Uncoated Paper for Continuous Ink-Jet Printers

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Abstract

This article discusses images printed with a high speed continuous ink-jet printer on uncoated paper using dye-based inks. For such images print quality and waterfastness depend highly on paper additives. Optimizing paper properties requires tradeoffs. For example, increased print waterfastness leads to a large loss of print optical density. With improved waterfastness also comes more print raggedness. Color-to-color bleed and black print quality generally are opposed to each other. Why the trade-offs occur and ways of overcoming them are discussed.

Total cationic charge dictates waterfastness but limits ink coverage, which contributes to lower optical density. Increased sizing lowers waterfastness because of an inability of the ink to interact with cationic charges in the paper. Increased sizing improves black print quality but sometimes leads to lower optical density because of even less ink coverage. Concurrently, higher sizing often lowers color-to-color print quality by increasing bleed. Using and changing additives that alter the absorption and adsorption of inks adjusts the balances of properties. For example, just reducing surface starch levels significantly increases optical density for a given level of waterfastness.

Introduction

Continuous ink-jet printers provide individual full color digital images on every printed page at incredible speeds [1]. A large percentage of the printing occurs on uncoated paper. Use of uncoated paper with dye-based inks, as with the Versamark printers from Kodak, makes it difficult to obtain the desired print properties of high print optical densities (ODs), sharp images, and waterfastness (WF). Additives in the paper greatly enhance these qualities. However, tradeoffs exist between the desired results. This article describes paper additives that enhance OD, WF, and print quality and that change the balance of properties.

Paper samples for the current work were made on either a pilot paper machine equipped with a puddle size press or by treating pre-made paper on a bench top size press.

A Canon Pixma iP6000 desk-top ink-jet printer loaded with Versamark inks served to simulate Versamark printing. The test pattern used contained a notched black circle for testing waterfastness and solid areas of cyan, magenta, yellow, and black for measuring ODs. The test pattern also contained black dots, magenta dots, and black dots on a yellow background for obtaining ink-spread and edge-raggedness of printed areas. A Verity IA image analysis system provided measurements of the dot spread and edge-raggedness [2]. A densitometer provided ODs. WF was measured by soaking black printed areas in deionized room temperature water for 60 seconds followed by air drying. Two measurements are common for WF, a loss of black OD and bleed of black ink into unprinted areas. With almost any type of mordant black OD does not decrease with the water soak and in fact usually increases. Therefore, in the current work waterfastness was quantified by the black OD imparted to an unprinted area. A typical starting black OD in an unprinted area of white paper is 0.04 to 0.05.

Waterfastness

Figure 1 gives examples of poor, fair, and good WF samples with optical densities of 0.38, 0.11, and 0.05. The figure shows how the ink can bleed in water.

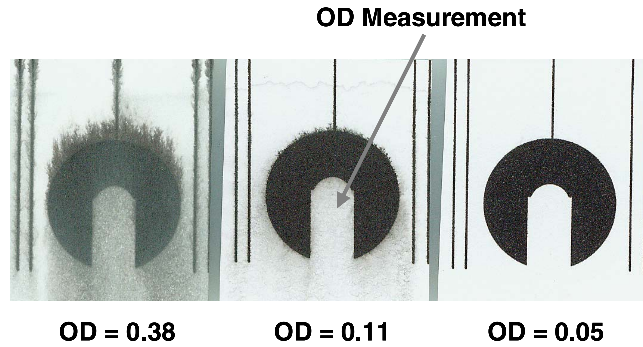

Figure 1. *Poor, Fair, and Good Waterfastness Following Water Soak*

Addition of a cationic polymer to the paper provides WF. Figure 2 shows the WF obtained from paper samples containing cationic mordants of varying charge density added at various levels. The results are plotted by total charge in the paper, which equaled the charge density of the mordant times its concentration in the paper in dry pounds per ton of dry paper. The broad conclusion is simple, for similar paper samples the level of WF largely depends on the total cationic charge in the paper regardless of the charge density of the mordant.

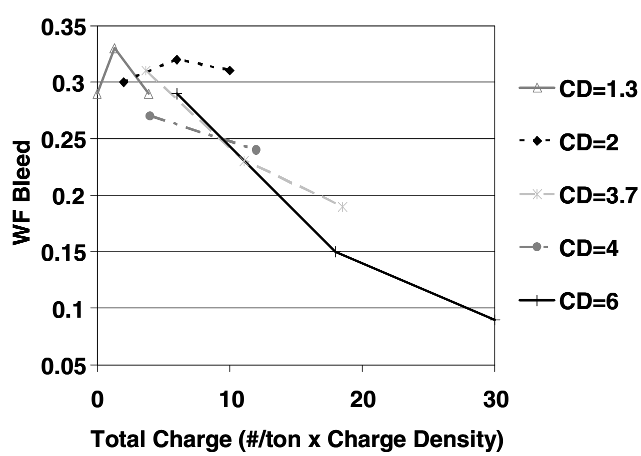

Figure 2. *Waterfastness vs. Total Cationic Charge (Mordant Charge Density Times Addition Level to Paper in Pounds Per Ton)*

For the remainder of the work presented here a Hercules Incorporated cationic polymer mordant (M-5018) served as the primary mordant for WF. It provides a high charge density of greater than 8 meq/g at a low cost. By comparison, the charge density of poly(diallyldimethyl ammonium chloride) is 6.1. A typical paper addition level of M-5018 in paper to get excellent WF for Versamark prints is 0.8 to 1.0% on a dry basis on 80g/m^2 paper.

The paper samples in Figure 2 were similar. However, paper properties do not remain the same from mill to mill or grade to grade. For example the water hold-out (sizing) may vary greatly. Hercules offers many products that impart sizing to paper. The Hercules Sizing Test (HST) measures the rate ink penetrates through paper.

Figure 3 shows that with equal mordant level WF depends highly on the paper sizing, as measured in seconds by the HST. The higher the sizing the worse the WF. Therefore, to obtain optimum WF in a paper the HST value should be kept low. It doesn't matter if the high HST value comes from internal or surface sizing agents.

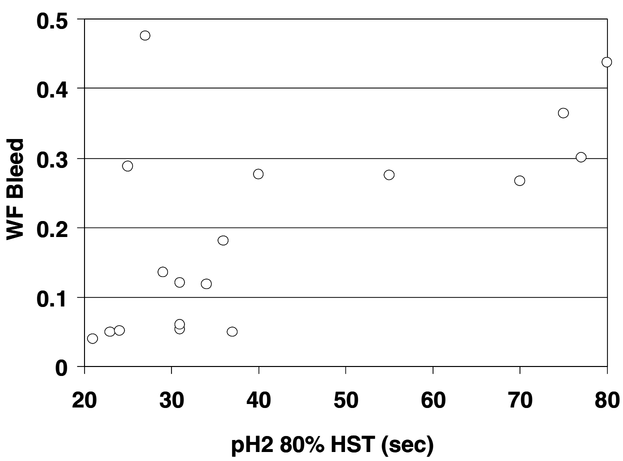

Figure 3. *Waterfastness vs. Degree of Sizing*

The effect of sizing can be understood by considering the mechanism of obtaining WF with a mordant. Cationic groups from a mordant in a paper bind strongly with the anionic dye molecules of an ink and render them insoluble in water. To be bound each dye molecule must find and associate with a cationic site. Increased sizing holds the ink toward the surface of the paper and limits its spread such that not all dye molecules reach a cationic site. They therefore remain free to redissolve in water. Changes in papermaking conditions or additives that result in a change in sizing will affect WF.

Waterfastness and Black Print Quality

For almost as long as paper has been ink-jet printed papermakers and suppliers have realized that tradeoffs occur between print properties [3]. Figure 4 presents the WF of samples versus the corresponding black OD. Ideally one wants high black OD and a low value for WF; however, the opposite occurs. One can usually increase OD by increasing sizing but as already shown this leads to lower WF. Two explanations were considered for the tradeoff. The first was interaction of the ink with the cationic polymer. However, the presence of cationic polymer did not change the light absorption spectrum of the dyes. The second cause considered was a large decrease of drop spreading such that adjacent dots of ink failed to connect together. There was some evidence for this problem as increased sizing sometimes decreased black OD. But, when looking at WF versus print quality, dot size became larger as WF improved, indicating that more spreading occurred with mordant present. Micrographs showed a third and less obvious explanation. As seen in Figure 5, with mordant in the paper, surface fibers showed through because of less ink coverage. Additionally, in both samples soft wood fibers appeared to be poorly covered by ink. It is possible, but yet unproven, that starch and mordant concentrate between fibers and draw the ink off the fiber surfaces.

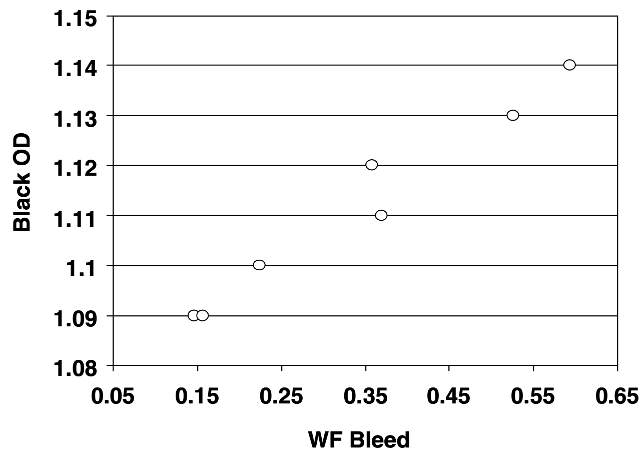

Figure 4. *Waterfastness vs. Black Optical Density*

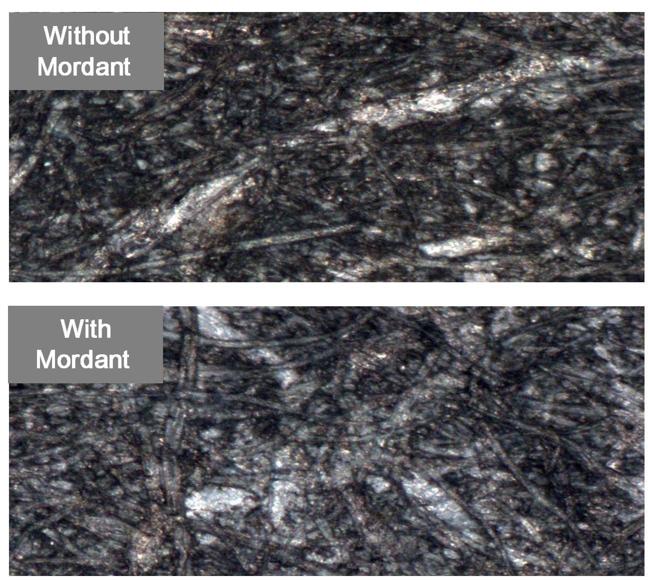

Figure 5. *Micrographs Showing Ink Distribution in Prints Without and With Mordant*

Figure 6 shows WF versus black OD for a series of samples with various additive combinations, including different levels of mordant, different mordants, different levels of sizing, the addition of fillers, and the use of different starches. Most of the printed samples fell on a line similar to the trend observed in Figure 4. However, four changes provided improvement. First the addition of 0.25% magnesium chloride (a divalent salt) with 1% M-5018 gave an improved WF for a given level of black OD. It is likely the magnesium ion helped anchor the dye or it tied up other materials in the paper that would interact with some of the cationic sites of the M-5018. Calcium chloride, another divalent salt, gave a similar improvement. Addition of hydroxyethylcellulose (HEC), an absorbent natural polymer made by Hercules, with M-5018 also improved the balance. A subsequent experiment showed HEC did not raise the OD but improved the WF for a given HST. The simplest change, and the most promising, was a reduction of the amount of starch added with the M-5018. Adding no starch led to an OD of 1.13 and a WF value of about 0.05. Reducing the starch level in half also helped but to a lesser extent. The final, and less practical modification, was the addition of uncooked starch instead of cooked starch. The starch was slurried into water containing the M-5018. With 9% uncooked ethylated starch the OD was 1.13 and the WF was 0.03. Other starches that did not dissolve under size press conditions gave similar results and a mixture of uncooked and cooked starch also gave an improvement. It is likely the uncooked starch absorbed the ink.

The reason why removing starch improved OD and WF remains unknown; however, in keeping with the theory expressed above less starch may lead to less ink being drawn off the tops of fibers. Use of less starch may also lead to a different distribution of M-5018.

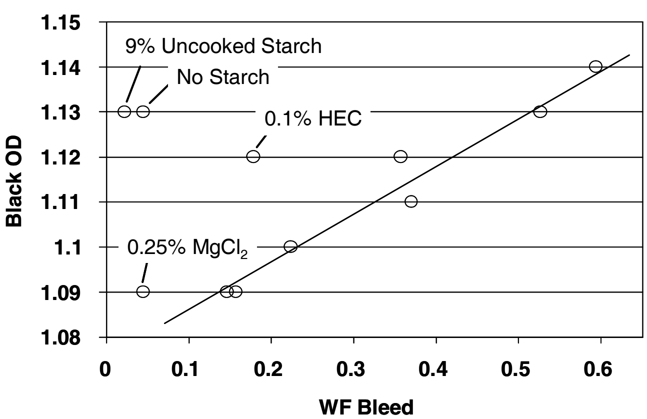

Figure 6. *Waterfastness vs. Black Optical Density*

As noted above, improvements of WF were accompanied by an increase in image dot gain, which generally means a decrease in print quality. The cationic polymer mordant does not stop the spread of ink. The mechanism of ink-spread may occur much faster than the anchoring of the ink. Related work on anchoring of pigment-based ink-jet inks indicates that to prevent ink spread and absorption into the paper the anchoring mordant must dissolve rapidly when the ink is applied [4]. Polymers, in general, do not dissolve rapidly.

Black versus Black-on-Yellow Print Quality

Another well-known tradeoff in ink-jet printing is black print quality versus color-to-color print quality. The latter is generally measured with black printing on a yellow background. Experiments showed that as sizing increased black print quality, as measured by dot size or edge raggedness, improved; whereas, black-on-yellow print quality became much worse. The results are shown in Figure 7.

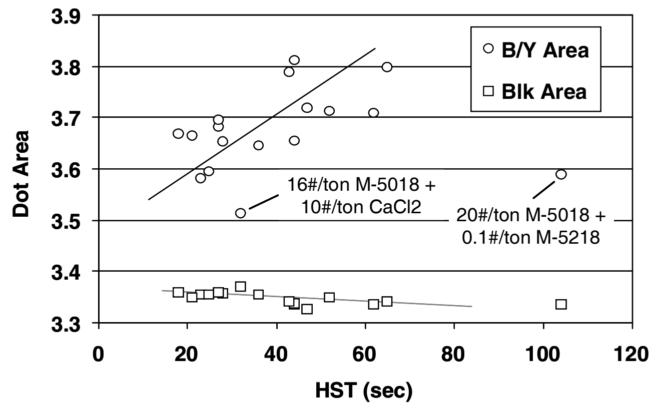

Figure 7. Black Dot Area and Black- on-Yellow Dot Area vs. HST

Two samples broke the trend. Adding 0.5% calcium chloride with 0.8% M-5018 provided much improved black-on-yellow print quality while not significantly degrading black print quality. Using a liquid reactive sizing agent (Hercules M-5218) at the surface instead of no sizing agent or in place of a styrene/acrylic latex sizing agent also broke the trend. Again black-on-yellow print quality improved without sacrificing black print quality. In addition the sizing efficiency on a dry addition basis of the reactive sizing agent was far better than a styrene/acrylic latex sizing agent. The M-5218 sizing agent allowed for an increased level of sizing without a large loss of black-on-yellow print quality. However the increased sizing did reduce WF.

In another set of experiments, the ability of the M-5218 sizing agent to improve the balance between the black and black-on-yellow print qualities was confirmed. Likewise, the use of polyvinylalcohol in place of some or all of the starch or the addition of 0.75% ground calcium carbonate at the size press also enhanced the balance.

Conclusions

The WF of Versamark prints with dye-based inks depends mostly on total cationic charge and level of sizing. Several tradeoffs of properties occur with uncoated papers. Mordants that improve WF lead to less ink coverage of fibers on the surface of the paper and therefore lower print optical densities. The WF versus OD balance was improved by adding magnesium or calcium chloride, by addition of uncooked starch, and by simply reducing starch levels. A similar tradeoff occurs with WF and print quality. Black print quality versus black-on-yellow print quality are also counter to each other. Again, adding a divalent salt improved the balance as did the use of a liquid reactive sizing agent in place of a styrene/acrylic latex sizing agent. Replacing starch with polyvinylalcohol also provided an enhancement.

References

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[4] US Patent 6207258B1, Hercules Incorporated.

Author Biography

Daniel F. Varnell received his PhD in polymer science from Pennsylvania State University in 1982 and holds a position of Research Fellow at Hercules Incorporated. His research career spans projects on graphite fibers, photoresists, solder masks, new laminate materials, and internal and surface sizing agents for paper. He has authored numerous papers and patents, including a well-known patent on the use of divalent salts for ink-jet printing. At least half a dozen products in the paper industry can be credited to his work.