# Influence of Coating Pigment Porosity on Inkjet Color and Lightfastness Performance

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Keywords: Inkjet Coating, Color Gamut, Pore Size, Coating Pigments

The coating structure of the print substrate strongly influences ink setting speed and uniformity, which in turn affects the quality of the final image, such as color saturation, optical density, color gamut and image resolution. Fumed silica is one of the most important inorganic oxides used for high performance, microporous inkiet media. Because of its fine particle size and high levels of microporosity, fumed silica is capable of absorbing high amounts of fluid. However, fumed silica coatings are known to produce "cracks" in coating, which may contribute to low gloss at higher coat weights. Its costly ingredients have also limited its use by the industry. Previous studies reduced the occurance of coating cracks by mixing fumed silica with less costly conventional pigments. Changes in pigment composition and type produced different coating layer microstructures. The main objective of this study was to evaluate the effect of coating porosity on inkiet color and lightfastness performance. In this work, fumed silica was blended with precipitated calcium carbonate (PCC). The ratio of fumed silica to PCC used was 100:0. 85:15. 70:30, and 55:45. The coatings were applied using a cylindrical laboratory coater (CLC) to obtain a coat weight of 12 g/m<sup>2</sup> on one side. The roughness and specular paper gloss were tested and compared. Coated paper samples were printed on different digital printers, and the color reproduction capability was evaluated in terms of color gamut and optical density. A O-Sun Xenon test chamber was employed to evaluate lightfastness. It was found that the less expensive compatible pigment, PCC, blended with fumed silica pigments did yield coatings with equal or better smoothness and paper gloss (until 30% addition). Also, the addition of PCC in the coating formula tended to increase the UV resistance of the coating with a slightly higher pH value of coating. However, the color reproduction capability of inkjet media was still controlled by the porosity properties of the coating.

### **1. Introduction**

Today, inkjet printing technology has become the dominant printing method for commercial large format and desktop small format printing of photos, graphic art, and documents, as well as being a valuable proofing device. Inkjet printing provides unique advantages of high color gamut, high image quality, and print on demand at affordable prices (Chen & Burch, 2007; Lee, Joyce & Fleming, 2004, 2005).

Unlike solvent-based liquid or paste ink systems used in conventional printing, the present ink systems used for inkjet printing are water based, containing 65% to 95% water. In order to absorb a high amount of ink quickly and produce high-quality color images with inkjet printers, specialty media are required (Chapman & Michos, 2000; Lee, et al., 2004, 2005).

Over the past few years, there have been a variety of different coating formulations and technologies developed to meet the needs of inkjet printing. Former studies indicated that the optical properties and printability of microporous inkjet coated paper is strongly controlled by the pigment types used in the coating formulations. For instance, the specialty structured synthetic silica is one of the most important inorganic oxides used to produce the desired properties for high quality glossy inkjet coated paper. Its characteristics of small particle size and large surface area provide special pore structures and surfaces to rapidly absorb the aqueous ink vehicle away from the surface and into the porous microstructure. Silica has been used for its porous structure and hydrophilic characteristics (Batz-Sohn, Storeck & Scharfe, 2004; Khoultchaev & Graczyk, 2001; Monie & Krupkin, 2006; Chen & Burch, 2007).

Fumed silica pigment particles have little or no internal microporosity, that is, the particles are not porous themselves. However, packing these fine particles (typically lie below 1µm) forms interparticular voids and capillaries in the coating layer and makes it possible to absorb the water of the ink droplets within fractions of a second (Batz-Sohn, et al., 2004). Although fumed silica pigments play a vital role in the production of high quality glossy ink jet coated media, their costly ingredients, low make-down solids, and considerable binder demand have limited more widespread use of them. In order to obtain the absorption properties of the silica and increase productivity at the same time, the method of blending with lower cost of conventional coating pigments was proposed (Lee, Joyce & Fleming, 2004, 2005; Vikman & Vuorinen, 2004). For example, calcium carbonate in ground and precipitated forms has been engineered as a substitute for silica pigments. A new generation of precipitated calcium carbonate (PCC) used in inkiet receptive media has high surface area. In the meantime, PCC for ink-jet receptive media has been synthesized with an increase in coating solids; that is, less dryer capacity is required. The blending with PCC

in the silica coating pigments becomes a lower cost alternative (Lee, et al., 2004, 2005; Vikman & Vuorinen, 2004; Superka & Bashey, 2005).

It is well known that the pore structure of a pigment can have a significant influence on the print quality of the final printed images. The porosity characteristics of coatings are the key in production of differentiating products and their end-use performance. The nature of the coating components is also important in controlling the lightfastness properties of the print. The type of pigment affects the pH of the coating, which has been shown to have an influence on lightfastness (Vikman, 2001). The addition of PCC in the fumed silica coating will definitely change the pore structure of coating media. The porosity of the coating colors controls the way inks penetrate through the paper, which in turn determines the color reproduction capability of ink-jet media (Ishii, et al., 2001; Bandyopadhyay, 2001). Silica is able to trap the large volume of water in the ink by its microporous structure. PCC, on the other hand, traps the colorant portion of the ink droplet and relies on the base sheet to be receptive to the water phase vehicle portion that remains. When blending fumed silica pigments with PCC, the optimum combination of fumed silica and PCC blending coating color needs to be investigated. In order to obtain good color reproduction, it is necessary to understand how coating pigment porosity impact ink-iet color reproduction when quality/cost matrix coatings are employed.

# 2. Methodology

Commercial pigment samples of fumed silica (Cabot PG001) and precipitated calcium carbonate (Imerys OptiCal 400) were studied. Precipitated calcium carbonate (PCC) was chosen due to its high pH property, which was compatible with fumed silica pigment, as well as its high glossing property (Lee, et al., 2005). The particle size of fumed silica pigment was 192.6 nm, while the precipitated calcium carbonate had a larger particle size of 350 nm. The physical properties of the pigments are shown in Table 1.

Table 2 lists the properties of the coating formulations used in this study. The binder used in the coating formulation was partially hydrolyzed polyvinyl alcohol (PVOH, from Celvol). Formulations were prepared using a 4:1 pigment-to-binder ratio. In order to study the influence of coating pigment porosity on inkiet color reproduction, coatings were prepared at different fumed silica and precipitated calcium carbonate pigment ratios (100:0, 85:15, 70:30, and 55:45, respectively). 1.5 pph of carboxymethyl cellulose (CMC) was added to each coating to increase its viscosity. The final solids content of the coatings was controlled in the range of 29% to 31%. The viscosities of the coatings were measured using a Brookfield RVT digital viscometer (#4 spindle at100 rpm). The addition of PCC in the fumed alumina coating increased the viscosity of the coating.

Sample	Solids Content, %	Color	Specific Gravity, g/cm <sup>3</sup> , 25°C	Particle Size, nm	pH
Fumed Silica (FS)	30	White	1.19 - 1.20	Mean: 192.6; Std. Dev.: 62.7 (32.6%)	9.9 - 10.9
Precipitated Calcium Carbonate (PCC)	72	White	1.65 - 1.90	Mean: 349.5; Std. Dev.: 135.6 (35.5%)	9.2

Table 1: The physical properties of pigments as supplied

Sample	Pigments	Parts	Final solids content, %	Viscosity, cp (100 rpm, #4 spindle)	pH
FS	Fumed Silica	100	29.01	171	10.09
FSP1	Fumed Silica/PCC	85:15	29.78	212	10.22
FSP2	Fumed Silica/PCC	70:30	30.23	272	10.16
FSP3	Fumed Silica/PCC	55:45	29.54	302	10.16

Table 2: Properties of Coating Formulations

The physical properties of the base sheet were basis weight of 82.67 g/m<sup>2</sup>, Parker Print Surf roughness of 6.5  $\mu$ m, TAPPI brightness of 83.75%, and paper gloss (at 75°) of 15.60%. Coatings were applied using a cylindrical laboratory coater (CLC) at a speed of 3000 fpm to obtain a coat weight of 12 g/m<sup>2</sup> on one side. In order to further investigate the influence of calendering on optical density and color gamut, some coated inkjet papers were calendered on a soft-hot nip calender through two and three nips at 123 kN/m and 62°C before performing any gloss measurements.

Paper gloss was measured at 75° using a Novo-Gloss™ Glossmeter based on TAPPI standard T 480. A Parker Print-Surf (PPS) tester was employed to measure the roughness of the coated sheets. An Autopore IV 9500 mercury porosimeter, which measures the incremental increase of volume penetrated as the pressure rises, was employed for the porosity-related characteristic measurements. The average pore size and porosity were used as parameters in analyzing the results.

Samples were then printed on two different printers: an Epson Stylus Pro 4000 printer with UltraChrome K3 pigmented inks and a HP Z3100 printer with Vivera pigment-based inks. Also, the addition of PCC reduced the positive charge of the coating layer in this experiment. For fumed silica coatings, in order to optimize the adsorption of the negatively charged dye-based ink on the coating surface, a surface modification with special cationic polymers had to be employed (Batz-Sohn, Storeck & Scharfe, 2004; Chen & Burch, 2007). In this study, a dye-based inkjet printer was not included in the test and discussion.

ICC profiles were generated for these coated papers. A 5" x 9" RGB chart was printed on the coated sheets. Those printed charts were then measured with an i1iO spectrophotometer and ICC profiles were generated by using ProfileMaker software. The gamut volumes achieved from both inkjet printers on the coated papers were derived from ColorThink 3.0 Pro software. The color reproduction capability was evaluated by two specific parameters, optical density and color gamut volume. Higher optical density and wider color gamut is desirable to provide better color reproduction capability.

Lightfastness tests were accomplished by exposing the prints to artificial sunlight for 25, 50, 75, and 100 hours with a Q-Sun Xenon lamp equipped with a Daylight-Q filter. The test chamber was used at irradiance settings of 0.68 W/m<sup>2</sup>/nm at 340nm (noon summer sunlight) and

63°C for black standard temperature (BST). The color values in CIE L\*a\*b\* color space of color patches were measured before, during and after exposure using an X-Rite i1iO spectrophotometer (D50/2° standard illuminant). Results of accelerated lightfastness tests for the different coating formulations were interpreted in terms of change of color gamut volume and color difference.

# 3. Results and Discussion

### 3.1. Coated Paper Properties

Roughness and paper gloss measurements for each of the coatings are shown in Figure 1 and Figure 2. As shown in Figure 1, both the pigment composition and calendering influenced the roughness of the coatings. Before performing calendering, the smoothest surface was found in the coating formulation prepared at 85:15 ratio (FSP1). Typically, coatings with small pigment particles scatter more light and fill the voids within the coating and base paper, thereby resulting in a smoother paper surface. Despite having a smaller particle size, the coating with fumed silica did not produce the smoothest surface as expected, probably due to the presence of cracks in the fumed silica coating. Calendering significantly increased the smoothness of coated paper. It was observed that the addition of PCC yielded coatings with equal or better smoothness until 30% addition, compared to the coating with fumed silica alone. In this study, roughness consequently increased with increasing portions of PCC added in the coating.

For the paper gloss properties, as shown in Figure 2, the fumed silica coating produced the highest gloss before performing calendering. The gloss of the uncalendered papers consequently decreased with increasing portions of PCC added in the coating. Calendering enhances gloss by closing the larger pores in the coating layer (Wikström, Bouveng & Rigdahl, 2002; Larsson & Engström, 2007). Gloss also increases due to base smoothing as well as closing of coating pores. It was seen that once calendered, the addition of PCC to the fumed silica coatings increased the paper gloss, but there are not significant differences when higher degrees of calendering are applied. After performing calendering, the paper gloss improved from lower than 36% to higher than 65%, which is acceptable for the commercial grade of inkjet paper (> 55%) (Lee, Joyce & Fleming, 2005).



Figure 1: Parker Print-Surf Roughness measurement, µm



Figure 2: Paper gloss measurement at 75°. %

Fumed silicas are known to produce "cracks" in coatings, which are caused by shrinkage of the coating layer and may contribute to low gloss at higher coat weights (Wu, et al., 2008). Scanning electron microscopy (SEM) images of the FS and FSP3 sample are shown in Figure 3, at 200X magnification. As expected, the FS coating sample produced "cracks" in the coating. Calendering improved the smoothness, but was not beneficial to cracks. The addition of PCC to the fumed silica coatings did reduce the "cracks phenomenon" by filling the internal void volume of the fumed silica, which was confirmed by SEM and which is in accordance with former research results (Lee, et al. 2005).



Figures 4 and 5 illustrate the average pore size and porosity properties for each coating, respectively. The porosityrelated characteristics confirmed that the addition of the larger, rhombohedral-shaped PCC pigments to the fumed silica coatings opened the structure of the coating layer. Average pore size and porosity increased with increasing portions of PCC in the coating.





# 3.2. Optical Density

Optical densities of black plotted for the Epson 4000 K3 printer and the HP Z3100 VIVERA printer are shown in Figure 6 and Figure 7, respectively. The density values are lower for the PCC blends versus the fumed silica alone. The addition of PCC roughened the paper surface and opened the coating structure, resulting in poorer ink hold-

out. Although calendering improves smoothness and increases paper gloss, it can cause compression of the coating layer, which in turn affects the ink setting properties. In some cases, higher degrees of calendering caused compression and resulted in lower density. The other colors followed similar trends (as shown in Appendix I).





### 3.3. Color Gamut

Recently, gamut volume with a given printing device has been proposed as a measure of the quality of paper and its coating (Chovancova, et al., 2004, 2005). Color gamut comparisons for each coating are illustrated in Figure 8. Again, the gamut volume of coating samples decreased with increasing portions of PCC in the coating. The coating color with fumed silica as the sole pigment provided a larger color gamut. For the Epson 4000 printer, higher degrees of calendering compressed the coating layer and yielded a smaller gamut volume. For the HP printer, however, applying calendering tended to increase gamut volume for the PCC blends samples. The gamut volume for each coating formulation and two inkjet printers is displayed in Appendix I.



Figure 9 illustrates the color gamut comparison of PCC blended pigments without calendering. The coatings with

increasing portions of PCC tend to have a smaller color gamut in the yellow and magenta areas.



# 3.4. Effect of Coating Pigment Porosity on Color gamut volume

**Reproduction** Pearson's correlation coefficient was used to measure the association between coating pigment porosity and color attributes. The correlation analysis between gamut volume/optical density and porosity-related characteristics for two inkjet printers is summarized in Table 3. It shows that the gamut volume and optical density of coated papers significantly correlates with pigment porosity for the Epson printer at the 0.05 level, with the exception of the black optical density. It shows that there is a strong negative relationship between gamut volume and pigment porosity. That is, the less porous the paper is, the larger the gamut volume it has. For the HP printer, a strong negative relationship was found between average pore diameter and gamut volume, as well as magenta and yellow optical density. Overall, coatings with smaller average pore size and porosity provided better ink holdout capabilities, resulting in higher optical density values. The same trend was observed in the gamut volumes. Smaller pore sizes yielded improvements in color. The addition of PCC roughened the paper surface and opened the coating structure; the ink was absorbed unevenly into the surface of the sheet, resulting in a smaller gamut volume.

		Epson	Printer		HP Printer				
	Ave. Pore	Diameter	Porosity		Ave. Pore Diameter		Porosity		
	Sig.	Ŷ	Sig.	Ŷ	Sig.	Ŷ	Sig.	Ý	
Gamut Volume	0.069	-0.931	0.033	-0.967*	0.017	-0.983*	0.255	-0.745	
Cyan	0.115	-0.885	0.006	-0.994*	0.099	-0.901	0.298	-0.702	
Magenta	0.056	-0.944	0.030	-0.970*	0.048	-0.952*	0.063	-0.937	
Yellow	0.071	-0.929	0.021	-0.979*	0.022	-0.978*	0.218	-0.782	
Black	0.200	-0.800	0.070	-0.930	0.061	-0.939	0.198	-0.802	

\* Correlation is significant at the 0.05 level (2-tailed).

Table 3: Pearson correlation between coating pigment porosity and color attributes (Y represents Pearson's correlation coefficient)

# 3.5. Lightfastness Tests

Table 4 shows gamut volume results before and after exposure. The lightfastness of an inkjet print depends on the chemical composition of the media surface and the diffusion/migration of the colorant into the coating layers. Acidic pH values can favor the hydrazo form of certain azo dyes. The azo form has a better light fastness (Lavery, et. al, 1999). The addition of PCC in the coating formula

tended to increase the UV resistance of the coating with a slightly higher pH value of coating. Figure 10 illustrates color changes after light exposure for 100 hours. As shown in Figure 10, the FSP1 coating (FS:PCC = 85:15) with Epson pigmented inks was the most stable chromophore, whereas the FS coating (FS:PCC = 100:0) with Epson pigmented inks was the least stable.

Samples		Gamut	Decrease [%]	
		Before	After	After 100Hrs exposure
	FS	347,194	281,187	19.01
Epson	FSP1	314,282	271,395	13.66
Printer	FSP2	311,557	256,543	17.66
	FSP3	292,193	235,005	19.57
	FS	478,476	393,401	17.78
HP	FSP1	461,032	386,013	16.27
Printer	FSP2	461,032	385,876	16.30
	FSP3	412,237	339,825	17.57

Table 4: Gamut volume results before and after exposure.



### 4. Conclusions

The commercial ink jet application highly relies on coating pigments to deliver the proper combination of physical and chemical properties. The fumed silica coatings blending with pigments were tested. It shows that the less expensive compatible pigment, PCC, blended with fumed silica pigments is capable of vielding coatings with equal or better smoothness and paper gloss (until 30% addition). The addition of PCC to the fumed silica also reduced the presence of cracks in the coating. However, the pore structure of a pigment is still the key on the color reproduction of the final printed images. Although the tested coating formulations have guite similar average pore size and porosity, their porosity-related characteristics still affect the way color reproduced. In general, a fumed silica coating, with a smaller particle size and a smoother surface, offers lower absorption and leaves the colorant near the paper surface, thereby yielding higher optical density and wider color gamut. The addition of PCC to the coating roughened the paper surface and opened the coating structure, yielding lower optical density and smaller color gamut. Negative relationships were observed between gamut volume/optical density and porosity-related characteristics. That is, the less porous the paper is, the larger the gamut volume and higher the optical density it has. The presence of pigment in the coating formula controlled the lightfastness properties of the print. It was found that the FSP1 coating (FS:PCC = 85:15), which has a higher pH value, tended to have better light stability. Coating formulation impacted the individual inkjet process colors differently. The HP Z3100 VIVERA Inks were held near the surface of the tested coating, resulting in higher gamut volume.

### Acknowledgements

The authors thank Mr. Matt Stoops for help with the coating trial and Sun Chemical Corporation for help with the printing test. Sincere appreciation is also expressed to the Cabot Corporation for donation of fumed silica samples and the Imerys Minerals Ltd. for donation of PCC samples.

### 5. Appendix

		Optical de	nsity and co	lor gamut mea	isurement		
Sample		Calendering	Cyan	Magenta	Yellow	Black	Gamut Volume
	Base paper	0 nip	0.95	0.94	0.99	1.25	232,500
		0 nip	1.54	1.46	1.24	1.77	461,400
	FS	2 nips	1.20	1.34	1.18	1.64	362,300
		3 nips	1.18	1.41	1.16	1.84	347,200
		0 nip	1.35	1.36	1.20	1.69	418,400
Encon	FSP1	2 nips	1.11	1.29	1.12	1.62	321,600
Epson V2 intra		3 nips	1.09	1.28	1.12	1.66	314,300
K5 liiks		0 nip	1.26	1.33	1.15	1.61	393,300
	FSP2	2 nips	1.11	1.28	1.11	1.57	316,600
		3 nips	1.07	1.25	1.10	1.35	311,600
	FSP3	0 nip	1.17	1.20	1.03	1.39	344,100
		2 nips	1.04	1.19	1.09	1.42	294,700
		3 nips	1.04	1.17	1.08	1.38	292,200
	Base paper	0 nip	0.94	1.01	0.92	1.16	216,400
	FS	0 nip	1.45	1.57	1.20	2.11	565,100
		2 nips	1.29	1.59	1.17	1.48	493,100
		3 nips	1.29	1.58	1.17	1.46	478,500
	FSP1	0 nip	1.27	1.43	1.12	1.48	453,500
HP Z3100		2 nips	1.25	1.52	1.15	1.39	466,900
VIVERA Inks		3 nips	1.31	1.52	1.16	1.45	461,000
		0 nip	1.22	1.38	1.11	1.33	438,600
	FSP2	2 nips	1.24	1.50	1.15	1.41	448,400
		3 nips	1.20	1.46	1.13	1.37	461,000
		0 nip	1.21	1.38	1.07	1.26	410,600
	FSP3	2 nips	1.28	1.48	1.15	1.37	431,900
		3 nins	1.12	1.41	1.08	1.31	412,200

Appendix: Color Reproduction Capability

# 6. References

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(first received: 25.03.2012)





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