Influence of silica and alumina oxide on coating structure and print quality of ink-jet papers

HYUN-KOOK LEE, MARGARET K. JOYCE, PAUL D. FLEMING, AND JAMES E. CAWTHORNE

ABSTRACT: Advances in ink-jet printing have resulted in a new generation of ink-jet printers, which can print faster, at wider widths, producing four-color images close to photographic quality. Ink-jet printing papers must respond to these changes through quick ink absorption, minimizing ink bleeding and wicking, while retaining favorable ink optical density.

Amorphous and precipitated silica and silica gels, prepared by the acidification of a solution of sodium silicate, are commonly used in premium matte coated ink-jet papers. Aqueous coatings for paper or paperboard applications use traditional coating pigments such as clay, calcium carbonate, and titanium dioxide. However, for matte coated ink-jet papers, precipitated and gelled silica are used for their unique morphological properties. The structure of these pigments provides an internal and packing porosity that enables the rapid diffusion of liquid inks into the coating layer. The rapid uptake of the ink immobilizes the anionic dyes at the surface of the coating. This accumulation of dye at the surface allows high optical print densities to be achieved. The particle size of precipitated and gelled silica is typically in the 3-16 mm range. Particles of this size significantly reduce gloss, which limits their use in glossy ink-jet media. Thus, they are primarily used in matte grades.

This study compared coatings of non-porous fumed silica, aluminum oxide, and precipitated silica in ink-jet media. We used a blade coat process on a cylindrical lab coater (CLC) rather than the cast coat process. We focused on the contribution of pigment chemistry, functionality, and particle size on coating structure, and coating influences on ink-jet print quality. The pigments used are commercially available and, because of this work, currently being used commercially.

Application: This paper can help to guide coating formulators in the contribution of pigment characteristics to coating structure for matte coatings of ink-jet papers that can be on-machine coated.

The quality of non-impact printing is improving because of advances in technology that increase print resolution and printing speed. Color printers are now common in the home and office. These trends are placing increasingly stringent requirements on the paper coating to take advantage of the improved printing technology. To date, research in the area of paper coatings for ink-jet printing has concentrated on examining the paper properties required for good print quality [1]. The results of these studies have shown that good print quality depends very much on the structure and the surface properties of the dry coated paper.

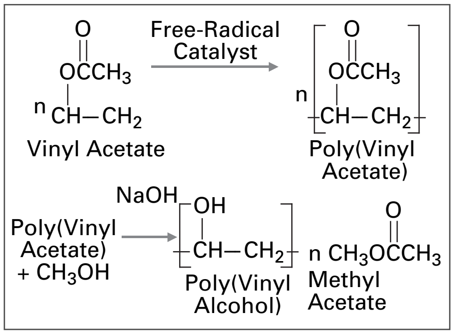
To understand some of the demands placed on a coating during this printing process, a basic understanding of some of the typical ranges of ink and print properties is required. For a typical narrow-format, home or office ink-jet printer, the ink fluid contains 2-5 wt.% dye or pigment, 2%-5% surfactants and additives, 30% humectant (ethylene glycol or diethanolamine), and 65% water. The important ink-fluid properties that contribute to the quality of the printed image are surface tension and viscosity [2].

Thus, because approximately 65% of the desktop ink-jet ink is water, media for ink-jet paper must have the following properties [3]:

- Ink applied to the recording paper must be absorbed without running and must not smudge
- Ink dots formed on the paper must have high contrast and bright color tones
- Ink dots must be suitably described in the direction of the paper surface; the dots should be almost round, with sharp edges
- Media must have excellent smoothness and gloss so that sharp images and high resolutions can be obtained.

Preparing coating for ink-jet paper is very different from preparing coating for conventional printing paper. The coating for ink-jet paper must absorb large volumes of water from ink drops. The ink has to be fixed on the surface of ink-jet paper to avoid bleeding or smudging when the ink drop hits the substrate. The ink drop should move evenly in the lateral direction to produce a clear edge for contrast and image fidelity [4, 5].

Fumed, pyrogenic silica is produced by flame hydrolysis of silica tetrachloride or tetrafluoride. The result is an aerosol of small primary particles, typically 7-40 nm in diameter. These particles stick together by hydrogen bonds, forming aggregates, and the aggregates form into micron-sized agglomerates. Porosity is created by virtue of the packing of the dense particles into secondary structures. These secondary particles are shear sensitive, thus shear can destroy the inherent porosity that gives them their inherent absorptivity [6].



1. The chemistry of polyvinyl alcohol ink-jet formulations.

Plain or surface-sized paper	Low cost, good monochrome text, poor color (limited coverage, poor gamut, high bleed, strike-through, cockle/curl)
Coated matte paper	Higher cost, good color gamut, fast dry time, excellent resolution, 100% coverage
Coated glossy paper	Very high cost, nanoporous, slow dry time
Cast coated paper and resin coated paper	Very high cost, highest gloss, photorealistic image

I. Four major classifications of ink-jet papers.

Although precipitated silica is prepared by mixing sodium silicate and mineral acids, the reaction system is typically sheared during the silicate polymerization process. Because of the pH and temperature of the reaction system, which favor silicate dissolution and reprecipitation, the primary, nonporous particles grow in size to 5-100 nm. Because of the shear forces applied during the reaction, the developing network between these particles is continually broken down, and the primary particles are again only weakly bonded together, as in the case of fumed silica. Conceptually, fumed and precipitated-silica agglomerates resemble a cluster of grapes rather than the sponge structure of the silica gels. Gel-precipitate hybrids, or high structure factor precipitated silicas, are prepared by additional treatment with soluble silicates, and this treatment encourages siloxane bonding between the primary particles. This method of secondary treatment for network development produces agglomerates that are still somewhat shear sensitive, and does not yield materials with as much porosity as that which can be achieved in silica gels.

The affect of coating properties on ink-jet print quality depends on the micro- and macro-porosity of the coating [7]. Because the ink contains a large volume of water, the coating must be capable of quickly absorbing and holding water to set the ink quickly and provide good print quality. Penetration of water into the base sheet results in fiber swelling, which can distort the image and thereby reduce the print quality. Undesirable cockling of the sheet can also occur. Conventional coatings, which are designed primarily for solvent-based liquid or paste inks, rather than water and dye holding ability, are largely inadequate for use in color ink-jet printing papers.

Ink density is an important quality control indicator in the printing process. Ink density affects the final visual quality, color gamut, and color fidelity. The main factor identified with color density is the concentration of colorant in the ink. Other major factors determining ink densities are ink dot coverage on the coating surface and colorant concentration at the surface. In the interaction of the colorant with coated paper, electrostatic interactions play the key role in colorant-coated paper interactions. The nature of the anionic dyes and the oxides will determine the print quality of the ink-jet printing, because electrostatic interactions of colorant with coated media occur between the anionic groups of dyes and the oxides. The binding energies of the dyes are greatly increased by electrostatic interactions, resulting in a high binding strength [8-10].

Conventional coating media from conventional pigments, such as kaolin, calcium carbonate, and titanium dioxide, are primarily limited by their available void fraction for liquid uptake (0.2-0.4 µm) and the narrow pore diameters for fluid flow (0.02-0.04 µm). For example, special methods [8, 11] have to be applied to improve the water uptake—and therefore drying—of ink-jet inks when using precipitated calcium carbonate (PCC) pigments in the coating. Thus, coating technologies using silica pigment and polyvinyl alcohol (PVOH) have been developed [7]. Precipitated and gelled silica pigments are matte pigments, so they are not suitable for glossy ink-jet grades.

PVOH is produced through the hydrolysis of polyvinyl acetate (**Fig. 1**). It can possess different physical and chemical properties due to varying polymerization of the intermediate polyvinyl acetate, which affects the molecular weight of the polyvinyl alcohol [12, 13]. Other structural variables, which may also be manipulated during the manufacturing process, include branching, spatial orientation or tacticity, and the distribution of the hydroxyl and remaining acetate groups along the polymer backbone chain. Branching, which is low compared to corn starch, may vary from one supplier's product to another. Sequencing of the residual acetate groups, depending on the process, could be used to prepare PVOH, in either block or random form. However, the structural variables that most significantly affect its use in paper coatings are the degree of hydrolysis and molecular weight.

Ink-jet printing places demands on paper that are quite different from those required by conventional contact printing methods [3]. Most ink-jet printers require low viscosity and low solids ink to achieve proper jetting. Thus, to obtain images with sufficient optical densities, relatively large volumes of these inks are required. High liquid loading presents a peculiar problem to the design of an optimum ink-jet coated paper.

Ink-jet papers can be classified into four major categories, as shown in **Table I**. Depending on the grade, the coating formulation, application process (air knife, pre-metering size press, rod, or blade), and coating, cost can vary substantially [7].

OBJECTIVES

This study used two fumed silicas, alumina and precipitated silica in ink-jet coating formulations. Previously, coatings based on these pigments were shown to be applicable at high speed (650-1000 m/min) and to provide good ink-jet print quality [8, 9, 14, 15]. Pigment particle size and packing are also very important for such coatings [16].

Following these earlier results, we sought to better understand the contribution of coating properties on coating structure and print quality. The objectives of our research were as follows:

- To study influence of fumed silicas, aluminum oxide, and precipitate silica on optical properties of coated paper and printing properties.
- To study the surface properties of the coatings using dynamic contact angle measurements, and the porous structure of the coating using mercury porosimetry.

EXPERIMENTAL DESIGN

The base paper (basis weight: 75 g/m^2) was obtained from International Paper (Otis, Maine) for the cylindrical lab coater (CLC) trials. The base paper was determined to be a neutrally sized paper with a Hercules sizing value of 69 s (TAPPI 530 pm-89). Brightness was 87.2% (TAPPI T 452 om-92), gloss was 6.4% (TAPPI T 480 om-92), and roughness was 3.93 microns (TAPPI 555 pm-94).

For use in the experiments, we obtained two fumed silicas (A and B) of varying surface areas, one aluminum oxide pigment with a surface area similar to pigment A, and precipitated silica. **Table II** shows the physical properties of the pigments.

The binder in the coating formulation was a partially hydrolyzed, low viscosity PVOH alcohol. We chose this PVOH to optimize the coatings solids by minimizing the interaction between pigments and PVOH. Polyvinyl alcohols with a higher degree of hydrolysis are known to interact more strongly with silica pigments, thus limiting the coating solids that can be obtained. They are also less hydrophilic, thus reducing the ink absorption properties of the coating and hence, print quality.

We prepared PVOH solutions at 32%-33% solids by adding the required amount of dry PVOH powder to cold water under agitation and heating the mixture to 185°F. The solution was held at this temperature for 35-40 min to assure complete dissolution and hydration of the PVOH. We then added a defoamer (Foam Master VF, Henkel). The solids content of the solution was measured using a CEM Labwave 9000 microwave moisture analyzer.

Sample	Solids Content, %	Color	Specific Gravity, 25°C	Surface Area, m^2/g	Particle Size, µm	pH
Aluminum Oxide	40	White	1.40	55	0.160	3.8-4.2
Fumed Silica, A	30	White	1.20	90	0.225	10.0-10.3
Fumed Silica, B	25	White	1.20	170	0.135-0.155	9.0-10.0
Precipitated Silica, powder	97	White	2.10	250-280	2-3	6.5-7.5

II. Physical properties of supplied pigments.

We added the slurried pigments after the solution had cooled to 40°F. The precipitated silica coating was prepared at a pigment-to-binder ratio of 1.75:1. The fumed alumina and silica coatings were prepared at a 4:1 ratio under slow agitation. The higher surface area of precipitated silica pigment required more binder for sufficient adhesion and cohesion. (We observed dusting at lower binder addition.) The coatings were mixed for 20-30 min and the pH was measured. The coating viscosities were measured using a Brookfield RVT digital viscometer (#5 spindle @ 100 rpm).

The base papers were blade coated using a CLC speed of 610 m/min. Coatings were prepared using the two fumed silicas (A and B) of varying surface areas, an aluminum oxide, and precipitated silica. We used 0.1% potassium hydroxide to increase the low pH (4.4) of the aluminum oxide coating formulation. **Table III** shows the coating properties of each formulation. Four different coat weights were applied: 6 ± 1 g/m^2, 9 ± 1 g/m^2, 12 ± 1 g/m^2, and 15 ± 1 g/m^2.

We measured the brightness, gloss, roughness, and air permeability (porosity) of the papers. The brightness of the papers was measured using a Technidyne brightness meter and TAPPI T 452 om-92. Gloss was measured using a Hunter 75° glossmeter according to standard TAPPI T 480 om-92. The surface roughness and permeability of the sheets were measured using a Parker Print Surf (PPS) tester (TAPPI T555 pm-94).

The rate of liquid absorption of the papers was measured using a First 10 Angstrom dynamic contact angle measuring device.

The samples were printed on an Epson Stylus Pro photo-realistic ink-jet printer, using a proprietary test print pattern created with Adobe software [8, 9, 14-16]. The print densities of the samples were then measured using an X-rite 408 densitometer.

Coating	pH	Solid Content, %
Aluminum Oxide + PVOH	8.82	27.18
Fumed Silica, A + PVOH	9.26	31.75
Fumed Silica, B +PVOH	9.25	27.00
Precipitate Silica + PVOH	6.50	27.00

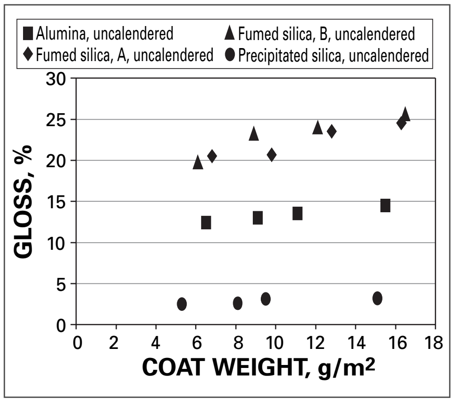
III. Coating formulation properties.

The pore volume and pore size distribution of coated papers were measured using a Micromeritics mercury intrusion porosimeter.

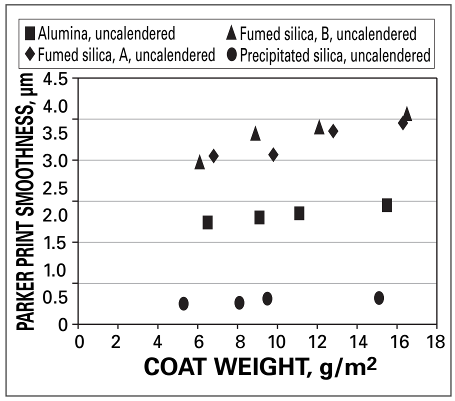
RESULTS AND DISCUSSION

Typically, small pigments and narrow size distribution pigments produce more gloss. That results because the smaller pigments fill the surface irregularities, providing a smoother surface with more compact air boundary surfaces [17]. For uncalendered samples, the gloss of the precipitated silica coating was much less than the gloss of the fumed silica (A and B) and alumina coatings. The gloss of all increased with coat weight (**Fig. 2**). This result indicates that, although the precipitated silica and fumed silica particles have similar shapes, the precipitated silica coating surface has much lower gloss because of the larger particles of precipitated silica. On the other hand, fine, particle-size fumed silicas and alumina oxide tend to orient and pack together tightly, producing a microsmooth surface. **Figure 3** shows that the roughness (PPS smoothness) of the precipitated silica coating was higher than that of the fumed silica (A and B) and alumina coatings.

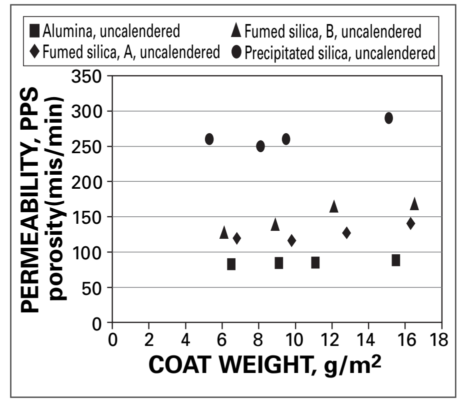
Figure 4 shows the permeabilities (PPS porosities) of the coated papers as a function of coat weight and pigment type. It is evident that permeability increased with coat weight. The high permeability of these coatings is attributed to the clustered particle arrangement.



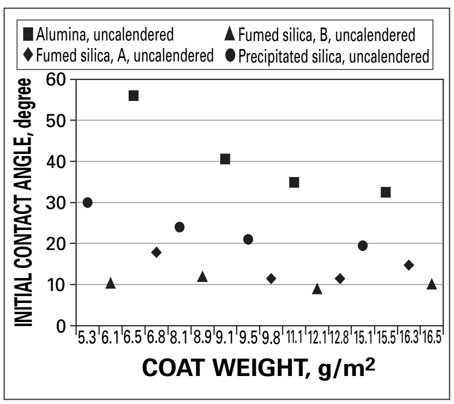
2. *Influence of pigment on gloss.*



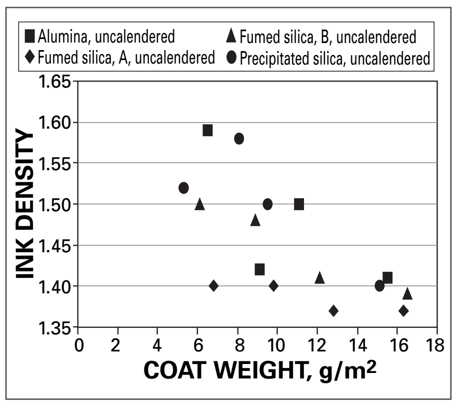
3. *Influence of pigments on roughness.*



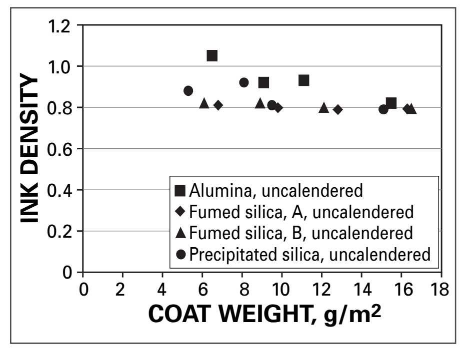
4. *Influence of pigments on permeability (PPS porosity).*



5. *Influence of pigments on contact angle.*

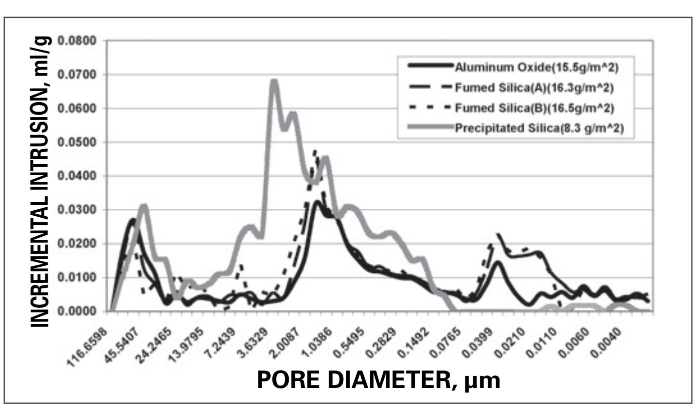


6. *Influence of pigments on black ink density.*



7. *Influence of pigments on magenta ink density.*

As coat weight increases, the thickness of the coating layer also increases, providing more passageways for air to flow. As a result, permeability increased. The permeability of precipitated silica coating was much higher than that of the fumed silica coatings and the aluminum oxide coating. The larger particles of precipitated silica increased the size of air voids between particles. Therefore, increased air voids impart more air-flow pathways.

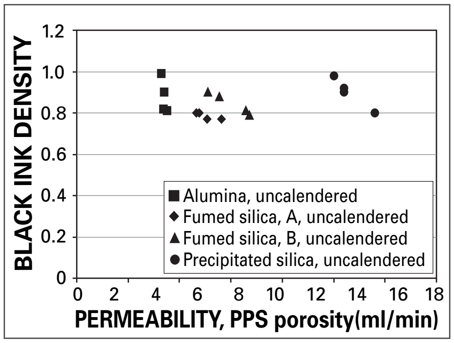


8. *Influence of pigments on pore size distribution.*

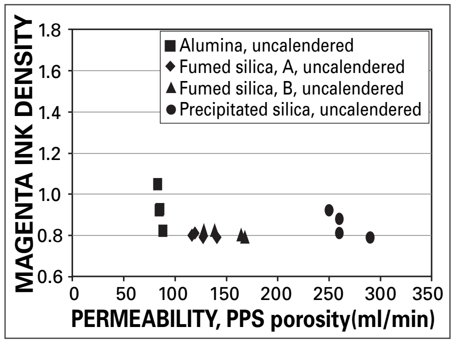
We performed initial contact angle measurements and printing studies to determine if the rate of liquid absorption and print quality were adversely affected. The initial contact angle of each sample was measured to estimate the rate of liquid absorption into the sheet and to study the influence of pigment type on the surface energy of the sheet. As seen in **Fig. 5**, the initial contact angle decreased with increasing coat weight. This corresponds to the permeability results, which showed that permeability also increased with coat weight. Once again, the initial contact angle of the aluminum oxide coating was highest. The higher initial contact angles are believed to be caused by base sheet effects. The base sheet was highly sized (Hercules size test=120 s). As coat weight increases, the base sheet coverage increases and the available void spacing increases to promote wetting.

The coated papers were printed on an Epson Stylus Pro photo-realistic ink-jet printer. **Figures 6** and **7** present the ink densities of the printed samples. For all samples, the black and magenta ink densities for the alumina samples were higher than those of the fumed silica coatings (A and B) and the precipitated silica samples. Coat weight had little effect on the ink densities of the samples. For all samples, the density of the black ink was higher than the density of the magenta ink.

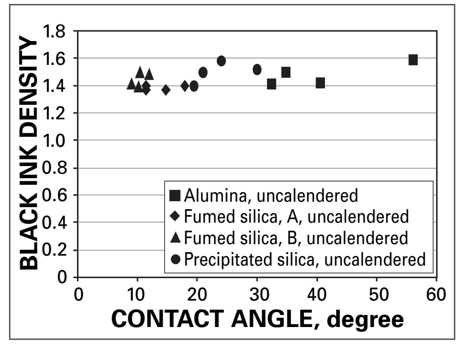
The porosity of the coated layers was obtained using a Micromeritics mercury porosimeter. **Figure 8** shows the pore size distributions, median pore diameters, and total intrusion volumes. The precipitated silica samples had a wide pore size distribution curve because the larger particles of the precipitated silica made a wide porous structure in the coating layer. This is consistent with the permeability data.



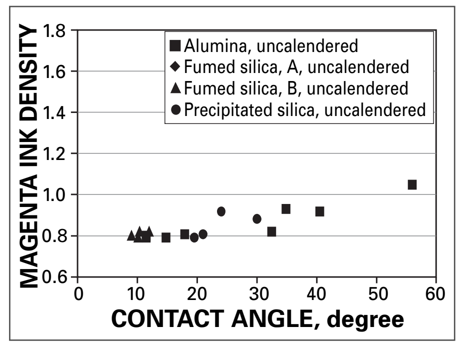
9. Permeability influences on black ink density.



10. Permeability influences on magenta ink density.



11. Initial contact angle influence on black ink density.



12. Initial contact angle influence on magenta ink density.

Figures 9 and **10** show the influences of permeability on ink density for the black and magenta ink. They indicate that the permeability of the coating layer did not significantly affect ink density. Likewise, **Figs.** **11** and **12** show the effect of contact angle on ink density. Both black and magenta ink densities of alumina oxide samples were higher than those of the silica samples (Figs. 11 and 12). The coating layers of aluminum samples have higher cationic charges compared to the cationic charge of silica coating layers. It is attracted more strongly to the negatively charged dye of ink-jet ink. This keeps the dyes nearer to the top of the coating surface, which produces higher optical print density [18]. The differences of the pore structure probably play a role on the development of ink density as well.

CONCLUSIONS

The results obtained from this study indicate that optical properties, such as gloss, were affected by pigment type and coat weight. The correlation between improvements in optical properties and smoothness indicate that the property improvements resulted from an increase in surface coverage with coat weight. Permeability increased with coat weight.

The dry coating properties were also influenced by pigment type, particle size, and coat weight. We believe the low solids of the coatings prevent the smooth application of the coating, due to base sheet roughening by the absorption of coating water and shrinkage during drying.

Print quality, as measured by ink density, was strongly dependent on pigment type and correlated well with pore size distribution results. Coat weight did not significantly affect these properties. The difference in print quality between the two colors—black and magenta—indicates differences between the two inks and confirms the need to perform print studies on multiple printers with multiple colors. The permeability and liquid absorption do not significantly affect the ink density. **TJ**

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INSIGHTS FROM THE AUTHORS

This research marks our effort to find a pigment capable of providing high gloss and vibrant ink-jet print quality. Based on our formulation experience, we knew that cationic additives are used to fix the dyes in the ink-jet inks to the coating surface, and that gloss is affected by the refractive index of the pigment and particle size. Using this knowledge, we selected fine particle aluminum oxide and fumed silica pigments for this application.

This research supports fundamental research done in the past on coating gloss that showed gloss to be dependent on smoothness and index of refraction. Coating cracks discovered on the surface of the silica-coated papers supported findings of past research; however, the interrelationship between coating cracks and particle size had not been presented in prior work. The application of alumina oxides in glossy ink-jet coatings had not been previously reported, although their unique characteristics made them well suited for this application. Advances in pigment processing and particle classification techniques sparked the discovery of the proper pigments for this application.

The most difficult part of this research was determining the best way to combine the coating components. The coating components were strongly interactive, so we needed to develop a methodology to combine them. Determining the amount of and type of binder needed to balance the printing and coating properties also took a considerable amount of time.

The most surprising and interesting discovery was that a glossy ink-jet paper could be prepared in a one-coat process with a minimum level of calendering. Mills will benefit by discovering the benefits of using silica and alumina pigments in the formulation of glossy ink-jet papers.

The next step of this research has already been taken: products are being sold commercially. The benefits of using the pigments in combination with conventional coating pigments has already been studied by our research group and will be published soon.

Lee (photo unavailable), Joyce, Fleming, and Cawthorne are with the Department of Paper Engineering, Chemical Engineering and Imaging, Center for Coating Development, Western Michigan University, Kalamazoo, Michigan 49008. Email Fleming at dan.fleming@wmich.edu.

Joyce

Fleming

Cawthorne