The Hilltop Review http://www.wmich.edu/gsac/publications
2005, Volume 1 All Rights Reserved

Evaluation of Dye and Pigment Based Ink Jet Ink Sets

VERONIKA CHOVANCOVA
Department of Paper Engineering, Chemical Engineering and Imaging
Western Michigan University

Abstract

The development of high performance inkjet printers and inks is advancing rapidly. Manufacturers seem to introduce their new technology inks to the market on an almost daily basis. Chemists in ink laboratories are still fighting with the issue of combining a wide gamut of dye-based inks with the lightfast and weather resistance qualities of pigment-based inks into new-age ink formulations.

Three different inkjet printers and inks were investigated in this work: the Epson Stylus® Pro 5000, using a dye-based ink set, the Epson Stylus® Pro 5500, employing Archival ink technology, and the Epson Stylus® Photo 2200, with 7-color UltraChrome™ inks. A number of different commercial substrates were sampled. Printability tests were carried out to test and evaluate ink/printer/substrate interactions. Particle size analyses of the three ink types were investigated. Color gamuts and ICC profiles for each of the different printer/ink/substrate sets were compared. In addition, the accuracy of each printer's color profile was investigated. The results of the profile accuracy measurements were expressed in terms of CIE $L^*a^*b^*$ coordinates and Root Mean Square (RMS) □E. Results of accelerated lightfastness tests for the different ink sets were interpreted in terms of change of profile and color gamut.

Introduction

There has been and will continue to be wide development of novel technologies in manufacturing inks and substrates, and due to that, an expansion of inkjet printing technology into desktop, outdoor and industrial applications[1,2].

Epson has recently introduced two types of pigment-based inks. They combine the advantages of both dye and pigment based inks in their formulations. Both their Archival and UltraChrome™ ink systems represent new ink solutions, where each pigment particle is encapsulated in a resin. This technology offers many advantages over conventional pigment and dye based inks. The primary advantages being those of uniform particle shape and particle size, greater color gamut, advanced optical density, exceptional gloss for photo prints, enhanced lightfastness and support for a wider range of media.

Pigment based inks tend to satisfy the requirements of most ink jet printing demands; but the suitable combination of ink and substrate is still crucial. Inkjet inks require a fine particle size, due to possible clogging of the printing head. For low viscosity inks there is a tendency of particle migration with time[3]. Pigment based inks behave differently than dye-based inks. The spreading behavior of these inks is determined by the hydrodynamic properties such as the Weber or Reynolds's number. On the other hand, in pigment-based inks, after initial spreading, the pigment particles coagulate on the surface of the microporous layer, creating a filter cake that limits the penetration of the carrier liquid. This results in longer absorption times and recessed dots that stay on the top of the substrate layer, and affect all the other printability properties[4].

Also, the precision of color reproduction depends on the image processing, e.g. color separation, rendering intent, and on the stability of the printing process, which usually is carried out with the help of an ICC profile and Color Management Modules[5-9]. In order to understand the whole process, the influence of paper properties on color reproduction has to be taken into consideration. The grade or type of the substrate used will definitely affect the results of the profile calculations and therefore the printing gamut[10,11].

Procedures and Results

All the printers (Epson Stylus Photo 2200, Epson Stylus PRO 5000, Epson Stylus PRO 5500) were profiled as CMYK devices on the six selected substrates (Epson Archival Matte, Epson Premium Luster Photo, Epson Premium

Kodak Glossy, Kodak Satin Paper), using a GretagMacbeth SpectroScanT spectrophotometer (in reflection mode), Gretag-Macbeth ProfileMaker 4.1.5 and the ECI2002 Random Layout CMYK Target[10]

Sample test prints were produced from Adobe InDesign. In “Color Settings” the CMYK working space was set to the appropriate ICC profile. The prints were made with color management set to source space as proof and the applicable CMYK profile for the print, with the intent set to Absolute Colorimetric for the sample output (the “proof space” is the only management that allows the intent to be manually set). Therefore, all output was set for an absolute colorimetric intent.

Density Tests

The samples for all substrates were measured with an XRite 530 SpectroDensitometer. Paper density, Solid density and Dot Area were measured for each sample. The dot area as measured and calculated by the device includes both mechanical and optical gain. Also listed in the results is the difference “Dot Gain” assuming the actual dot size to be a true 20%.

Particle Size Measurements

A NICOMP 370 Submicron Particle Sizer was used to measure the particle size of all the ink sets. As expected, no particles were detected in the dye-based ink set for the Stylus PRO 5000. The measured particle sizes of all pigmented inks are found in Table 1.

Table 1. Particle Size of All Ink sets.

Particle Size	**C (nm)**	**M (nm)**	**Y (nm)**	**K (nm)**
PRO 2200	119	172	74	99
PRO 5500	141	190	123	113
PRO 5000	Dye	Dye	Dye	Dye

ICC Profile Test

Profile accuracy tests were carried out using the following steps. The values of the ColorChecker® target in Photoshop with the profile applied for each paper sample were checked first. This was accomplished by selecting a large portion of each patch and then recording each of the $L^*a^*b^*$ values from the “Histogram” portion of the “Info” palette. The Mean values obtained from the histogram were converted to actual $L^*a^*b^*$ values. Using the GretagMacbeth SpectroScanT, $L^*a^*b^*$ measurements were made for each of the sample patches of the ColorChecker® target for all of the substrates and for each of the sample printers. Employing the formula for color difference “ΔE”[11],

$$\Delta E = \sqrt{\left(L_1^* - L_2^*\right)^2 + \left(a_1^* - a_2^*\right)^2 + \left(b_1^* - b_2^*\right)^2} \qquad (1)$$

The original $L^*a^*b^*$ values of the ColorChecker® target (Target values) were compared with the values from Photoshop with the profile applied (Profile values). These values were also compared with the actual values measured from the printed ColorChecker® portion of the verification samples produced from InDesign, and finally the original values were compared with the values measured from the ColorChecker® Target (Test values). The resultant values for Delta E are listed in Table 2.

Table 2. RMS ΔE Results.

EPSON Paper	**Target vs. Profile**	**Profile vs. Test**	**Target vs. Test**	**IT8/7 Test**
Photo 2200				
Archival Matte	2.42	2.11	2.54	7.55
Luster Photo	1.48	2.8	2.87	4.39
Glossy Photo	1.33	1.65	2.02	3.79

EPSON Paper	**Target vs. Profile**	**Profile vs. Test**	**Target vs. Test**	**IT8/7 Test**
PRO 5000				
Archival Matte	1.1	1.8	2.02	7.38
Luster Photo	0.91	2.09	2.3	3.27
Glossy Photo	2.04	2.55	3.59	4.86
PRO 5500				
Archival Matte	4.5	1.37	4.55	12.86
Luster Photo	1.01	1.85	1.92	8.33
Glossy Photo	1.38	1.89	2.17	9.66

RMS ?E

KODAK	**Paper vs. Profile**	**Target vs. Test**	**Profile vs. Test**	**Target Test**	**IT8/7**
Photo 2200					
Satin 1.52	1.56	1.99	6.8		
Glossy Photo	1.26	1.93	2.16	6.67	
PRO 5000					
Satin 1.24	5	5.17	5.43		
Glossy Photo	1.18	5.76	5.87	6.18	
PRO 5500					
Satin 4.78	2.3	5.77	13.06		
Glossy Photo	3.33	2.05	4.28	11.31	

IT8/7-3 Subset Test

The subset part of the IT8/7-3 chart was included in the verification page layout. The $L^*a^*b^*$ values of the patches were measured with the GretagMacbeth SpectroScanT and compared with the original data of IT8/7-3 chart in order to investigate the quality of the profiles made for each scanner/ printer/paper set. The resulting RMS □E’s are also shown in Table 2.

Color Gamut Comparison

Using CHROMiX ColorThink 2.1.2, the profile gamuts for each of the printers were graphically compared in this order: Epson Photo 2200, Epson Stylus PRO 5000, Epson Stylus PRO 5500 (Figures 1-2). The axis represents the CIELab color space: from “-a” (green) to “+a” (red) and from “-b” (blue) to “+b” (yellow) colors.

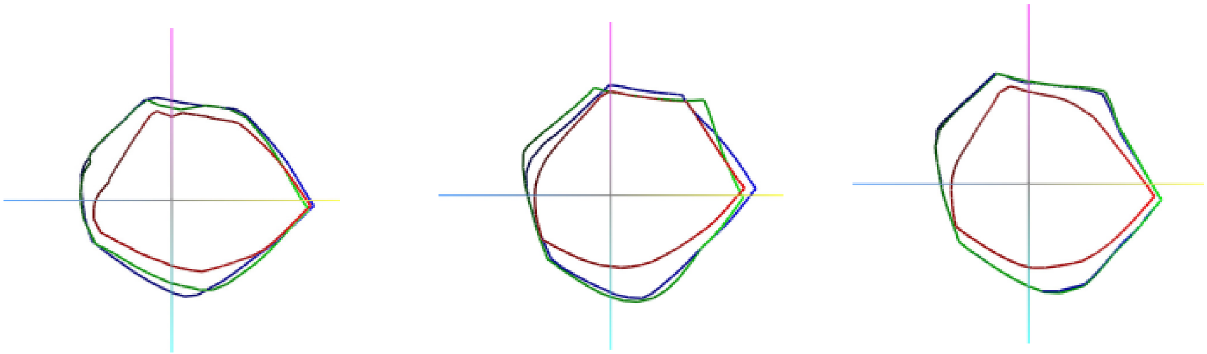

Fig. 1. Gamut projection plots for Epson papers, Matte (red), Luster (green) and Glossy (blue) from different printers 2200 (left), PRO 5000 (middle), PRO 5500 (right).

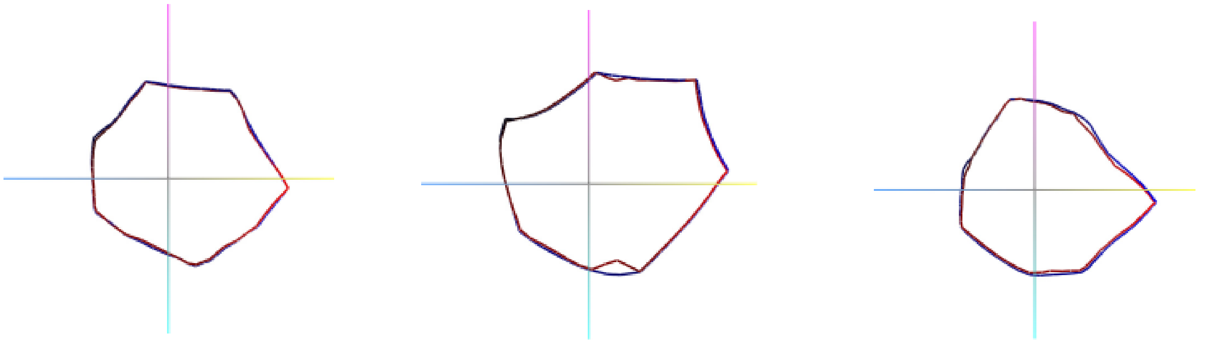

Fig. 2. Gamut plots for Kodak papers Satin (red) and Glossy (blue) from different printers 2200 (left), PRO 5000 (middle), PRO 5500 (right).

Then we compared the similar substrates, glossy and matte/Satin, from each printer to each other. The results were combined and are shown on the 3D gamut plots (Figures 3-4).

Figure 3

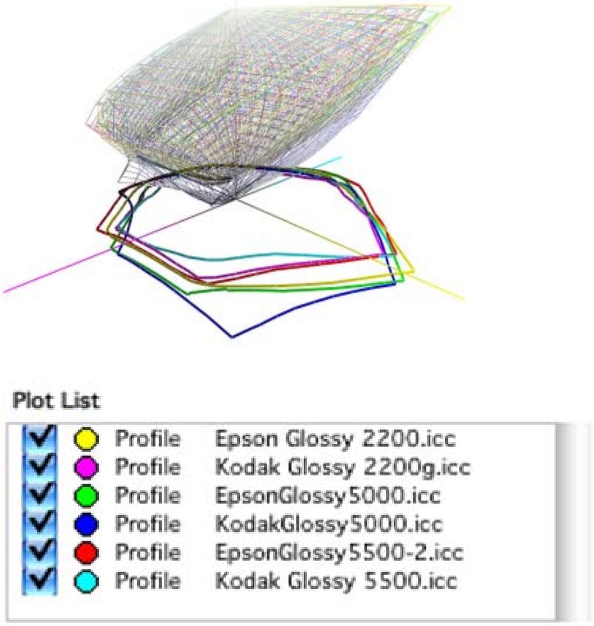

Figure 4

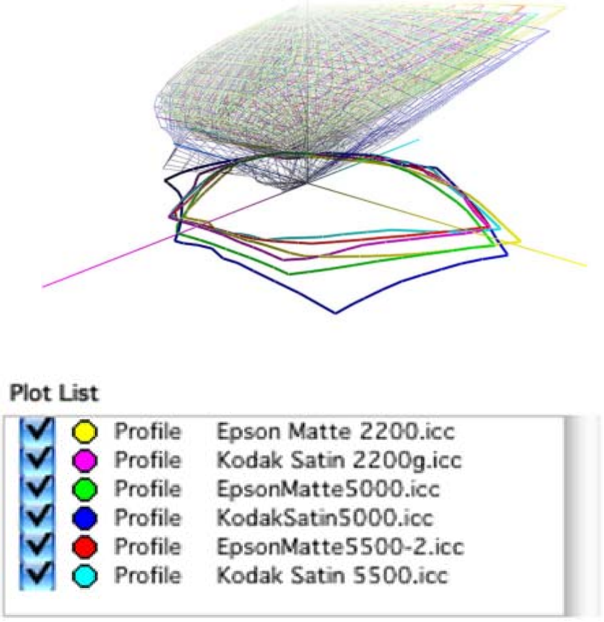

Fig. 3. Gamut plots of glossy substrates from all printers.

Fig. 4. Gamut plots of matte substrates from all printers.

Fading Tests

The patches of the ECI 2002 Random Layout CMYK Target were measured with the GretagMacbeth SpectroScanT before they were put into the fade meter. They were submitted to 129,600 kJ/m^2 of energy over 48 hours with the uncoated quartz glass filter configuration and measured again. This represents about 4.5 months (June) of daylight exposure in Florida (36 hrs @ 765 W/m^2)[12].

The $L^*a^*b^*$ values of the printed patches for all the printers on Archival Matte substrate 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 3).

Table 3. □E values before and after fading test for different printers and papers.

Printer	**Paper**	**Average □E**	**RMS □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[13,14]. Examination of the data shows that there is a systematic shift toward yellow and green. The Epson 2200 shows an average □b* of 1.57, while the Epson 5500 shows an average □b* of 1.89. Thus, for the pigmented inks, most of the average □E results from the systematic □b* shift, reflecting the drop in the OBA[15,16] contribution (see below). The Epson 5000 shows an average □b* of only .77, but the average □L* is 6.96. Therefore, that □E is mostly due to actual ink fading.

Again, the profile gamut plots for the papers are given in Figure 5. Figure 5 shows the gamut plots before and after the fading test.

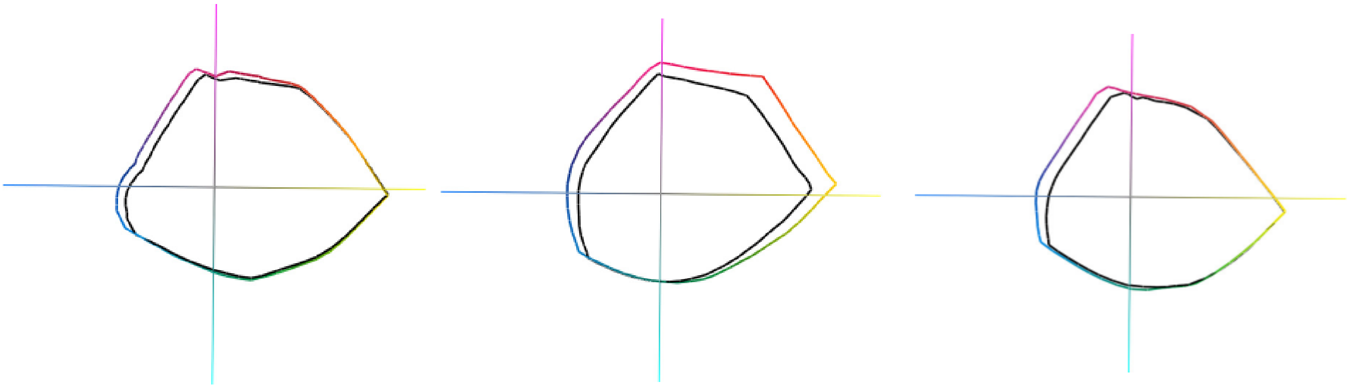

Fig. 5. Comparisons of projections of the color gamuts before (full color) and after (black) fading test for pigment-based Epson 2200 (left), dye-based Epson 5000 (middle) and pigment-based Epson 5500 (right).

Note that the Epson 5000 shows a significant decrease in color gamut because of the dye-based nature of the used inks. The printers with the pigmented inks, the Epson 2200 and 5000, show the aforementioned shift towards yellow, but little decrease in gamut.

The Epson Stylus Photo 2200 printer together with the Epson Archival Matte substrate provides best results for this part of the research. This set was chosen for further investigation of the fading properties. 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 bellow. In this case, the color shift is even more significant in the yellow region of the spectrum.

Fig. 6. Comparisons of color gamuts before and after fading test for Epson 2200 and Archival Matte substrate.

From the gathered information we decided to look at the changes in properties of the plain substrate. $L^*a^*b^*$ values of the substrates before and after the tests were taken. ☐E calculations for obtaining the range of color difference are shown in the Table 4.

Table 4. Average and RMS ☐E values before and after fading test for different printers and papers.

Substrate		**L***	**a***	**b***	**?E**
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	**Before**	95.9	0.8	-4.0	**4.91**
(long term test)	**After**	95.8	-0.6	0.7	

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 the Epson Archival Matte substrate, claiming the best archival properties, Epson Glossy substrate, Kodak Glossy substrate and for Kodak Satin substrate are shown in Figures 7 to 10.

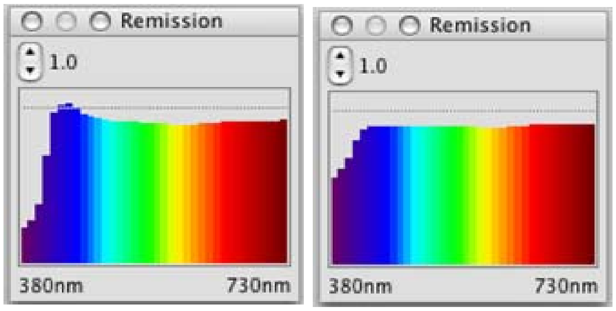

Figure 7. Reflection spectra of Epson Archival paper before (left) and after fading (right).

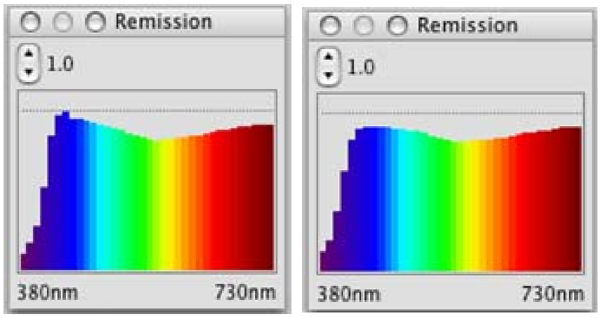

Figure 8. Reflection spectra of Kodak Satin Matte paper before (left) and after fading (right).

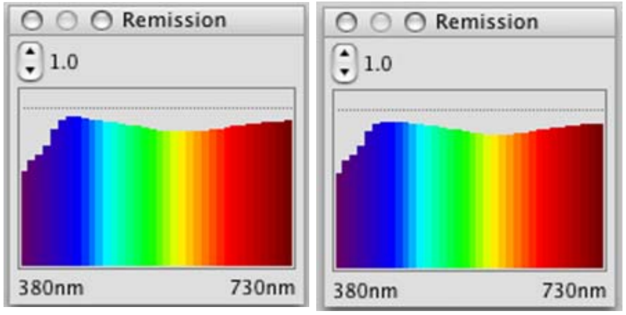

Figure 9. Reflection spectra of Epson Premium paper before (left) and after fading (right).

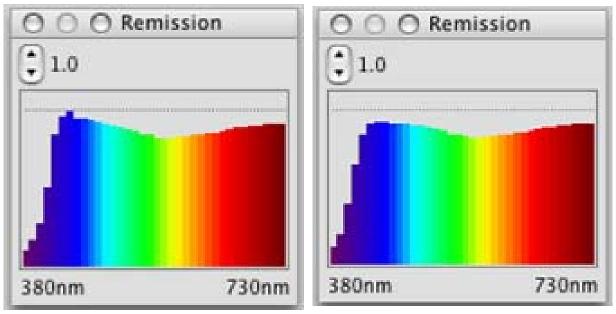

Figure 10. Reflection spectra of Kodak Glossy Glossy paper before (left) and after fading (right).

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 Satin papers. Optical Brightening Agents (OBA) are fluorescent materials that absorb in the ultraviolet and emit in the blue[15,16]. 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 4 that the majority of the OBA neutralization has occurred in the first simulated 4.5 month period, with little (barely significant) additional change in the remaining simulated 8.5 months.

Other Properties of Printer/ Substrate Combinations

Other properties of the Printer and substrate combinations are given in other research paper. In particular, the paper roughness by Parker Print Surf, profilometer and Atomic Force Microscopy [17,18,19].

Discussion

The procedures used with the densitometer and the measurements obtained by that method produced comparative values for the 20% dot area on all of the samples, and all measurements were of comparative values for all of the papers and inks. The matte samples from all printers did represent a lower density than those of the luster and glossy samples. The dot gain seemed relatively consistent for all colors on all samples.

The comparison of the difference in □E values for the original $L^*a^*b^*$ ColorChecker® target to those of the values calculated in Photoshop indicate small dissimilarities in almost all cases. The □E values for most of the patches on all substrates and from all printers were found to be generally less than two. Exceptions include the dark patches when printed on the matte papers and when printed from the Photo 2200 and PRO 5500 using pigment based inks. In the case of the pigment based ink printers (Epson 2200 and Epson 5500) the average and RMS □E were always higher for the matte substrates than for the luster, satin and glossy substrates. This is most likely due to out of gamut colors for the matte substrates.

The □E values for the comparison of the patches calculated in Photoshop to those measured with the SpectroScanT show similar values to the differences between the original values and the values from Photoshop in the case of the Epson papers. The only exception is the Epson Stylus PRO 5000 in combination with Kodak substrates.

Comparisons of the measured samples in most cases very closely approximate the values of the original ColorChecker® reference values, with the largest variances indicated on the glossy papers printed from the PRO 5000 and the matte from the PRO 5500. Matte paper printed from the PRO 5500 produced the largest variances of all the samples.

In comparing the profile gamuts it was noted in all cases that the matte paper profile represented the smallest gamut whereas the luster and glossy papers were generally similar and contained the complete matte gamut. Comparing the printers to each other on the same substrate the Photo 2200 generally included a similar size gamut to that of the PRO 5000 printer and dye based inks but the PRO 5500 represented the smallest color gamut. It could be seen that the Photo 2200 with its pigment-based inks is able to provide a color range that very closely matches that of the dye based prints from the PRO 5000.

The smaller gamut produced by the PRO 5500 printer may have something to do with the older technology and/or the advertised better archival properties of the ink set used by that printer. The fact that the pigment based inks used in the Photo 2200 printer closely match those of the dye based inks of the PRO 5000 is noteworthy, but it can be expected that the archival properties as advertised for this ink set may not be as good as those of the PRO 5500. It should also be noted that the increased archival properties of the matte paper in combination with archival pigment based inks produce the smallest color gamut of the samples analyzed.

Taking into the consideration the Kodak paper, there is no difference in gamut size between glossy and satin substrate. In addition, Epson vs. Kodak paper gamuts did not show any significant discrepancies in the terms of color gamut size. It is seen from Figurers 3 and 4 that the widest gamut was obtained when printed from the Epson Stylus PRO 5000 dye based inkjet printer followed by Epson Photo 2200 and Epson Stylus PRO 5500, both pigment based inkjet printers.

After the printouts were submitted to the fading test it could be seen that the gamuts decreased. The Epson 5000 showed a significant decrease, while the 2200 and 5500 showed small changes. In the case of the Epson Archival Matte and as well the Kodak Satin substrate, it was found that, even without any change in ink composition, the color performance will change because of the loss of brightener effect. This led to a systematic shift toward the yellow, especially when exposed to longer time tests, as shown in Figure 6. This deviation was not seen when inspecting the glossy substrates.

The particle size of the pigment based inks were found to be in the range <190 nm, most of them bellow 150 nm, showing smaller particle sizes for the PRO 2200 ink set than for the Photo 5500 ink set. The Particle Sizer's light detector was not able to distinguish any intensity in the case of the PRO 5000-ink set, which is consistent with the dye based ink system of the printer. The color gamut decreases with particle size, with the smallest particle size, the Epson 5000 dye, having the largest gamut, while the largest particle size, the Epson 5500, gives the smallest gamut. However, the dye based ink in the 5000 showed significant fading from only a simulated 4.5 month exposure.

Conclusion

Different inkjet printers and their corresponding ink sets were studied in terms of printability tests, ink/printer/substrate interactions, particle size analyses, color gamut comparisons, the accuracy of printer's color profile, and fading tests. It can be definitely said that the new technology of the manufacturing the inks with pigment particles encapsulated in specific resins is able to approach the properties of the dye based inks, especially in the term of gamut width. The particle size of the pigment in these inks is small enough to provide the color range that could match that of the dye based inks and also reach the gamut of digital silver halide photo on conventional photo paper[2]. Also, it has to be mentioned that the increased archival properties of the matte paper in combination with archival pigment based inks reflect in the smaller color gamut than the gamut of glossy paper. The pigment based inks show much better lightfastness than the dye-based inks, but for some substrates there is a drift towards the yellow as optical brighteners lose their effect.

For future work we suggest to investigate the substrates which do not include optical brighteners in their composition, e.g. art paper. Also, there is a newer dye based ink set becoming available, with enhanced archival properties. HP has created a new generation of inks to achieve over 100 year predicted indoor lightfastness performance, while simultaneously improving the color gamut over previous products.[20]

References

1. M. Usui, H. Hayashi, K. Hara, T. Kitahara, “The Development of Pigment Ink for Plain Paper”, *Proceedings of IS&T NIP18*, San Diego, California, 2002, pg. 369.
2. K. Takemoto, S. Kataoka, K. Kubota, “High-Gloss and Wide Color Gamut Pigmented Inks for Ink-Jet Printing”, *Proceedings of IS&T NIP19*, New Orleans, Louisiana, 2003, pg.237.
3. P. Rose, N. Walker, “The Influence of Pigment Selection on Particle Size and Migration Stability in Aqueous Inkjet Inks”, *Proceedings of IS&T NIP19*, New Orleans, Louisiana, 2003, pg.190.
4. G. Desie, O. Pascaul, T. Pataki, P. de Almeida, P. Mertens, S. Allaman, A. Soucemarianadin, “Imbibition of Dye and Pigment-based Aqueous Inks into Porous Substrates”, *Proceedings of IS&T NIP19*, New Orleans, Louisiana, 2003, pg. 209.
5. Commission Internationale de l’Eclairage (CIE) Proceedings 1931, Cambridge University Press, Cambridge, 1932. Commission Internationale de l’Eclairage (CIE) *Proceedings 1963* (Vienna Session), Vol. B., Committee report E-1.4.1, Bureau Central de la CIE, Paris, 1964.
6. CIE, “Colorimetry,” CIE Pub. no. 15.2, Centr. Bureau CIE, Vienna, Austria, 1986.
7. A. Sharma, *Understanding Color Management*, Delmar Thomson Publishing, Clinton Park NY, 2004.
8. Paul D. Fleming and Abhay Sharma, “Color Management and ICC Profiles; Can’t Live Without It So Learn To Live With It!”, *Gravure Magazine*, August 2002, p56.
9. O. Norberg, M. Anderson, “The Influence of Paper Properties on Color Reproduction and Color Management”, Proceedings of IS&T NIP19, New Orleans, Louisiana, 2003, pg. 836.
10. European Color Initiative, “Guidelines for device-independent color data processing in accordance with the ICC-Standard”, http://www.eci.org/eci/en/060_downloads.php.
11. *CIE, Recommendations on Uniform Color Spaces, Color-Difference Equations, Psychometric Color Terms, Supplement No. 2 of CIE Publ. No. 15* (E-1.3.1) 1971, (Bureau Ventral de la CIE, Paris 1978).
12. William R. Schaeffer, Catherine Leroy, Ming Fan, “UV-Curable Products with Superior Outdoor Durability”, http://www.sartomer.com/wpapers/5061.pdf.
13. Epson”Stylus Pro 5500", downloaded from: http://www.ldr.com/products_new/epson_styluspro5500.shtml.
14. Epson, “UltraChrome Ink”, downloaded from: http://www.epson.com.au/whats_new/story_148.asp.
15. Burak Aksoy, Margaret K. Joyce and Paul D. Fleming, “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, 2003).
16. Burak Aksoy, Paul D. Fleming and Margaret K. Joyce, “New Measures of Whiteness that Correlate with Perceived Color Appearance”, *Applied Optics*, in press.
17. Renmei Xu, Paul D. Fleming III and Alexandra Pekarovicova, “The Effect of Ink Jet Papers Roughness on Print Gloss and Ink Film Thickness” *Proceedings of the IS&T NIP20: International Conference on Digital Printing Technologies*, Salt Lake City, 2004, p439-444.
18. T555 om-99 *Roughness of Paper and Paperboard (Print-surf Method)*, TAPPI, (1999).
19. T. Enomae, P. Lepoutre, TAPPI J., Vol. 78, No. 10 173 (1995).
20. S. Jakobs, A. Duparre, M. Huter, H.K. Pulker, Thin Solid Films, 351, 141 (1999). Alexey Kabalnov, Charles Dupuy, Jay Gondek, Je-Ho Lee, Ranjit Bhaskar, and David Berfanger, “Gamut and Permanence of New-Generation Dye-Based Inks”, Proceedings of the IS&T NIP20: International Conference on Digital Printing Technologies, Salt Lake City, 2004