Dye and Pigment Ink Jet Image Stability and Permanence

Ray A. Work, III, Work Associates, Inc. Hockessin, Delaware and Russell T. Brown, DuPont Imaging Technologies, Wilmington, Delaware

Abstract

As ink jet ink and media technologies continue to evolve the issues of image stability in the short term and image permanence in the long term become more complex. With the widening availability and variety of pigmented and dye based ink jet inks and new media incorporating micro or nano porous ink jet coatings, new performance trade offs are being experienced by customers who buy and use these products. This paper will explore some of these trade offs, the reasons for some of these differences, their importance in end use applications and the potential for overcoming the resulting deficiencies with continued product development.

Introduction

Probably the most demanding application of ink jet printing is pre-press proofing. The term “proofing” has come to mean different things to different people. In commercial printing in the pre-press workflow the term “proofing” is used for everything from checking the results of work during the design process to “imposition proofing”, checking the layout of images and text as it will appear on a press sheet, to a “contract proof” used by the printing customer and commercial printer as the basis for the their business contract, what you see is what you will pay for.

In all cases it is important that the “proof” correctly represent the digital image so that the hard copy produced can be used with confidence as a communication tool. For a print to achieve this goal it must be predictable and stable in the characteristics important in that application. In the most color critical application, the “contract proof”, this is particularly important.

We have conducted a number of studies on commercial proofing products to characterize the stability of the color they achieve in order to determine to what extent they may meet these critical color needs. These findings and some tests to try to understand the causes of the observed changes provide some insight into the whole problem of color control and color stability of digitally produced images. We believe this information will help all who are trying to achieve good ink jet images, i.e. images that correctly represent the color the creator of the image intended both at the time of printing and at the time it is used.

Color Stability Test

Test Target - We have developed over many years of evaluating systems for color stability a 288-color target (Figure 1).

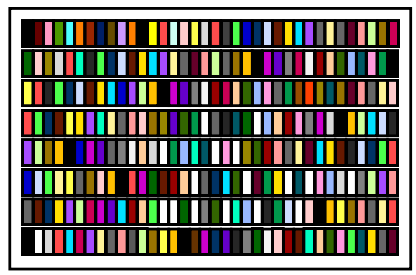

Figure 1

The colors on the target represent L*a*b* values near each axis, well within the normal printable gamut of an ink jet printer and outside the normal printable ink jet primary colors. The choice of colors is made to insure that many permutations of black, cyan, dilute cyan, magenta, light magenta and yellow are included on the target at various mixture ratios where a six ink set is used.

Test Setup – The physical set-up of the room and samples are as illustrated below (Figure 2).

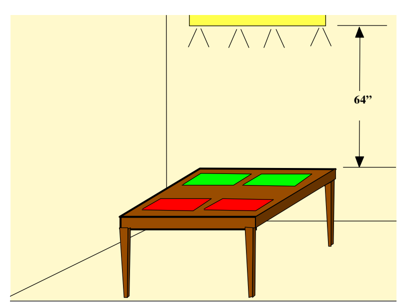

Figure 2

Exposure conditions are on a table exposed by with D50 lights with 525+ 75 LUX illumination (office-like conditions). Samples were illuminated 24 hours/day, 7 days/week with temperature 70deg F and 40% Relative Humidity. A number of samples were tested for up to 28 days. This is the normal maximum useful life of a “proof”.

Results of Daylight Tests – The tests were run on three systems:

1. A commercial drop on demand ink jet printer using dye ink and micro porous media,
2. A commercial continuous flow ink jet printer using dye ink and polymeric swellable media,
3. An analog proofing system using pigments

Figure 3 shows the average delta E for each system compared to one hour after printing.

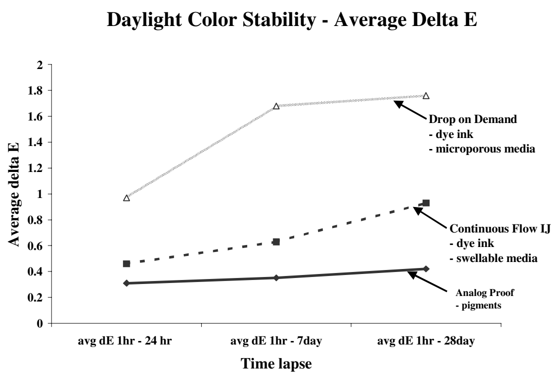

Figure 3

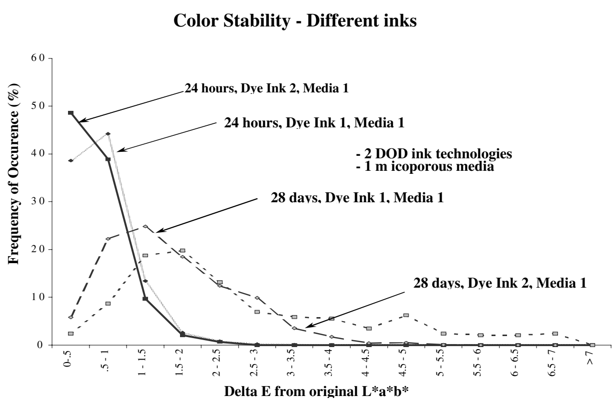

Figure 4

The goal for proofing is no measurable change. We have found however that a delta E of 1.5 or less for the 28 day period is acceptable to most proofing customers. The averages for #1 exceeds that target change by a small amount while #2 and #3 are within that range for the full 28 days. Taking the averages can be misleading however. If we look at each of the 288 color squares the numbers of color squares that change more than 1.5 delta E units we get a very different picture.

Figure 4 shows a plot of the number of colors within the 288 colors tested which display a delta E shift in the ranges shown on the x-axis.

Note that all of the analog proof color squares remained at delta E of 1.5 or less and the continuous flow ink jet was only slightly poorer. The drop on demand ink jet had more than half of the colors greater than 1.5 delta E with a number of the squares showing delta E values of up to 4! This is seriously objectionable in proofing applications.

This information is interesting but is it the ink the media or the printer that causes the drop on demand system to perform so poorly. Figure 5 shows a comparison of two completely different drop on demand printing technologies with the commercial dye based inks supplied for them by the printer manufacturers at one day and 28 days.

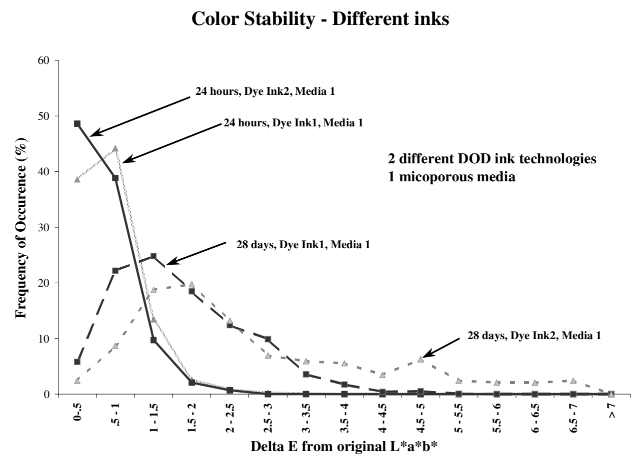

Figure 5

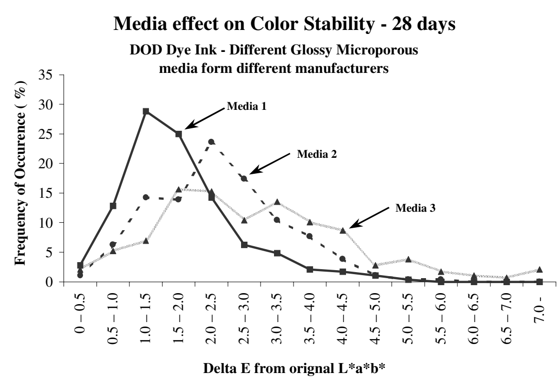

Figure 6

In this case the two different printers were used to print the 288 color squares on the same commercial micro porous media. At 24 hours they appeared to behave well and about the same as one another. At 28 days not only did both show poor stability but also the new dye ink/printer system showed delta E values up to 7! By anyone’s analysis this is very poor stability and would result in complaints from customers using these systems for much less demanding applications than proofing. So we see differences in the ink/printing technology systems what about the media.

Figure 6 shows the performance of one of the drop on demand printers with dye inks on three different micro porous glossy media.

In 28 days they all showed poor performance but all three were significantly different in their color shifts. Imagine an end user developing a set of ICC profiles for his new printer/ink/media combination at 24 hr. after printing and then try to match a print one month later. The end user might blame the printer manufacture or the ink manufacturer or the media manufacturer for changing their products and causing his colors to shift while it was really an unstable ink/media system.

Dark fade – So what is causing the problem of instability? We see changes between drop on demand printer/ink systems and types of glossy micro porous media with constant printer/ink type. We need to do more work to determine what may be causing the differences. Figure 7 shows some dark fading results of a test between our initial three test materials, drop on demand ink jet with dye ink on micro porous media, continuous flow ink jet with dye ink on swellable media and analog pigment.

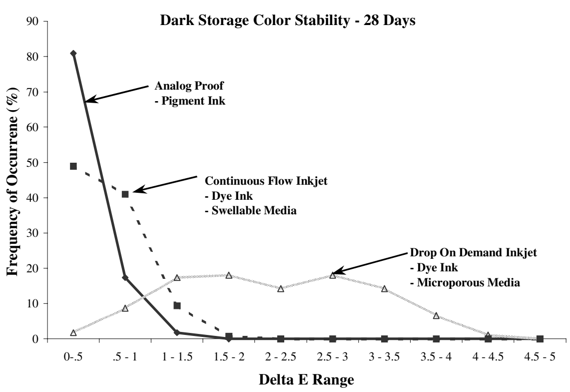

Figure 7

Here we see serious changes in the dark fade results with the drop on demand ink on micro porous media. This suggests a chemical and not light induced color change mechanism. Oxidation from air, ozone, nitrogen oxides, sulfur oxides and the like can cause the bleaching of dyes and that is what is probably happening here. In other studies (1) it has been shown that the cyan dye in many ink jet inks is particularly susceptible to decolorization by air, particularly polluted air. In addition but to a lesser extent many magenta dyes show a tendency to decolorize as well but they do so at a slower rate. The yellow dyes commonly used in ink jet inks appear not to be affected as easily. So while most of the end user's attention has been directed at light stability much of the damage to the color in dye based ink jet prints has been caused by air. But wait! What about the dye inks in the continuous flow ink jet? They did not show nearly as much fading! Why not? Are they somehow different? Yes, the coatings are different in their composition and ink absorption. The main contribution to the increased stability is not the dyes or the ink formulations but the polymeric, swellable media. It is theorized that upon drying the polymer coating seals the surface of the media protecting the dyes that are now inside the coating from the effects of the air. The same result is reported (2) when micro porous media is either mounted under glass or otherwise protected from air. In either case, the air contribution to fading is slowed.

Conclusions

So what does this mean in the practical world beyond proofing? It means that if you have an unstable system you cannot control color! To achieve good color when a color ink jet print is viewed, shortly after printing or much later the color must be stable. Not only stable in the long term but also in the short term or color calibration efforts will be futile. How do you calibrate a moving target? You cannot. So the lessons to be learned from this work are:

1. Primary and secondary colors alone are insufficient in a test target to characterize color changes.
2. Measurement of average color shift of 288 colors is not sufficient to characterize objectionable color shifts
3. Commercial dye inks on several commercial glossy micro porous media do not provide good stability.
4. Light fastness alone is not the only and sometimes not the greatest concern to those making color stable ink jet prints.
5. A careful choice of materials with good testing is required to control color in ink jet prints.
6. Pigments can offer added short term and long-term stability to ink jet prints.[3]

The Future

As we look forward to the development of better inks and media that will allow us to achieve better images we can be optimistic. Once identified, ink and media developers attack problems and make improvements. Just a few short years ago all dye based ink jet inks lacked even short-term light fastness. In some cases magenta dyes lasted only a few hours when exposed to sunlight. Dramatic improvements have been made so that some ink and media systems can provide light fastness equal to silver halide photographic prints. Once the problem was identified, the chemical reaction of air with dyes on microporous media became a priority among media developers and improved products are already beginning to show up on the market. With continued stability improvements, microporous media will give the performance advantages of shorter dry times and excellent color quality without unacceptable color stability.

Pigments offer even more stability in both light fastness and resistance to degradation by air. Pigment ink developers continue to design better ink jet inks with increased color gamut without sacrificing their superior light fastness. Media developers are now designing media coatings for pigments. Consequently we are now seeing a rapid closing of the gap in color and image performance between pigments and dyes. These improvements will carry ink jet to new heights of performance well beyond silver halide in color and stability.

References

1. Private communication Rochester Institute of Technology Research Corporation (RITRC)
2. Results of Henry Wilhelm tests (www.wilhelm-research.com) and subsequent tests at RITRC
3. Ray A. Work, III "Color Pigmented Ink Jet Inks: New Developments and New Applications" *IS&T NIP 15 International Conference on Digital Printing Technologies*, Orlando, FL October 1999, p. 149-150.

Biographies

Dr. Ray A. Work, III has recently retired from DuPont Imaging Technologies and was New Business Development Manager in DuPont Color Proofing. He holds BS and PhD degrees in Chemistry and has held a variety of positions in DuPont in research, management and business for over the past 28 years. He holds 7 US Patents and has over 20 publications. Dr. Work is a frequent speaker at conferences and symposia world wide on the subject of ink jet inks and ink jet printing. He has formed a consulting business, Work Associates, Inc. (see http\\:www.workassoc.com)

Russell T. Brown is responsible for ink jet media development and qualification for DuPont Color Proofing. He holds a BS degree in Mechanical Engineering and has held various positions in manufacturing, marketing, research, and supply chain in his more than 12 years with DuPont. For the past 7 years he has focused on developing digital proofing solutions for DuPont utilizing dye sublimation, continuous flow ink jet and drop on demand ink jet technologies.