Predicting the Light Stability of Contemporary Photographic Print Materials

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ABSTRACT

The light stability of six contemporary photographic print materials was investigated. Two silver halide, one dye sublimation transfer, one liquid toner electrophotographic, one dye based and one pigment based inkjet material on nanoporous RC paper were exposed by a set of narrow band LED covering the visible spectrum. In the accelerated ageing chamber, the samples are exposed at ambient environmental conditions. The colorants in the prints exhibit different fading properties, but all colorants are most sensitive in the wavelength range 400 to 550 nm. Pigment based systems are considerably more stable than dye based systems. The absorbance losses of the colorants per unit of exposure (1 kJ/ cm^2) represent the sensitivity of the colorants to the specific wavelength of light.The sensitivities at different wavelengths are used to predict fading of a white light LED. The method assumes that the changes of narrow band wavelength exposures are additive and that a white light exposure can be simulated by adding photon-energy corrected intensities of narrow wavelength light. Significant fading of at least one colorant is observed for all investigated print materials at 70 kJ/cm^2 exposure.The method predicts absorbance changes of the colorants well for most of the investigated print materials except for silver halide photographic prints. In silver halide prints, fading at longer wavelength is not independent of the presence of light around 400 nm and absorbance losses are not additive. The fading of the colorants depend also on the destruction of sacrificial UV absorbers which are present in the top layer. It is important to clearly identify a material as predictions are only valid for a specific colorant on a particular base material. The method can proabably be extended to other types of print materials, particularly fragile materials, but may not be suitable for complex image structures such as paintings. The conclusions from of the LED exposures can help to select the least destructive lighting for prints on display.

KEYWORDS (light stability testing, contemporary photographic print materials)

RECEIVED 04/02/2025; **REVISED** 13/03/2025; **ACCEPTED** 15/03/2025

1. Introduction

Colour photographic prints are among the more delicate objects in museum collections and require particular care when on display (Beltran et al.2021). If display lighting is kept low, it reduces the visual impact intended by the artist. Prolonged exposure to light will degrade the colours. Particularly for LED lighting, the choice of acceptable light levels, duration of display and best relative spectral irradiance (RSI) are of concern. Some institutions try to balance the visual impact and the degradation by adapting the lighting individually to certain objects (Kore and Durmus, 2024). Others optimize the RSI to reduce degradation (Lunz et al., 2017) for particular objects. There have been approaches to predict photodegradation for classes of materials by looking at the energy of the exposure light (Luo et al., 2018) as the only cause for fading. Yoo at al.(2023) find that different materials have different fading characteristics that have to be taken into consideration. Photodegradation of print colorants is a photoactivated chemical reaction that depends on the excitation energy, but also on the presence of oxygen and other environmental gases (Zhao et al., 2021). The individual properties of the colorants, their particular excitation states and photodegradation pathways are important. As Groenevelt et al (2023) remarks ”Additionally, it was found that oxygen is required in the photodegradation of these specific dyes with VIS light, but not with UV radiation, again indicating that the photofading mechanism can be different depending on the irradiation wavelength”. Many researchers find that light with shorter wavelength is more destructive than light with longer wavelength (Saunders and Kirby, 1994). A general recommendation is that for accelerated ageing, the exposure light source RSI should closely match the display light in the final application. There is a wealth of accelerated ageing test data of photographic print materials with different light sources, such as fluorescent and Xenon light for silver halide materials (Wilhelm and Bower, 1993) or inkjet prints (Wilhelm, 2004), fluorescent light for face mounted inkjet prints (Blaschke-Walther and Dobrusskin, 2015), and UV radiation for UV curing inkjet materials (Maretić et al. 2021). There are few studies with white light LED exposure (Ishizuka et al., 2019a). As there are many different types of LED lighting currently available, many fading experiments with different LED would need to be done to represent the many different RSI of commercial LED.

The following study investigates the light stability of contemporary photographic prints in different spectral regions. Based on the measurement of the sensitivity of colorants to different wavelength of light, it is possible to predict fading for different types of white light exposure, allowing to select light sources that lead to slower fading of colorants. The study also allows to rank the light stability of typical contemporary photographic print materials, in particular when exposed to LED light.

2. Materials and Method

The method was previously described by Hofmann and Hofmann-Sievert (2022 and 2024.).

2.1. *Experimental set-up*

The exposures were done in an accelerated ageing chamber with 18 narrow band LED and 6 white LED.

A diagram of the experimental set up and an enlargement of the optical path for one LED are given in Fig 1 and b.

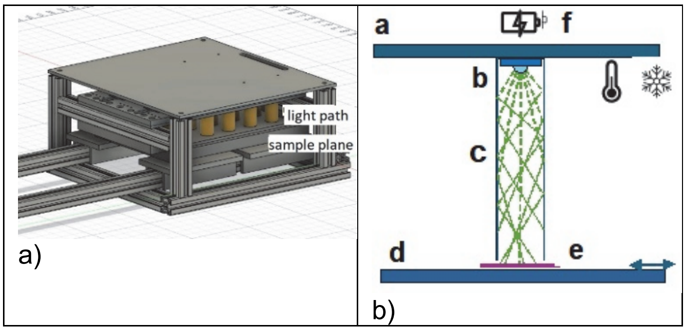


Fig. 1) a) view on exposure chamber b) illumination spot of single LED: (a) cooled optics mounting plate (b) LED on support, with lens, (c) hollow light guide with liner, (d) sample support (sliding) (e) flat sample, (f) regulated power supply

The chamber is kept in an air conditioned room. The light guides for the LED lamps in Fig 1b) are designed to homogenously illuminate the area of the test patch shown in Fig 3 a. Each patch is illuminated by a different LED. Two LED each had the same centre wavelength. All narrow band LED had a typical width at half maximum of 30 nm. The narrow band LED spun a wavelength range of 380 nm to 620 nm. Fig. 2 shows their emission characteristics and the white light LED 4000 K emission as a comparison. The RSI of the LED was measured by an Ocean Optics 2000$^{®}$ spectrometer with UV-VIS radiation guide fibre. A thin polyester foil protected the prints against pollutants. Some of the photographic materials have open porous surfaces that absorb environmental pollutants, particularly ozone, which degrades colorants fast (Reber and Hofmann, 2005).The total irradiance of each LED was measured offline at the sample plane and through the protective foil with a Gentec XLP12–3S–H2–INT-D0® power meter. The narrow band LED had irradiances in the range of 15 to 40 mW/cm^{2}. Four different white LED were used in the chamber. The LED with a correlated colour temperature (CCT) of 5000 K had an irradiance of 77 mW/cm$^{2.}$, the others had irradiances between 19 and 26 mW/cm^{2}.

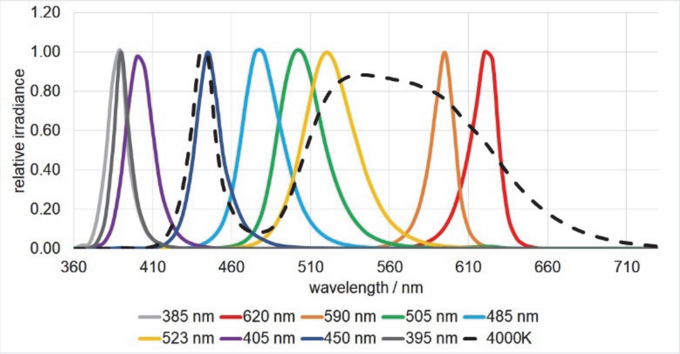


Fig. 2) Emission wavelength of the narrow band LED and of the white LED 4000 K.

The exposure chamber was held at 24 °C ± 2 °C by water cooling. The relative humidity range was 38% to 52%. These conditions are close to typical environmental conditions in homes (Bugner et al, 2006) and in agreement with (ISO 18937, 2023).

2.2. *Materials*

Six different contemporary photographic print materials were investigated: two inkjet (IJ) materials, a dye-based IJ print (IJD)(Epson ET2650® printer on HP Everyday Photo Paper®) and a fine art pigment print on lustre RC paper (IJFA), two chromogenic photo papers (Photo A and Photo B) on glossy RC paper, a dye sublimation transfer print (D2T2) and a liquid toner electrophotographic pigment print (EP) on glossy 200 g/m^2 paper. The samples were provided without further detail by participants of an ISO TC42, WG5 committee's Interlaboratory Test to validate a new version of a standard. They are current commercially available products.

2.3. *Test pattern and homogeneity*

The test sample consisted of paterns with a medium Y,M,C and greywedge shaped patch as shown in Fig 3a. The maximum absorbance of the main colorant before exposure (Amax 0) was about 0.7, the value of a medium light colour as recommended by (ISO 18950, 2021). A white patch in the center was measured in addition. The test pattern was repeated in 6 rows (1-6) and 4 columns (A-D) on the sample page as shown in Fig. 3 b . Each of the 24 patterns was exposed by a different LED.

For some materials, the print patches of yellow, magenta, cyan, and grey were made by pure colorants, for others they consisted of one predominant colorant with smaller amounts of the other colorants. For silver halide prints, grey is a mixture of the three dyes in the layers. Although the dye based ink set for IJD had a black dye, the grey print patch was a mixture of Y,M,C only (see Fig. 4 c). In the case of the IJFA and the D2T2 print, black/grey was a mix of all four colorants. A typical example of the enlarged print patterns of two magenta patches and one grey are shown in Fig. 4 a-c.

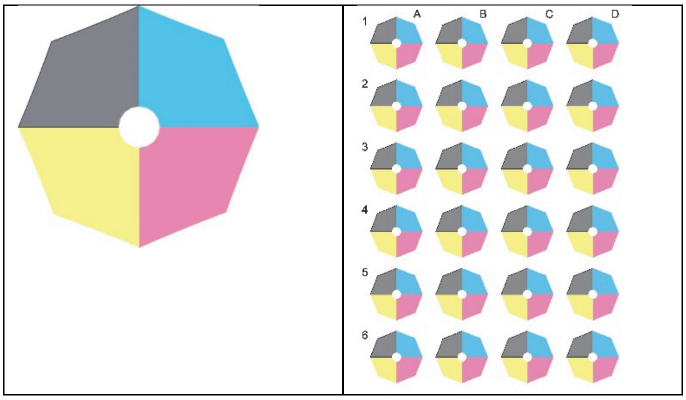


Fig. 3. a) Individual print patch b) test samples with 24 patterns to accommodate the 24 LED exposure spots of the accelerated ageing chamber.

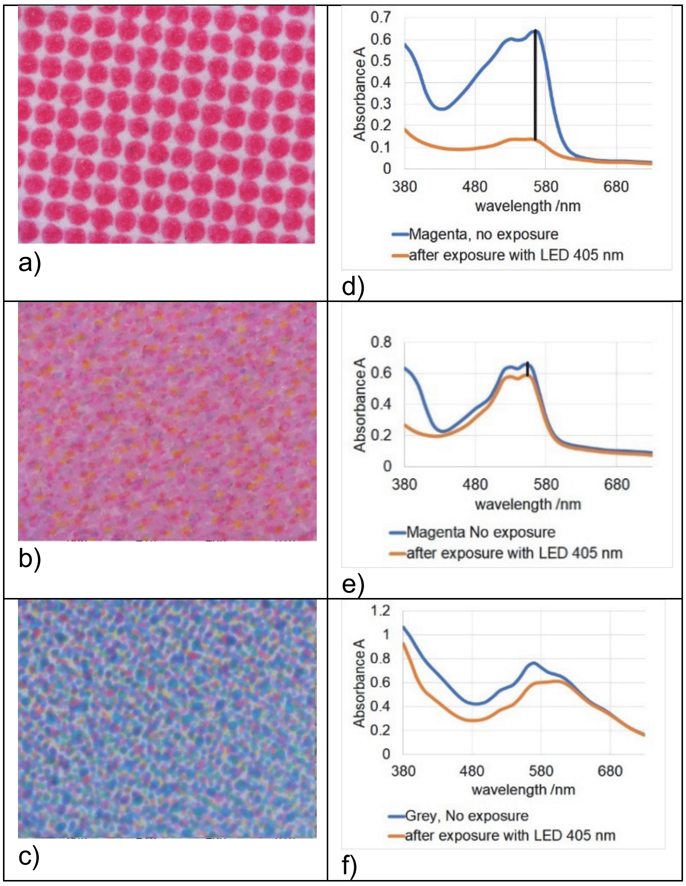


Fig. 4. a) - c) enlargements of an original printed patch with 0.4 mm spot a) EP magenta b) IJFA magenta, c) IJD grey- d)-f) corresponding absorbance spectra before and after exposure d) EP 60 kJ/cm^2 exposure e)IJFA 70 kJ/cm^2 exposure f) IJD 35 kJ/cm^2 exposure. The black line indicates where ΔA_{max} is measured.

The patches were measured in reflectance with a Gretag Macbeth iPro spectral densitometer, which has a fixed filter condition of 'no UV' M2 according to ISO 2009. The measurement range of the reflectance spectrum is 380 nm to 700 nm and the optical measurement geometry is 0°/45°

on a 4.5 mm aperture. A white Melinex® backing was used. To estimate the homogeneity of the test patterns the reflectance spectra were converted into colour coordinates (D50, 2°) The calibration of the iPro is done on a certified, Gretag Macbeth proprietary and instrument specific white tile in absolute white on all 36 wavelengths. Short term reproducibility for this instrument is given by the manufacturer as 0.1ΔE* (D50, 2°) and inter instrument error as 1.0 ΔE* (max), both in CIE 1994 colour space. Colour differences on the test samples were calculated in CIE 1976 space according to recommendations from Ishizuka et al.(2019b).

Before the first exposure, the CIELAB values of the Y,M,C,B wedge patches of 24 colour patterns were averaged respectively. The deviations from the average of the individual colour patches were between 0.2 and 1.2 colour difference in the CIE 1976 (ΔE*) colour space. These variations are small enough to not have a major effect on the fading curves. Colour coordinates were only used to determine the homogeneity of the unexposed print patches.

As colour coordinates do not discriminate between the different dyes present in certain print patches (Fig 4 b and c), they could not be used for the evaluation of colorant fading. The change of the maximum absorbance of the colorant, ΔA_{max} , as shown for magenta in Fig 4 d and e, is used as the y-value of the fading curve. The yellow dye present in the magenta print patch Fig 4 b has no absorbance at the wavelength of 560 nm such that changes at this wavelength are only due to magenta dye reactions.

If the spectra of the pure colorants are known, the analytical spectral densities of dyes in a mixture can be calculated (Kowaliski, 1977) for any mixture, for example for a grey shown in Fig 4 c. However, in our study we focused on colour patches with one predominant colorant and a maximum of 20% of other colorants present. The grey colour patches were not used for the prediction of white LED fading.

2.4. *Test procedure*

All test patches on a sample were measured before exposure, positioned in the light exposure chamber and exposed at subsequent intervals of time. After each exposure interval, the sample was pulled out, measured and repositioned for the next exposure cycle. The intervals were selected according to the light stability of the sample. The test was continued until a significant change in A_{max} on all colorants could be observed for at least one narrow band wavelength exposure. Typical experiments took 2 to 6 weeks for any one material.

We define ΔA_{max} as the absorbance after exposure with x kJ/cm² ($A_{max\,x}$) minus the absorbance before exposure ($A_{max\,0}$). ΔA_{max} was plotted for each colorant and for each narrow band exposure source against the total exposure to derive the fading curves for each wavelength. Two typical fading curves of the exposure of D2T2 with 385 nm radiation are shown in Fig. 5. At a very small exposure, the signal stays below the noise level of the experiment. With further exposure, the absorbance loss becomes linear. The negative slope of this linear part is the sensitivity to the exposure wavelength (Sensi). Further exposure leads asymptotically into bleaching towards the white paper background.

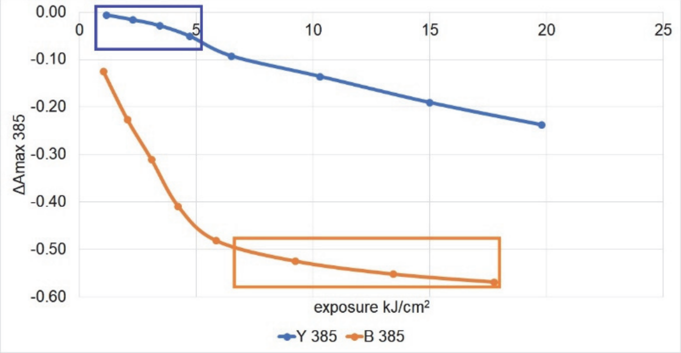


Fig. 5: Fading curves of D2T2 Y and B colorants at 385 nm. The blue rectangle shows measurement noise level, the orange rectangle shows bleaching to white.

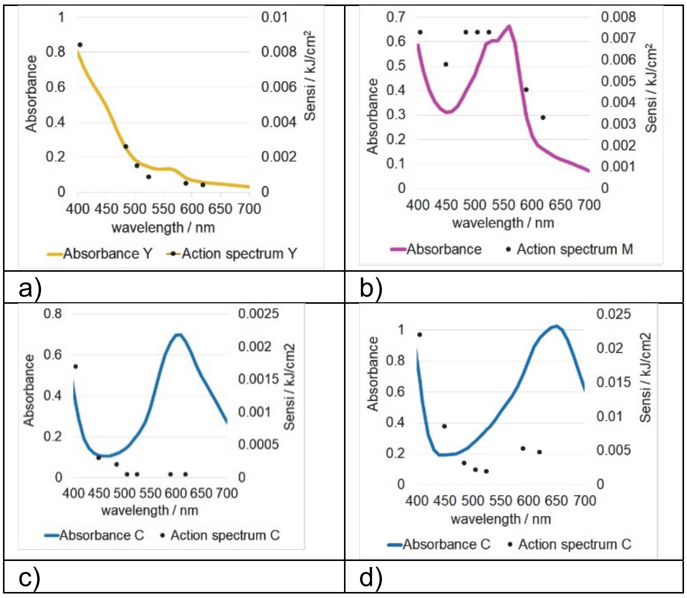
The plot of Sensi as a function of exposure wavelength is referred to as the action spectrum.

3. Results

3.1. *Action spectra*

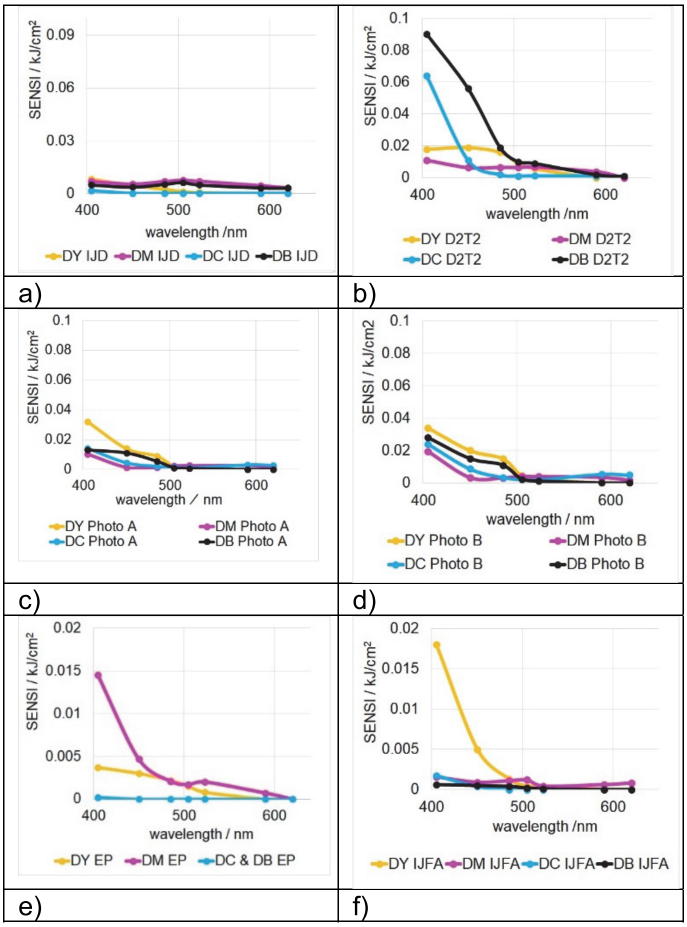
Action spectra and absorbance spectra are related. The first prerequisite for a photochemical reaction to occur is the absorption of light. Most of the absorbed energy is dissipated as heat and only some will lead to chemical reactions (Groeneveld et al., 2023). The action spectrum represents the part of the absorbed light that leads to a reaction, in our case changes in A_{max}. The action spectra and the absorption spectra of different colorants are plotted in Fig. 6 a-d.

While for the yellow colorant, light absorbed over the whole absorption range leads to changes in A_{max}, for the magenta colorant, the maximum of the A_{max} changes is shifted to the lower wavelength of the absorption range. Weyermann et al (2006) find that all colorants are most sensitive at their maximum absorption, others report that certain colorants only react when exposed to light in the blue green wavelength range.



a) b) c) d)

Fig. 6 a-d. Absorbance spectra (solid lines) and action spectra (black points) of a) Y IJD b) M IJD c)C IJD d) C Photo B.



a) b) c) d) e) f)

Fig. 7 a-f. Action spectra of the colorants of photographic print materials, a) IJD b) D2T2 c) Photo A d)Photo B.e) EP f) IJFA.

For the particular IJD cyan colorant shown in Fig. 6 c, degradation reactions are caused solely by exposure of light below 450 nm which is typical for phthalocyanines (Lerwill et al., 2015; Hattori et al., 2012). The behaviour depends on the chemical structure of the colorant. The Photo B cyan in Fig. 6 d also reacts partially to light in the range 550 to 600 nm and probably belongs to a different class of dyes.

The action spectra for the Y, M, C and Grey patch (DY,DM,DC,DB) of all investigated print materials are plotted in Fig. 7 a-f. D2T2 is the least light stable print material due to cyan and grey that are quite sensitive to the short visible wavelength range between 400 and 500 nm. Silver halide (Photo A and Photo B) and IJD prints have rather similar fading properties. The colorants fade at comparable rates, thus lightening the print.

The y-axis scale of the action spectra of the pigment prints in Fig. 7 e and f is one fifth of the scale in Fig. 7 a-d, which means the fading is about five times smaller. The fading of the pigment prints is not very balanced, though. The IJFA sample loses the yellow colorant and the EP loses the magenta colorant, while the other colorants are very stable, leading to a visible colour shift. In many of the materials tested, most of the degradation is caused by light in the wavelength range 400 to 520 nm, even if the maximum of the absorbance of a colorant is higher than 520 nm.

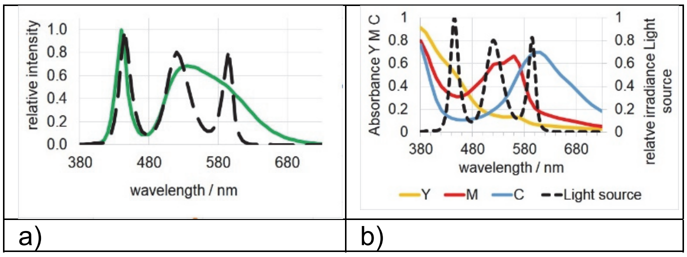
3.2. *Prediction of fading under white light exposure*

The goal of this study was to develop a tool which can predict fading for a white light LED exposure. Two steps are needed to make a prediction based on the action spectra. In a first step, the amount of narrow band exposure which can simulate the white light has to be determined. In a second step, ΔA_{max} has to be derived from the action spectra of the colorants for a virtual exposure to the white light source.

3.2.1. *Simulation of white light exposure*

With the narrow band LED emission spectra as factors and the white light LED spectrum as target, a (Generalized Reduced Gradient (GRG) nonlinear fit was done.The results for the LED 5000 K are shown in Fig. 8 a.

With a limited number of narrow band LEDs it is not possible to exactly match the white light LED spectrum. For the purpose of colour reproduction, such a match would be unacceptable. However, the exact relative irradiance of the exposure light is less important for degradation reactions as long as the light causes the same electronic excitation of the colorant as the reference light (Feller, 1994) and (Groenevelt et al., 2023).



a) b)

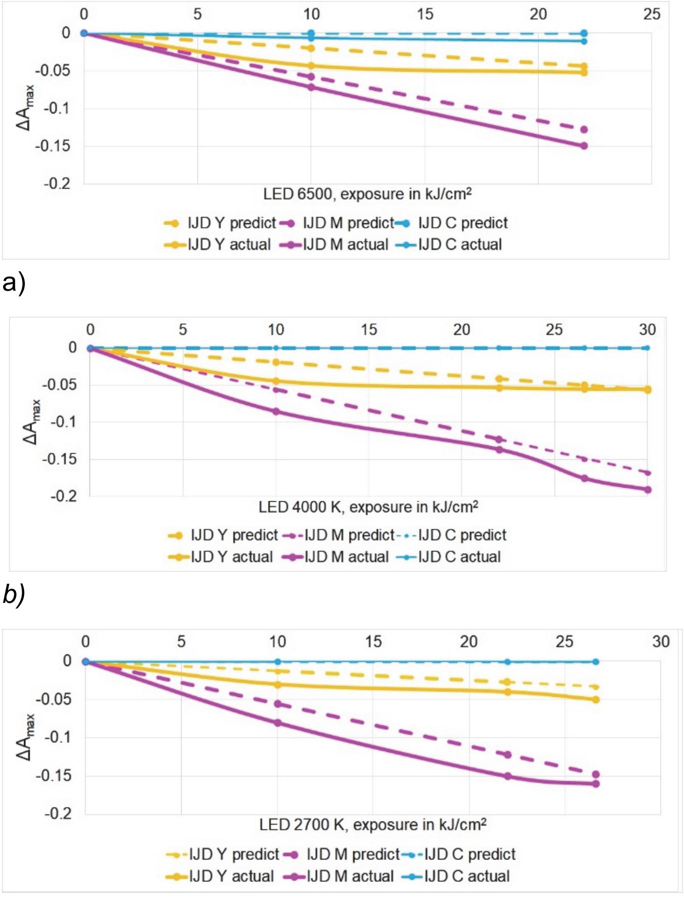
Fig. 8 a) spectrally matched curve (dashed line) compared to the RSI of the actual LED 5000 K (green solid line), b) spectrally matched curve (dashed line) and absorbance of the IJD Y,M,C colorants (solid lines).

Imaging colorants have broad absorption spectra (Aceto et al, 2014) and the narrow band LED do essentially excite one of the absorption bands of the three colorants as shown in Fig. 8 b. It is known from laser fluorescence spectroscopy (Zaffino et al., 2017) that the exposure light does not have to illuminate the whole absorption range, or even the maximum absorbance, to excite colorants.

Apart from the appropriate wavelengths, the GRG fit provides a factor for each narrow band LED which represents how much that LED contributes to the white light spectrum. In the case of the LED 5000 K shown, the factors are 0.01 at 405 nm, 1.0 at 450 nm, 0.8 at 523 nm and 0.81 at 590 nm. As the intention is to match electronic excitation by the white light and not colour, the factors are weighted by the photon energy (Yoo et al., 2023). To predict absorbance changes, they need to be multiplied by the value of the action spectrum and by the overall total exposure at which the comparison is done.

3.2.2. *Prediction of absorbance changes for three LED*

To predict the overall ΔA_{max} change of a white light total exposure of x kJ/cm^2, one needs to calculate the corresponding $\Delta A_{max\ ,\ nm}$ loss for each of the narrow band LED. The weighted factors from 3.2.1 are multiplied with the value of the action spectrum at the particular wavelength, $\Delta A_{max,nm.}$ One unit of the action spectrum is equivalent to the loss of A_{max} at 1 kJ/cm^2 exposure at that exposure wavelength. For a total exposure of 50 kJ/cm^2, for example, one needs to multipliy the value of the action spectrum by 50. This calculation is repeated for each of the narrow band LED and the $\Delta A_{max,nm}$ losses for each excitation wavelength are added to the total change of ΔA_{max} for each exposure. Fig. 9 shows the results of the predicted losses for one material, IJD, compared to the actual losses (ΔA_{max}) measured in the exposure unit for the three white LED (5000 K, 4000 K, 2700 K). Experimental errors can be estimated from the exposures made with the two LED of the same RSI. Those errors were about ±0.02 for all colours. The action spectrum method predicts qualitatively and quantitatively the fading of all three colorants for the three LED with different RSI. As can be seen in Fig. 9 a-c , the predictions agree quite well with the actual fading.



a)

b)

c)

Fig. 9. Predicted (dashed line) vs. actual (solid line) fading of IJD colorants under white light exposure a) LED 6500 K, b) LED 4000 K c) LED 2700 K

The case of an LED with CCT 5000 K was selected for the prediction of fading of the different photographic materials of this study. Bright LED 5000 K are often found in offices and in general lighting but also sometimes in museum lighting (Feltrin et al, 2019).

For most of the print materials shown in Fig. 10 a-d, the prediction of fading based on action spectra works well for all colorants. For the pigment material IJFA, the tested white light exposure was too small for a reliable comparison. For the silver halide print Photo A the predictions are acceptable for yellow and magenta but not for cyan.

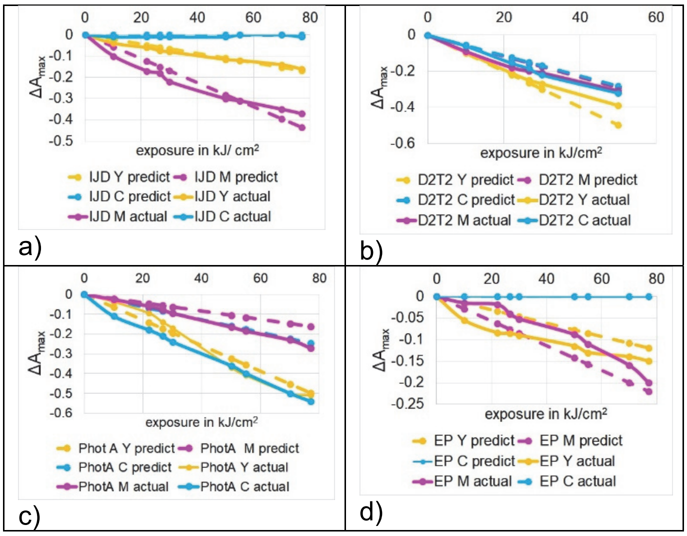


Fig.10. Predicted (dashed line) vs. actual (solid line) fading of print materials for LED 5000 K exposure a) IJD, b) D2T2, c) Photo A, d) EP.

4. Discussion of Results

Many silver halide colour materials have a UV protective layer (Marchesi, 2005; Pénichon, 2013; Rogers, 2007), which is slowly degraded by short wavelength light (García et al, 2010). When the cyan colorant is exposed with the narrow band LED at 620 nm, there is no degradation of the UV protection and the actual density loss is underestimated compared to a white light exposure where red light and short wavelength light are present and the UV protection is degraded.

The example of the silver halide prints points to one of the limits of stability prediction. The method assumes additivity of narrow band fading over a specific exposure range. Decomposing protective colourless additives, strong interactions with other colorants or strong interference with the layer matrix are non-additive factors that hamper prediction. Furthermore, the predictions are only valid if the light degradation is the only factor of destruction of the imaging colorant. In some locations other reactants could attack the colorants in the dark, for example the pollutants that Thickett and Grøntoft (2023) have found in the museum environment.

The prediction can only be made for a specific colorant of a print and only applies to this specific material. It is thus important to unambiguously identify photographic print techniques (Cattaneo et al., 2022; Eom and Lee, 2023) and even colorant types of prints (Silva, 2022) to use it.

The method is particularly suited to print materials with thin layers and a limited number of colorants. The method will probably not be applicable to very complex image structures such as paintings (Dal Fovo et al, 2024). On the other hand, it is suited to very fragile and heat sensitive materials as the exposure takes place at ambient conditions.

Apart from testing a method to predict fading, another aim of this study was to provide quantitative data for the fading of contemporary photographic print materials when exposed to LED light. There are very few published data for fading of photographic prints under LED light as there is no commercial equipment for such tests. One study (Ishizuka et al., 2019a) looks at certain of the materials investigated here with a LED 5000 K and LED 4000 K accelerated light fading chamber. Unfortunately, the authors average the results over all types of materials as their aim is to compare the two light sources. The same set of photographic print materials as in our study was investigated by Duan (Duan, 2024) with a microfadometer (MF). The MF with a Xenon light source was set up to only expose to very small, nearly invisible colour changes, a range of exposure which cannot be reliably tested in our equipment. The ranking of colorant stability in the MF experiment did not agree with long-term Xenon exposures and with the stability ranking of this study. In a paper of Luo et al (Luo et al 2018) inkjet and photographic samples were exposed, but it is not specified if the inkjet sample was a pigment or a dye based print. In addition, the exposure was stopped at about 1.5 Mluxh, about a 5th of the smallest exposure step used in our study, which does not allow a comparison. Eric Luden (Luden, 2018) presents ranges of stability for contemporary photographic materials that are mainly based on Wilhelm Imaging Research studies (Wilhelm, 2025). The Wilhelm data are based on a variety of tested paper and ink combinations of a particular photographic print class, exposed with fluorescent light. The author specifies light stability in years of expected display life before clearly visible fading occurs. Clearly visible fading in this context corresponds to about an average colour difference of 7 in the CIE 1976 (ΔE*) colour space (Ishizuka, 2019b). The average colour difference is the sum of the colour differences of the Y,M,C,B colour patch before and after the expsoure, devided by the number of colours. The display condition of Wilhelm (Wilhelm, 2025) is specified as 450 lux for 12h/day. The LED 5000 data of this study were converted to these conditions and are shown below in comparison to the data from Luden and Wilhelm (Luden, 2018).The condition ‘no UV’ was selected, as the LED 5000 K has no UV emission.

The ranking of stability derived from the two different test methods correlates quite well, bearing in mind that the same class of materials was tested but not exactly the same material types, and that the two light sources have a different RSI.

Tabel 1 Comparison of LED 5000 K fading data with published fluorescent light fading data, units are years until visible degradation occurs.

Material	This study	Wilhelm data /no UV
IJD	13-16	0.3-82
D2T2	11-12	0.3-82
IJFA	137-142	>200
EP	62-66	29-54
Photo	23-25	20-60

The comparison also suggests that a reasonable ranking can be done by accelerated ageing of only a few critical colours. The current study works with only one lightness level per primary colour channel, where as the Wilhelm test target consists of 135 colour patches distributed over the whole colour space. The restriction to very few test patches helps in testing historic photographic materials. As it is not possible to reprint test targets on historic materials that are no longer commercially available, existing and rare expendable printed samples have to be used for testing. The ISO 18950 standard (ISO, 2021) describes how to sample a very limited number of test patches on historic expendable print samples. This study suggest that for a rough ranking of stability, even fewer test patches could be useful.

Though action spectra Fig 7 a-f have been determined by LED exposure, the sensitivity to the particular wavelengths of light are valid for all light sources and some general conclusions can be drawn for museum lighting. Conservators limit the illuminance levels of lighting for prints on display depending on the print light stability. This approach worked well as long as incandescent halogen and indoor daylight were the predominant light sources. New types of light sources, such as LED, have widely varying spectral irradiance. Luminance in combination with spectral irradiance should be taken into account to select the most benign display lighting. We can conclude from the action spectra that most photographic colorants exhibit much stronger fading in the wavelength range from 400-450 nm than at higher wavelengths. To improve display print life, blue light should be kept to the absolute minimum needed for acceptable colour reproduction. For daylight and halogen light sources, the use of cut-on filters with wavelegths of 420 nm is general practice in museum display. Using even longer cut-on wavelengths such as 430 to 440 nm would protect prints even more. An interesting case is the dye sublimation print, D2T2 of this study. According to it’s action spectrum in Fig. 7 b, when exposed with white light in the range from 400-600 nm, for example daylight, the cyan colorant will fade rather fast, as the cyan is very sensitive in the wavelength range 400-450 nm. This would lead to a strong red cast. However, as there is no light below 450 nm in most white LED, the D2T2 cyan stability much improved when displayed under LED lighting. This shows that for certain materials appropriate display light sources can be found that reduce degradation.

Many LED lamps have an excitation wavelength with a maximum at 450 nm, a part of which is converted to longer wavelengths by phosphors. For museum display, LED with a very high conversion to green and red light (warm LED light) should be used. Additional filtering as for daylight sources should be envisaged. The use of high luminosity blue LED is very detrimental to print stability and should be avoided. Particular care should be taken for all dye based photographic prints as they are considerably more light sensitive than pigment based systems.

5. Conflict of interest declaration

The authors declare no conflict of interest..

6. Funding source declaration

The construction of the equipment was funded by the Innosuisse funding agency under the grant Inno-Eng 47431.1.

7. Acknowledgment

We gratefully acknowledge Eduard Baumann for the spectral match module. I am thankful to Jürgen Jung of Agfa-Gevaert NV, convenor of ISO TC42, WG 5, and the whole WG 5 international team for providing the sample set and for many fruitful discussions. Our special thanks go to Henry Duan from NARA for the many interesting discussions about fading methods.

8. Short biography of the author(s)

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Manfred Hofmann - • Dr. Manfred Hofmann has worked for the Swiss chemical society Ciba as analytical chemist, later directed a laser laboratory to investigate light based materials processing. After a novel laser marking project, he developed photopolymer materials and process parameters for 3D Printing, As the business shifted he cofounded a separate company, which later became a part of 3D Systems Inc.

Licensing terms

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