



Water Fast Ink Jet Print Using an Acrylic /Nano-Silver Ink

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ABSTRACT

A color ink jet printing with improved water fastness property was produced using an acrylic/nano silver resin in the ink's formulation. Introduced resin was a nano-composite (acrylic/nano silver) emulsion which was prepared via mini-emulsion polymerization of acrylate monomers in the presence of silver nano-particles. The water fastness properties of the prints were assessed by the ASTM /F2292-03 water fastness test standard. The results indicated that nano composite resin increased water fastness property of the printed paper and provided a water insoluble printed image on the paper. Furthermore, by introducing acrylic/nano-silver resin in the ink formulation, the hue of printed image was darker than plain acrylic resin. Prog. Color Colorants Coat. 4(2011), 79-83. © Institute for Color Science and Technology.

1. Introduction

In the last two decades, the interest in ink-jet printing in industry has been increased; especially drop-on demand (DOD) ink jet printing system [1-6]. Ink jet printers are widely used in small business and home office applications due to their economic, low space demand, substrate independence, easy integration with existing production lines and high-quality color output. The two most popular types of DOD ink jet printers are thermal [1-3] and piezoelectric [4-5] printers. Thermal ink jet printer which is used in this research utilizes a number of resistors to eject droplets of ink through nozzles. In addition, the attention should be paid to the interaction of the ink and the print media [7]. Printing inks with ink jet printers are usually aqueous solutions and the print media

are usually paper.

Currently the highest possible dot resolution for commercial ink jet printers is 4800 dpi (with an ink dot diameter of less than 5.3 micron); however, the resolution of the printed image is controlled not only by the dot arrangement of the ink jet but also by the printing media. Three basic elements are important for ink jet printing quality which are as follows; printed head, ink formulation, and printing media.

In case of ink formulation, dyes in some respects are superior to pigments for a number of well-known reasons. Pigment particles are significantly (about six order of magnitude) larger than dye molecules. Pigment based inks are, basically, finely ground particles suspended in a transfer medium. It is evident that, dye based inks will yield good color gamut and avoid jet

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nozzle clogging because of their molecular characteristics. But bleeding may occur when the image is exposed to water.

In case of printing substrate, adequate ink absorbency, drying speed, and water fastness are very important to make high quality color images. Insufficient ink absorbency results in color haziness and subsequently a blurry image. Low drying speed lets ink droplets to spread on the paper surface and results in color bleed. Poor water fastness shortens the exposed lifetime of printed items in humid or rainy environments [8]. Many researches have been done to improve the quality of ink jet printing by improving individual elements such as developing improved water fast dye sets, [9-13] or trying new materials. In the latter, the new materials such as cationic polymers [14-19], mixed metal cations in the form of their sulfates [20], cationic metal-organic charge complexes [21], or nano particle metal oxides [19], within paper coating formulations or adding nitril which have quaternary or tertiary amines added the ink's formulation [23] were used. However, water fastness remains a concern for papers. Good water fastness requires a critical balance of properties. For example, ink jet printers require water soluble dye systems to avoid jet nozzle clogging which may be obtained through dyes with improved solubility. The water solubility of dyes is a cause of poor image water fastness. One method to improve water fastness is to attach dyes chemically to the media surface during printing by coating the paper with silica pigments [22], poly vinyl alcohol binders (PVA), kaolin and cationic polymer additives which are typically expensive [19,24-29].

Research on improving water fastness properties for ink jet prints has focused on the paper coating formulations. In contrast, little attention has been drawn on the ink formulation. Therefore, the present study has focused on the ink composition which uses the nano-composite (acrylic/nano-silver) resin as a binder to improve the water fastness of ink jet prints.

2. Experimental

The water soluble "IRGASPERSE Jet Cyan" dye was purchased from Ciba. Co-solvents (diethylen glycol (DEG) and isopropyl alcohol) and potassium persulfate (KPS) as initiator was purchased from Merck. Polyvinylpyrrolidone (PVP, MW 40,000) was obtained from Merck. The industrial grades of Methyl methacrylate (MMA), Butyl acrylate (BA) and Acrylic acid (AA) were used. The analytical grade colloidal

nano-silver particles having a specific area of 120-180 $\text{m}^2.\text{g}^{-1}$, Cetyl alcohol (CA), Sodium dodecyl sulfate (SDS), Nonylphenol polyethylene glycol ether as a nonionic surfactant were also used.

The pH, surface tension and viscosity of inks were characterized using 827 pH Metrohm meters, Tensiometer K100MK2 and Brookfield DVII respectively. The spectral reflectances of the samples were measured using Gretag Macbeth Spectrophotometer ColorEye 7000A in the range of 360nm and 750nm with 10nm intervals.

2.1. Resins Preparation

Acrylic/nano-silver resin which is used in Ink 2 formulation was prepared as follows.

A mini-emulsion of colloidal nano-silver particles with emulsifiers, distilled water and acrylic monomers was prepared by ultra-sonication. Then, the mixture was polymerized via emulsion copolymerization in a glass reactor at 75°C. An initiator solution was added slowly to start the polymerization reaction. Subsequently the mixture was stirred for three hours and the final resin was obtained by cooling the system down to room temperature. Figure 1 and 2 show TEM and SEM images of nano silver particles embedded in the acrylic polymers.

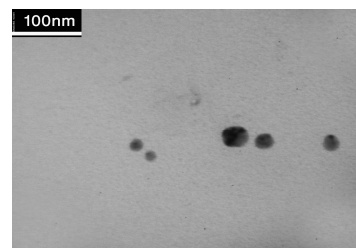


Figure1: TEM image of nano-composite resin.

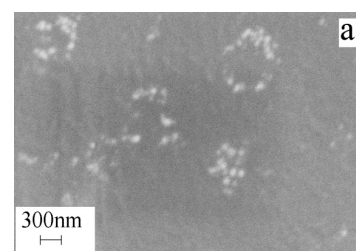


Figure 2: SEM image of nano-composite resin.

Table 1: The formulation of inks.

	Ink 1(%Wt)	Ink 2 (%Wt)
IRGASPERSE Jet Cyan	2.8	2.8
Diethylen glycol (DEG)	20	20
Isopopylacclcohol	17.2	17.2
Acrylic emulsion resin	1	-
Nano- composite resin	-	1
Distilled water	59	60

Table 2: The physical properties of inks.

	Ink 1	Ink 2
pH	7.5	7.5
Viscosity	0.0025Pa*s	0.0025Pa*s
Surface Tension	0.035N/m	0.035N/m

Acrylic emulsion resin without nano-silver particles which is used in Ink 1 formulation was prepared via a similar synthesis procedure. More detailed recipe and procedure for synthesizing acrylic/nano-silver resin and acrylic emulsion resin have been presented in our previous work [30].

2.2. Printing of the Ink on the Substrate

To examine the influence of the nano-composite (acrylic/nano-silver) resin on the water fastness of ink jet printing, Ink 1 (without nano-composite resin) and Ink 2 (with nano-composite resin) were prepared and then solid single color area was printed on the plain white paper using a HP Deskjet 5150 thermal ink jet printer. Then the water fastness properties of nano-composite ink jet print and acrylic emulsion ink jet print were compared. The inks formulation and their physical properties are shown in Tables 1 and 2, respectively.

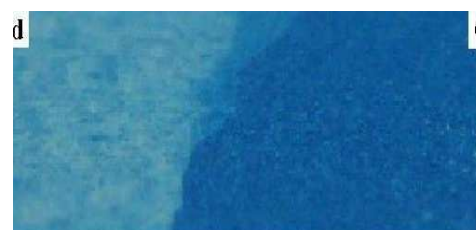
3. Results and discussion

The water fastness properties of the prints were assessed

by the ASTM /F2292-03 water fastness test standard [31]. Figure 3 shows the spectral reflectance of the printed inks before and after exposing the printed image to water. Color coordinates of the samples under D65 illuminant and 1964 CIE standard observer are given in Table 3.

Figure 3 and Table 3 indicate that the lightness of the nano-composite ink is less than the acrylic emulsion ink. Consequently, using nano-composite resin may result in darker inks. Therefore, there is a bathochromic shift by using nano-composite resin compared to acrylic resin (10nm) which might be related to nano-silver material presence in nano-composite resin.

In addition, color change of the patches before and after washing computed by CIELAB 1967 color difference formula was shown as a measure of water fastness in Table 3. Results provided in Table 3 show that the color change via exposing water in ink 2 is about 3 CIELAB units lower in comparison to ink1. Therefore, the water fastness of nano-composite ink is better than acrylic emulsion ink. This result can be also visually seen from Figures 4 and 5.

**Figure 4:** The print image (nano- Composite resin) before (a) and after (b) exposing the prints image to water.**Figure 5:** The print image (acrylic emulsion resin) before (C) and after (d) exposing the prints image to water.**Table 3:** CIELAB values of inks (Illuminant D65).

Name	L*	a*	b*	h°	ΔE* (CIELAB)
Ink1(before washing)	60.8	-25.2	-43	239.6	
Ink1(after washing)	74.3	-22.0	-32.2	235.6	17.57
Ink2(before washing)	51.4	-18.7	-39.1	244.5	
Ink2 (after washing)	62.5	-17.8	-30.4	239.6	14.1

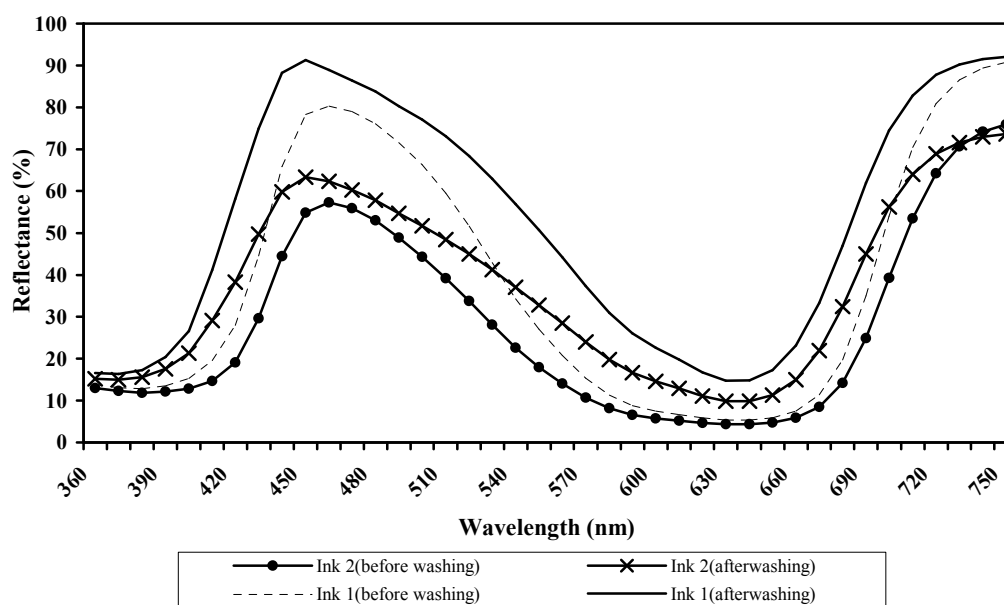


Figure 3: Reflectance percentage of inks.

Consequently, substituting nano-composites for acrylic emulsion resins can improve water fastness of printing inks. Once the printed paper by Ink 2 was dried, the nano Ag^+ were bound to polar hydroxyl group of paper via electrostatic interaction, because the electron rich oxygen atom of polar hydroxyl group of paper are expected to interact with the electropositive transition metal cation. Not only the hydroxyl group anchors silver ions tightly onto the paper via ion-dipole interaction, but also stabilizes the nano-silver cation. These may suggest that in this case the interaction between paper and nano-

composite resin gives the better result in ink jet printing.

4. Conclusions

The water fastness and the hue of ink jet prints were improved by adding the acrylic/nano-silver resin to the formulation of ink jet ink. The acrylic/nano-silver resin increased water fastness of the printed paper and the color stability of the inks upon exposure to water can be improved. The lightness of the nano-composite ink is also less than acrylic emulsion ink. Consequently, using nano-composite may result in darker inks.

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