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Generic investigation of the light stability of printing colours using action spectra

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Abstract

The paper presents a method on how to predict the fading of particular printing colours based on action spectra. The action spectra are measured in a custom-built exposure chamber equipped with narrow band LED covering the visible light range. The action spectra are used to predict broadband exposure to 'white light' of a particular application. As a first example, the predicted fading curves are compared with actual fading data obtained using white-light LED. In the next step, the action spectra are applied to predict fading for the same sample set when exposed to a commercial, LC37-filtered Xe-arc light source, as specified in ISO 18937-2. The action spectra of colour print materials reveal that the main degradation reactions are caused by radiation below 420 nm, some degradation happens in the wavelength range 420 nm to 550 nm and very little degradation is caused by light above 550 nm. A severity factor to estimate the degrading potential of light sources for the material class of colour photographic and printing materials is developed.

Introduction

Digital printing is often used in demanding applications, such as outdoor signage, labels and in-window display. Such commercial applications require a display life of several months to years. As most prints are protected from water and pollution, the degradation of displayed prints is mostly caused by light, including glass filtered indoor direct or indirect daylight or LED illumination from backlit panels or indoor lighting. Print material and dye manufacturers routinely test printed inks, substrates and protective film materials, mainly with commercial weathering devices using Xenon-arc lamps. The Xenon-arc lamp radiation can be filtered to match, for example, the relative spectral irradiance (RSI) of indoor or outdoor illumination. The RSI is a measure of how the power of a light source is distributed across different wavelengths, expressed as a ratio to the peak power energy. One of the challenges is that the results from white light exposure are only valid for the specific RSI, that was used in the test. For example, the degradation obtained by an illumination using a UV cut-off filter to predict fading under simulated indoor light cannot predict degradation when a considerable amount of UV irradiance is present, like in outdoor illumination.

In this paper we would like to present a method with which one can predict fading under light with different spectral power distributions. The method has been applied to the samples of an interlaboratory test conducted in ISO/TC 42 (Photography), WG5 to validate a new version of a light stability test method specified in ISO 18937-2 [1]. The test samples were unprotected photographic print materials, each representing a particular contemporary digital imaging print technique, i.e. inkjet dye-based printed on nanoporous paper (IJD), inkjet pigment-based printed on fine arts paper (IJFA), liquid toner electrophotography (EP), dye diffusion thermal transfer (D2T2) and dye sublimation print on textile (DyeSub).

Experimental-set up

The design of the custom-built LED exposure chamber was described previously [2,3]. A schematic is shown in Fig 1.

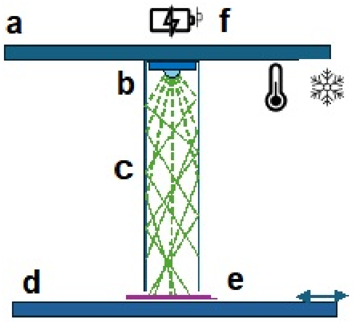


Figure 1: *schematic of the illumination spot of one single LED channel: (a) cooled mounting plate, (b) LED on a support with a lens, (c) hollow light guide with a highly reflective liner, (d) sample support (sliding), (e) flat sample, (f) regulated power supply*

The test pattern was composed of four colour patches including Y, M, C, BK of medium lightness, which are arranged as quadrants, with an unprinted white area in the centre. Replicates of these test patterns were positioned under the various narrow band LED channels, spanning the wavelength range from 380 nm to 620 nm. The exposure unit also comprised four different types of white light LED. The set-up was kept at slightly higher than ambient temperature (27°C to 30°C) and a relative humidity in the range 45% to 55 %. The spectral absorbance, A = 1/ log (Remission), was measured for each of the colour spots after each exposure step. The sample was then placed back into the exposure unit for another cycle until a significant loss of absorbance could be observed. The patches were measured with an X-rite i1Pro spectral photometer, which has a fixed filter condition M2 ('UV cut') according to ISO 13655 [4].

It is difficult to print pure colour patches as many printer drivers do not allow this setting. The printed medium lightness colour patches were either made up of one pure colorant or of a mixture of two or three colorants, as shown in the enlargement of a magenta patch of an EP print and an IJFA print in Fig 2 a and 2 b respectively. If colour differences in terms of CIE ΔE were used for the evaluation, the changes of the three colorants in the IJFA patch would be measured. Measuring the colorant absorbance at its maximum wavelength A_{max}, allows to differentiate between the fading of the colorants. The change for a particular colorants $\Delta A_{\max(i)}$, is calculated according to equation (1)

$$\Delta A_{\max(i)} = A_{\max(i)} - A_{\max(0)} \qquad (1)$$

where i = 1 … n marks the intermediate sampling points and 0 the beginning.

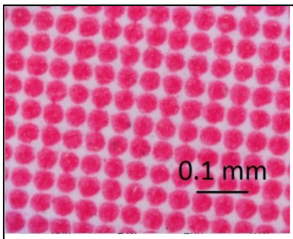
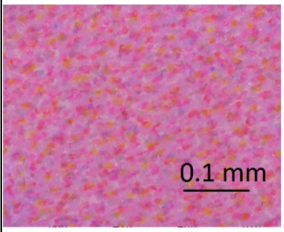
	

Figure 2 a. *enlargement of magenta patch of the EP print*	***Figure 2 b.*** *enlargement of magenta patch of the IJFA print*

Action Spectra

The total exposure was divided into approximately ten discrete steps with intermediate colour measurements after each sampling step. Fig 3) shows a full set of the fading curves for the exposure of the IJD magenta patch with 450 nm, 485 nm and 505 nm LED's, respectively, represented as the change of the peak absorbance $A_{\max}$ of the colorant as function of exposure. . Each type of LED is present twice in the chamber to check for the experimental repeatability of the colour fading experiment: Experimental errors can be estimated from the exposures made with the two LED of the same RSI. Those errors in the measurement of absorbance were about ±0.02 for all colours.

The linear part of the fading curves is used to determine the slope, which represents the sensitivity of the printed patch to fading under a particular narrow-band LED illumination. This slope is given by the change of absorbance $A_{\max}$ due to a radiant exposure H in units of kJ/cm^2. For a very small exposure, the signal does not surpass the noise level of the experiment (blue rectangle). For very long exposures (yellow rectangle), the dye increasingly bleaches out and the peak absorbance nearly reaches the level of the white substrate of the print. In that range the fading is no longer linear with exposure.

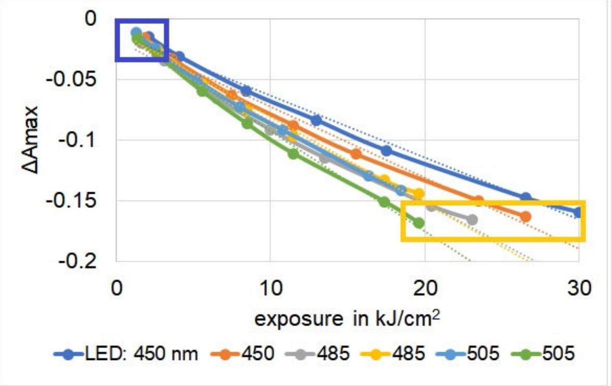


Figure 3: *Fading curves of IJD magenta for exposure at 450 nm, 485 nm and 505 nm. The blue rectangle shows measurements within noise, the yellow rectangle shows the onset of bleaching*

The slopes, i.e. $\Delta A_{\max} / \Delta H$, determined for the quasi-linear sections of the fading curves are shown as dotted lines, A plot of the negative slope over the center wavelengths of the narrow band LED exposures, $-\Delta A_{\max} / \Delta H$, is called the action spectrum of a colorant. See Fig. 4 for the action spectrum of the IJD colorants. The action spectrum of a colorant represents the part of the spectral range, where radiation causes degradation, in our case the fading, of a colorant.

Absorption spectra and action spectra are related but different. The absorption of radiation is the first requirement for colorant degradation. Not all of the absorbed light will however lead to a chemical reaction such as fading, some of it will be converted to heat in the specimen. In general, as shown in Fig 4, radiation in the short wavelength region causes much more degradation at same exposure than radiation at wavelengths higher than 550 nm.

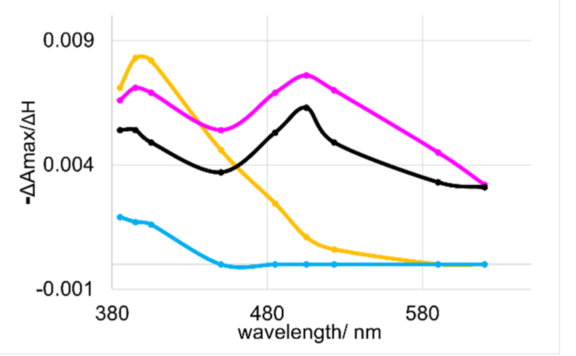


Figure 4. *Action spectra of IJD colorants CMYK, units of the y-axis are 1/kJ/cm^2*

A particularly striking case, in which absorbance spectra and action spectra differ very much, are many cyan dyes, particularly phthalocyanine dyes [5], the cyan colorants used in many modern printing techniques. Fig 5 a) shows spectral absorbance and the action spectrum for cyan in the D2T2 print and Fig 5 b) for cyan in the IJD print. Their main light absorption is in the red wavelength range from 550 nm to 700 nm (blue line), but the degradation reactions are nearly exclusively caused by UV radiation and blue to green light of wavelength 400 nm to 550 nm (black dots).

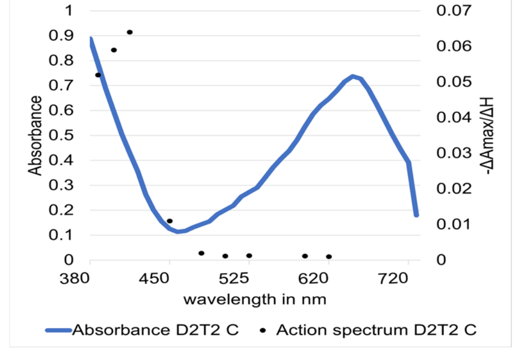


Figure 5 a: *spectral absorbance and action spectrum of D2T2 cyan*

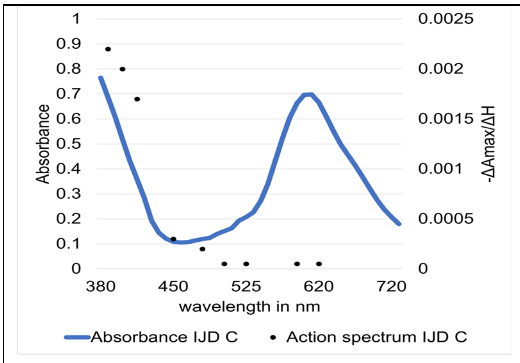


Figure 5b. *spectral absorbance and action spectrum of IJD cyan*

Severity factor of light sources

The concept of relative severity has been introduced in ISO/TS 21139-22 [8] and allows comparing the strength of light fading under different relative spectral irradiance in terms of photometric quantities, namely by the ratios of luminous exposure. A 'general' action function has been derived from a wide range of colorants typically used in photographic print materials: For a large set of experimental data of colour photographic prints materials the losses of Status A optical density were measured in a series of light fading tests with different relative spectral distributions, namely Xe-arc exposure with different UV cut-on filters. These data could be correlated considering the spectral product of the spectral absorbance, the RSI of the test light-source and the action function as a weighting factor for each wavelength. In this way the 'relative severity' of light sources at the same level of illuminance (klx) could be ratioed. The relative severity represents the relative density losses over the range of photographic colorants on average. The analysis was limited to the spectral range between 300 nm and 750 nm.

Results

While the interlaboratory comparison (ILC) test of ISO/TC42 WG5 aimed to validate the Xenon-arc exposure condition 'general indoor display' according to according to ISO 18937-2, when implemented with L37 and/or SC37 filtering. In that ILC test the same set of materials was exposed as with the aforementioned LED chamber including, an Inkjet dye-based print on nanoporous paper (IJD), an inkjet pigment-based print on Fine art paper (IJFA), an electrophotographic print on resin coated paper (EP) and a dye diffusion thermal transfer D2T2 print. There were some minor differences in the experimental procedure due to the need of different test target: (i) The samples patches had slightly different lightness values CIELAB L* (1976) at t = 0 of the test. (ii) The test laboratory using the LED exposure chamber measured differences as changes in the maximum absorbance, whereas the laboratory with filtered Xenon-arc exposure measured differences in Status A densities. Specimen temperature and relative humidity were rather comparable. The main difference was the RSI of the test light source. One lab exposed with narrow band LED and a white LED with a CCT of 5000 K as described before, the other lab with a LC37-filtered Xenon-arc as described in ISO 18937-2.

Severity: LED exposure vs Xe-arc exposure

The LED 5000 K and LC37-filtered Xenon-arc have a very different RSI's as shown in Fig. 6.

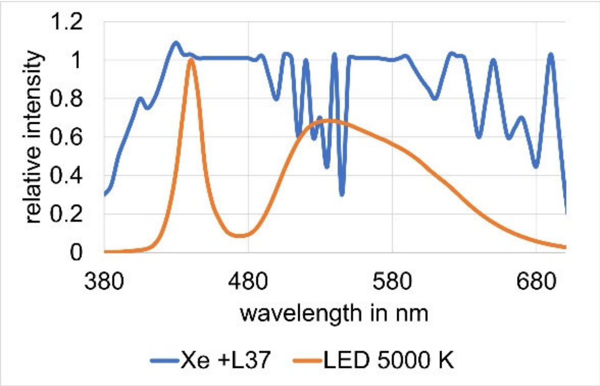
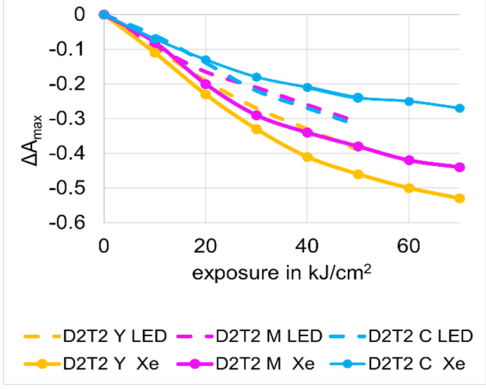


Figure 6: *relative spectral distribution (SPD) of the two exposure light sources LC37-filtered Xe arc and the LED 5000K*

But they have both strong emissions in the blue and in the green spectral range. The LED 5000K has no emission in UV at all. Nevertheless, as can be seen in Fig 7a-d), the severity of fading with the two light sources for the tested print materials is rather similar. At same overall irradiance, the L37-filtered Xenon-arc exposure shows similar fading as the LED 5000 K light. Most colorants fade slightly, and the fading is around 30 % to 50% faster under the L37-filtered Xenon-arc exposure. An exception is the IJD magenta, which seems to fade slightly faster under LED light than under filtered to Xe-arc light. Overall, these two light sources would be considered to have rather similar severity factors.



a)

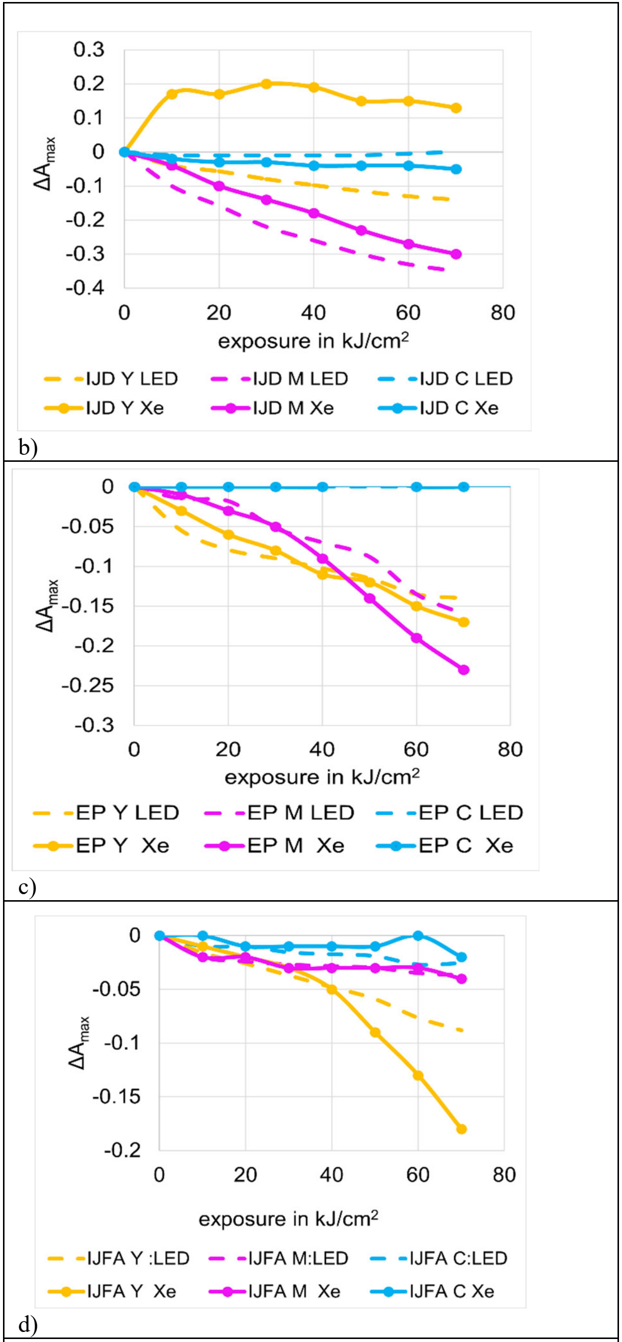


Figure 7: *actual fading for Xe arc (solid line) and LED (dashed line) exposure, a) D2T2, b) IJD, c) EP, d) IJFA*

Prediction of Fading

When the sensitivity of a colorant to the different wavelengths is known, one can predict fading with light sources with different relative spectral irradiance, under the assumption that the degradation effects at the different wavelength are additive. As shown in a previous publication [2] this additivity holds true for many print materials. An exception, for example, are materials which have sacrificial additives. This is typically the case for chromogenic silver halide photo papers that have UV absorbers. For such a case the fading of the colorant at longer wavelength depends partially on the fading of the protective layer at much shorter wavelength, and therefore the fading effects are not independent from each other.

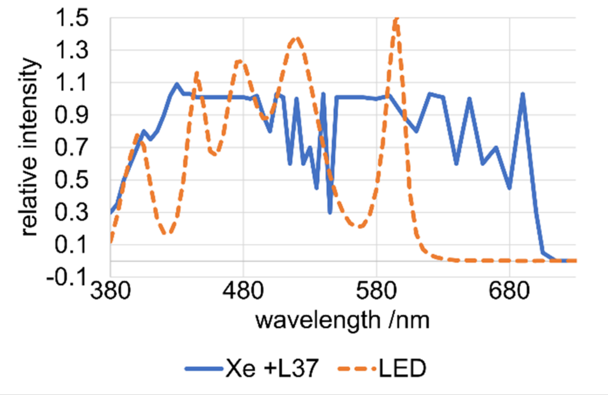


Figure 8: *Calculated best fit of narrow band LED to Xe-arc with LC 37 filter*

In a first step, the narrow band LED exposures have to be matched to the light source to be predicted. This is shown in Fig 8 a) for the case of a Xenon plus L37-filter case. A GRG non-linear fit (MS Excel) allows to express any white light exposure by a combination of narrow band exposures, as applied in the LED chamber. The limited number of LED's does not allow a perfect spectral fit as it would be required for a colorimetric match. However, the exact match of the relative spectral irradiance of two exposure light sources is less important for degradation reactions as long as both light sources excite the same electronic transitions of the colorant [6,7]. In Fig 9 the emission of the LED absorbance spectra of the typical IJD colorants are plotted together to show the good overlap between emission and absorption. The narrow band wavelength results have to be weighted by photo energy. The weighted absorbance changes at the respective narrow band wavelength are added to predict the overall fading of a white light source

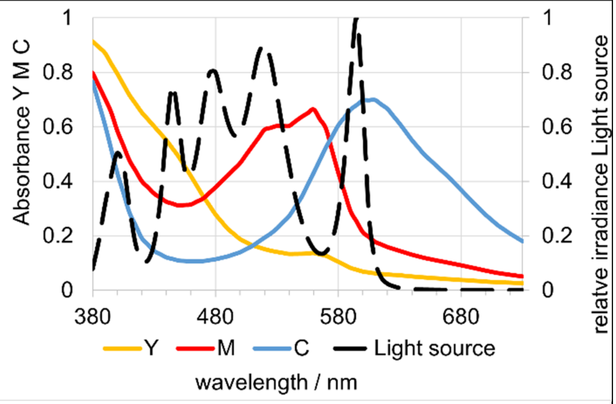
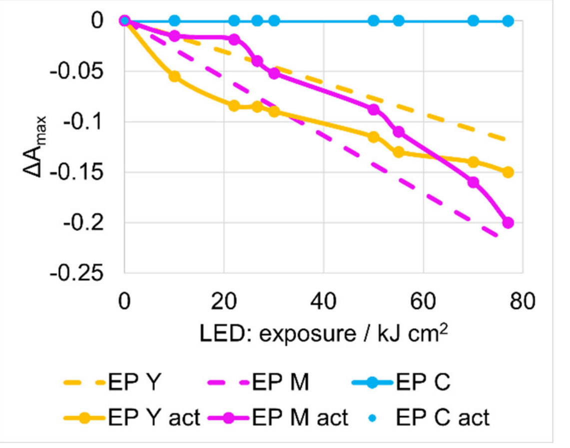


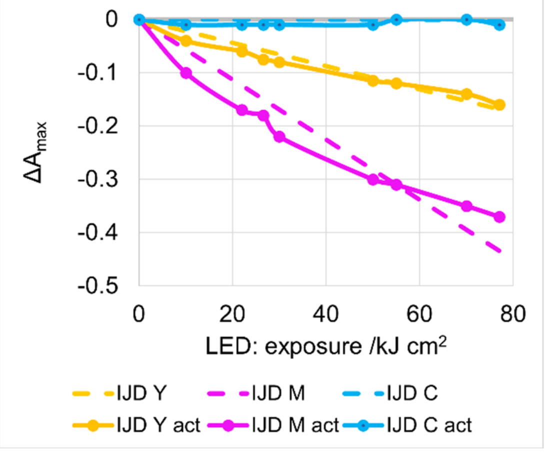
Figure 9: *LED exposure wavelength compared to IJD colorant absorbance spectra*

Actual exposure vs predicted exposure

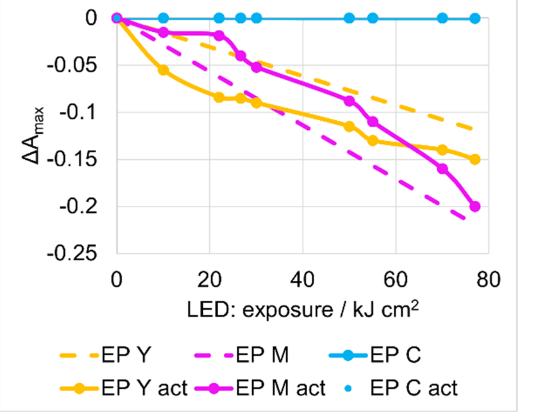
The prediction for each of the three colorants Y, M, C was made based on the action spectrum method as described above. Fig 10 a-d) show the predictions and actual fading results for the white LED 5000 K exposure and all four print materials. Predictions are shown as dashed (linear) lines, exposure results as solid lines. The agreement is quite satisfactory in most cases.



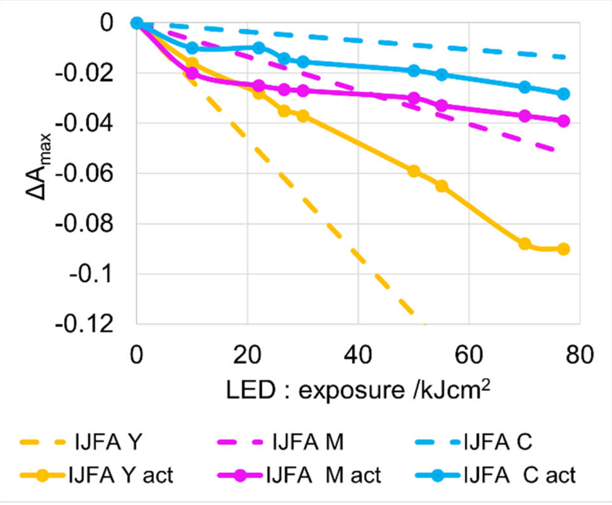
a)



b)



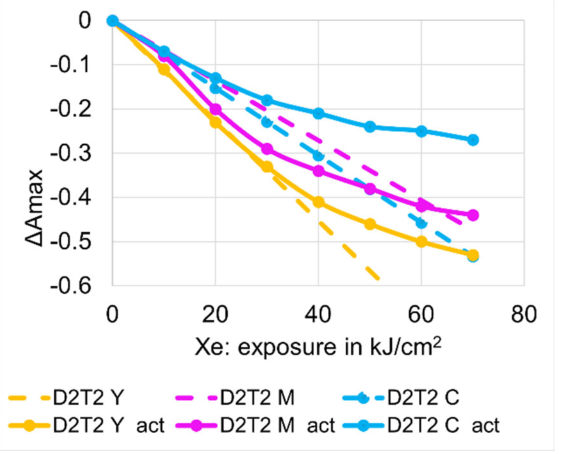
c)



d)

Figure 10: *predicted fading (dashed line) and actual fading (solid line) for LED exposure a) D2T2, b) IJD, c) EP, d) IJFA*

The same approach was then applied for the prediction under L37-filtered Xe-arc exposure. Fig. 11 a-d) shows the results for all four print materials. For rather fast fading materials such as D2T2, the actual fading at higher exposures diverts from the prediction, as the colour patch reaches the bleaching level at which the absorption is significantly reduced, and the original fading curves are no longer linear. More stable materials such as the pigmented EP and IJFA samples show some noise at very low exposure, as for some colorants the absorbance changes are very small.



a)

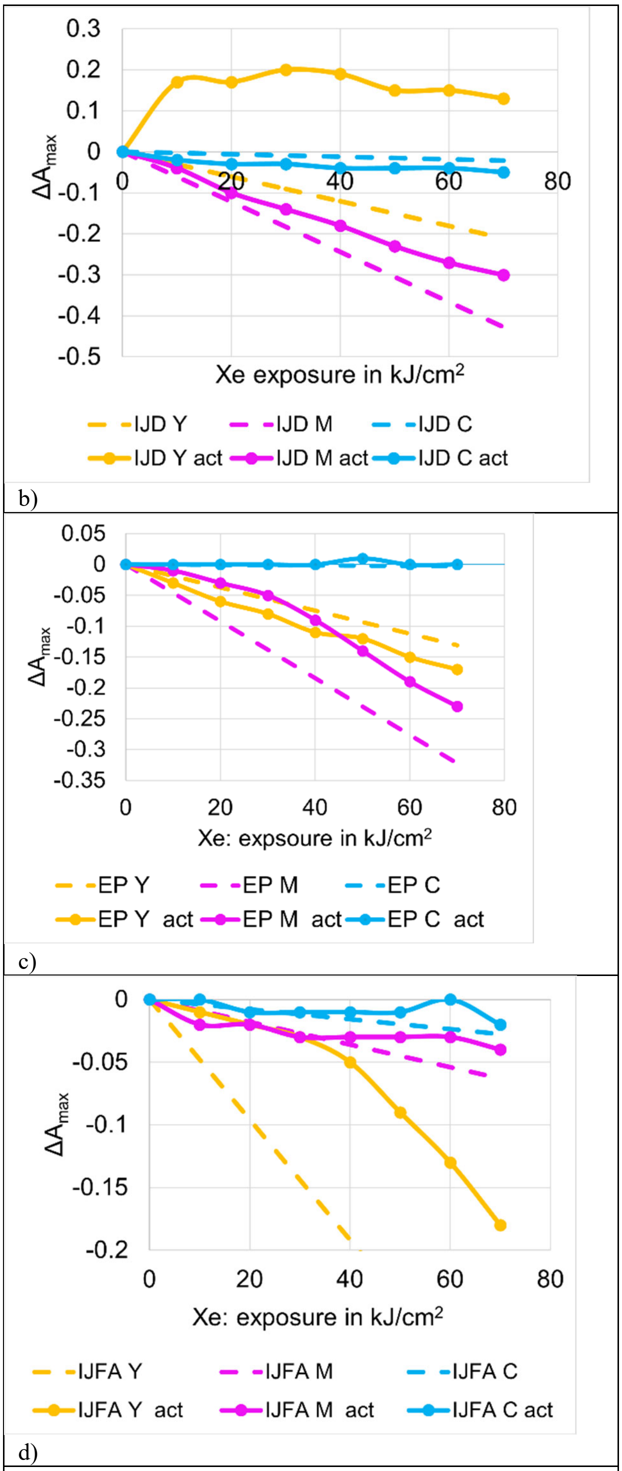


Figure 11: *predicted fading (dashed line) and actual fading (solid line) for Xe-arc exposure a) D2T2, b) IJD, c) EP, d) IJFA*

For certain colorants, the actual fading curve diverts appreciably from the prediction. This is the case of L37-filtered Xenon-arc fading of the IJD yellow, Fig 11b. Actual experiments show an increase whereas the action spectra method predicts a relatively strong decrease. The LED exposure in Fig 10b shows the expected and predicted decrease of yellow absorbance. This suggests that other processes and not only the destruction of colorants have occurred.in the Xenon arc experiment. Fig 12 a and 12 b show an enlargement of a printed yellow patch of the IJD sample before and after exposure to Xenon arc light. The increase in DY is due to lateral bleeding of Y dots during exposure in the chamber. Fig 12b also shows the low stability of the IJD magenta colorant compared to cyan and yellow.

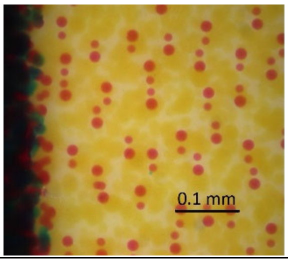
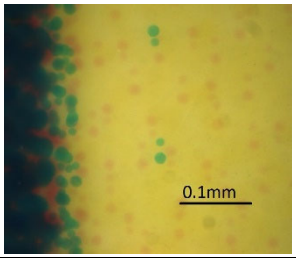
	

Figure 1b. *enlargement of an original printed patch of IJD yellow before exposure*	***Figure 1c*** *enlargement of an original printed patch of IJD yellow after exposure with Xenon arc light*

Conclusions

The study shows that light fading predictions are possible based on action spectra if those are derived from the exact material type, the same dye/substrate combination. In many applications the exact materials combination is not known. General conclusions about colorant fading can be made based on ’average’ action spectra of a certain class of materials, in our case photographic colour print materials. This allows qualifying the destructive potential of light sources in terms of severity factors, and the current investigation provides guidance to improve the method currently described in Annex A of ISO/TS 21139-22 [8]. In another application, the method can help to choose the best trade-off between colour rendering and protection of prints under museums and commercial display locations. In agreement with the literature [6,7], it was found that the wavelength range from 380 nm to 420 nm is the most destructive and causes considerably more degradation than light in the wavelength range 420 nm to 550 nm. Based on this study, light with wavelengths above 600 nm does not cause any degradation in the colorants investigated.

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