a low incident UVA irradiance (∼1.65 mW cm^{-2}). In contrast, the same ink on commercial self-cleaning glass, under the same irradiation conditions takes ca. 1800 s to change from blue to pink.

Brown and Darwent[22] have previously demonstrated that it is possible to photocatalyze the irreversible reduction of azo dyes, such as methyl orange (see Scheme 1), using colloidal TiO_2 under anaerobic conditions.

Encouraged by this finding, a selection of azo dyes, namely, acid violet 7 (AV7), methyl orange (MO), and basic blue 66 (BB66), were assessed as possible alternative redox dyes to Rz, via a series of photocatalytic activity indicator inks, otherwise identical to the Rz ink. Table 1 lists the outcome of a simple screening test of all four inks on highly active, thick sol−gel titania paste films, STOClimasan paint, and the much less active commercial Activ self-cleaning glass. The time taken to fully bleach the ink was assessed both by eye and also by monitoring one or more of the RGB color components

Figure 2. Photographs demonstrating the color change of each ink upon UVA irradiation (I_0 = 3.26 mW cm^{-2}) through a printed transparency film, on STOClimasan Color paint. Both AV7 and MO were irradiated for 30 min, whereas BB66 and Rz were irradiated for approximately 0.1 min.

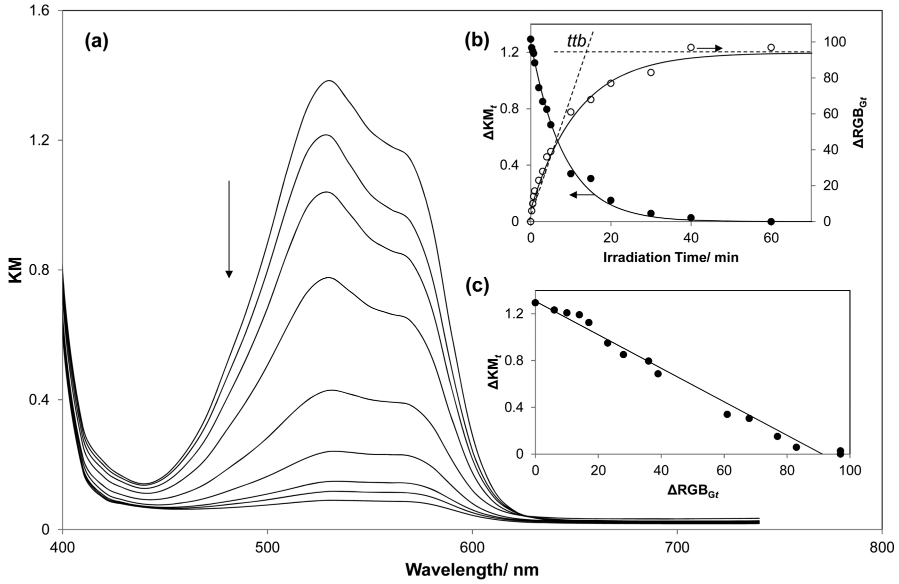


Figure 3. (a) Change in the diffuse reflectance spectrum of the AV7 ink on STOClimasan Color photocatalytic paint, irradiated with a UVA irradiance of 3.26 mW cm^{-2}. (b) Plot of the change in Kubelka−Munk units, ΔKM, at 530 nm (●), and also the change in the green RGB value, ΔRGB$_{Gt}$, (○) as a function of irradiation time. (c) Plot of ΔKM$_t$ vs ΔRGB$_{Gt}$, showing a linear relationship.

extracted from the digital images recorded by using a hand-held scanner. Table 1 also lists the RGB color value used to monitor each reaction, that is, the color value that gave the biggest change over the course of the bleaching of each dye. From the results in Table 1, both Rz and BB66 were found to be unsuitable for assessing highly active photocatalytic surfaces, such as the sol−gel film or the STOClimasan paint even when using a modest UVA irradiance of 1.65 mW cm^{-2}. Indeed, in order to monitor/assess the photocatalytic bleaching of these inks, the UVA light irradiance had to be significantly reduced (0.15 mW cm^{-2}), and the samples prepared and handled in the dark prior to irradiation. The BB66 and Rz inks were, however, very good for monitoring the photocatalytic activity of commercial self-cleaning glass, such as Activ, under modest UVA irradiation (1.65 mW cm^{-2}). In contrast, MO and AV7 inks were much too slow to change color (over 120 min) when used with Activ, but both worked equally well on the photocatalytic paint and sol−gel films, showing complete color loss after 60 min of irradiation (irradiance, I = 1.65 mW cm^{-2}).

Figure 2 shows photographs of the color changes observed upon irradiation of each of the inks on STOClimasan paint samples when irradiated through a black and white negative which allowed different levels of UV light through. Thus, the clear sections (such as the "sky") allow most of the UV light through and was responsible for the greatest color change in the ink i.e. typical bleaching complete after 30 min. The pitch black images (such as the tree and sun) allowed the least of the UV light through and so resulted in little or no change in color of the inks. The images that were gray in the negative, for example, the "sea", allowed some of the UV light through and so ensured some photocatalyzed bleaching of the underlying ink. Thus, the ink-coated paint samples were irradiated through a printed transparency film, effectively allowing three different UV light irradiances (in this case) to irradiate the sample at the one time, thus allowing the picture to develop. The use of printed transparencies as UV light filters will be discussed later. From the results of this work the AV7 ink was chosen for further assessment with regard to the STOClimasan photocatalytic paint, due to the more striking nature of the observed color change when compared to the MO ink.

Monitoring Ink Color Changes. The progress of each photocatalyzed dye-bleaching reaction was monitored using both diffuse reflectance and a hand-held digital image scanner. Figure 3a shows a typical collection of diffuse reflectance spectra collected over irradiation time, when irradiated with 3.26 mW cm^{-2} UVA light. Figure 3b shows the change in Kubelka−Munk units, ΔKM$_t$, at 530 nm (from diffuse reflectance monitoring) and the change in the green, ΔRGB$_{Gt}$, color value (obtained from analysis of the digital images generated by the hand-held scanner) as a function of irradiation time, t. It was observed that in both cases the bleaching of the

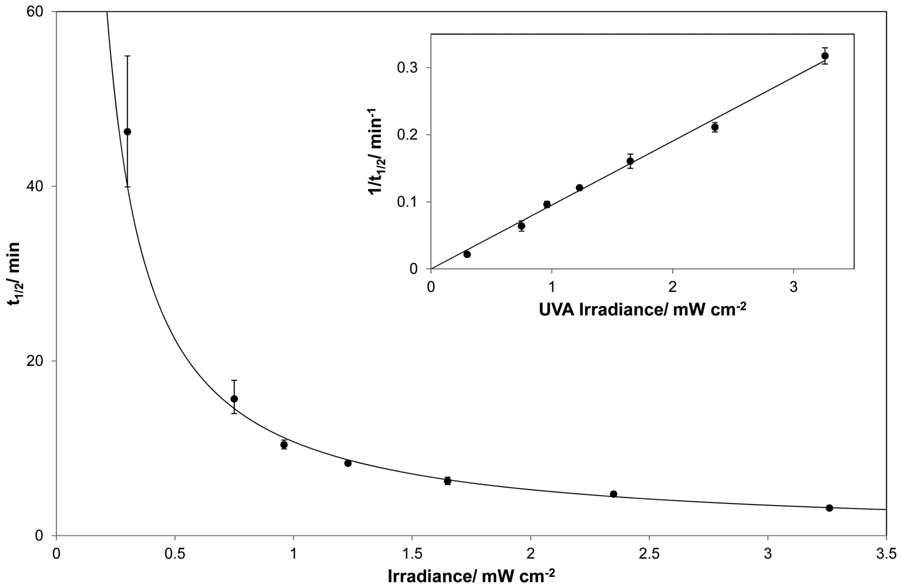


Figure 4. Plot of the time taken for the AV7 ink to lose half its color, $t_{1/2}$, as a function of UVA irradiance. The inset graph shows a plot of $1/t_{1/2}$ vs UVA irradiance, showing a linear dependence.

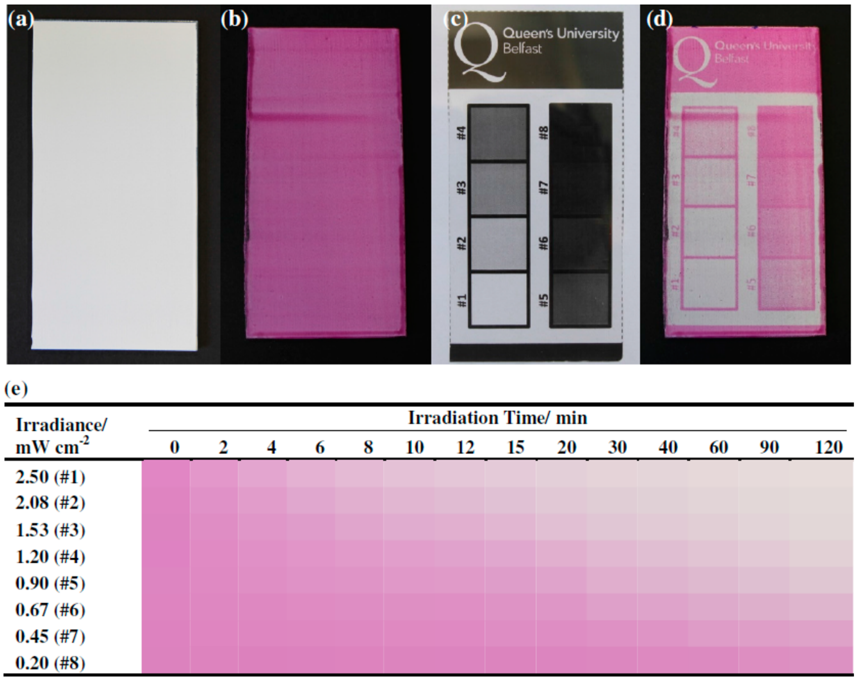


Figure 5. (a) 5 × 10 cm^2 glass sheet coated with STOClimasan Color photocatalytic paint. (b) Paint sample coated with AV7 ink. (c) Printed acetate filter. (d) Coated paint sample after 30 min of irradiation. (e) Color change observed over time for each incident UVA irradiance.

AV7 ink followed first order kinetics. The kinetics of the photobleaching process appear to be approximately first-order, as a natural log plot of the decay data in Figure 3b reveals a good straight line ($R^2 = 0.998$) over 2 half-lives. In addition, a plot of the data in Figure 3a in the form ΔKM_t vs ΔRGB_{Gt}, shown in Figure 3c, reveals a linear relationship between these two parameters. The linear relationship observed between ΔKM_t and ΔRGB_{Gt} suggests that the hand-held scanner can be used to monitor the bleaching of the dye, since ΔKM_t is proportional to dye concentration, and to monitor the rate of bleaching, just as effectively as a more expensive, lab-based, diffuse reflectance spectrophotometer.

A simple, inverse, measure of the first-order rate constant, k_1, for photobleaching, is the time taken for the dye to lose half its color, $t_{1/2}$, since $t_{1/2} = \ln 2/k_1$. And another measure of rate is time taken to bleach, ttb, which may be estimated by extrapolating the two linear regions in the ΔRGB_{Gt} vs time plot and identifying their point of intersection. ttb approximates to ca. $2t_{1/2}$. Thus, using the data in Figure 3b, $t_{1/2}$ for AV7 on STOClimasan Color photocatalytic paint is 6 min, using a UV irradiance of 3.26 mW cm^{-2}. ttb values for the various inks on photocatalytic paint and a sol−gel film are given in Table 1.

Light Irradiance Study. The photocatalytic bleaching of the AV7 ink on STOClimasan photocatalytic paint was assessed using a range of different UVA irradiances (3.26−0.30 mW

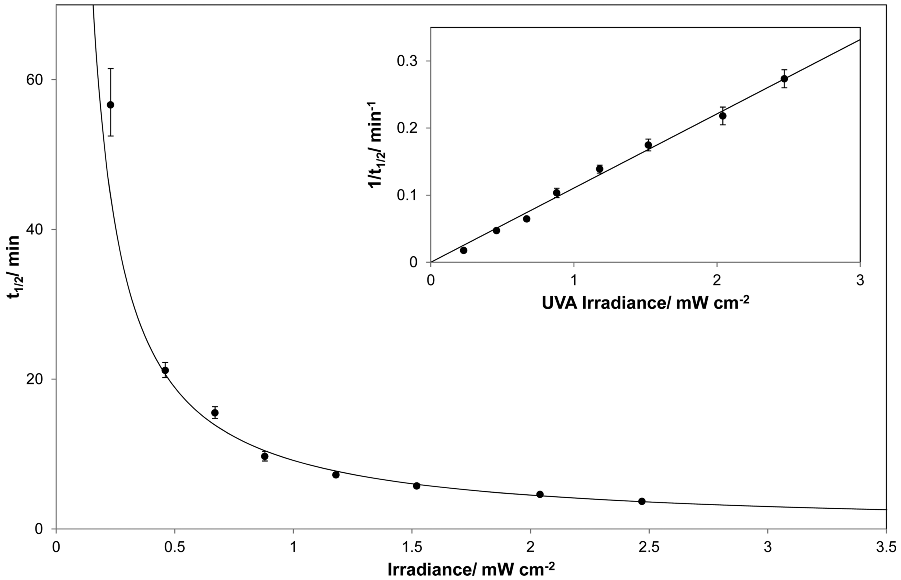


Figure 6. Plot of the time taken for the AV7 ink to lose half its color, $t_{1/2}$, as a function of incident UVA irradiance provided by the printed filter. The inset graph shows a plot of $1/t_{1/2}$ vs UVA irradiance, showing a linear dependence.

cm^{-2}), achieved by varying the distance the Blak-Ray XX-15BLB UV bench lamp from the sample.

Thus, in another set of experiments, a hand-held scanner was used to measure the variation in RGB$_{Gt}$ with irradiation time for AV7 coated STOClimasan paint slides, subjected to different UV irradiances. Each data set was then analyzed to determine the value of $t_{1/2}$ and the plot of $t_{1/2}$ vs irradiance is illustrated in Figure 4.

In semiconductor photocatalysis, the dependence of the rate (proportional to $1/t_{1/2}$ since it is, in turn, proportional to k_1) of the process upon irradiance, I^{θ}, is complicated, as θ is usually found to lie in the range $0.5 \leq \theta \leq 1$.[23] Values of $\theta \rightarrow 1$ are usually found under low irradiance conditions, or in the presence of a very effective hole or electron scavenger since, under these conditions, electron−hole recombination is not the dominant process. In this work, the vast excess of the electron donor, glycerol, in the ink film ensures $\theta \rightarrow 1$, and so $1/t_{1/2} \propto I$ as indicated by the inset diagram in Figure 4, a plot of the data in the main diagram in the form: $1/t_{1/2}$ vs I. In contrast, values of $\theta \rightarrow 0.5$ are usually found in photocatalysis when high irradiances are used and electron−hole pair recombination is the dominant process.

Printed Transparency Film Filter. The assessment of the photocatalytic activity of a surface as a function of UV irradiance can be made even simpler and quicker using a printed neutral density filter on a transparency film (3M transparency film sheets (CG3360)). Thus, it is achieved by simply printing a range of deepening gray squares onto a sheet of overhead transparency acetate ranging in "gray" tone from white/clear (RGB 255, 255, 255) to black (RGB 0, 0, 0). Such a filter has the benefits of being cheap, disposable, simple to make, and easily customized to provide a wide range of irradiance values falling on a single sample using the same incident UVA irradiance falling on the filter, negating the need to run multiple experiments at various distances from the lamp, say, when carrying out a study of photocatalytic rate upon irradiance.

The ability of the printed filter to allow simultaneous monitoring of the photocatalytic bleaching of the AV7 ink over a range of incident UVA irradiancies was demonstrated using a 5×10 cm^2 sheet of 3 mm thick glass coated with STOClimasan Color photocatalytic paint. Figure 5a and b shows pictures of the paint sample before and after coating with the AV7 ink, respectively. Figure 5c shows the printed overhead transparency filter, through which the UV irradiation of the paint-coated sample film (Figure 5b) was performed. The overhead transparency created 8 different UVA irradiance values, varying from 0.20 to 2.50 mW cm^{-2}, measured using a hand-held UVX digital UV intensity meter fitted with a 365 nm sensor head, that fell upon the underlying AV7 coated, STOClimasan paint film. The filter was removed periodically, and the extent of the photocatalytic bleaching of the AV7 ink was measured using a portable hand-held scanner. Figure 5d is a photograph of the AV7/paint film after 30 min of irradiation, and Figure 5e is a chart of the color changes recorded as a function of irradiation time for each square filter, as monitored by the hand-held scanner.

Figure 6 shows a plot of the time taken for the dye to lose half its color, $t_{1/2}$, at each incident UVA irradiance provided by the printed filter, as determined using the ΔRGB$_{Gt}$ values obtained from the digital scans as a function of irradiation time, t. The inset plot of $1/t_{1/2}$ vs UVA irradiance illustrates a linear dependence, as previously observed in the initial irradiance study (see Figure 4), where the distance from the light source was varied to achieve the same variation in irradiance. The use of a negative, such as shown in Figure 5c, to vary the irradiance on a single photocatalytic film, in one run, is a much more simple and less labor intensive approach than varying the irradiance on different samples, by varying the distance between the light and the sample, to study the kinetics of the photocatalytic bleaching of the AV7 ink as a function of irradiance.

The above study also suggests that the ink is ideally suited for studying films of photocatalyst with patches/areas of different activity, say due to different photocatalytic coating thicknesses or anatase/rutile/amorphous crystalline phase ratios. This feature of the photocatalyst indicator ink to identify different areas of activity on the same film will be helpful in developing activity-surface characterization correlation studies which are necessary for optimal film activity production.

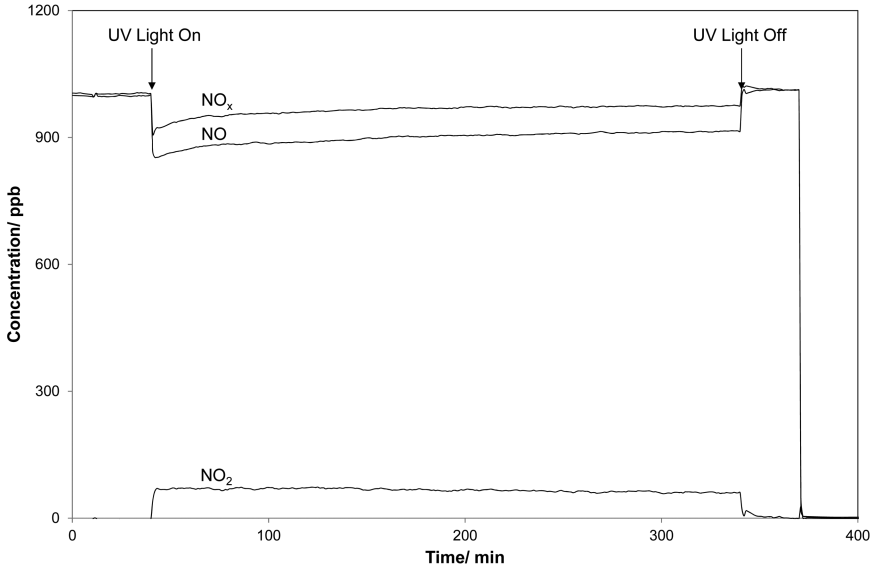


Figure 7. Plot of the concentration of NO$_x$, NO, and NO$_2$ during the ISO test (ISO 22197-1:2007) of the STOClimasan Color paint on glass under an irradiance of 2.80 mW cm^{-2}.

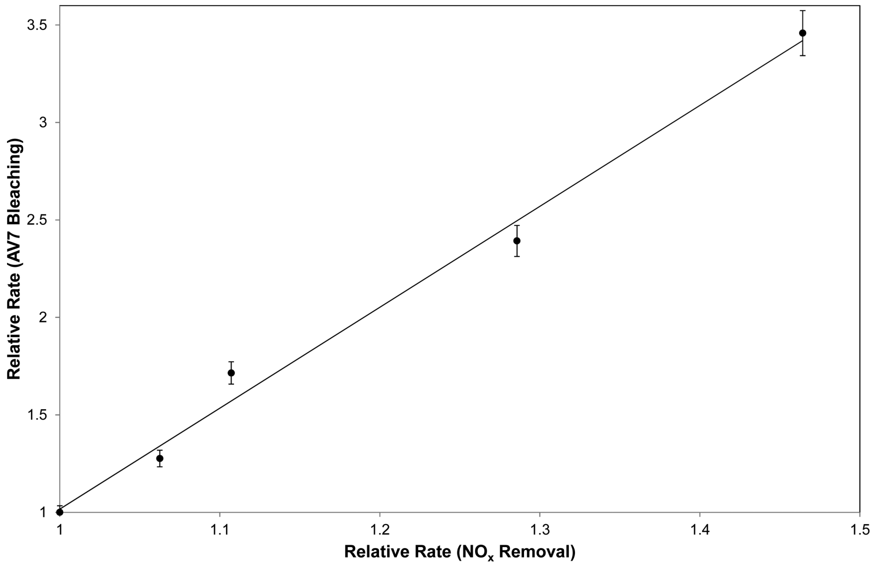


Figure 8. Plot of the relative rate of bleaching of AV7 (obtained from the ink tests) vs the relative rate of NO$_x$ removal under the same irradiances.

Upon visible light irradiation of photocatalyst films with a coating of AV7 ink using 2 × 8 W Hybec cool white bulbs with 2 Optivex 400 nm filters in place, to cut out the UV component, (irradiance = 10900 Lux), no color loss was observed for the AV7 ink, for either sol−gel titania or STOClimasan Color paint photocatalyst films, indicating no visible light activity of the STOClimasan Color paint when assessed for photocatalytic activity using the AV7 ink. These results also show that the photoinduced color loss measured in the previous experiments is due to photocatalysis and not photolysis of dye-photosensitization bleaching mechanisms involving the AV7 dye. A similar observation of lack of visible light activity is also observed for the photocatalytic destruction of stearic acid.

NO$_x$ Analysis. A popular method of assessing photocatalytic activity is the NO$_x$ test, in which a photocatalytic film is exposed to UV light in a stream of NO (typically 1 ppm) for a period of time (e.g., 3 h) and the amount of NO removed, via

$$4NO + 3O_2 + 2H_2O \xrightarrow[h\nu > E_{bg}]{SC} 4HNO_3 \qquad (1)$$

and NO$_2$ generated, via

$$2HNO_3 + NO \xrightarrow[h\nu > E_{bg}]{SC} 3NO_2 + H_2O \qquad (2)$$

are monitored. This test is the basis of the ISO 22197-1:2007, and a typical set of data are illustrated in Figure 7. Thus, Figure 7 illustrates a typical outcome from the NO$_x$ analysis, obtained at an irradiance of 2.80 mW cm^{-2}, showing the amount of NO removed, NO$_2$ generated, and hence the amount of NO$_x$ photo-oxidized/removed by the paint sample.

The ability of the self-cleaning photocatalytic paint to remove NO$_x$, that is, a current ISO standard,[5] was measured over a similar range of incident UV irradiances as used above.

As with the AV7 ink test, the number of moles of NO_x removed by the paint, as measured by this ISO test, n_{NO_x}, was found to be proportional to the incident UV irradiance, I.

A plot of the relative rate of photocatalysed bleaching of AV7 (obtained from the ink tests) (i.e., $t_{1/2}(I)/t_{1/2}$ (I = 0.84 mW cm^{-2})) vs the relative number of NO_x removed under the same irradiance conditions (i.e., $n_{NO_x}(I)/n_{NO_x}$ (I = 0.84 mW cm^{-2})), as shown in Figure 8, reveals a linear correlation between the ink tests and the NO_x ISO test, although note the gradient is not unity, indicating that the AV7 test is more sensitive to changes in irradiance than the NO_x removal test.

CONCLUSIONS

As the Rz ink was found to be too easily reduced via photocatalysis to facilitate the easy measurement of the activity of an example of a commercial photocatalytic paint and a high-activity sol−gel TiO_2 film, a screening of other potentially alternative inks for the purpose, utilizing different azo dyes as the indicator, revealed AV7 to be the most suitable replacement for Rz when studying high active photocatalytic surfaces (i.e., activity > 40 times greater than that of Activ self-cleaning glass).

The monitoring of the photocatalytic bleaching of the AV7 ink on STOClimasan Color photocatalytic paint using both diffuse reflectance and a portable hand-held scanner revealed a linear correlation between the change in diffuse reflectance absorbance units and the change in RGB color green value. This, therefore, suggests that the kinetics of the photocatalytic bleaching of AV7 can be successfully monitored using a cheap, simple to use, piece of general office equipment, namely, a hand-held scanner, just as effectively as a much more expensive diffuse reflectance UV/vis spectrophotometer. The use of a hand-held scanner has the advantages of being able to assess self-cleaning surfaces outside the laboratory, and does not require the same technical knowledge and skill as needed when using most spectroscopic methods, such as diffuse reflectance spectrophotometry.

A linear dependence was found for the photocatalytic bleaching of the AV7 ink on UVA irradiance, and the photocatalytic bleaching of the AV7 ink followed first order kinetics. The use of a printed transparency filter successfully demonstrated a route to monitor the photocatalytic bleaching of the AV7 ink over a range of UVA irradiances in one simple experiment. This work also suggests that the ink would be very effective in structure−activity and optimization studies. Work using the Rz ink on glass has recently been used very effectively just for this purpose.[24]

A comparison of the time taken to bleach half the color of the AV7 ink and the number of moles of NO_x removed under the same irradiance revealed a linear correlation within the UVA irradiance range used in this study (0.84−2.80 mW cm^{-2}). This suggests there is a possible correlation between the response of the photocatalytic activity indicator ink and a standard ISO used to assess the ability of a film to photocatalyse the removal of NO_x.

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Pilkington. http://www.pilkington.com (accessed July, 2013).

(2) Italcementi Group. http://www.italcementigroup.com (accessed July, 2013).

(3) TOTO. http://www.toto.com.hk (accessed July, 2013).

(4) STO. http://www.sto.co.uk (accessed July, 2013).

(5) *ISO 22197-1: 2007, Fine ceramics, advanced technical ceramics − test method for air-purification performance of semiconducting photocatalytic materials − part 1: removal of nitric oxide*; International Organization for Standardization: Geneva, Switzerland, 2007.

(6) *ISO 10678: 2010, Fine ceramics, advanced technical ceramics − determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue*; International Organization for Standardization: Geneva, Switzerland, 2010.

(7) *ISO 10676: 2010, Fine ceramics, advanced technical ceramics − test method for water purification of semiconducting photocatalytic materials by measurement of forming ability of active oxygen*; International Organization for Standardization: Geneva, Switzerland, 2010.

(8) Mills, A.; Hill, C.; Robertson, P. K. *J. Photochem. Photobiol., A* **2012**, *237*, 7−23.

(9) Mills, A.; Wang, J.; Lee, S. K.; Simonsen, M. *Chem. Commun.* **2005**, *21*, 2721−2723.

(10) Ink Intelligent. www.inkintelligent.com (accessed June, 2013).

(11) Laufs, S.; Burgeth, G.; Duttlinger, W.; Kurtenbach, R.; Maban, M.; Thomas, C.; Wiesen, P.; Kleffmann, J. *Atmos. Environ.* **2010**, *44*, 2341−2349.

(12) Kolarik, J.; Toftum, J. *Build. Environ.* **2012**, *57*, 396−402.

(13) Águia, C.; Ângelo, J.; Madeira, L. M.; Mendes, A. *J. Environ. Manage.* **2011**, *92*, 1724−1732.

(14) Maggos, T.; Bartis, J. G.; Liakou, M.; Gobin, C. *J. Hazard. Mater.* **2007**, *146*, 668−673.

(15) STO. http://www.stoshop.co.uk/products/item/stoclimasan-color (accessed June, 2013).

(16) Mills, A.; Elliott, N.; Hill, G.; Fallis, D.; Durrant, J. R.; Willis, R. L. *Photochem. Photobiol. Sci.* **2003**, *2*, 591−596.

(17) Mills, A.; McFarlane, M. *Catal. Today* **2007**, *129*, 22−28.

(18) Ink Intelligent. http://www.inkintelligent.com/wp-content/uploads/2013/06/RGB_Extractor.xlsm (accessed June, 2013).

(19) KRONOS. http://www.nl-ind.com/khome.nsf/KRONOSvlp-Cleaningwithlightpdf (accessed Oct, 2013).

(20) Orth-Gerber J.; Kisch H. Titanium dioxide photocatalyst containing carbon and method for its production. U.S. Patent 2005/0226761 A1, Oct 13, 2005.

(21) Zabek, P.; Eberl, J.; Kisch, H. *Photochem. Photobiol. Sci.* **2009**, *8*, 264−269.

(22) Brown, G. T.; Darwent, J. R. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1631−1643.

(23) Mills, A.; Wang, J.; Ollis, D. F. *J. Catal.* **2006**, *243*, 1−6.

(24) Kafizas, A.; Adriaens, D.; Mills, A.; Parkin, I. P. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8367−8375.