Effect of Silica Pore Characteristics on Inkjet Print Attributes

Sanjay A. Monie, Beate C. Stief and Natalia V. Krupkin; Grace Davison, W.R. Grace and Co., Conn.; Columbia, MD/USA

Abstract

Simple pore-volume measurements are not sufficient to fully understand the absorption of inkjet inks into microporous inkjet media, especially as manifested in print artifacts such as ink coalescence, ink bleed and ink drying time. In this paper, we will investigate the influence of other pore characteristics such as pore size and distribution on the aforementioned print attributes, using porous silica pigments, both commercial and under development. This paper will also look at the influence of coat-weight in overcoming bleed and coalescence and its implications for microporous coating design.

Introduction and Background

As the inkjet media market is gradually transitioning to microporous coatings, primarily based on silica or alumina, it is important to fully understand the mechanisms of ink uptake by these coatings, especially as printers get faster, and the demands on the coatings to contain the ink-liquids grow. One of the primary functions of a microporous coating is to rapidly absorb the aqueous ink vehicle away from the surface and into the porous microstructure.

Previous studies have looked at the penetration kinetics of ink into porous media from a more theoretical standpoint[1, 2]. Desie et al.[1] explain ink penetration on the basis of Darcy's law, which describes the vertical absorption of a drop initially at rest into a porous layer, and the Davis-Hocking model, which describes the kinematics of absorption in terms of the Lucas-Washburn equation. These authors have proposed that three main phases are involved in ink absorption into a microporous coating: inertial spreading, absorption, and evaporation of the liquid. Strictly speaking, these phenomena primarily apply to dye-based inks, where the predominant mechanism of ink uptake is capillary wicking. In the case of pigmented inks, the study shows the formation of a filter cake on the surface of the microporous layer, absorption through which becomes the rate-limiting step in ink absorption, rather than a capillary wicking process by the coating. Previous studies at Grace Davison have looked at pigmented inks and their interaction with porous silica media in greater detail[3, 4].

Previous studies have also characterized the effect of silica pore size and distribution on color density and dot formation characteristics of microporous inkjet coatings [5, 6].

In this study, two commonly observed print defects – coalescence and bleed, will be examined in terms of the pore structure of silica-based microporous coatings. Bleed is a phenomenon in which the ink migrates laterally within the coating, causing colors to run into each other. Coalescence is a phenomenon where the ink pools on the coating surface and dries before it can be absorbed by the coating. Sheets with a tendency for coalescence may also have longer drying times.

Experimental

In this study, eight silica slurries were studied. Five of these (A, B, C, D, E) were porous silica slurries made by Grace Davison. The remaining three (F, G, H) were fumed silica slurries from other suppliers. Table 1 reports the physical properties of the samples used in this study.

These materials were made into a simple pigment-binder coating using a polyvinyl alcohol from Kuraray (Poval® PVA-235). The pigment/binder ratio was kept high at 85:15 to maximize the effect of the pigment. All the coatings were made at the same % solids so as to get reliable coat-weights in the laboratory drawdowns. The coatings were then drawn-down on a transparent Melinex® 454 substrate using a K Control Coater (RK Instruments) with wire-wound rods. The sheets were then printed on an Epson Stylus Photo 870 printer (dye-based), which we have found to be the most demanding printer in terms of ink-lay down, allowing us to see differences in print performance. The print-settings used were best quality for 'Photo Quality Inkjet Paper'.

The porosities of all the silica slurries were characterized using nitrogen adsorption porosimetry (BET method) and mercury penetration porosimetry. The nitrogen porosimetry was conducted on a Tristar 3000 Analyzer (Micromeritics Instrument Corp.). Mercury porosimetry was conducted on an Autopore 9520 (Micromeritics Instrument Corp.)

Table 1: Materials and Key Physical Properties

Sample ID	Description	Solids (%)	pH	APS (μm)
A	Silica Slurry (Grace)	25	8.7	0.39
B	Silica Slurry (Grace)	26	7.5	0.34
C	Silica Slurry (Grace)	25.4	9.1	0.37
D	Silica Slurry (Grace)	25.8	9.0	0.34
E	Silica Slurry (Grace)	25.3	6.6	0.32
F	Fumed Silica Slurry	20.3	9.5	0.23
G	Fumed Silica Slurry	23.9	3.9	0.27
H	Fumed Silica Slurry	37.8	2.4	0.23

Results

Print Performance and Observed Defects

Table 2 lists the primary print defect observed for each of the samples studied. Samples A, C and F showed a clear tendency towards bleed, whereas B, D, E, G and H showed a tendency towards coalescence. A comparison with the typically reported pore-volume (Nitrogen BET at 0.967 P/Po) shows that the occurrence of these defects cannot be simply correlated with the pore-volumes.

Table 2: Samples and Observed Print Defects

Sample ID	PV (cc/g)	Primary Print Defect
A	0.64	Bleed
B	0.63	Coalescence
C	0.76	Bleed
D	0.71	Coalescence
E	0.84	Coalescence
F	0.87	Bleed
G	0.67	Coalescence
H	0.51	Coalescence

The prints from the various samples on the Epson 870 printer at an intermediate coat-weight (~ 12-15 gsm) are provided as an Appendix at the end of this paper. At these coat-weights, the print defects were readily distinguishable, while not being as severe as at the lowest coat-weights (~ 7-8 gsm). Bleed is typically observed in the test pattern as bulging of the color blocks, and/or lack of edge definition in the lady's picture, and/or feathering and running of the color bands into the adjacent colors. Coalescence is usually observed as discrete circular spots, especially common in the green and blue patches. The diameters and pattern of the spots can vary.

Effect of Porosity on Bleed and Coalescence

In order to relate these phenomena to the pore structure, the samples were analyzed using nitrogen adsorption and mercury porosimetry. These data provided detailed information on pore-volume as a function of pore-size distribution in the coatings. Figure 2 shows the cumulative pore-volume as a function of average pore-diameter for nitrogen adsorption, and Figure 3 shows the cumulative pore-volume as a function of average pore-diameter for mercury penetration.

Nitrogen adsorption is especially sensitive to micro- and mesoporosity (i.e., pores up to ~ 500 Å), and mercury porosimetry is better able to characterize larger 'macropores' (>> 500 Å). Figures 2 and 3 show both sets of data in general agreement. A comparison of these data with the print defects reported in Table 2 shows that for samples A, C and F, which have the smallest pores, the primary print defect is bleed. As the pore-size distribution tends towards larger pores (Samples B, D, E, G and H) the primary print defect is coalescence. As mentioned earlier, these defects do not correlate with the pore-volumes reported in Table 2.

The following mechanism for these effects is proposed. In the case of the samples with smaller pores, the theory suggests that there is a greater driving force for capillary wicking. As a result, the rate of uptake of ink into the coating is rapid downwards towards the substrate. However, if the ink reaches the substrate, as in the case of low coat-weights, it starts to migrate laterally, resulting in bleed. Depending on the extent to which this occurs, the severity of bleed can vary. In the case of the samples with larger pores, there would be a smaller capillary driving force to pull the ink into the coating. As a result, the residence time of the ink on the coating surface is longer. The excess amount of ink that is unable to penetrate the coating before it dries results in coalescence. The particular appearance of coalescence on the surface will be affected by the surface-energy and wetting behavior of the coating surface. In samples prone to coalescence, bleed was observed as a secondary defect. Since coalescence appears to be a phenomenon influenced by competing rates of ink-penetration and drying, some ink will penetrate into the coating and may manifest itself as bleed. However, in these samples, coalescence is the primary defect.

Mercury porosimetry was also performed on the coated sheets to confirm that the coating process did not alter these conclusions. The same trends in the porosity data were found to hold true for these samples.

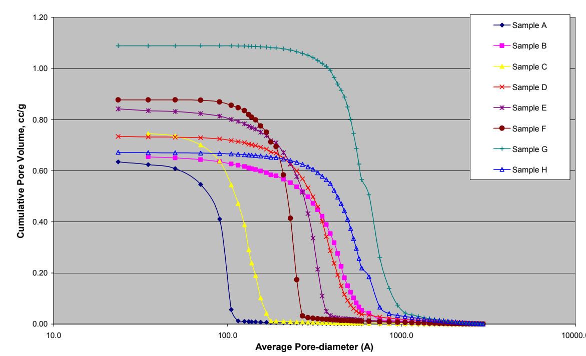


Figure 2. *Nitrogen adsorption pore-volumes of various samples.*

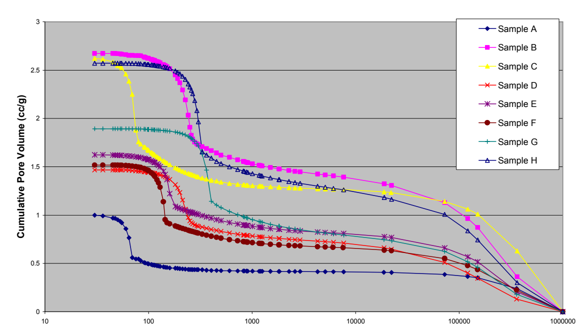


Figure 3. *Mercury porosimetry pore-volumes of various samples.*

Influence of Coat-weight on Print Defects

In evaluating these print defects, three different coat-weights were targeted, a low coat-weight (~ 7-8 gsm) where any print-defects would be most severe, an intermediate coat-weight (12-15 gsm), where differences between bleed and coalescence may be more easily differentiable, and a high coat weight (~ 25 gsm), to see if these print defects could be effectively eliminated by increasing the coat-weight.

In order to study the effect of coat-weight on these print artifacts, all the printed samples were rated for degree of bleed and coalescence on a scale of 1 – 5 (1 = Best). Figures 4 and 5 show the degree of coalescence and bleed of the printed sheets vs. the coat-weights, respectively. In the case of coalescence, as seen in Figure 4, Samples B, G, and H (which have the largest pores), have problems with coalescence at all three coat-weights tested. Samples A, C and F, which have mostly small pores do not show a coalescence problem. For samples D and E, which have an average pore-size between the two extremes, there is some degree of coalescence at low coat-weights, but is largely overcome at coat-weights around 25 gsm. These data show that for samples with very large pores, coalescence might be a difficult problem to solve at a reasonable coat-weight.

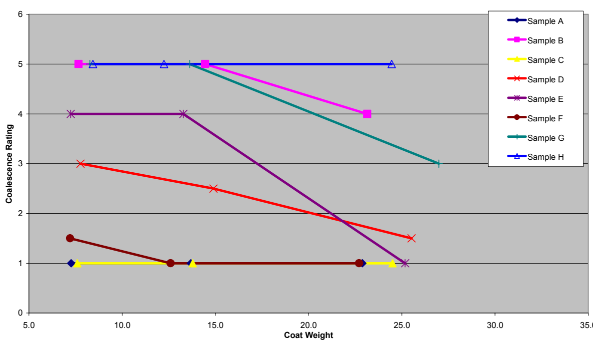


Figure 4. *Effect of Coat-weight on Coalescence Rating of Samples*

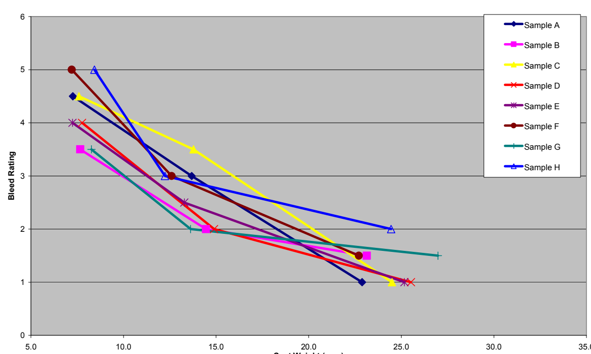


Figure 5. *Effect of Coat-Weight on Bleed Rating of Samples*

In the case of bleed, as seen in Figure 5, all the sheets show some amount of bleed at the low–coat weights. Samples, A, F and C, which have the smallest pores, show significant bleed at the lowest coat-weight, but not as much at higher coat-weights. Sample H with large pores, showed a significant amount of bleed at the lowest coat-weight, but also severe coalescence. In samples B, D and E also, which have larger pores, bleed was present as a secondary defect at the lowest coat-weights, but coalescence was the primary defect. As discussed before, this indicates that even though coalescence was the primary defect for these samples, the low coat-weight was insufficient to accommodate the volume of ink that was able to penetrate the coating, resulting in bleed. In all cases however, there was a progressive improvement in bleed with increasing coat-weight.

These two plots indicate that for those samples that had very large pores, there was a problem with coalescence that was not easily solvable simply by increasing coat-weight. By contrast, for samples with smaller pores, an increase in coat-weight clearly alleviated any tendency towards bleed in these coatings.

Conclusion

In summary, it may be concluded that regardless of the total pore volume, the pore-size distribution plays an important role in the ability of a microporous coating to absorb the inkjet ink. Where much of the pore-volume resides in the form of microporosity, the ink is able to penetrate the coating relatively rapidly, and bleed is the primary print artifact that is observed when the coat-weight is insufficient. On the other hand, if a majority of the pore-volume is contained in macropores, there is a tendency for ink to reside on the surface longer, resulting in coalescence as the primary print artifact.

Increasing the coat-weight of the coating can largely alleviate bleed, but coalescence is more difficult to address by coat-weight alone. Therefore, simply choosing pigments that have high pore-volumes may not ensure that the coating will be able to effectively and rapidly absorb the inks as print speeds increase. Pigments that have a significant amount of porosity contained in micro- and mesopores make the best candidates for microporous coatings.

References

[1] G. Desie, G. Deroover, F. De Voeght and A. Soucemarianadin, “Printing of Dye and Pigment-Based Aqueous Inks Onto Porous Substrates”, J. Imaging. Sci. and Technol., 48 (5), 389 (2004).

[2] A. Marmur and R. D. Cohen, “Characterization of Porous Media by the Kinetics of Liquid Penetration: The Vertical Capillaries Model”, J. Coll. and Interface. Sci., 189, 299 (1997).

[3] W. Storbeck, D. Dietrich and R. Schneider, Fixation of Pigmented Black Ink on Matte Coated Ink-Jet Substrates, Proc. NIP-21, pg. 306. (2005).

[4] D. M. Chapman, Design Considerations for Matte-Coated Microporous Media for Pigmented Inks, Proc. NIP-19, pg. 598. (2003).

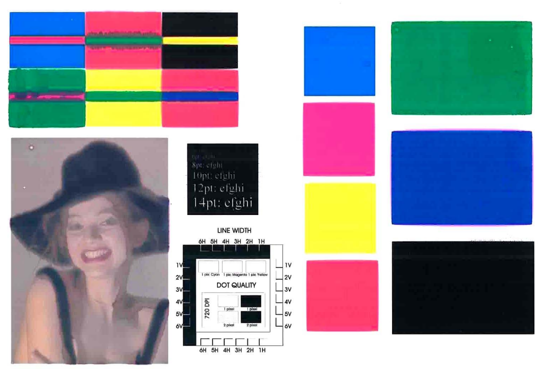
[5] M. C. Withiam, “Silica Pigment Porosity Effects on Color Ink Jet Printability”, Recent Progress in Ink Jet Technologies II (IS&T, Springfield, VA), pg. 493 (1999).

[6] H.K. Lee, M. K. Joyce, P.D. Fleming and J.E. Cawthorne, “Influence of Silica and Alumina Oxide on Coating Structure and Print Quality of Ink-Jet Papers”, TAPPI Journal, 4 (2), 11 (2005).

Author Biography

Sanjay Monie received his Ph.D. in Materials Science from the Pennsylvania State University (1996). Since then he has been involved in media development for inkjet printing, working on inkjet coating formulation at Westvaco Corporation (now MeadWestvaco) and since 2002 at Grace Davison, focusing on the development of microporous pigments. He participates on the ISO Subcommittee on Image Permanence Standards *for Digital Printing (IT9/TG-3/WG-5) and is a member of IS&T. He has also previously served as Section Chair for the Delaware Valley Chapter of TAPPI.*

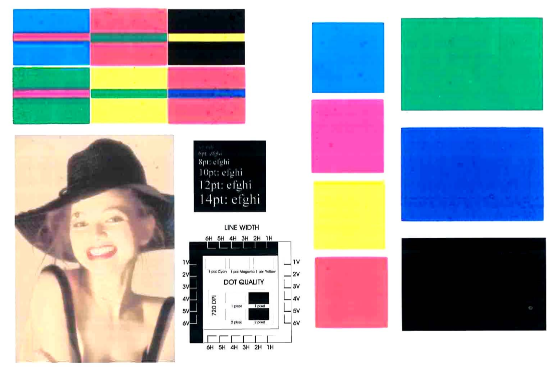
***Appendix**: Prints showing Bleed and Coalescence (Coat-weight : 12-15 gsm, Epson 870 Printer)*



Sample A - Bleed

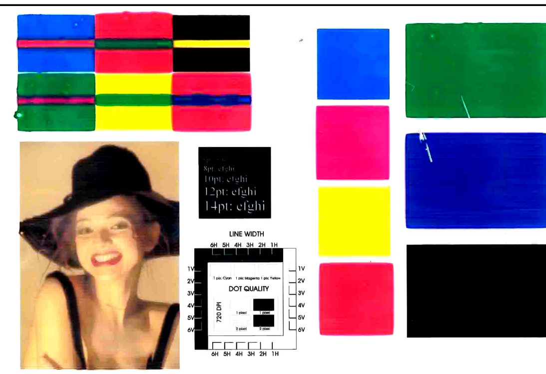
Sample B - Coalescence

Sample C - Bleed

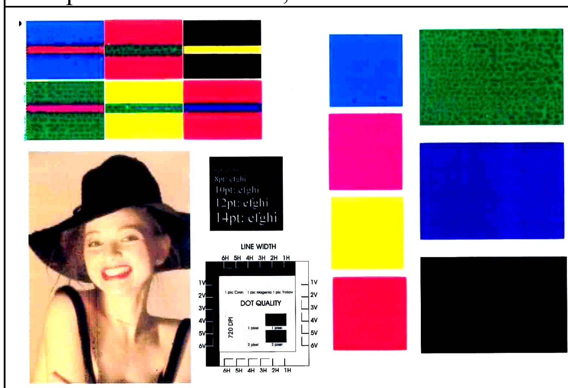


Sample D - Coalescence

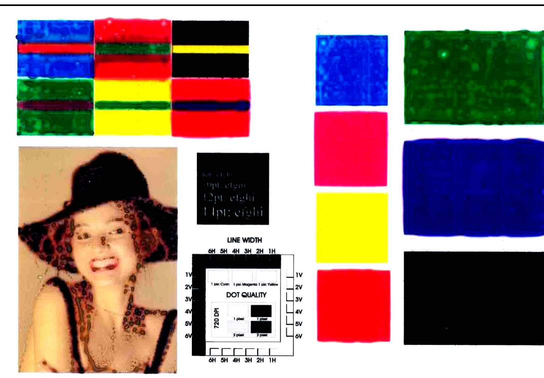
Sample E – Coalescence, some bleed



Sample F - Bleed



Sample G - Coalescence



Sample H – Coalescence, some bleed