# Use of a Chemically Modified Clay as a Replacement for Silica in Matte Coated Ink-Jet Papers

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## INTRODUCTION

New techniques for modifying the surface of ink-jet papers are continuously being developed.[1-5] Constant changes in the market, in both narrow and wide format, demand that ink-jet papers evolve to handle a new generation of ink-jet printers that can print larger image sizes at higher speeds while generating four-color images at near photographic quality.[2] The affordability of ink-jet printers, furthermore, has placed them at the forefront of home-use digital printing technology. Thus, the demands on the paper substrate to respond to a variety of ink-jet operating conditions, while yielding a quality printed product, is higher than ever.

An ink-jet substrate, coated or uncoated, must demonstrate a series of unique properties to produce a quality printed image. The difficulty in formulating a coating for an ink-jet printing substrate, compared to conventional printing papers, comes from the need to handle the large volume of liquid (water), approximately 90% of the initial drop, associated with each ink drop.[1,3] Once the ink drop is accepted by the substrate, the ink must adhere without running or smudging. The ink drop should spread uniformly in all lateral directions to generate sharp edges for print contrast and image fidelity.[4,5] The substrate should also have adequate smoothness to promote high print densities and, subsequently, bright images.[5] Finally, the paper should minimize bleeding and wicking tendencies, while promoting the quick absorption of the ink vehicle to set the dye onto the coated surface.[5] This absorption and rapid setting promotes better print densities. To achieve these required paper properties, it is becoming commonplace to rely on specialty coatings to produce the necessary coating structure to deal with the various demands of ink-jet printing.

New techniques for modifying the surface of ink-jet papers are continuously being developed. The affordability of ink-jet printers has placed them in the forefront of home-use for digital printing technology. Thus, there is a demand on the paper substrate, whether coated or not, to respond to a variety of ink-jet operating conditions, while continuing to yield a product with high print quality.

Coating formulations for ink-jet papers currently utilize precipitated or gelled silica with polyvinyl alcohol (PVOH) as the binder. This silica and PVOH formulation generates good optical, surface, and print qualities, yet leaves a lot to be desired from a runnability and coating preparation standpoint. The modified clay pigment offers potential as a substitute particle for the silica pigment in matte grades of ink-jet paper. The modified clay pigment offered significant improvements in coating preparation and runnability. The modified clay, however, could not match silica in producing the surface and bulk coating properties required for generating high print quality without the addition of a cationic additive.
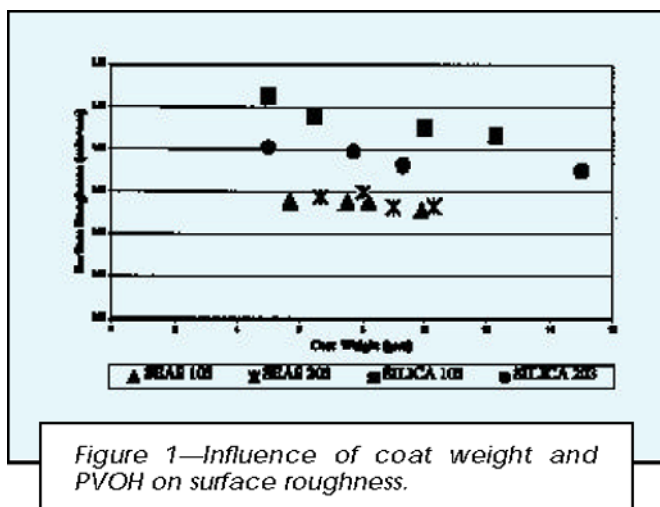
Figure 1—Influence of coat weight and PVOH on surface roughness.

Coating formulations for ink-jet papers currently utilize precipitated or gelled silica[6,7] with polyvinyl alcohol[8] (PVOH) as the binder. Silica is the pigment of choice in ink-jet coating due to its high internal porosity and high surface area. The internal porosity[7] drives the capillary action and controls the rate of liquid penetration into the coating structure. The faster the uptake of the liquid vehicle from the ink, the quicker the ink sets, allowing for faster print throughput. The macro-porosity generated from the packing of the silica-PVOH coating provides the interparticle network of pores required for controlling the bulk flow of water into the coating. The high surface area of the silica pigment, associated with its high internal porosity, dictates the use of polyvinyl alcohol as the binder. The high surface area of the surface enhanced aluminosilicate (SEAS) and silica pigments requires the high binding strength to maintain the adhesion of the pigments to the paper substrate and the cohesion of the pigments within the coating layer. Polyvinyl alcohol, therefore, is the preferred binder, since it has the highest binding strength of all binders, roughly 1.5-2 times the binding strength of latex. If other binders, such as latex and starch, were utilized, the significant increase of binder present to maintain adhesion and cohesion in the formulation will have a negative impact on optical properties and ink receptivity.[8-11] PVOH is also a hydrophilic polymer, which aids in the absorption of the ink. The limitations of silica and PVOH are their low makedown solids[7]: silica (25-30%); and binder (15-30%), which limits the attainable solids for the coating formulation (25-30%). The costs of silica and PVOH are also high in comparison to conventional coating pigments and other binders.

The development of a modified kaolin pigment, known as SEAS, has provided a possible alternative to the use of silica. The key improvements in the SEAS are the development of increased pore volume and surface area over conventional and engineered kaolin. These alterations are fundamental for generating the absorbance, ink holdout, and other properties essential for ink-jet printing.[12]

This investigation evaluates the modified clay pigment as a substitute particle for silica in matte grades of ink-jet paper. The modified clay pigment should offer improvements in coating makedown and runnability, in terms of attainable levels of solids, pigment to binder ratio, and rheological properties, compared to silica.

## EXPERIMENTAL DESIGN AND METHODOLOGY

Before beginning the experimental work, a commercially produced base sheet for the coating work was obtained and characterized. The uncoated commercial base paper was obtained from International Paper Company, and its basis weight was determined to be 75 g/m². The base paper had a low Hercules Sizing Test (HST) value (TAPPI standard test method T-530 pm-89) of 65 sec for sizing.

The HST time value is a measure of how long it takes for a colored acid-dye, at a known concentration, to penetrate the substrate being tested. The time is directly associated with the time it takes for the dye to reduce the reflectivity the instrument is reading to 80% of the initial reflectance value. The brightness was 85% with an opacity of 91% and a surface roughness (PPS at 500 kPa) of 5.20 microns. PPS is the designation for the Parker-Print Surf measuring device.

The modified clay (Digitex) was obtained from Engelhard Inc. For comparison, the two types of silica obtained were a gelled silica, Sylojet P612 from Grace Davison, and a precipitated silica, Optisil 3225 from Huber. The different types of silica provide a good comparison to industry practices for this grade.

The experimental program was divided into four distinct phases: (a) screening design, (b) application of the selected coatings using a cylindrical laboratory blade coater, (c) characterization of the optical and surface properties of the coating, and (d) printing and print testing of the modified clay coated as well as silica control to a commercial silica coated sheet.

The screening phase of this experimental design was an attempt to generate a basic understanding of the modified clay pigment, its potential, and its limitations. The pigments were prepared by first dispersing the dry
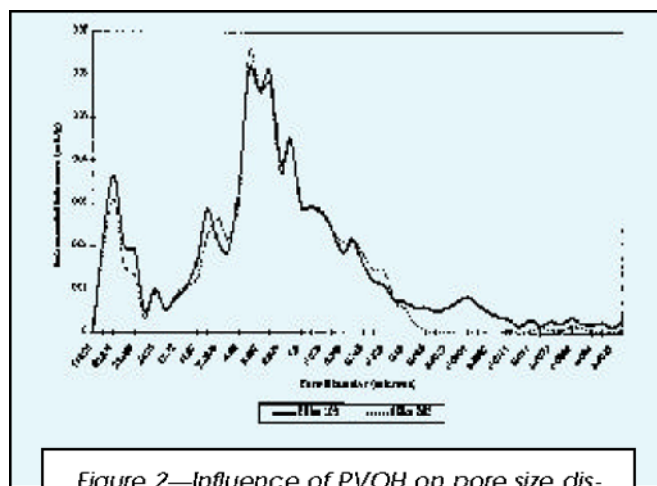


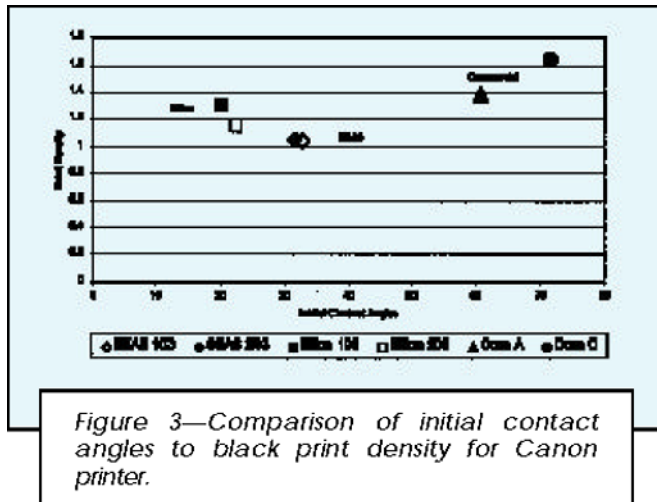Figure 2—Influence of PVOH on pore size distribution of silica.

Figure 3—Comparison of initial contact angles to black print density for Canon printer.

pigment with distilled water at 25°C under agitation. The pigment was added slowly to a high-speed Cowles disperser, and then allowed to mix for 30 min at a constant rotational speed of 45 revolutions per minute. For the modified clay, the target was a 52% solids level. The silicas were targeted to a solids level of 25% for the gelled silica (Grace, Sylojet P612) and 27% for the precipitated silica (Huber, Optisil 3225). Once adequate pigment dispersion was obtained, the binder was added to the pigment slurry.

The polyvinyl alcohol solutions were prepared at 31.5% solids by adding the dry PVOH particle to the appropriate amount of 25°C distilled water under agitation. Defoamer (Foam Master, VF) was added to the water, before adding the polyvinyl alcohol, to help limit the amount of foam generated during the cooking of the polyvinyl alcohol. The polyvinyl alcohol was cooked with indirect steam to a temperature of 90-95°C where it was held for 30 min. The polyvinyl alcohol was then cooled to below 40°C before mixing it with the slurried pigment. The Brookfield viscosities of the coatings were then measured using a Brookfield RVT viscometer with a #4 spindle at 100 rpm and 25°C.

The modified clay was initially mixed with the partially hydrolyzed PVOH, Airvol 203, at pigment to binder ratios ranging from 10:1 to 6:1 at 40% solids. Drawdowns with Meyer rods of various wire sizes were performed to determine at what pigment to binder ratio dusting began due to the poor adhesion of the pigment to the substrate. Rheograms using the Hercules Hi-Shear Viscometer were also performed. The combination of the rheological and drawdown testing identifies an acceptable rheological, % solids, and pigment to binder ratio from a simple application standpoint.

The coating formulations identified during the screening phase for the modified clays were produced in large batches for application on a cylindrical laboratory coater, CLC. The base paper was blade-coated using the CLC-6000 at a speed of 2600 ft/min. Replicate measurements were obtained for the four different applied coat weights, ranging from 6 to 12 g per square meter for both the Airvol 103 and 203 coatings. The silica control samples were run on the CLC at the same speed as the modified clays. A generic coating formula-

tion for the silica, provided by the companies that supplied the pigments, was used for running the control samples. The gelled silica, failed to adhere to the base sheet even at a pigment to binder ratio of 1:1. The precipitated silica, however, did adhere with only slight dusting at a pigment to binder ratio of 1.75:1 at 27.5% solids. Two precipitated silica coatings were prepared using the PVOH Airvol 103 and 203. Additional studies were also performed after incorporating a cationic fixative,[13] PolyDADMAC, at 5% by weight of pigment to the coating.

Phase 3 involved the testing of the basic coating properties of the samples produced on the CLC. For the purpose of comparison, two commercial matte-coated ink-jet papers were tested along with the CLC samples to allow for a commercial comparison. The samples were subjected to two passes through a soft-nip calender at 6 psi. The coated side contacted the metal cylinder on the first pass and soft roll on the second pass. The basic surface coating properties of brightness, surface roughness, air permeability (PPS porosity), opacity, gloss, and dynamic contact angle were measured on all of the samples. The dynamic contact angle was performed using distilled water. All testing was performed according to TAPPI standard test methods. Mercury porosimetry (Micromeretics' Autopore II 9220) measurements were performed on the samples to provide information regarding the pore size distribution of the coating.

In Phase 4, the commercial and CLC samples were printed and the basic print properties of print density, dot gain, and roundness were evaluated. The samples were printed on three different drop-on-demand printers.[14,15] Two of the printers, the Canon BJC 4300 (360 dpi) and Canon BJC 5000 (720 dpi), were thermal printers,[14,16] while the Epson Color Stylus Pro (720 dpi resolution) was a piezoelectric [14,15] printer. The variance in the three printers allowed for an evaluation of the influence of printer type and resolution on final print quality for the various coated samples. The test pattern has evolved over time as similar print testing has been performed. It was created with a combination of Adobe Illustrator, Photoshop, and PageMaker. Print testing
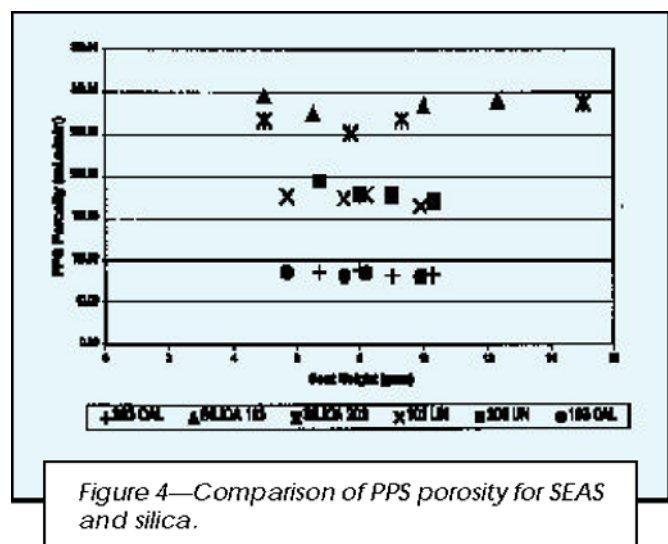


Figure 4—Comparison of PPS porosity for SEAS and silica.

Figure 5—SEM of surface of silica-PVOH (103) coating.



Figure 6—SEM of surface of silica-PVOH (203) coating.

was performed on both the black and magenta colors. Print density and dot gain were measured using an X-Rite 408 densitometer, which has the Murray-Davies[17] equation built into the electronics. The roundness of the dots was evaluated using Image Pro Plus image analysis software.

## RESULTS AND DISCUSSIONS

One of the major benefits associated with the use of the modified clays for the matte-coated ink-jet papers is the improvement in coating runnability. The runnability of a coating refers to both the makedown and application operations. In pigment preparation, a significant difference in attainable levels of solids was evident, which played a significant role in application solids. The modified clay (SEAS) could be prepared at 52% solids, 57% if a cationic fixative was added initially, compared to silica's limitation of 20-25% solids. The high interactivity of the PVOH binder with the SEAS[8-10] limited application solids to only 38%, however, if the SEAS are used with a binder of weaker bonding strength, or mixed with other pigments in formulating a non-ink-jet coating, higher application solids are obtainable. The increase in solids at application reduces the amount of water that must be removed in the dryers. Additionally, a significant impact in running speed was noticeable for a change in the degree of hydrolysis for the PVOH binder. The fully hydrolyzed PVOH (Airvol 103) generated more interaction within the coating and consequently allowed for an increase in speed from 2600 ft/min to 2900 ft/min, while maintaining coat weight control in the 6 to 12 gsm range.

Calendering had a significant impact on the development of all optical and surface properties. Calendering reduced surface roughness and decreased the permeability and porosity of the sheet by compacting and leveling the peaks and valleys of the coating. The compaction of the coating layer during the calendering operation also increased the initial contact angle of the modified clay samples, making them comparable to the silica samples. The end result of the surface modifications through calendering was a significant improvement in the print densities for the modified clays.

Surface and optical properties—gloss, surface roughness, opacity, and air permeability—demonstrated no significant differences between the commercial grades and the samples coated in the laboratory. Figure 1 illustrates that coat weight did not influence the development of surface roughness, however, the type of polyvinyl alcohol slightly influenced the surface roughness for the silica pigment. The partially hydrolyzed PVOH 203 produces a lower roughness than the fully hydrolyzed PVOH. This is due to fewer hydrogen bond interactions occurring between the silica particle and the partially hydrolyzed polyvinyl alcohol.[9,11] When drying occurs, therefore, the binder shrinkage associated with the fully hydrolyzed PVOH will cause the increase in surface roughening. Accordingly, the SEAS does not demonstrate any change in the surface roughness characteristic with the increasing interactivity of the binder.

The brightness of the commercial grades was significantly higher (approximately 92 for all) than the laboratory samples due to the use of optical brightening agents[9] as additives in the commercial coating formulations. The upper limit for brightness development through pigment use alone ranges from 86 to 90% depending upon the characteristics of the pigment used. Since polyvinyl alcohol is an excellent carrier of optical brightening agents, they were added to the SEAS coating and generated brightness levels comparable to the commercial grades tested. Although the optical and surface properties play a significant role in how the substrate and printed image appear to the user, print quality, in terms of setting the ink, is completely dependent upon the surface chemistry and absorption tendencies of the coating layer.

The hydrophilic/hydrophobic surface chemistry of the coating plays an important role in the development of image quality. The development of the contact angle, which controls the spread of liquid on the surface, and its influence on the spread and adherence of the ink on the surface, can be characterized by the Young-Dupre Equation.[18,19]

$$W_{SLV} = \gamma_{LV} \left(1 + \cos\theta\right) \tag{1}$$

The porosity of the coating also impacts the measured contact angle since the volume of the ink droplet is

reduced by ink penetration into the coating layer. The rate of ink penetration can be explained by the integrated form of the Lucas-Washburn equation[20]:

$$l^2 = \frac{\gamma r\,(\cos\theta)\,t}{2\eta} \qquad (2)$$

where l = depth of ink penetration; r = pore radius; t = time; $\gamma$ = surface tension; $\theta$ = contact angle; $\eta$ = viscosity (ink).

The generation of print quality requires the management and balance of surface tensions and porosity to produce the desired set of surface wetting and ink penetration characteristics. All of this is controlled by the interaction between the media and ink droplet. In generating high print quality, the rate of ink penetration must be modified to allow for sufficient surface wetting to occur.

Mercury porosimetry was performed on a select number of samples to determine the influence of the controlled variables on the pore size distribution within the coating layers. The porosimetry testing was performed on two commercial sheets, the silica control sheets, at both polyvinyl alcohol levels, and the SEAS samples, at both calendering and polyvinyl alcohol levels. The samples used for comparison were all at approximately the same coat weight (8.3 gsm), except for the commercial samples whose coat weight is unknown.

Figure 2 shows a significant impact on the pore size distribution for the silica when the degree of hydrolysis for the polyvinyl alcohol was increased. The major change was in the amount of smaller sized pores, which should increase liquid penetration, while tending to filter out the relatively large hydrated dye molecules. The total pore area was larger for the polyvinyl alcohol that had a higher degree of hydrolysis. This can be related to the increased interactivity between the particle and binder.

The calendering operation shifted the pore size distribution of the modified-clay samples. The number of very large pores (greater than 20 microns) remained approximately the same, while a shift occurred in the pore size distribution below 20 microns. The shift increased the number of smaller pores within the coat-

ing structure. The retention of the large pores generated the necessary volume to hold the large liquid intake into the sheet. The elimination of the mid-size pores (between 10-20 microns) and the increase of smaller pores decreased the depth of penetration of the ink into the coating layer. With comparable pore networks, print density should be the same, yet silica was still the better of the two.

The difference in print density between the silica and SEAS must be related to the surface energy. The relationship between the initial contact angle and the print density for the black ink is shown in Figure 3. The silica samples had a lower initial contact angle, but demonstrated increased print densities for both the black and color inks. Silica's low contact angle is related to the high Parker Print Surf porosity displayed in Figure 4. PPS porosity represents the limitation of liquid penetration into a substrate since air perfectly wets all materials. Figures 5-8 are SEM pictures of the coating surfaces for the SEAS and silica coatings. Figures 5 and 6 show the silica samples that had significant surface cracks that were produced by the high interaction between the PVOH and silica during drying, while the surface of the SEAS' coatings did not indicate the same phenomena. Initial contact angle measured for the silica, therefore, was lower than the actual contact angle because of the increased water penetration into the coating which resulted from increased surface roughness and apparent surface permeability.

Initial contact angles are measures of the initial wetting of the average surface by the ink. Changes in the contact angle may occur from dissolution of the coating materials into the liquid, as well as evaporation of the water and absorption into the surface. Initial contact angle should not be significant with regards to print density beyond whether the surface was wetted or not. The silica, with its high level of polyvinyl alcohol, improved the print density by keeping more of the colorant dye and pigmented ink at the coating surface and controlling the rate at which it penetrated into the surface.

Comparison between the print density and delta contact angle was performed to determine if any absorption or spreading phenomenon, beyond its influence on the
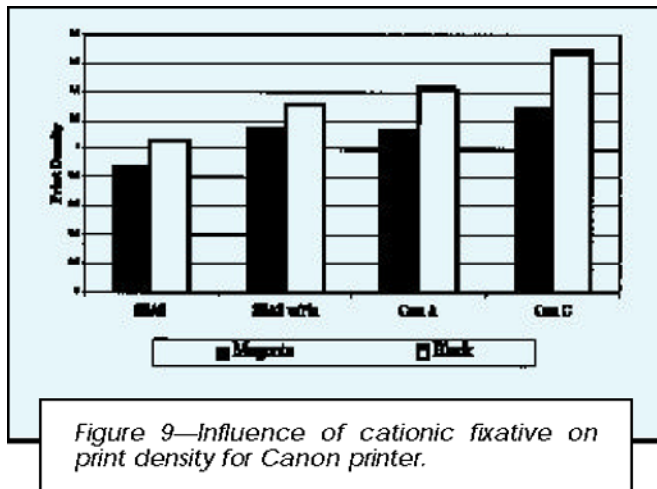
*Figure 9—Influence of cationic fixative on print density for Canon printer.*

development of the initial contact angle, over a short time influenced the final print density. There was no significant impact of the delta contact angle on the development of print density. The wettability of the coating surface, via the initial contact angle, seems to be the key factor for print quality development.

There were no similarities between the laboratory-coated silica and modified-clays to the commercial samples. The lack of knowledge in regards to the commercial papers' coating formulation and an application method make it difficult to isolate what in particular differentiates the commercial paper from the laboratory prepared samples. There are several potential explanations for why the commercial papers can have such large pores, yet maintain print density. The large pores are still responsible for the intake of the large amount of liquid (water and humectants), yet surface chemistry modifications, such as the use of cationic fixatives or other additives, seems to have set the colorant at the surface.

It was determined, therefore, to follow the known commercial practice of adding a cationic fixative, in this case diallyl dimethyl ammonium chloride (PolyDADMAC), to try and match the SEAS print quality the silica produced as well as commercial standards. Cationic fixatives are a common additive in the production of ink-jet papers to help attach or fix the anionic dye in the ink-jet ink to the surface of the coated substrate and improve print density. The cationic fixative works by interacting with the anionic ink to fix the colorant to the surface.[13] The cationic fixative performed as predicted. The print density improved significantly for all colors. *Figure* 9 illustrates that substantial improvement in print density makes the SEAS-based coating with cationic fixative competitive with both commercial grades tested.

The substrate plays a large role in developing print quality, as previously discussed, but so does the choice of printer. Printers vary based upon the composition of the ink chosen by the individual manufacturers. The print density for black was best with the piezoelectric Epson printer, while the thermal Canon printers provided the best color densities. Visual inspection of the ink cartridges for the two printers offered some insight

as to why there was such a dramatic difference in print quality. The colored dyes, used to print cyan, magenta, and yellow, appear diluted for the Epson cartridges. Conversely, the Epson cartridge appears to contain more carbon black pigment. It is this variance in ink composition from one printer to another that complicates the development of a single ink-jet medium that will satisfy all users.

## CONCLUSIONS

The research investigated the application of a modified clay pigment (SEAS) in matte-coated ink-jet formulations. The optical, surface, and print properties of the coatings were compared to a standard commercial sheet. The following conclusions were made from evaluating the data:

(1) SEAS provide a significant improvement in make-down solids over silica.

(2) Calendering significantly improved the optical, surface, and printed properties for the SEAS.

(3) The fully hydrolyzed polyvinyl alcohol offered some benefits from a runnability standpoint, but did not have a significant impact on the final optical, surface, and print properties for SEAS.

(4) The relationship between the initial contact angle and print densities, regardless of ink type, was not significant. The absorption and spreading phenomenon, characterized by the delta contact angle, did not impact the final print density. The increased presence of polyvinyl alcohol and/or silanol groups on the silica have more impact.

(5) The piezoelectric printer produced higher black print densities with the pigmented (carbon black) black inks, while the thermal printers generated better print densities using the dye-based ink.

(6) The SEAS did not match the print properties that the silica pigment could generate, without the use of additives in the coating formulation.

(7) The use of cationic fixatives dramatically improves final print densities, regardless of color or printer, without any adverse influences on the rheology and application of the SEAS coating and competes well with samples produced commercially.

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