Seeking New Alternatives: The Evaluation of Precipitated Silicate and Silica for Inkjet Media

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Abstract

New or alternate materials are of interest to formulators striving to gain an edge in inkjet printable media whether it is in performance or cost. Much of media development activity lies in bridging the gap between copy paper and photo quality media. These mid-range products are required to have a competitive edge in performance while maintaining a consumer friendly price. Formulators need a selection of materials in order to actualize media products that accomplish these objectives.

This paper examines the performance of precipitated silicate, precipitated silica, and calcium carbonate in inkjet media. Following well established guidelines in formulating an ink receptive coating, these alternate materials are utilized as the primary pigment in a matte formulation. The resulting coating takes advantage of absorptive properties and particle sizes to create a porous structure useful in inkjet printing.

Introduction

Inkjet media specific paper first came on the scene with the objective matching the performance of silver –halide photo paper in look and feel. It was learned early on that premium inkjet print quality was achieved when the substrate was covered with an ink receptive coating with sizable pores, high porosity, and good wetting profiles. [1] Silica gel's high porosity makes it a natural choice. Achieving a high level of porosity led to high color gamut, excellent optical density, and reduced bleeding and wicking. Whether the silica is used as a single pigment system or part of a combination, it can be stated that gel, fumed, and colloidal silica are the primary performance components of inkjet coatings and that silica has been very difficult to replace without sacrificing quality.

Now that many industrialized nations are fully immersed in the digital age, a variety of digital technologies are being employed in commercial print houses where analog processes once reigned. Thus, new applications for inkjet printing have risen in high speed web printing. This has also created a need for media that can handle the particular aspects of high speed, inkjet printing.

Conventional printing paper is designed to provide optimum printing with analog inks that contain significantly lower levels of ink vehicle. These types of papers do not have the capacity or porosity to achieve the quick dry times to set inkjet inks. The additional dry time becomes critical on the high speed presses as the ink dry times then determine the speed of the printer. The challenge is to balance the ink dry times with print properties of color gamut, optical density, bleeding and strike through. [2] All while keeping media costs suitable for the application.

High-speed web inkjet printing has opened the door to alternative materials and pigment manufacturers have spent a great amount of time developing products that may be suitable for the application by modifying and engineering new versions of traditional pigments. Modified, engineered, and precipitated structures have high surface area and internal pore volume. Utilization of these types of materials in a coating should create a porous structure that traditional pigments, like clay, were unable to achieve. Knowing what was learned from photo-quality media, the porous coating structure is crucial for achieving the fast dry times and good print quality.

Experimental

The silicates and silica selected for this study were chosen because their precipitated structures have high surface area and demonstrate an ability to absorb liquids while having the potential to be economically suitable for commodity papers. The properties of the silicates and silica are summarized in Table 1. Silicate A is a precipitated sodium aluminum silicate. Silicate B is a precipitated calcium silicate. Silicate C is a precipitated magnesium silicate. Silica D is modified precipitated silica. ECC is a calcium carbonate.

Table 1. Properties of Trial Materials

Material	Surface Area (m2/g)	pH (5%)	Oil Absorption (g/100g)	Particle Size (microns)
Silicate A	100	10.7	185	9
Silicate B	60	10.5	175	7.5
Silicate C	50	10	60	5.7
Silica D	165	6	230	18
ECC	70	9	105	2.4

The starting point of this experiment utilized a standard inkjet formulation containing polyvinyl alcohol (PVOH), polyvinylpyrollidone (PVP), and cationic mordant. Polyvinyl alcohol is frequently chosen as the binder for inkjet coatings because the pigments employed for optimum print quality are high surface area materials with significant binder demand. Exercising a strong binder like PVOH allows the formulator to lessen the binder content allowing for maximum pigment effect. [2] The PVOH employed throughout this experiment was Poval PVA-235 manufactured by Kuraray. It is a super high molecular weight, partially hydrolyzed PVOH. Data advocates super-high molecular weight PVOHs, such as PVA 235, to produce coatings with minimal cracking. [4] PVP controls ink spreading, bleeding and holds it at the surface. [5] Finally, the ink is fixed and immobilized to the media through the use of a cationic mordant. The addition of a polymeric amine results in improved print properties such as, gamut, optical density and permanence. [6]

Although binders are considered the glue of the formulation, they must be considered carefully because they impact the resulting surface chemistry and porous structure. This is especially true for PVOH with its hydrophilic nature which assists in absorption of water based inks leading to reduced wicking and bleeding. Although both fully hydrolyzed and partially hydrolyzed PVOHs are used in inkjet formulations, partially hydrolyzed PVOH gives better optical density and dry times when used with silica pigment. [2] The binder's impact doesn't end there. Low molecular weight PVOH can be absorbed into the pores and reduce the efficiency of the ink absorption thus affecting print quality. [7] Lastly, PVOH affects the coating structure and influences the overall average pore size. [6]

Many researchers have demonstrated that alternate materials require only a portion of the PVOH utilized in traditional porous coatings encompassing silica. [8, 9, 10] Therefore, it was surmised that each material should be formulated at three binder levels to discover the optimum level for each material for coating strength and performance. Three formulations were prepared with pigment binder ratios of 100:10, 100:30, and 100:50. The pigment PVP ratio was kept constant at 100:30 and the cationic addition remained constant throughout the experiment at 1.44 %. The final solids content was kept constant at 14.45 %.

The formulations were coated onto Syntheape paper, a non-porous synthetic paper, using an automatic coater fitted with a 100 μm KBar to ensure an even coating with a target coat weight of 9 gsm was produced. The paper was dried in an oven at 110°C for 20 minutes.

The experimental coated Syntheape papers were printed on a Hewlett Packard Officejet Pro K5400 and Epson Stylus Photo R300 with an ImageExpert test pattern. A commercially available Hewlett Packard sheet of 175 gsm was also printed as a reference. Each print was assessed for a range of inkjet print criteria. X-Rite 938 Spectrodensimeter measured the color gamut and optical density. Optical density was calculated from the sum of measured C, M, Y, and K optical densities. Gamut was calculated from the sum of the absolute value of CIE a* and b* parameters for C, M, Y, B, R, and G colors. For optical density and gamut, a higher number represents a better value. Other print properties were assessed using Imagexpert analysis software. The properties were measured on a scale of 1 – 6 with lower numbers representing better print quality.

Results and Discussion

Coating Characteristics

It was observed, with the exception of Silicate A, that the experimental formulations have a few undesirable characteristics. Silicate B appeared to be incompatible with the inkjet formulation resulting in a poor dispersion and solids separation. The resulting coated sheets had poor patchy coverage. This material was deemed unsuitable for this experiment and eliminated from further evaluation. Silica D and ECC had a hard settlement requiring vigorous remixing prior to coating the Syntheape. Silicate C produced a soft settlement which required only slight remixing to prepare for draw downs. Silicate A produced limited settlement and did not require any additional mixing.

Table 2. Formulation Viscosity

Formulation	Viscosity (cps)			
	10rpm	20rpm	50rpm	100rpm
A @ 100:10	0	20	28	40
A @100:30	380	350	260	212
A @ 100:50	240	350	336	288
C @ 100:10	0	10	24	36
C @ 100:30	620	440	260	206
C @ 100:50	1040	770	522	408
D @ 100:10	0	10	28	46
D @ 100:30	100	130	136	140
D @ 100:50	320	330	332	320
ECC 100:10	0	0	12	24
ECC 100:30	640	620	480	342
ECC 100:50	240	250	244	238

The viscosity of the remaining formulations is presented on table 2. The lowest binder level of 100:10 presented some challenges in obtaining an even coating on the Syntheape due to the very low viscosity. This would indicate that the total solids content could be increased for silicate and calcium carbonate formulations at low binder levels. This would be advantageous for improved runnability on a coater and increased coat weights applied to the substrate. The other binder levels developed adequate viscosity for coatings.

Pigment to Binder Ratio

The next step was to determine which binder level worked synergistically with the materials to produce optimum print quality. The color gamut and optical density for the papers printed on the HP K5400 can be found in Figures 1 and 3. The color gamut and optical density for the papers printed with the Epson R300 can be found in Figures 2 and 4. The data indicates that each experimental material responds differently to the level of PVOH. Silicate A performed consistently on both printers with an optimum level of PVOH at 30 parts. Silica D with 30 parts of PVOH was determined

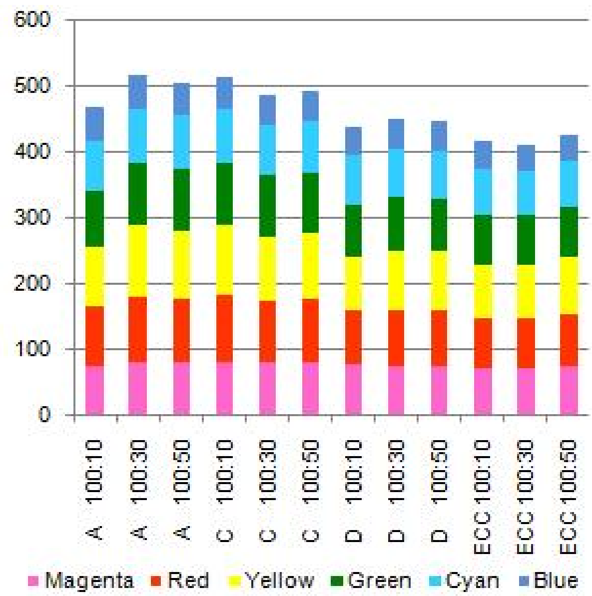

Figure 1. *Color gamut on Officejet K5400*

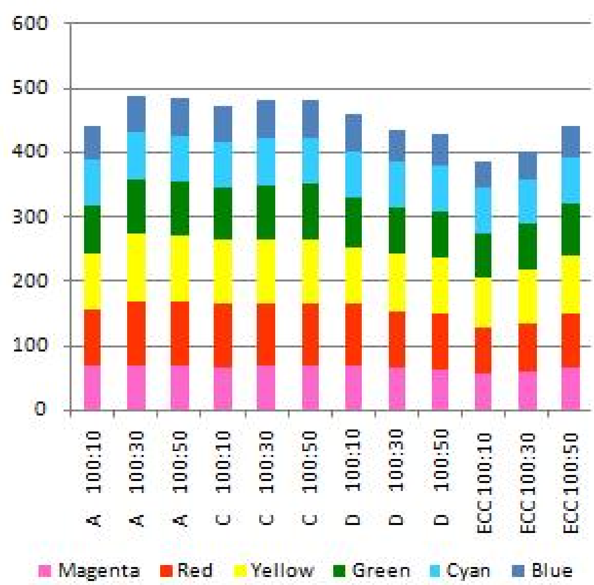

Figure 2. *Color gamut on Photo Stylus R300*

to be the optimum level because it gave the best optical density on both printers and the best color gamut on K5400. Silicate C achieved its best results in optical density with 10 parts of binder on both printers. Lastly, the ECC performed best at a level of 50 parts of binder on both printers. This was an unexpected result as most experiments with calcium carbonate formulate 10 parts or less of PVOH. [8, 9, 10]

Print Quality

An ink receptive coating that can deliver truly good print quality must excel in all of the print attributes. A print with perfect line roughness and no color to color bleed will be

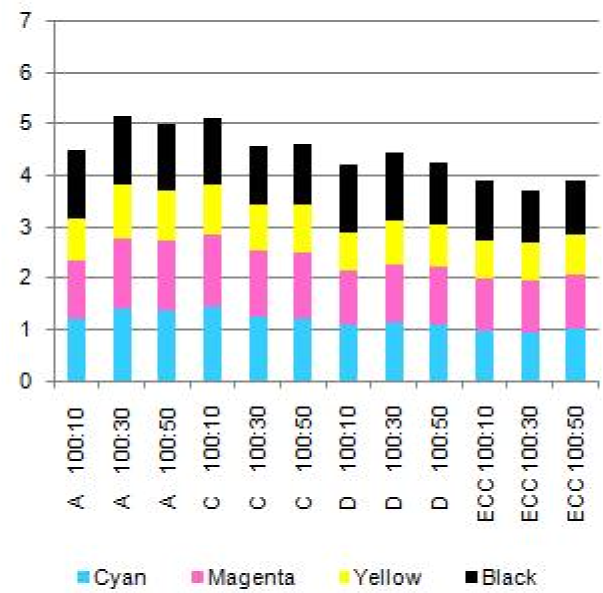

Figure 3. *Optical Density on Officejet K5400*

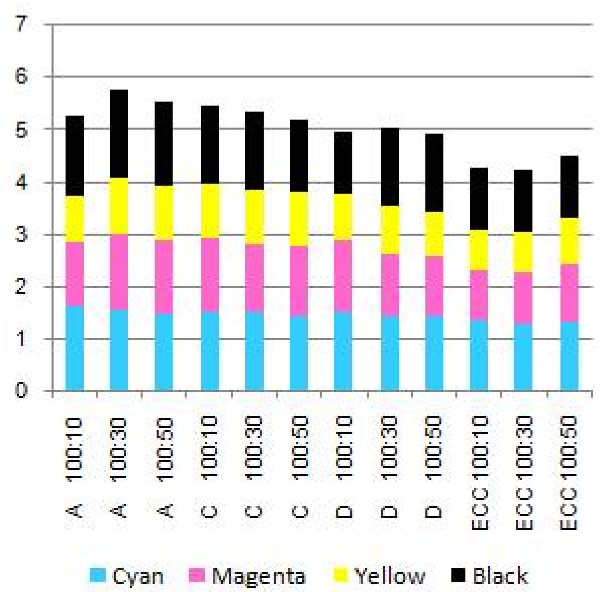

Figure 4. *Optical Density on Photo Stylus R300*

viewed as insufficient if the optical density is poor. The opposite holds true as well. Preventing the penetration of ink into the coating results in higher optical densities but unless the ink is immobilized quickly, the resulting print will be blurry as well as bright. Therefore, there is no one attribute which is more important than the other.

This fact is especially apparent in the ECC evaluation. The bleed and line roughness results on the ECC is only marginally worse than the other materials. Subjective visual evaluation of the sheets also indicates that the print quality of the ECC is comparable to the other materials except in optical density and color gamut. Figure 5 demonstrates the visual effect of poor optical density and color gamut achieved by the

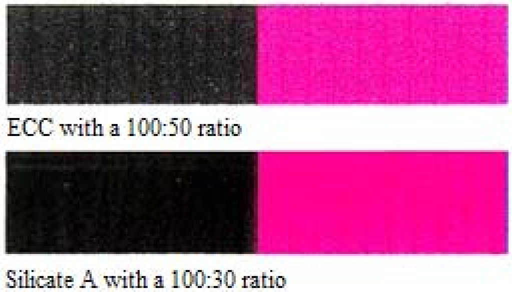

Figure 5. *Black and magenta blocks printed by Officejet K5400.*

ECC. The gamut and optical density results shown Figures 1 – 4 indicates that the calcium carbonate utilized in this study produced much lower optical densities and gamut than the other materials. Calcium carbonate formulations with low contact angles result in a high absorption rate that leads to low optical densities because the ink is absorbed before the colorant can be fixed at the surface. [10] It is likely that the absorption of the colorant into the porous coating leads to a reduced color gamut as well.

Silica D performs well on both printers in the areas of line width and line roughness but is similar to ECC in that its optical density and color gamut are poor. The color gamut is shown in Figure 6. The oil absorption for Silica D is 230 g/100 g. This is the highest oil absorption of experimental

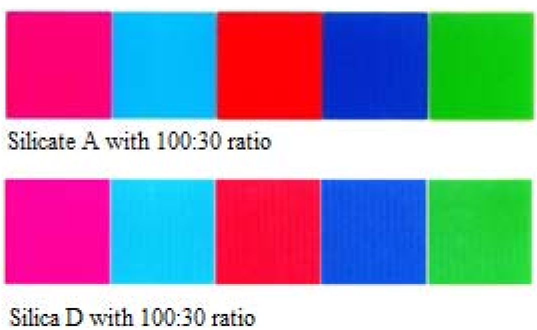

Figure 6. *Color gamut prints by Officejet K5400.*

materials as shown in table 1. It is surmised that the optical density and color gamut suffered because the ink was able to penetrate beyond the surface of the coating due to the high absorption property of Silica D.

It has been the goal in the inkjet market to produce a universal sheet to work with all printer inks. This is a challenging task, as is demonstrated in the print analysis shown in Figures 7 and 8. The Silicate A performs the best on the HP K5400 printer and the worst on the Epson R300 printer in print analysis. The print quality of the ECC printed with the K5400, which is the worst, is equal to the best result on the R300 achieved using Silica D. In the case of Silicate A, the 100:10 ratio had better bleed and line roughness than the 100:30 ratio. This is demonstrated in Figure 9. So, although both printers use dye based inks, their chemistries interact

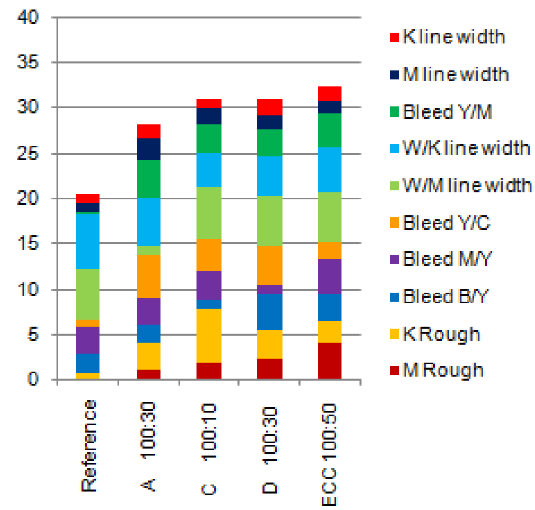

Figure 7. *Print analysis of prints from the Officejet K5400*

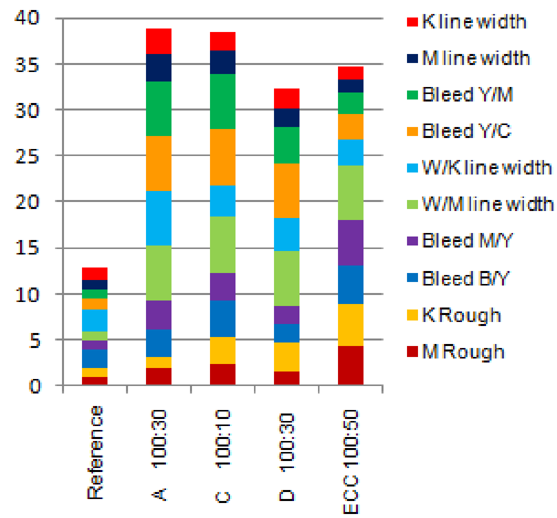

Figure 8. *Print analysis of prints from the Photo Stylus R300*

differently with each of these materials. Further optimization is needed of the other components of the formulation to create an acceptable universal coating.

Conclusion

Four of the five materials evaluated showed an ability to create an ink receptive coating that works with dye based inkjet printers. Although none of the materials performed consistently throughout the evaluation, Silicate A had the best overall performance. ECC and Silica D had poor optical density and color gamut and would need further examination to determine if those properties could be improved by adjusting the fixative.

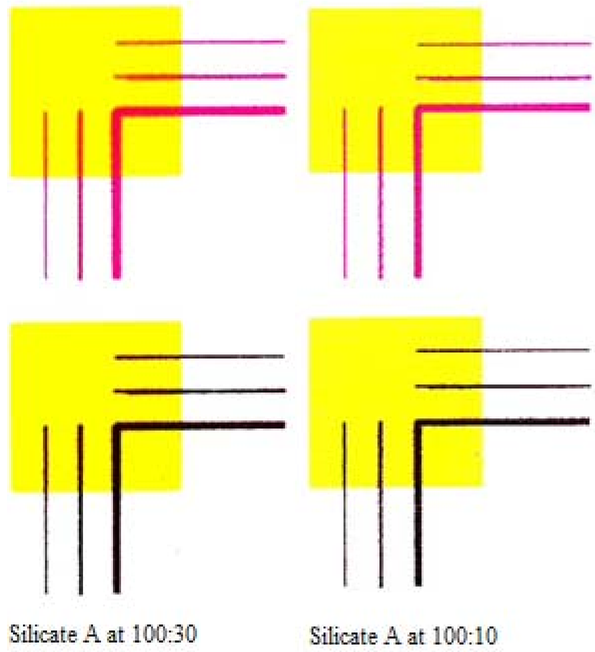

Figure 9. *Line width and bleed from papers printed on Photo Stylus R300.*

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