Application of Nano Pigments in Inkjet Paper Coating

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Abstract

Coated inkjet paper is one of essential factors that dominate inkjet print quality. Coating pigments are the most abundant component that impacts coating layer performance. In high-end coated inkjet paper, fumed silica is the primary pigment in coating formulations, because of its ideal ink absorption and optical appearance. Other pigments have also been widely introduced into silica coating colors. In this study, two nano scale pigments, clay and ground calcium carbonate, were added into a commercial inkjet coating formulation respectively. Meanwhile, two conventional pigments, #1 clay and precipitated calcium carbonate were applied into the formulation as references. All of the formulations were coated paper and paperboard base sheets via a cylindrical laboratory coater. A systematic evaluation has been applied including paper surface conditions, optical properties and printability. These two nano scale pigments were found to increase optical and print performance. Specifically, the nano clay was expected to replace polyethylene layers of premium inkjet paper.

Introduction

Compared with two major digital printing methods inkjet and laser, inkjet is expected to gain the market in the future, and acts as the primary selection to nibble the offset market. The advantage of inkjet printing is obvious that the simplicity design is easy to obtain process reliability. Further, the low procurement, wide format and fast print speed are also interesting to the customers [1]. Specially, inkjet has a print quality advantage, because of its wide color gamut and high print density [2]. Stationary print head (MemJet and HP Edgeline), has been found to significantly improve print speed and quality which will attract customers in the near future. Inkjet print performance is mainly dominated by ink, printer and substrate [3]. Ideally, a substrate should absorb aqueous inkjet ink droplets immediately and minimize ink droplet spreading to obtain high image resolution. Further, to achieve high print density and gloss, the colorants (dye or pigment) should be accumulated on the top of the substrates as near as possible. Currently, colored inkjet printing has to be applied to well-designed coated substrates.

Figure 1 illustrates the construction of premium photographic inkjet coatings [4] [5]. The protective layer is to prevent the image for scratching and finger print, and also improve lightfastness. It is also a porous layer to boost ink penetration. The first imaging layer carries most of colorants, and fixes the ink droplets instantly with minimum horizontal spreading. The second imaging layer mainly takes the rest of the ink, which requires a sufficient ink reservoir. Usually, both imaging layers apply high cost pigments, such as silica and alumina as the primary coating pigments [1]. High strength binders, e.g. polyvinyl-alcohol (PVOH), are applied to bind these pigments with high price [6]. Two extruded polyethylene layers are used to prevent ink penetration to the core sheet in most premium inkjet papers. The films are also a benefit to paper optical property and dimensional stability. The complex yields high manufacturing cost, which significantly limits large scale application. The mainstream of coated inkjet paper seldom applies polyethylene layers.

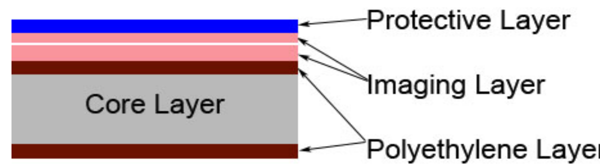

***Figure 1**: Photographic inkjet paper coating construction*

Meanwhile, many other pigments have been introduced into coating formulation to replace part of silica and/or alumina. The incentives are varied; some are set to reduce the manufacturing cost, and the others are to improve coating runnability or specific properties. Even some pigment suppliers promote modified conventional pigments or low resolution printing (e.g. 600 dpi) which eventually replace silica and alumina [7]. In this study, two nano-sized pigments, nano thickness clay (NCY) and nano particle size ground calcium carbonate (NCC) were added into a silica based coating formulation. Conventional clay (CY) and precipitated calcium carbonate (PCC) are also substituted into the same formulation for alternate references. With the acceptance of inkjet printing on paperboard in some packaging areas, both paper and paperboard are used as coating base sheets.

Methodology

A commercial coating formulation for premium glossy inkjet was applied as the control (CON) in Table 1. Fumed silica was the solo pigment in the control color. With a quick screen experiment on optical properties and coating rheology, all of four tested pigments were decided to replace 10 PPH of silica. Detail of formulation is listed in Table 1.

A fumed silica dispersion is provided from Cabot (CAB-O-SPERSE PG01, 30 wt %, Ph = 10), with particle size of 189 nm. Conventional clay is #1 clay from J.M. Huber. The nano thickness engineered clay slurry is from Imerys (Barrisdurf LX, 59 wt %, pH = 6.2). PCC is Alba gloss from Omya with particle size of 1.7 µm. NCC is nano sized ground calcium carbonate slurry (59 wt %, pH = 9.3), an experimental product from an undisclosed supplier. The primary binder is partially hydrolyzed polyvinyl alcohol from Celanese (Celvol 203S, 30 wt %). The co-binder is hydrophobic surface starch from National Starch (FilmKote 54, 15 wt %). An optical brightening agent (OBA) from Clariant is also employed (Leucophor FTS). The solid content of final coating colors is between 27.5~31 %. All of color dispersions were adjusted to pH 10 by NH_4OH.

The paper base (PB) sheet is a sized paper, which has 116 seconds reading from ink resistance test (TAPPI T530OM-02), and basis weight of 66 g/m^2. Paper PPS roughness and porosity are 3.15 µm and 16.5 ml/min (1000 Pa, soft backing), respectively. TAPPI brightness is 90.75%, and paper gloss (at 60°, MD) is 5.6%. The paperboard base (PBB) is applied with pre-coated recycle paperboard with basis weight of 357 g/m^2. Paperboard PPS roughness and air porosity are 3.1 µm and 11 ml/min (1000 Pa, soft backing), respectively. TAPPI brightness is 76.69%, and paperboard gloss (at 60°, MD) is 10.4%.

Table 1: Coating Formulations.

Coating Colors	CON	CY	NCY	PCC	NCC
Ingredients	Dry Parts Added				
Fumed Silica	100	90	90	90	90
Clay		10			
NCY			10		
PCC				10	
NCC					10
PVOH	10	10	10	10	10
Starch	10	10	10	10	10
OBA	2	2	2	2	2

The coating processes were completed via a short dwell, blade type cylindrical laboratory coater (CLC) at 2500 ft/min, single pass. The coating weights of two types of base sheets are 10gsm (paper) and 15gsm (paperboard), respectively. Coated paper and paperboard samples were calendered using a soft nip calender at 170°F, 250 PLI and 2 nips. All samples were conditioned for 24 hrs at 50% RH and 23 °C (73.4 °F) before testing.

Brookfield viscometer and Hercules rheometer were used to predicate the coating runnability. The samples surface conditions were performed with FTÅ200 (dynamic contact angle) and EMCO 30 (ultrasonic water penetration). Paper roughness was measured using a PPS ME-90 (1000 kPa, soft backing) based on TAPPI T555-OM-99. The air porosity was also tested by the PPS at same condition. Paper brightness was measured with a Brightimeter Micro S-5 based on TAPPI T452-OM-98. Paper gloss was measured at 60° using a BYK Gardner Glossmeter based on TAPPI T480-OM-99. Epson Stylus Photo 2200 printer was used for print evaluation. It applies Ultrachrome 4-picoliter pigment ink, at 720 dpi resolution. ORIS Color Tuner 5.5.1, printer RIP software from CGS Publishing was applied to achieve controlled CMYK tint colors. Optical density was measured using an X-Rite 530 SpectroDensitometer on 100% tints. Print gloss was measured on 100% Cyan tint using BYK Gardner Glossmeter (at 60°). A TC3.5 CMYK test chart was printed to determine sample color reproduction performance. These charts were measured with an X-Rite EyeOne IO Spectrophotometer. The generated ICC profiles were used to calculate color gamut volumes using CHROMiX ColorThink 3.0 Pro software. Print mottle was calculated from Verity IA Print Target with an HP ScanJet 4050 scanner [8]. ImageXpert imaging system was applied to observe dot quality and color bleeding.

Results Analyses and Discussions

Paper Surface Condition Evaluations

The differences of paper and paperboard roughness and air porosity are negligible without considering the base variance. The results are seen in Table 2. The reason is clear that only 10 PPH test pigments have been added into coating colors. These limited dosages could not influence these properties in such a large scale.

Table 2: Paper PPS roughness and air porosity.

CON		CY		NCY		PCC		NCC	
PB	PBB	PB	PBB	PB	PBB	PB	PBB	PB	PBB
.9	1.4	.8	1.4	.8	1.4	.8	1.1	.7	1.2
.1	.2	.1	.1	.0	.1	.1	.1	.1	.1
2.6	6.7	3.4	6.3	4.1	6.7	3.1	5.7	3.4	6.5
.1	.9	.3	.9	.4	.9	.3	.5	.2	.5

Paper roughness and STD: microns (top two rows); paper air porosity and STD: ml/min (bottom two rows)

Paper contact angle and ultrasonic water penetration experiments unveiled how these pigments affect wetting and absorption. These tests were only measured on paper base coated samples. Figure 2 illustrates the contact angle movement curves on samples during 10 seconds test. The water droplet volume curves recorded the droplet volumes fluctuation during the penetration. These readings were normalized by their initial values.

Pigment NCY presented significant barrier performance, even with such small amounts. For example, the quick decline of the curves in Figure 2indicates fast ink penetration and wide ink spreading. NCY, the top lines of Figure 2, had the least decline curves among all of samples. Its blocking function was also admitted during the ultrasonic water penetration. The ultrasonic water penetration test provides two parameters; t_B is the time with maximum transmission, which is the elapsed wetting time; t_S is the time with most negative gradient, which refers to peak absorbency time. In Table 3, NCY had the highest t_S time, which indicates a barrier behavior. Figure 3 records the ultrasonic wave intensity curve versus time (10 seconds). Many employ this chart to explain paper sizing [9]. NCC presents a relatively fast penetration rate (or intensity declining sharply), comparing with others. It could be interpreted that NCC increased the ink penetration rate. However, this hypothesis needs to be confirmed with other experiments.

As suppliers claimed, NCY is designed to replace wax and/or polymer films in packaging, where a barrier is needed. According to the illustration of photographic coating construction in Figure 1, the primary function of polyethylene layer builds a barrier to further ink penetration into the core sheet. The current extrusion process and other treatments (e.g. corona surface treatment) definitely prevent its wide application. Therefore, applying NCY to replace polyethylene film seems to be attractive and feasible. It will be instrumental to the environment and paper recycling. For certain situations, such as print packaging paperboard with inkjet, NCY coating layer could carry a barrier function for both packaging and printing purposes. Certainly, this experiment was not enough to discover the pros and cons, such as the effect on optical properties.

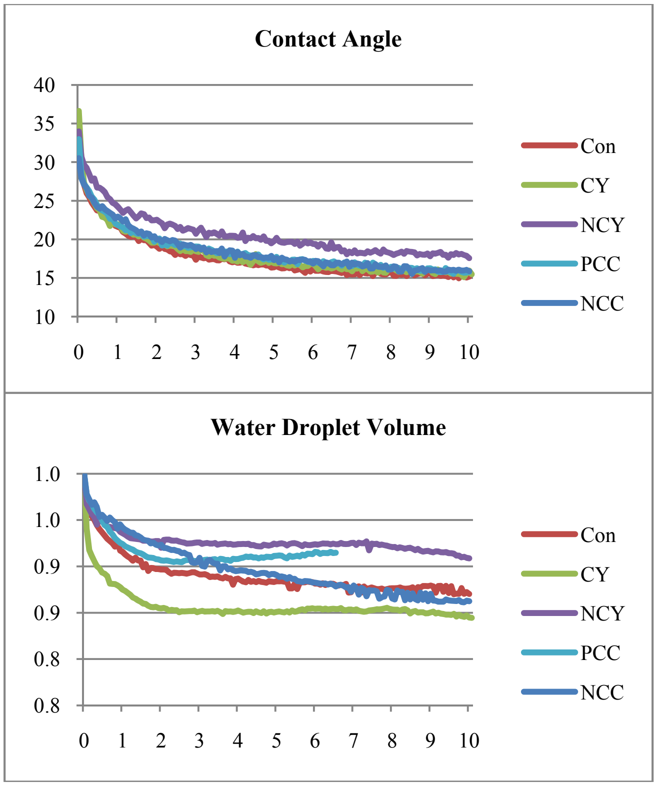

Figure 2: Paper surface contact angle and water droplet volume curves.

Table 3: Ultrasonic Water Penetration

Sample	CON	CY	NCY	PCC	NCC
t_B: *ms*	442	678	182	593	457
t_S: *s*	3.9	3.6	5.4	2.9	4.1

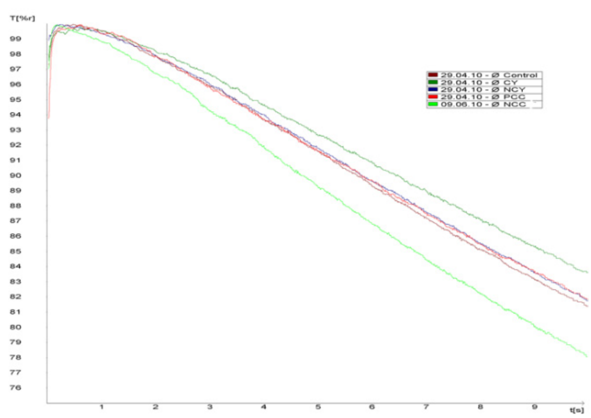
Figure 3: Ultrasonic water penetration.

Paper Optical Property Evaluations

Paper brightness influences print contrast and color reproduction; and indeed it is one of significant factors for print appeal [10]. Figure 4 shows whether pigment type or particle size did not significantly affect the paper brightness of samples. With only 10 PPH loads of the other pigments, silica dominated the pigment influence on paper brightness.

Paper gloss also impacts print contrast and the perception of print "depth" [11]. Generally; pigment and binder properties significantly affect paper gloss within a coating formulation. In this glossy finish formulation; CY slightly decreased the paper gloss in both base sheets, see Figure 5. NCY, PCC and NCC likely had the ability to increase paper gloss; apparently on paper board base, which had high coating weight. It's said that PCC can increase paper gloss due to "healing" of silica cracks [12]. Hypothetically, the two nano pigments did the same work as PCC did.

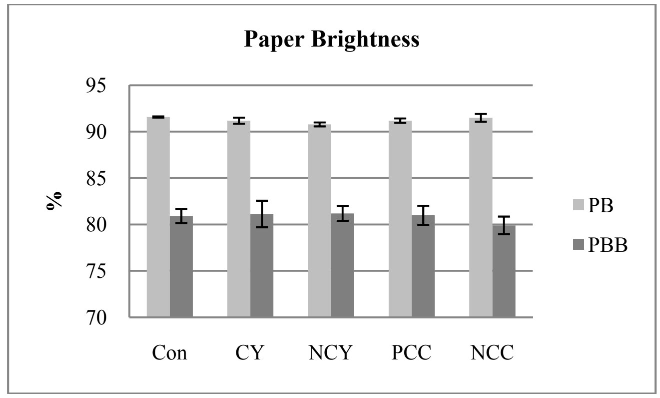

Figure 4: Paper brightness.

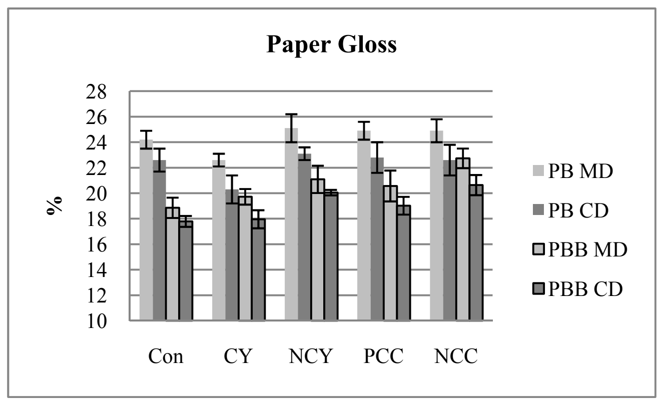

Figure 5: Paper gloss.

Printability Properties Evaluations

Print density and color gamut are two common attributes to determine the print quality [13]. In this print evaluation, CMYK solid color print densities are illustrated in Figure 6. Whether on paper or paperboard, the differences between samples were negligible, which indicated the tested pigments having weak impact on print density. The reason could be interpreted that 10 PPH foreign pigments did not alter the print density appreciably. Paper based samples had overall higher values than paperboard, because paperboard could trap more colorants beneath the coating layer. Hence, less colorant contents decrease the density values.

In Figure 7, paper based samples present comparable color gamut values with the control. However, NCY, PCC and NCC yield a higher reading on paperboard sheets, compared with CON and CY; PCC had the highest. The differences were related to the coating weight. The paper base sheet was only 10 GSM which significantly less than the counterpart, 15 GSM. Even only applying 720 dpi print resolution, paper based samples could not hold such large ink volumes. Therefore, some color patches (composite colors) were smeared which did reduce the accuracy of color gamut volumes. This issue revealed a fact that the minimum coating weight was important. For certain measurement, e.g. TC3.5 CMYK test chart, a minimum coating weight versus print resolution table should be set up. Unfortunately, none of test standards has discussed the issue.

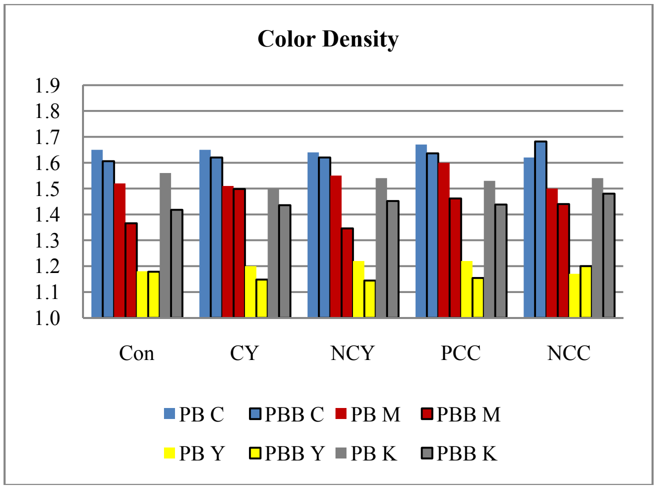

Figure 6*: Print density.*

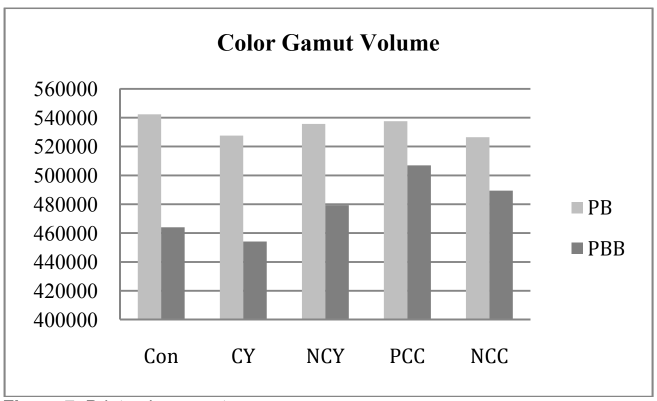

Figure 7*: Print color gamut*

Print gloss is illustrated in Figure 8, which was measured from solid cyan tint of each sample. Delta gloss reflects the gap between print gloss and paper gloss which is also illustrated in Figure 9. For paper based samples, the CON had the highest gloss; although the difference with others was not significant. On the paperboard samples, all of NCY, PCC and NCC obtained higher value than CON and CY's. This phenomenon was corresponding with the gains on their paper gloss, as previous discussing. Specially, paperboard based sample obtained larger delta gloss than paper based did; even the first ones had lower paper gloss than the later ones. Since there were no other clear factors between two kinds of samples, we concluded that the coat weight played an important effect on these results.

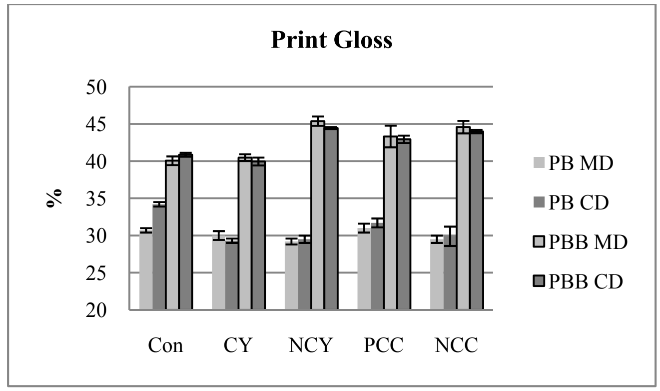

Figure 8*: Print gloss.*

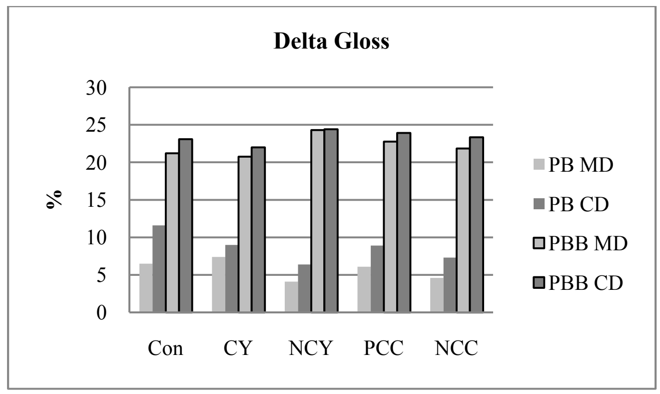

Figure 9*: Delta gloss.*

Print mottle is a major issue of printability which could be related to every print factor [14]. In this experiment, paper surface physical properties, such as surface roughness, air porosity, surface energy and ink penetration are the major concerns. In Figure 10, both CY and NCY produced lower print mottle on both substrates, comparing with the others. Since both pigments are platy shape, which distinguishes them from others, clay plays as a good coating ingredient to reduce mottling [15]. Meanwhile, paperboard samples had higher print mottle than paper ones, which should be associated with its rough surface.

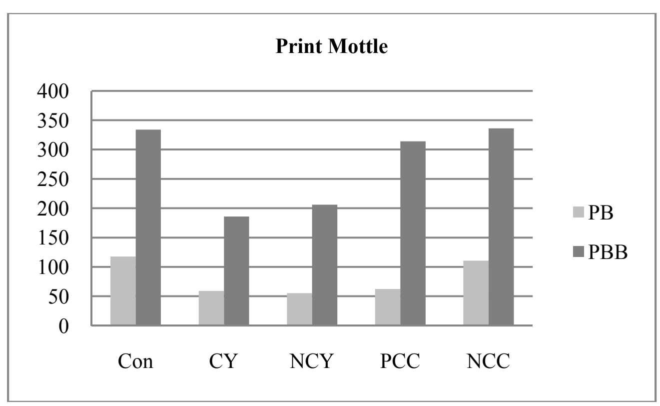

Figure 10*: Print mottle.*

To evaluate the detail of dot fidelity and print resolution, a single pixel matrix was created in Adobe Illustrator. An eight-pixel blank gap between to two solid tints was used to determine color bleeding, in Figure 11. Yellow tint was applied because the ink cartridge has two units for each CMK color. Only paper based samples underwent this test.

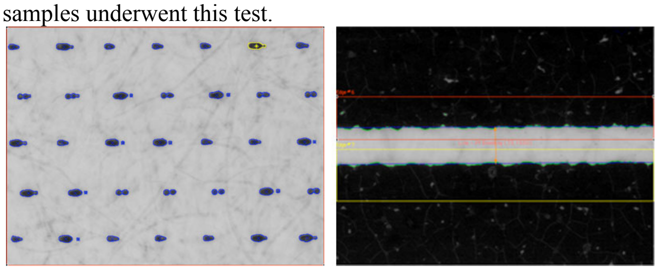

Figure 11*: Print dot fidelity and color bleeding.*

Conventionally, the one with small dot radius and high roundness represents a high print resolution. From Table 4, all of samples had almost the same values, which should be believed with the same print resolution. However, the color bleeding test led a converse conclusion. The wider gap width indicates less ink spreading (from solid area), or meaning better print resolution. CON and NCY had the widest gap and was able to obtain good print resolution. NCC had the narrowest width that meant poor performance. In addition, NCY performance was matched to the prediction from its contact angle curve. Considering the conclusion from the dot and bleeding analysis, the conflicting results meant both methods were insufficient. A reliable method for inkjet print should be explored in the future.

Table 4: Print dot fidelity and color bleeding

	CON	CY	NCY	PCC	NCC
Roundness	.73 ± .13	.75 ± .15	.78 ± .13	.79 ± .13	.76 ± .14
Radius*	9.2 ± 3	8.8 ± 3.3	9.2 ± 3.5	8.8 ± 3.3	8.9 ± 3
Bleeding*	73.2	71.6	73.2	72.1	70.1

**Unit: Pixel*

Conclusions

This experiment concentrated on two nano-sized pigments, NCY and NCC, to determine their performance in a glossy premium inkjet coating formulation. Two base sheets, paper and paperboard, were applied. NCY presented an interested potential application in inkjet coatings. NCY could boost paper gloss and print gloss, especially with a high coat weight. It was found to increase color gamut and reduce print mottle. It was also beneficial to print resolution, due to better color bleeding performance. Moreover, its barrier nature could be used to replace the polyethylene film in premium inkjet substrates. Although this experiment did not really work on this purpose, its predicted values on cost saving and environmental issue seem meritorious. NCC were found to improve paper gloss and print gloss as PCC did, which could be associated with reducing silica cracking phenomenon. However, no other positive impact is found.

Meanwhile, two conventional test methods, color gamut volume and print resolution, were found to lack efficiency under certain test conditions. A minimum coating weight should be considered in case of ink smearing. Conventional dot fidelity analysis might not be suited to inkjet print evaluation, due to large volume ink droplet and low viscosity.

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