https://doi.org/10.24867/GRID-2022-p11 Original scientific paper

ACCELERATED PHOTODEGRADATION OF DYE-BASED INK-JET PRINTING INKS IN AN AQUEOUS SOLUTION AND ON A SUBSTRATE

Barbara Blaznik [1], *Franci Kovač* [2], *Grega Bizjak* [3], *Sabina Bračko* [1]
[1] *University of Ljubljana, Faculty of Natural Sciences and Engineering, Ljubljana, Slovenia*
[2] *University of Ljubljana, Faculty of Chemistry and Chemical Technology, Ljubljana, Slovenia*
[3] *University of Ljubljana, Faculty of Electrical Engineering, Ljubljana, Slovenia*

Abstract: *When studying the process of photodegradation, we often deal with the durability of the individual ink colour components, the durability of the printing material or the durability of the ink on the printing material. Less frequently, ink degradation in the solution is compared to the print. However, it is essential to consider all the crucial external and internal factors that influence the photodegradation process in the context of the durability of printed materials. When studying photodegradation, external factors such as light, temperature and humidity are relatively easy to control. On the other hand, the control of internal factors in the photodegradation process is much more complex since the internal factors are related to the composition of the ink used, the substrate and the physical and chemical processes between them. The study aims to analyse the complex degradation process of prints made with an ink-jet printer compared to the degradation of the same inks in an aqueous solution. The study included two types of paper and an ink-jet printer using dye-based inks. A high-pressure mercury lamp was used to irradiate and accelerate the degradation process, and a specially adapted reactor was used to irradiate solutions and prints. The results showed how short-wave UV radiation significantly influences the changes of the printing material, ink and prints. In some cases, the difference between the ink stability in solution and ink stability on the printing material can be observed. The effect of paper on the durability of the print is, however, negligible in the case of short-wave UV radiation. The process of photodegradation of the paper under UV radiation was mainly manifested by the loss of specific surface and optical properties.*

Key words: UV-C radiation, photodegradation, dye-based ink, ink-jet printing

1. INTRODUCTION

Photodegradation is an interactive process between light and material since this process takes place only when the material can absorb light (Feller, 1994; Steiger & Brugger, 1999). Among the most crucial factors affecting the lightfastness of colourants are dye concentration, degree of aggregation, pigment particle size, chemical and physical structure of the printing material, energy between the colourant and the printing material, spectral distribution of the light source and composition of the atmosphere, including relative humidity as well as the presence of pollutants in the air (Zollinger, 2003).

Light fastness has always been of interest, although the photodegradation process has not been fully explained yet (Zollinger, 2003; Giles, 1965; Padfield & Landi, 1966; Vikman et al, 2005). During irradiation with average daylight, samples are exposed to a broad spectrum of energy levels of electromagnetic waves [Feller, 1994; Wypych, 2008]. Exposure to a more significant proportion of UV radiation leads to accelerated chemical degradation of materials (Aydemir & Yenidoğan, 2018). Many processes accompanying the degradation of organic materials depend on temperature; therefore, the degradation rate is directly proportional to the increase in temperature (Feller, 1994; Blaznik, Gregor-Svetec & Bračko, 2017). Moisture further accelerates the degradation process (Bamfield, 2001; Wypych, 2008). The joint contribution of humidity and temperature is mainly expressed in changes in materials' mechanical properties (Černič, 2008; Fellers et al, 1989). Also, the presence of oxygen in the surroundings negatively affects the degradation process. After all, oxidation is the fundamental reason for the decomposition of organic materials. The combined influence of heat and light forms free radicals that initiate a chain reaction and accelerate materials' deterioration (Feller, 1994).

Prints made with an ink-jet printer represent a complex system in terms of print analysis, as they connect an infinite number of combinations of printing materials, colourants, and other internal and external factors (Jürgens, 1999). The purpose of our research was to study the photodegradation of ink-jet inks in an aqueous solution as well as prints made with an ink-jet printer under the influence of a high-pressure mercury lamp, which was used to accelerate the photodegradation process. Using appropriate analytical methods, we have monitored the colour changes, ink amount and its half-life as well as the substrate's roughness. Consequently, we evaluated the influence of the immediate environment of the ink and dye on the process of degradation.

2. METHODS

The Epson L130 (T2) printer was included in our experimental part, which uses water-based ink-jet printing inks. The printer contains four cartridges with four dye-based primary colour inks.
A sample of individual dye-based ink (C, M, Y, K) was taken directly from the cartridge using the syringe and diluted 1:3000 with water. Four colour fields (C, M, Y, K) with a resolution of 2400 dpi were printed on plain office and permanent paper.
The office paper was labelled PPO and was produced by Officeline under the name Super Quality paper. PPO has a grammage of 80 g/m^2, and according to the manufacturer, the use of paper PPO is versatile. Permanent paper (TPI) with a grammage of 80 g/m^2 was produced by the Institute for Pulp and Paper in Ljubljana and labelled as ICP-PP1. Paper TPI was made in accordance with the standard for durable papers EN ISO 9706 and ISO 11108. According to the ISO 4287 standard, we measured the roughness on the upper side of the paper. A TR2000 profilometer (Time Group Inc. China) was used for measurements.
The high-pressure mercury lamp was used to irradiate water solutions of ink and prints (Figure 1). Due to the heating of the lamp, the lamp was water-cooled. 30 ml of dye solution was poured into the reactor and exposed for 15 minutes to the radiation of the lamp. That approach enabled us to maintain the liquid samples' temperature between 16 and 20 °C, although they were only 2 cm away from the lamp. For the prints, the reactor needed to be modified. Therefore, a stand with an aperture was constructed to ensure a uniform distance from the radiation source and 50 ml of water was added to the reactor to maintain the temperature.

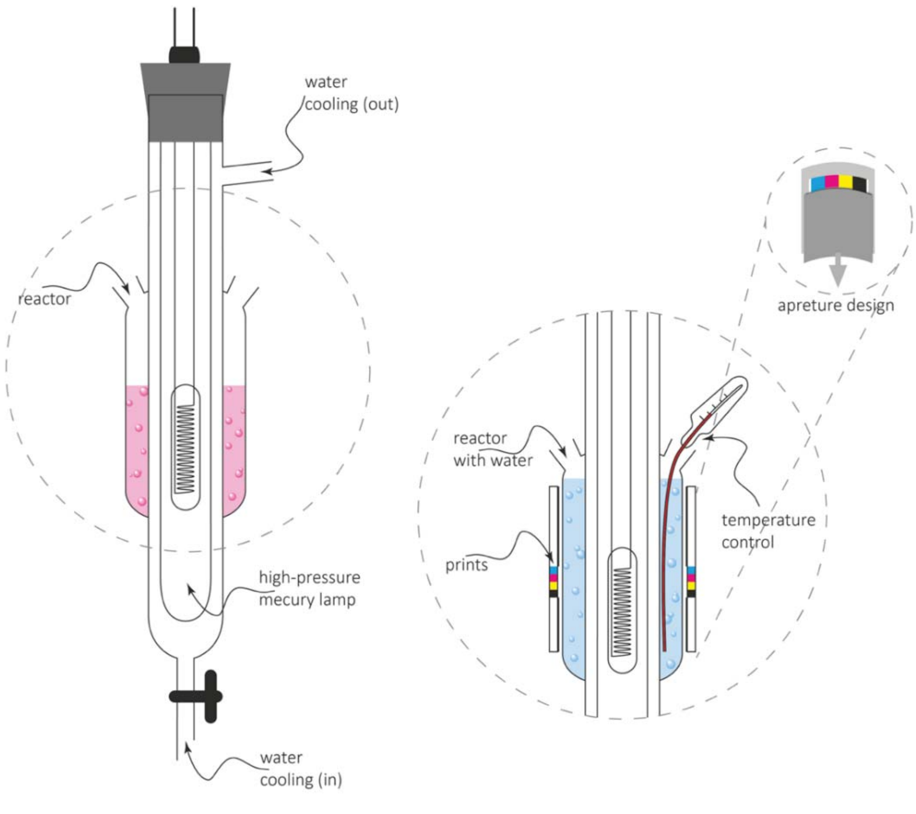

Figure 1: Scheme of reactor during operation of the high-pressure mercury lamp for liquid samples and prints

After the exposure, for the liquid samples, the measurements of absorption in two repetitions in the range between 380 in 730 nm were performed using UV/VIS spectrophotometer Cary 1E (Varian, USA). For prints, the measurements were performed in accordance with ISO 13655 standard on white backing, 45°:a:0° and 10° observer using spectrophotometer iOne (X-Rite, USA). From the measured values of the reflection, the colour differences were calculated using the CIEDE2000 equation 1 (Commision Internationale de L'Eclairage, 2018).

$$\Delta E_{00}^{*} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T\left(\frac{\Delta C'}{k_C S_C}\right)\left(\frac{\Delta H'}{k_H S_H}\right)} \quad (1)$$

The ink amount (IA) in the aqueous solution was calculated according to equation 2. The IA represents ink amount in %, A_i represents the absorption value after the irradiation, and A_0 represents the absorption value before irradiation.

$$IA\ [\%] = \frac{A_i}{A_0} \times\ 100\ \% \quad (2)$$

According to the Beer-Lambert law, the ink amount (IA) on the substrate was calculated according to equation 3, where the IA represents ink amount in % on the substrate, and R_i represents the reflection value after the irradiation, and R_0 represents the value of reflection before irradiation.

$$IA\ [\%] = \frac{log\left({}^{1}/_{R_i}\right)}{log\left({}^{1}/_{R_0}\right)} \times\ 100\ \% \quad (3)$$

3. RESULTS AND DISCUSSION

3.1 Ink-jet ink in aqueous solution

The spectra presented in figure 2 are related to the colour change after irradiation with a high-pressure mercury lamp. Considering the width of the absorption bands, the number of absorption maxima and the previous studies (Blaznik et al, 2021; Blaznik et al, 2022) carried out on these samples, we conclude that the inks included in the survey represent a mixture of different colourants used by the manufacturer to achieve the desired ink properties. From the absorption spectra, we detect a shift of the absorption maxima towards shorter wavelengths in the case of cyan, yellow, and black inks. The absorption maxima decreased most for black ink (18%, λ = 594) and the least for cyan ink (5%, λ =695).

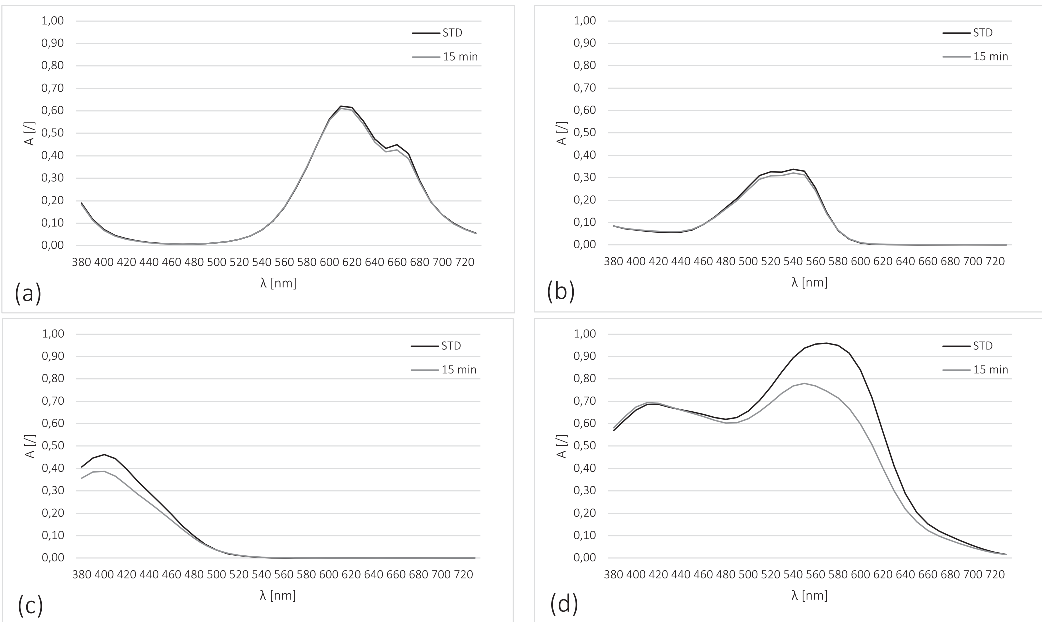

Figure 2: Absorption spectra of cyan (a), magenta (b), yellow (c) and black (d) inks in aqueous solution before (STD) and after 15 minutes of exposure to the high-pressure mercury lamp

The ink amount (IA) in the solution after irradiation was determined using equation 2 (Table 1) based on the absorption values measured. The IA values show that the most significant change after irradiation occurred with the black ink in an aqueous solution, as the amount decreased to 78 % of the initial absorbance.

By monitoring the rate of photodegradation and calculating the slope (k) of the line, the degradation rate and half-life ($t_{1/2}$) were determined (Table 1). According to the results (Blaznik et al, 2021; Blaznik et al

2022), the photodegradation reaction likely follows the pseudo-first-order kinetic model for best fit. The degree of photodegradation was most notable in the case of the black and yellow inks. On the other hand, the degradation of cyan ink was less evident.

Table 1: Ink amount (IA), coefficient (k) and half-life ($t_{1/2}$) of ink samples in aqueous solution under the influence of a high-pressure mercury lamp

	IA [%]	k [s^{-1}]	$t_{1/2}$ [min]
EC	98	–0.0013	533
EM	95	–0.0035	198
EY	84	–0.0118	59
EK	78	–0.0165	42

3.2 Substrate

From figure 3a, we can conclude that PPO paper contains optical brightening agents, which disintegrate after irradiation with a high-pressure mercury lamp. Therefore, changes in the colour of the paper were observed mainly on the b^* axis, i.e., on the yellow-blue axis, as the hue of the paper shifted from slightly bluish towards yellow. On the paper TPI (Figure 3b), we detected changes in a broader part of the short-wave spectrum and consequently yellowing of the paper ($\Delta b^* > 2.5$).

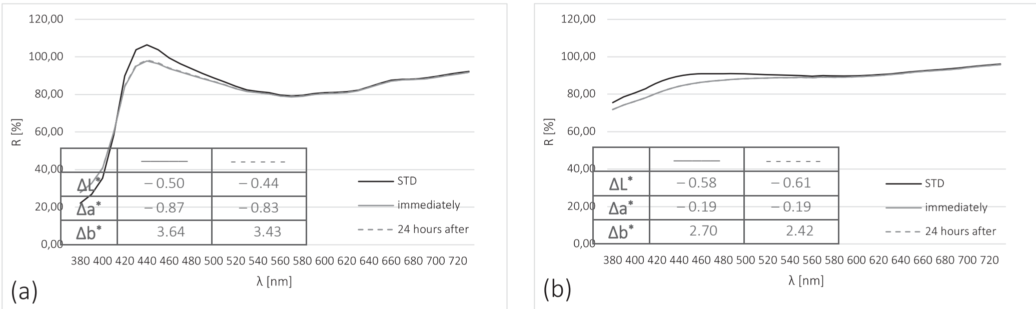

Figure 3: Reflection spectra of office paper PPO (a) and permanent paper TPI (b) before (STD) and immediately after exposure to the high-pressure mercury lamp

Table 2 shows the calculated values of colour differences (ΔE^*_{00}) and roughness (Ra) changes before and after irradiation with a high-pressure mercury lamp for PPO and TPI papers. After 15 minutes of irradiation, more significant differences in roughness were measured for paper PPO. Regarding colour differences, we noticed a slightly more significant difference in colour on paper TPI.

Table 2: Roughness (Ra) of substrate PPO and TPI before (STD) and 24 hours after exposure. Colour difference (ΔE^*_{00}) of substrate immediately and 24 hours after exposure to the high-pressure mercury lamp

	Paper	Ra [/]		ΔE^*_{00} [/]	
		STD	after 24 hours	immediately	after 24 hours
Substrate	PPO	2.92	3.25	1.30	1.21
	TPI	3.12	3.25	1.58	1.43

3.3 Ink-jet ink on substrate

Under the influence of the high-pressure mercury lamp, the so-called bronzing or red shift of cyan prints (Figure 4) occurred. Bronzing of cyan disappeared after 24 hours. The phenomenon of bronzing of prints is usually the result of the dye's structural characteristics and some external factors such as ozone (Bugner, 2002; Fujie et al, 2009), which was a by-product of the operation of the high-pressure mercury lamp. Therefore, the reflection of all prints and substrates was measured twice, immediately after exposure.

Figure 4: Bronzing of cyan prints

The most representative bronzing effect after UV light exposure is visible on the cyan prints (Figure 5a, b). The comparison of the reflectance curve of different colours (CMYK) on different substates (TPI, PPO) shows that it was not so much dependent on printing material as on colour (Figure 5a–5h).

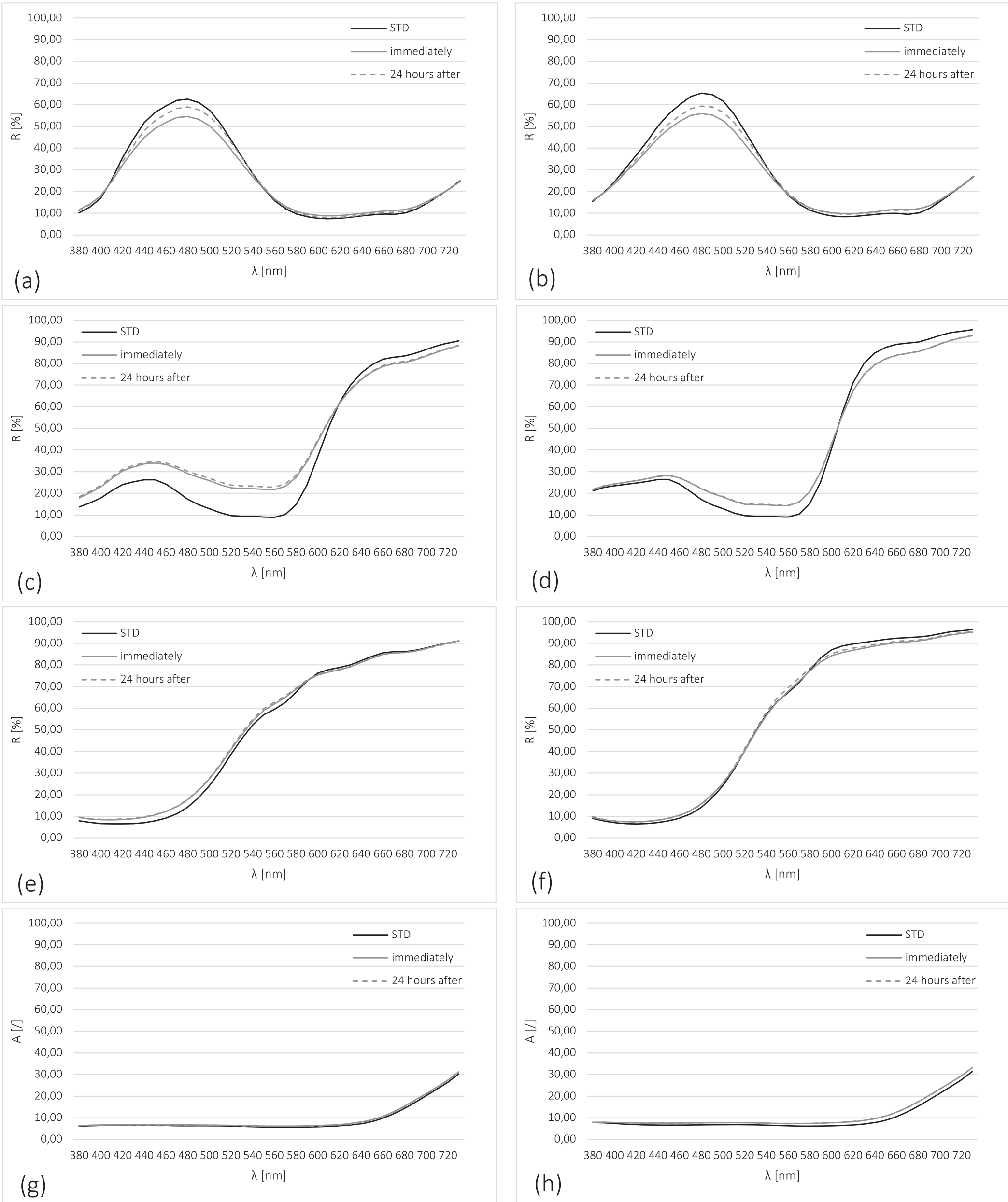

Figure 5: Reflection spectra of cyan (a, b), magenta (c, d), yellow (e, f) and black (g, h) prints on office paper PPO (left column) and permanent paper TPI (right column) before (STD), immediately and 24 hours of exposure to the high-pressure mercury lamp

Table 2 shows calculated values of ink amount (IA) and colour differences for the prints. The IA was calculated according to equation 3. According to the results (Table 2), changes in the value 24 hours after irradiation can be observed due to the bronzing, the most significant changes in IA are observed on the cyan prints. Also, the positive influence of the printing material can be observed since, using a TPI paper, the IA values are higher. Magenta prints are considered the least durable; however, the use of TPI paper gave better results. The decrease of IA on magenta prints is significant both on TPI (IA = 81 %) and even more on PPO paper (IA = 61%).

Regarding the colour differences of the prints (Table 2), we find that, in line with expectations, the most significant colour differences occurred on magenta prints ($\Delta E^*_{00,M,PPO} > 12$ and $\Delta E^*_{00,M,TPI} > 5$). We can also find out how the value of ΔE^*_{00} changed 24 hours after the irradiation. A colour change can be observed, especially on cyan prints, resulting from the bronzing of the cyan print after irradiation with a UV lamp. In the case of magenta prints on paper PPO, notice that the ΔE^*_{00} increased by almost 1 after 24 hours of irradiation. Comparing the colour differences of prints on TPI paper, we can find that ΔE^*_{00} values immediately after irradiation and 24 hours after irradiation are somehow more constant compared to prints on PPO paper.

Table 2: Colour difference (ΔE^*_{00}) of prints on office (PPO) and permanent paper (TPI) immediately and after 24 hours of exposure to the high-pressure mercury lamp

	Paper	IA [%]		ΔE^*_{00} [/]	
		immediately	after 24 hours	immediately	after 24 hours
EC	PPO	94	98	2.27	1.05
	TPI	94	95	2.79	1.42
EM	PPO	64	61	12.04	12.96
	TPI	81	81	5.25	5.47
EY	PPO	91	90	2.16	2.29
	TPI	95	95	1.22	1.09
EK	PPO	97	98	1.15	0.82
	TPI	93	93	2.72	2.65

4. CONCLUSIONS

The degradation process of ink-jet inks in solution depends on internal factors such as the dye's chemical structure, the dyes' catalytic effect and the presence of various solvents in the accompanying liquid. According to the results, short-wave UV-C radiation had no significant impact on the cyan ink in the solution or the prints. However, bronzing of the cyan print indicates that several inter-related processes occur during the exposure to radiation, which can influence the durability of the prints and can also affect the testing procedure.

In an aqueous solution, black ink exhibited inadequate durability, which was probably due to the catalytic effect due to some of the components, as black inks consist of a mixture of different colourants to achieve the desired colour shade. However, the same ink mixture printed on paper did not show as significant colour changes as in a solution.

Surprisingly, the magenta in the solution proved to be relatively stable, but it still holds first place among the least durable inks on the print, regardless of the substrate used.

Therefore, we conclude that when researching the fastness of prints, it is crucial to consider the composition of the ink, which is usually a mixture of several dyes that influence each other and behave unexpectedly in different environments. It is inevitable to consider both characteristics of dye or ink alone as well as its resistance and durability when applied to the substrate.

5. REFERENCES

Aydemir, C. & Yenidoğan, S. (2018) Light fastness of printing inks: A review. *Journal of graphic engineering and design.* 9 (1), 37–43. Available from: doi:10.24867/JGED-2018-1-03

Bamfield, P. (2001) *Chromic phenomena : technological applications of colour chemistry*. Cambridge: The royal society of chemistry.

Blaznik, B., Kovač, F., Bizjak, G. & Bračko, S. (2022) Fastness of dye-based ink-jet printing inks in aqueous solution in the presence and absence of oxygen. *Color research and application*. 1–7. Avaliable from: doi:10.1002/col.22797.

Blaznik, B., Kovač, F., Bizjak, G. & Bračko, S. (2021) Fastness of black dye-based ink-jet printing inks in aqueous solution in the presence and absence of oxygen. In: *Book of abstracts*. AIC 14th Congress, Milano 2021, August 30th – September 3rd 2021. Online edition. Milano: International Colour Association (AIC), 2021. pp. 124. Avaliable from: file:///C:/Users/library/AppData/Local/Temp/AIC_2021_abstr.pdf. [Accessed 25th 2022]

Blaznik, B., Gregor-Svetec, D. & Bračko, S. (2017) Influence of light and temperature on optical properties of papers. *Cellulose chemistry and technology.* 51 (7/8), 755–764.

Bugner, D. E. (2002) Papers and films for ink jet printing. In: *Handbook of imaging materials*. 2nd ed. New York, Marcel Dekker, pp. 603–627.

Commision Internationale de L'Eclairage. (2018) CIE 015:2018. CIE – technical report : Colorimetry, 4th ed. Viena: Commision Internationale de L'Eclairage. Available from: doi:10.25239/TR.015.2018

Černič, M. (2008) *Trajnost in obstojnost dokumentnega gradiva na papirju.* Phd thesis. University of Ljubljana.

Feller, R. L. (1994) *Accelerated aging : photochemical and thermal aspects.* Los Angeles, Getty Conservation Institute.

Fellers, C., Iversen, T., Lindström, T., Nilsson, T. & Rigdahl, M. (1989) *Ageing/Degradation of Paper: A literature survey*. Stockholm.

Fujie, Y., Hanaki, N., Fujiwara, T., Tanaka, S., Noro, M., Tateishi K, Usami, K., Hibino, A., Wachi, N., Taguchi, T. & Yabuki, Y. (2009) Development of high durability cyan and magenta dyes for ink jet printing system. In: *Fujifilm research & development*. Minamiashigara, Kanagawa : Intellectual property technology division, intellectual property division, research & development management headquarters, FUJIFILM Corporation, pp. 35–42.

Giles, C. H. (1965) The fading of colouring matters. *Journal of applied chemistry*. 15 (12), 541–550. Available from: doi:10.1002/jctb.5010151201

Jürgens, M. C. (1999) *Preservation of ink jet hardcopies*. Rochester: Capstone Project, Cross-Disciplinary Studies, Rochester Institute of Technology.

Padfield, T. & Landi, S. (1966) Light-fastness of the natural dyes. *Studies in conservation*. 11 (4), 181–196. Available from: doi:10.1179/sic.1966.022

Steiger, R. & Brugger, P. A. (1999) Photochemical studies on the lightfastness of ink-jet systems. In: Hanson, E., (ed.) *Recent progress in ink jet technologies II*. Society for Imaging Science and Technology, pp. 321–324.

Vikman, K., Iitti, H., Matousek, P., Towrie, M., Parker, A. W. & Vuorinen, T. (2005) Kerr gated resonance Raman spectroscopy in light fastness studies of ink jet prints. *Vibrational spectroscopy*. 37, 123–131. Available from: doi: 10.1016/j.vibspec.2004.08.002

Wypych, G. (2008) *Handbook of material weathering.* 4th ed. Toronto, ChemTec Publishing.

Zollinger, H. (2003) *Color Chemistry : Syntheses, properties and applications of organic dyes and pigments.* 3rd ed. Weinheim, Verlag Helvetica Chimica Acta.