



## The Effect of Reactive Dye Structure on the Ink-Jet Printing of Cotton

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### ABSTRACT

**T**he purpose of this study was to investigate the effect of the structure of reactive dye on cotton ink-jet printing. Cotton fabric was printed upon with three commercial cellulosic reactive dyes, which are based on the similar chromophore and possess different numbers of reactive and anionic groups. Colour yield and absorbed dye fixation of the printed cotton were evaluated at various pH values. The ink-jet printing was carried out on a HP DeskJet 5150 printer at 1200 dpi, and then the printed cotton fabrics were air dried and put into a steamer to fix the reactive dye on to the cotton fabric. The results indicated that the absorbed dye fixation levels increased by decreasing the numbers of anionic groups and appeared to be dependent on the number of the reactive group. All reactive dye based inks are demonstrating excellent colour fastness to washing and dry/wet crocking. The light fastness of each reactive dye based ink fixed to cotton fabrics was moderate. Prog. Color Colorants Coat. 7(2014), 19-26. © Institute for Color Science and Technology.

### 1. Introduction

Nowadays, the interest in ink-jet printing on textile has been increased both at academic and industrial levels. Benefits of ink-jet printing include customization, high speed, flexibility, cleanliness, eco-friendliness, substrate independency and easy to integrate with existing production lines [1-3]. Cotton is the most widely used natural textile fibre in the world and it commonly printed by the reactive dye based ink. Commercial ink-jet reactive inks are usually based on dyes with low to moderate fixation properties (generally mono-functional reactive dyes) [4-8]. The application method in ink-jet printing method is totally different from the conventional

printing method. In ink-jet printing thickener, urea and alkali are applied to the fabric by a pre-padding process. Steam fixation, washing-off and drying are performed following the ink-jet printing stage. Most researches on ink-jet printing on textile overwhelm on improving the fixation of the reactive ink by modification of reactive dye [9] and fabric [10,11] or using fixation-enhancement chemicals [5,12,13]. As the first step toward the design of novel reactive inks for cellulose and before embarking on a synthetic programme, an attempt was made to identify the structural features associated with good reactive printing performance on cotton fabric.

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Therefore, the effect of dye structure changes, including the number of reactive groups and the degree of sulphonation were evaluated on the printing properties.

## 2. Experimental

### 2.1. Materials

The fabric used was 100% singed, desized, scoured and bleached cotton plain weave fabric (98 g/m<sup>2</sup>) which was supplied from Broojerd Textile Company, Iran. Sodium Alginate was provided by Sigma-Aldrich Company, Germany. The commercial anionic reactive dyes, Table 1 were kindly supplied by DyStar Company, Germany. A non-ionic detergent, Synperonic BD 100, Univar, UK, was used in the wash-off process. All other chemicals used in this work were of laboratory grade as received from Merck Company, UK.

### 2.2. Equipments and instruments

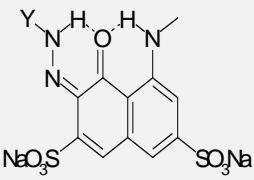
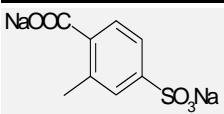
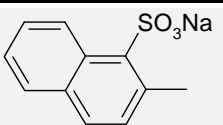
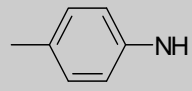
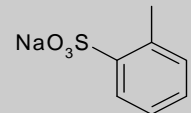
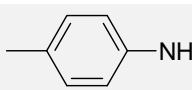
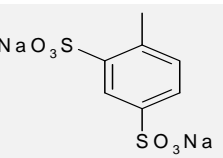
A laboratory padder, Kimia Behris Company, Iran, was applied for pre-treatment solution on the fabrics after which they were then dried in an Ecocell oven. The fabric was ink-jet printed using a HP DeskJet 5150 printer. A laboratory steamer that was supplied by Kimia

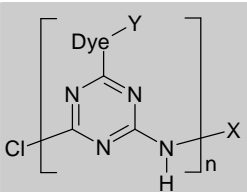
Behris Company, Iran, operating at the atmospheric pressure was used for fixation. The dye concentration in the washing baths was determined by absorbance measurements at  $\lambda_{\max}$  using UV Ikon 923Double Beam UV/Visible spectrometer. The pH, surface tension and viscosity of inks were characterized using 827 pH Metrohm meters, Tensiometer K100MK2 and Brookfield DVII viscometer, respectively.

### 2.3. Fabric pre-treatment

The pre-treatment paste was prepared using 150g sodium alginate made from a stock sodium alginate solution, which was made ready by dissolving sodium alginate (50g) in de-ionised water (0.95 dm<sup>3</sup>), sodium bicarbonate (8g), and urea (10g). Then the paste was made up to a weight of 200g with de-ionised water [13-15], which was subsequently mixed thoroughly. The pre-treatment was padded onto the cotton fabric using a padding machine with an even pressure of 2.6 kg/m<sup>2</sup> and a constant padding speed of 2.5 rpm until a pick-up of 80% was achieved. The pre-treated fabrics were dried in an oven at 80°C, and then conditioned before ink-jet printing [13-15].

Table 1: Commercial anionic reactive dye used in printing cotton.

Ink	Dye	No. of anionic groups	Dye	n	X	Y
1	Procion Red PX-3B	4		1		
2	Procion Red H-E3B	6		2		
3	Procion Red H-E7B	8		2		



### 2.4. Ink-jet printing

The ink-jet printing was carried out on a HP DeskJet 5150 printer at 1200dpi using the ink formulation as shown in Table 2. The ink was made up to 1 dm<sup>3</sup> with de-ionised water, printing was carried out at four different pH values (5, 6, 7, 8) using McIlvaine buffers, as shown in Table 3 [16]. The three anionic reactive dyes were of commercial grade. The viscosity values for the ink-jet inks were between 2.1 and 2.9 cps which are in the acceptable range for textile ink-jet printing inks [17]. The surface tension values of the formulated inks were in the range of 28-31 mNm<sup>-1</sup> which are within the normal range for typical commercial ink-jet inks in textile printing [18].

### 2.5. Fixation

After printing, the fabrics were air-dried and then put into a steamer. All the printed fabrics were treated with superheated steam at 110°C for 10 minutes for colour fixation [6].

### 2.6. Washing off

The steamed fabric samples were washed with cold water and then washed in 10g/dm<sup>3</sup> non-ionic detergent (Synperonic BD) until all the un-reacted dyes and chemicals were removed from the fabric surface [6,15].

### 2.7. Determination of absorbed dye fixation

The percentage of absorbed dye fixation was determined using a method adapted from previously established methodology for textile dyeing with reactive dyes [5, 19-20].

Two identical square pattern printed fabrics with a size of 10cm × 10cm at 1200dpi were used to estimate the percentage of fixation; one was printed with the reactive ink on 100% polyester fabric. This printed fabric was washed off immediately after printing to obtain the total amount of the dye printed on the fabric and the solution was diluted with de-ionised water to 0.5 dm<sup>3</sup> to calculate the absorbance of the printed dye solution. The other one was printed with reactive ink on cotton, fabric for batching, followed by washing to obtain the amount of the dye washed off after the fixation process and the washing solution was diluted with de-ionised water to the same volume of 0.5 dm<sup>3</sup>. The percentage of absorbed dye fixation was determined according to Equation (1):

$$\% F = \frac{A_0 - A_1 - A_2}{A_0} \times 100 \quad (1)$$

where A<sub>0</sub> is the absorbance of the printed dye solution, A<sub>1</sub> is the absorbance of the first wash-off solution and A<sub>2</sub> is the absorbance of the soaping liquor at the wavelength of the maximum absorption (λ<sub>max</sub>).

**Table 2:** Basic printing ink recipe.

Ingredient	g/dm <sup>3</sup>
Reactive dye	100
N-methyl morpholine N-oxide	300
2- pyrrolidone	20
Propan-2-ol	25

**Table 3:** Composition of the McIlvaine buffers in a total volume of 100 cm<sup>3</sup>.

pH	0.2 M Na <sub>2</sub> HPO <sub>4</sub> (cm <sup>3</sup> )	0.1 M citric acid (cm <sup>3</sup> )
5	51.50	48.50
6	63.15	36.85
7	82.35	17.65
8	97.25	2.75

## 2.8. Determination of color fastness

Color fastness properties, which are determined by the stability of the dye-fibre system, present an interesting property for quality printing in terms of practicality. For the evaluation of colour fastness properties, the colour fastness to light, washing and crocking of the ink-jet printed fabrics were determined by AATCC Test Methods 16-2001, AATCC Test Method 61-2001 and AATCC Test Method 8-2001, respectively.

## 3. Results and discussion

### 3.1. Effect of pH on the percentage of absorbed ink

According to the equilibrium shown in Figure 1, the cellulose ionisation changes depending on the pH within the fibre.

By raising the pH of the ink, the probability of reaction with cellulose increased due to the increase in the ionisation of cellulose to cellulosate, Figure 2.

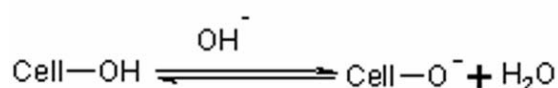


Figure 1: Formation of cellulosate anions.

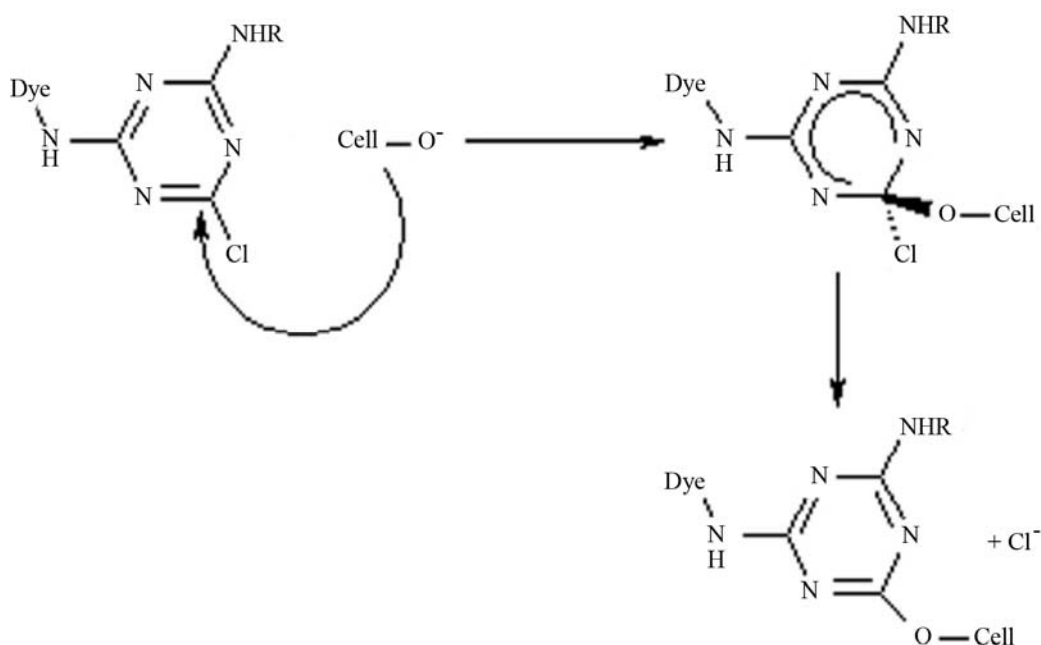


Figure 2: Fixation reactions occurring for a halo-s-triazine type dye (Procion P/HE).

Therefore, it was necessary to determine the best applicable pH for each ink type in order to achieve the optimum ink fixation for that individual ink formulation. A series of prints were evaluated in buffers of different pH values. Buffers of pH 5, 6, 7 and 8 were made as described above (section 2.4).

According to Table 4, the percentage of absorbed dye increases with pH. Therefore, the reactive dye based inks, regardless of the type of dye used, fix more efficiently on cotton fabric at pH 8.

### 3.2. Effect of anionic group numbers in reactive dyes on the percentage of absorbed ink

To investigate the influence of the number of sulphonic groups of reactive dyes on the printing of cotton, two bi-functional monochlorotriazinyl cellulosic reactive dyes were employed; Procion Red H-E3B (Ink 2) and Procion Red H-E7B (Ink 3). The results were compared for each dye with a different number of 6 and 8 sulphonic groups respectively.

According to Figure 3, the absorbance of the different percentages of fixation of Procion Red H-E3B, which possesses six sulphonic acid groups was better than that of Procion Red H-E7B, which possesses eight sulphonic acid groups.

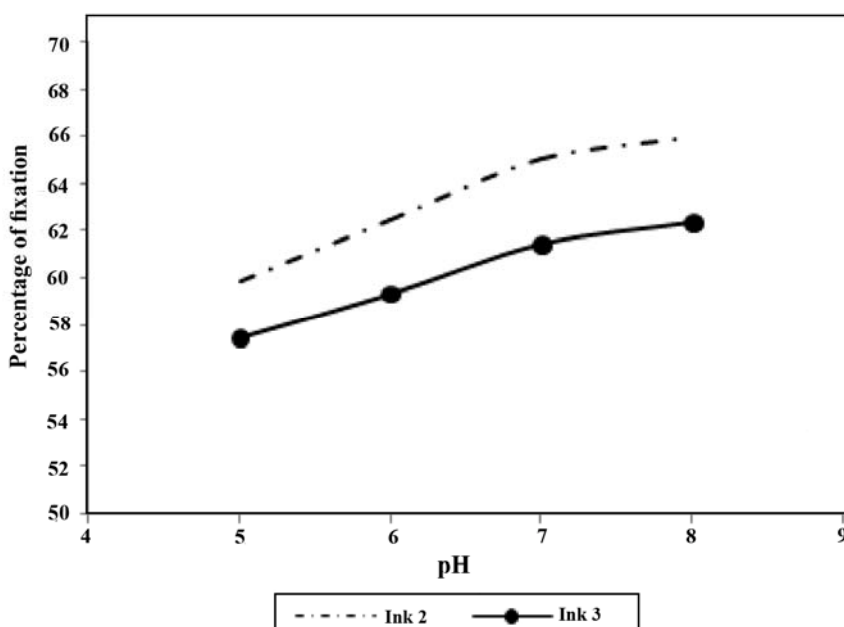


Figure 3: The percentage of absorbed Ink2 and Ink3 onto cotton fabric at different pH values.

Table 4: Percentage of the absorbed dye on printing of non-pre-treated cotton fabric with commercial anionic reactive dye based inks ( $\lambda_{max}=550$ ) at different pH values and pre-treated cotton fabric with commercial anionic reactive dye based inks.

pH	Cotton Fabric	%F	Ink 1	Ink 2	Ink 3
5	non-pre-treated	%F	52.09	59.87	57.49
6	non-pre-treated	%F	56.51	62.5	59.35
7	non-pre-treated	%F	61.2	65.03	61.47
8	non-pre-treated	%F	62.09	66.01	62.38
-	pre-treated	%F	63	67	64

Thus, the percentage of absorbed dye on printed cotton was decreased by increasing the sulphonation degree of the reactive dyes.

These results were attributed to an increased electrostatic repulsion between the dye (sulphonate groups) and fibers (cellulosate anion). Increasing the sulphonation degree of the reactive dyes resulted in higher solubility of the dyes. Therefore, the number of anionic groups played an important role in the percentage of absorbed dye on the printed cotton fabrics.

### 3.3. Effect of reactive group numbers in reactive dyes on the percentage of absorbed ink

In order to gain some insight into the influence of the reactive groups number of reactive dyes on the printing of cotton, two monochlorotriazinyl cellulosic reactive dyes were employed; Procion Red P-8B Red (Ink 1), and Procion Red H-E3B (Ink 2). Each dye has a different number of reactive groups, mono- functional monochlorotriazinyl and bis-monochlorotriazinyl, respectively. All are based on a similar chromophore,

being derived from a sulphonated 2-aminonaphthalene, (diazo component) and H-acid, (coupling compound). Figure 4 depicted that the absorbance of the percentages of fixation of Ink 1 (Procion Red H-E3B), which is based on bis-monochlorotriazinyl reactive groups was better than Ink 2 (Procion Red P-8B). Therefore, by increasing the number of reactive groups attached to the dye molecule, the percentage of absorbed dye on printed cotton fabric was increased.

### 3.4. Color fastness properties

The results of color fastness to light, washing and crocking of the printed fabrics are given in Table 5. The change in the shade and the degree of cross-staining was assessed visually using gray scale. As seen from the results in Table 5, there are no changes in the shade of the printed samples as well as no staining on the adjacent cotton in case of dry crocking. There is just a little staining on adjacent cotton in case of wet crocking. As expected, the wash fastness of each ink fixed to cotton fabrics was very good. The light fastness of each printed fabric was moderate.

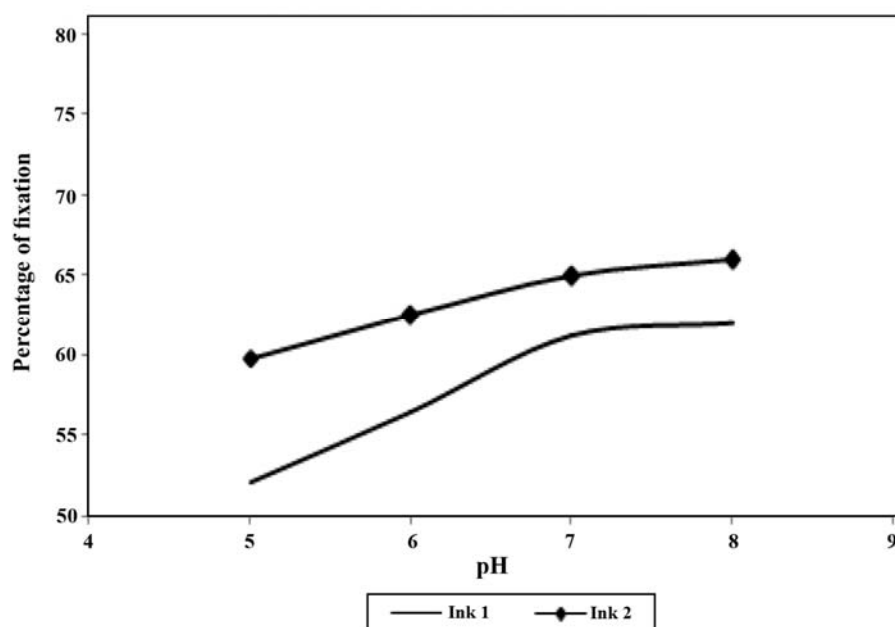


Figure 4: The percentage of absorbed Ink1 and Ink2 onto cotton fabric at different pH values.

**Table 5:** Color fastness (light, washing, crocking) properties of the printed cotton fabrics.

Ink	Light	Washing						Crocking		
		Staining on multi-fibre fabric						Change	Wet	Dry
		Wool	Cotton	Acetate	Nylon	Acrylic	Polyester			
1	4	5	5	5	5	5	5	4-5	4	5
2	4	5	5	5	5	5	5	4-5	4	5
3	3-4	5	5	5	5	5	5	4-5	4	5

#### 4. Conclusions

The results revealed that the structure of reactive dye in ink formulation plays an important role on percentage of absorbed dye on printing cotton. At pH 8, essentially the number of cellulosate anion groups increased, which are highly nucleophilic and reactive to electrophilic reactive groups. The results demonstrated that the number of anionic groups on dye molecule in the ink formulation played an important role in the percentage of absorbed dye on the printed cotton. As the degree of sulphonation

of the reactive dye increased, the percentage of absorbed dye on printed cotton was decreased due to an increase of electrostatic repulsion between the dye (sulphonate group) and fiber (cellulosate anion). Furthermore, the number of reactive groups in the reactive dye is an important factor in the absorption of dye on printed cotton. As the reactive groups on the reactive dyes increased, the percentage of absorbed dye on printed cotton was increased.

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