Particle Size Effects in Pigmented Ink Jet Inks

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

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Introduction

Until recently, those involved in the business of producing large format ink jet 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 caused by large pigment particles or agglomerates clogging the channels and/or nozzles of the ink jet heads.

With the launch of the new Kodak Professional Large Format 2000 series printer, 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 that are approximately one-tenth the size of other manufacturers' pigmented inks. In theory, inks containing these pigment particles with average particle sizes of 50 nm or less, should show improved image quality and improved printhead reliability (i.e., less nozzle clogging) when compared to inks containing significantly larger particles. The purpose of this study was to determine the effect of pigment particle size on various ink properties and printing performance attributes. Specifically, this study considered the effects of pigment particle size on dispersion stability, optical density, color gamut, gloss, and lightfastness. The effects of pigment particle size were evaluated for cyan, magenta, and yellow inks. Additional studies are underway to quantify the effect of pigment particle size on printhead jetting reliability.

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Materials

In this study, cyan, magenta, and yellow pigments were used. The cyan is a Kodak proprietary siloxane-bridged aluminum phthalocyanine obtained from the Synthetic Chemicals Division of Eastman Kodak Company.[1] The magenta pigment is pigment red 122 (PR 122), a quinacridone-type pigment obtained from Sun Chemical Company as Sunfast Magenta 122. The yellow is pigment yellow 74 (PY 74), a non-benzidine yellow obtained from Clariant Chemical Company as Hansa Brilliant Yellow 5GX-03. Sodium N-methyl-N-oleoyl taurate (OMT) was obtained from Rhone-Poulenc and was purified by the Synthetic Chemicals Division of Kodak. Diethylene glycol (DEG) and glycerol were obtained from Acros Chemical Co. and Aldrich Chemical Co., respectively.

Methods

The pigments were milled using a variation of the process described by Czekai and Bishop.[2] The milling formulations for the cyan, magenta, and yellow pigments, respectively, were 21, 20, and 20 wt% pigment, 13, 6, and 2.5 wt% OMT, with the balance being de-ionized water. For each pigment, 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, magenta or yellow, and the larger cut will be referred to as "large" cyan, magenta or yellow.

Inks were prepared from the different particle size fractions by adding the pigment concentrate with stirring to a mixture of deionized water, DEG, and glycerol. The final cyan, magenta, and yellow ink formulations are given in Table I.

TABLE I. Cyan, Magenta, and Yellow Ink Formulations

Color	Wt% Pigment	Wt% OMT	Wt% DEG	Wt% Glycerol
Cyan	2.25	1.35	7.95	12.05
Magenta	2.60	0.78	10.80	7.20
Yellow	2.25	0.28	6.36	9.64

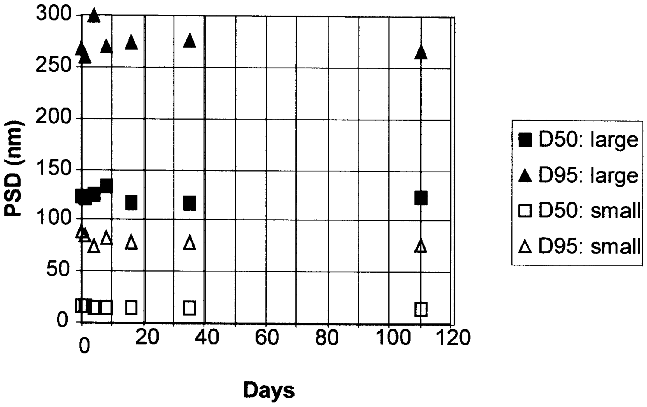

Figure 1. Cyan inks incubated at 60°C: PSD vs. time.

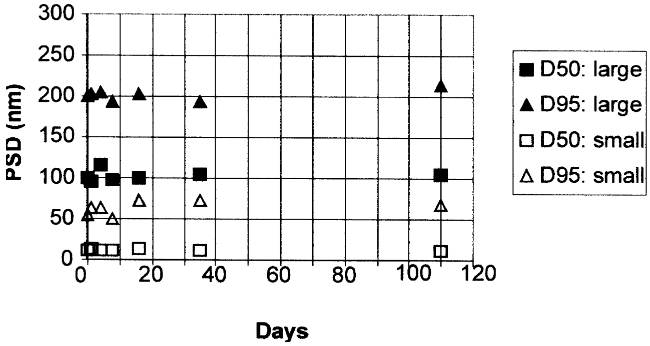

Figure 2. Magenta inks incubated at 60°C: PSD vs. time.

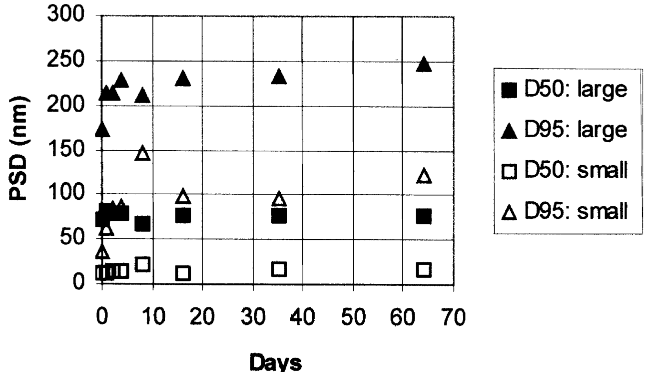

Figure 3. Yellow inks incubated at 60°C: PSD vs. time.

TABLE II. 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
Large cyan	49	122	267	486
Commercial A	54	108	356	688
Commercial B	57	98	178	344
Commercial C	86	145	223	289

TABLE III. Particle Size Distributions for the Magenta Inks of this Study along with Several Commercially Available Pigmented Magenta Inks

Ink	D_{10} (nm)	D_{50} (nm)	D_{95} (nm)	D_{100} (nm)
Small magenta	9	11	55	122
Large magenta	46	100	201	344
Commercial A	67	146	326	688
Commercial B	44	70	124	243
Commercial C	188	335	749	1375

TABLE IV. Particle Size Distributions for the Yellow Inks of this Study along with Several Commercially Available Pigmented Yellow Inks

Ink	D_{10} (nm)	D_{50} (nm)	D_{95} (nm)	D_{100} (nm)
Small yellow	9	11	37	122
Large yellow	33	73	173	344
Commercial A	67	146	326	688
Commercial B	43	85	216	409
Commercial C	82	148	254	409

Pigment particle size distributions (PSDs) were measured on a Leeds and Northrup Microtrac-UPA 150 ultrafine particle size analyzer. To simulate the effect of shipping and handling, the inks were subjected to a "freeze/thaw" test. This test involves holding the inks for 24 hr at –20°C, then for 24 hr at 60°C, measuring particle size, and repeating this cycle four times. Samples were examined for sediment and then shaken prior to sampling for the PSD measurements. Shelf-life of the inks was evaluated by incubating samples of inks at several temperatures and evaluating them 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 Ektajet 50 semigloss paper MW8, resin-coated photo paper. Optical density and color gamut were determined by previously disclosed methods.[3] Gloss was measured on a BYK Gardner microgloss meter acccording 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

The particle size distributions for the large and small cyan, magenta, and yellow inks are given in Tables II, III, and IV. Also included in the tables are the PSDs of several commercially available pigmented inks. It should be noted that the commercially available cyan inks all appear to contain copper phthalocyanine as the cyan pigment. In the tables, 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 distribution, and D_{100} is the size of the largest particles in the distribution. Table V shows the effect of freeze/thaw cycling on the particle size (D_{50} and D_{95}) of the cyan, magenta, and yellow inks, respectively. Figures 1, 2 and 3 show the effect of incubating the inks at 60°C on the pigment particle size.

Figure 4 compares the reflection spectra of the large and small inks. Table VI summarizes the effect of particle size on optical density and gloss, and Table VII compares the color gamut achieved with the small inks to that achieved with the large inks. In Table VIII, the

TABLE V. The Effect of Four Freeze/Thaw Cycles on the Inks of this Study

Ink	Initial D_{10}	Final* D_{50}	Initial D_{95}	Final* D_{95}
Large cyan	122	114	267	243
Small cyan	16	14	89	80
Large magenta	99	102	196	195
Small magenta	13	12	68	60
Large yellow	73	65	173	208
Small yellow	11	14	37	87

*Final: after four freeze/thaw cycles; 1 cycle = 24 hr at –20°C then 24 hr at +60°C

TABLE VI. A Comparison of Optical Density and Gloss for the Inks of this Study

Ink	Optical density	60° gloss
Small cyan	2.08	65
Large cyan	1.23	72
Small magenta	2.22	96
Large magenta	1.76	85
Small yellow	2.00	113
Large yellow	1.67	93

TABLE VII. A Comparison of Color Gamut for the Inks of this Study

Ink combination	Color gamut
Large cyan, large magenta, large yellow	53,390
Small cyan, small magenta, small yellow	70,728

TABLE VIII. Effect of Increasing Pigment Concentration in Large Cyan Ink

Pigment Size	Wt% pigment	Optical density	Color gamut*
Large	2.25	1.28	59,838
Large	3.00	1.73	67,963
Large	3.50	1.68	65,897
Large	4.00	1.63	65,119
Small	2.25	2.07	70,728

*The small magenta and small yellow inks were used in combination with the indicated cyan inks for the gamut calculations.

effects of increasing the pigment concentration in the large cyan ink on the optical density and the color gamut are presented. Figure 5 compares the reflection spectrum of the small cyan ink at 2.25% pigment concentration with the large cyan ink containing a higher pigment concentration. In Fig. 6, the lightfastness results for the yellow inks are compared.

Discussion

Historically, the inks developed for the first commercially successful thermal drop-on-demand ink jet printers employed off-the-shelf dyes as colorants. Dyes are colorants that 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 that are essentially insoluble in the ink solvent(s). It is important to note that the lightfastness

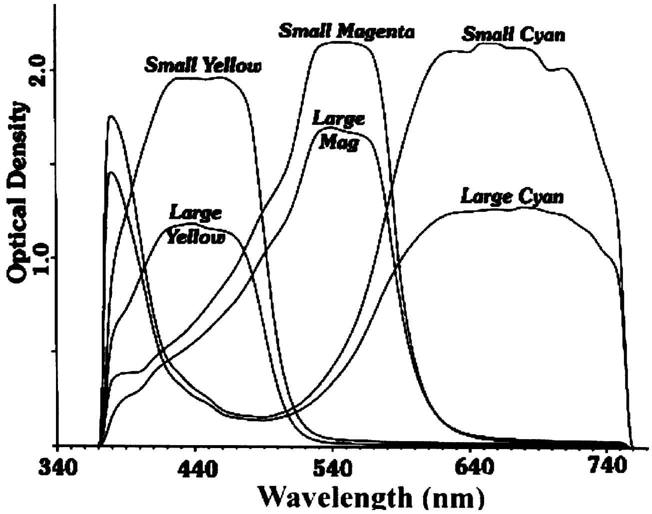

Figure 4. A comparison of reflection spectra for the small and the large cyan, magenta, and yellow pigmented inks.

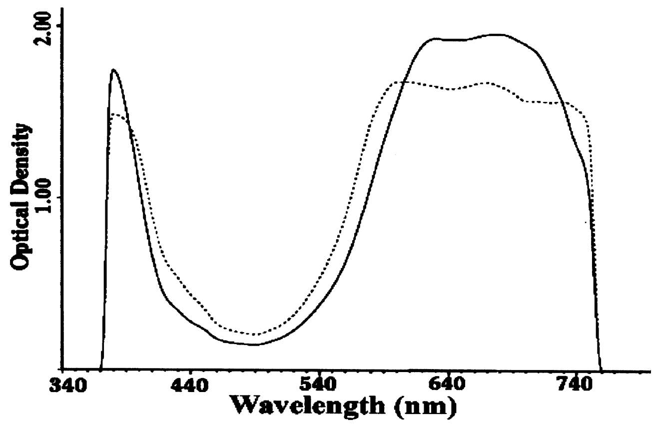

Figure 5. Reflection spectra of large cyan ink containing 3.5% pigment (dashed) and small cyan ink containing 2.25% pigment (solid).

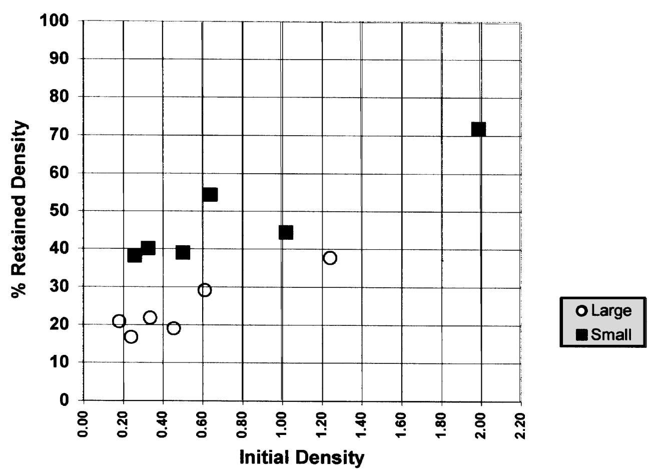

Figure 6. Yellow lightfastness data: % retained density after 8 weeks exposure to 50 Klux high-intensity daylight.

properties of pigments vary; some are extremely lightfast, while others fade as quickly as dyes.

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 between the commercially available inks and inks produced by this process, such as the pigment, dispersant, and humectant types and levels, so that it becomes 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 hoped to better understand which attributes are strongly affected by pigment particle size.

Our goal was to prepare a set of cyan, magenta, and yellow inks with PSDs comparable to those being offered with the Kodak Professional 2000 series printers ("small inks"), and, for comparison, a set of cyan, magenta, and yellow inks with average particle sizes approximately ten times larger than the small inks ("large inks"). The large inks were designed to simulate other manufacturers' commercially available inks. Tables II, III, and IV indicate that we achieved that goal.

The first requirement of a pigmented ink is for the pigment dispersion to be stable (i.e., no significant change in PSD) 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. The effect of freeze/thaw cycling on D_{50} and D_{95} for the cyan, magenta, and yellow inks is shown in Table V.

The data indicate that the freeze/thaw cycling had essentially no effect on the particle size of the large and small magenta and cyan inks. In addition, the optical density of a D-max patch printed with each magenta and cyan ink, before and after freeze/thaw cycling, exhibited essentially no change as a result of the treatment. The data indicate that there was some growth in the yellow inks as a result of the freeze/thaw testing. This growth was not observed in yellow inks that were stored at room temperature for up to one year. The growth is most apparent in the larger fractions of the small yellow ink.

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 estimate 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. Figures 1 and 2 show the effect of incubating the cyan and magenta inks at 60°C. As shown in Figs. 1 and 2, there was no significant particle growth in the large and small cyan and magenta inks over reasonable times at 60°C. Additional studies indicated no particle growth in the cyan and magenta inks for temperatures up to 80°C. Thus, as was the case with freeze/thaw cycling, there does not appear to be an effect of particle size on shelf-life for the magenta and cyan inks.

In Fig. 3, the effect of incubating the yellow ink at 60°C is presented. For both the small and large yellow ink, the D_{50} value remains constant throughout the experiment. However, significant growth is observed in the D_{95} value initially in the incubation period for both small and large inks, then the particles grow more slowly.

Evaluation of the large particles using scanning electron microscopy indicates that large particles are not agglomerates of small particles, but rather they are plate-like in appearance. This suggests that the pigment is ripening with time. It appears that both large ink and small ink undergo the ripening phenomenon, which appears to be a property of this pigment type, and is not due to particle size effects *per se*. We are currently evaluating how to prevent ripening in this pigment dispersion.

The image quality attributes that we evaluated with respect to particle size included optical density, gloss, and color gamut. Figure 4 indicates that the maximum optical density achieved using the large inks is significantly lower than the maximum optical density that can be achieved using the small inks. The lower densities result in a significant reduction in color gamut (Table VII). In theory, increasing the pigment concentration in the large ink should increase the optical density and improve the color gamut. This was done with the large cyan ink, and the results are given in Table VIII. The pigment concentration of the large cyan ink was increased from the standard level for the small cyan pigment of 2.25%, to 3.00%, 3.50%, and 4.00%. The data indicate that increasing the pigment concentration of the large cyan ink does increase the optical density; however, it is not possible to achieve as high an optical density or as large of a color gamut with the large pigment as with the small pigment. In addition, when the pigment concentration was increased to 4.00% severe imaging artifacts, i.e., banding, were observed, which resulted in a decrease in optical density and the resulting color gamut. This is attributed to the fact that the cartridges are not designed to fire such high concentrations of pigment. In Fig. 5, it is also apparent that another effect of increasing the pigment concentration is to broaden the absorption curve of the ink, which is undesirable and will reduce color gamut.

As expected,[6] the gloss levels of the small magenta and yellow inks were higher than the gloss levels of the corresponding large magenta and yellow inks. However, the large cyan ink exhibited 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. This unexpected observation is currently under investigation.

One of the concerns with using pigmented inks in ink jet systems has been that the color gamut would not be acceptable. However, as demonstrated above, the use of very small pigment particles results in a color gamut that approaches the best color gamuts achieved with dye-based inks (i.e., 76,000).

After having determined that the use of small pigment particles is required to achieve an acceptable color gamut, it was important to investigate the claims[7] that pigmented inks containing very small pigment particles would exhibit poorer lightfastness than inks containing larger pigment particles. To determine the effect of pigment size on lightfastness, step wedges of all the inks were printed with densities ranging from D-min to D-max. The large and small cyan and magenta inks were exposed for 16 wk to a high-intensity Xenon source filtered with window glass, which is estimated to be equivalent to > 50 yr of indoor exposure, and none of the inks faded significantly. Thus for the cyan and magenta, there appears to be no effect of pigment particle size on lightfastness in the system studied.

In Fig. 6, the results of exposing the small and large yellow inks for 8 wk under the same conditions are presented. There are several things to note in this graph. First, the yellow pigment used is not as lightfast as either the magenta or the cyan tested in this study, and a significant level of fade was observed for both the large and small pigment. Second, the large pigment appears to fade more than the small pigment, which is in contrast to the claim referenced previously. Third, the degree of fade was a function of the starting density of the image. This is particularly apparent in the data for the small yellow, where the high-density step retained about 70% of its initial value, while the lower density steps only retained 40–50% of their initial value.

Summary

We have initiated a study of particle size effects in pigmented ink jet inks. In this study, dispersion stability, image quality, and lightfastness were evaluated for two C,M,Y sets of inks: one set containing pigment particles with average particle size <50 nm, and one set containing pigment particles with average particle size ~100 nm. The results of this study indicate that reducing the average pigment particle size in the ink from ~100 nm to less than 50 nm significantly improves image quality, and the reduction does not adversely affect the lightfastness of these pigments. Specifically, the following effects of particle size were noted:

- For the large and small cyan and magenta inks, no particle size growth was observed when the inks were subjected to either freeze/thaw cycling or incubation for extended periods at temperatures up to 80°C;
- For the yellow ink, particle growth was observed in both the small and large inks when the inks were subjected to either freeze/thaw cycling or incubation for extended periods at 60°C;
- The color gamut for the C,M,Y ink set containing small pigment particles was significantly higher than the color gamut for the ink set containing the large pigment particles. It was not possible to adjust the formulation of the ink containing the large pigment particles and achieve as large a color gamut as was measured with the inks containing the small pigment particles.
- After 16 wk of high-intensity exposure, the large and small cyan and magenta inks exhibited essentially no fade. After 8 wk of high intensity exposure, both the large and small yellow inks exhibited significant fade.

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References

1. M .T. Regan, U.S. Patent 4,311,775 (1982).
2. D. Czekai and J. Bishop, U.S. Patent 5,679,138 (1997).
3. D. Santilli, D. E. Bugner, A. D. Bermel, and D. J. Oldfield, U.S. Patent 5,738,716 (1998).
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,* IS&T, Springfield, VA, 1996, pp. 405–408.
7. R. A. Work III, *5th Annual Ink Jet Printing Workshop*, Information Management Institute, Boston, MA, March 27–29,1996.