Engineered Pigments for Inkjet Receptive Media

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Abstract

Silica, kaolin and calcium carbonate pigments have been engineered for inkjet receptive media. These pigments have been synthesized by a range of companies to create a surface that produces improved quality for inkjet printing paper. Precipitated Calcium Carbonate (PCC) has been available for several years for inkjet coatings but had application limitations with regard to coat weight and coater speeds due to low solids content. To address this limitation, a second generation of PCC for inkjet receptive media has been synthesized with a significant increase in solids content.

The second generation pigments have been evaluated on pilot as well as commercial coaters with great success. Increased pigment solids yield increased coating color solids which, in turn, allow this pigment to run at higher coat weight and higher coater speed on standard coating equipment. The new PCCs can successfully create matte grade papers with improved coater productivity relative to the traditional synthetic silica coatings.

This paper will compare PCC hand coated drawdowns and commercially available inkjet sheets coated with silica, kaolin and/or calcium carbonate through a series of inkjet print evaluations and image analysis. The commercially coated sheets were characterized by XPS surface analysis to determine pigment and binder content.

Introduction

Non-impact digital printing demand has increased significantly in recent years with the massive increase in inkjet printing at home and at the office. With increasing market demand, the demand on the paper requirements has increased as well. Multipurpose plain paper is unsuitable for good quality inkjet printing since it causes numerous problems such as feathering, wicking, color bleeding, low color density, strike-through, and cockle/curl (Malla). To alleviate these problems, inkjet papers are coated with inkjet receptive pigments. Inkjet receptive pigments enhance the printability results that were obtained by traditional multipurpose papers. With increasing quality demands, advancements have been made in the pigments for inkjet receptive media. No longer is silica the only player in this market; additional pigments have been synthesized to address the quality demands and paper costs. Calcium carbonate in ground and precipitated forms and kaolins have been specifically engineered by a range of companies to create a surface that produces an improved quality/cost matrix for inkjet printing paper. Conventional kaolins and carbonates, which typically have low surface areas, are not suitable for inkjet printing. Higher surface area pigments are required to match or surpass the print quality of traditional silica pigments.

Background

High surface area Precipitated Calcium Carbonate (PCC) for use in inkjet receptive media was introduced to the public in 1997 by Specialty Minerals Inc. with the trademark JETCOAT® 30 PCC. This PCC is a high surface area, reticulated structure that has been processed to trap inkjet ink colorant while allowing the vehicle to penetrate to the base media below. With much higher surface area than typical coating PCCs, JETCOAT® 30 PCC gives comparable print quality results to silica but a lower system cost. The lower cost is due partially to much lower binder demand; this PCC requires one-third the amount of polyvinyl alcohol (PVOH) compared to silica in the same inkjet applications (Donigian, et al.). Silica can require 30 to 40 parts of PVOH binder while only 5 to 12 parts of PVOH are recommended for a JETCOAT® 30 PCC formulation (the parts of PVOH are dependent on sizing of the basestock). Silica has been used for its porous structure and water loving characteristics and is able to trap the large volume of water/solvent in the ink applied by the inkjet printer (Chapman). This requires a thicker coating film and proportionally greater cost reflected in the greater binder demand (Donigian, et al.). PCC, on the other hand, "traps" the colorant portion of the ink droplet and relies on the base media to be receptive to the water phase vehicle portion that remains.

Literature suggests that surface enhanced aluminosilicates (SEAS) such as Digitex ™ (Longo) can be formulated at upwards of 50% coating color solids for MSP (metered size press) applications for inkjet receptive paper. SEAS may have an advantage with regard to solids, but the brightness and CIE b* values are lower than PCCs as a result of the yellowed clay. SEAS often require 20 parts of PVOH and a co-binder which can be far more costly than the recommended starting formulation of 7 parts of PVOH as a sole binder for PCC.

Silica pigments in the form of amorphous, precipitated, fumed or gel sell for \$2.00 to \$4.00 per pound (Rooks) which has opened the market for lower cost alternate pigments such as kaolin and calcium carbonate for matte, semi-gloss, and photographic inkjet grades. Kaolins and calcium carbonates have higher coating color solids than silica. Silica slurries alone do not flow well at solids levels above 15% to 20% (Rooks) while JETCOAT® 30 PCC slurry is available at 25% solids. PCC coating colors can be made with PVOH, starch, latex or combinations of the three binders. PCC coatings have been incorporated in a wide range of inkjet papers and coating formulations from metered size press (MSP), blade, rod, airknife and cast coaters to create paper grades in all levels of the inkjet paper pyramid. JETCOAT® 30 PCC has excellent printability, but may have application limitations with regard to coat weight and coater speed due to the 25% solids. To address this limitation, SMI has produced PCCs at 35% to 45% solids. The commercially produced pigments have been evaluated on pilot as well as commercial coaters with great success. Increased pigment solids yield increased coating color solids which, in turn, allow this second generation pigment to run at higher coat weight and higher coater speed on standard coating equipment with no loss in inkjet print quality. A higher solids coating color requires less dryer capacity than a lower solids coating color, which is an added benefit.

Pigment Blends

There is a synergistic effect between silica and the second generation PCC. Blends of dry silica and PCC impart a two-fold benefit to the formulations: first, the coating color solids increase relative to the silica alone and, second, the inkjet attributes of the silica and PCC blend further enhance the print quality of the paper. A synergistic relationship also holds true for PCC and SEAS. SEAS can be added as a dry co-pigment with the predominant portion remaining PCC. This can increase the coating color solids thus increasing the coater speeds. Blending the two pigments can increase the brightness and CIE b* values of the coating color relative to SEAS as the sole pigment. The binder demand will decrease as PCC content increases in a SEAS and PCC blend as well as in a silica and PCC blend.

Experimental

A series of inkjet pigments were characterized, dispersed and formulated in standard inkjet formulations. The "natural" pigments were characterized for surface area (BET); the dispersed pigments were characterized for percent solids and Brookfield viscosity prior to formulating. The pigments were formulated in a typical inkjet coating color with partially hydrolyzed PVOH, cationic additive and AZC crosslinker. The coatings were drawn down on uncoated basestock, dried with a heat gun and allowed to condition in a CTH room prior to printing. The laboratory coated paper samples were printed on a range of narrow format inkjet printers from Hewlett Packard, Epson, Canon and Lexmark. The samples were evaluated for optical density and color bleed. They were also compared to commercially available samples purchased from a local office supply warehouse, which were identified by XPS surface analysis.

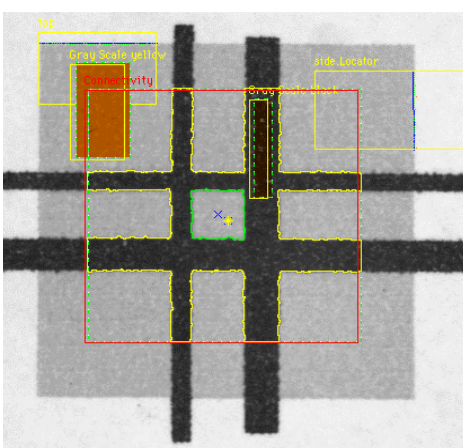

Image 1. Color bleed analysis

Equipment

XPS - The XPS (X-ray Photoelectron Spectroscopy) analyses were performed on a Kratos XSAM 800 spectrometer. The instrument was run in the fixed analyzer transmission (FAT) mode. Surface concentrations were calculated from the peak areas of the element region using sensitivity factors provided by Kratos Analytical. The high-resolution carbon spectra were peak fitted, after Shirley-type background subtraction, using peaks with a 75% Gaussian and 25% Lorenzian shape. The analysis chamber during data acquisition had a pressure in the mid 10^{-9} torr range.

XPS is a surface sensitive technique with an analysis depth of 5-50 Å. Samples are bombarded with x-rays causing electrons to be emitted. The electrons, which evolve without energy loss, originate from the top few monolayers. The spectrometer separates these electrons according to their kinetic energy. The energies of the photoelectrons depend not only on the element from which the electrons originate but also upon the chemical environments of that element. This is particularly true for carbon and permits a more detailed resolution of surface carbon in its oxidation states.

KDY ImageXpert - ImageXpert™ is an automated image quality measurement system, which provides a precise and objective means of quantifying the image quality performance of imaging devices or media (KDY Manual). ImageXpert™ is a machine-vision based system that produces repeatable and reliable quantitative results with consistency that cannot be achieved though inherently variable subjective evaluations performed by human observers. Evaluating the color bleed, also known as spreading and feathering, of the printed image via image analysis creates a quantitative value, which can be compared objectively to other samples. Image 1 is an illustration of the color bleed measurement taken with the ImageXpert software.

Preparation of Pigment Slurry and Coating Color

The PCC pigments were dispersed with unique dispersant chemistries, to create three distinct pigments. The kaolin pigment was dispersed with polydadmac as recommended by the supplier. In accordance with the manufacturer's instructions, the kaolin was added to the water with a portion of the dispersant already present within the water. The kaolin readily dispersed into the water and the dispersant. Additional dispersant was added to fully disperse the kaolin to a slurry solids of 48.8%.

The silica pigment was received as a powder and dry added to create PCC and silica blends. Both the silica and kaolin blends were 90:10, 80:20 and 70:30 ratios with the PCC being the dominant pigment. The coating colors with PCC as the sole pigment readily mixed with the binder and additives. The coating colors with pigment blends required some additional dispersant to create a homogeneous slurry and to control viscosity. In the case of silica and PCC blends, additional dispersant was required if greater than 10 pph of silica was present. Without the additional dispersant, the coating was lumpy and the drawdown was very rough. The kaolin and PCC blends readily dispersed with no additional dispersant. Both the kaolin and the silica were received as "dry" pigment and added as such to attain maximum coating color solids.

Table 1: Coating Colors for Hand Drawdowns

Slip Material	1	2	3	4	5	6	7	8
PCC 1	100							
PCC 2		100		90	80	70	90	80
Silica				10	20	30		
Clay			100				10	20
PVOH	7	7	30	7	7	7	7	7
Cationic	2	2	2	3	4	5	3	3
Crosslinker	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Table 2: XPS Surface Analysis of Commercial Sheets (atom %)

Samples	1	2	3	4	5	6	7	8	9	10
C (total organic)	17.6	37.4	24.6	39.9	58.9	55.5	59.6	59.5	60.4	58.5
CHx	8.7	24.6	13.1	22.2	13.9	28.8	15.2	15.5	16.8	14.6
C-O	6.5	10.7	8.7	12.1	37.1	17.4	35.8	36.3	34.9	35.1
C=O	1.4	0.81	1.7	2.2	7.9	5.1	7.7	7.7	8.1	7.1
O-C=O	1	1.3	1.1	3.4	ND	4.2	0.89	ND	0.55	1.7
C (CO3)	ND	ND	11.1	0.52	ND	5	0.43	ND	0.24	0.39
Ca	ND	ND	13.2	0.03	0.47	5.1	0.55	0.52	0.7	1.3
Si	7.7	15.4	0.09	12.4	0.29	0.04	0.2	0.24	0.15	0.07
Al	12.3	ND	0.16	0.08	0.1	0.45	ND	0.09	0.09	ND
F	0.01	1.2	ND	ND	ND	ND	ND	ND	ND	ND

Printer Specifications

The printers that were incorporated in this evaluation were Hewlett Packard 6540, Hewlett Packard 970C, Epson C86, Epson 890, Canon IP4000, and Lexmark Z705. All samples were printed in the factory default settings with the assumption that the average consumer often does not alter the settings that are present at printer installation. The average consumer buys the paper for the quality; he/she does not adjust the printer settings unless instructed to by the paper manufacturer.

Print Quality Measurements

An in-house test form derived from Hewlett Packard's original inkjet testing criteria was analyzed as the print target. The two key print quality parameters for this study were optical density/color appearance and color bleed. Optical density was evaluated utilizing a standard ink densitometer, while the color bleed was evaluated utilizing an image analysis package (hardware & software) called ImageXpert (Wolin).

Conclusions

XPS Analysis

For this study three grades of commercial ink jet paper were evaluated: photographic, matte and multipurpose. By measuring the surface concentrations of particular organic and inorganic surface elements, the surface coatings could be determined. XPS surface analyses were performed on these sheets to identify the surface coatings. Table 2 illustrates the XPS results of several commercial papers evaluated in this study. For the photographic grade papers, three different surface coatings were identified that appear to be comprised of calcium carbonate (sample3), silica (sample 2), pseudoboehmite (sample 1) or a fluorinated surfactant. The matte grade inkjet sheets are coated with calcium carbonate (sample 6), silica (sample 4), pseudoboehmite/aluminum oxide or a blend of these pigments. Alumina is used in inkjet coatings similar to silica, a special commercial type alumina, pseudo-boehmite (AlO_2H) is used as an aqueous dispersion for high end inkjet grades (Vikman). The AlO_2H was identified through XPS analysis of the higher atom % of Al rather than Si which is typical of clay. The multipurpose office papers are coated with calcium carbonate, clay or a blend.

Print Quality Analysis

The print quality was evaluated by two specific parameters, optical density and color bleed. The higher the optical density value the brighter the printed image, while the lower the color bleed value the greater the tendency of the ink to remain in place and not wick or spread. The print quality was far superior with the commercially produced photographic inkjet sheets than with any other sample evaluated in this study. The photographic samples contain high-end pigments, binders, additives and multiple coating layers to produce the high quality, which increases cost of the coating color. PCC pigments or blends of PCC and other engineered pigments are a lower cost alternative. The matte commercial samples performed fair for optical density and color bleed. The multipurpose samples performed better than the matte grade, which may be a result of the surface chemistry rather than the pigment selection. Multipurpose sheets may be surface treated with a cationic starch which will readily attract the anionic ink. The laboratory hand drawdowns performed equal to or better than some of the commercially produced sheets due to the pigment content. Chart 1 illustrates the optical density of selected samples printed on the HP 6540. The commercial samples are characterized as follows: samples 1,2 and

3 are photo quality, samples 4, 5, 6 and 7 are matte to semi-gloss and samples 8, 9 and 10 are multipurpose. These commercially produced samples were compared to hand coated drawdowns containing several engineered pigments. XPS analysis demonstrated that the samples, which contained specialty additives and pigments, performed better than those that contained only starch coated/surface treatments.

The PCC hand coated samples 1 and 2 performed much better than the sample 3 with clay as the sole pigment. Blending the two pigments, 7 and 8 increased the optical density compared to sample 3. Two commercial samples, 3 and 6, contained calcium carbonate as the dominant pigment, and performed similarly to the laboratory hand coated samples 1 and 2, which were SMI's PCC. Sample 3 is a photographic quality paper containing PCC and it prints much like multi-layer photographic papers containing silica and/or aluminum oxide. Sample 6 is a matte grade paper containing PCC, which has comparable black values and better cyan values than some photographic grades containing silica and/or aluminum oxide pigments.

The uncalendered hand drawdowns had excellent optical density due to the ink trapping mechanism of the PCC. Blending the PCC with dry pigments increased the coating color solids and created print results that were better than some of the commercial matte and multipurpose samples. Blending PCC and silica resulted in slight increases in black and cyan values. This type of blending can also yield higher gloss results with appropriate calendering and binder selection to create semi-gloss and/or photographic quality inkjet sheets.

The XPS analysis of the commercially produced inkjet sheets demonstrated that silica is not the only player in the market; calcium carbonate and alumina are utilized in many inkjet grades. The laboratory hand coated results illustrate that PCC can be utilized in all grades of inkjet papers and when the formulations are optimized, high quality inkjet paper can be produced with PCC (Chart 1).

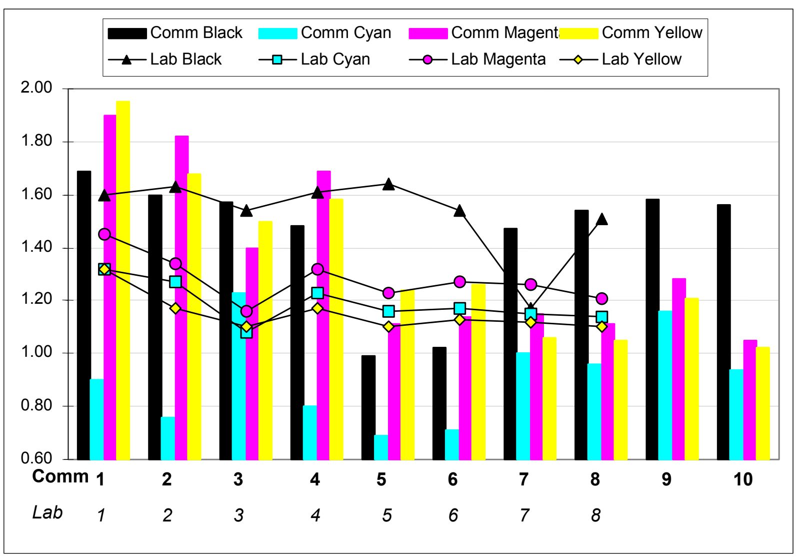

Chart 1. Print Results Hewlett Packard 6540

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Author Biography

Annmarie Superka is currently a Scientist at Specialty Minerals Inc. and a 1995 graduate of Allegheny College. During her eight-year career at SMI, she has authored and contributed to several papers on inkjet printability. As the global technical coordinator of the JETCOAT product line, she focuses on customer support and product optimization. She and a colleague have recently developed and filed patents for second generation PCC inkjet pigments