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The Dyeing Behaviour of Cotton Modified with Chloropropionyl Chloride and Related Compounds

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ABSTRACT

Cotton fabric was esterified with chloropropionyl chloride followed by reaction with amines, in order to introduce primary, secondary, tertiary and quaternary amino residues. The reactive dyeing properties of these chemically modified fibres were studied, especially from the point of view of dyeing in the pH region 5–7 without added electrolyte.

The conditions employed to introduce amino residues on the chloropropionated cotton appeared to affect the ultimate mode of attachment of the amino group. These reactions have been studied and a reaction scheme proposed involving the chloropropionic acid acting as a leaving group under severe amination conditions.

INTRODUCTION

Processes for efficient dyeing of cellulosic fibres with reactive dyes under neutral pH conditions in the absence of salt would exhibit the following advantages:

(1) higher fixation efficiency, because of reduced reactive-dye hydrolysis under neutral pH conditions;
(2) polyester/cotton blends could be dyed in a one-step, one-bath dyeing procedure using reactive and disperse dyes, thus saving time and energy;

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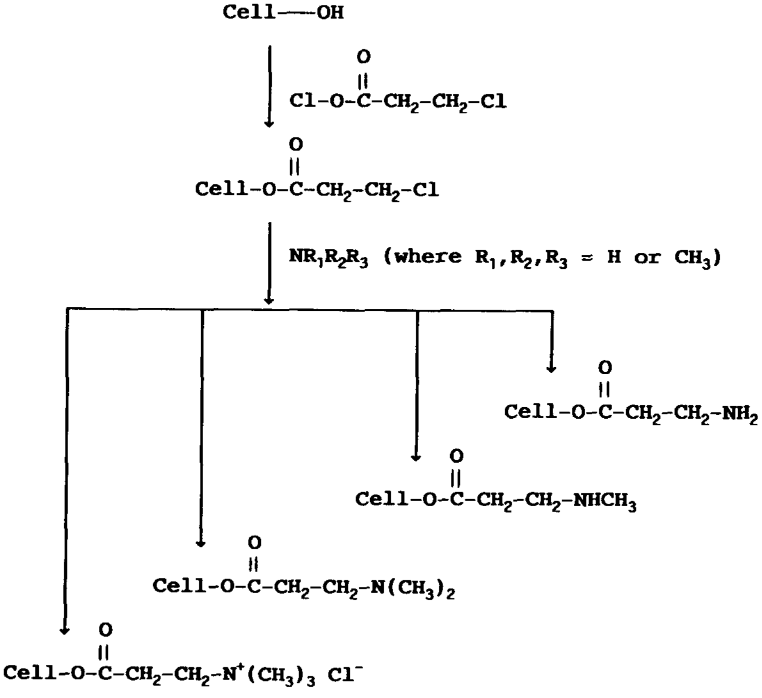
(3) environmental effluent problems reduced, due to minimum formation of hydrolysed dye and the absence of salt.

Chemical modification of cellulosic fibres is a promising route to achieve neutral dyeing with reactive dyes. In an earlier paper[1] it was demonstrated both in theory and in practice that it was necessary to introduce functional groups that are capable of increasing both the substantivity and the reactivity of reactive dyes.

The majority of reported chemical modifications that increase the substantivity of anionic dyes for cellulose are based on the incorporation of amino groups in the fibre.[2-6] An earlier paper of the authors[7] described the preparation of a variety of cellulose derivatives using amine reactions with *N*-methylolacryl-amide-treated cotton. This study describes results using a different bridging system to incorporate amino residues into cotton.

In this study the four different types of amino groups (primary, secondary, tertiary and quaternary) were introduced into cotton by means of the reaction of cellulose with chloropropionyl chloride, followed by substitution of the terminal β-chloro groups by different amines (ammonia, methylamine, dimethylamine and trimethylamine). It is the aim of this study to give further support to the previous theoretical analysis,[1] as well as to clarify the sort of



Scheme 1

amino group which should be introduced, to achieve neutral dyeing of cellulosic fibres with reactive dyes in the most efficient way.

The initial intention was to modify cellulose according to Scheme 1.

The above objective was achieved under certain conditions of amine reaction with the chloropropionyl ester, but under other conditions an anomalous reaction was noted.

EXPERIMENTAL

Materials

Bleached and unmercerized cotton fabrics were used throughout the work. All dyes and auxiliaries used were of commercial grade. Chloropropionyl chloride (CPC), sodium thiosulphate, mercuric oxide and potassium sulphate were Analar reagent grade materials; sodium hydroxide, sulphuric acid (98% w/w), hydrochloric acid (36% w/w), dimethylformamide (DMF), ammonia ($d = 0{\cdot}880$), methylamine (25–30% w/w, aqueous solution), dimethylamine (40% w/w, aqueous solution) and trimethylamine (25–30% w/w, aqueous solution) were laboratory reagent grade materials.

Acylation of cotton with chloropropionyl chloride (CPC cotton)

Cotton fabric was treated in a DMF solution containing 10% (v/v) of CPC; the treatment was carried out with mechanical stirring in a glass reactor, housed in a water bath at a given temperature for 2 h; the fabric was then rinsed thoroughly in tap water and dried in the open air.

Preparation of aminized cotton

The CPC cotton was further treated in an aqueous solution containing 10 g/litre of NaH_2PO_4 and 'V' ml of the selected amine; the treatment was carried out in 500-ml sealed stainless-steel dyepots housed on a Rotadyer (John Jeffreys, Rochdale, UK) laboratory dyeing machine at a liquor to goods ratio of 20:1.

Treatments were commenced at 50°C, rising to 100°C over 30 min, and maintained for various times, t (min), at this temperature.

The samples were then rinsed thoroughly in tap water and dried in the open air. The specific treatment conditions employed with each amine are listed in Table 1.

TABLE 1
Conditions for Amination of CPC Cotton

Amines	*V* (*ml/litre*)	*t* (*min*)
Ammonia ($d = 0{\cdot}880$)	150	120
Methylamine (25–30%)	175	60
Dimethylamine (40%)	125	60
Trimethylamine (25–30%)	175	180

Dyeing of the treated cotton

All dyeings were carried out in 100-ml sealed stainless-steel dyepots housed in the Rotadyer at a liquor to goods ratio of 20:1. Dyebaths were set at pH 5 (NaH_2PO_4 buffer, 10 g/litre), and no further electrolyte addition was made. In some cases dyeing was performed at pH 7 ($Na_2HPO_4 + NaH_2PO_4$ buffer mixture). Dyeing was commenced at 50°C, the temperature was raised to the boil over 25 min (2°C/min) and dyeing was continued at the boil for a further 60 min.

The dyed samples were then rinsed thoroughly in tap water and cut into two equal portions. One of these portions was soaped in a solution containing 5 g/litre of the non-ionic detergent, Sandozin NIE(S), and 2 g/litre of sodium carbonate at the boil for 15 min (liquor ratio 50:1).

Measurements

Exhaustion

The uptake of dye by each type of aminized 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 using a UV–visible spectrophotometer (Philips Pye Unicam PU8600). Dyebath exhaustion was calculated using the following equation:

$$\text{Exhaustion}\ \% = 100(1 - A1/A0)\%$$

where $A0$ and $A1$ are the absorbances of dye solution before and after the dyeing process, respectively.

Dye fixation

Measurement of the extent of dye fixation of the reactive dye on both treated and untreated cotton was carried out by stripping any unfixed dye from the dyed material using a 25% aqueous pyridine solution (100°C, liquor ratio 10:1). This stripping treatment was carried out repeatedly using fresh, aqueous pyridine solutions until no further dye was removed. The K/S valued of the stripped, dyed samples were then measured using the ICS Micromatch colour measurement system, from which the extent of fixation of dye was calculated using the following equations:

$$\text{total dye applied fixed } (T\%) = \text{dye exhaustion } (\%) \times (C2/C1)$$

$$\text{degree of fixation of dye absorbed } (F\%) = (C2/C1) \times 100\%$$

where $C1$ and $C2$ are the K/S values of dyed samples before and after stripping, respectively.

Total nitrogen determination

The total nitrogen content of the treated fibre was measured according to ASTM Standard D1013-81[8] (standard test method for total nitrogen in resins and plastics).

Weight gain

The samples (before and after CPC treatment) were dried at 70°C to constant weight and then weighed immediately in an electronic balance that measures to six decimal places. The weight gain was calculated using the following equation:

$$R(\%) = (W2 - W1)/W1 \times 100\%$$

where $W1$ and $W2$ are the weights of samples before and after CPC treatment, respectively.

FTIR spectra

IR analysis of both treated and untreated cotton was carried out using the Perkin–Elmer 1740 infrared Fourier transform spectrometer, using the diffuse-reflectance attachment to obtain IR spectra.

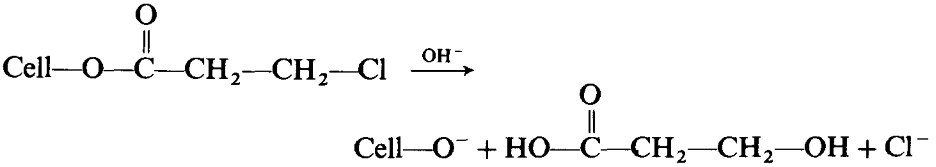
Determination of CPC fixation on cotton by ion-exchange chromatography

The extent of reaction of CPC with cotton was measured both by weight gain and by ion-exchange chromatography. In the latter case a Varian 2510 HPLC pump and a Varian CM-2 conductivity monitor with PRP-X100 IC anion column were used. The mobile phase used in this analysis consisted of 2 mmol/litre of phthalic acid and 10% of acetone (pH 5, conductivity approximately 180 μS/cm). The flow rate for this analysis was 7·5 ml/min and the volume for each injection was 10 μl.

RESULTS AND DISCUSSION

Establishment of a method to determine the extent of CPC reaction with cotton using ion-exchange chromatography

Determination of the extent of CPC reaction with cotton could be done by measuring weight gain, but this method is time consuming. In the present work efforts have therefore been made to establish a simpler method based on ion-exchange chromatography. Chloride ion concentration can be easily measured using this technique.[9] After reaction of cellulose hydroxyl groups with CPC, one chlorine atom is introduced per molecule of reacted CPC. The chlorine atoms may be readily liberated from the CPC cotton by simply treating the substrate with an aqueous solution of potassium hydroxide. The molar concentration of chloride ion in the solution is equal to that of the chloropropionyl ester bound to the cotton according to the hydrolytic Scheme 2.



$$\mathrm{Cell{-}O{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}CH_2{-}CH_2{-}Cl} \xrightarrow{\mathrm{OH^-}} \mathrm{Cell{-}O^-} + \mathrm{HO{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}CH_2{-}CH_2{-}OH} + \mathrm{Cl^-}$$

Scheme 2

For quantitative measurement when using this instrumentation it is necessary to use an internal standard to avoid errors. In the present case

TABLE 2
Reproducibility of Relative Chloride Concentration [RCl]

Number	*Duration of treatment (h)*	*Area of $(OH^- + K^+)$ peak*	*Area of Cl^- peak*	*[RCl]*
1[a]	5	2 008 753	664 641	330·8
2[a]	5	2 021 406	667 821	330·4
3[a]	5	2 006 333	661 145	329·5
4[a]	0	1 982 776	137 400	69·3
5[a]	0	2 011 202	139 351	69·3
6[b]	3	2 093 371	290 483	138·8
7[b]	3	2 089 561	290 856	139·2
8[b]	3	2 096 375	293 510	140·0

[a] Solution treatment.
[b] Fabric treatment.

TABLE 3

The Change of Relative Chloride Concentration with Treatment Time

Time (*h*)	*Area of chloride peak*	*Area of* $(OH^- + K^+)$ *peak*	*[RCl]*
0	137 400	1 982 774	69·3
1	695 678	2 121 618	327·9
2	709 704	2 161 016	328·4
3	786 364	2 139 742	367·5
4	806 968	2 157 853	373·9
5	667 821	2 021 406	330·4
6	830 853	2 274 442	365·3

both OH^- and K^+ give a single peak that may be employed as a constant internal standard.

In order to obtain an accurate indication of chloride ion concentration relative to total $[OH^-]$ and $[K^+]$, a parameter—relative chloride concentration [RCl]—was employed:

$$[\mathrm{RCl}] = \frac{\text{area of chloride peak}}{\text{area of } (\mathrm{OH}^- + \mathrm{K}^+) \text{ peak}} \times 1000$$

The reproducibility of the [RCl] data obtained from the instrument was checked by repeated injection of the same sample under identical chromatographic conditions. The samples analysed were the solutions obtained by treating chloropropionic acid (0·5%) in 5 g/litre KOH aqueous solution for 0 and 5 h, respectively, and by treating CPC cotton under the same conditions at a liquor to goods ratio of 20:1 for 3 h. The data collected and the [RCl] values are given in Table 2. It can be seen that the reproducibility of [RCl] values was very good.

The confirmation that hydrolysis of C—Cl bonds in the CPC cotton is complete under the above-mentioned conditions was obtained by treating chloropropionic acid under the same conditions for various times. The chloride ion concentration in the solution was measured using ion-exchange chromatography. Table 3 gives the results.

The data in Table 3 suggests that treatment of CPC cotton under the above-mentioned conditions for 3 h would lead to complete hydrolysis of all C—Cl bonds. These conditions were therefore used for all the later studies.

Effect of temperature on CPC–cellulose ester yield

During the reaction of cellulose with CPC the reaction temperature was kept as low as possible so that a suitable amount of CPC–cellulose ester could be

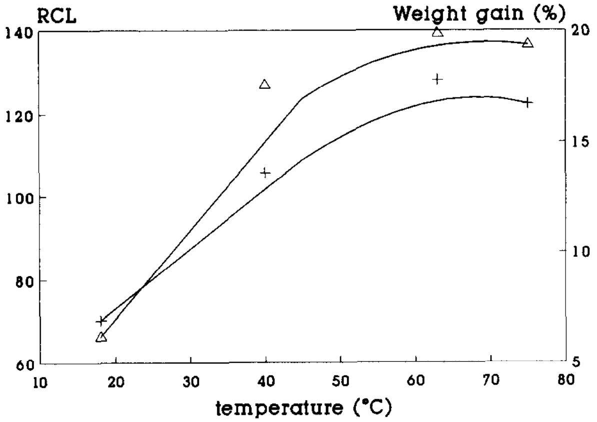


Fig. 1. The effect of temperature on the yield of cotton–CPC ester (△, relative chloride concentration [RCl]; +, weight gain).

produced without altering the other desirable properties of cotton. The ester yield on cotton after reaction was determined both by weight gain and chloride ion analysis (ion-exchange chromatography). The results are shown in Fig. 1. It can be seen from Fig. 1 that, at 60°C, a reasonable ester yield was obtained. The handle and other physical properties of the cotton fabric after CPC treatment under this particular condition was observed to be equivalent to that of untreated cotton fabric. All further experiments were therefore carried out at 60°C.

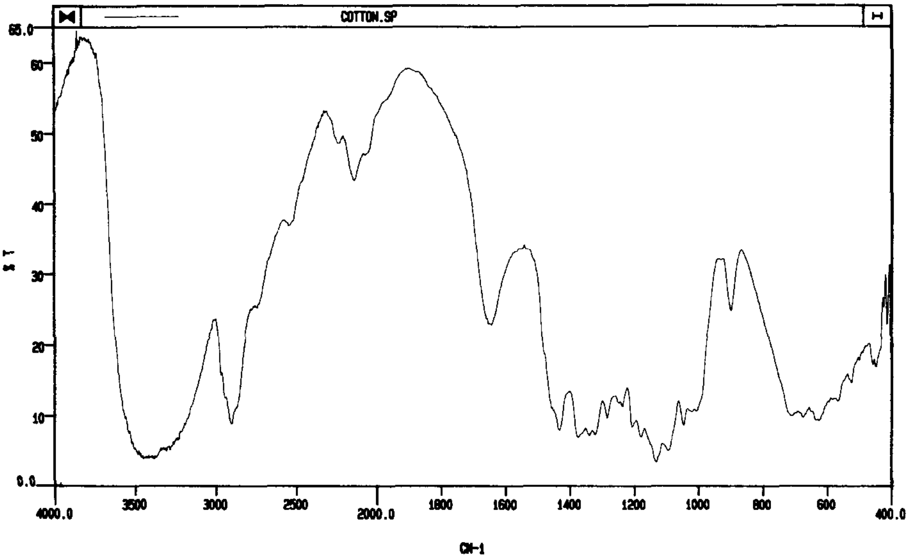


Fig. 2. FTIR spectrum of untreated cotton.

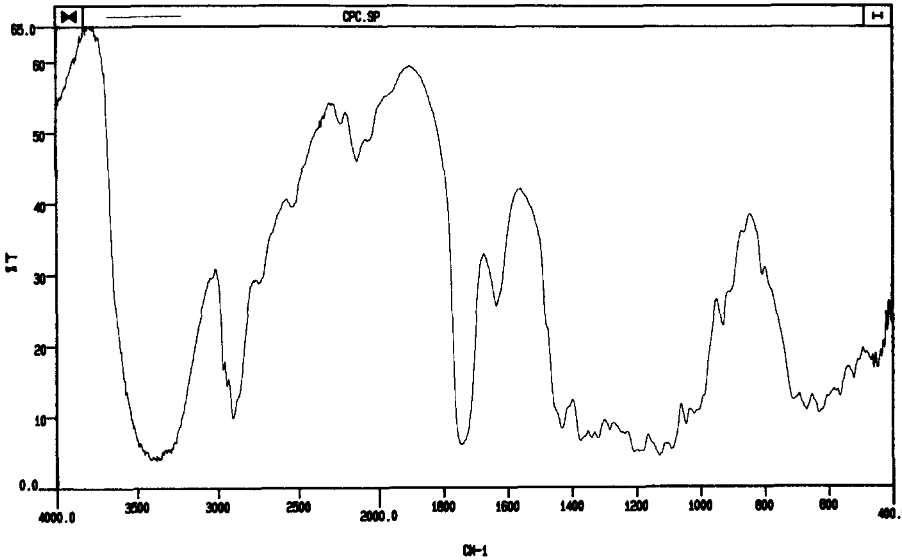


Fig. 3. FTIR spectrum of CPC-treated cotton.

The formation of CPC–cellulose ester was confirmed by the diffuse FTIR spectra of both untreated and CPC-treated cotton. Figures 2 and 3 show the spectra of both fabrics and Fig. 4 is the spectrum obtained by computer subtraction of Fig. 2 from Fig. 3. A strong absorbance attributable to the ester bond is apparent at 1746 cm^{-1}, and some evidence exists for the carbon–chlorine bond at 790 cm^{-1}.

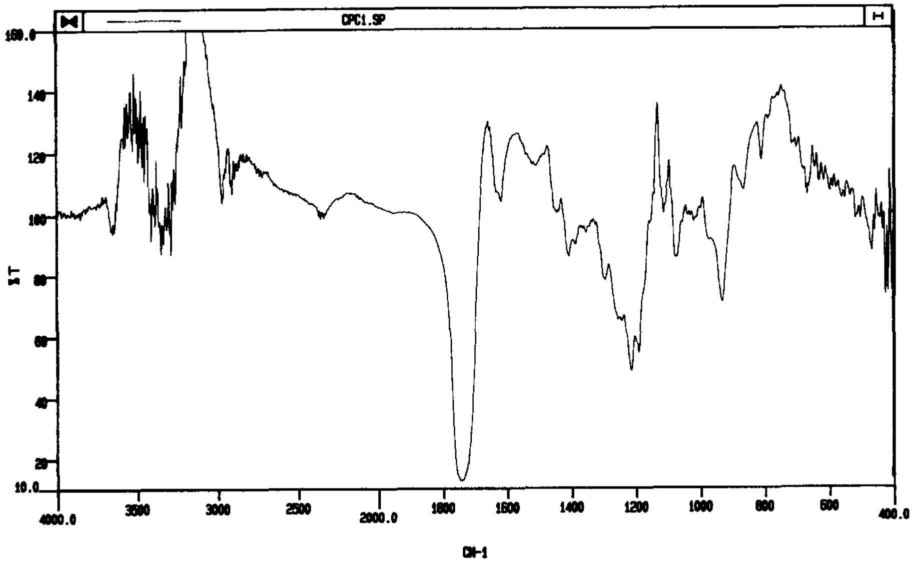


Fig. 4. FTIR spectrum obtained by subtracting untreated cotton from CPC-treated cotton.

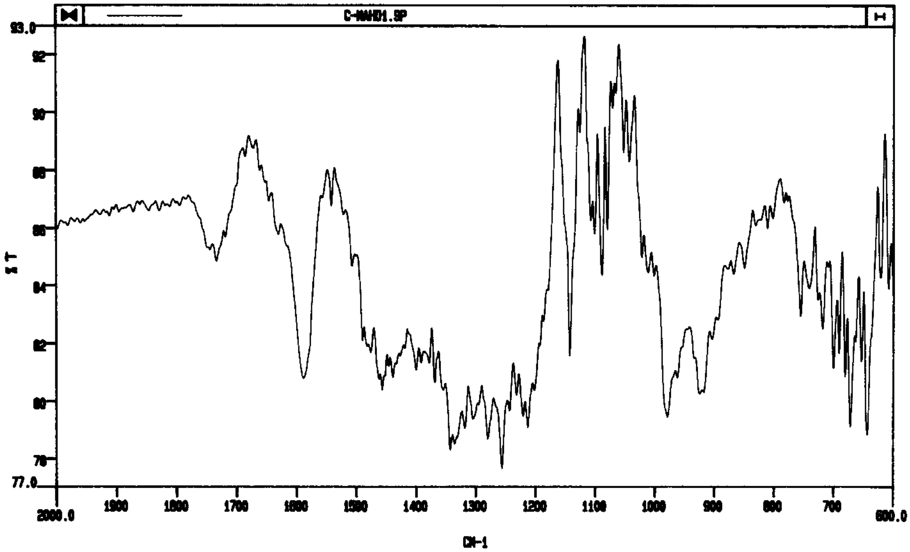


Fig. 5. FTIR spectrum obtained by subtracting untreated cotton from substrate I (methylamine reaction with CPC cotton at the boil).

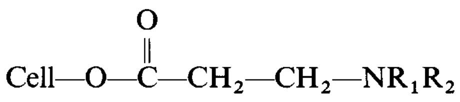
Substrate properties produced by the CPC/amine treatment

Two phenomena were observed following investigation of CPC/methylamine-treated cotton.

(1) Neutral dyeing, without salt, of Procion Red MX-G (CI Reactive Red 5—ICI) on CPC/methylamine-treated cotton gave high colour yields and the dyeings were very fast, being resistant to alkaline soaping (Table 4). This was surprising if one assumes the ester linkage remained intact during the amination; if present, ester residues are likely to be easily saponified during the boiling alkaline clearing treatment at the end of the reactive dyeing process.

(2) CPC cotton gave a strong IR absorbance at about 1740 cm^{-1}, indicating the presence of ester bonds in this substrate (Fig. 4), but this peak disappeared after the substrate was further treated with boiling aqueous methylamine solutions under the conditions described in the experimental section (Fig. 5). The other amines described in Table 1 gave similar IR analysis when they were applied to CPC cotton at the boil.

It is suggested from the above observations that the substrate obtained after amination under boiling conditions is *not*



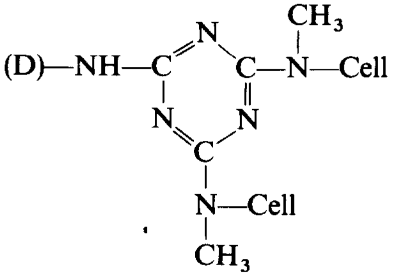
$$\text{Cell—O—}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{—CH}_2\text{—CH}_2\text{—NR}_1\text{R}_2$$

but rather has the following structure:

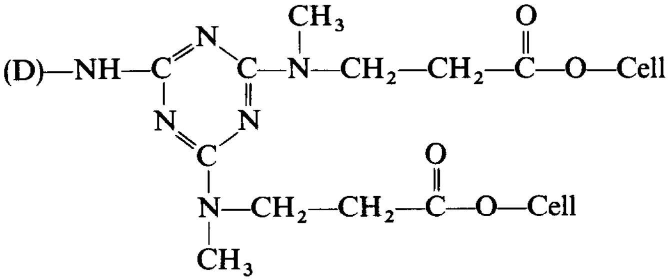
$$\text{Cell—NR}_1\text{R}_2 \qquad \text{I}$$

where R_1 and R_2 may be either H or $—CH_3$.

The dichloro-*s*-triazine reactive dye is thus bonded to the fibre in the following manner (if the amine used was methylamine):



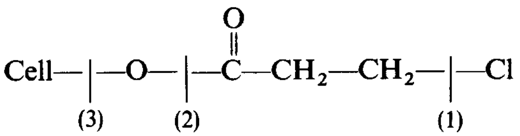
rather than



where (D) represents a sulphonated chromophore.

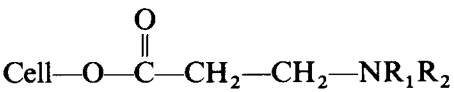
No coloration could be produced when dyeing chloropropionated cotton, which had not been subsequently aminated, under the above salt-free, weakly acidic conditions, thus excluding the possibility that the fast dyeings obtained on the aminated substrates might be due to a modification derived, somehow, from the CPC treatment.

CPC cotton has the following structure:



$$\text{Cell}\underset{(3)}{—|—}\text{O}\underset{(2)}{—|—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—CH}_2\text{—CH}_2\underset{(1)}{—|—}\text{Cl} \qquad \text{II}$$

Under the conditions used for amination of CPC cotton only the three positions indicated above could possibly be involved in reaction with the amine. In fact, the chlorine atom (position (1)) should be readily replaced by highly nucleophilic amines to form a substrate of the following structure:



$$\text{Cell—O—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—CH}_2\text{—CH}_2\text{—NR}_1\text{R}_2 \qquad \text{III}$$

This substrate would still give a strong IR ester absorbance at about

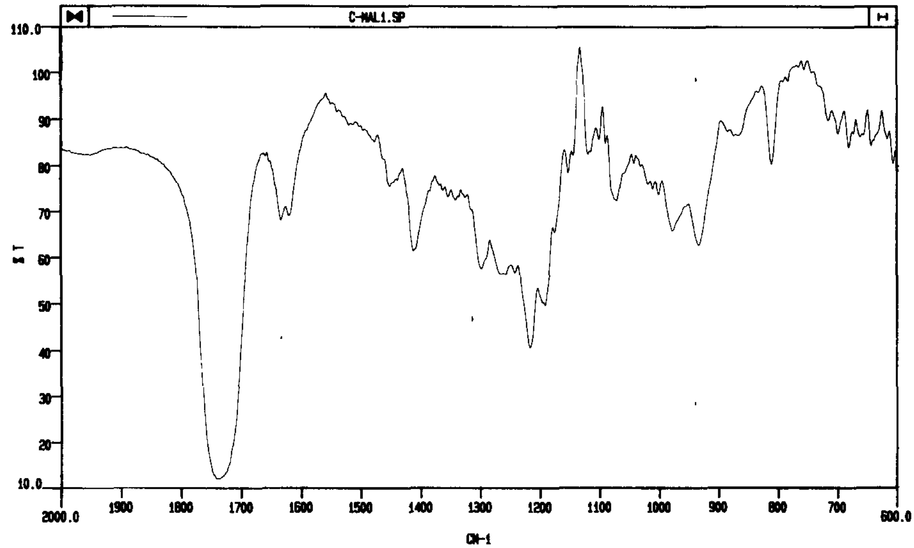


Fig. 6. FTIR spectrum obtained by subtracting untreated cotton from substrate **III** (methylamine reaction with CPC cotton under mild conditions).

1740 cm^{-1}. It was subsequently shown that substrate **III** could indeed be produced by carrying out the amination under much milder conditions (10 ml/litre of 25–30% methylamine aqueous solution and at 50°C for 1 h). Figure 6 shows the FTIR difference spectrum produced by subtracting the spectrum of untreated cotton from this latter treated cotton; the strong ester band is intact at 1740 cm^{-1}, new bands attributed to secondary amines appear at 1584 cm^{-1} and the carbon–chlorine band has disappeared. Dyeings with reactive dyes on substrate **III** were found to show poor alkaline wet fastness (Table 4); this was expected, since the ester bonds would not be stable under alkaline conditions.

Furthermore, when the above modified substrates (**I** and **III**) were treated with an aqueous solution containing 20 g/litre of sodium carbonate at a

TABLE 4

Colour Yield of Procion Red MX-G (2% owf[a]) Dyeings on Different Substrates (Methylamine 25–30% was Used for Amination)

Substrate code	*Amination conditions*		*Colour yield*	
	Amine concentration (g/litre)	*Temperature (°C)*	*Before soap (K/S)*	*After soap (pH 10·5) (K/S)*
I	175	100	12·63	11·95
III	10	50	19·72	8·72

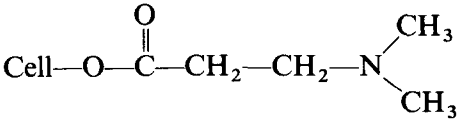
[a] On weight of fibre.

TABLE 5
Colour Yield of Procion Red MX-G (2% owf) Dyeings on Different Substrates (Methylamine 25–30% was Used for Amination) Following Alkaline Hydrolysis Treatment

Substrate code	*Amination conditions*		*Colour yield*	
	Amine concentration (g/litre)	*Temperature (°C)*	*Before soap (K/S)*	*After soap (pH 10·5) (K/S)*
I	175	100	11·03	10·57
III	10	50	0·21	0·19

liquor to good ratio of 20:1, at the boil for 1 h and then dyed with Procion Red MX-G under the same dyeing conditions (pH 5, no salt), the substrate aminized under severe conditions (**I**) still gave a good colour yield, whilst the other exhibited no coloration (Table 5), indicating that the ester bond had been hydrolysed (confirmed by FTIR).

Further evidence that the dyed substrate showing high wet fastness is not substrate **III** is obtained from the dyeing behaviour of CPC/dimethylamine-treated cotton. When amination was carried out by using dimethylamine under milder conditions (7 ml/litre of 40% aqueous dimethylamine solution, 50°C, 1 h), the following substrate was obtained (FTIR spectrum confirms ester bond still intact):

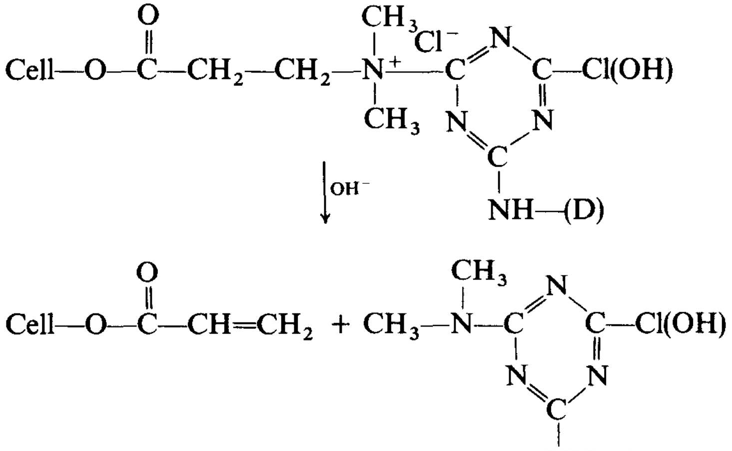


IV

Dyeings of Procion Red MX-G on this substrate were readily decolourized by alkaline soaping because of β-elimination and ester hydrolysis reactions. The β-elimination reaction proposed is shown in Scheme 3.

This type of β-elimination was previously observed when studying the dyeing behaviour of *N*-methylolacrylamide/dimethylamine-treated cotton.[7] Other literature has also discussed this type of reaction.[10] However, when CPC cotton was treated with dimethylamine under the more severe conditions described in the experimental section, dyeings on this substrate were surprisingly fast to alkaline soaping (Table 6).

If cleavage during amination of substrate **II** was to take place at position (2), cellulose itself would be reformed, which certainly would not improve the neutral dyeability of this fibre in the absence of high electrolyte concentration.



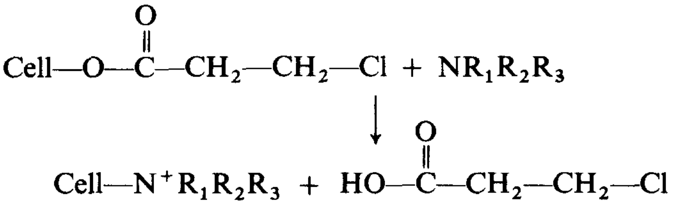
Scheme 3

TABLE 6

Colour Yield of Procion Red MX-G (2% owf) Dyeings on Different Substrates (Dimethylamine 40% was Used for Amination)

Substrate code	*Amination conditions*		*Colour yield*	
	Amine concentration (g/litre)	*Temperature (°C)*	*Before soap (K/S)*	*After soap (pH 10·5) (K/S)*
I	125	100	10·31	8·39
III	10	50	14·72	1·40

The above discussion indicates that the only possible cleavage site in substrate **II** following amination at the boil would be position (3) and the substrate produced would be type **I**. Karrer and Wehrli[11] produced type **I** amino celluloses by means of tosylation of cotton with toluene-4-sulphonyl chloride followed by a further treatment with amines; in this case the leaving group is toluene-*p*-sulphonic acid and the amino nucleophile is attached through carbon to the cellulose. The present system must therefore follow a similar mechanism to that proposed by Karrer and Wehrli.[11] We thus propose the following (Scheme 4).



$$\text{Cell—O—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—CH}_2\text{—CH}_2\text{—Cl} + \text{NR}_1\text{R}_2\text{R}_3 \longrightarrow \text{Cell—N}^+\text{R}_1\text{R}_2\text{R}_3 + \text{HO—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—CH}_2\text{—CH}_2\text{—Cl}$$

Scheme 4

TABLE 7
Nitrogen Contents and Dye Exhaustion/Fixation Values on Different Substrates (Procion Red MX-G, 2% owf)

Amine used	*Nitrogen (%)*	*Exhaustion (%)*		*Fixation (%)*	
		pH 5	*pH 7*	*pH 5*	*pH 7*
Ammonia	0·0088	16·0	20·4	13·3	20·3
Methylamine	0·0344	72·9	66·3	69·0	63·8
Dimethylamine	0·0133	51·8	54·3	42·2	48·2
Trimethylamine	0·0300	20·1	48·5	14·1	40·7

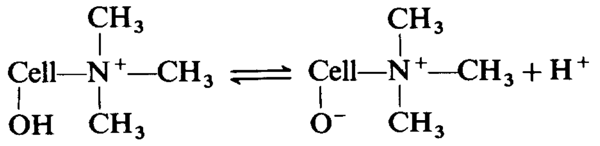
Relation of exhaustion and fixation values to total nitrogen values

A comparison of total nitrogen fixed and subsequent reactive dye exhaustion/fixation according to the type of amine residue involved with substrate **I** was attempted, but it was difficult to draw meaningful conclusions because of the large differences in bound nitrogen. Ammonia gave the least bound nitrogen values, indicating the lower nucleophilicity of this amine (Table 7).

As far as the reactivity towards CPC cotton was concerned, methylamine is the strongest nucleophile of the four amines. This can be clearly seen from the time taken to achieve significant reaction (Table 1) and the total nitrogen values (Table 7).

The cellulose-bound quaternary amino group is the only one which is incapable of reacting with reactive dyes. As expected, it gives the lowest fixation values under pH 5 dyeing conditions as its mode of action will be to promote dye exhaustion, but, since few nucleophilic sites are available at pH 5, little fixation occurs (Table 7).

Another interesting observation is that the exhaustion and fixation values in the case of these quaternary amino-modified substrates increase sharply with rising pH, whilst the other amino-modified substrates do not. This again indicates the overriding importance of the presence of nucleophilic amino residues in cotton when dyeing under neutral pH conditions using reactive dyes—presumably the reaction sites for the dye on the quaternary ammonium-modified cotton dyed at pH 7 are cellulosate anions. These are probably present at moderately high concentrations under neutral conditions in this modified substrate, due to the bound cationic residue promoting ionization of adjacent cellulose hydroxyl groups.



$$\underset{\mathrm{OH}}{\mathrm{Cell}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{N^+}}}-\mathrm{CH_3} \rightleftharpoons \underset{\mathrm{O^-}}{\mathrm{Cell}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{N^+}}}-\mathrm{CH_3} + \mathrm{H^+}$$

CONCLUSIONS

Cotton may be effectively esterified with CPC to give a reactive substrate that can undergo further reactions with a variety of amines. Thus a series of primary, secondary, tertiary and quaternary amino residues were covalently incorporated into the fibre. These modified amino celluloses were found to be promising substrates for neutral to slightly acidic dyeing with reactive dyes in the absence of electrolyte. The methylamine treatment showed optimum colour yield and fixation.

If the amination reaction was carried out in such a way as to leave the ester linkage intact, the alkaline stability of the dye–fibre bond was found to be weak, giving low fixation values. However, under certain more severe conditions of amination an anomalous reaction occurred, incorporating the amino residues in a different manner. Reactive dyeings on these latter substrates exhibited excellent alkaline stability. Evidence has been obtained that, during the boiling reaction of the amine and esterified substrate, nucleophilic displacement of either chloropropionic acid or its β-elimination product, acrylic acid, occurs and that the amino nucleophile is directly attached to the cellulose. This proposed reaction is supported by FTIR studies and analysis of reactive dyeing behaviour.

Evidence is presented which shows that neutral to weakly acidic fixation of reactive dyes in the absence of salt varies according to the type of amino group incorporated. The apparent order of amino group efficiency is

$$\text{secondary} > \text{tertiary} > \text{quaternary} > \text{primary}$$

However, the low, primary, amino group content realized thus far is most likely distorting this conclusion; earlier work[7] using a different method to introduce primary amino residues to the fibre gave excellent reactive dyeing results.

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