Influence of Pigment Particle Size and Packing Volume on Printability of Glossy Inkjet Paper Coatings

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Abstract

The optical properties and printability of ink jet coated papers are influenced by smoothness, surface chemistry and pore structure of the surface coating layer. To control these properties, the coating formulator must select the proper pigment(s) and binder(s), the two main components of any coating. For glossy ink jet papers, small particle, large surface area fumed silica and aluminum pigments have been shown to provide the desired properties for high quality glossy ink jet coated papers. However, their high cost and low make-down solids, in comparison to conventional pigments, has limited their use by the industry to these specialty grades.

The focus of this study was to determine if the costs and application solids of fumed silica and alumina coatings could be improved by extending the pigments with less expensive compatible pigments. The effects of the resultant change in packing volume and particle size distribution on the optical properties and printability were determined. Blends capable of providing equal or better gloss and printability, at a reduced cost, were sought.

It was determined that up to 30 parts of the fumed silica and alumina could be replaced with less expensive compatible pigments, without significant loss to the optical and printing properties of the glossy ink jet paper.

Introduction

Inkjet printing has proven to be the first digital technology that has achieved an acceptable level of color quality at an affordable price for the majority of home/office end users (1). As a result, there is a demand for ink jet media with intermediate and high gloss finishes, so that the ink jet printed image may resemble a photographic image. It is expected that as image quality improves and throughput speeds increase, ink jet printing will continue to expand into more printing markets and may begin to challenge electrophotography in many high-end applications. A key to meeting the needs of this evolving market is the development of coated ink jet media capable of providing the desired glossy image characteristics of photographic papers.

Another key optical property for photo quality papers is brightness. Brightness is important for print contrast. The higher the brightness, the higher the contrast between the paper and printed image, hence the “snappier” the image. For the paper industry, absolute brightness is defined as the reflectance of blue light peaking at a wavelength of 457 nm in terms of a perfectly reflecting, perfectly diffusing surface. The brightness of pigment-coated paper is heavily dependent on the brightness of the raw stock. Therefore, the raw stock should have brightness as close as possible to that of the dried coating layer. The principal coating components that influence brightness are the pigments, binders, additives, and the relative proportion of each used in the coating formulation (2). Optical brighteners (3-5) are commonly used in these grades. Papers with brightness values greater than 90, and as high as 100, are currently being marketed.

According to TAPPI standards (6), gloss is defined as the 75° spectral reflectance of light at $\lambda = 550$ nm. Based on this definition, coating gloss is optimized by increasing the refractivity of the coating layer, while minimizing the roughness of the coated surface layer.

The scattering coefficient is the fraction of light incident upon an infinitesimally thin layer of the material that is scattered backwards by that layer, divided by the basis weight of the layer. It is expressed in reciprocal basis weight units. Kubelka and Munk (7) provided a direct mathematical relationship between scattering absorption, and opacity.

The original theory of Kubelka and Munk was developed for light diffusing and absorbing infinitely wide colorant layers. Due to its simple use and to its acceptable prediction accuracy, this model is very popular in industrial applications. The concept is based on the simplified picture of two diffuse light fluxes through the layer, one proceeding downward and the other simultaneously upward (5,8,9).

Recent research in our laboratory by Lee et al (10,11) and Ramakrishan (12) showed that fumed metallic oxide pigments are capable of producing semi-gloss and high-gloss ink jet papers with acceptable print quality after calendering. In these works, it was found that the gloss of fumed alumina pigments was higher than fumed silica. An important finding of Ramakrishan’s studies was that the gloss of the ink jet papers increased with an increase in silica particle size, which does not follow the findings for conventional pigments. The loss in gloss with reduction in silica particle size was attributed to the presence of coating cracks. The cracks were shown to result from drying stresses, which increased with an increase in silica surface area. Cracking was not present in the alumina coatings, resulting in the alumina coatings providing higher gloss values at equal coat weights.

Ink density is an important performance parameter in the printing process. Ink density impacts the final visual quality, color gamut, and color fidelity. The main factor identified with color density is the concentration of colorant in the ink. Other major factors determining ink density are ink dot coverage on the coating surface and colorant concentration at the surface. In the interaction of the colorant with coated paper, electrostatic interactions play the key role in colorant-coated paper interactions. The nature of the anionic dyes and the oxides will determine the print quality of the ink jet printing, since electrostatic interactions of colorant with coated media occur between the anionic groups of dyes and the oxides. The binding energies of the dyes are greatly increased by electrostatic interactions, resulting in a high binding strength(13,14)

Ink gloss depends on the smoothness of the substrates and the smoothness of the ink layer. Another factor contributing to the smoothness of the printed film is the amount of vehicle on the surface. If the pigment particles are completely covered by a level film of the vehicle, a good approximation to a mirror surface usually results irrespective of the smoothness of the substrates or of the ink(15). However, the use of dyes rather than pigments in ink jet inks makes the former more relevant than the latter.

Generally, optical properties and printing properties improve with increases in the coat weight, since increasing coating materials improve properties of the coated surface. For example, reflectance of light and ink absorption both increase with increased coat weight.

The objective of this research was to determine if less expensive compatible pigments could be blended with fumed alumina and silica pigments to yield coatings with equal or better glossing and printing properties. The influence of pigment blending on the packing volume of the coating was studied and the relationship between packing volume and ink jet print quality was determined.

EXPERIMENTAL DESIGN

Selected pigments were obtained from several pigment companies. Aluminum oxide (AO), fumed silica (FS), precipitated calcium carbonate (PCC), ultrafine ground calcium carbonate (UFGCC), alumina trihydrate (ATH), and baumite were studied. The physical properties of the pigments and the ratio of the pigments used are shown in Table 1.

The binder used in the coating formulation was a partially hydrolyzed, low viscosity, polyvinyl alcohol (Airvol 203, Air Products Inc.). This polyvinyl alcohol was chosen to optimize the % coating solids by minimizing the interaction between pigments and PVOH and to promote the ink receptivity of the coating layer to the water based ink jet inks. Solutions of polyvinyl alcohol were prepared at 30% solids by adding the required amount of dry PVOH powder to cold-alkaline water (pH 9.0-10.0) under agitation and heating the mixture to 185ºF. The solution was held at this temperature for 35-40 minutes to assure complete dissolution and hydration of the PVOH. A defoamer was then added (Foammaster VF, Henkel, Inc.). The solution was cooled to 40ºF before adding the slurried pigments at a slow rate of agitation. The coatings were mixed for 30 minutes and the pH and viscosity measured. Coatings containing different fumed and conventional pigment ratios (50:50, 70:30, and 80:20, respectively) were prepared and draw downs made using various Mayer rods.

Table 1. The Physical Properties of Pigments as Supplied

Sample	Solids Content	Color	Specific Gravity	pH	Refractive Index	Avg. Particle size (nm)
AO	40%	White	1.40	3.8-4.2	1.76	160
FS	30%	White	1.20	10.0-10.3	1.46	225
PCC	70%	White	2.72	9.0-10.0	1.58-1.63	544
UFGCC	75%	White	1.92	9.0-10.0	1.58	600
Baumite	30%	White	1.1-1.3	4.0-6.0(5% sol)	1.65-1.66	200
ATH	65%	White	2.42	6.70	1.57	400

From this initial study, it was determined that PCC and UFGCC were the two most compatible pigments for blending with fumed silica due both to their high pH requirements and high glossing properties. For the fumed alumina, baumite and alumina trihydrate performed best. It was also determined that substitution levels greater than 30 parts of these pigments into the coating, greatly diminished the gloss of the coatings, to where the coating gloss would not be acceptable for this commercial grade of ink jet paper. Based on these finding, the coatings for cylindrical laboratory coating studies, (CLC), applications were prepared at a 70:30 ratio, a pigment-to-binder ratio of 7:1 and final solids of 30 ±1%.

The coatings were applied to a 75 g/m^2 commercial base paper using a Cylindrical Laboratory blade coater at a speed of 2000 fpm. For each sample, the basepaper was pre-dried at 25% power for 10 s and post-dried at 100 % power for 60 s. Four different coat weights were applied: 6 g/m^2, 8 g/m^2, 10 g/m^2, and 12 g/m^2.

The brightness values of the papers were measured using the standard procedure(16) on a Technidyne Brightness meter. Gloss was measured using a Hunter 75º gloss meter according to the standard procedure(6).

The samples were printed on an Epson Stylus 900, Hewlett Packard 932C and Canon S450 ink jet printers using a proprietary test print pattern created with Adobe software [(10-13)]. The printed images were bars of four solid colors (cyan, magenta, yellow, and black). The Epson 900 is a piezoelectric printer with a resolution of 1440 x 720dpi. The HP 932c is a thermal ink jet printer with a resolution of 2400 x 1200 dpi. The Canon S450 printer is thermal ink jet printer with a resolution of 1440 x 720 dpi. Print gloss was measured using a Gardener 60º Micro-Gloss meter. Print density was measured using a X-Rite 408 densitometer. Roundness was measured at 30% tone scale by using a Hitachi HV-10 camera and ImagePro Plus, version 3.0, was used for image detail analysis [(10-13, 16)].

Table 2. Ratio of pigments used.

Sample	Pigments	Parts	Viscosity* (cP)	pH
Sample A	Fumed silica UFGCC	70 30	572	9.2
Sample B	Fumed silica PCC	70 30	254	9.7
Sample C	Aluminum Oxide ATH	70 30	984	5.9
Sample D	Aluminum Oxide Baumite	70 30	1766	6.9
Sample E	Fumed Silica	100	72	9.8
Sample F	Aluminum Oxide	100	1231	8.1

*Viscosity=Brookfield viscosity, RPM:100, spinindle:#4

The coated samples were calendered on one side, through 3 nips at 123 kN/m and 60°C.

Result and Discussion

The influence of coat weight and pigment type on brightness is shown in Figure 1. Both the coat weight and pigment type influenced the brightness of the coating. The addition of the calcium carbonate to the fumed silica improved the coating brightness. The addition of ATH increased the brightness of the fumed alumina. Comparison of the brightness data to calculated light scattering coefficient values for the data showed a strong correlation (See Figure 2).

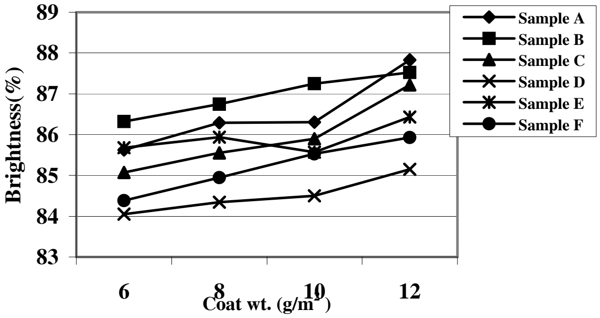

Figure 1. Brightness Comparison of each coating formulation .

The scattering coefficients of the coatings were calculated using the following equations [(8)]:

From the measurements of R_0 and $C_{0.89}$

$$a= 0.5(R_{0.89} +(R_0 - R_{0.89} +0.89)/(0.89R_0)) \quad (1)$$

$$b= 0.5(1/R_\infty - R_\infty) \quad (2)$$

$$x = (1-aR_0)/ bR_0 \quad (3)$$

$$R_{0.89} = R_0 /C_{0.89} \quad (4)$$

$$R_\infty = a-(a -1)^{1/2} \quad (5)$$

$$sW =(0.5/b)[\ln(x+1)/(x-1)] \quad (6)$$

$$S=sW/W \quad (7)$$

$R_{0.89}$ = reflectance of the layer which has behind it a surface with reflectance of 0.89.
R_0 = reflectance of the layer with ideal black background
$C_{0.89}$ = $R_0 /R_{0.89}$ = TAPPI opacity, as a fraction
sW = scattering power
W = basis weight
S = light scattering coefficient (LSC)

From the above equations, it is seen that brightness is influenced by the amount of light scattered and absorbed. Light is absorbed when colored matter is present. Scattering is influenced by the surface area of the pigments and the number of air-to–pigment interfaces due to the higher degree of refractivity between the two interfaces. Scattered light, to some extent, can mask the visual effect of colored impurities.

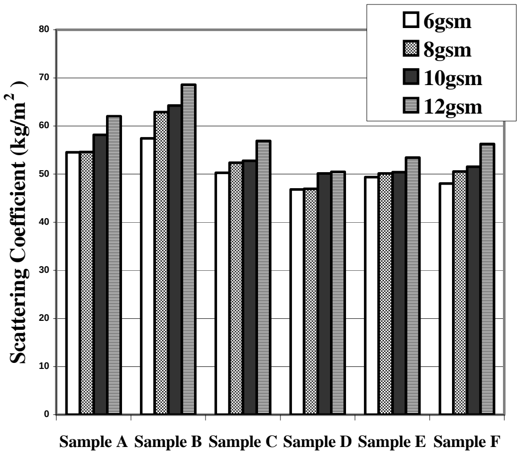

Figure 2. Influence of Scattering Coefficient on Coat Weight.

The addition of carbonate significantly increased the LSC of the silica coatings, improving the coating brightness and gloss (Figure 3). The addition of ATH to the fumed alumina coating resulted in a slight increase in the LSC with a corresponding increase in coating brightness. The increase in brightness with LSC value indicates that addition of the carbonates and ATH increases the air voids in the packing structure enabling more light to be scattered. This is consistent with Figure 4, which shows the influence of pigment addition on coating PPS porosity.

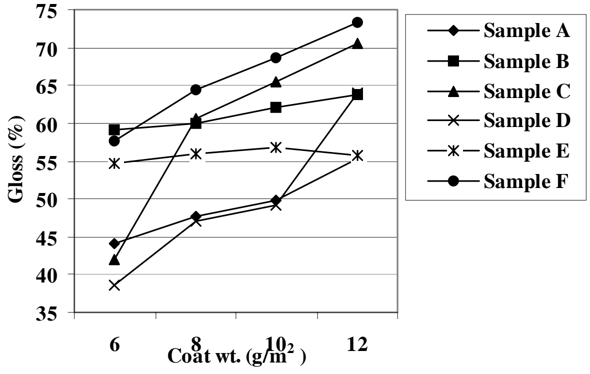

Figure 3. Gloss Comparison of Each Coating Formulations.

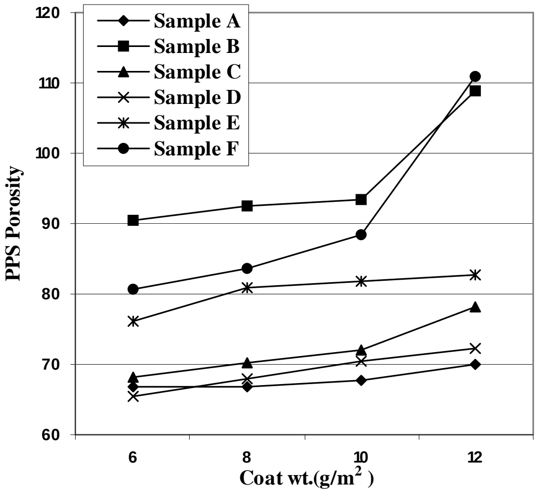

Figure 4. PPS Porosity comparison of each coating formulation

The results indicate that the addition of the larger pigments to the fumed silica coatings increased the porosity of the coating layer, enabling the coating to scatter more incident light. As a result, the brightness, gloss, and opacity (Figure 5) of the coatings increased. Unlike the fumed silica coatings, the LSC of fumed alumina coatings were not significantly changed by the addition of the ATH and baumite pigments. The gloss of the fumed of alumina was the highest of all the samples tested. The addition of PCC to the fumed alumina enabled glosses comparable to the fumed alumina to be obtained.

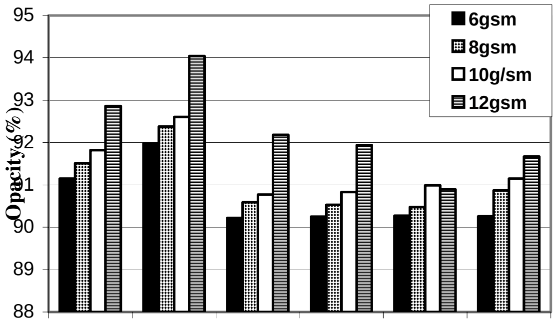

Figure 5. Opacity comparison of each coating formulation.

Since gloss is a function of surface smoothness, the higher gloss could be indicating that fumed alumina (sample F) formed a smoother coat layer.

Chinmayanadam [(18)] has shown gloss to be a function of the refractive index and the wavelength of incident light, as well as the surface roughness:

$$\text{Gloss} = I/I_o = f\,(n,i)\ \exp[-(4\pi\sigma\cos(i)/\lambda)^2] \qquad (8)$$

I and I_o are the specularly reflected and incident light intensities, f(n,I) is the Fresnel coefficient of specular reflection as a function of refractive index n and angle of incident light I, σ as the standard deviation of the surface roughness, and λ is the wavelength of incident light.

Application of this equation to the results indicate that the refractive index of sample F is sufficient to provide acceptable commercial glosses, if the proper alignment of the particles (in the case of platey pigments such as ATH) or smoothness of the coating layer is achieved. Small particles not only scatter more light, but better fill the microvoids within the coating and base paper, to provide higher smoothness than large and/or chunky particles. Although calendering improves smoothness, and hence gloss, it can have the negative effect of compressing the coating layer, adversely affecting the ink receptivity and consequently print quality of the paper.

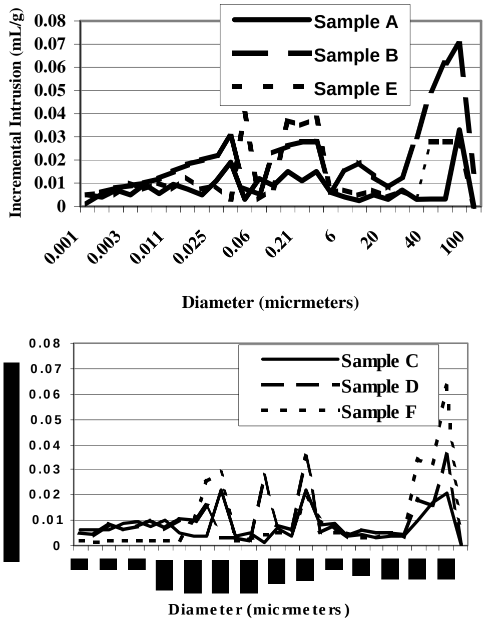

Figure 6. Pore Size Distribution by Mercury Intrusion Porosimeter (Coat weight: 12 g/m^2)

The pore size distributions of the samples are shown in Figure 6. The LSC and Parker print porosity results for the fumed silica coatings correlate well to the Hg porosimetry data. The results confirm that the addition of the needle shaped PCC (aragonite) with the grape-like silica clusters open the coating structure. The resultant structure was found to increase the print density and ink gloss of the samples (Figures 7,8). The results indicate that the new packing structure enables the ink dye to be fixed and dried closer to the coating surface. The ink density and gloss values of the fumed silica coatings were found to be higher than the fumed alumina coatings. In the case of ink density, the differences are probably not significant, the increased ink gloss for the silica samples is most likely due to the ink filling in the cracks known cracks in the silica based coatings (12-14). This filling occurs because these inks are either dye based or small pigment based (19,20) (~100nm for the HP black).

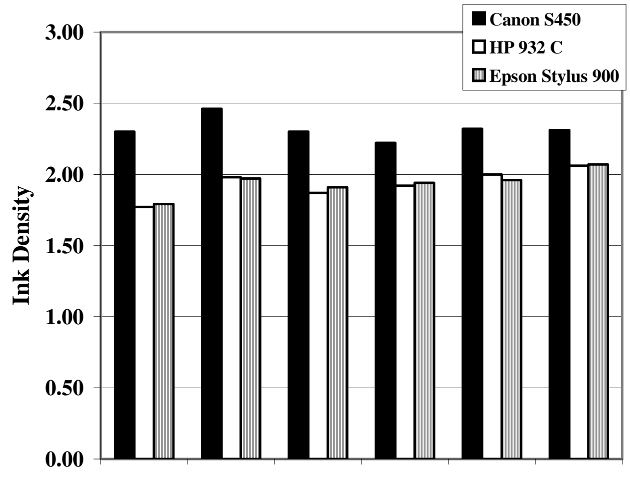

Figure 7. Ink-Density Comparison of Each Coating Formulations (Coat wt. : 12 g/m2, Color: Black)

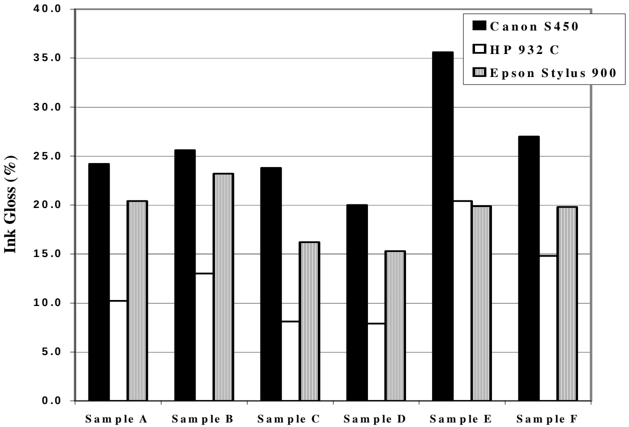

Figure 8. Ink-Gloss Comparison of Each Coating Formulations (Coat wt.: 12 g/m2, Color: Black)

The dot roundness results for black dots are shown in Table 3. Roundness was defined in reference 17. Roundness near one is ideal because it indicates that he ink spreads uniformly, and thus is a measure of coating uniformity. If the roundness is 1, it means the dots are perfect circles. Values of roundness less than 1.0 indicate lack of roundness. Therefore, the closer the value of roundness is to 1, the better the quality of the dots.

From Table 3, most of the low coat weight samples have a smaller roundness values. That is to say, ink dots smeared on the coating layer because coating layers in the low coat weight are not able to hold ink dots well and coatings applied for the low coat weight samples didn't cover the substrate perfectly. The roundness values of Canon printer samples were better than the roundness values of HP and Epson printer samples.

Table 3. Dot Roundness of samples

Canon S450

	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
6 g/m^2	.99	1.00	.97	.92	1.00	.95
8 g/m^2	1.00	1.00	.98	.89	1.00	.99
10 g/m^2	1.00	1.00	.96	.83	1.00	.99
12 g/m^2	.99	.99	.95	.80	1.00	1.00

HP 932C

	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
6 g/m^2	.93	.79	.83	.87	.96	.81
8 g/m^2	.90	.87	.85	.83	.96	.88
10 g/m^2	.85	.85	.88	.74	.92	.92
12 g/m^2	.99	.87	.85	.71	.97	.86

Epson Stylus Color 900

	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
6 g/m^2	.95	.99	.90	.80	.99	.91
8 g/m^2	.94	.98	.91	.79	1.00	.90
10 g/m^2	.97	1.00	.90	.81	.99	.92
12 g/m^2	.99	.90	.89	.69	.94	.86

Conclusions

The results obtained from this study indicate that the optical properties, brightness and gloss, were affected by pigment type and coat weight. Improvements in optical properties indicate that brightness improvements were due to an increase in scattering coefficient with large particle size and gloss improvements were due to increase in smoothness and refractive index.

The print properties were also influenced by pigment particle size and packing volume. Print qualities as measured by ink density and ink gloss were strongly dependent on pigment particle size and packing volume. Inks used in the printers influenced printing qualities.

Calendering improved the smoothness of the surfaces. Ink gloss and ink density consequently increased. It is believed that the low solids of the coatings prevents the smooth application of the coating due to base sheet roughening by the absorption of coating water. Research is therefore needed to determine ways to control the penetration of the coating water into the base sheet. Base sheet sizing, coating solids, the application and formulation of a base coating, and coating rheology should be considered for topics of future studies.

From the results of these experiments, it is evident that the coatings of fumed metallic oxide and conventional pigments had as good optical properties and printing qualities as the coatings of fumed metallic oxides.

Acknowledgement

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Biography

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