Gamut and Permanence of New-Generation Dye-Based Inks

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Abstract

Both dye and pigment-based inks have been used successfully to optimize the overall performance of ink-jet printers, the output of which is approaching and surpassing traditional silver halide photographs. The formulation of these inks strives to simultaneously address traditional image quality concerns like color vividness and grain, as well as such print characteristics as photo permanence, dark storage stability, and gloss uniformity. Addressing these multiple concerns often involves making a large number of trade-offs. For dye-based inks, improved color gamut has been traditionally compromised by decreased light-fade stability, because lightfast dyes tend to be less chromatic. In this paper, a discussion of a new generation of inks developed by Hewlett Packard is given.[1] By careful selection of dyes, the new HP ink set achieves >100 year predicted light fastness performance while simultaneously improving color gamut over previous products.

Introduction

Image quality, durability, and storage stability are three major attributes of ink-jet prints that attract the attention of customers and have driven a continuous improvement in ink-jet technology over the past twenty years.[2-5] Herein, we consider the term image quality to be broadly defined as how an image looks immediately after it has been printed, including aspects of color vividness and preference, color accuracy, dynamic range, grain, bronzing, gloss uniformity and illuminant sensitivity. By durability we refer to the print's ability to withstand short-term exposure to environmental stress, including the stability of a print to water dripping on the print and to finger smudge. Lastly, by storage stability or permanence we refer to the stability of a print during long-term exposure to environmental conditions, including storage both under display conditions and in the dark. Among the factors affecting storage stability are fade under action of light and atmospheric gases, as well as color changes caused by humidity. 'Dark fade', that is, the fade or staining of samples when stored in photo albums, also attracts considerable attention.[5]

Two major ink-jet ink technologies, dye-based and pigment-based, are being used to address these design concerns. As has been discussed recently, with the multiplicity of trade-offs involved, there exists currently no single ink-jet technology which delivers all the attributes in one package.[2-6] Pigmented inks tend to produce more permanent and durable images with the downside of somewhat reduced image quality on glossy media because of reduced gamut, lower gloss uniformity and the tendency of pigments to bronze. On the other hand, dye-based inks tend to produce superior image quality on glossy media with the trade-offs often being related to the reduced durability and permanence.

By careful selection and blending of dyes, HP has created a new generation of inks (referred to herein by their ink cartridge numbers HP 95, HP 97, HP 99 and HP 100)[1] to achieve >100 year predicted lightfastness performance, while simultaneously improving the color gamut over previous products. This paper deals primarily with HP's recent advances in these aspects of ink-jet ink formulation. Note that gas-fastness aspects are not discussed below because the HP swellable media technology is substantially free of gasfastness issues regardless of colorants used.[7]

Experimental Conditions

Data will be presented to benchmark the performance of the new HP ink set with respect to previous products. We briefly present the conditions under which these data were obtained**.**

Light fade experiments were conducted internally at Hewlett Packard and, in part, by Wilhelm Imaging Research, Iowa. The conditions of the light fade experiments are given in Table 1. In the internal HP studies, HPUV Indoor Actinic Exposure Systems (Atlas Material Testing Technology LLC) were used. Wilhelm's WIR v3.0 Endpoint Criteria set and assumptions for the daily light exposure were used in the analysis.[5, 8] In brief, the system failure is defined as the first failure among twelve failure criteria, measured as based on the light fade of the CMY colors in neutral patches and as primary colors at the optical densities of 0.6 and 1. The assumption of 1971 kLux-hours exposure per year was used.

Table 1. Lightfade Experimental Setup

Conditions	HP internal	Wilhelm Imaging Research
Temperature	28 ± 1° C	24° C
Relative Humidity	30 ± 2 %	60%
Light intensity/source	60 – 90 kLux, cool white light	35 kLux, cool white light
Air gap between the sample and the glass	No air gap; glass on top of the sample	5 mm
Sample dry-down before the test	2 weeks	2 weeks
Failure criteria	WIR v3.0 Endpoint Criteria set[8]	*Same*

Color gamut is presented in CIE 1976 L*a*b* color coordinates that were measured using a Gretag-MacBeth spectrophotometer assuming D50 illumination and a 2° standard observer. Unless otherwise noted, all the prints were generated on HP Premium Plus Photo Paper Glossy with HP Deskjet 6500 series printer in best mode.

Results and Discussion

Lightfastness-Vividness Trade-Off for Magenta Dyes

Historically, it has been the magenta dye that has presented the most challenge for the permanence of inkjet prints. Magenta dyes used in ink-jet come from many different classes.[9-11] The four main classes are (1) xanthene (rhodamine) dyes; (2) H-acids; (3) gamma-acids; and, (4) metal complexes of azo dyes.[12-16] It is interesting to note that choosing from these four classes of dyes represents a direct trade-off between lightfastness and color vividness, as is shown in Figure 1. It has been recognized that one solution to this problem is to utilize different dyes for the dark and light inks in 6-ink printing systems.[17] By doing so, one can substantially decouple lightfade stability and color gamut, that is, the permanence will be primarily carried by the dyes in the light inks, and the color gamut will be provided by the more chromatic but less permanent dyes in the dark inks. Obviously this decoupling of attributes is not an option for 3 ink systems.

Another approach that has been pursued for some time is to utilize dye blends.[18,19] Typically, one of the dyes in the blend delivers the color vividness, while another provides the lightfastness improvement. However, this path represents a trade-off and can deliver an exceptional result only when the dyes in the blend show beneficial chemical or photo-chemical interactions with each other. Although both increases and decreases in lightfastness have been observed for blends of dyes, compared to the dyes separately, little is known about the nature of the interaction. Some dyes show autocatalytic fade in the presence of the other dyes; for example, Archiva Magenta dye fades more quickly in presence of phthalocyanines, as reported by Schüttel and Hofmann.[20] On the other hand, it has been discovered that some xanthene dyes can become considerably more lightfast when blended with metal complex dyes.[21,22] Blends of xanthene and metal complex dyes are more lightfast than the similar blends of metal complex dyes with more light-stable H-acids. The xanthene – metal complex dye blends also are brighter, which obviously provides a much better balance between chroma and lightfastness.

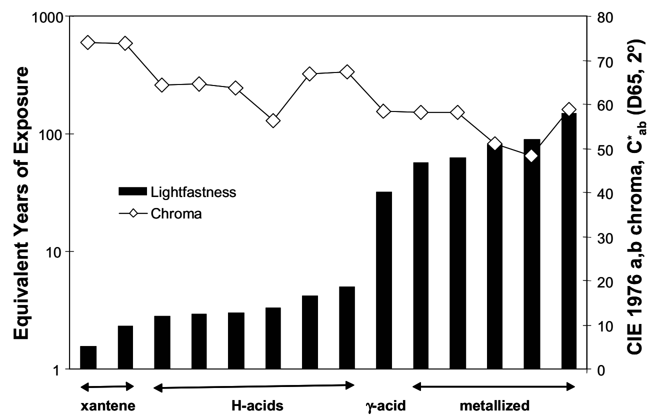

*Figure 1. Predicted lightfastness plotted in comparison to chroma (C*ab) for various magenta dyes on HP Premium Plus Photo Paper, Glossy. Predicted lightfastness is measured at optical density 0.5. No glass protection was used during accelerated fading.*

Figure 2 illustrates the stabilization of lightfastness in magenta dye blends which were made with four different bright magenta dyes paired with the same lightfast dye. Dyes 1 and 2 are xanthenes and Dyes 3 and 4 are H-acids.

The magenta dye blends were formulated based on the ratios of the peak absorbances of the dyes. The absorbances in the blend were 0.15 for the bright dye and 0.1 for the dye-stabilizer, at 1:10000 dilution. The lightfastness performance of magenta blends, and that of the individual dyes, was measured at an initial OD of 0.6, without glass protection. The xanthene Dye 1 is the least lightfast of four fugitive dyes; however it benefits the most from blending with the lightfast dye. On the other hand, despite the fact that the H-acid Dye 4 is the most lightfast of the four fugitive dyes, it benefits the least from the blend.

The exact mechanism of stabilization for xanthene dyes by metallized dyes remains unclear, but it is likely related to radiationless quenching of the excited state of the fugitive dye. The luminescence behavior of the xanthene dye supports that hypothesis. A very sharp transition in the light fade stability is seen above and below the lumen-escence threshold, indicating that quenching of the excited state is linked to the lightfade stability. The luminescence can be self-quenched by increasing the concentration of the dye, or by adding a second dye-quencher.

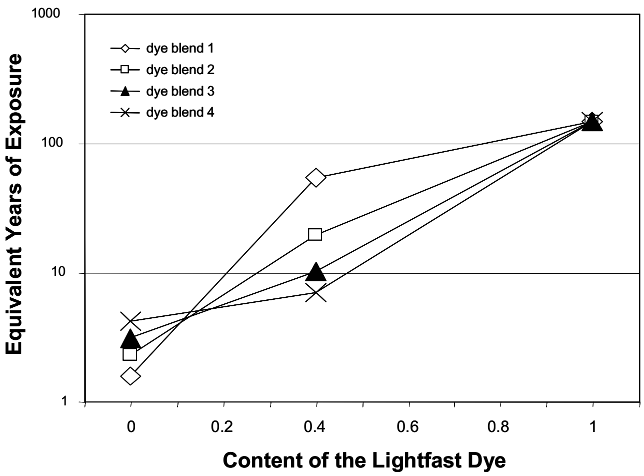

Figure 2. Lightfastness of pure non-blended dyes compared to the 3 : 2 blend by absorbance units at optical density 0.6 without the glass protection. The lightfast dye is the same for all the four blends. The stabilizing effect is observed for Blend 1, and to a lesser degree, for Blend 2. No stabilization is seen for Blends 3 and 4.

Color Space Optimization and Comparison with HP Deskjet 5550 Performance

Optimizing inks for a large, well-shaped printer gamut requires consideration of the effects of ink mixing. Simply optimizing for high chroma cyan, magenta and yellow inks does not necessarily give a large, usable color gamut. The job of each primary ink is to absorb approximately one third of the color spectrum, and pass the other two thirds.

Inks used in printing systems typically contain *unwanted absorption*, absorption of light in a region of the spectrum where complete transmission is expected. Unwanted absorption limits both the usable density of primary inks, and the chroma of both the primary and secondary colors. It is widely recognized that the chroma of primary colors in a printer gamut is important, however, when printing from additive digital sources (such as digital cameras and their associated additive RGB spaces), the chroma of secondary colors is actually of higher importance. This is because the colorspace of the source data does not contain high-chroma CMY colors, but will contain high-chroma RGB colors. Given that candidate inks for an individual primary of equal chroma may produce secondary colors of different chroma after mixing with other primaries, ink color optimization must also consider the chroma of secondary colors, as well as the fit to the gamut of source image data.

Improved optimization techniques were employed to help deliver the best size and shape for the color gamut of the new inkset. Figure 3 compares the a*b* projections of color space for the 3-ink and 6-ink outputs of the HP Deskjet 5550 printer using HP 57 and HP 58 ink cartridges with that of the new HP Deskjet 6500 using the HP 95 and HP 99 ink cartridges. Color gamut measurements are reported in Table 2 for both HP Printing (plain) Paper and HP Premium Plus Photo Paper Glossy. One can see that the new inkset delivers a significant extension of the gamut on both media.

Table 2 shows that the new inkset also delivers substantially improved lightfastness, in particular, when the 3-ink systems are compared to each other. Because the dark inks of the HP 95 ink cartridge are substantially more lightfast, the new 6-ink system in the HP Deskjet 6500 shows a more uniform fade across the color ramp, as compared to the inks used in the HP Deskjet 5550. Figure 4 shows the percent of retained optical density for magenta after 73 years of accelerated fade for the two 6-ink systems; note the differences at higher OD where the dark inks are used.

Table 2. Comparison of Gamut Volumes and Lightfastness Performances of HP Deskjet 5550 and HP Deskjet 6500 on HP Premium Plus Photo Paper Glossy

Printing system	Gamut volume, Lab units	Time to failure, years
HP Deskjet 5550, 3-ink, HP57 ink cartridge	597,550	15-18 [6, 24]
HP Deskjet 6500, 3-ink, HP 95 ink cartridge	623,000	82 [26]
HP Deskjet 5550, 6-ink, HP 57 & 58	624,410	73 [23, 24]
HP Deskjet 6500, 6-ink, HP 95 & 99	651,420	>100 [26]

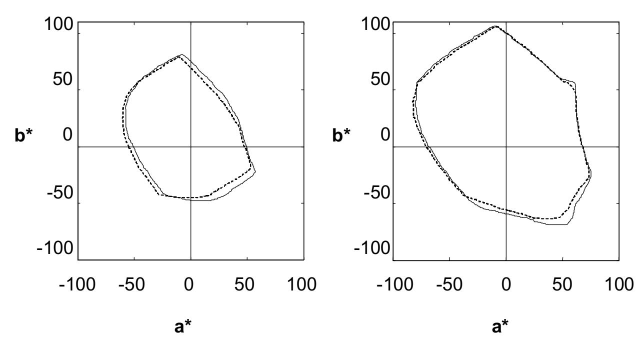

Figure 3. Comparison of the a b* projections of color spaces for new HP Deskjet 6500 (solid line) and HP Deskjet 5550 output (dashed line). Left: 3-ink outputs on HP Printing Paper (plain); Right: 6-ink outputs on HP Premium Plus Photo Paper Glossy.*

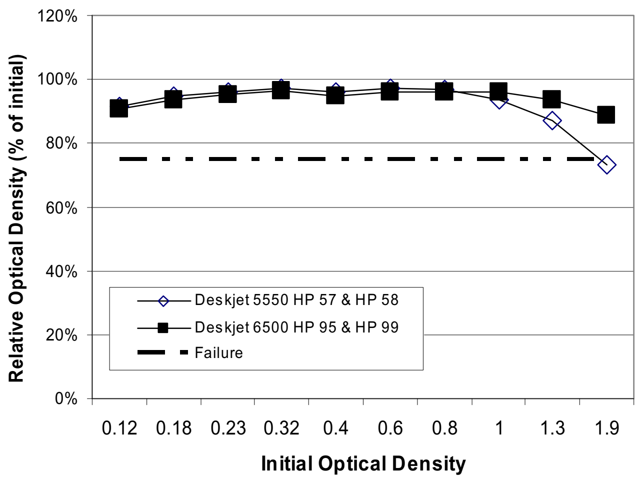

Figure 4. Fade of the magenta ink in two 6 ink systems over a range of initial optical densities: the HP Deskjet 5550 versus HP Deskjet 6500. The vertical axis shows the percent in optical density remaining after 73 years of accelerated fade when printed on HP Premium Plus Photo Paper Glossy.

Comparison with Other Ink-Jet Systems and Silver Halide Photographs

Table 3 compares the lightfastness performance of several ink-jet and silver halide systems. One can see that the performance of the new ink set substantially surpasses previous performance of Hewlett Packard products and matches/surpasses the performance of pigmented systems.

Figure 5 compares the color gamut obtained with the HP Deskjet 6500 using the HP 95 and HP 99 ink cartridges with that of traditional silver halide prints. It is worthwhile noting that the new HP inkjet system substantially surpasses traditional silver halide in both light fastness and color gamut.

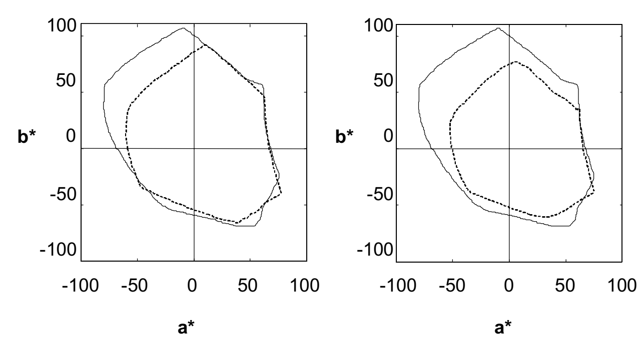

Figure 5. Comparison of the color gamuts of the HP Deskjet 6500 with the HP 95 and HP 99 pens (6 ink printing) on HP Premium Plus Photo Paper Glossy (solid lines) and the gamut of representative AgX systems (dashed lines): Kodak Duralife (left) and Fuji CrystalArchive (right) outputs

Table 3. Lightfade Comparison of Several Inkjet and Silver Halide Systems. All Data from Wilhelm Imaging Research , Inc.

Printing system and ink	Media	Lightfast-ness,years
Lexmark Z65 (dye)	Ilford Printasia Photo Glossy Paper	6 [23]
HP Photosmart 145; HP Deskjet 5550, 3-ink, HP 57 ink cartridge (dye)	HP Premium Plus Photo Paper Glossy	15-18 [6,24]
Epson 960 (dye)	Epson ColorLife SemiGloss	27 [23]
Canon S900 (dye)	Canon Photo Paper Pro	38 [23]
HP DeskJet 5550, 6 ink HP 57 & HP 58, (dye)	HP Premium Plus Photo Paper Glossy	73 [23, 24]
Epson Stylus Pro 4000 (pigment)	Epson Premium Glossy Photo Paper	85 [25]
Epson PictureMate Personal Photo Lab (pigment)	Epson PictureMate Glossy Photo Paper	104 [6]
HP Deskjet 6500, 3-ink, HP 95 ink cartridge (dye)	HP Premium Plus Photo Paper Glossy	82 [26]
HP Deskjet 6500, 6-ink, HP 95 & HP 99 (dye)	HP Premium Plus Photo Paper Glossy	> 100 [26]
HP Deskjet 8450, 8-ink, HP 95, HP 99 & HP 100 (dye)	HP Premium Plus Photo Paper Glossy	> 100 [26]
Kodak Ektacolor Edge Generations paper	n/a	19 [6, 27]
Fujicolor Crystal Archive Type One	n/a	40 [6, 27]

Conclusions

By careful selection and blending of dyes, HP has generated a new generation of inks which achieve >100 year predicted light fastness performance, while simultaneously improving in the color gamut over previous products. The new dye-based system provides light fastness performance compare-able to existing pigmented systems on the market, while being free of drawbacks often found in pigmented systems such as gloss non-uniformity and bronzing. The new HP ink set system also substantially surpasses traditional silver halide in both light fastness and color gamut.

References

1. For simplicity and consistency in this document, the new ink set will be referred to using the North American ink cartridge number designators. Specifically, the dark dye load inks, found in the tri-color (CYM) ink cartridge, are referred to as the HP 95 ink cartridge. The HP 97 ink cartridge contains the same ink as the HP 95 ink cartridge. The light cyan, light magenta and black inks found in the photo ink cartridge are referred to as the HP 99 ink cartridge. The light gray, dark gray and black inks found in the gray photo ink cartridge are referred to as the HP 100 ink cartridge. Different ink cartridge number designators may be found in other regions of the globe.
2. Miller, N. HP Ink-Jet Photo Prints: Memories for Generations. Hewlett Packard Company Web Site, http://www.hp.com/sbso/product/supplies/img/lightfastness.pdf 2002.
3. Miller, N.; Rolly, L. HP Ink-Jet Technology : Designing Inks for Photo Printing, Hewlett Packard Company Web Site, http://www.hp.com/hpinfo/newsroom/press_kits/2004/pma/fs_ink_tech.pdf 2003.
4. Epson Answers: Ink-Jet Printers: http://www.knoware. epson. com/pages/EpAns.htm; Seiko Epson Corporation, 2001-2002.
5. Wilhelm, H. The Permanence and Care of Color Photographs: Traditional and Digital Color Prints, Color Negatives, Slides, and Motion Pictures; Preservation Publishing Company: Grinnell, Iowa, 1993.
6. Wilhelm, H, Proc. Ann. Conf. Imaging Soc. of Japan, Japan Hardcopy 2004, Tokyo, Japan, 2004, 81-84.
7. Thornberry, M.; Looman, S. Proc. IS&T's NIP 19 2003, 426-430.
8. Wilhelm, H. Final Program and Advance Printing of Paper Summaries, IS&T's 12th International Symposium on Photofinishing Technology, 32-37, Orlando, Florida, 2002; Wilhelm, H. Proc. IS&T's NIP 19 2003, 444-449.
9. Gregory, P.; Gordon, P. F. Organic Chemistry in Color; Springer-Verlag, Ed.: Berlin, 1983.
10. Gregory, P. Surface Coatings International, Part B: Coatings Transactions 2002, 85(B1), 9-17.
11. Bauer, W.; Baumgart, D.; Zoller, W. American Ink Maker 1998, 76(10), 53-59.
12. Byers, G. W. Magenta dyes for ink-jet inks; USA Patent # 5980622, 1999.
13. Evans, S.; Weber, H. Metal complex for ink jet ink; USA Patent #6001161, 1999.
14. Yamada, M.; Yoneyama, T.; Chino, T. Metal-chelated dyestuff for inkjet recording and aqueous inkjet recording liquid using the same, USA Patent Application #20030088077, 2002.
15. Gregory, P. In: Comprehensive Coordination Chemistry II, J. A. McCleverly, T. J. Meyer, M. D. Ward, Eds. Elsevier-Pergamon, Amsterdam, Vol. 9, (2004), 549-579.
16. Stoffel, J. L.; Morris, P. C. Use of hydrolyzed Reactive Red 23; USA Patent #6458195, 2002.
17. Burch, E.; Kabalnov, A.; Miller, N.; Dupuy, C.; Niu, B.-J.; Wang, P.; Guo, S.; Tyrell, P.; Deardurff, L. Proc. IS&T's NIP 18 2002, 342-347.
18. Deardurff, L. A.; Austin, M. E.; Lauw, H. P. Ink-jet inks for improved image quality, USA Patent #5788754, 1998.
19. Johnson, L.; Lauw, H. P.; Pawlowski, N. E.; Shields, J. P.; Skene, J. M. Thermal ink-jet inks having reduced black to color and color to color bleed, USA Patent 5536306, 1996.
20. S. Scühttel and R. Hofmann, Proc. IS&T's NIP15 1999, 120-123.
21. Wang, P.; Kabalnov, A. Patent Pending.
22. Kabalnov, A.; Dupuy, C. Patent pending.
23. LaGesse, D. Are Photos Finished?, US News and World Report, 2003; Vol. 134, pp 66-70, 72-74.
24. Wilhelm Imaging Research; Hewlett-Packard Deskjet 5550 – Print Permanence Ratings, http://www.wilhelm-research.com/WIR_HP5000_2003_07_31.pdf, 2004.
25. Wilhelm Imaging Research; Epson Stylus Pro 4000 – Print Permanence Ratings, http://www.wilhelm-research.com/WIR_Ep4000_2004_05_01.pdf, 2004.
26. Wilhelm Imaging Research, ongoing experiments.
27. The numbers as reported in Ref. 6 are somewhat reduced compared to the previously reported [5, 23] (22 years for Kodak Ektacolor Edge 8 and 60 years for Fujicolor Crystal Archive) as based on the newer experimental data generated with WIR v3.0 Endpoint Criteria set [8] (H. Wilhelm, personal communication).

Biography

Alexey Kabalnov holds a PhD degree in chemistry from Moscow State University, Russia with the specialization in colloids and surface chemistry. Since 1998, he has been working for Hewlett Packard Company in Corvallis, Oregon primarily on the formulation of color inks. He authors about 50 scientific publications and patents. He is a member of the American Chemical Society and serves on Advisory Boards of Langmuir (American Chemical Society Journal for Colloids and Surfaces) and Journal of Dispersion Science and Technology.