Light Fastness of Pigment-based and Dye-based Inkjet Inks

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Abstract

This paper focuses on the ability of pigment-based, dye-based inks and paper substrates to maintain accurate color over time due to the exposure to simulated sunlight. The testing of a number of ink/substrate combinations, utilizing the ECI 2002 Random Layout CMYK target for the printed samples was done. The samples were exposed to the simulated equivalent of 4.5 months of sunlight in Florida. The ΔE values of the samples were calculated in order to observe the color changes attributed to the fading of the inks/substrates. The Epson Matte paper printed with Epson 5000 resulted in largest ΔE, thus this ink has the least fade resistance. A longer term fade test has indicated that most of the color shift has occurred in the earlier time period of exposure. It was also found that difference in the color appearance upon exposure, was not solely due to the ink fading, but also due to color change of substrate itself.

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Introduction

The ability of pigment- and dye-based inks to maintain accurate color strength over time due to light exposure and subsequent fading is an important research topic (Wilhelm, 1993). Resistance to fading is significant in several situations. The archiving of sensitive documents is one focus of research pertaining with fading and light fastness. Another field in which the subject is of importance is the world of digital photography, where consumers are now producing ink jet prints of digital photographs (Wilhelm, 2004). In both of these cases, inks and papers used for archival purposes (or purposes dependent upon color accuracy) should be reliable in their light-fastness because of the need for long-term storage. Photographic prints from digital files are also expected to maintain accurate color over a moderately lengthy period. (Wilhelm, 1993; 2004)

The digital age may decrease the need for paper-based document storage, but archived papers should still resist fading (Wilhelm, 2002). Families wishing to create albums from digital images expect their photographs to maintain brightness and clarity. Light-fastness of inks and papers is relevant in all situations requiring document storage over a moderate period in suboptimal conditions. Archived documents have a higher probability of being properly stored (low light exposure, non-extreme temperatures, and moderate humidity) than a family's digital photos. Still, since both situations would benefit from little degradation of the document over time, research into the ideal papers and inks for proper light-fastness is necessary.

The use of relatively new and widely-available ink-jet technologies for the creation of archive-quality documents, along with choices between pigment-based (Usui, 2002; Takemoto, 2003; Rose, 2003; Desie, 2003) and dye-based inks (Desie, 2003; Kabalnov, 2004; Oki, 2004), asks for research into the methods to achieve optimal light-fastness (Wilhelm, 2002).

Light fastness is not simply determined by the colorant used in the ink. Light fastness also depends upon the protective properties of the ink vehicle, the ink's exposure time, the atmospheric conditions during the exposure, the light intensity during the exposure and properties of the substrate. Most importantly, the fading or yellowing of the substrate affects all of the print colors, especially tints. There is also variability between different pigments. Inorganic pigments tend to resist fading better than organic pigments (Eldred, 1995).

Previously, Chovancova (2004, 2005) presented different measures of printability of various ink jet printers using dye-based and pigment-based inks. Specifically, the Epson Stylus Pro 5000 (with dye-based inks), the Epson Stylus Pro 5500 (with archival inks), and the Epson Stylus Photo 2200 (with UltraChrome inks) were investigated. These experiments were conducted on six different substrates: Epson Archival Matte, Epson Premium Luster Photo, Epson Premium Glossy Photo, Kodak Glossy, Kodak Satin Paper, and experimental substrates (Chovancova, 2004; 2005). The samples were measured using a spectrophotometer both before and after fading simulations. They were submitted to 129,600 kJ/m^2 of energy over 48 hours (at 765 W/m^2) with the uncoated quartz glass filter configuration and measured again. This represents about 4.5 months of daylight exposure in Florida (Atlas, 1997; Schaeffer, 2005). This study indicated that the optical brighteners in the Archival Matte and Kodak Satin papers had been mostly degraded, ultimately shifting the perceived color of the images without regard for the ink composition (Chovancova, 2004; 2005). While a higher degree of resistance was expected from the pigment-based ink, it was obvious that a ΔE value of almost 3.0 was large for inks rated to withstand more than 75 years of archiving (Epson, 2005a; 2005b).

The goal of this project was to simulate the changes that occur when printed samples are subjected to sunlight exposure for extended period of time. This was done using measurement of the ΔE (the change in color) of the ECI 2002 Random Layout CMYK test chart (European Color Initiative, 2005) between two conditions: their original, unexposed prints and prints after fading. Utilizing ICC profiles and the associated color gamut gives a measure of the entire color space in the permanence evaluation. McCormick-Goodhart (McCormick-Goodhart, 2003) presented a method of evaluating image stability based on $L^*a^*b^*$ measurements, but these were based on measurement of gray midtone patches. The reproduction and permanence of gray balance is very important (Fleming, 2004), but a measure of the effects on saturated colors is also necessary.

Experimental

The experimental design is similar to the earlier study (Chovancova, 2004; 2005). This is reviewed in the following:

- Print the ECI 2002 profile chart (random) using different substrates on Epson Photo 2200 and Stylus 5500 pigment-based inkjet printers and Epson 5000 dye-based inkjet printer.
- Measure charts using the GretagMacbeth SpectroScan spectrophotometer.
- Submitted charts to controlled amounts of energy using an Atlas Fade meter.
- Measure charts again using the GretagMacbeth SpectroScan.
- The original versions and the faded versions of the respective charts were compared using GretagMacbeth MeasureTool.

Results and Discussion

The L*a*b*values of patches of the ECI 2002 Random Layout CMYK Target printed on five different substrates were measured with the GretagMacbeth SpectroScan. Then, they were put into the Atlas Fade meter and submitted to 129,600 kJ/m^2 of energy over 48 hours at 765 W/m^2 with the uncoated quartz glass filter configuration and measured again. This represents about 4.5 months of daylight exposure in Florida in June (Atlas, 1997, Schaeffer, 2005).

The $L^*a^*b^*$ values of the printed patches for all the printers on the different substrates before and after the tests were taken from the data file and the ΔE calculation was performed to obtain the range of color difference between them. **Table 1** summarizes the results for all printers and papers used in this experiment.

Table 1. Average and RMS ΔE values before and after fading test for different printers on various papers

Printer	Paper	Average ΔE	RMS ΔE
Photo 2200	Archival Matte	2.20	2.74
PRO 5000	Archival Matte	10.62	11.34
PRO 5500	Archival Matte	2.19	2.76
Photo 2200	Epson Glossy	1.30	1.52
PRO 5000	Epson Glossy	8.73	9.65
PRO 5500	Kodak Glossy	3.04	3.44
PRO 5500	Kodak Satin	2.90	3.45

The average ΔE for the Epson 2200 is uniformly small in all three channels, with $\Delta L^* = .20$, $\Delta a^* = -.67$ and $\Delta b^* = .57$. On the other hand, the largest contribution to ΔE for the Epson 5000 is from $\Delta L^* = 4.59$, with $\Delta a^* = 2.59$ and $\Delta b^* = -1.31$. Thus most of the color change is true fading, although there is a small color shift towards red and blue.

The average ΔE for the Kodak Glossy paper on the 5500 printer has almost equal contributions from all channels, with $\Delta L^* = 1.17$, $\Delta a^* = -1.31$ and $\Delta b^* = 1.91$. These tend to follow the change in the paper color during light exposure (**Table 1**). The pigmented inks change colors much less than the dye inks, as expected. However, values ΔE ~ 3 for the pigmented inks are larger than expected for inks rated at more than 75 years of archiving (Epson, 2005a; 2005b). Examination of the data shows that there is a systematic shift toward yellow and green. The Epson 2200 shows an average Δb^* of 1.57, while the

Epson 5500 shows an average Δb^* of 1.89. Thus, for the pigmented inks, most of the average ΔE results from the systematic Δb^* shift, most likely reflecting the drop in the optical brighteners contribution. The Epson 5000 shows an average Δb^* of only 0.77, but the average ΔL^* is 6.96. Therefore, that ΔE is mostly due to actual ink fading.

The average ΔE for the Kodak Glossy paper on the 5500 printer has almost equal contributions from all channels (**Table 1**), with $\Delta L^* = 1.16$, $\Delta a^* = -1.13$ and $\Delta b^* = 1.89$. The Kodak Glossy and Satin papers show virtually identical performance for this printer. The color change for this paper also tends to follow the change in the paper color during light exposure (**Table 1**).

The gamut plots of Epson Matte substrate printed from all three printers before and after the fading test are illustrated at the **Figure 1**.

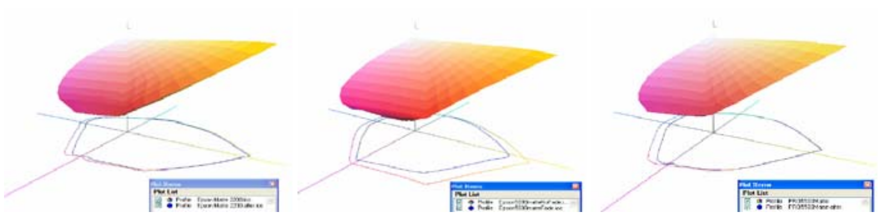

Figure 1: Comparison of color gamuts before and after fading test for Epson 2200 (left), Epson 5000 (middle) and 5500 (right) for Epson Archival Matte substrate.

The Epson 5000 shows a significant decrease in color gamut in addition to fading. The printers with the pigmented inks, the Epson 2200 and 5500, show the aforementioned shift towards yellow, but little decrease in gamut.

The Epson Stylus Photo 2200 printer together with the Epson Archival Matte substrate was chosen for further investigation of fading effects. This substrate with the printed chart from the 2200 was submitted to longer time light exposure equivalent to 13 months (June) of daylight exposure in Florida (104 hrs at 765 W/m^2). The gamut plot of this test is shown in **Figure 2**. In this case, the color shift is even more significant in the yellow region of the spectrum.

After receiving this information, we decided to look at the changes in properties of the non-printed substrates. In previous work done by Aksoy and Fleming, the important role of optical brighteners and their effect on paper whiteness was studied (Aksoy, 2003; Aksoy, 2005). Fading test of non-printed substrates was done, and $L^*a^*b^*$ values of the substrates before and after the tests were taken. ΔE calculations for obtaining the range of color difference are shown in the **Table 2**.

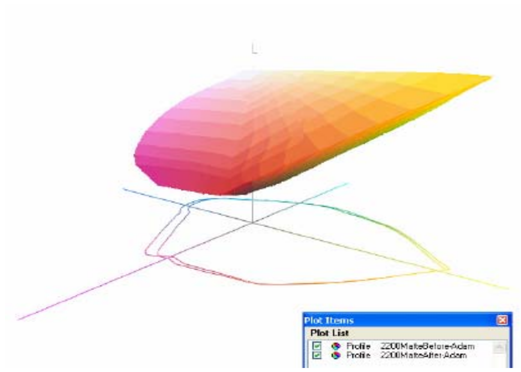

Figure 2: Comparison of color gamuts before and after fading test for Epson 2200 and Archival Matte substrate.

The GretagMacbeth MeasureTool 5.0.0 software was used to compare the spectra of the substrates before and after the fading test. The spectra for Epson Archival Matte substrate and for Kodak Satin substrate before and after fading test, are shown in **Figures 3-6**. These were chosen because they claim the best archival properties.

Table 2: $L^*a^*b^*$ values and average ΔE values of non-printed paper substrates before and after fading test.

Substrate		L*	a*	b*	ΔE
Epson Archival Matte	**Before**	96.1	0.8	-4.3	**4.34**
	After	95.8	-0.4	-0.1	
Kodak Satin	**Before**	93.3	0.7	-6.3	**2.49**
	After	93.4	-0.1	-3.9	
Epson Premium Glossy	**Before**	94.6	-0.4	-3.9	**0.50**
	After	94.4	-0.6	-3.5	
Kodak Glossy	**Before**	92.8	0.3	-6.7	**2.66**
	After	93.7	0.1	-4.2	
Epson Archival Matte (long term test)	**Before**	95.9	0.8	-4.0	**4.91**
	After	95.8	-0.6	0.7	

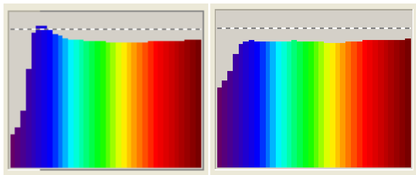

Figure 3: Spectrum of Epson Archival Matte.

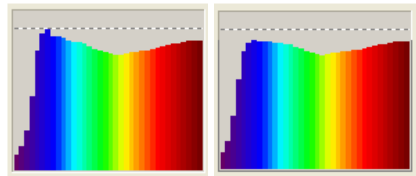

Figure 4: Spectrum of Kodak Satin.

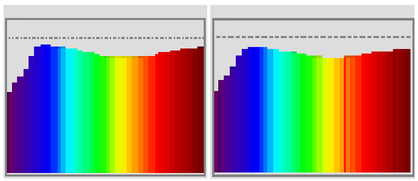

Figure 5: Spectrum of Epson Premium Glossy.

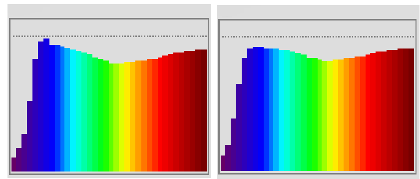

Figure 6: Spectrum of Kodak Glossy.

The spectra and the $L^*a^*b^*$ values of these substrates suggest that the contribution of optical brighteners, added to improve the perceived whiteness of the paper, has been degraded for the Archival Matte paper and greatly diminished for the Kodak Glossy and Satin papers. There is little or no effect for the Epson Glossy paper. Optical Brightening Agents (OBA) are fluorescent materials that absorb in the ultraviolet and emit in the blue region of visible spectrum, which is the source for the blue peak in the spectra and the negative values of b^* before the fading test. This means that, regardless of the permanence of the printed dye or pigmented ink, there will always be some shift in the perceived color of printed images. Note from **Table 2** that the majority of the OBA degradation for the Archival Matte paper has occurred in the first simulated 4.5 month period, with little (barely significant) additional change in the remaining simulated 8.5 months.

Conclusion

Fade testing of ink jet inks and archival substrates on a short-term testing timeline showed that the Epson Matte paper printed with Epson 5000 resulted in largest ΔE, thus this ink has least fade resistance. A longer term fade test has indicated that most of the color shift has occurred over the earlier time period. Difference in the color appearance was not solely due to ink fading, but also due to change of paper substrate itself. This was most likely due to decomposition of optical brighteners present in paper substrates.

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References

Aksoy, B., Joyce, M.K. and Fleming, P. D.
2003 "Comparative Study of Brightness/Whiteness Using Various Analytical Methods on Coated Papers Containing Colorants", *TAPPI Spring Technical Conf. & Trade Fair*, (Academic, Chicago, May 12-15).

Aksoy, B., Fleming P. D. and Joyce, M. K.
2005 "New Measures of Whiteness that Correlate with Perceived Color Appearance", Applied Optics, In press.
Atlas,
1997
"Suntest CPS Operating Manual".
Chovancova, V., Howell, P., Fleming III, P. D. and Rasmusson, A.
2004 "Printability of Different Epson Ink Jet Ink Sets," *Proceedings of the IS&T NIP20: International Conference on Digital Printing Technologies*, p. 457-463.
2005 "Printability of Different Epson Ink Jet Ink Sets," In press, *Journal of Imaging Science and Technology*.
Desie, G. Pascaul, O. Pataki, T. de Almeida, P. Mertens, P. Allaman, S. Soucemarianadin, A.
2003 "Imbibition of Dye and Pigment-based Aqueous Inks into Porous Substrates", *Proceedings of IS&T NIP19*, New Orleans, Louisiana, p. 209.
Eldred, N.R.
1995 "What the Printer Should Know About Ink," 2nd ed., Pittsburgh, GATF, p. 30, 135.
Epson
2005a "Stylus Pro 5500",
http://www.ldr.com/products_new/epson_styluspro5500.shtml.
Epson
2005b "UltraChrome Ink",
http://www.epson.com.au/whats_new/story_148.asp.
European Color Initiative
2005 "Guidelines for device-independent color data processing in accordance with the ICC-Standard",
http://www.eci.org/eci/en/060_downloads.php.
Fleming, P. D., Jewell, H. and Khandekar, A. D.
2004 "The Leverage of Gray Balance in Controlling Perceptual and Quantitative Colorimetry", *Journal of Graphic Technology*, **3**, p. 43.
Kabalnov, A., Dupuy, C., Gondek, J. Lee, J.-Ho, B. R. and Berfanger, D.
2004 "Gamut and Permanence of New-Generation Dye-Based Inks", *Proceedings of the IS&T NIP20: International Conference on Digital Printing Technologies*, Salt Lake City, p.705-709.
McCormick-Goodhart, M. and Wilhelm, H.
2003 "A New Test Method Based on CIELAB Colorimetry for Evaluating the Permanence of Pictorial Images", *Proceedings of the IS&T's Thirteenth International Symposium on Photofinishing Technologies*, June 16, p.25-30.
Oki, Y., Kitamura, K., Aoyama, T., Hanmura, M. and Fukumoto, H.
2004 "The Inkjet Prints Permanence of the Latest Dye Ink"**,** *Proceedings of the IS&T NIP20: International Conference on Digital Printing Technologies*, Salt Lake City, p. 710-713.

Rose, P. Walker, N.
2003 “The Influence of Pigment Selection on Particle Size and Migration Stability in Aqueous Inkjet Inks”, *Proceedings of IS&T NIP19*, New Orleans, Louisiana, p.190.

Schaeffer, W. R., Leroy, C., Ming F.
2005 “UV-Curable Products with Superior Outdoor Durability”, http://www.sartomer.com/wpapers/5061.pdf.

Takemoto, K. Kataoka, S. Kubota, K.
2003 “High-Gloss and Wide Color Gamut Pigmented Inks for Ink-Jet Printing”, *Proceedings of IS&T NIP19*, New Orleans, Louisiana, p.237.

Usui, M., Hayashi, H. Hara, K. Kitahara, T.
2002 “The Development of Pigment Ink for Plain Paper”, *Proceedings of IS&T NIP18*, San Diego, California, p. 369.

Wilhelm, H., Brower, C.
1993 *“The Permanence and Care of Color Photographs*: *Traditional and Digital Color Prints*, *Color Negatives*, *Slides*, *and Motion Pictures”*, Preservation Publishing Company, Grinnell, Iowa.

Wilhelm, H.
2002 “How Long Will They Last? An Overview of the Light-Fading Stability of Inkjet Prints and Traditional Color Photographs”, *Proceedings of the IS&T 12th International Symposium on Photofinishing Technology, pp. 32–37, Orlando, Florida, February 20–21,* p. 32-37.

Wilhelm, H.
2004 “A Review of Accelerated Test Methods for Predicting the Image Life of Digitally-Printed Photographs - Part II”, *Proceedings of the IS&T NIP20: International Conference on Digital Printing Technologies*, Salt Lake City, p.664-669.