The Influence of Diluted Inks and Drying on the Lightfastness of Dye Based Ink-Jet Prints

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Abstract

Since the market introduction of several wide-format ink-jet printer models, that offer 6-12 different ink channels, the use of diluted inks (mostly cyan and magenta) has become widespread. Main advantage of such a printer is an improved print quality in highlights. However, the challenge for ink and media developers to keep lightfastness and image permanence with these systems on a constant high level has often been underestimated.

In diluted inks, the ratio of solvent to dye increases considerably. For the same image, more ink is applied, with a direct consequence on dot pattern and, as will be shown, on lightfastness of single colors and via catalytic fading on mixed colors.

A large part of professionally made prints are laminated for better protection. Higher throughputs, faster printers and porous, "fast-dry" media mislead to shorter waiting times between printing and lamination. This can have a severe impact on lightfastness.

Keywords: lightfastness, ink solvent, drying time, lamination, diluted inks.

Introduction

In *previous papers*^{1,2}, we have discussed different aspects of the lightfastness of soluble dye based ink-jet prints, as a function of ink composition (dyes, solvents), media components (polymers, layer design, addenda) and environmental conditions (temperature, humidity). Several mechanisms of dye fading, based on photooxidation or photoreduction have been described, and the importance of the equilibrium of dye aggregation/deaggregation to stabilize imaging dyes has been demonstrated.

The *present paper* discusses some fundamental aspects of lightfastness which can - to a large degree - be controlled by how a print is printed and handled. To optimize lightfastness of ink-jet prints means not only to choose the right ink, media and printer combination, but also to select most favorable printer drivers and handling methods. Recently, this has gained in importance by a fast growing market of different printers, offering e.g. 6-, 8- or 12-color printing heads for the use of additional inks in order to

improve color rendition or graininess in highlights, or by the use of "faster drying" ink-jet media which allow higher printing speed and throughput. Some of these printer systems gave at first sight contradictory and surprising results in image permanence and lightfastness.

From Halftone to Continuous Tone

Ink-jet prints are – in contrast to traditional photography - built up by a fine pattern of small dots (20-100 μ m dot diameter). Depending on printer and printer settings, dots are placed in a controlled halftone pattern. Dye coverage of the paper surface varies from a few percents in highlights to full coverage in dark areas. It is an important advantage of a halftone print that the part of the light energy that reaches the print surface "between the dots" is ineffective and does not contribute to dye fading. Figure 1 shows a comparison of printed color densities vs. paper surface coverage of a set of cyan inks with different concentrations of the same dye.



Figure 1: Surface coverage as a function of printed density

All three inks of a commercially available ink-set (relative dye ratio 100:30:10) have separately been used to print step wedges (21 steps) on a glossy, resin coated paper with a wide format printer. Color densities have been measured with a standard densitometer (Status A) and the relative dye coverage of the paper surface has been determined with imaging analysis software on a patch of 5 mm². The result is shown in Fig. 1 (open squares).

To demonstrate the protective effect of the halftone pattern, the step wedges have been irradiated in an Atlas light fading equipment up to 30'000 kluxh (detailed fading results are given in Fig. 2). A plot of relative fading vs. printed density, normalized to the fading at maximum density of the respective ink, is included in Fig. 1 (filled circles).

By the simple decision to move towards continuous tone by printing highlights of an image with a higher number of more diluted ink dots, the lightfastness of low and medium densities is reduced up to a factor of two.

Diluted Inks and Single Dot Fading

Whereas the apparent reduction of lightfastness described above is not dye-dependant, another complication related to diluted inks can be observed with some dyes. Many of today's very lightfast, soluble ink-jet dyes are selfstabilizing by aggregation². Similar to pigments, where lightfastness is given by the particulate structure of the dye, permanence of soluble dyes is increased by aggregation of the dye in the layer. High quality ink-jet media and inks are optimized together to facilitate this reaction. Two of the most important variables to control aggregation are relative dye and solvent concentrations in the drying dot in the imaging layer. The negative effect of a decreased dye concentration and/or an increased solvent concentration on dye aggregation and therefore on lightfastness is demonstrated in Figures 2 and 3.



Figure 2: Fading of cyan at different concentrations

Figure 2 shows the density loss vs. the printed density for the three different dye concentrations on the step wedges described above after an irradiation of 30'000 kluxh (incl. UV cut-off filter and day/night cycles to simulate indoor conditions). Control measurements of the dot size before and after irradiation were made to estimate the effect of color bleed on fading results. For all non-laminated prints in this paper, the influence is negligible. As can be seen from the different slopes in the high density region of the three curves in Fig. 2, fading of the higher diluted inks is stronger than expected based on surface coverage alone. In fact, the observed lightfastness of low densities is reduced up to a factor of 6.

To better visualize the real lightfastness of the diluted inks, the surface coverage effect can be subtracted by calculation. Figure 3 shows the relative fading after this correction vs. surface coverage.



Figure 3: Calculated "single dot fading"

The curves represent the level of fading within the fraction of surface covered by ink dots. This "single dot fading" is expected to be independent of surface coverage or print density. In fact, the curves in Fig. 3 are almost flat. The fading ratio of the three dye concentrations is approx. 1:2:3.

A careful adjustment of dye, ink and media can reduce this dilution effect on lightfastness considerably. To demonstrate this, the experiment has been repeated with a dye, known for its efficient aggregation on the same media and printer. Figure 4 shows the corresponding three fading curves after subtracting the halftone effect.



Figure 4: Alternative dye with lower sensitivity to dilution

The dye concentration in these inks is clearly less important. Interestingly, both dyes at full concentration (100% curves in Fig. 3 and 4) show a comparable lightfastness. The suitability of a dye for the use in diluted inks can therefore not be predicted from its lightfastness in a concentrated ink.

Catalytic Fading

The phenomenon of catalytic fading and its possible mechanisms are well-known in the field of ink-jet³. The term describes the often made observation that combinations of dyes (mixed colors) fade faster than single dye colors alone. Typically, the magenta of a 3-color gray or a blue fades considerably faster than pure magenta or magenta in red. The decay is "catalyzed" by the presence of cyan. The result is a print with a greenish gray and blue, whereas the rest of the image would still be very acceptable. Less common are dye combinations showing accelerated cyan fading in presence of magenta, resulting in a reddish discoloration.

Figure 5 shows a case of very strong catalytic fading of a magenta in presence of cyan, with otherwise good lightfastness.



Figure 5: Magenta dye with strong catalytic fading

Step wedges have been printed with cyan and magenta from the same set of commercially available inks, already used in the experiments before. A glossy, resin coated media has been chosen, which was known for its catalytic fading problem. After printing the wedges have been irradiated in the Atlas up to 30'000 kluxh. Whereas single colors are very stable, the magenta loss in blue (green channel) is approx. 8 times higher.

This observation can be explained by a dye-dye interaction, which destabilizes magenta. The dyes have to be mixed on the image for catalytic fading to take place. From Fig. 5, it is visible that catalytic fading is negligible at densities below 0.5. The reason is the low overlap of dots at low densities.

Changing to diluted inks means again placing a higher number of dots, with as a consequence, a better mix of colors already at low densities. In Figure 6 the same mediadye combination as in Fig. 5 has been printed with the diluted inks. Shown is the low density region, only.



Figure 6: Influence of dilution on catalytic fading

The three magenta inks alone (dotted lines) show a similar behavior as cyan in Fig. 2. Catalytic fading in medium and low concentrated blue (mixed from diluted magenta and cyan) appears at lower densities. The visual sensitivity for color imbalance in highlights is very high. Therefore the rejection limit of an image is reached already after a very short exposure time, despite the good lightfastness of single, concentrated inks.

As shown in Fig. 7, changing the magenta dye reduces catalytic fading considerably. (A similar improvement can also be reached by selecting another media).



Figure 7: Magenta dye with lower level of catalytic fading

Print Protection by Lamination

Lamination is widely accepted as a protection against UV and water. To shield against outdoor UV-exposure, there exists a broad range of UV-absorbent laminates. However, ink-jet dyes are not only faded by UV, but also by visible light. Indoors, where UV-levels are very low, lamination is not very efficient against fading.

As solvent loads and humidity levels are other very important factors for lightfastness, we would even expect that lamination in non-optimal conditions can have a negative impact on lightfastness. Entrapped humidity and solvents in a laminated image have to be considered as factors that can reduce the lightfastness of a print. The main mechanism is similar as described above - hindered dye aggregation or increased deaggregation.

Figure 8 shows results of light stability tests on prints which have only been partially dried before laminating.



Figure 8: Fading of partially dried laminated prints

Four different, commercially available media – two polymer based products (media 1 and 2) and two microporous, ceramic products (3 and 4) - have been printed with a dye based ink. After printing the images were dried at 20°C/45%rH or at 60°C/40%rH during 1, 4 or 24 hours. The prints were then cold-laminated and afterwards irradiated in an Atlas up to 10'000 kluxh (UV filtered, day/night cycles). None of the prints was lightfast after 1 hour drying at room temperature. Only media 2 was sufficiently dry after four hours. Heating to 60°C accelerated the lightfastness via improved drying considerably.

This experiment demonstrates the importance to assure drying of ink-jet prints before laminating. Prints should not only be "dry-to-touch". Microporous, fast absorbing imaging layers, which absorb ink through capillary forces instead of polymer swelling are "dry when leaving the printer". As shown by media 3 and 4, this does not mean, that the prints are fit to be laminated without an additional drying period. The low lightfastness of the unlaminated control sample of the microporous media 4 is partially caused by the humidity uptake during the night cycle in the Atlas.

Conclusion

The quality standard expected from ink-jet prints has increased a lot during the recent years. Top quality media and inks, carefully developed and optimized in parallel, assure a lightfastness, which can exceed the permanence of traditional photography. Important developments in controlling the photochemistry of dyes, inks and media have contributed a lot.

However the final quality of a printed image is still controlled to a large extent by the know-how of the printing lab. This has been widely accepted for quality issues like image preparation, image composition, color balance or image mounting. More surprisingly, lightfastness or image permanence are also strongly dependent on the art of printing. Lowest graininess in highlights, reached by using diluted inks, is an example of an improvement with a possible, unexpected drawback. Especially in the wideformat market with viewing distances of one meter and more, the negative impact on lightfastness may not be justified.

Acknowledgement

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Biography

Stefan Schüttel received his Ph.D. degree in Chemistry from the University of Berne, Switzerland in 1990. After a postdoctoral fellowship at the University of Washington, Seattle, he joined Ilford Imaging Switzerland in 1993. His work has primarily focused on ink-jet media development, including polymer chemistry, imaging permanence and coating technology.