The Water Resistance of Aqueous Ink Jet Graphics and Factors Pertaining to Media Design

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Abstract

In the realm of aqueous ink jet media the inherent differences between porous and polymeric, or "dense", media is well studied and documented.[1] *Features of both media types pertaining to ink compatibility, drying time of aqueous inks and image stability have been investigated. Another inherent difference between the two media types is the degree of water resistance each imparts to an image composed of water-soluble dyes. Literature provides evidence that porous media formulations can provide better water resistance to water-soluble dyes than media formulations comprising solely of water- soluble polymers.*[2] *This paper presents further studies with an objective of explaining the properties that porous coatings have, that provide the better water resistance. Moreover, it is demonstrated how these properties can be engineered into polymer design. By choosing polymer components that influence the polymeric infrastructure it is possible to create a hydrophilic polymer that forms a water insoluble film. This is shown to impart water resistance to water-soluble dyes. It is believed that this new technology challenges previous notions that a hydrophilic/hydrophobic balance is necessary for ink sorption/water resistance. Consequently, the system does not require the use of external cross linkers, a method employed to create such a balance in water-soluble films*

Introduction

Two types of media design commonly co-exist in the market place today–porous and polymer dense. These types can be distinguished by the method in which they dry the aqueous ink printed thereon. Coating formulations for porous media employ a significant portion of insoluble ceramic particles. It is the intent that when the porous coating formulation is applied, the dried coating will have a certain pore volume. The internal pores of the ceramic particles and the interstitial pores that form in between the particles create this. This pore volume and increase in surface area, in turn, creates the driving force behind the drying of the aqueous ink. Polymeric coatings dry the ink through controlled swelling of the receptive coating. Swelling and subsequent contraction of the coating upon application of the aqueous ink produces the absorption and drying effect. Matching ink to media parameters such as solubility parameters, and swell indices of the receptive coating to the water and co-solvents present in the ink are important formulation criteria for polymer dense coatings. Figure 1 below is a simplified schematic of the two media types.

This paper explores only the inherent differences between the two receptive coatings in terms of the water resistance both afford to dye based aqueous jet inks. From exploring why the two receptive coatings behave differently in this aspect, a new polymer technology has been developed that seeks to exploit the findings.

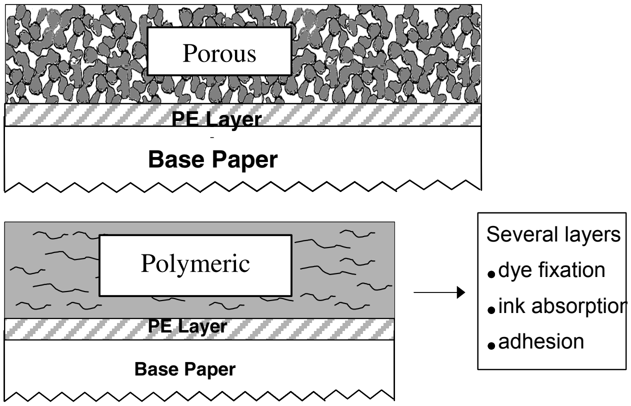

Figure 1. Schematic of porous and polymeric dense media.

Experimental Test Methods

Commercial media was viewed under SEM and subsequently subdivided into the class of porous or polymer dense. For the purposes of this paper the commercial media are designated as CM A, CM B and CM C for the polymeric types and NP A for the porous type. The water resistance of commercially available media and experimental coatings was measured using the test methods "water drip" and "water immersion". The tests are described in detail.

Water Drip Test

Color blocks of red green and blue, 2 × 2 cm in dimension, were printed on the media with a HP 5550 desktop printer. The color blocks were printed at 100% print density. The prints were allowed 24 hours to dry under controlled environmental conditions of 70°F 50% RH. The CIE L*a*b* color values of the unprinted area present directly below the color blocks was measured using an X-Rite TR938 spectrophotometer. The prints were placed at 45° angle and 2.0 mls of water was dispensed onto the center of each color block. The water was allowed to run down the print and into the unprinted area below. After the test sample had dried for a further 24 hours the CIE L*a*b* color values in the stained, formerly defined as the unprinted area, were measured. The results are reported as Delta E (see equation below) and interpreted as the amount of colorant that had washed from the color block into the unprinted area. (The higher the Delta E, the more color washed from the print, the less water resistant the printed color).

Water Immersion Test

Color blocks of red green and blue, 2 × 2 cm in dimension, were printed on the media with a HP 5550 desktop printer. The color blocks were printed at 100% print density. The prints were allowed 24 hours to dry under controlled environmental conditions of 70°F, 50% RH. The CIE L*a*b* color values of the color blocks were measured using an X-Rite TR938 spectrophotometer. The samples were mounted onto a rigid support, such as stainless steel, in order to make them rigid and easy to submerge in water. A pan was filled with distilled water, equilibrated to room temperature, to a depth of 2 inches. The prints on the support were placed print side up in the pan of water. A timer was set for 10 minutes. After 10 minutes elapsed the print and support were removed from the water bath. Immediately, after removal, a wet cotton swab was rubbed over one portion of the print encompassing all the colors. The number of double rubs taken to completely remove the printed area was recorded. The non-abraded portion of the print was left to dry naturally and the CIE L*a*b* color values of the color blocks were re-measured. The amount of color change is reported as a Delta E value, which is directly proportional to the amount of color lost from the print during water immersion.

Delta E values were calculated using the equation:

$$\text{Delta E} = \sqrt{((L2-L1)^2 + (a2-a1)^2 + (b2-b1)^2)}$$

Cross-sectional Photomicrographs

With an aim of inspecting ink absorption on media, cross-sectional photomicrographs were taken of printed samples. Printed media samples (HP 5550) were cut with a razor blade. A cross-section of the sample was then viewed and photographed using a Carl Zeiss microscope.

Coating Preparation

Experimental coatings were made in the following way. Aqueous preparations under investigation were drawn down onto either a polythene coated paper substrate for the water drip test or untreated bi-axially orientated polyester for the water immersion test. The aqueous preparations were applied with a Meyer bar so that a 20-micron coating thickness was obtained after oven drying. All coatings were dried at a temperature of 200°F for 5 minutes.

Results and Discussion

Experiment 1: Comparison of Commercial Media

Commercial media, polymeric and porous, were subjected to the water drip test. Figure 2 provides the results.

It is evident that in two of the three cases the polymeric commercial media "CM A" and "CM B" afford less water resistance to the secondary colors than the commercial porous media "NP A". "CM C", another commercial polymeric media, almost equals the water resistance of the porous media in this test. Subjecting the same media to the water immersion test produced an entirely different result. All three media based on a polymeric design completely dissolved and no color measurements could be taken after removal from the water bath. Figure 3 shows the result for the porous media, the one that survived the test; allowing measurement of the color change and wet double rub resistance.

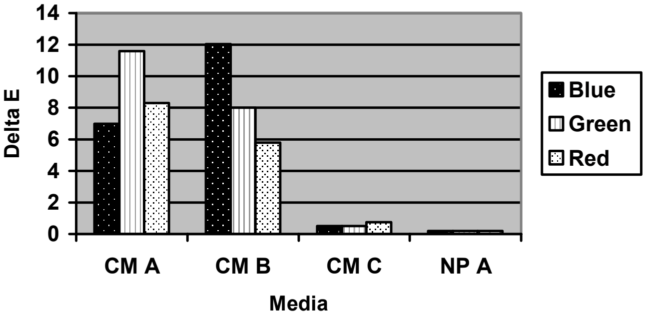

Figure 2. Water drip test results for commercial media.

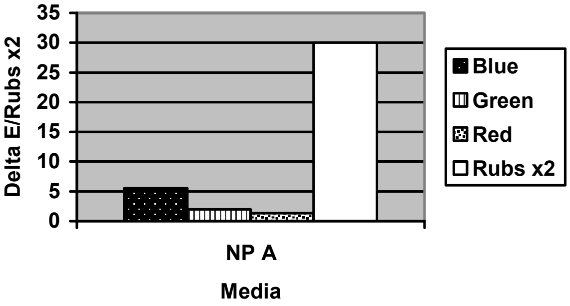

Figure 3. Water immersion test results for a commercial porous media.

It is obvious that the two tests significantly distinguish porous and polymeric commercial media. It is interesting to note that commercial media C was almost equal to the porous media in the drip test but the receptive coating on this media was much more water soluble than that on the porous media. Although it appears known that to achieve a "good" result in the water immersion test the water solubility of the coating needs to be retarded, for example, by covalent cross linking the receptive polymer[3] or by using a more hydrophobic polymer in the coating formulation.[4,5] The results of this experiment suggest that this is not the only design factor that requires consideration. On examining cross sections of the prints, a fundamental difference between them was found that correlated well with the drip test results. This is the ability of the dyes to penetrate into the receptive coating and they embed further into CM C and NP A. It is proposed that porous media is advantageous because the dyes are embedded in a water insoluble matrix, hence, a good result in both tests is observed.

Experiment 2: Experimental Coatings and Dye Fixation

It is documented that the addition of cationic polymers to a receptive coating formulation, either as an additives or as part of the main binding system, improves the water resistance of printed dyes.[6] The theory stands to reason. Dyes common in aqueous jet inks are anionic; example classifications are H-acid, gamma-acid, xanthene or copper complexes. (Some typical dyes and their chemical structures are shown below in Figure 4). It is reasonable to suggest that these anionic dyes can form zwitterionic complexes with cationic polymers. This interaction competes with the dye's water solubility and is consequently observed as a fixation between the dye and cationic polymer. Another theory is the anionic dye is flocculated in an environment of counter charge and/or lower pH.

Hence adopting the characteristics more akin to a pigment than a dye. Again, this explains a reduction in water solubility. Whatever the theory, the net result, in terms of water resistance, is the same. This experiment explores the effect of polymeric cationic additives in a water-soluble and an experimental water-insoluble receptive polymer, with a view to explaining their function.

Coating formulations were prepared so that the only experimental variables were those depicted in the matrix below (figure 5). Coated media was subsequently prepared from these formulations. (See experimental section for details).

The percentage values of the various Glascol® F additives is the solid weight of additive on solid weight of acrylic binder.

Acrylic 1 = hydrophilic water soluble binder
Acrylic 2 = experimental hydrophilic water insoluble binder (CGPS 360 ex. Ciba S.C.)

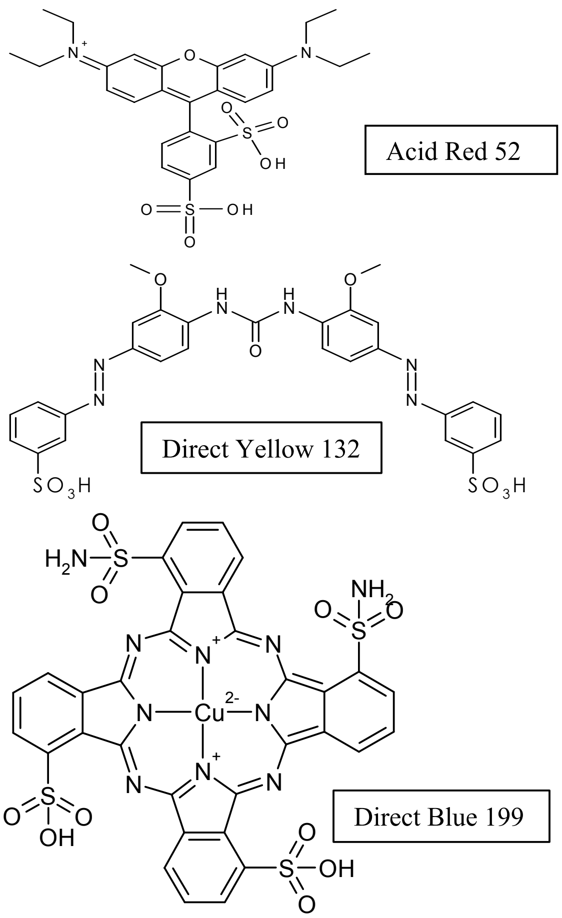

Figure 4. Acid Dyes

Cationic Additive / Resin Binder	Glascol® F 111		Glascol® F 120		Glascol® F 207		Glascol® F 211	
Acrylic 1	1.50%	3.0%	1.50%	3.0%	1.50%	3.0%	1.50%	3.0%
Acrylic 2	1.50%	3.0%	1.50%	3.0%	1.50%	3.0%	1.50%	3.0%

Figure 5. Experimental coating formulations.

The properties of the Glascol® F materials are:

Product	Charge Type	Charge Density/ milli equivalents / 100 g
Glascol® F 111	Cationic	333
Glascol® F120	Cationic	337
Glascol® F 207	Cationic	206
Glascol® F 211	Cationic	239

Figure 6. Charge properties of the Glascol® F cationic mordents.

Water Drip Test

The graph below depicts the results for the water drip test for the blue at 100% print density. (Only the results for the blue are shown as this is deemed a representative result).

Three observations are noteworthy. Firstly a large difference is seen between the water-soluble and water insoluble acrylic controls (0% mordant). The water-soluble acrylic, acrylic 1, loses less ink than the water insoluble acrylic 2. Secondly, the effectiveness of the mordant in fixing the dye, therefore, diminishing Delta E is not solely a function of charge density but mostly a function of it's environment. For example, Glascol® F 207 is more effective in acrylic1 than in acrylic 2. Thirdly, via extrapolation, it is suggested that at some higher concentration of mordant the data points will converge. For this test, at some higher concentration of mordant, the role of the mordant type and the nature of it's polymeric environment will become indiscernible.

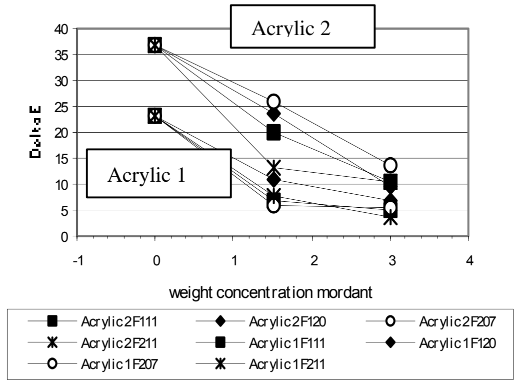

Figure 7. Water drip test results for blue.

Water Immersion Test

The amount of ink loss due to water immersion for all test samples and all secondary colors is shown in figure 8 and a fundamental difference can easily be assigned to the water solubility of the polymeric receptive coating. The water insoluble polymer, acrylic 2, out performs the water-soluble acrylic 1 in this test. The benefits of the cationic mordant, however, are less pronounced. Even though ink loss can be reduced in a water insoluble coating, those of lower charge density promote ink loss in a water-soluble counterpart. This infers that the coating maintaining its integrity during water immersion is paramount. Fixation of the dye is secondary.

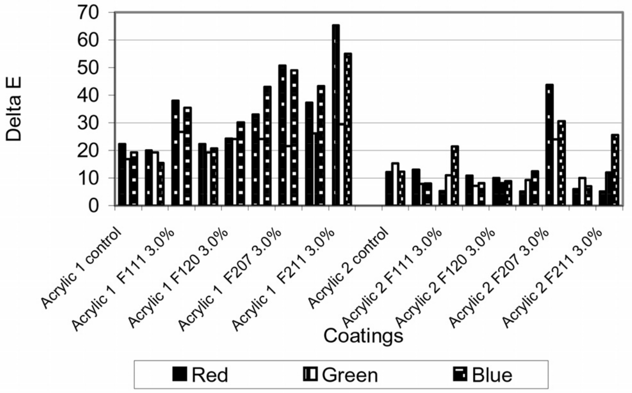

Figure 8. Water immersion test results for secondary colors.

Their wet rub resistance after water immersion also differentiated acrylic 1 and 2. The unprinted acrylic 1 coating was easily removed; acrylic 2 remained undamaged after 100 double rubs. A result that is easily explicable. Acrylic 1 and 2 were chosen for the study because of their extremes in water solubility; 1 is water-soluble, 2 is not. Both are hydrophilic.

The test method, however, specifies, "…rubs required to remove the wet printed area". Here differences are seen. For all acrylic 2 coatings the red print was irremovable, the green print varied slightly and the blue fluctuated the most; as a function of mordant type and concentration. Figure 9 below displays two sets of superimposed data-the amount of blue ink loss during water immersion (Delta E) and the number of wet double rubs taken to remove the same blue color block. Obviously, no correlation exists between the two measurements. For acrylic 2 / cationic mordant combinations it is possible to consider the blue ink fixation and wet rub resistance independently.

Consistently, the samples of higher mordant concentration fail the "100 double rub" test. Since the coating is irremovable, it is the dye that is being wiped away from the surface of these coatings. The chemical structure of a typical blue dye is bulky, compared to other acid dyes (see figure 4), and it can only be concluded that higher mordant levels further hinder the absorption of this large dye molecule. If the dye is absorbed into a water insoluble coating it can be protected from wet abrasion. as well as constructively interact with the mordant. Glascol® F211 added to acrylic 2, at a level of 1.5%. is a good example where this has happened (see below).

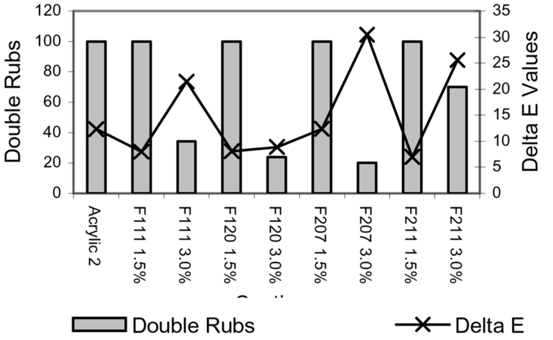

Figure 9. Water immersion test result. Blue ink loss and wet rub resistance.

Conclusion

There is evidence that the water resistance of dye based ink jet images can be largely influenced by the receptive coating formulation on the media. Of those tested, commercial porous media has better water resistance than media coatings based on a polymeric design. From analysis and experiments, coupled with the evaluation of a novel polymer, it is concluded that water resistance can be considered wholly as three interdependent factors, shown in figure 10.

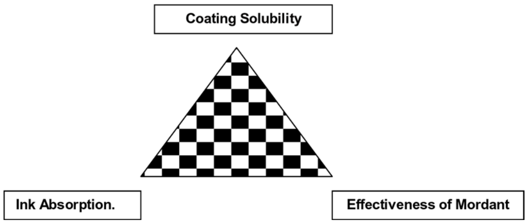

Figure 10. Factors affecting water resistance of coated media.

With this in mind, an ideal exists for optimum water resistance. Ideally, the receptive media coating must absorb all the dye in the ink, encapsulate and fix it, but be totally water insoluble. The results show that test example "acrylic 2", CGPS 360 from Ciba, approaches this criteria, especially when used in combination with a Glascol® F cationic mordant. No external cross linkers have been used to attain this step forward. Covalent cross-linking is successful at limiting water solubility but may retard dye absorption and hence limit the observed water resistance of dye-based images. It has been shown that the new polymer technology provides good ink absorption into a water insoluble film.

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