

Particle Size Effects in Pigmented Inkjet Inks

D. E. Bugner and A. D. Bermel
Eastman Kodak Company, Rochester, NY

Abstract

Eastman Kodak has recently announced breakthrough nanoparticulate ink technology which offers the best of both dye-based and pigment-based inks. These ultrafine pigmented inks exhibit average particle sizes an order of magnitude smaller than other commercially available pigmented inkjet inks. In this paper, we will discuss the effects of colorant particle size on reliability, image quality, and durability in an inkjet printing system. Comparisons will also be made to conventional dye-based inks.

Introduction

Until this year, those involved in the business of producing large format inkjet prints have had to choose between two different types of ink sets depending on requirements of the intended application. For the highest image quality applications, dye-based inks have been preferred, but for signage applications where durability, especially lightfastness, is required, pigmented inks have become a very popular option. In addition to image quality limitations such as inferior color gamut and differential gloss, pigmented inks have also exhibited poorer reliability than dye-base inks, presumably due to some form of dispersion instability leading to channel or nozzle clogging.

With the launch of the new Kodak Professional 2000 series Large-Format Inkjet system, there is no longer a need to choose between dyes and pigments. This value proposition is made possible by a breakthrough in pigmented ink technology which yields pigment particle sizes which are approximately one-tenth the size of other manufacturers' pigmented inks. The smaller pigment particles result in more stable dispersions and more reliable jettability of the printhead. Other direct benefits are higher optical densities, greater transparency, more uniform gloss, and a larger color gamut, especially when printed on the matched, glossy, resin-coated photo paper. With the ability to produce pigment dispersions with average particle sizes well under 50 nm, we have undertaken a detailed study of the effect of pigment particle size on various ink properties and printing performance attributes. In this first report on pigment particle size effects, we will discuss the effects of the particle size of a cyan pigmented ink on dispersion stability, optical density, color gamut, gloss, and lightfastness.

Materials and Methods

Materials

The cyan pigment used for this study is a proprietary siloxane-bridged aluminum phthalocyanine obtained from the Synthetic Chemicals Division of Eastman Kodak.[1] Sodium N-methyl-N-oleyl taurate (OMT) was obtained from Rhone-Poulenc and was purified by the Synthetic Chemicals Division of Eastman Kodak. Diethylene glycol (DEG) and glycerol were obtained from Acros and Aldrich, respectively.

Methods

A mixture of pigment (21 wt%), OMT (13 wt%) and de-ionized water (balance) were milled using a variation of the process described by Czekai. et al.[2] Particle size was monitored as a function of milling time, and two cuts were chosen with differing particle size distributions. The smaller cut will be referred to as "small cyan", and the larger cut will be referred to as "big cyan".

Inks were prepared from the different particle size fractions by adding the pigment concentrate with stirring to a mixture of de-ionized water, DEG, and glycerol. The final inks contain 2.25 wt% pigment, 1.35 wt% OMT, 7.95 wt% DEG, 12.05 wt% glycerol, and the balance de-ionized water.

Particle size distributions (PSDs) were measured on a Leeds and Northrup Microtrac-UPA 150 Ultrafine Particle Size Analyzer. Freeze/thaw cycling was carried out by holding the inks for 24 hr at -20°C followed by 24 hr at 60°C (one cycle). Samples were examined for sediment and then shaken prior to sampling for PSD measurements. Shelf-life was evaluated by incubating samples of inks at several temperatures and evaluating for sediment, filterability, and PSD as a function of time.

For image quality and lightfastness evaluations, the inks were loaded into a Hewlett-Packard model 51626A printhead and printed onto Kodak Type LF MW8 glossy, resin-coated photo paper. Optical density and color gamut were determined by previously disclosed methods.[3] For the color gamut calculations, a standard reference set of pigmented magenta, yellow, and black inks with similar formulations were used in combination with the two cyan inks prepared for this study. Gloss was measured on a BYK Gardner microgloss meter according to ASTM D523. Lightfastness was evaluated by exposing targets comprising several printed densities ranging from D_{min} to D_{max} with a 50 Klux Xenon source filtered with window glass.[4] Optical densities were measured before and after differing lengths of exposure, and lightfastness is expressed as the percent retained optical density, corrected for D_{min}.

Results and Discussion

Results

The particle size distributions for the two inks are given in Table 1, along with several commercially available cyan pigmented inks. It should be noted that the commercially available cyan inks all appear to contain copper phthalocyanine as the cyan pigment. In the table, the columns labeled D_n represent the size of the particles at the *n*th percentile of the distribution. Thus, the column labeled D_{50} is typically referred to as the average or mean particle size of the distribution, and D_{100} is the size of the largest particles in the distribution. Figure 1 shows the effect of freeze/thaw cycling on the average (D_{50}) particle size of the two inks, while Figure 2 shows the effect of time at 60°C on the same inks. No sediment was noted for these samples throughout these tests.

Figure 2 compares the reflection spectra of the two inks, and Table 2 summarizes the effect of particle size on optical density, color gamut, and gloss.

Discussion

Historically, the inks developed for the first commercially successful thermal drop-on-demand inkjet printers employed off-the-shelf dyes as colorants. Dyes are colorants which are soluble in the solvent(s) or vehicle used to make the ink. Each molecule of the dye is surrounded by the solvent(s) and is separated from other dye molecules. For applications requiring weatherability, especially lightfastness, pigmented inks have become increasingly popular. In contrast to dyes, pigments are colorants which are essentially insoluble in the ink solvent(s).

Pigmented inks are normally prepared in a two-step process. In the first step, a mixture of pigment and water is milled or otherwise mechanically sheared in the presence of a dispersant or stabilizer. During this step, the clumps of as-received pigment particles are broken down into their primary particles. The primary particles become coated with the dispersant molecules and are thereby stabilized against re-aggregation and/or settling. The pigment concentrate thus produced is then diluted in a second step to a working strength ink by addition of co-solvents, called humectants, and other addenda, such as surfactants or biocides. Commercially available pigmented inks produced by this method generally result in average particle sizes in the range of 100-200 nm, with particle size distributions often extending to greater than 400 nm.

By using a new type of milling process, we have been able to produce inks with much finer particles.[2] Comparisons of inks produced by this process with commercially available pigmented inks have revealed several noticeable advantages to the smaller particle size distributions. However, there are many other differences, such as pigment, dispersant, and humectant, such that it is difficult to isolate specific particle size effects on the various performance attributes. By preparing two inks with virtually identical chemical compositions, differing only in their particle size distributions, we hope to be able to better understand which attributes are strongly affected by pigment particle size. As a starting point we chose cyan ink for this study. Future studies will focus on the other colors, and possible intercolor particle size effects.

Our goal was to prepare one cyan ink with a PSD comparable to that being offered with the Kodak Professional 2000 series printers (small cyan), and one ink with D_{50} approximately ten times larger (big cyan), simulating a commercially available pigmented ink. Table 1 indicates that we achieved that goal.

Table. 1. Particle size distributions for the cyan inks of this study along with several commercially available pigmented cyan inks.

Ink	D_{10} (nm)	D_{50} (nm)	**D_{95} (nm)**	**D_{100} (nm)**
Small Cyan	13	16	**89**	**204**
Big Cyan	49	122	**267**	**486**
Commercial A	54	108	**356**	**688**
Commercial B	57	98	**178**	**344**
Commercial C	86	145	**223**	**289**

The first requirement of a pigmented ink is that the pigment dispersion is stable over a reasonable range of temperatures and times. Two types of studies were carried out to evaluate dispersion stability: freeze/thaw cycling and Arrhenius testing.[5] Freeze/thaw cycling, as defined above, is essentially a “shipping and handling” simulation. Figure 1 shows the effect of freeze/thaw cycling on D_{50}. The plot indicates that for this particular ink composition, both particle size inks appear to be stable to freeze/thaw perturbations. Examination of the rest of the PSD for these inks indicates no clear effect of particle size on freeze/thaw stability. Finally, the optical density of a D_{max} patch printed with each ink before and after freeze/thaw cycling exhibited essentially no change in optical density as a result of the treatment.

Arrhenius testing is a tool for estimating shelf-life for formulations that are sensitive to time and temperature. The basic concept is to measure the rate of a given phenomenon, in this case particle size growth, at three or more temperatures. For well-behaved systems with a single mechanism of degradation, these data can be used to calculate an energy of activation for the process, which in turn allows one to calculate the time, or shelf-life, at any temperature within the range tested, that the dispersion will remain stable. For the two cyan inks studied, there does not appear to be any significant particle growth over reasonable times at temperatures up to 80°C. Figure 2 shows the 60°C data. Thus, as was the case with freeze/thaw cycling, there does not appear to be an effect of particle size on shelf-life for these inks.

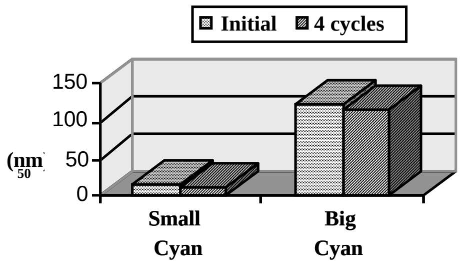

Figure 1. The effect of 4 freeze/thaw cycles on the cyan inks of this study.

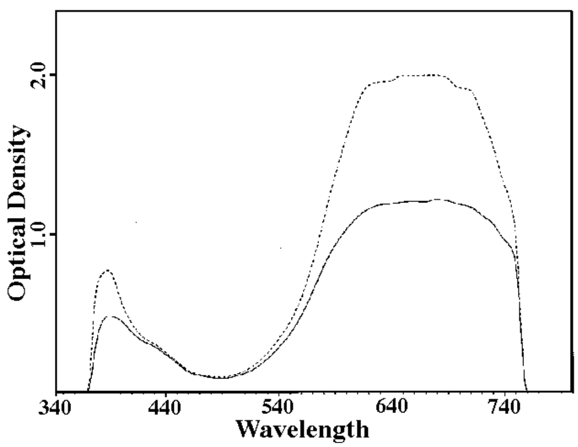

Figure 2. A comparison of the reflection spectra for the small cyan (dashed line) and the big cyan (solid line) pigmented inks.

The image quality attributes that we evaluated with respect to particle size included optical density, color gamut, and gloss. Figure 2 indicates that the primary effect of particle size, all else being kept equal, is a greatly diminished optical density for the big cyan ink, nearly one-half of the small cyan ink. In turn, this has an adverse impact on color gamut (Table 2). In theory, one could increase the pigment concentration to increase optical density, but it is unclear at this point whether (a) one can reach the same optical density with a higher concentration of the larger pigment dispersion, or (b) even if one could, would the absorption curve be adversely broadened, or (c) what other rebalancing of the formulation would be required because of the higher pigment concentration and what impact would this have on all of the other relevant ink and system level attributes. These questions are currently under evaluation.

Interestingly, the big cyan exhibits a slightly higher gloss value than the small cyan ink at an angle of 60°. This observation was also confirmed at 20° and 85° viewing angles as well. We expected to see just the opposite.[6]

Table. 2. A comparison of optical density, color gamut, and gloss for the cyan inks of this study.

Ink	Optical Density	**Color Gamut**	60° **Gloss**
Small Cyan	2.08	**70,380**	**65**
Big Cyan	1.23	**58,577**	**72**

In the area of durability, we were interested in verifying claims[7] that very small particle size pigmented inks would exhibit poorer lightfastness. At the present time, we have treated step wedges of each ink to 8 weeks of high intensity exposure as described above. Thus far, neither the big nor the small cyan ink has faded significantly. Treatment is ongoing.

In summary, we have initiated a study of particle size effects in pigmented inkjet inks. In this report, two cyan pigmented inks with significantly different particle size distributions were prepared and evaluated in the areas of reliability, image quality, and durability. The following effects of particle size were noted:

- neither ink exhibited particle size growth when subjected to either freeze/thaw cycling or incubation for extended periods at 60°C;
- the small cyan ink displayed a significantly higher optical density and color gamut than the big cyan ink, while the big cyan ink gives slightly higher gloss values; and
- after 8 weeks of high intensity exposure, neither ink has faded significantly.

We are also currently evaluating particle size effects for magenta and yellow pigmented inks. Thus far, the results for magenta and yellow are consistent with those described above for cyan. We will communicate the results of these studies at a future date.

Acknowledgments

The authors would like to acknowledge the following colleagues for their assistance in this study: D. Oldfield, T. Rosa, J. Santiago, L. Seaman, and P. Minchak. The authors would also like to thank the Professional Imaging Division of Eastman Kodak for funding this work.

References

1. M. T. Regan, *U.S. Patent 4,311,775* (1982).
2. D. Czekai, et al., *U.S. Patent 5,478,705* (1995).
3. D. Santilli, D. E. Bugner, A. D. Bermel, and D. J. Oldfield, *U.S. Patent Pending.*
4. ANSI/NAPM Standard IT9.9 (1996).
5. S. Arrhenius, *Z. Phys. Chem.*, **4**, 226 (1889).
6. F. Pesenti, J. C. Hassler, and P. Pepoutre, *IS&T's NIP12: International Conference on Digital Printing Technologies,* New Orleans, 1996, pp. 405-408.
7. R. A. Work III, *5th Annual Ink Jet Printing Workshop,* Information Management Institute, March 27-29, 1996.