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Light Emitting Diodes (LED) for Aqueous Light Bleaching of Paper

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Abstract: High performance daylight LED lamps are compared with HID lamps for light bleaching of paper. The LED can be placed in closer proximity to the object than the HID lamps, causing a significantly increased, uniform light exposure. Two commercial LED systems with 4000 K and 6500 K colour temperature were installed in a convertible test device with a polypropylene tray in default exposure distance of 10 cm and 20 cm. A HID lamp in 60 cm and 120 cm distance served as a reference. Samples of two naturally aged rag papers were bleached with both LED systems and with the HID while immersed in water. All three light sources increased brightness (CIELAB L*), though the LEDs with 4000 K colour temperature were most effective. They had no negative effect on the molar mass and the cellulose carbonyl group content while LEDs with 6500 K colour temperature caused molar mass decrease and carbonyl group increase. LEDs of a 4000 K or similar colour temperature are a promising option for improved light bleaching of paper, reducing the treatment and aqueous exposure time and eliminating UV radiation.

Keywords: innovation, LED technology, bleaching, LED, light bleaching

1 Introduction

Light bleaching, historically practiced by sunlight exposure, was rediscovered in conservation in the 1970s (Branchick et al. 1982; Keyes 1982; Smith 2009) and has since become a recognised bleaching method (Brückle 2009b; Hofmann et al. 1991; Schaeffer et al. 1997). The intensity of light exposure determines the rate of bleaching action (Feller et al. 1982; Palmer Eldrige 1982; van der Reyden et al. 1988). With sunlight and fluorescent tubes, the noted drawback concerns the potentially long duration of aqueous exposure (Baker 1982, 1986; Saur-Aull 1996; Brückle 2009a;

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Henniges and Potthast 2009), due to their low light intensity (Gowland and McAusland 2003). The first light source with significantly higher luminous flux was the high-intensity-discharge lamp (HID) introduced by Perkinson (2001). The illuminance was adjusted by the distance between the wetted or immersed object and the lamp. The 300 W HID lamps in this study provide a maximal illuminance of about 50,000 lx when used at the nearest recommended distance to the object of 60 cm. However, other published data suggests that HID laps with greater power are capable of reaching levels as high as 100.000 lx (118.000 lm, 120°, 60 cm) (Schopfer 2012). Due to the high thermal radiation emitted by all HID lamps, they must not be placed closer to the object to avoid heat accumulation and corresponding negative effects on the object, in particular protein sizing and media (Schaeffer 1991).

Light emitting diodes (LED) offer several advantages over the established light sources. Invented over 30 years ago, they have gone through a tremendous development toward a high level in efficacy and luminous flux. Today, they are present in countless lighting systems for indoor and outdoor applications. The currently available LED chips (≤1 cm^2) are significantly smaller than any traditional light source. High-performance LEDs by far exceed all other sources in their illumination potential (Figure 1). The efficacy of LEDs also tops most other

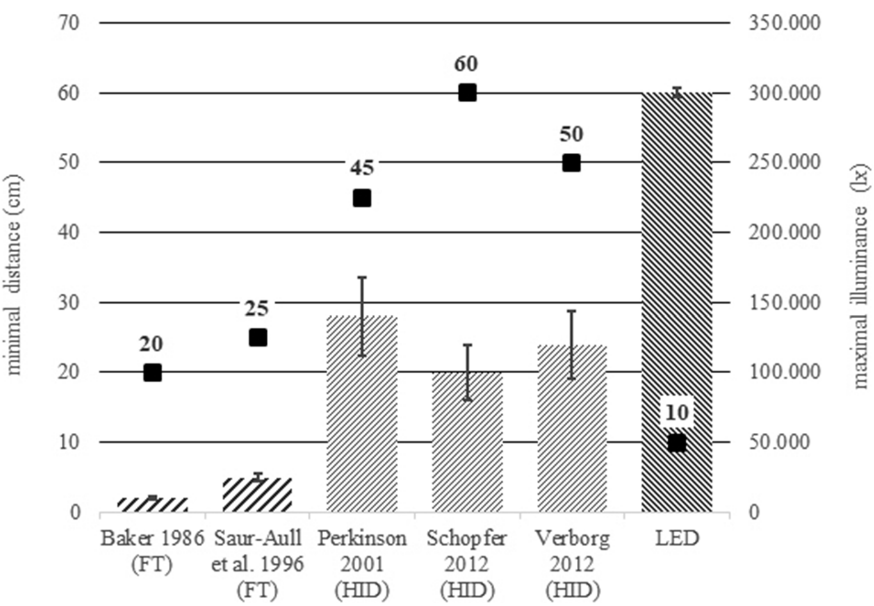

Figure 1: Illuminance of LED in comparison to fluorescent tubes (FT) and high-intensity discharge lamps (HID) according to published studies (see references). Bars indicate achievable illuminance in lux (lx); dots indicate the closest recommended distance (cm). Error bars indicate fluctuations in illuminance due to setup and ageing of the lamps.

lighting technologies. Available in a wide range of specifications and pre-assembled modular systems, they have replaced numerous traditional lighting technologies also in museum lighting (Garside et al. 2017; Herzberg 2015; Michalski et al. 2012; Miller and Druzik 2012). Considering the past development, it seems likely that luminous flux and efficacy will see further increases in the future. Due to their monochromatic light emission, LEDs usually do not emit ultraviolet (UV) radiation, which is found in the emission of all other light sources used in bleaching. UV radiation has an accelerating effect on paper bleaching but also on cellulose degradation independent of the visible (VIS) light intensity (Feller et al. 1982; van der Reyden 1988).

For these reasons, LEDs are an interesting alternative radiation source for light bleaching. This study focuses on the characteristics of modular LED systems, their possible application in bleaching, their effectiveness and the cellulose stability. They are also compared to HID lamps available in the lab.

2 Light emitting diodes (LED)

2.1 Technology

LEDs are made of semiconductor crystals that can allow or block the flow of electrons depending on direction of the applied current (Appendix A). When an aligning current of sufficient voltage is applied to the crystals, they emit light. The light emission increases with increasing voltage until a maximum is reached. The emitted light is of a specific wavelength which depends on the elemental composition of the crystal. To produce white light, a LED with a peak in the shorter wavelengths (blue) is combined with a phosphor-based filter layer that transforms a part of the blue emission into light with greater wavelengths. The mixed light appears white (Dohlus 2015). The thickness and composition of the filter determines the colour temperature and spectral composition of the white light. Unlike other light sources, white LED do not emit high levels of infrared radiation. The energy that is not transformed into light remains in the crystal in form of heat. The diodes are usually attached to an aluminium board as a thermal transmitter (Figure 2) that absorbs the process heat and avoids overheating and disintegration of the crystal. Due to their power, high-performance LED usually require additional cooling units such as heat sinks and fans.

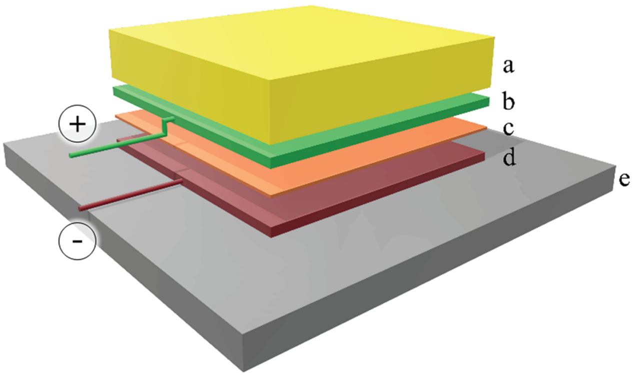

Figure 2: Model of a white light LED semiconductor: (a) the phosphorous filter covering a crystal containing (b) the p-doped layer, (c) the active area that emits radiation under aligning electrical current and (d) the n-doped layer. The semiconductor is attached to (e) the substrate.

2.2 Selection criteria for the tested LED modules

Given the complexity of the field and the limits of time and resources it was necessary to narrow the search to essential specifications for the selection process.

2.2.1 Physical shape

Pre-assembled LED modules and components are available in a vast variety of sizes and specifications, ranging from small single LED chips to complex multi LED modules. Theoretically, any given LED chip or module could be chosen for incorporation in the study. We concluded that a commercially available, modular system would offer the best comparability and reproducibility. Pre-assembled modules with multiple LEDs both simplify the construction of larger units with consistent illumination and minimize the risk of malfunction. LED are best arranged in a grid pattern to obtain even illumination and a homogeneous bleaching effect.

2.2.2 Luminous flux

The quantity of VIS emitted by a light source is characterised by the luminous flux. The unit lumen (lm) is defined as the product of the luminous intensity of one candela (cd) per steradian (sr). The luminous flux does not represent the actual energy emitted by the light source. UV and IR radiation are not included and must be considered separately. The unit for the light intensity on a given surface is the illuminance in lux (lx). Depending on the distance between light source and surface it represents the energy of VIS per square metre (1 lx = 1 lm/m^2). A LED module was sought with a luminous flux comparably to or higher than the HID lamps present in the lab. The illuminance (lx) could be amplified by placing the LEDs in much closer distance to the object than the 60 cm recommended for the HID (Schopfer 2012) since the thermal radiation (IR) emitted by the LED is significantly lower.

2.2.3 Luminous efficacy

The luminous efficacy is expressed in lumen per Watt (lm/W). It quantifies the energy of the emitted luminous flux (lm) in relation to the radiant flux (W) of a given light source. The efficacy is in correlation with parameters like colour temperature (K) and colour rendering index (R_a) since it exclusively represents the part of the consumed energy that is transformed into VIS. Current literature mentions the highest value theoretically achievable for white light to be 250–370 lm/W (Murphy 2012). However, an ideal monochromatic green light of 555 nm is believed to be able to transform 100 % of the energy into light which would represent 683 lm/W (Wyszecki and Stiles 2000). The higher the efficacy of a light source, the more energy is transformed into VIS and the less energy is emitted as thermal radiation or UV. Fluorescent tubes reach levels of around 50–70 lm/W (Baker 1986; Saur-Aull 1996). With about 80–118 lm/W, HID lamps show a higher luminous efficacy (Perkinson 2001; Schopfer 2012). Most current LED chips show levels of efficacy between 130–180 lm/W. The most efficient ones currently reach levels of around 200 lm/W, which might even further increase with future technical developments. For this study, a LED with the highest available efficacy, considered the second most important criteria following luminous flux, in combination with excellent overall performance concerning the noted criteria was chosen.

2.2.4 Colour temperature

The spectral or wavelength composition of white light, i. e. colour temperature or Kelvin (K), encompasses the infrared spectrum (3,200 K) at the low end, the VIS range, and UV at the high end (8,000 K) (Dohlus 2015; Heinz 2009). The higher the colour temperature of a light source, the greater the amount of blue light and the higher the energy that is transmitted by the light. Blue light must play an important role for the success of a light bleaching as it carries the most energy in the VIS spectrum but is not as damaging as UV radiation.

2.2.5 Colour rendering

The colour rendering index CRI (R_a) indicates the ability of a light source to reproduce the spectral range of natural daylight that ensures accurate colour perception. The highest possible CRI (R_a = 100) equals day light. Spectral deviations cause inaccurate colour perception. The CRI is related to the colour temperature. Up to a colour temperature of 5,000 K, the spectral composition of artificial light is compared to the black body of the corresponding temperature. Above 5000 K, natural daylight is taken as the standard (Dohlus 2015). The CRI is not directly related to the bleaching effect of the light. For example, LED with low CRI but high frequency such as monochromatic blue light can be more effective for paper bleaching than white light. However, a high CRI is important for observing colour change of the object during treatment.

2.2.6 Radiant flux

The electric energy consumed by a light source in a given time is called radiant flux. The unit Watt (W) is defined as the product of the energy in joules (J) per second (1 W = 1 J/s). Due to direct link between the already defined luminous flux and the generally high luminous efficacy the radiant flux was considered to be of secondary importance to the selection process.

3 Tested light sources

Two LED were selected, Aventrix and MiniMatrix, supplied by the international supplier LUMITRONIX® LED Technik GmbH (Hechingen, Germany). The modules can be assembled to create larger lighting both units.

3.1 Aventrix (AVX)

Originally designed for street lighting, the Aventrix 4 × 4 module (Figure 3) features 16 high-performance LEDs of the Nichia E21 series (NVSLE21AT; R70) (Lumitronix (1) 2017; Nichia (1) 2017) (summary of properties, see Table 1). The chips are mounted on

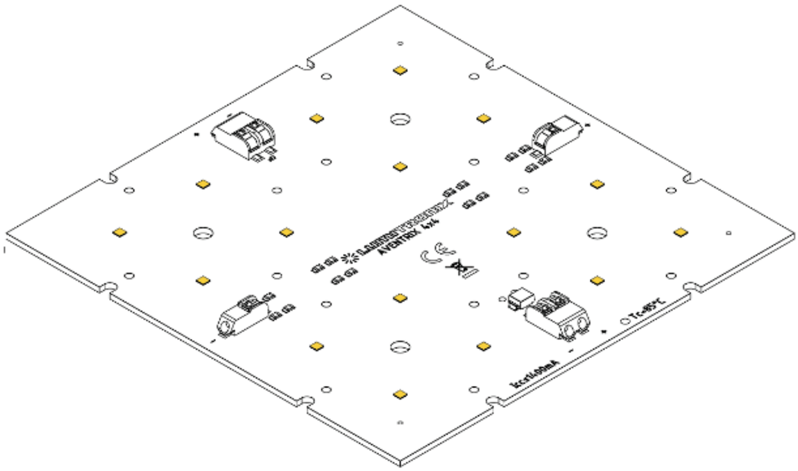

Figure 3: Aventrix 4 × 4 (AVX) module with 16 LED chips (yellow) mounted on an aluminium core circuit board (drawing courtesy of LUMITRONIX® LED Technik GmbH, 2017).

a square aluminium core circuit board (12 × 12 cm). With a maximum luminous flux of 7,785 lm per module, they provide a high level of luminous flux. The modules are dimmable by adjusting the voltage between 44 V and 48 V (DC). Each module consumes a total radiant flux of 68.8 W (Lumitronix (2) 2017). With a medium luminous efficacy of 136 lm/W, they are about 60 % more efficient than the HID lamps currently used in the lab (Lumitronix (1) 2017; Osram 2017). A square lighting unit of 1 m^2 requires 64 modules (8 × 8; 96 × 96 cm) and emits a total luminous flux of around 498,240 lm while consuming a radiant flux of 4,400 W. The modules can be attached either with screws though pre-drilled holes in the circuit board or with heat transmitting epoxy resin. The lifespan is estimated with above 60,000 h. With daily 8-hour use, the AVX will last 20 + years. Since most labs use light bleaching not continuously, the actual life span will be longer. Due to their high radiant flux, AVX need a passive cooling unit such as a heat sink to remove process heat and avoid heat accumulation as well as diminished performance.

3.2 Minimatrix (MMX)

The MiniMatrix system of the Nichia 757 series (NT2W757DRT; R8000) (Nichia (2) 2017) was designed for backlighting in architectural and advertising elements (Figure 4) (summary of properties, see Table 1). In the factory-made state, 126 segments, each 3 × 3 cm and featuring four LEDs, are connected in a 27 × 42 cm

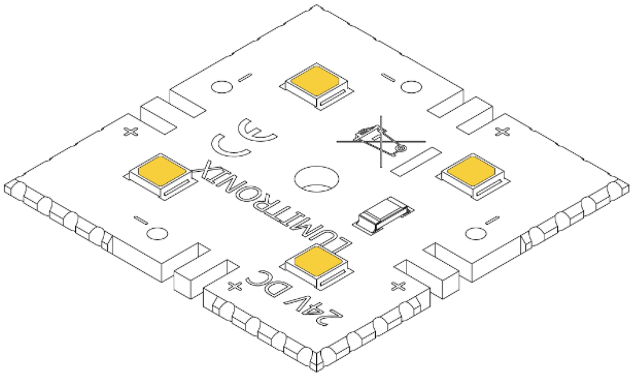

Figure 4: MiniMatrix (MMX) segment. Four LED chips (yellow) are mounted on honeycomb aluminium circuit board with perforated contacts around the outer edges. Additional gaps are added at each side for insertion of connecting bridges (drawing courtesy of LUMITRONIX® LED Technik GmbH, 2017).

Table 1: Characteristics of the MMX and AVX LED and the Osram HID.

	MiniMatrix (MMX) (Nichia NT2W757DRT; R8000)	Aventrix (AVX) (Nichia NVSLE21AT)	HID (Osram Power Star HQI TS 400 W/D; Norka Pollux 1 400W)
dimensions	30 mm × 30 mm	120 mm × 120 mm	579 mm × 318 mm
colour temperature	6,500 K	4,000 K	5,500 K
angle of radiation	120°	120°	–
segments/m^2	1,024	64	2
power consumption/ segment	0.48 W	68.8 W	400 W
power consumption/m^2	492 W	4,400 W	800 W
luminous flux/segment	78 lm	7,785 lm	35,000 lm
luminous flux/m^2	79,870 lm	498,240 lm	70,000 lm
Voltage	24 V	48.8 V	118 V
Amperage/Segment	0.002 A	1.4 A	4 A
Amperage/m^2	20 A	90 A	8 A
luminous efficacy	163 lm/W	136 lm/W	87 lm/W
colour rendering index (R_a)	>80	>70	>90
lifespan	>200,000 h	>60,000 h	12,000 h
external cooling	no	yes	yes
dimmable	yes	yes	no

module. By breaking the perforated joints between the segments, the module can be divided in any preferred number of segments. Each segment features electronic contacts on each edge. By attaching single segments or segment clusters with special board connectors, a module of a preferred shape can be built (Figure 5), for example to backlight single letters in an LED billboard (Lumitronix (3) 2017). Their spectral luminous efficacy of 163 lm/W is 96 % higher compared to the HID used in our study. Each segment provides a luminous flux of 78 lm. In a square lighting unit of 1 m^2 (32 × 32; 96 × 96 cm) they would emit a total luminous flux of 79,870 lm and consume a radiant flux of 492 W. The segments are dimmable between 20 V and 24 V. With daily 8 hour use, the MMX will last ca. 68 years. Since most labs use light bleaching not continuously, the actual life span will be longer, and exceed that of HID (Osram Powerstar HQI TS 400 W/D) 16 times. The segments are built of a lightweight honeycomb aluminium board. Because of their relatively high colour temperature, high efficacy and lower luminous flux, the MMX does not require external cooling. By attaching the modules with plastic spacers at a short distance to the supporting board, the airflow around the module ensures sufficient cooling.

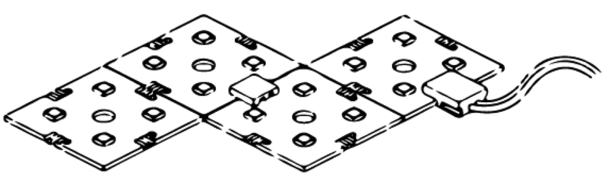

Figure 5: MMX segments held together by connectors that ensure power supply (drawing courtesy of LUMITRONIX® LED Technik GmbH, 2017).

3.3 HID lamps

The setup featured two cased 400 W HID lamps (Osram Power Star HQI TS 400 W/D bulbs in Norka Pollux 1 400 W) suspended over a sink by scissor mounts. The distance to a bleaching tray placed in the sink can be adjusted between 10 cm and 120 cm. A black curtain with inside reflective coating is closed with Velcro fasteners around the sink before treatment begins, so the unit can be safely operated by the conservator without direct exposure to the intense VIS/UV. Pre-heating 10 minutes to reach the maximum luminous flux of 35,000 lm is part of every treatment. After treatment termination, they must cool down for up to 20 minutes before they can be started again. During operation, tinted UV-filtering goggles for eye protection are required when opening the curtain. The colour temperature of the bulb is 5,500 K with a colour rendering index of $R_a > 90$. The luminous efficacy is about 87 lm/W. The two lamps can be adjusted and operated independently. For the test one HID lamp was used.

3.4 Differences between MMX, AVX, and HID

Both LED modules fulfil the desired properties (see 2.2) while they also show certain differences (Table 1).

By far the most obvious difference between the two modules is their luminous flux. Per module, the luminous flux of the AVX is 99 times higher than the MMX which is only in part due to dimensional difference. When calculated per $1\,m^2$, the AVX still reaches a luminous flux about 6 times higher than the MMX. Compared to two HID lamps illuminating $1\,m^2$, the MMX are slightly (14 %) and the AVX more than 7 times (712 %) more intense. Also, LED can be placed at a shorter distance to a substrate than HID, which allows an exponential increase in illuminance (lx), so it was expected that especially the powerful AVX would show a greater bleaching efficiency.

MMX segments are 1/16 the size of AVX, requiring 16 more segments of MMX than of AVX for a light bleaching unit of given dimension. A large number of segments may prove disadvantageous because the relatively frail connections between the segments may break, causing power disconnection. Segments can then only be reattached by inserting a separate connector, which requires extra space and disrupts the uniformity of light distribution. However, multi-segment modules allow more flexible uses.

MMX segments mounted on corrugated board are significantly more lightweight than the AVX mounted on solid board. Also, MMX shows a higher colour temperature and spectral distribution than AVX. While the AVX shows a sharp peak around 450 nm and a broad second peak around 590 nm, the MMX shows a more prominent sharp peak around 460 nm and a low curve peaking at 580 nm (Figure 6). The spectral luminous efficiency of MMX is slightly higher than that of AVX and is significantly higher than for the featured HID lamps.

4 Experimental

A test light bleaching unit was designed that features an aluminium profile frame, metal brackets for suspending a removable polypropylene tray at a desired distance from the light source, a set of four cooling fans and the LED source. The MMX and AVX modules and thermal transmission supplies each

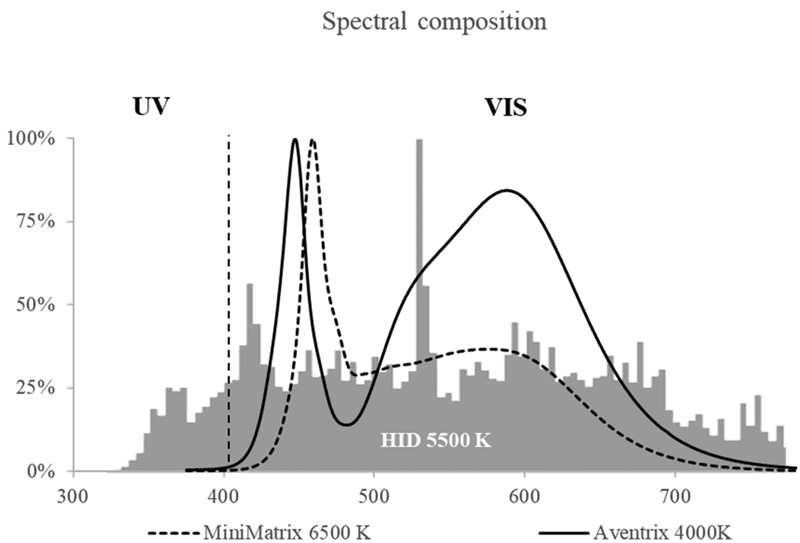

Figure 6: Light spectrum of the 4,000 K Aventrix 4 × 4 (AVX) with NVSLE21AT chip (R70) and 6,500 K MiniMatrix (MMX) with NT2W757DRT chip (R8000) compared to the Osram HID lamps (Power Star HQI TS 400 W/D); (after data by LUMITRONIX® LED Technik GmbH (2017) and Osram (2017)).

were mounted on a 1.5 mm aluminium plate (Figure 7). Each LED panel was connected via a lustre terminal and cable to an adjustable 300 W laboratory DC power supply. Since the DC power supply heats up during operation and with increasing power, the cable was sufficiently long (1.5 m) to avoid heat transfer to the LED modules. The LED modules were easy to mount and exchange in the frame. The MMX module featured 64 segments with a total luminous flux of 4,992 lm, the AVX module featured four segments with a total luminous flux of 31,140 lm and included an aluminium heat sink on the back. Although the LED spectrum is UV-free, at maximum intensity it is hazardous, requiring tinted goggles with 60 % light transmission rate during operation.

4.1 Test papers

Two naturally aged, blank papers with sufficient sheet dimension and intense, homogeneous discolouration were selected (Table 2). A bathophenanthroline test paper confirmed the absence of free iron(II) or iron(III)ions (Neevel and Reißland 2005). The surface pH, determined with a surface pH electrode and demineralised water (2 mL) in the centre of each sample in 16 (paper 1) and 14

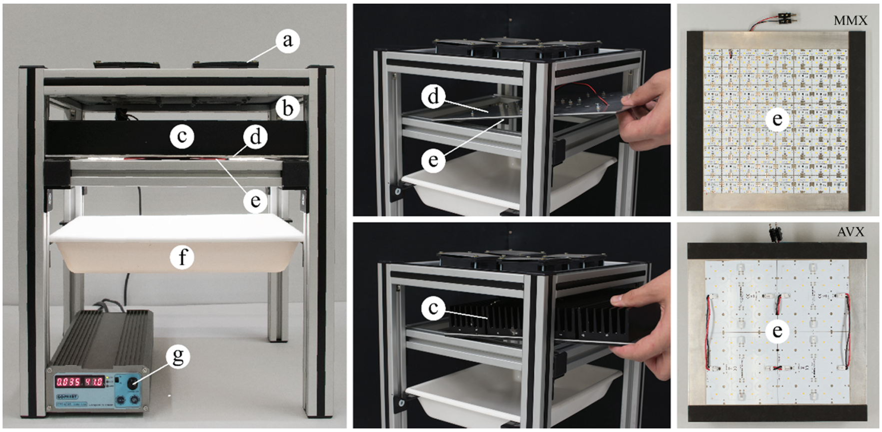

Figure 7: Light bleaching test device with (a) cooling fan, inserted in (b) corrugated cardboard, (c) heatsink, attached to (d) aluminium plate supporting the (e) LED module (here: AVX). The distance between the LED and the tray (f) is adjustable between 3–30 cm. The DC power supply (g) serves as an on-off control and determines the illuminance by setting the desired voltage.

Table 2: Spot test results for test papers.

Test	paper 1	paper 2
water drop	2–3 min.	<5 sec.
Biuret	positive	negative
bathophenanthroline	negative	negative
pH	6.17 ± 0.11	6.17 ± 0.21

(paper 2) repeat measurements showed an average pH of 6.17. Three colour measurement areas (2 cm diameter) were marked on each sample.

Paper 1 is a handmade, late 18th- to early 19th-century rag paper that was gelatine-sized as indicated by a Biuret test (Mayer 2018) and slow water absorption. It is relatively thick and probably intended for letterpress printing. The sheet (40 × 40 cm) showed a homogeneous dark yellowish discolouration. It was divided into 16 samples measuring 6 × 20 cm each.

Paper 2 is a thin handmade rag paper, likely from the early twentieth century and likely unsized or weakly sized as it tested negative for gelatine and showed a rapid water absorption. The sheet (28 × 48 cm) showed a relatively homogeneous light yellow discolouration. It was divided into 14 samples measuring 6 × 14 cm each.

4.2 UVA content and illuminance of the tested light sources

The energy of UVA radiation emitted by the LED and HID (mW/m^2) as well as its correlation with the luminous flux (µW/lm) was determined with an ELSEC 764 photometer (Table 3). The HID emits a significant level of UV radiation as illustrated in Figure 6. At a distance of 60 cm the exposure is 18,700.80 mW/m^2 with a ratio to the VIS of 423.00 µW/lm. At 120 cm distance, the exposure dropped by 60 % to 7101.00 mW/m^2 but the ratio of 405.60 µW/lm remained. For both LEDs, the relative amount was too low to be displayed by the photometer, indicating that there is no UV radiation in the emitted light. The small amount of W/m^2 is likely due to daylight UV transmitted through the room windows during measurement. The HID was used unfiltered for UV in this study.

Table 3: UV radiation determined for both settings of the tested light sources (five measurements each).

type	mW/m^2	standard deviation	µW/lm	standard deviation
HID 60 cm	18,700.80	±159.89	423.00	±0.50
HID 120 cm	7,101.00	±14.20	405.60	±4.19
MMX 10 cm	6.88	±0.29	0.00	±0.00
MMX 20 cm	3.16	±0.17	0.00	±0.00
AVX 10 cm	137.00	±1.71	0.00	±0.00
AVX 20 cm	53.60	±0.15	0.00	±0.00

The homogeneity of the LED illuminance was checked by exposing undeveloped cyanotype paper to the LED sources at the closest chosen treatment distance (10 cm) (Figure 8). One quadrant of the paper was covered with Marvelseal® 360 before the start of exposition. The remaining quadrants were covered, respectively, after 2, 5 and 10 minutes. The exposed paper sheets were developed in demineralised water and air-dried. Any variances in the developed cyanotype's blue colour would represent uneven exposure caused by lower or higher illuminance. Both cyanotypes were evenly developed (disregarding a small contamination-induced error in the bottom left segment of MMX), indicating a homogeneous LED light distribution.

4.3 Treatment

Test papers 1 and 2 were treated as summarized in Table 4.

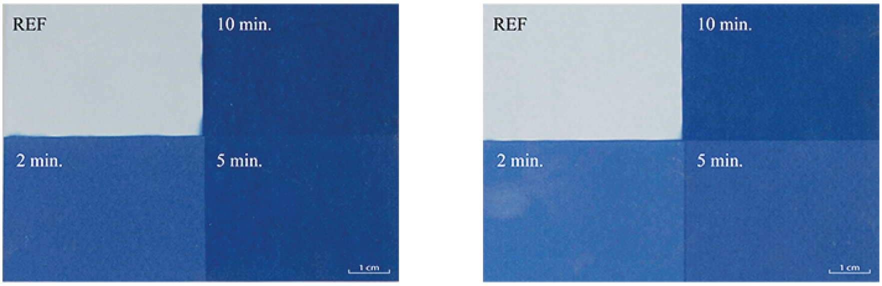

Figure 8: Cyanotype papers (each 7 × 10 cm) developed after different exposure durations under AVX (left) and MMX (right), to verify homogeneous illuminance at a short distance (10 cm).

Table 4: Abbreviations and corresponding treatments (read: treatment-exposure distance-short or long duration) including luminous exposure levels for papers 1 and 2 (except: REF and REF-G). See Figure 9 for results.

Treatment group	Abbreviation	Treatment	Luminous exposure (lxh)
0	REF	paper 1 and 2, reference, no treatment (paper 1: 2 samples at different sheet positions)	–
	REF-G	paper 1, reference, 3 × 15 min immersion washed (IW) (paper 1: 2 samples at different sheet positions)	–
1	HID-2–1	IW + HID, 120 cm, 2 h	35,266
	MMX-2–1	IW + MMX, 20 cm, 2 h	103,286
	AVX-2–1	IW + AVX, 20 cm, 2 h	269,362
2	HID-2–2	IW + HID, 120 cm, 4 h	70,532
	MMX-2–2	IW + MMX, 20 cm, 4 h	206,572
	AVX-2–2	IW + AVX, 20 cm, 4 h	538,725
3	HID-1–1	IW + HID, 60 cm, 2 h	87,730
	MMX-1–1	IW + MMX, 10 cm, 2 h	192,892
	AVX-1–1	IW + AVX, 10 cm, 2 h	593,460
4	HID-1–2	IW + HID, 60 cm, 4 h	175,459
	MMX-1–2	IW + MMX, 10 cm, 4 h	385,783
	AVX-1–2	IW + AVX, 10 cm, 4 h	1,186,919

4.3.1 Colour measurement

CIELAB colour was measured with a Datacolor Check II spectrophotometer with a D65/10° illuminant. Each sample was measured 3–5 times on 3 marked spots

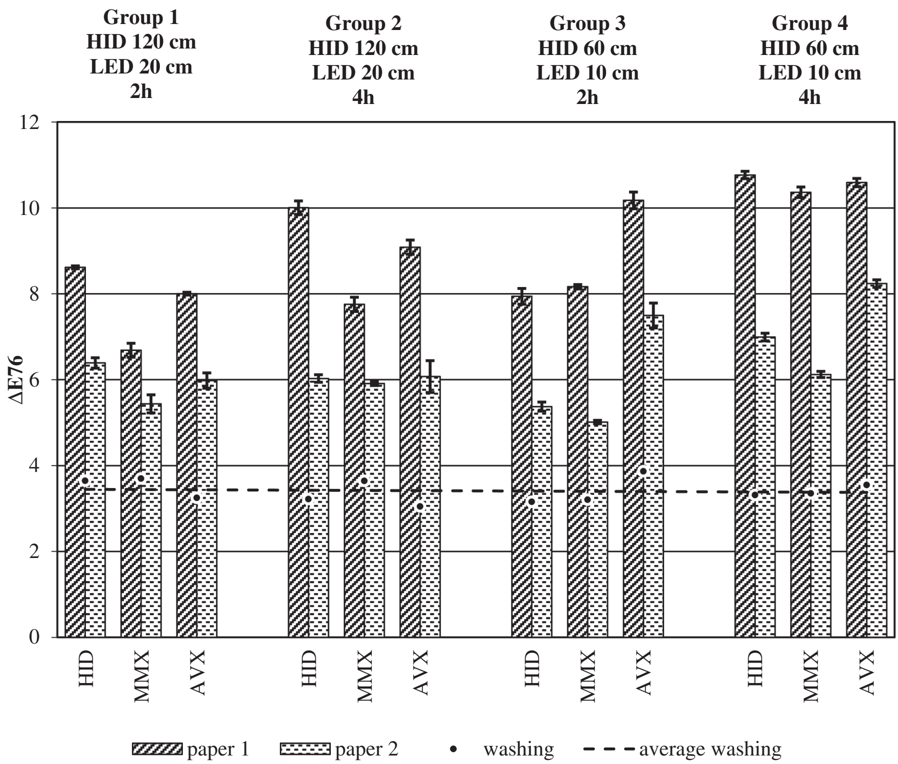

Figure 9: Colour distance (Δ_E, CIE1976) of paper 1 and 2 after four different bleaching treatments (see Table 4) compared to washed papers (dots and dotted line). See also Figure 10.

before treatment, after washing and after bleaching. The colour difference (Δ_E) was calculated according to the CIE_{76} standard. The degree of colour change is equivalent to brightening in our bleaching study. According to Has and Newman (1995), values of $\Delta_E > 2.5$ represent the minimal colour change distinguishable for the human eye. Values over $\Delta_E > 5.0$ mostly lead to perception of a different colour shade and above $\Delta_E = 10$ a new colour appears

4.3.2 Washing

The samples 2–15 of paper 1 and 2–14 of paper 2 underwent three 15-minute immersion washing treatments. Each bath consisted of 3 L of demineralised water adjusted to pH 9.0 with a saturated calcium hydroxide solution. The washed samples were air-dried.

4.3.3 Bleaching

The illuminance of each bleaching setup was determined with an ELSEC 746 photometer. The average of five measurements was used to calculate luminous exposure lxh (Table 4). Four samples, two of each paper were exposed to one light source and at one of two exposure distances. Samples were immersed in a white polypropylene tray, avoiding overlap. The bath consisted of 200 mL demineralised water adjusted to pH 9.0 with a saturated calcium hydroxide solution. During exposure, the water was exchanged every 30 minutes and the samples were rotated. The first sample set was removed after 2 h exposure, the second sample after 4 h exposure. All bleached samples underwent deacidification by immersion in a calcium hydrogen carbonate solution for 30 minutes and were then air-dried.

4.3.4 Molar mass and carbonyl group content of the cellulose

Molar mass and carbonyl group content according to Röhrling et al. (2002) were determined for paper 1, which showed more differentiated bleaching results than paper 2 and which was more convenient to sample due to its larger format. It was assumed that any possible negative impact on the cellulose would be most prominent with the most intensively light-exposed sheets HID-1–2, MMX-1–2, AVX-1–2 (see Table 4), which were chosen for analysis (1 × 6 cm removed from the top edge). Each of the measurements was repeated twice and the average was determined.

5 Results

All treated samples show a brightness increase (measured as colour differences Δ_E) (Figure 9). Immersion washing alone increased the brightness of both papers about Δ_E = 3.37 (±0.21), which is a slight, though perceptible change. The brightness increase effected by bleaching shows more diverse results. Both papers' brightness increased with intensified exposure. Brightening was more intense for bleaching at a shorter distance or over a longer time. Furthermore, paper 1 showed a greater brightness increase than paper 2 (Figure 10).

For samples in group 1 that were bleached at the far distance and for the shortest time, the average bleaching effectiveness can be ranked HID above AVX above MMX, though the difference between HID and LEDs is statistically significant only for paper 1. Group 2 samples which were bleached at the same

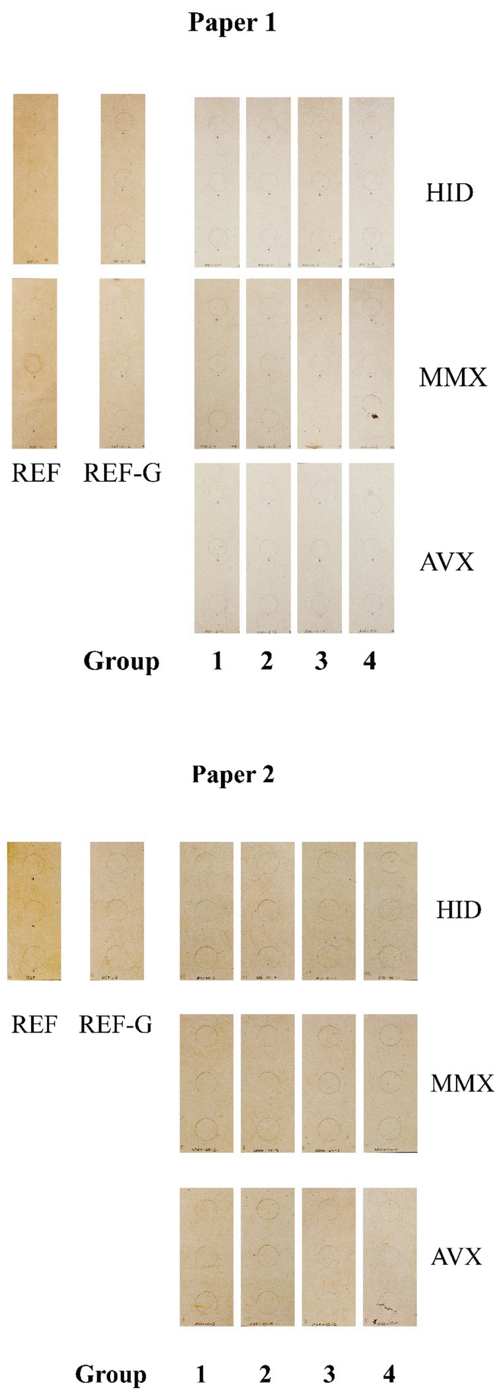

Figure 10: Paper 1 (top) and paper 2 (bottom) after four different bleaching treatments (groups, see Figure 9, treatment ID, see Table 4). Colour measurement spots are marked with pencil.

distance for 4 h, results were quite similar, effectiveness was similar for HID and AVX and better than for MMX. Paper 1 was bleached with HID and AVX intensely, while paper 2 showed no significant brightness increase. The MMX showed the lowest brightening effect on paper 1.

In group 3, which was bleached at the minimum exposure distance and for 2 h, the AVX modules effected a brightness increase that was about 28 % (paper 1) and 40 % (paper 2) more intense than the HID. This is the most significant absolute brightness increase achieved within 2 h of exposure. MMX and HID achieved no significant brightness increases for paper 1, and only a slight one for paper 2. Within group 4, which was bleached at the same distance for 4 h, HID and MMX effected a significantly greater brightness increase than in group 3. For paper 2, a similar ranking like in group 3, with an overall increase of brightness, can be observed with HID being 19 % lower than AVX. The difference between the brightening achieved by AVX when compared to HID and MMX indicates that for those two light sources the exposure time was not long enough to reach the full potential brightening.

When comparing the four groups, the most significant overall colour change (equalling brightening) of paper 1 was $\Delta_E \geq 10$. It was achieved by HID in both distances after 4 h exposure, by MMX in 10 cm distance after 4 h and by AVX in 10 cm distance after 2 h and 4 h. All papers underwent a colour shift in the same direction: They became brighter (ΔL), less red (Δa) and less yellow (Δb). Washing caused a greater ΔL increase for paper 2 than for paper 1.

The weight average molar mass showed a decrease for HID by 15 % (±1.29 %) and for MMX-bleached papers by 17 % (±1.32 %) while for AVX there was no notable change (Figure 11). The carbonyl group content, an indicator for

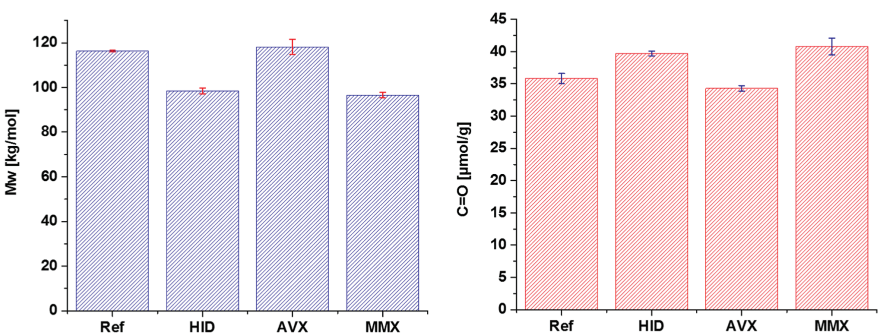

Figure 11: Results of cellulose analysis. Left: Molar mass (kg/mol) of the untreated reference (REF), and the three samples with the highest exposure for each light source (e. g. smallest distance and longest exposure: HID-1–2, MMX-1–2, AVX-1–2). Right: Carbonyl group content (µmol/g) of the untreated reference (REF), and the three samples.

oxidation of the cellulose, was increased after HID bleaching by 11 % (±1.02 %) and after MMX bleaching by 14 % (±3.17 %), but was slightly decreased for the AVX sample.

6 Discussion

Although a significant bleaching effect could be observed for both tested LED sources, they showed notably different performances. Especially Aventrix 4 × 4 (AVX) was highly efficient in reducing discolouration. Due to its luminous flux of 31,140 lm and the resulting high illuminance, the bleaching efficiency was considerably higher than that achieved with the MiniMatrix (MMX). HID in 60 cm distance showed a similar brightening effect as AVX in 20 cm distance. However, this is most likely due to its UVA content, which makes up, in bleaching, for its low illuminance (see Figure 1). Therefore, the paper brightening achieved by HID may not be related only to the VIS but also to UV which was not filtered in this study. The significant drop in molar mass of the HID exposed samples when compared to the reference confirms the known fact that UV radiation causes photocatalytic breakdown of the cellulose, as noted by Verborg (2012). A corresponding slight increase in carbonyl group content furthermore illustrates the UV radiation-related cellulose oxidation. For the AVX bleached samples, no significant negative effect on the cellulose was evident despite the intense illumination. With MMX, the molar mass dropped significantly, and carbonyl group content increased. Since this cannot be linked to UV radiation, the high amount of blue light present in the spectrum might be the reason for the cellulose breakdown and oxidation. It can be assumed that the different colour temperature of the two LED sources had a more significant effect of the cellulose than the illuminance. The blue light content, known as a key factor for light damage, must also be considered a risk factor concerning cellulose damage during light bleaching. However, this connection is not entirely conclusive due to the relatively small sample size.

The most intense brightening occurred at 10 cm distance during the first 2 h exposure, indicating that the high illuminance increased the rate of bleaching. Compared to AVX, the MMX showed a lower performance in brightening the paper, explainable by its lower illuminance. The applied external cooling with heat sinks and fans was effective in keeping the operating temperature of the AVX within the acceptable range.

7 Conclusion

The present study demonstrates that high-performance LEDs have a great potential of raising the efficacy and sustainability of artificial light bleaching of paper. The high luminous flux and outstanding long lifespan make them an interesting light source for bleaching. The absence of UV radiation in the emitted spectrum and the low level of emitted thermal radiation allow LED sources to be placed in a much closer distance to the object than any other light source. The wide angle of radiation of 120° ensures a homogeneous illumination even in close distance. Especially when LED with moderate colour temperature, i. e. lower short-wave VIS content, and high luminous flux, like the AVX, are applied, excellent brightening results with no notable negative effect on the cellulose substrate can be expected. Since increased oxidation of the cellulose likely accelerates the extent of colour reversion (Burgess 1982), the results confirm the importance of minimizing short-wave VIS (blue light). Thus, the total intensity of the applied radiation may not be as important for the preservation of the cellulose as the spectral composition of the applied radiation. The AVX in this regard proved the better choice than the MMX. Nevertheless, the studied effects need to be complemented by subsequent research. Certainly, the influence of the colour temperature on the degradation of the cellulose and the relation between illuminance and bleaching need further attention. As LEDs are likely to replace most common light sources in the future, they hold significant potential for paper conservation practise.

The LED modules can be constructed to units of any size, weight and power. Effective cooling of the LED is always an important construction feature. LED are generally safer than HID since they operate at lower voltage, do not emit UV and can be dimmed to any desired luminous flux. No pre-heating or cooling breaks are needed, allowing the conservator to pause the exposure any time during the treatment. The illuminance can be adjusted to meet the treatment requirements through voltage adjustment without changing the setup. Furthermore, by masking parts of the object during treatment and adjusting the illuminance, light bleaching at different rates is possible at shorter exposure times than those that are common with other light sources. LED exposure has some health hazards, as the intense illumination can cause stress and dizziness. Protective eyewear, such as tinted goggles or light-blocking shields must be considered as a safety precaution, especially when working with illuminances over 25,000 lx.

A series of ready-to-use countertop and overhead LED bleaching units is in the process of construction and will be marketed by Belo Restaurierungsgeräte GmbH.

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References

Baker, C.: *Practical methods for sun and artificial light bleaching paper*. The Book and Paper Group Annual 1 (1982).

Baker, C.: *The double-sided light bleaching bank*. The Book and Paper Group Annual 5 (1986).

Branchick, T. J., Keyes, K., Tahk, F. C.: *A study of the bleaching of naturally aged paper by artificial and natural light*. In: Preprints, American Institute for Conservation of Historic and Artistic Works (AIC), 10th annual meeting, Milwaukee WI, Book and Paper Group, Washington DC: AIC, 1982: 29–29.

Brückle, I.: *Bleaching in Paper Production versus Conservation*. Restaurator 30 (2009a): 280–293.

Brückle, I.: *Bleaching Paper in Conservation: Decision-Making Parameters*. Restaurator 30 (2009b): 312–332.

Burgess, H. D.: *Relationships between color production in cellulose and the chemical changes brought about by bleaching*. In: Postprints, American Institute for Conservation of Historic and Artistic Works (AIC), 12th Annual Meeting, Milwaukee WI, Book and Paper Group, Washington DC: AIC, 1982: 20–28.

Dohlus, R.: Lichtquellen. Berlin: DeGruyter, 2015.

Feller, R. L., Lee, S. B., Bogaard, J.: *The darkening and bleaching of paper by various wavelengths in the visible and ultraviolet*. In: Postprints, American Institute for Conservation of

Historic and Artistic Works (AIC), 12th Annual Meeting of AIC, Milwaukee WI, Book and Paper Group, Washington DC: AIC, 1982: 65–81.

Garside, D., Curran, K., Korenberg, C., MacDonald, L., Teunissen, K., Robson, S.: *How is museum lighting selected? An insight into current practice in UK museums*. Journal of the Institute of Conservation 40,1 (2017): 3–14.

Gowland, J., McAusland, J.: *Some notes on light-bleaching, humidification and steamers*. Paper conservation news 106 (2003): 4–5.

Has, M., Newman, T. *Color management: Current practice and the adoption of a new standard*. Whitepaper 1, International color consortium, 1995.

Heinz, R.: Grundlagen der Lichterzeugung – Von der Glühlampe bis zum Laser. Rüthen: Highlight Verlag, 2009.

Henniges, U., Potthast, A.: *Bleaching revisited: Impact of oxidative and reductive bleaching treatments on cellulose and paper*. Restaurator 30 (2009): 294–320.

Herzberg, H.: *Exhibition in correct light – quality features of artificial lighting for use in museums*. Restauro 121 (2015): 55–61.

Hofmann, C., van der Reyden, D., Baker, M. *Comparison and evaluation of bleaching procedures – the effect of five bleaching methods on the optical and mechanical properties of new and aged cotton linter paper before and after accelerated aging*. The Book and Paper Group Annual 10, 1991.

Keyes, K. M.: *Alternatives to conventional methods of reducing discoloration in works of art on paper*. In: Postprints, American Institute for Conservation of Historic and Artistic Works (AIC), 12th Annual Meeting, Miwaukee WI, Book and Paper Group, Washington DC: AIC, 1982: 100–104.

Lumitronix (1): Datenblatt Aventrix 4 × 4. Hechingen: Lumitronix LED-Technik GmbH, 2017. https://lumstatic.com/Ya/DR/RpKMgv_Opi8j1dHyXg.pdf (accessed 6. 2018).

Lumitronix (2): Aventrix LED-Module für Straßen-, Tunnel und Hallenbeleuchtung – Macht die Nacht zum Tag. catalogue no. 99458, Hechingen: Lumitronix LED-Technik GmbH, 2017. https://lumstatic.com/IS/kv/wiL9GMlf43qUpfbe6Q.pdf (accessed 6. 2018).

Lumitronix (3): LumiMatrix & MiniMatrix LED-module – Das kreativste Lichtsystem der Welt. catalogue no. 99459, Hechingen: Lumitronix LED-Technik GmbH, 2017. https://lumstatic.com/Tl/7k/qu8l5CkX4BrGMcs_3Q.pdf (accessed 6. 2018).

Mayer, D. (eds.): Spot Tests (PCC). AIC Conservation Wiki (online resource) Washington DC, 2018. http://www.conservation-wiki.com/wiki/Spot_Tests_(PCC)#Protein_Adhesives (accessed 6. 2018).

Michalski, S., Tétrault, J., Hagan, E., Tse, S.: *Seeing the light! An overview of CCI's work on lighting*. Reflections on Conservation 1 (2012): 37–39.

Miller, N. J., Druzik, J. R.: Demonstration of LED Retrofit Lamps at an Exhibit of nineteenth Century Photography at the Getty Museum – Final Report Prepared in Support of the U.S. DOE Solid-State Lighting Technology Demonstration GATEWAY Program. Richland WA: Pacific Northwest Laboratories, US Department of Energy, The J. Paul Getty Museum and Getty Conservation Institute, 2012. http://apps1.eere.energy.gov/buildings/publications/pdfs/ssl/getty_museum_gateway_final.pdf (accessed 6. 2018).

Murphy, T. W.: *Maximum spectral luminous efficacy of white light*. Journal of Applied Physics, American Institute of Physics 1 (2012): online resource; (accessed 6. 2018).

Neevel, J. G., Reißland, B.: *Bathophenanthroline indicator paper: Development of a new test for iron ions*. PapierRestaurierung – Mitteilungen der IADA 6,1 (2005): 28–36.

Nichia (1): *Specifications for warm white LED – NVSLE21AT*. catalogue no. 170418, Tokushima: Nichia Corporation, 2017.

Nichia (2): *Specifications for white LED – NT2W757DRT*. catalogue no. 130523, Tokushima: Nichia Corporation, 2017.

Osram: *Familiendatenblatt powerstar HQI-TS*. Osram GmbH, 2017. https://www.osram.at/osram_at/produkte/lampen/hochdruck-entladungslampen/halogen-metalldampflampen-mit-quarztechnologie/powerstar-hqi-ts-excellence/index.jsp (accessed 6. 2018)

Palmer Eldrige, B.: *A sun bleaching project*. In: Postprints, American Institute for Conservation of Historic and Artistic Works (AIC), 12th Annual Meeting, Miwaukee WI, Book and Paper Group, Washington DC: AIC, 1982: 52–55.

Perkinson, R.: *An alternative light source for light bleaching in paper conservation*. The Book and Paper Group Annual 20 (2001): 27–30.

Reyden, D. van der., Mecklenburg, M., Baker, M., Hamill, M.: *Update on current research into aqueous Light bleaching at the conservation Analytical Laboratory*. In: The Book and Paper Group Annual, vol. 7. Washington DC: AIC, 1988.

Röhrling, J., Potthast, A., Rosenau, T., Lange, T., Ebner, G., Sixta, H., Kosma, P.: *A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 1. Method development*. Biomacromolecules 3 (2002): 959–968.

Saur-Aull, Barbara.: *Konstruktion und Einsatz einer Lichtbleichanlage*, Thesis (unpublished), Stuttgart, Germany: State Academy of Art and Design, 1996.

Schaeffer, T. T.: *Effect of aging on an aqueously light bleached, mixed pulp paper*. The Book and Paper Group Annual 10, 1991.

Schaeffer, T. T., Blyth-Hill, V., Drutzik, J. R.: *Aqueous light bleaching of modern rag paper – an effective tool for stain removal*. Paper Conservator 21 (1997): 1–14.

Schopfer, J. M.: *Light bleaching with HID lamps*. Restaurator 33 (2012): 287–328.

Smith, A. W.: *Bleaching in paper conservation*. Restaurator 30 (2009): 223–249.

Verborg, M.: *Light bleaching with metal halide lamps – effects on naturally aged paper*. Restaurator 33 (2012): 329–355.

Wyszecki, G., Stiles, W. S.: Color Science – Concepts and Methods, Quantitative Data and Formulae, 2nd. New York: Wiley-Interscience, 2000.

Zusammenfassung

Leuchtdioden als alternative Lichtquelle für die wässrige Lichtbleiche von Papier

Die vorliegende Studie untersucht die Eigenschaften von Leuchtdioden (LED) für den Einsatz in Lichtbleichbehandlungen im Vergleich zu den bekannten HID-Lampen. Aufgrund ihrer geringen Wärmeabgabe können LEDs näher am Objekt platziert werden als HID-Lampen; dies vervielfacht die Lichtintensität auf dem Papier. Zwei modulare LED-Systeme mit 4000 K und 6500 K Lichttemperatur wurden ausgewählt und in ein Testgerät eingebaut. Proben von zwei natürlich gealterten Hadernpapieren wurden mit den LED-Modulen in einem Bad gebleicht, und die Ergebnisse wurden mit Proben verglichen, die mit HID-Lampen gebleicht wurden. Die Farbe aller Papierproben wurde vor und nach der Behandlung mit einem Spektralphotometer im CIELAB-Farbraum bestimmt. Alle drei getesteten Lichtquellen erhöhten die Helligkeit der historischen Testpapiere; die maximale Helligkeit wurde jedoch mit LED schneller erreicht als mit HID. LED mit einer Farbtemperatur von 4000 K haben darüber hinaus keinen negativen Einfluss auf die Molmasse und den Carbonylgruppengehalt der Cellulose. Bei den LED mit 6500 K Farbtemperatur konnte ein leichter Abfall der mittleren Molmasse sowie eine leichte Erhöhung des Carbonylgruppengehalts beobachtet werden. Dies führt zu der Schlussfolgerung, dass LED mit mittlerer Farbtemperatur eine interessante Option für eine verbesserte Lichtbleiche von Papier darstellen, da die Behandlungszeit, d.h. die wässrige Behandlung des Objekts, signifikant verringert werden kann.

Resumé

Diode électroluminescente (LED) - une source de radiation alternative dans le blanchiment à la lumière aqueux du papier.

La présente étude évalue les propriétés des diodes électroluminescentes (LED) et leur utilisation dans les traitements de blanchiment légers, en comparaison avec les lampes à décharge DHI dont l'utilisation est bien établie. En raison de leur faible émission de chaleur, les LED peuvent être placées plus près de l'objet que les lampes à décharge DHI; ce qui permet d'accroître l'intensité de la lumière sur le papier. Deux systèmes LED modulaires avec une température de lumière de 4000 K et 6500 K ont été choisis et installés dans un appareil de contrôle. Des échantillons issus de deux papiers chiffons vieillis naturellement ont été blanchis dans un bain d'immersion, à l'aide de modules LED et HID à des fins de comparaison. La couleur des échantillons de papier a été mesurée avant et après traitement à l'aide d'un spectrophotomètre dans l'espace colorimétrique CIELAB. Les trois sources lumineuses testées améliorent la luminosité des échantillons papier, mais à différents degrés. Le blanchiment à l'aide d'une LED à la température de couleur de 4000 K résulte en un éclaircissement plus intense, si l'on compare aux deux autres sources lumineuses. En outre, les LED ayant une température de couleur de 4000 K n'exercent pas d'impact négatif sur la masse molaire et la teneur en groupes carbonyle de la cellulose; contrairement aux LED de température de couleur de 6500 K, qui causent une diminution de la masse molaire et une augmentation générale du nombre de groupes carbonyles. Ceci permet de conclure que les LED à la température de couleur modérée représentent une option intéressante pour un blanchiment amélioré du papier, car le temps de traitement, c'est-à-dire l'immersion aqueuse de l'objet, peut être diminuée de manière significative.

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Appendix A

Principles of light emitting diodes

The semiconductor crystals used in LED are made of silicon. It is a tetravalent metalloid of the carbon group (IV) with four valence electrons (Figure A1). A pure siliceous-based crystal is inert. All four valence electrons are bound in the crystal lattice, which prevents movement of electrons through the lattice. By modifying the crystal through forced contamination (doping) with atoms of elements with a differing number of valence electrons, a local over- and under-saturation occurs. This forced imbalance enables electrons to move within the crystal lattice. If, for example, gallium, a group III acceptor, is added, one of the silicon's valence electrons remains unsatisfied triggering an attraction of electrons to the so-called "hole" and thereby creating a local positive charge (p-doping) at the nearby silicon atoms. Added phosphor, a group V electron donor, creates a surplus of electrons because one of its valence electrons remains unpaired resulting in a local negative charge (n-doping). A diode is a crystal containing a predominantly p-doped and an n-doped layer (Heinz 2009).

When no external electric current is applied, the charges in layers neutralise each other. In the area between the layers, free electrons of the n-doped area move towards the p-doped area filling the "holes". Due to this effect, the charges close to the border are neutralised forming an area that inhibits any further movement of electrons. This area is known as the p-n junction (Figure A1a). Under the influence of an applied electric current, the charged layers interact with the electrons. If the applied electric current opposes the charge of the layers, the electrons from the n-doped layer move towards the applied positive charge and the electrons from the applied negative charge are forced into the p-doped layer. Due to the further neutralisation the p-n junction expands and a flow of electrons through the lattice is inhibited (Figure A1b). When an electric current similar to the charge of the layers is applied electrons of the n-doped layer are pushed towards the p-n junction and the p-doped layer. The p-n junction decreases with increasing voltage. With sufficient voltage applied the p-n junction is eliminated. Electrons can pass through the crystal. By interacting with the holes of the p-doped layer a so-called band gap occurs. Electrons move into their excited state and once they return to normal state a part of the energy is transformed into radiation (Figure A1c). The remaining energy is transformed into heat that is absorbed by the crystal and transferred to the aluminium board and the attached cooling unit.

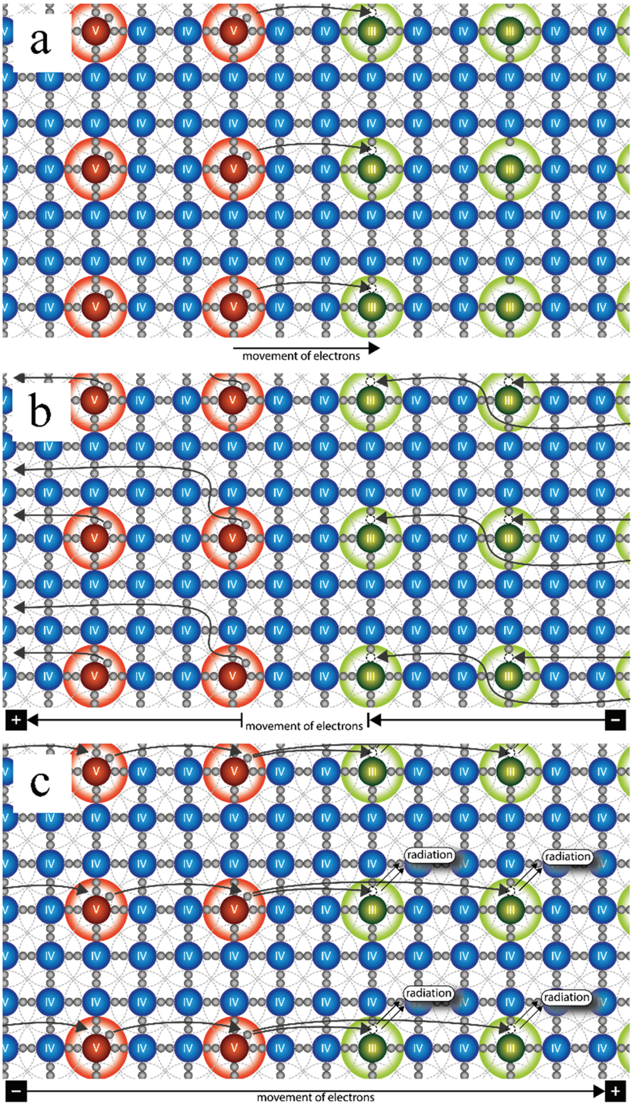

Figure A1: Semi-conductor crystal with an n-doped layer (left; in red) and a p-doped layer (right; in green). (a): p-n-junction under normal condition. (b): increased p-n-junction under electric current opposing flow direction. (c): irradiation reaction under electric current matching flow direction (after Heinz 2009).