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

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**Keywords:** Image Permanence, Inkjet, Archival

**Abstract**

The digital age may seem to have diminished the need for paper-based document storage, but there are still many situations that call for color accuracy in inkjet applications. Examples of these circumstances include: individuals wishing to create photo albums from digital images, and any type of document printed on archival papers. After taking digital photos and sending them to an inkjet printer, people expect their photographs to maintain brightness, clarity, and color. Documents printed on archival papers are intended for long-term storage with little change in color. Light fastness of inks and papers is relevant in all situations requiring document storage over a moderate period in suboptimal conditions.

This paper focuses on the ability of pigment-based and dye-based inks to maintain accurate color strength over time due to the exposure of printed samples to simulated sunlight. It proposes the testing of a number of ink/substrate combinations, utilizing the ECI 2002 Random Layout CMYK target for the printed samples. The printed samples were measured using a spectrophotometer. The samples were exposed to the simulated equivalent of 4.5 months of sunlight in Florida. The samples are again measured, and the results compared to the original measurements. The $\Delta E$ values of the samples were calculated in order to observe the color changes attributed to the fading of the inks/substrates.

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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 important 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 warranted.

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, Desei, 2003) and dye-based (Desei, 2003, Kabalnov 2004, Oki, 2004) inks, begs for research into the methods to achieve optimal light-fastness (Wilhelm, 2002). The benefits of this research will be the measured effect of light on various inks and papers, allowing for documented and predictable results for anyone who chooses to use these inks and papers for archival or color-managed intents. As a result of this research, consumers and businesses will be able to make informed decisions regarding document archival and photograph storage.

## Goals and Objectives

The goal of this project is to simulate the changes that occur when printed samples are subjected to sunlight exposure for extended periods. A certain amount of fading is expected, due to the aging of the substrate and to ink interactions with the elements, namely humidity, natural light and non-ideal temperatures. However, it will be interesting to see the specific amounts of fading in relation to the composition of the inks and substrates. Sunlight should have a measurable impact on the color of the substrate, due to the radiation's interactions with fibers, optical brighteners, and other elements of the paper. In addition, sunlight will interact with the components of the ink—including the colorant—causing fading to a certain degree. Any conclusions that can be drawn from specific combinations of inks, substrates, and exposure time will be welcome.

The objective of this research is to measure the ΔE (the change in color) of the ECI 2002 (European Color Initiative, 2005) Random Layout CMYK test chart between two conditions: their original, unexposed condition and their post-exposure, faded condition. Based upon the Delta E values achieved, and factoring in exposure time, conclusions may be reached concerning several factors: the color strength and stability of pigment- and dye-based inks, and any effect upon the optical brighteners in substrates. Pigment-based inks should resist fading better than dye-based inks.

## Background and Literature Review

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), we presented different measures of printability of various dye-based and pigment-based ink jet printers. Specifically, we investigated 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). We also studied six different substrates: Epson Archival Matte, Epson Premium Luster Photo, Epson Premium Glossy Photo, Kodak Glossy, Kodak Satin Paper, and experimental substrates with experimental coatings. While our discussions involved various measures of printability, some preliminary results on ink fading were presented.

The samples were measured using a spectrophotometer both before fading simulations. They were submitted to 129,600 $kJ/m^2$ of energy over 48 hours (@ 765 $W/m^2$) with the uncoated quartz glass filter configuration and measured again. This represents about 4.5 months (June) of daylight exposure in Florida (Atlas 1997, Schaeffer, 2005). The samples' before and after measurements were compared using profiling software to display changes in terms of spectra color gamut and specific L*a*b* color values. The color variations were then compared between the various inks and substrates, and results recorded.

The key findings of the preliminary study indicated that the optical brighteners in the Archival Matte and Kodak Satin papers had been mostly neutralized, ultimately shifting the perceived color of the images without regard for the ink composition. While a higher degree of resistance was expected from the pigment-based ink, it was felt that a ΔE value of almost 3.0 was large for inks rated at more than 75 years (Epson, 2005a, 2005b).

## Experimental Design

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 substrated 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

The patches of the ECI 2002 Random Layout CMYK Target printed on five different substrates were measured with the GretagMacbeth SpectroScan before they were put into the Atlas fade meter. They were submitted to 129,600 $kJ/m^2$ of energy over 48 hours (@ 765 $W/m^2$) with the uncoated quartz glass filter configuration and measured again. This represents about 4.5 months (June) of daylight exposure in Florida (Atlas 19xx, 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 $\Delta E$ calculation was performed to obtain the range of color difference between them. Table 1 summarizes the results for Epson Archival Matte paper.

Table 1. Average and RMS $\Delta E$ values before and after fading test for different printers on Archival Matte paper.

| Printer | Paper | Average $\Delta E$ | RMS $\Delta E$ |
|---|---|---|---|
| **Photo 2200** | Archival Matte | 2.20 | 2.74 |
| **PRO 5000** | Archival Matte | 10.62 | 11.34 |
| **PRO 5500** | Archival Matte | 2.19 | 2.76 |

Table 3 does show that the pigmented inks change colors much less than the dye inks, as expected. However, values ~ 3 for the pigmented inks are larger than expected for inks rated at more than 75 years (Epson, 2005a, 2005b)! Examination of the data shows that there is a systematic shift toward yellow and green. The Epson 2200 shows an average $\Delta b^*$ of 1.57, while the Epson 5500 shows an average $\Delta b^*$ of 1.89. Thus, for the pigmented inks, most of the average $\Delta E$ results from the systematic $\Delta b^*$ shift, reflecting the drop in the OBA[20,21] contribution (see below). The Epson 5000 shows an average $\Delta b^*$ of only .77, but the average $\Delta L^*$ is 6.96. Therefore, that ΔE is mostly due to actual ink fading.

Table 2 summarizes the results for the Epson 2200 and 5000 printers on Epson Glossy paper. The average ΔE for the 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.

Table 2. Average and RMS ΔE values before and after fading test for different printers and Epson Glossy paper.

| Printer | Paper | Average ΔE | RMS ΔE |
|---|---|---|---|
| **Photo 2200** | Epson Glossy | 1.30 | 1.52 |
| **PRO 5000** | Epson Glossy | 8.73 | 9.65 |

Table 3 summarizes the results for Kodak Glossy paper and the Epson 5500 printer. 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 (see Table 4 below).

Table 3. Average and RMS ΔE values before and after fading test for different printers and Kodak Glossy paper.

| Printer | Paper | Average ΔE | RMS ΔE |
|---|---|---|---|
| **PRO 5500** | Kodak Glossy | 3.04 | 3.44 |

Table 4 summarizes the results for Kodak Satin paper and the Epson 5500 printer. The average ΔE for the Kodak glossy paper on the 5500 printer has almost equal contributions from all channels, 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 (see Table 4 below).

Table 4. Average and RMS ΔE values before and after fading test for different printers and Epson Luster paper.

| Printer | Paper | Average ΔE | RMS ΔE |
|---|---|---|---|
| **PRO 5500** | Kodak Satin | 2.90 | 3.45 |

Figure 1 shows the gamut plots before and after the fading test.

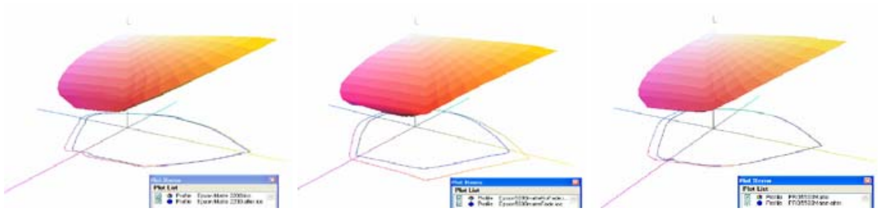

Figure 1. Comparisons of color gamuts before and after fading test for Epson 2200 (left), Epson 5000 (middle) and 5500 (right).

Note that 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 @ 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.

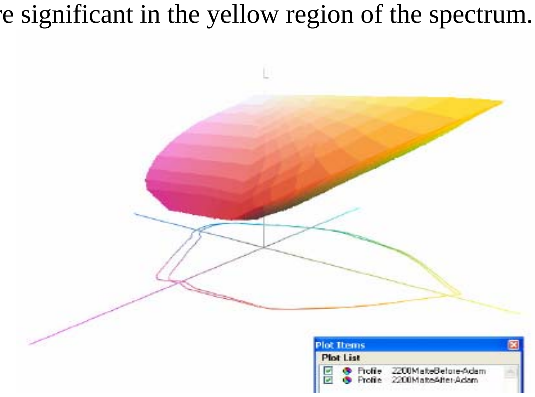


Figure 2. Comparisons of color gamuts before and after fading test for Epson 2200 and Archival Matte substrate.

From this information, we decided to look at the changes in properties of the plain substrates. $L^*a^*b^*$ 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 5.

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, claiming the best archival properties, and for Kodak Satin substrate are shown in Figures 3 to 6.

Table 5. Average and RMS ΔE values before and after fading test for different printers and papers.

| 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 | |

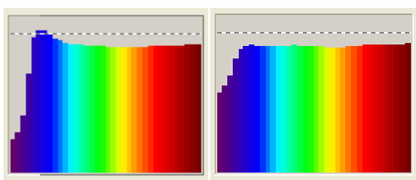

Figure 3. Spectrum of Epson Archival Matte.

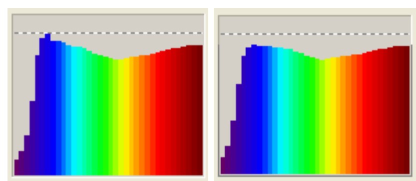

Figure 4. Spectrum of Kodak Satin.

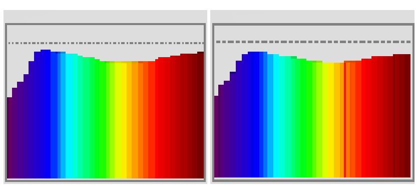

Figure 5. Spectrum of Epson Premium Glossy.

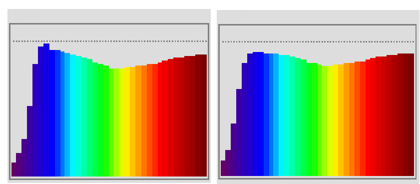

Figure 6. Spectrum of Kodak Glossy.

The spectra and the $L^*a^*b^*$ values suggest that the contribution of optical brighteners, added to improve the perceived whiteness of the paper, has been neutralized 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 (Aksoy, 2003, 2005). This 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 perceive color of printed images. Note from Table 5 that the majority of the OBA neutralization 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 has yielded interesting results. A longer term fade test has indicated that most of the color shift has occurred over the earlier time period.

The results presented here and earlier (Chovancova, 2004, 2005) provide a general frame work for assessing image permanence. Utilizing ICC profiles and the associated color gamut gives a measure of the entire color space in the permanence evaluation. 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.

Acknowledgement: We thank GretagMacbeth, X-rite and Electronics for Imaging for donation of Color measurement/management hardware and software.

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