doi: 10.1111/cote.12011

Single-phase ink-jet printing onto cotton fabric

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Received: 28 February 2012; Accepted: 31 May 2012

Coloration Technology
Society of Dyers and Colourists

The current commercial application of ink-jet reactive inks to cotton fabrics requires pretreating with pad liquor containing a thickener, urea and alkali prior to printing. In this study, attempts have been made to develop a reactive ink-jet print in a single-phase process by adding an organic salt to the ink formulation and hence removing the need to pretreat fabrics. This approach utilises inks containing both a reactive dye, in this case Procion Red H-E3B, and an organic salt such as sodium formate, sodium acetate, sodium propionate or tri-sodium citrate. The behaviour of a novel reactive ink formulation for ink-jet printing on to cotton fabric was evaluated at different pH vlaues. The results at optimum pH indicated that printed non-pretreated fabrics with ink containing organic salts exhibited a higher level of reactive dye fixation than printed pretreated fabric containing no organic salt ink. The yielded prints demonstrate excellent colour fastness to washing and dry/wet crocking properties. The light fastness of the printed fabrics was improved by adding an organic salt to the ink formulation.

Introduction

In the last two decades, digital ink-jet printing has found an increasing number of applications in the printing of textiles. It is foreseen that the traditional flat or rotary screen-printing and roller printing techniques may be superseded by digital printing technologies in the near future [1–7]. Cellulosic fabric can be printed on with reactive dye-based inks [8–10]. Commercial ink-jet reactive inks are based on dyes with low to moderate fixation properties, therefore maximising the dye fixation for economic and environmental reasons is considered to be very important. Generally, reactive dyes are applied to cellulosic fabrics in the presence of an alkali to promote the fixation of the dye to the fabric through covalent bond formation via the reaction of the cellulosate anions with the reactive groups of the reactive dye molecule. In ink-jet printing, none of the conventional printing chemicals, such as alkali, urea and thickener, can be directly incorporated into the ink formulations [10,11]. If reactive dye-based ink formulations incorporate an alkali, then not only can the ink cause corrosion of the printhead nozzle, but it would also have an extremely limited storage life, as the dye rapidly hydrolyses to a non-reactive form, leaving behind a precipitate that will block the nozzle. In order to prevent dye hydrolysis, a stable ink formula containing purely the dye should be prepared and applied to cotton substrates, which have been pretreated with a printing paste, which contains an alkali, urea and thickener [12–14].

Application of the pretreatment process is thought to be disadvantageous in practice, as the pretreatment process is environmentally unfriendly, energy intensive and time-consuming; additionally, the print pastes have a short shelf life because of their pH.

Previous studies have detailed the increase in reactive ink fixation through the modification of reactive dyes [15] and fabrics [11,16–20], as well as the use of fixation-enhancing chemicals in the pretreatment process [11,16,21–23].

Recently, some biodegradable organic salts have been used as an exhausting and fixing agent for dyeing cotton with reactive dyes to improve the fixation of dye. Such a process offered the potential of lowering costs through the reduction of the amount of chemicals and energy consumed [24–26].

Consequently, the aim of this work was to formulate a reactive dye-based ink containing a biodegradable organic salt such as sodium formate, sodium acetate, sodium propionate or tri-sodium citrate, which will promote the degree of reactive dye fixation, with the further intention of producing a reactive ink-jet print in a single-phase process, by eliminating the necessity of fabric pretreatment.

Experimental

Materials

The fabric used was 100% singed, desized, scoured and bleached cotton plain weave fabric (98 g/m^2), supplied by Broojerd Textile Company (Iran). Sodium alginate was provided by Sigma-Aldrich (Germany). The dye (Procion Red H-E3B) used for printing cotton was kindly provided by DyStar (Germany) (Figure 1). A nonionic detergent, Synperonic BD 100 (Univar, UK) was used in the wash-off process. Organic salts (Table 1) and other chemicals used were received from Merck (Germany).

Equipment and instrumentation

A laboratory padder (Kimia Behris Company, Iran) was applied for the pretreatment solutions on to the fabrics, after which they were dried in an Ecocell (Germany) oven. The prepared ink was filtered through 0.45 and 0.2 μm Sartorius (Germany) Minisart filters. The fabric was ink-jet printed using a HP (USA) DeskJet 5150 printer. A laboratory steamer, supplied by Kimia Behris Company, operating at

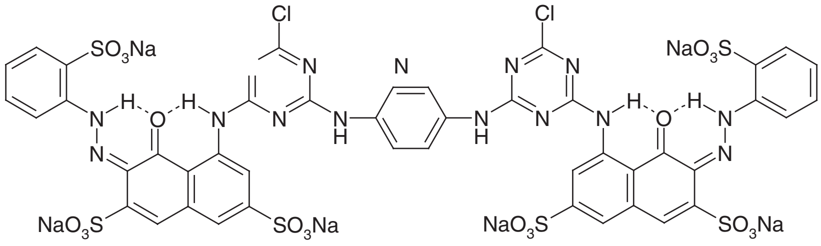


Figure 1 The structure of Procion Red H-E3B

atmospheric pressure was used for fixation. The dye concentration in the washing baths was determined by the absorbance measurements at λ_{max} using an ultraviolet (UV) Ikon 923 Double Beam UV–visible spectrometer (Kontron, France). The reflectance measurements of the prints were determined using a GretagMacbeth (USA) spectrophotometer ColorEye7000A with d/8º measurement geometry under the following conditions: measurement wavelength range 400–700 nm, measurement area 10 mm in diameter, and the specular component included (SCI) measurement mode. The CIELab values were computed under D65 illuminant and SCI 1964 (10°) standard observer. The Fourier Transform infrared (FTIR) spectrum [Perkin-Elmer (USA) Spectrophotometer Spectrum One], in the range 400–4000 m^{-1} was used. The pH, surface tension and viscosity of the inks were characterised using 827 pH Metrohm (Switzerland), Tensiometer K100MK2 (Krus, Germany) and Brookfield (USA) DVII meters, respectively. The colour fastness to light, washing and crocking of the ink-jet printed fabrics were determined by AATCC Test Methods 16-2001 [27], AATCC Test Method 61-2001 [28] and AATCC Test Method 8-2001 [29], respectively.

Fabric pretreatment

The pretreatment paste was prepared using 150 g sodium alginate made from a stock sodium alginate solution, which was made ready by dissolving sodium alginate (50 g) in deionised water (0.95 dm^3), sodium bicarbonate (8 g) and urea (10 g). The paste was then made up to a weight of 200 g with deionised water [11,21,23,30], which was subsequently mixed thoroughly. The pretreatment was padded on to the cotton fabric using a padding machine with an even pressure of 2.6 kg/m^2 and a constant padding speed of 2.5 rpm until a pick-up of 80% was achieved. The pretreated fabrics were dried in an oven at 80 °C and then conditioned before ink-jet printing [11,21,23,30].

Ink-jet printing

The ink-jet printing was carried out on a Hewlett Packard (HP) thermal ink-jet printer (HP DeskJet 5150) at 1200 dpi as a solid square pattern, to allow easy colour measurement, using the ink formulations as illustrated in Table 2. The organic salt was then added to the basic printing ink formulation at the different concentrations. The ink was made up to 1 dm^3 with deionised water. Printing was carried out at four different pH values (pH 5, 6, 7 and 8) using McIlvaine buffers, as shown in Table 3 [31]. The anionic reactive dye used in this study was Procion Red H-E3B. The prepared ink was filtered through a 0.45 μm filter, and then through a 0.2 μm filter to prevent clogging the nozzles before being poured into the cartridge. In the preparation process for ink-jet printing of cotton, firstly a new cartridge was unfilled by opening and washing, then it was loaded with the ink formulation. Subsequently, the filled cartridge was placed into the printer. The substrate was a piece of cotton glued to paper, which was cut to a size just slightly smaller than the paper to provide uniform edges.

The viscosity values for the ink-jet inks were between 2 and 2.8 cps, which are in the acceptable range for textile ink-jet printing inks [32]. The surface tension values of the formulated inks were in the range of 28–31 mN/m, which are also within the values of typical commercial ink-jet inks for textile printing [33].

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 min for colour fixation [16,21]. The steamed fabric samples were washed with cold water and subsequently washed again in 10 g/dm^3 of nonionic detergent (Synperonic BD) at 60 °C for 10 min

Table 1 Organic salt used for printing cotton

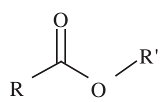
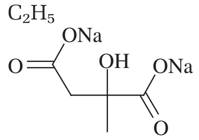
Ink	Organic salt		*R*	*R'*	No. of carboxylate groups
1	Sodium formate		H	Na	1
2	Sodium acetate		CH_3	Na	1
3	Sodium propionate		C_2H_5	Na	1
4	Tri-sodium citrate			Na	3

Table 2 Basic printing ink recipe

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

Table 3 Composition of McIlvaine buffers in a total volume of 100 cm^3

pH	0.2 M Na_2HPO_4 (cm^3)	0.1 M citric acid (cm^3)
5	51.50	48.50
6	63.15	36.85
7	82.35	17.65
8	97.25	2.75

until all the unreacted dye and other chemicals were removed from the surface of the fabric [21,33].

Determination of absorbed dye fixation

Evaluation of percentage of absorbed dye fixation from the ink-jet printing technique used a methodology adapted from previously established procedures for textile dyeing with reactive dyes [16,34,35]. Two equal square pattern printed fabrics of 10 × 10 cm at 1200 dpi were used to determine the per cent fixation; one was printed with the reactive ink on 100% polyester fabric and the other was printed with reactive ink on cotton. The printed polyester fabric with the reactive ink was washed off immediately after printing, to obtain the total amount of the dye printed on the fabric, and the wash-off solution was diluted with deionised water to 0.5 dm^3. The printed cotton fabric with reactive ink was used for steaming followed by washing to obtain the amount of the dye washed off after the fixation process, and the wash-off solution was diluted with deionised water to 0.5 dm^3. The percentage of absorbed dye fixation was determined according to Eqn 1, in which A_0 is the absorbance of the printed dye solution, A_1 is the absorbance of the first wash-off solution and A_2 is the absorbance of the soaping liquor, which was diluted with deionised water to 0.5 dm^3, at the wavelength of the maximum absorption (λ_{max}).

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

Results and Discussion

Effect of pH on printing performance

According to the equilibrium shown in Figure 2, in the presence of water, depending on the pH within the fibre, the cellulose will be ionised to a lesser or greater degree.

When the pH of the ink was raised, the ionisation of cellulose to the cellulosate anion increased, thus increasing the chance of reaction with cellulose over the competitive hydrolysis reaction of the reactive dye. Consequently, pH is a key variable in influencing the level of fixation of the reactive dye-based ink on cotton fabric. It was thus necessary to determine the best application pH for each ink type in order to achieve optimum dye fixation. A series of prints was evaluated, in buffers of different pHs, to determine the optimum application pH. A pH higher than 8 hydrolysed the reactive dye and might be damaging to the printhead and cartridge. Therefore, buffers of pH 5, 6, 7 and 8 were made as described in the 'Ink-jet printing' section and reactive dye inks containing an organic salt were used to print on to non-pretreated cotton fabrics. The results shown in Table 4 indicate an increase in percentage of absorbed dye with increasing pH. Therefore, the reactive dye-based inks, regardless of the type of organic salt used, fix more efficiently on cotton fabric at pH 8.

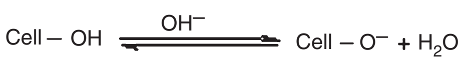


Figure 2 Formation of cellulosate anions

Effect of organic salts on absorbed dye fixation

Tables 4 and 5 indicate that printed non-pretreated cotton fabric with ink containing organic salt exhibited a higher level of reactive dye fixation than printed non-pretreated cotton fabric containing no organic salt ink.

The results in Table 5 show that the degree of dye fixation on non-pretreated cotton fabric at the optimum pH in the cases of adding sodium formate, and tri-sodium citrate in ink formulation, is as high as those achieved with printing non-organic salt ink on pretreated cotton fabric. Therefore, the reactive ink-jet prints in a single-phase process are developed by adding an organic salt in the ink formulation and hence removing the need to pretreat fabric.

To justify the fixation improvement, the following theory could be suggested. On the one hand, at the optimum pH condition (pH 8), essentially the numbers of cellulosate anion groups are increased; these are highly nucleophilic and reactive towards the electrophilic reactive groups. On

Table 4 Percentage of absorbed dye on printing of cotton fabric with organic salt (20 g/dm^3) and reactive dye-based ink at different pH and with different concentration of organic salt at pH 8

pH	Organic salt concentration	%*F*			
		Ink **1**	Ink **2**	Ink **3**	Ink **4**
5	20 g/dm^3	59.77	59.51	59.13	59.6
6	20 g/dm^3	60.45	60.34	59.93	61.7
7	20 g/dm^3	65.61	63.98	63.72	65.85
8	20 g/dm^3	67.87	65.25	64.95	68.04
8	15 g/dm^3	65.73	65.05	64.89	66.01
8	10 g/dm^3	65.16	64.89	64.87	65.24
8	5 g/dm^3	64.93	64.69	64.68	65.02

Table 5 Percentage of absorbed dye on printing of pretreated fabric with ink (without organic salt) and non-pretreated cotton fabric with Ink **1** and Ink **4**

No.	%*F*
Ink (without organic salt and non-pretreated fabric)	49.8
Ink (without organic salt) pretreated fabric	67.01
1 (non-pretreated fabric)	67.87
4 (non-pretreated fabric)	68.04

the other hand, at this high pH all the sulphonic acid groups in the commercial anionic reactive dye (Procion Red H-E3B) will be de-protonated and hence anionic, which caused electrostatic repulsion with the anionic cellulosate groups. Incorporation of organic salts in the ink formulation may suppress negative charge build-up at the fibre surface by its cations, thereby assisting absorption of the dye on to the fabric. Under these conditions, the electrostatic repulsion between dye and fibre would be minimised and the available nucleophilic cellulosate anions will be reactive towards the electrophilic reactive groups.

Table 4 shows tri-sodium citrate has the highest percentage of fixation compared with other organic salts. The obtained result may be attributed to the higher ionic strength and better stability of tri-sodium citrate for reaction between a monochlortriazinyl dye and the cotton fabric as tri-sodium citrate is a polycarboxylic sodium salt and contains more cations per mol than monocarboxylic sodium salt.

Additionally, comparing the results obtained from sodium formate, sodium acetate and sodium propionate indicates that, as the number of electron donating groups near the carboxyl group increase, the level of reactive dye fixation decreases. This can be attributable to the reduction of the acidity of the carboxylic acid group.

Furthermore, the results in Table 4 show that, as the concentrations of organic salt are increased, the percentage of absorbed dye will increase, which may be attributable to countering the more negative charge of the fabric by the salt's cation.

Therefore, the high percentage of ink fixation to printed non-pretreated cotton fabric, attained either by increasing the number of cation groups or the concentration of the organic salt, parallel to raising the pH in the ink formulation, could support the above-mentioned theory.

Table 6 The colorimetric data for printed cotton with reactive ink under D65 illuminant and CIE1964 (10°) standard observer

No.	L^*	a^*	b^*	C^*	h^o
Ink **1**	71.29	46.63	−4.80	48.92	342.38
Ink **2**	72.80	44.81	−5.46	47.40	340.95
Ink **3**	76.33	37.04	−5.54	40.18	337.23
Ink **4**	67.09	52.17	−2.67	53.68	346.34
Ink (without organic salt) pretreated fabric	69.45	39.34	−8.58	43.51	334.71

Effect of organic salts on colorimetric properties

Table 6 shows the colorimetric data of non-pretreated cotton, which had been printed with reactive ink containing an organic salt at the optimum pH. The printed cotton sample with reactive ink containing sodium formate and tri-sodium citrate has a darker shade (lower L^* value) and higher chroma value (C^*) than the others. This shows that the degree of dye fixation, in the case of adding sodium formate and tri-sodium citrate as an organic salt, is higher than adding sodium acetate and propanoic acid. The hue ($h°$) values of all inks containing a different type of organic salts are similar. The ranges of hue angle are 334.7–346.3.

Colour fastness properties

Colour 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 of the printed samples, colour fastness to light, dry and wet crocking and to washing at 60 °C were determined. As seen from the results in Table 7, there were slight changes exhibited in the shade of the printed samples and, at the same time, no staining on the adjacent multi-fibre fabric was observed in the case of washing at 60 °C. Furthermore, there was no staining on the adjacent cotton in the case of dry crocking. Slight staining was seen on the adjacent cotton in the case of wet crocking. The light fastness of the printed fabrics was improved by adding an organic salt (tri-sodium acetate) in the ink formulation; finding the exact reason to justify the improvement of light fastness may require further study. Colour fastness properties of all printed samples thus show excellent dye–fibre stability and no decrease in the quality is observed when using the organic salts in the ink formulations.

Conclusions

Cotton fabrics can be pretreated with aqueous liquors containing an alkali, urea and a thickening agent, via a pad–dry process to yield a suitable substrate for subsequent ink-jet printing with reactive dyes. By incorporating a suitable organic salt in the ink's formulation, the printed cotton fabric offers higher levels of reactive dye fixation than printed non-pretreated cotton fabric containing no organic salt ink. The reactive dye-based inks, regardless of the type of organic salt used, fix more efficiently on cotton fabric at pH 8. The results demonstrated that organic salts such as

Table 7 Colour fastness (light, washing, crocking) properties of the printed cotton fabrics

Ink	Light	Washing (Staining on multi-fibre fabric)						Crocking		
		Wool	Cotton	Acetate	Nylon	Acrylic	Polyester	Change	Wet	Dry
1	4–5	5	5	5	5	5	5	4–5	4	5
2	4–5	5	5	5	5	5	5	4–5	3–4	5
3	4–5	5	5	5	5	5	5	4–5	4	5
4	5	5	5	5	5	5	5	4–5	4	5
Pretreated fabric (without organic salt)	4	5	5	5	5	4–5	5	4–5	3–4	5

sodium formate and tri-sodium citrate, when added to the ink's formulation, improved reactive ink-jet printing in the single-phase process on cotton fabric. Furthermore, the degree of dye fixation was as high as that achieved with pretreated cotton fabrics. The number of carboxylic acid groups and electron donating groups near the carboxyl group are key parameters in influencing the level of fixation and the colorimetric data of the reactive dye-based ink on cotton. It was readily demonstrated that high percentages of fixation attained with organic salt, which has higher ionic strength, would support that cations from the salts can counter the negative charge of the fabric, thereby facilitating absorption of dye anions on to the fabric. In all cases, excellent wash and dry/wet crocking fastness properties were achieved, and light fastness was improved by adding organic salt to the ink formulation.

References

1. K Chapman, *Am. Assoc. Text. Chem. Color. Rev.*, **2** (2002) 12.
2. S Ervine, B Siegel and K Siemensmeyer, *Text. Chem. Color. Am. Dyest. Rep.*, **32** (2000) 26.
3. K Siemensmeryer, B Siegel, S Ervine and J Bullock, *NIP 15: Int. Conf. Digital Print. Technol.*, Orlando, FL, USA (1999) 280.
4. A L Eckman, *AATCC Rev.*, **4** (8) (2004) 8.
5. H Ujiie, *Digital Printing of Textiles*, 1st Edn (Cambridge: Woodhead Publishing, 2006).
6. S Gupta, *Indian J. Fibre Text. Res.*, **26** (2001) 156.
7. M van Parys, *Melliand Texilber./Int. Text. Rep.*, **83** (2002) E96.
8. E P A Kumbasar and M Bide, *Dyes Pigm.*, **47** (2000) 189.
9. I Petrinic, N P R Andersen, S Sostar-Turk and A M Le Marechal, *Dyes Pigm.*, **74** (2007) 512.
10. S O Aston, J R Provost and H Masselink, *J.S.D.C.*, **109** (1993) 147.
11. Q Fan, Y K Kim, A F Lewis and M K Perruzi, *J. Imaging Sci. Technol.*, **47** (2003) 400.
12. L S Moser, *J. Text. Apparel Technol. Manag.*, **3** (2003) 1.
13. P J Hauser, *Advances in Treating Textile Effluent* (Vienna: InTech, 2011).
14. A Walters, D Santillo and P Johnston, *An Overview of Textile Processing and Related Environmental Concerns* (Exeter: Greenpeace Research Laboratories, 2005).
15. X F Li and W C Tincher, *Text. Chem. Color. Am. Dyest. Rep.*, **1** (1999) 37.
16. A W Kaimouz, R H Wardman and R M Christie, *Dyes Pigm.*, **84** (2010) 79.
17. M Kanik and P J Hauser, *Color. Technol.*, **119** (2003) 230.
18. Y Zhang, S Westland, V Cheung, S M Burkinshaw and M R S Blackburn, *Color. Technol.*, **125** (2009) 357.
19. A V D Eltz, A Schrell and W H Russ, *US5348557* (Germany: Hoechst AG, 1994).
20. G F Hutter, G Fand and M D Matzinger, *US6156384* (New York: Westvaco Corporation, 2000).
21. C W M Yuen, S K A Ku, P S R Choi and C W Kan, *Color. Technol.*, **120** (2004) 320.
22. C W M Yuen, S K A Ku and C W Kan, *J. Appl. Polym. Sci.*, **107** (2008) 1057.
23. C W M Yuen, S K A Ku, C W Kan and P S R Choin, *Color. Technol.*, **123** (2007) 267.
24. N S E Ahmed, *Dyes Pigm.*, **65** (2005) 221.
25. S A Abo Farha, A M Gamal, H B Sallam, G E A Mahmoud and L F M Ismail, *J. Am. Sci.*, **6** (10) (2010) 109.
26. H G Prabu and M Sundrarajan, *Color. Technol.*, **118** (2002) 131.
27. *AATCC Test Method 16-2001 Colour Fastness to Light* (Research Triangle Park: AATC, 2001).
28. *AATCC Test Method 61-2001 Colour Fastness to Washing* (Research Triangle Park: AATC, 2001).
29. *AATCC Test Method 8-2001 Colour Fastness to Crocking* (Research Triangle Park: AATC, 2001).
30. C W M Yuen, S K A Ku, P S R Choi and C W Kan, *Fibers Polym.*, **5** (2004) 117.
31. A Vogel, *A Textbook of Quantitative Inorganic Analysis* (London: Longman, 1944).
32. S Daplyn and L Lin, *Pigm. Resin Technol.*, **35** (2003) 307.
33. H R Kang, *J. Imaging Sci.*, **35** (1991) 179.
34. K F Morris, D M Lewis and P J Broadbent, *Color. Technol.*, **124** (2008) 186.
35. J A Bone, T T Le, D A S Phillips and J A Taylor, *Color. Technol.*, **124** (2008) 117.