Photocatalyst Activity Indicator Ink for high activity self-cleaning films such as paint.

First Working Draft

Contents

1. Scope

This CEN norm specifies a test method for the qualitative or semi-quantitative evaluation of the photocatalytic activities of photocatalytic surfaces, the active component of which is a semiconducting photocatalyst, such as titanium dioxide. The test measures how long the colour, or component of the colour, of a photocatalyst activity indicator ink takes to bleach when deposited onto the surface of the photocatalytic surface and irradiated subsequently with UVA light. This norm is intended for use with all photocatalytic surfaces in flat, smooth sheet form, including: glass, paint, tiles, concrete and fabric that fit this description.

2. Normative references

The following references are indispensable for the application of this document. For dated references, only the edition applies. For undated references, the latest edition of the referenced document applies.

ISO 10677:2011: Fine Ceramics – Ultraviolet light source for testing semiconductor photocatalytic materials,

3. Terms and definitions

Photocatalytic

Ability to photosensitise a chemical transformation, change in water-droplet contact angle or destruction of a biological species under UVA irradiation.

Ambient Conditions

Room temperature = 18-21 °C and relative humidity (RH) = 40-70 %.

4. Symbols

G_t = normalised green component value of the coloured, i.e. RGB, digital image of the ink film on the photocatalyst material under test at time *t* after irradiation;

ttb = time taken to photocatalytically bleach the normalised green component of the selected central digital image of the ink film on the photocatalyst material under test.

5. Principle

A photocatalyst activity indicator ink is deposited as a film by K-bar coating onto the surface of a material, such as glass, paint, tiles, concrete or fabric, with a

photocatalytically active surface. Upon exposure to UVA, with a defined irradiance, from a defined source, the film changes colour, which is measured periodically via digital photography, either using a digital camera or hand-held scanner. Analysis of the centre of each digital image of the ink film (100 × 100 pixels) reveals a value for the green component of the digital image (which is comprised of red, green and blue elements). A plot of the normalised parameter, G_t, versus irradiation time, *t*, allows the time taken to bleach the green component of the image to be determined, i.e. *ttb*.

Up to eight identical samples (plus 2 blanks for reference, i.e. otherwise identical samples but with no photocatalyst component/coating) are run at any one time, and from the five active samples that have the most similar *ttb*, with a standard deviation that is < 20% of the average value, the average is taken. (if the standard deviation is > 20%, the coating process must be repeated until this condition is satisfied). The average value of *ttb* so obtained is taken as a measure of the photocatalytic activity of the sample.

6. Materials and method

6.1 *Preparation of the photocatalyst activity indicator ink*

The ink is made by dissolving 0.15 g hydroxyethyl cellulose (HEC) into 9.85 g high purity (conductivity ≤ 2 μS cm^{-1}) water to give a solution of 1.5 wt.%. 1 g of Glycerol is added and dissolved followed by 25 mg Acid Violet 7 and 20 mg polysorbate 20 surfactant. The ink is stirred with a magnetic stirrer for a minimum of 8 hours. The ink should be stored in a fridge and used within 2 weeks of its preparation. Before the ink is used it should be removed from the fridge and allowed to stir on a magnetic stirrer at room temperature for 1 hour.

6.2 *Sample Preparation (for paint only)*

For paint sample preparation it is recommended that no. 4 K-bar (0.51 mm diameter wire wound rod from RK Print) is used to draw-down a layer of paint to cover a glass microscope slide, 26 mm × 76 mm. The freshly coated paint is then left to dry in the dark under ambient conditions for no less than 30 minutes and used without further treatment. If the paint sample has been pre-prepared, a minimum sample surface area of 25 × 25 mm must be used.

6.3 *Sample Cleaning (not paint)*

A minimum sample surface area of 25 mm × 25 mm must be used. If the sample is a smooth, relatively non-porous material such as a tile or glass then each sample is cleaned by wiping lightly with a water-soaked tissue and allowed to dry for 60 minutes in the dark under ambient conditions before being coated with the indicator ink. The tissue must be a silicone free tissue. If the sample is relatively porous such as concrete, then the sample should be rinsed with high purity water (conductivity ≤ 2 μS cm^{-1}) and allowed to dry for 60 minutes in the dark under ambient conditions. If a porous sample is freshly prepared (and therefore pristine) then the sample does not need to be rinsed with water.

6.4 *Coating the sample with the ink*

Once dry, the clean samples are then coated with the ink. Thus, a typical 25×25 mm sample is secured to an impression bed (i.e. a clipboard) and a line of ink ~0.5 cm wide deposited along and next and central to the top edge of the sample – a typical amount being ~ 70 mg**.** A wire wound rod (K-bar No. 3) is then used to coat the ink onto 8 high activity samples (in the round robin, commercial self-cleaning paint was used to generate the data at the end of this document) by a drawdown method. All samples are then left for ca. 60 minutes at room temperature in a dry, completely dark container, before use.

6.5 *Sample irradiation and digital photography*

The 8 samples (plus 2 blanks) are irradiated with UV-A light from a BLB or BL lamp, under ambient conditions of temperature and humidity, i.e. T = 18-21 °C and RH = 40-70 %, with an UVA irradiance of 2 mW/cm^2 derived from a UV light source, defined by normalised ISO 10677:2011. The change of colour, G_t,*(vide infra)* is monitored via digital photography using either a digital camera or hand-held scanner. The minimum irradiation time interval for a sample is 30 s. If a sample changes the colour of the ink completely (from blue to pink or colourless), instantly, upon contact with the ink, in the absence of illumination, the surface is defined as 'reactive' and the test is not appropriate. If a sample changes the colour of the ink completely (from blue to pink or colourless) in less than 120 s of irradiation, then the sample's activity is too high for this test and the test should be conducted using an irradiance of 0.5 mW/cm^2 and if the UV light induced colour change occurs still in < 120 s – this test is not appropriate.

The colour change of the sample is monitored digitally so that there are at least 4 images/points between the start of a measurable colour change and the point where no further change in G_t is observed. Conversely, if no visual colour change is observed after the first 5 measurements (compared to the results of an ink film on a blank) then the initial exposure time should be doubled (e.g. from 30 to 60 seconds) and the process repeated until a visual change can be observed. If the sample shows no change (i.e. < 5 % change in the value of G_t *at t=0*) after 120 min, the sample is defined as 'not photocatalytically active' by this test and an ink test for a less active material (e.g. the BB66 ink test) should be used instead.. If a digital camera is to be used instead of scanner then constant lighting conditions must be used – as can be created in a portable photostudio for example. All digital images must have a resolution of 300 dpi at least.

6.6 *Image Analysis*

Software is used to extract the average RGB values from each sample in each image. The central 100×100 pixels of each image of the ink on the sample under test for irradiation time *t*, are selected for such analysis and the average values of each of the *RGB* components determined, i.e. values: $RGB(red)_t$, $RGB(green)_t$, and $RGB(blue)_t$. The averaged $RGB(green)_t$ component at irradiation time, t, is normalised to G_t using the equation:

$$G_t = RGB(green)_t / (RGB(red)_t + RGB(green)_t + RGB(blue)_t)$$

So as to generate a series of G_t , irradiation time, *t*, values, a plot of which usually reveals two straight line components from which a value of the time taken to bleach the G_t component, i.e. *ttb*, can be calculated. The straight line components are chosen as (a) the steepest part of the curve and (b) the flattest point of the curve after the main part of the colour change has occurred (see example data).

7. Test report

The standard score (*z*) for each sample is calculated using $z = |x - \mu| / \sigma$, where *x* is the observed raw *ttb* value and μ and σ are the mean and standard deviation respectively.

Starting with the original data set (usually the 8 active samples, and so 8 *ttb* values), the sample with the highest standard score is eliminated from the dataset and the average and standard score of the now refined data set are then

recalculated and the next sample eliminated from the dataset; this process of reducing/refining the data set is then repeated until there are only 5 sample times left in the dataset. At this point the average value of *ttb* for these 5 most consistent samples in an 8 sample test is taken as a measure of the photocatalyst activity of the material under test under the specified UV irradiance conditions. Note that, if for this data set the ratio of σ/μ is > 0.20 then a new batch of samples must be recoated and the process of refining the data set repeated. This cyclic process of recoating and refining stops only when a 5 sample data set is created for which: σ/μ is ≤ 0.20. The final report should comprise: the digital images of the 5 samples, a plot of G_t vs. t for the 5 samples and a record of the average *ttb* (μ) and its error (σ), in seconds.

Annex A: typical experimental data

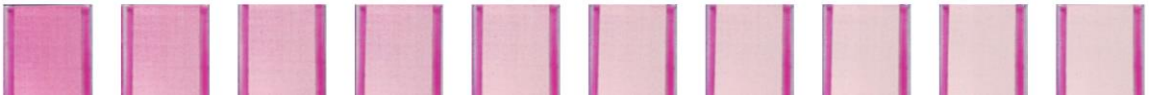

Figure 1. - A typical set of digital images of a photocatalytic film on a sample of commercial photocatalytic paint (image shown from every 60 seconds).

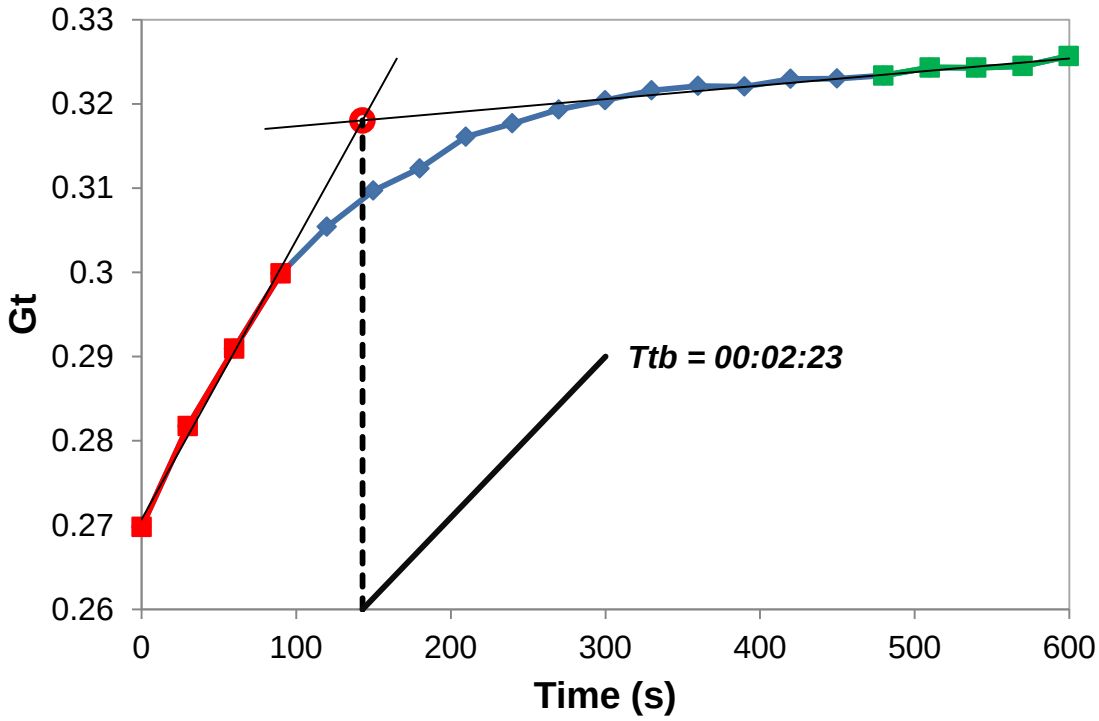

Figure 2. – (a) The normalised green component of the digital images shown in **Figure 1** plotted vs. time in seconds, with the calculated intersection of the two lines displayed as a red circle, from which a *ttb* of 2m 23s (143 seconds) was determined.

Annex B: Example dataset

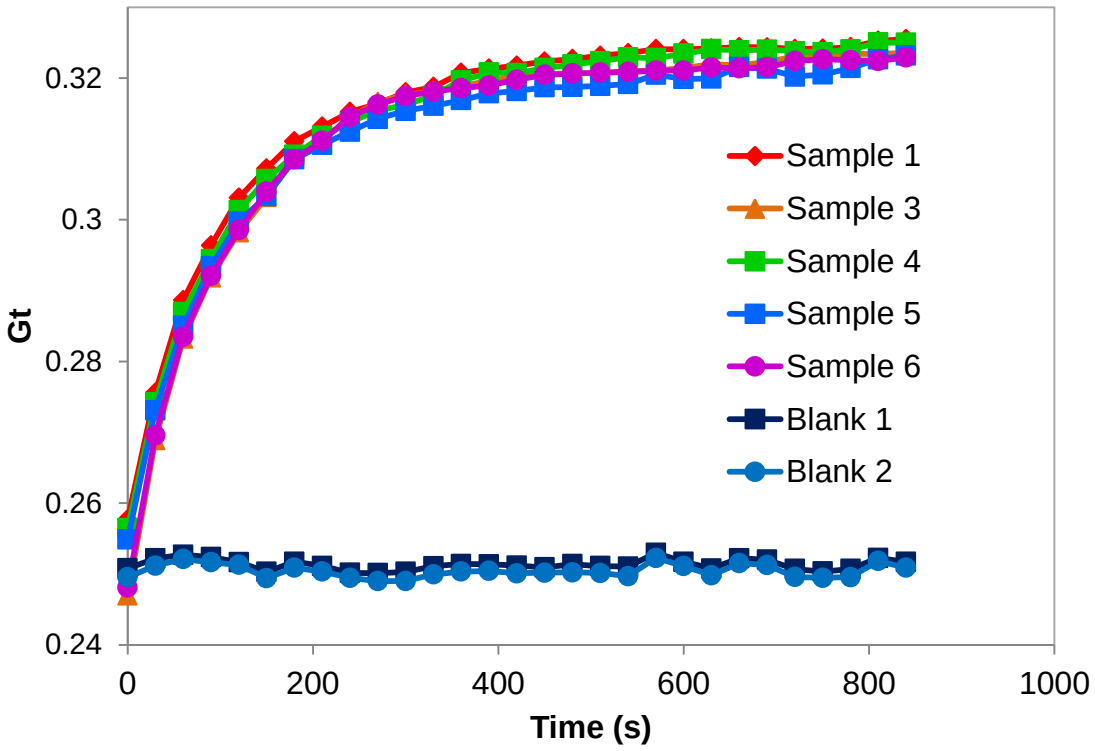

Figure 3. – The normalised green component (G_t) vs. time curves for 5 of the best samples (from 8). The average, standard deviation and % standard deviation ($\sigma/\mu \times 100$) are shown below:

average (s)	135
std. dev. (s)	1
% standard deviation	1

Annex C: Intergroup test results

Table 1. – Average time to bleach (*ttb*) in seconds.

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6
Sample 1	152	133	124	144	97	
Sample 2	142	135	148	141	90	
Sample 3	137	137	139	145	107	
Sample 4	128	134	120	139	106	
Sample 5	143	134	145	144	99	
Average /s	140	135	135	142	100	
Std. Dev. /s	9	1	13	2	7	
Average across groups				130 (2m 10s)		
Std. Dev. Across groups				18 (13 %)		

Group 1 – QUB

Group 2 – DIT

Group 3 – Cristal

Group 4 - ICT

Group 5 – Aalborg