

ORIGINAL ARTICLE

Investigation into the reaction of reactive dyes with carboxylate salts and the application of carboxylate-modified reactive dyes to cotton

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Abstract

Ink-jet printing of cellulosic fabrics with reactive dyes typically requires that the fabric is pretreated with alkali, prior to printing, to facilitate efficient fixation of the dye. In this paper we evaluate the use of sodium formate and other carboxylate salts as a neutral (pH 6.5) pretreatment process. The thickened, prepared-for-print pad liquor contained at least 50 gdm⁻³ of the selected carboxylate salt and was applied to the cotton fabrics by a pad-dry procedure. The fabric was then ink-jet printed with reactive dye inks, followed by standard steaming and washing-off processes. The pH of the carboxylate salt pretreatment was 6.5 and the aqueous extracts from the print fabrics at the end of the steaming process remained at pH 6.5. It was observed that even at pH 6.5, in the presence of selected carboxylates, significant reactive dye fixation could be achieved on a cotton substrate, whereas in the absence of the carboxylate, very little or even zero fixation was achieved. Infrared and capillary electrophoresis analyses of model reactions of reactive dyes with the carboxylate salts indicated that reactive ester residues were formed, and which subsequently promoted reaction with the cellulosic substrates. In addition to improving reactive dye fixation in ink-jet printing, the carboxylate-modified dyes were also demonstrated to improve long-liquor dyeing properties on cotton substrates. As an extension of this carboxylate-based printing process, the incorporation of lithium acetate (100 gdm⁻³) into the ink formulation was further studied and it was demonstrated that the necessity for a preparative pretreatment process could be eliminated.

1 | INTRODUCTION

The use of sodium formate to promote reactive dye fixation in cotton/polyester printing with the Remaron system, a mixture of selected reactive dyes and disperse dyes, was developed by scientists at Hoechst AG.¹ This work was patented as a process in which fibres were pad-dyed or printed with a padding liquor or print paste containing a reactive dye, a disperse

dye, an alkali metal salt of formic acid, a printing or dyeing auxiliary, carrier, levelling agent and/or a dispersing agent, and the printed fabric was subsequently fixed by dry heat or a steam heating process. The patent claimed that sodium formate is preferably used in amounts of 5–50 g/kg of paste or liquor, and the printed material is dried at below 100°C before dyestuff fixation. Weyer² subsequently showed that in the presence of sodium formate (25–30 g/kg), vinyl sulfone

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and sulfatoethyl sulfone (SES) dyes could covalently fix on cotton cellulose under mild processing conditions (10 minutes of steaming at 140°C), with no addition of alkali being necessary. However, no explanation or reaction mechanism was provided to account for this surprising effect.

Horrobin,³ in researching the shelf life of the early 2,4-dichloro-*s*-triazine Procion M dyes (DCT dyes) in dry powder form, found that acetate buffers accelerated hydrolysis of these powders. By contrast, phosphate pH 5 buffer had no detrimental effect and gave sufficient stability for these dyes to be commercialised. Perhaps unsurprisingly, there was little published regarding this poor reactive dye powder stability in acetate buffer and that it could be related to the acetate anion acting as a nucleophile, converting the chloro-*s*-triazine residue to a more reactive aceto-*s*-triazine residue. However, a later study by Rayle and Fellmeth⁴ did indicate that chloro-*s*-triazines reacted with alkyl carboxylates to form an acyl-*s*-triazine that subsequently could be reacted with an alkylamine to form the alkylamide and the hydroxy-*s*-triazine. In parallel, Rucker and Guthrie⁵ described improvements in the exhaust application of reactive dyes to cotton by replacing inorganic salt with carboxylate salts. In particular, potassium citrate gave improved levels of exhaustion and fixation. Again, no explanation was offered regarding the chemical mechanism responsible for the marked improvements. More recently, at the 2013 AIC conference, Lewis et al⁶ reported that 50 g/kg of sodium formate, or other selected carboxylates, could be applied as a cotton fabric pad-dry pretreatment for optimum fixation of ink-jet printed reactive dyes following 10 minutes of steaming at 104°C.

In the current paper we explore the chemical nature of the reaction of carboxylates with a variety of reactive dyes. A model β -SES dye was prepared and reacted with various carboxylate salts to monitor reaction outcomes using Fourier Transform Infrared (FTIR) spectroscopy. Commercially available reactive dyes were also reacted with various carboxylate salts and the products were evaluated using capillary electrophoresis (CE). This paper also details the surprising improvements in fixation of commercially available reactive dyes when combined with carboxylate salts and applied in ink-jet printing.

2 | EXPERIMENTAL AND METHODS

2.1 | Materials

1-aminobenzene-4- β -SES and 1-aminobenzene-4- β -hydroxyethyl sulfone were kindly supplied by Sumitomo Chemicals; 2-naphthol and all other chemicals were purchased from

Aldrich Chemical Co. Ltd. The cotton fabric was a plain weave bleached cloth (130 g/m²) supplied by Whalleys of Bradford. Commercially available reactive dyes were supplied by the following dye manufacturers: Remazol (Dystar); Procion P/PX (Dystar); Cibacron F (now Novacron F; Huntsman); Cibacron C (Ciba); Sumifix Supra (Sumitomo); and Drimarene K (Clariant, now Archroma).

2.2 | Synthesis of a model SES dye

The following model dye (SES dye I) was synthesised according to the method described in the literature (Figure 1).⁷

2.2.1 | Diazonium salt manufacture

1-aminophenyl-4-sodiosulfatoethyl sulfone (5.6 g; 0.02 M) was stirred in 300 cm³ of distilled water, to which 2.4 cm³ of 35% hydrochloric acid (0.03 M) was added. The suspension was cooled to below 5°C and 37 cm³ of a 0.5 M aqueous sodium nitrite solution was added over 20 minutes. The excess nitrous acid was destroyed by the addition of 10% (w/w) aqueous sulphamic acid.

2.2.2 | Coupling with 2-naphthol to produce model SES dye

2-naphthol (2.65 g; 0.18 M) was dissolved in 50 cm³ of 0.2 M aqueous sodium hydroxide solution then added to the above diazo component, the temperature being maintained between 0 and 5°C. The pH of the mix was adjusted to 7 by the addition of dilute (0.1 M) aqueous hydrochloric acid and stirring continued for 1 hour at 0-5°C. The mix was then left to reach an ambient temperature and 40 g of solid sodium chloride was added to precipitate the desired product, which was filtered and dried overnight at room temperature.

When required, conversion of SES dye to the more reactive vinyl sulfone form was achieved by adding 0.5 M sodium carbonate solution to an aqueous solution of the dye, raising the solution pH value to 11 while the solution temperature was maintained at 20°C. The solution was stirred well for 90 minutes and the pH value was maintained at 11 by addition of sodium carbonate solution as necessary. In this way, the hydrogen sulfate anion was eliminated and the vinyl sulfone reactive group was generated. Finally, the reaction solution was adjusted to pH 6 and the vinyl sulfone dye was precipitated from the solution. The precipitate was filtered, washed with deionised water, then dried.

The hydroxyethyl sulfone derivative of the model SES dye was prepared in a similar manner to the sulfatoethyl dye,

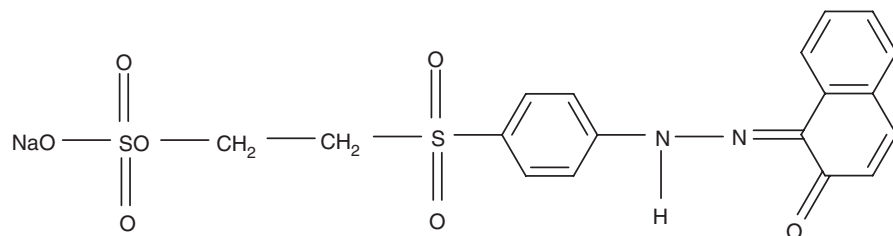


FIGURE 1 Structure of model sulfatoethyl sulfone dye

but in this case 1-aminobenzene-4- β -hydroxyethyl sulfone (4.02 g; 0.02 M) was diazotised and coupled to 2-naphthol.

2.3 | Model SES dye reaction with sodium formate

The SES dye (4 g) was dissolved in 150 g of water, and sodium formate (1.2 g), dissolved in 50 g of water (pH 3.5), was added slowly. The solution was then gently stirred for 5 hours at room temperature. At this stage the product was still water soluble, indicating that it was not the vinyl sulfone dye, because it is insoluble in water. Potassium thiocyanate was added to salt out the sodium formate dye, which was then filtered and washed with acetone 5-6 times to remove residual potassium thiocyanate.

2.4 | Model SES dye reaction with sodium citrate

To further characterise the carboxylate/SES dye reaction, a similar experiment was performed using sodium citrate instead of sodium formate. The SES dye (4 g) was dissolved in 150 g of water and the pH was adjusted to 4-5 with sodium carbonate at 20-22°C. One gram of sodium citrate was dissolved in 50 g of water at pH 3-3.5 then added to the SES dye solution slowly over 3-4 hours. The solution was then gently stirred for a further 2-3 hours and 6 M hydrochloric acid was added to adjust the pH to 2.5. Potassium thiocyanate was added to salt out the sodium citrate dye, which was then filtered and washed with acetone 5-6 times to remove residual potassium thiocyanate.

2.5 | Modification of commercial reactive dyes with sodium formate and sodium citrate

Remazol Red RB, Remazol Brilliant Orange 3R, Cibacron Blue FR and Cibacron Red FB were selected for modification with sodium formate and sodium citrate.

Formate derivatives: the selected dyes (4 g) were dissolved in 150 g of water, and a solution of sodium formate (1.2 g) in 50 g of water (pH 3.5) was added slowly. The mix was left for 5 hours at room temperature. Potassium thiocyanate was

added to salt out the sodium formate dye, which was then filtered and washed with acetone 5-6 times to remove residual potassium thiocyanate.

Citrate derivatives: the selected dyes (4 g) were dissolved in 150 g of water and the pH was adjusted to 4-5. A solution of sodium citrate (1 g) in 50 g of water at pH 3-3.5 was added to the dye solution slowly over 3-4 hours. The solution was left for a further 2-3 hours at room temperature. Next, 6 M hydrochloric acid was added to adjust the pH to 2.5 and potassium thiocyanate was added to salt out the citrate dye, which was then filtered and washed with acetone 5-6 times to remove residual potassium thiocyanate.

2.6 | Cotton fabric preparation for subsequent ink-jet printing

Normally, cotton fabrics are prepared for ink-jet printing with reactive dyes by prepadding the fabric with a thickened liquor containing sodium carbonate or sodium bicarbonate; this activation method was included in the experimental design for comparison purposes only.

Carboxylate salts (100 gdm⁻³) were used to replace the above alkalis with the expectation that the processing pH conditions would remain at 6.5 and thus demonstrate the unusual reactive dye fixation on cotton under these slightly acidic conditions. The formate, acetate and lactate salts all kept the fabric pH at 6.5 throughout the process. However, two carboxylate salts did not exhibit this pH stability, with sodium trichloroacetate and sodium carbamate (derived from sodium cyanate) decomposing during steaming to liberate sodium hydroxide, thus raising the pH of the fabrics from 6.5 to 10.5.

Bleached 100% cotton woven fabric was padded to 100% wet pick-up with aqueous liquors containing 100 gdm⁻³ of the following: alkali salts (sodium carbonate or sodium bicarbonate), dye fixation “activators” (sodium carboxylate salts), or compounds capable of decomposing during steaming to generate an alkali (such as sodium trichloroacetate or sodium cyanate). The fabric was padded with a slightly acidic solution (pH 6.5) containing a dye activator (50 gdm⁻³), a propoxylated cellulose thickener, Cellcosan 2000 (8 gdm⁻³; Kelco), and the mild oxidising agent sodium meta-nitrobenzene sulphinate (20 gdm⁻³ Ludigol; BASF), to prevent any dye reduction that may occur during steaming of the prints. The pad

liquors were adjusted to pH 6.5 via the addition of either the appropriate carboxylic acid or hydrochloric acid. The padded fabrics were dried at 60°C for 3 minutes.

The printing inks were based on 100 gdm⁻³ reactive dye, 150 gdm⁻³ ethylene glycol, 20 gdm⁻³ propan-2-ol and 25 gdm⁻³ 2-pyrrolidinone adjusted to pH 6.5 and made up to 1 L with distilled water. The ethylene glycol evaporates during steaming and does not compete with cellulose nucleophiles for the electrophilic groups in reactive dyes. Some of the ink formulations exhibited only 1-2 days of storage stability before the dye was observed to precipitate in the ink, but this problem was resolved as required by inclusion of N-methylmorpholine-N-oxide (200 gdm⁻³) in the inks.

2.7 | Laboratory-based, ink-jet printing application

Prepared cotton fabrics were mounted on A4-size pieces of paper and ink-jet-printed on a HP 540 Deskjet printer using a tri-color cartridge filled with the corresponding red, blue and yellow reactive dye ink solutions. The printed fabrics were steamed (with a Mathis laboratory steamer) at 104°C for 10 minutes to promote the fixation reaction then rinsed with cold water. Finally, the prints were soaped at 100°C for 15 minutes with an aqueous solution of Sandozin NIE (2 gdm⁻³), rinsed in water then dried.

2.8 | Long-liquor dyeing

The unmodified reactive dyes and their formate- and citrate-modified forms were applied to cotton fabric in the Rotadyer (John Jeffreys) laboratory dyeing machine.

The original Remazol dye was much weaker in colour strength (*K/S*) than the carboxylate-modified dye due to its high salt content, typically *ca.* 50% dye content in the original dye. For both the original and carboxylate-modified dyes, the dye-bath was based on either 1% or 2% owf dye, 5% owf sodium acetate and 80 gdm⁻³ sodium sulphate, with a liquor ratio (LR) of 20:1 being used. The original unmodified reactive dye was dyed at 60°C using 2% owf dye, and after 30 minutes 30 gdm⁻³ trisodium phosphate was added to adjust the bath pH to 11.5. Dyeing was continued for a further 60 minutes at 60°C then the fabrics were rinsed, soaped and dried. Preliminary studies indicated the carboxylate-modified dye was of higher reactivity and was therefore applied at 1% owf in the same manner, but at 40°C.

Similar to the Remazol dyes, the original Cibacron F dyes were much weaker in *K/S* than the carboxylate-modified dye derivative due to the higher salt content, *ca.* 50%. The original dye was applied at 60°C using 2% dye owf, 5% owf sodium acetate and 80 gdm⁻³ sodium sulphate, and the cotton fabric was initially treated for 45 minutes at pH 7. Next,

30 gdm⁻³ trisodium phosphate was then added to adjust the pH to 11.5 and dyeing continued for 60 minutes at 60°C. Finally, the dyed fabric was rinsed, soaped then dried. The carboxylate-modified dye (1% owf) was applied in the same manner, except a lower temperature of 50°C was used.

The uptake of the dye by the cotton was measured by sampling the dyebath before and after the dyeing process. The absorbance of the diluted dye solution was measured at the wavelength of maximum absorption (λ_{\max}) of the dye and the percentage of dyebath exhaustion (%*E*) was calculated using

$$\%E = \frac{1 - A_1}{A_0} \times 100,$$

where A_0 and A_1 are the absorbance values of the dye before and after dyeing, respectively.

2.9 | Fixation

The extent of fixation of the reactive dye absorbed on cotton was determined by stripping any unfixated dye from the dyed material using 25% (w/w) pyridine in water solution (100°C, LR 10:1). The stripping treatment (2 minutes) was carried out repeatedly using fresh aqueous pyridine solution until no further dye was removed. CIELab colour coordinates (L^* , a^* , b^* , C^* and h) were calculated from the reflectance data for 10° observer and illuminant D65. The *K/S* values of the stripped, dyed samples were then measured at λ_{\max} using a Macbeth Colour Eye measurement system. Assuming *K/S* was proportional to the dye concentration on the fibre, the extent of fixation (*F*) of the dye could be calculated using

$$\%F = \frac{K_2/S_2}{K_1/S_1} \times 100,$$

where K_1/S_1 and K_2/S_2 represent the colour strength of the dyed fabrics before and after stripping, respectively; f_k is a visually weighted function of *K/S*, which indicates the colour strength of samples: the *K/S* values of treated fabrics were automatically converted to f_k values by the software.

An alternative use of the term "fixation" is sometimes used, which refers to the overall amount of original dye that is covalently bonded to the fibre. This overall fixation efficiency (*T*) is related to *F* (the fraction of exhausted dye fixed) by

$$\%T = \frac{\%E \times \%F}{100}.$$

2.10 | FTIR analysis

FTIR spectra were obtained using a Perkin Elmer 1725X FTIR spectrometer and a diamond cell attenuated total

reflection contact sampler. The spectral data collected were at a resolution of 4 cm^{-1} and the final spectra were an average of 200 scans. The samples were prepared by mixing 1 mg of the sample in 200 mg of potassium bromide.

2.11 | CE analysis of reactive dyes

A Dionex CES 1 electrophoresis instrument was used with a 10 mM potassium dihydrogen phosphate buffer adjusted with 1 M sodium hydroxide to pH 9.0. The analysis was performed in a fused silica capillary of 50 μm internal diameter, 20 kV power and 47 cm distance between injection and the ultraviolet-visible detector.^{8–10}

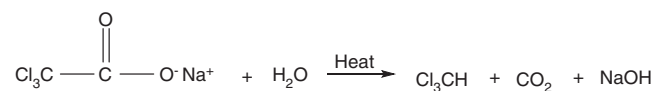
3 | RESULTS AND DISCUSSION

3.1 | Activator evaluation

Preliminary studies indicated that an activator concentration of at least 50 gdm^{-3} was required to give good reactive dye fixation following steaming at 104°C for 10 minutes. Accordingly, this level was used throughout the study. The activators investigated were sodium formate, sodium acetate, sodium propionate, sodium lactate, sodium benzoate, sodium malate, sodium citrate, sodium phthalate, sodium pyruvate, sodium tartrate, sodium malonate, sodium oxalate, sodium thiocyanate, sodium borate, sodium trichloroacetate and sodium cyanate. With all the activator buffers the initial pH was set to 6.5 and, with the exception of sodium cyanate and sodium trichloroacetate, the pH of an aqueous extract from the final printed fabric after steaming remained at pH 6.5. By contrast, for sodium trichloroacetate, decomposition occurred during steaming with the liberation of chloroform gas and the formation of aqueous sodium hydroxide (Scheme 1).^{11,12} Similarly, sodium cyanate, in moist steam, also decomposes by initially reacting with water to form sodium carbamate, which, being unstable in steam, evolves ammonia and carbon dioxide gas to form aqueous sodium hydroxide (Scheme 2).^{13,14}

Thus, in the case of sodium trichloroacetate and sodium cyanate activators, the pH of the final printed fabric water extracts was 10–11.

Typically, untreated cotton fabrics printed with reactive dyes exhibit practically zero dye fixation after steaming



SCHEME 1 Sodium trichloroacetate decomposition to chloroform, carbon dioxide and sodium hydroxide during steaming

(Figure 1). By contrast, the activators offering significant levels of reactive dye fixation were identified as sodium formate, sodium acetate, sodium propionate, sodium lactate, sodium benzoate, sodium cyanate, sodium borate and sodium trichloroacetate. The most promising activators, in terms of giving outstanding reactive dye fixation in this procedure, were sodium formate, sodium acetate, sodium cyanate and sodium trichloroacetate. In some cases (notably with bifunctional Remazol dyes), almost 100% reactive dye fixation could be achieved, with no colour being removed during the soaping-off process. Most dyes of medium reactivity were found to give rise to high levels of covalent dye fixation when applied to cotton in the presence of the selected activator. However, the lower reactivity monochloro-*s*-triazine dyes (Procion P/PX) were found to yield lower levels of covalent dye fixation. However, the degree of dye fixation could be considerably increased by incorporation of a tertiary amine catalyst in the pretreatment pad liquor with the tertiary amine forming a highly reactive quaternary dye intermediate, which will fix more efficiently.^{15–17}

3.2 | Ink-jet prints showing the effect of activators

Figure 2, showing ink-jet prints based on Remazol β -SES dyes, demonstrates the excellent colour yields achievable



SCHEME 2 Sodium cyanate decomposition to ammonia, carbon dioxide and sodium hydroxide during steaming

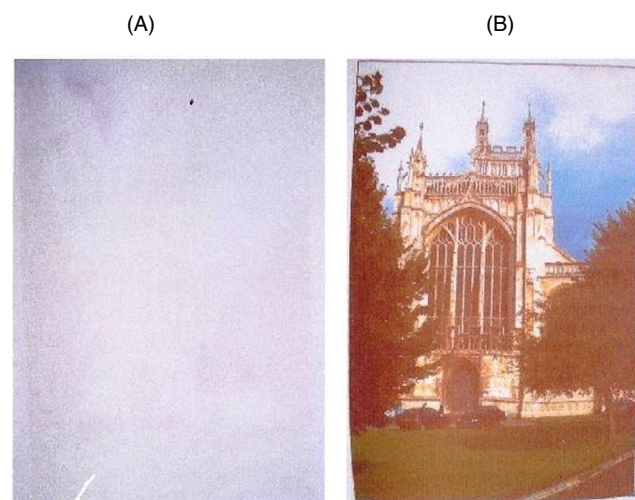
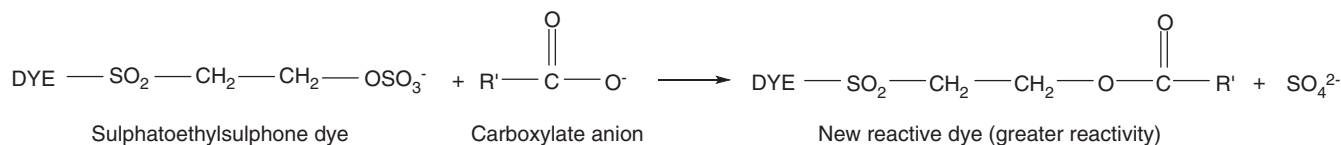
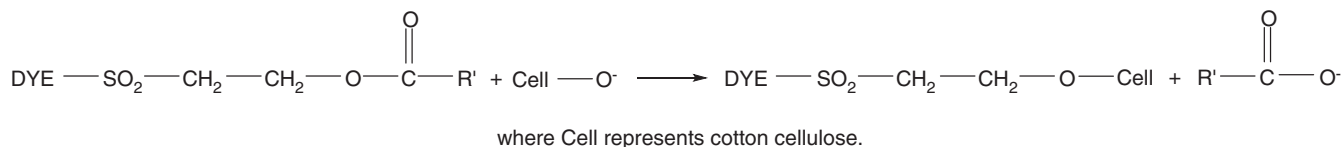


FIGURE 2 Untreated cotton (A) and sodium acetate pretreated cotton fabric (B) ink-jet-printed with Remazol dyes. Ink-jet cartridges containing 100 gdm^{-3} Remazol Red RB, 100 gdm^{-3} Remazol Brilliant Blue R and 100 gdm^{-3} Remazol Golden Yellow RNL



where DYE represents the dye chromophore and R' is H, alkyl or aryl.

SCHEME 3 Formation of a new reactive O-alkylcarboxyethylsulfone dye, where DYE represents the dye chromophore and R' is H, alkyl or aryl



SCHEME 4 Reaction of the O-alkylcarboxyethyl sulfone dye with cotton, where Cell represents cotton cellulose

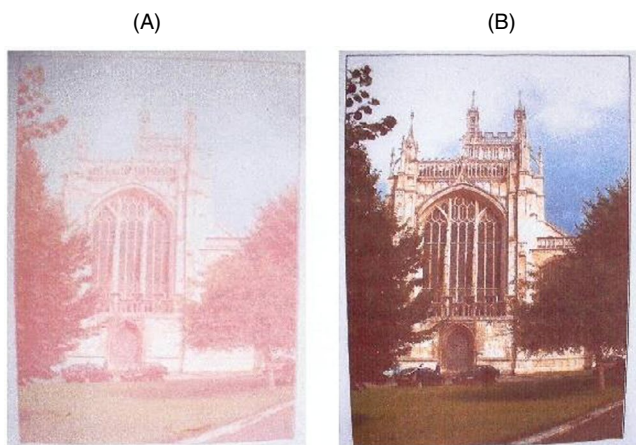


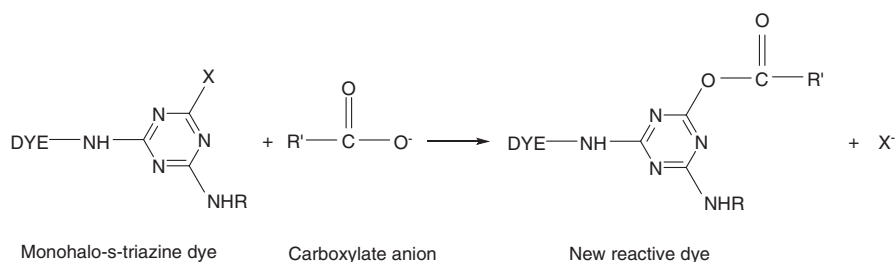
FIGURE 3 Untreated cotton (A) and sodium acetate pretreated cotton fabric (B) ink-jet-printed with Cibacron F dyes. Ink-jet cartridges containing 100 gdm⁻³ Cibacron Red FN-R, 100 gdm⁻³ Cibacron Blue FN-R and 100 gdm⁻³ Cibacron Yellow FN-2R

in the case of the sodium acetate activator pretreatment in comparison with the zero dye fixation achieved on untreated fabric. With the acetate activation of the Remazol dyes, the image of Gloucester Cathedral is colouristically strong and photorealistic.

The promotion of dye fixation at pH 6.5 is unexpected with the carboxylates because classical reactive dye application processes rely on additions of alkali to increase the concentration of the nucleophilic Cell-O⁻ groups. However, increased temperature can also achieve the same result, because raising the temperature from 25 to 100°C lowers the pK_a values of conjugate acids by up to 2 units,¹⁸ thereby increasing the concentration of Cell-O⁻ 100-fold. Moreover, dissociation of acids is also affected by ionic strength, so that an increase in salt concentration will also increase the dissociation of the proton from the cotton cellulose hydroxyl residue. These factors were utilised in a study of the neutral pH application of reactive dyes to cotton, where fixation levels, comparable with those achieved in standard alkali-promoted dyeing, were demonstrated.¹⁹

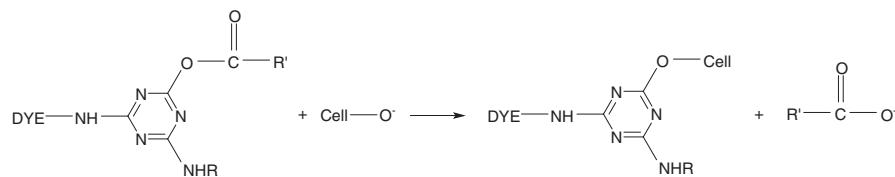
It is proposed that the reactions described in Schemes 3 and 4 are responsible for the excellent dye fixation occurring even at pH 6.5 and 100°C. Initially, the carboxylate anion forms an ester-based intermediate, which has greater reactivity towards cellulose than the original vinyl sulfone Remazol dyes.

This beneficial carboxylate effect was also found to be valid with other reactive dyes, for example, cotton was again pretreated with thickened sodium acetate (pH 6.5), dried then ink-jet-printed with fluoro-*s*-triazine Cibacron FN dyes.



SCHEME 5 Formation of a new reactive O-acyltriazine dye, where DYE represents the dye chromophore, X is Cl or F, R' and R' are H, alkyl or aryl

where DYE represents the dye chromophore, X is Cl or F, R' and R' are H, alkyl or aryl.



where Cell represents cellulose.

SCHEME 6 Reaction of O-acyl-s-triazine dye with cotton at pH 6.5, where Cell represents cellulose



FIGURE 4 Pretreated cotton fabrics ink-jet-printed with Cibacron F dyes. (A) Sodium bicarbonate (pH 8); (B) sodium carbonate (pH 11.5); (C) sodium trichloroacetate (pH 6.5→10.5); (D) sodium lactate (pH 6.5); (E) sodium formate (pH 6.5); (F) sodium cyanate (pH 6.5→10.5); and (G) sodium acetate (pH 6.5)

Figure 3 indicates that, on the carboxylate-pretreated fabric, excellent fixation was observed for the Cibacron FN dyes, even although the printing procedure was performed at pH 6.5; by contrast, very little dye fixation occurred on the untreated

cotton. The following halo-s-triazine dye-cellulose reactions are proposed (Scheme 5), based on the formation of an activated ester triazinyl intermediate, which reacts efficiently with cotton under slightly acidic conditions (Scheme 6).

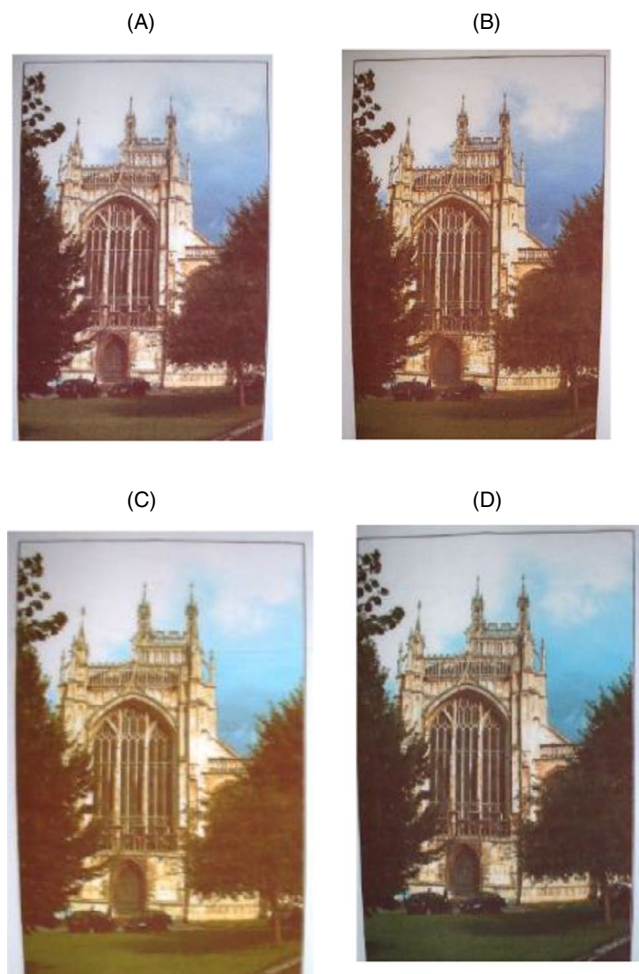


FIGURE 5 Lithium acetate (100 gdm^{-3}) non-prepared cotton fabrics ink-jet-printed with a range of reactive dyes. (A) 100 gdm^{-3} Cibacron Red C-R, 100 gdm^{-3} Cibacron Blue C-R, 100 gdm^{-3} Cibacron Yellow C-2R; (B) 100 gdm^{-3} Drimarene Brilliant Red K-4BL, 100 gdm^{-3} , Drimarene Brilliant Blue K-2R, 100 gdm^{-3} Drimarene Golden Yellow K-2R; (C) cyan cartridge: 85 gdm^{-3} Remazol Turquoise Blue G, 15 gdm^{-3} Remazol Brilliant Blue R; magenta cartridge: 75 gdm^{-3} Remazol Red BS, 25 gdm^{-3} Remazol Brilliant Blue R; yellow cartridge: 100 gdm^{-3} Remazol Golden Yellow RNL; and (D) 200 gdm^{-3} Sumifix Supra Turquoise Blue BGF, 100 gdm^{-3} Remazol Red BS, 100 gdm^{-3} Sumifix HF Yellow 3R

Whilst the acetate activation was encouraging, a wider range of activators were assessed for the Cibacron F dyes, and the resulting prints are shown in Figure 4. It is evident, for the monofluoro-s-triazine dyes, that the most intense prints were obtained, and hence the highest fixation efficiency, on the sodium trichloroacetate and sodium cyanate pretreatments, followed by sodium formate/sodium acetate, sodium carbonate and sodium bicarbonate, then finally sodium lactate. The bicarbonate prepared would have been rated higher but for the lower reactivity of the blue component, Cibacron Blue FN-R.

3.3 | “All-in” system for ink-jet printing with reactive dye-based inks

In seeking to improve on current technology, it would be a significant commercial advantage if the prepare-for-print-process stage for cotton fabrics could be eliminated. Ink formulations containing a dye activator plus reactive dye were therefore prepared and ink-jet printed onto unprepared (bleached only) cotton. However, when the activator was added to the ink as a sodium salt, precipitation of the reactive dye occurred. Therefore, the alternative highly water-soluble lithium acetate was identified as a suitable activator for inclusion with a reactive dye in a single ink formulation.

Following steaming of the printed fabrics at 104°C , then rinsing after soaping and drying, it was evident that the highest degree of reactive dye fixation was achieved for inks containing dyes of medium reactivity (Remazol, Cibacron F, Cibacron C, Sumifix Supra and Drimarene K). A suitable ink formulation developed for the one-step printing of cotton fabric was based on $100\text{--}200 \text{ gdm}^{-3}$ reactive dye, 100 gdm^{-3} lithium acetate, 200 gdm^{-3} N-methylmorpholine-N-oxide, 20 gdm^{-3} 2-pyrrolidinone, 25 gdm^{-3} propan-2-ol and 20 gdm^{-3} Ludigol, adjusted to pH 6.5 with acetic acid and the final volume adjusted to 1 dm^3 with distilled water. Following ink-jet printing, steaming and washing-off, very good dye fixation was obtained, with the pH of the wash-off liquors stable at 6.5. Figure 5 shows that excellent quality prints could be obtained using these “all-in” inks. It is significant that the omission of thickener did not give rise to the expected loss of print definition. However, as the inks are highly concentrated and the cotton substrate will rapidly absorb water, there is little likelihood of ink spreading following printing, and the steaming process clearly dissolves sufficient dye to allow diffusion and fixation of the reactive dye on the cotton cellulose.

3.4 | FTIR analysis of reactive dyes modified with carboxylates

The FTIR spectra of the starting model SES dye had the expected spectral intensities for the aromatic and aliphatic C–H stretch vibrations (3063 , 3000 and 2940 cm^{-1}), the CH=CH stretching vibrations for aromatic molecules (1622 and 1594 cm^{-1}), sulfonyl stretch (1135 cm^{-1}) and an S=O stretch associated with the sulphate anion (1005 cm^{-1}) (Figure 6). The controlled alkali conversion of the SES dye to the vinyl sulfone derivative produced obvious changes in the FTIR spectra (Figure 7), with the CH=CH out-of-plane bending vibration of the terminal alkene becoming evident at 981 cm^{-1} ; associated with this increase is the concomitant loss of the sulphato-vibrational signals and a relative increase in the

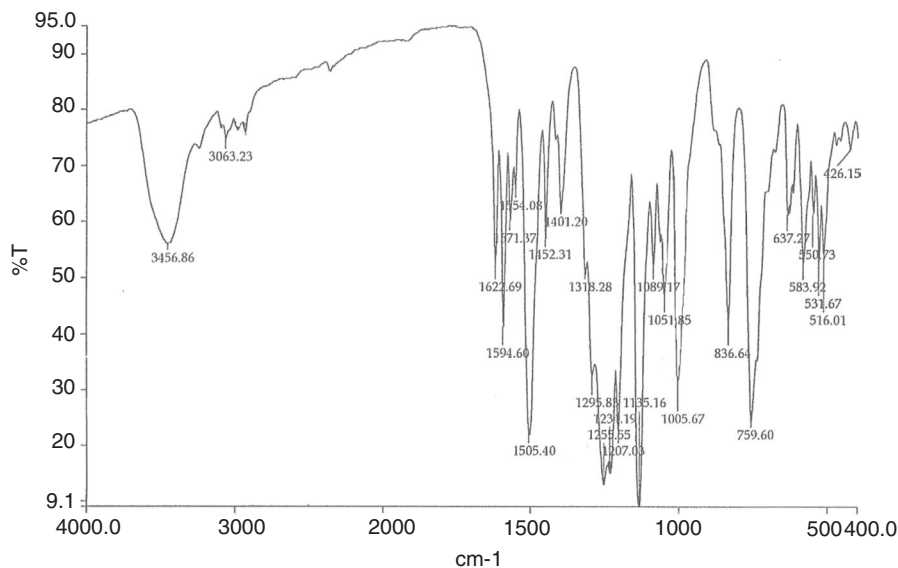


FIGURE 6 Fourier Transform–infrared spectrum of model sulfatoethylsulfone dye

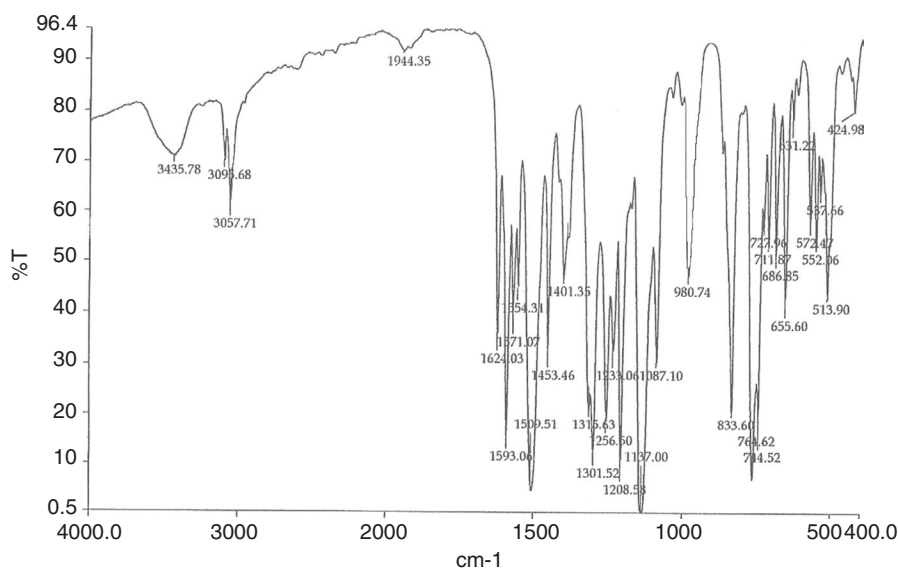


FIGURE 7 Fourier Transform–infrared spectrum of vinyl sulfone dye derivative

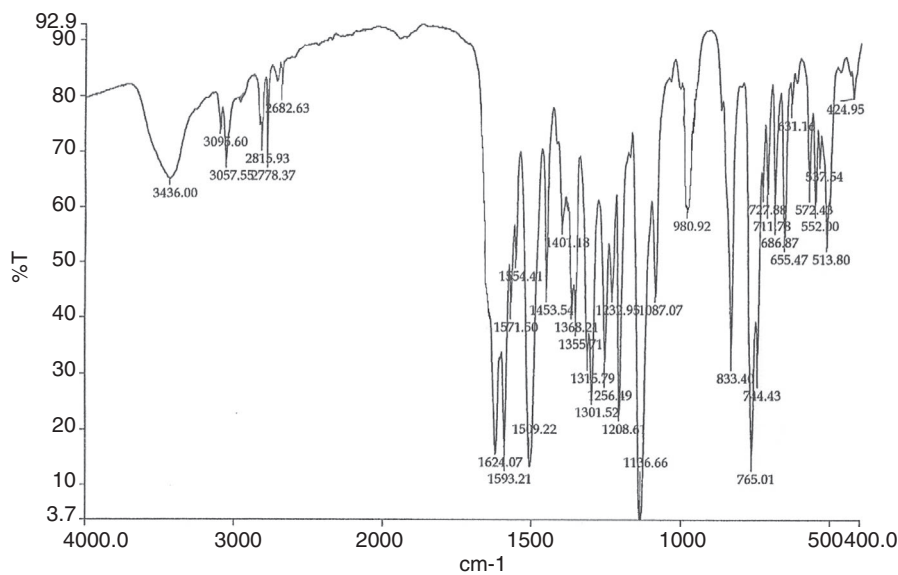
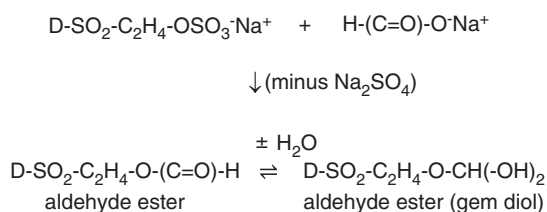


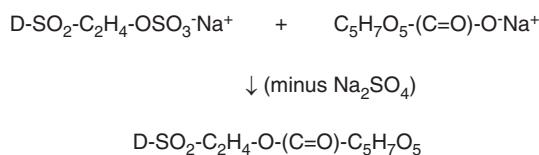
FIGURE 8 Fourier Transform–infrared spectrum of the formate-modified vinyl sulfone dye

aromatic C–H stretching vibrational intensity, due to loss of the aliphatic ethyl functionality. Similarly, examination of the FTIR spectrum (not shown) of the hydrolysed hydroxyethyl sulfone derivative of the SES molecule also confirmed the absence of the vibrations associated with the vinyl and sulfato functionalities.

Reaction of the formate nucleophile with the SES dye resulted in the loss of the sulfate ester vibrational signal at 1006 cm^{-1} in the FTIR spectrum (Figure 8). However, there was clear evidence for the presence of significant amounts of vinyl sulfone dye (vinyl stretching and bending signals evident at 3096 , 3057 and 981 cm^{-1} , respectively) in the dye mixture. The spectrum also indicated that the sulfate functionality had been replaced with a formate ester functionality, which exhibited aldehydic character when dry (typical C–H aldehydic stretch observed at 2816 and



SCHEME 7 Formation of formate aldehyde ester from sulphatoethyl sulfone dye



SCHEME 8 Formation of citrate ester dye derivative from sulfatoethyl sulfone dye

2778 cm^{-1}). However, when in aqueous solution, the gem diol, the hydrated form of the aldehyde, will predominate. Therefore, the expected carbonyl stretch vibration has shifted to lower frequency, 1645 cm^{-1} , due to the partial C–O nature of the carbonyl functionality. Scheme 7 shows the proposed reaction of formate with the SES model dye, but the isolation drying procedure, essential before the FTIR analysis stage, partially converts the formate ester back to vinyl sulfone.

To further characterise the carboxylate/sulfatoethyl sulfone dye reaction, a similar experiment was performed using sodium citrate instead of sodium formate (Scheme 8). Examination of the FTIR spectrum of the citrate ester-based dye indicated the presence of a new strong ester band at 1726 cm^{-1} (Figure 9). However, the presence of characteristic spectral intensity at 3096 , 3057 and 981 cm^{-1} indicates the citrate ester is again being partially converted back to the vinyl sulfone form on drying.

3.5 | CE analysis of selected commercially available reactive dyes and their carboxylate derivatives

Examination of the capillary electropherogram of the original SES form of Remazol Red RB indicated it was clearly a mixture, with the major species being the SES peak at 9.8 minutes (area 76%) and the smaller vinyl sulfone peak located at a retention time of 7.5 minutes (area 3.5%) (Table 1). The remaining low peak intensity signals were assigned to other unidentified contaminant species. The reaction of the SES dye with formate produced a new major peak at 11.1 minutes (area 78.3%) together with other unidentified low intensity peaks. Similarly, the citrate reaction with the SES dye resulted in a dominant new peak in the

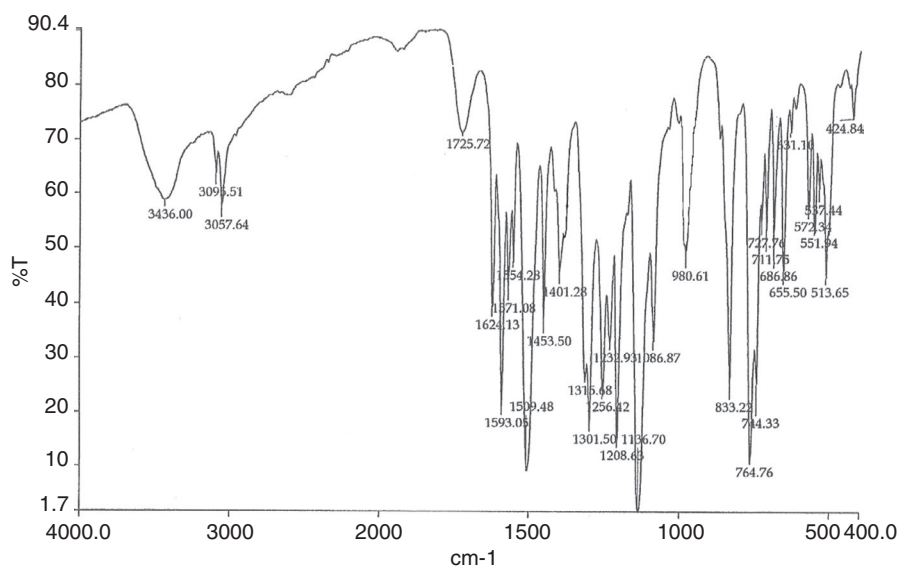


FIGURE 9 Fourier Transform-infrared spectrum of the citrate-modified vinyl sulfone dye

TABLE 1 Capillary electrophoresis (CE) analysis of formate- and citrate-modified Remazol Red RB and Remazol Brilliant Orange 3R reactive dyes

Dye	CE retention time of dye species (min) and peak intensity (%)			
	Sulfatoethylsulfone derivative	Vinyl sulfone derivative	Formate derivative	Citrate derivative
Remazol Red RB	9.8 (76.0%)	7.5 (3.5%)	11.1 (78.3%)	11.7 (75.7%)
Remazol Brilliant Orange 3R	5.7 (98.4%)	4.3 (96.5%)	N/A	7.0 (100%)

Abbreviation: N/A, not analysed

Dye	CE retention time of dye species, minutes and peak intensity, %	
	Fluorotriazine	Formate derivative
Cibacron Blue FR	8.5 (91.8%)	11.8 (98.9%)
Cibacron Red FB	9.5 (81.9%)	11.8 (79.8%)

TABLE 2 Capillary electrophoresis (CE) analysis of formate-modified Cibacron Blue FR and Cibacron Red FB reactive dyes

Coloration parameters	Reactive dye		
	Remazol Red RB, 2% owf	Remazol Red RB-Formate Dye, 1% owf	Remazol Red RB-Citrate Dye, 1% owf
Exhaustion <i>E</i> , %	85	98	98
Fixation <i>F</i> , %	82	98	97
Total efficiency <i>T</i> , %	70	96	95
Colour yield f_k	75	125	124

TABLE 3 Fixation and colour yield values following long-liquor dye application of 1%-2% owf Remazol Red RB dye and carboxylate dye derivatives to cotton fabric

Coloration parameters	Reactive dye		
	Cibacron Red FB, 2% owf	Cibacron Red FB-Formate, 1% owf	Cibacron Red FB-Citrate, 1% owf
Exhaustion <i>E</i> , %	85	93	97
Fixation <i>F</i> , %	82	99	99
Total efficiency <i>T</i> , %	70	92	97
Colour yield f_k	75	122	122

TABLE 4 Fixation and colour yield values following long-liquor dye application of 1%-2% owf Cibacron Red FB dye and carboxylate dye derivatives to cotton fabric

electropherogram at a retention time of 11.7 minutes (area 75.7%), with other unidentified low intensity peaks evident in the electropherogram.

Similarly, with the original Remazol Brilliant Orange 3R, the SES form was the major peak intensity in the electropherogram at a retention time of 5.7 minutes (area: 98.4%), with the vinyl sulfone form evident at 4.1 minutes (area: 1.1%) (Table 1). Conversion of the SES dye to the vinyl sulfone derivative resulted in the major peak intensity being at a retention time of 4.3 minutes with an associated peak area of 96.5%. Remazol Brilliant Orange 3R was also modified with sodium citrate and the reaction of the dye resulted in a new dominant citrate ester peak intensity at

7.0 minutes (area: 100%), and strongly supports the proposal for carboxylate activation of SES dyes (Scheme 3) and the formation of a new reactive group: the citrate ester of the vinyl sulfone.

The monofluoro-*s*-triazine dyes, Cibacron Blue FR and Cibacron Red FB, were also modified using the formate reaction, and the corresponding electropherograms indicated a shift in the retention time for the reactive Cibacron Blue FR parent dye from 8.5 (area: 91.8%) to 11.8 minutes (area: 98.9%) after reaction with formate to form the formyl triazine ester (Table 2). Similarly, for Cibacron Red FB, the retention time of the parent dye molecule in the CE data shifted from 9.5 minutes (area: 81.9%) to the major peak intensity at

11.8 minutes (area: 79.8%) following reaction with the formate nucleophile (Table 2). Coupled with the FTIR data, this provides strong evidence for the formate nucleophile readily replacing fluorine to form the formyl triazine ester.

3.6 | Application of carboxylate dyes in long-liquor dyeing of cotton fabric

Typically, the commercial Remazol Red RB and Cibacron Red FB dyes contain *ca.* 50% salt, while the formate and citrate derivatives are essentially salt-free. Therefore, to assess comparable dyeing levels the commercial dyes were applied at 2% owf, while the formate and citrate derivatives were applied at 1% owf. Further, as preliminary experiments indicated that the derivative dyes were more reactive than their commercial precursors, the Remazol derivatives were applied at 40°C rather than at 60°C, and the Cibacron derivatives were similarly applied at a lower temperature of 50°C rather than at the normal dyeing temperature of 60°C.

Examination of the dyed fabrics indicates the Remazol Red RB and Cibacron Red FB carboxylate-modified dyes gave clear improvements in exhaustion, dye fixation and colour yield (Tables 3 and 4). This preliminary long-liquor application study confirms that carboxylate-activated reactive dyes have the potential to improve reactive dyeing processes in terms of higher fixation efficiencies. However, it is evident that extensive further research is required into simplification of the preparation processes, storage stability of the derivatives and selection of the optimal carboxylate activator, as well as the need to benchmark the colour profile of the dye derivatives relative to the original commercial precursor dye.

4 | CONCLUSIONS

This study has shown that reactive dyes can be modified by reaction with a variety of sodium carboxylates and that the modified dyes gave improved fixation of reactive dye ink-jet formulations printed on cotton. Surprisingly, simple alkyl carboxylates such as formate, acetate and citrate provided promising dye fixation at pH 6.5.

Incorporating sodium trichloroacetate into the ink formulation also produced an excellent result with high dye fixation, but in this case the steamed fabric pH shifted on steaming to 11.0 due to hydrolytic decomposition, forming sodium hydroxide and chloroform. Similarly, sodium cyanate gave very high fixation of the reactive dye prints, but again decomposed to sodium hydroxide, carbon dioxide and ammonia during steaming. Clearly, the evolution of chloroform from sodium trichloroacetate would not be acceptable

commercially, whereas the decomposition products formed during steaming of the sodium cyanate-prepared cotton are environmentally acceptable.

Preliminary studies incorporating lithium acetate into the reactive dye printing ink formulation were successful in terms of the quality of the print, reactive dye fixation and print definition. The omission of the anti-migration thickener in the preparation for pretreatment did not appear to adversely affect image definition.

Infra-red analysis indicated that the model SES dye reacted with the formate and citrate anions to form esters, which also form significant amounts of the vinyl sulphone form of the dye on drying.

CE analysis of the carboxylate-modified Remazol and Cibacron F dye solution clearly demonstrated the presence of new ester-based derivatives. These solution-modified dyes were applied to cotton fabrics by long-liquor procedures and it was demonstrated that the exhaustion/fixation parameters were greatly improved following carboxylate modification.

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