Application of Polyolefin Dispersions in Paper Coatings

Roland Gong, Paul D. Fleming, Margaret Joyce and Erika Hrehorova; Western Michigan University, Kalamazoo, MI
Elizabeth Yuan and Sandy Mitton; Baker Hughes Incorporated, Sugar Land, TX

Abstract

The quality of inkjet printed color is significantly influenced by the substrate coating structure, which strongly affects ink-setting performance. Small amounts of coating additives are necessary and play an essential function, which in turn affects the substrates final surface structure, optical properties and printed color. The main objective of this study was to evaluate the performance of various polyolefin dispersions in paper coatings for inkjet papers and their effects on paper properties, inkjet printability and color. The polyolefin dispersions were added to a typical silica based coating formulation, and then compared to a control coating without a polyolefin additive. The coatings were applied to base sheets by a cylindrical laboratory coater. Coated papers were then calendered. To ascertain the mechanism underlying the effects of tested additives coating rheology, surface properties, optical properties, and print quality were measured. Based on the results, these additives provide increased paper brightness due to enhanced OBA efficiency, better lightfastness, and the potential for improved coating application.

Introduction

Among digital printing technologies, inkjet offers a high quality of color reproduction, resolution, and speed. This makes inkjet a leading digital printing method to challenge conventional printing for photo reproduction and high quality graphics. Generally, inkjet inks are aqueous, dye or pigment based, which are composed of 65-90% water [1]. Due to the drying mechanism, it is critical that an inkjet substrate absorbs ink instantly. Consequentially, substrate quality significantly influences inkjet printing quality. For inkjet paper, the coating structure and quality determine commercial inkjet paper grades and functions [2]. Many efforts have been made by manufacturers and researchers to approach high print performance; such as wide color gamut, optical density, sharpness or resolution, and archival properties.

During this experiment, four anionic and one nonionic polyolefin dispersions from Baker Hughes were tested. To prescreen these additives, drawdown coating tests were performed prior to application by a cylindrical laboratory coater (CLC). Due to the significant impact on coating rheology, the nonionic additive was removed after the prescreening. This paper reviews test results from the four anionic additives.

Methodology

Amorphous silica based coating formulations are widely applied on premium inkjet papers, due to their highly absorbent nature and brightness characteristics [3]. For this study, a typical silica based inkjet coating formulation was applied with and without polyolefin additives. The coating formulation is given in Table 1. Silica dispersion was Pyrogenic (Fumed) Amorphous Silica from Cabot (CAB-O-SPERSE PG 001, particle size: 188 nm, pH: 9.9-10.9). Polyvinyl alcohol (PVOH) was partially hydrolyzed from Celanese (Celvol 203 S). To maintain dispersion stability, PVOH pH value was modified with NH_4OH to be close to that of silica [4]. Starch was modified hydrophobic surface starch (Filmkote 54, National Starch). Optical brightening agent (OBA) was cationic, Leucophor FTS from Clariant. Additives tested included polyolefin dispersions A, B, C, and D (see Table 2). A control without additive was also tested. These names were also used to designate the coated paper samples. A total of five coating formulations were prepared. The final coating solid content was 26.5%-27.5%.

The base sheet used in the coating experiments was a sized paper. The physical properties measured for the base sheet were: basis weight of 62 g/m^2, Parker Print Surf roughness of 4.05 µm (1000 Pa, soft backing), TAPPI brightness of 86.8%, and paper gloss (at 75°, MD) of 14.3%.

Table 1: Typical Commercial Coating Formulations

Coating	Control	A	B	C	D
Ingredients	Dry Parts Added				
Silica	100	100	100	100	100
PVOH	10	10	10	10	10
Starch	10	10	10	10	10
OBA	4	4	4	4	4
A		4			
B			4		
C				4	
D					4

Table 2: Four Anionic Polyolefin Dispersions

	Chemistry	Viscosity (cps)	Solids (%)
A	Functional Polyethylene	10.0-15.0	22-25
B	Functional Polymer	10.0-20.0	18-20
C	Functional Polyalphaolefin	400.00	25-30
D	Functional Polymer	20-30	18-20

To identify the influence of tested additives on coatings, an AR 2000 Dynamic Stress Rheometer (TA Instruments) was used to study rheological properties at low shear rates. In addition, a Hercules Rheometer was used to determine rheological behavior at high shear rates (E Bob, 6600 max RPM and Spring Set at 200 kilo dynes-cm, 20.4 Sec).

The coatings were applied by a blade type, cylindrical laboratory coater (CLC) at 3000 ft (762 m) per minute. The target coating weight was 14 g/m^2. All the samples were calendered with the soft-hot nip calender through 2 nips, at 500 pli (1000 psi on gauge) and 71.1°C (160°F).

Paper roughness was measured by PPS ME-90 (1000 Pa, soft backing) based on TAPPI T555-OM-99. Air permeability, from PPS porosity was also measured under the same conditions. Brightness of coated samples was measured with a BrightiMeter Micro S-5 based on TAPPI Standard T452-OM-98 (457 nm light). Paper gloss was measured at 75° using a Novo-Gloss™ Glossmeter based on TAPPI standard T480-OM-99, in both machine direction and cross-machine direction. CIE L*a*b* value of paper samples were measured by X-Rite EyeOne IO SpectroDensitometer. To study the water absorption on coated papers, an ultrasonic water penetration test was performed using an EMCO DPM30. Dynamic contact angle tests, which were related to paper surface energy, were also performed by using FTA 200; and water drops spreading (simulating aqueous ink spreading) were observed too.

Samples were printed with an Epson Stylus Photo 2200 printer using an Ultrachrome 4-picoliter pigment ink. ORIS Color Tuner 5.5.1, one printer RIP software from CGS Publishing, was applied to achieve accurate CMYK tint color [5]. 100% and 20% CMYK tints were printed on each sample. Optical density was measured with an X-Rite 530 SpectroDensitometer on the 100% tint. Print gloss was measured on the 100% magenta tint using a Novo-Gloss™ Glossmeter (at 75°). A TC3.5 CMYK test chart was printed on each sample (at 720 dpi) to determine each samples color reproduction performance. These charts were measured with an X-Rite EyeOne IO Spectrophotometer. ICC profiles were then generated using Profile Maker 5.08 software. The color gamut volumes achieved from the coated papers were derived from CHROMiX ColorThink 3.0 Pro software. All samples were then exposed to over 48 hours to a xenon exposure system, Suntest CPS+, Atlas (@ 765 W/m^2) to determine fade resistance. The intensity of light exposure used is equal to 4.5 months of daylight (June) in Florida [6, 7]. The charts were then measured again to calculate their color gamut volumes [8].

An Epson premium photo glossy paper was selected as a reference for some tests. It is a typical resin coated photographic paper of five layer construction. The paper base weight was 250 g/m^2 and caliper was 10 mils.

Results and Discussion

*Brightness and CIE L*a*b**

The largest observed benefit of the polyolefin additives were higher brightness and improved L*a*b*. Paper brightness is related to print contrast and color reproduction, and is one of the key factors for print appeal. Fluorescence optical brightening agents (OBAs) are widely used in inkjet paper. OBAs increase brightness by absorbing light in the UV spectrum (340-370 nm) and re-emitting blue white visible light (420-470 nm) [9]. As shown in Figure 1, all of the tested polyolefin additives significantly increased the brightness of the paper samples. Additive D increased it the most.

In addition, samples containing polyolefin additives showed significantly lower b* values compared to the control. The lower b* values relate to a bluer undertone that contributes to perceived brightness. Additive B and D have the lowest value, as shown in Table 3. The precise mechanism is not yet clear. One potential mechanism is that these additives might carry or fix the OBA near the coating surface. Another could be that these additives enhance the cationic brightener efficiency. From their performance, it could be interpreted that these polyolefin additives function as efficient OBA carriers [9].

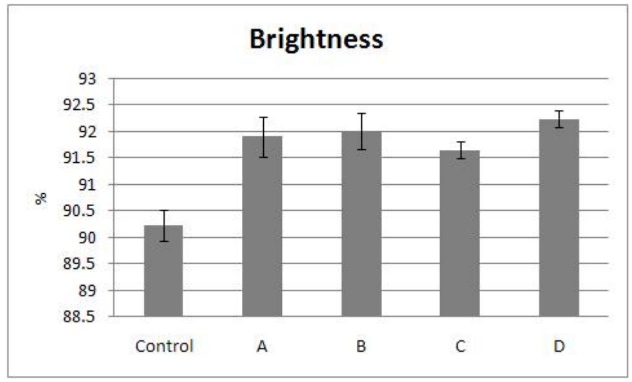

Figure 1: *Paper Brightness*

Table 3: CIE L*a*b*

	Control	A	B	C	D
L*	95.92 ± .08	96.08 ± .07	96.08 ± .08	95.98 ± .08	96.09 ± .04
a*	-.30 ± .08	-.09 ± .06	.12 ± .11	-.31 ± .06	.08 ± .04
b*	-1.24 ± .28	-2.59 ± .21	-2.95 ± .33	-1.64 ± .18	-3.02 ± .20

Lightfastness

Initially marketed inkjet photo paper had a poor lightfastness, or fade resistance. As the uses of digital cameras have grown, consumers want the digital output, from generally inkjet printers, to last as long as possible [10]. Many other documents also require the print to have better archival ability. According to Epson Corporation, a photo paper typically has a polymer layer that protects against fading caused by light and air pollution [11].

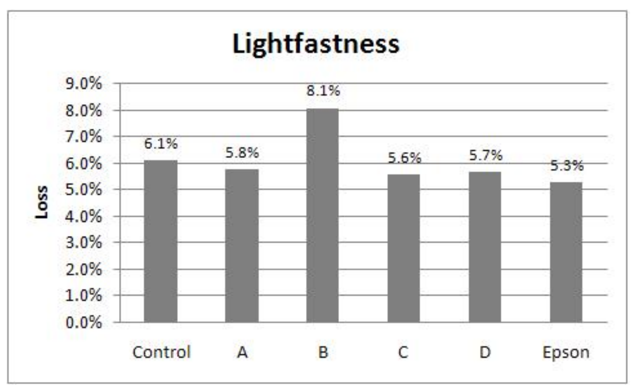

Figure 2: *Lightfastness*

In the lightfastness test performed in this experiment, polyolefin additives showed slightly lower color gamut loss when compared with the control, except for sample B. Furthermore, the performance is all very comparable to Epson photo paper. Compared to the commercially manufactured photo paper, with a protective layer and well-controlled quality, the effects of the three tested polyolefin additives were definitely positive. This further confirms the hypothesis based on the brightness test results: these additives function as efficient OBA carriers [9]. The results are shown in Figure 2.

Color Gamut & Optical Density

Except for color fidelity and optical density, print quality can be evaluated by the color gamut volumes [8]. A wider color gamut volume results in better color reproduction [6-8]. From Figure 3, tested samples showed color gamut volumes similar to those of the control, except for sample A, which is slightly lower. Additionally, all samples with polyolefin additives have better color reproduction in highlight areas (see Fig.4 top left region) and blue regions in 3D color space, compared to the control. The difference between sample A (lowest color gamut volume) and sample D (lowest b* value) with the control are shown in Figure 4. The lower color gamut volumes of the Epson paper is due to the higher absorbance of ink. In the optical density test, there were no significant differences in optical density between the control and the samples with additives. However, they also had better values than the commercial Epson ink jet paper. For instance, 100% black tint density on sample D (2.07) is 25% higher than the value on Epson (1.49).

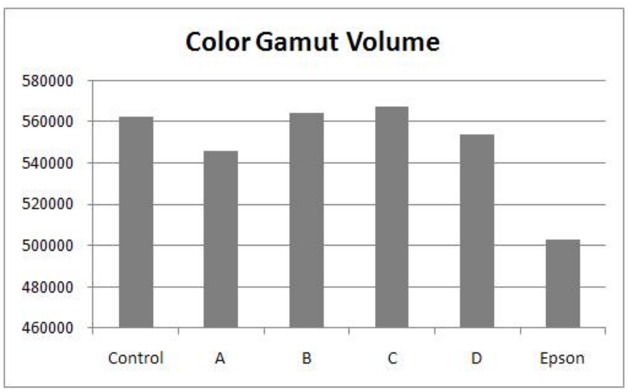

Figure 3: *Color Gamut Volumes*

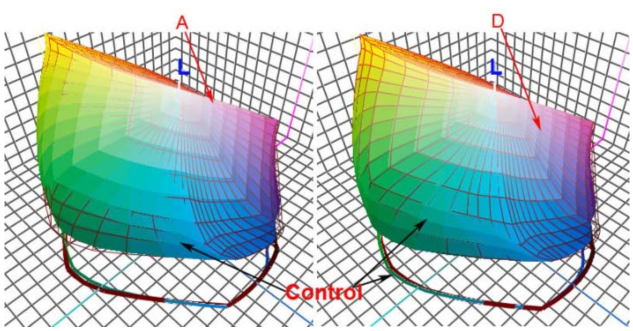

Figure 4*: 2 and 3 Dimensional Color Space. Left, Control (colored solid) vs. Sample A (red line frame). Right, Control vs. Sample D (red line frame)*

Rheology

Rheology significantly affects coating performance and process run ability [12]. Table 4 lists the coating rheology properties, which were derived from the rheological measurements. Three measurements, Oscillation Stress Sweep, Oscillation Frequency Sweep and Steady State Flow were performed; all are commonly used to analyze coating viscoelasticity and flow properties. Onset Point is a critical point where the elastic modulus (G') starts to decrease and the coating dispersion starts to flow.

Table 4: Coating Rheology Properties

	Control	A	B	C	D
Onset Point: Pa	2.4	2.9	3.2	3.7	2.2
G': Pa	169	162	340	187	108
Z.R.V *: KPa·s	11.2	19	41.8	29.7	4.3
I.R.V**: Pa·s	.09	.08	.08	.08	.05

** Zero-Rate Viscosity; ** Infinite-Rate Viscosity*

Figure 5 shows coating viscosity versus shear rate. Separate testing was done at both low and high shear rates and fitted onto one chart. Compared to the control, three of the additives slightly increased the coating viscosity at low shear rates. Additive D presented the lowest viscosity in the low shear rate range, which could allow an increase in coating solids content. Due to economic considerations, manufacturers prefer to apply coatings at the highest solids possible [13].

In addition, the control presented a slight dilatant behavior in the high shear range. This could contribute to poor run ability, especially using blade type coaters [14]. This dilatant behavior was not observed for the tested polyolefin additives.

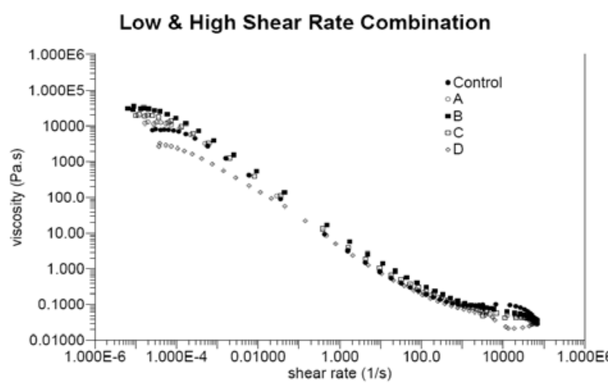

Figure 5: *Coating high and low shear rate vs. viscosity (Cross model)*

Roughness, PPS Porosity & Water Penetration

Although there is not a uniform interpretation for the ultrasonic water penetration test, some previous research has shown a correlation of these values to paper roughness, air permeability and wetting time [15]. In Table 5, two important parameters are shown. t_B is the time with maximum transmission, which is the elapsed wetting time; t_S is the time with most negative gradient, which refers to peak absorbency time.

Table 5: Ultrasonic Water Penetration & Paper Surface

Sample	Con*	A	B	C	D	E*
t_B: *ms*	308	307	107	323	87	37
t_S: *s*	3.6	4.6	5.4	7.3	6.3	0.28
R** microns	1.17	1.23	1.11	1.17	1.25	2.08
P***: ml/min	24.9	23.1	23.5	23.4	23.1	161

** Con: Control, E: Epson; ** Roughness, error ≤ ±5%; *** PPS Porosity, error ≤ ±10%.*

Samples B and D had moderately shorter initial wetting times. It was observed that all of the tested additives required more time to reach their peak absorbent time, compared with the control. From the long period absorption curves in Figure 6, all of the additives prolonged the water penetration time (or saturated time); with Additive C doing so the most. However, both paper roughness and air porosity were similar for all the samples. Therefore, these additives increase the samples hydrophobic properties, rather than decrease the air permeability. The net effect is that the additives reduce the ink penetration rate into the base paper.

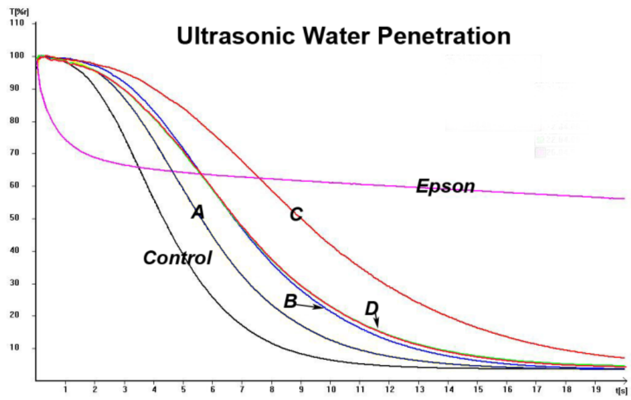

Figure 6: Ultrasonic Water Penetration in 20 seconds, Y axis is energy transmission rate (r %)

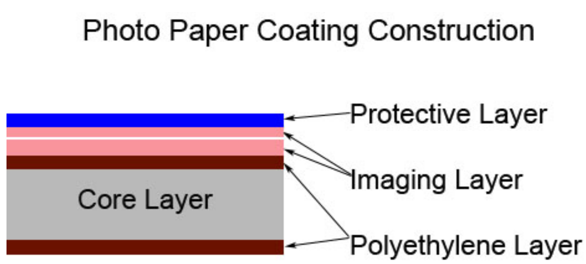

***Figure 7**: Typical Photo Paper Polyethylene Coating Construction*

Premium inkjet paper, such as Epson photo paper, normally adopts two imaging layers to provide sufficient ink capacity. The first imaging layer is set to fix ink droplets in place; the second layer absorbs additional ink (Figure 7). It also has two extruded polyethylene layers to eliminate ink penetration into the core paper layer and maintain dimensional stability; which also improves smoothness, gloss and anti-curling (back layer) properties [11, 16]. Hypothetically, choosing suitable additives for the second imaging layer might eliminate the need for the top polyethylene layer. If so, inline coating would become possible. However, this is beyond the scope of this paper.

Contact Angle

Figure 8 shows the change of water contact angle on the paper samples in 10 seconds. The angle change represents water spreading. The initial contact angles of the samples with additives are comparable to the control. The Epson paper has a higher initial contact angle because it has a low surface energy protective polymer layer. During the 10-second test, the contact angle of samples A, C and D showed a slower decline than the control, which indicates less ink spreading or ink immobilization. This could provide improved image resolution and sharpness, providing further support that polyolefin additives enhance the performance of the first imaging layer of the photo paper.

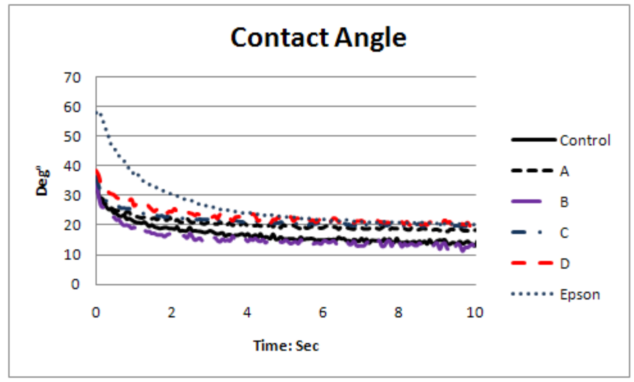

***Figure 8**: Surface Contact Angle*

The change of droplet volume was also recorded and it is shown in Figure 9. These data were normalized to their initial readings. Combining this data with the above contact angle results indicate that samples A, C and D have less ink spreading than the control. Compared to Epson paper, the contact angle of samples C and D declined slower, while the remaining drop volumes dropped faster than the Epson paper. This indicated that the ink droplet would be well fixed on the spot with less spreading.

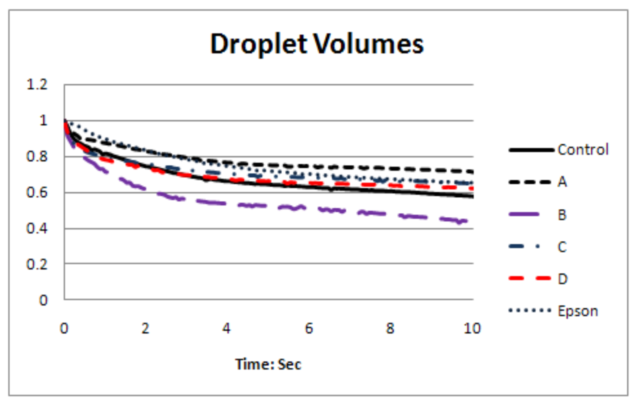

***Figure 9:** Water Droplets Remaining Volumes on Samples*

Conclusion

Overall, the four anionic polyolefin additives provided improved performance of the paper coatings. Additive D provided the best total performance with positives related to optical properties, print properties and run ability. Additives A, B, and C provided a mixture of positive and neutral test results.

All of the additives significantly increased paper brightness. We theorize that this is related to improved OBA efficiency. Additive D provided good lightfastness. It also provided the ability to control ink spreading, which would improve the image resolution. While all additives eliminated the dilatant behavior observed with the blank control coating, Additive D also reduced the viscosity at low shear rates, which might enable an increase of coating solids content.

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Author Biography

Roland Gong is the M.S. student of Paper and Imaging Science and Engineering; Department of Paper Engineering, Chemical Engineering and Imaging, Western Michigan University. Mr. Gong recieved his bachelor degree in Xi’An University of Technology, China. He had 10 years manufacturing and marketing experience in Imaging and Packaging industry. He has concentrated on new materials research in paper manufacturing, and digital printing materials improvement.