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Modification of Cotton with Nicotinoyl Thioglycollate to Improve its Dyeability

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ABSTRACT

Nicotinoyl thioglycollate (NTG) was synthesised and applied to cotton, producing a cellulosic fibre containing tertiary amine residues. The reactivity of NTG towards cotton was explored, so as to achieve an optimum NTG covalent reaction with the cellulose. The dyeability of the chemically modified cellulose with C.I. Reactive Red 120, a low reactivity, bi-functional monochlorotriazine (MCT) dye, in the absence of any electrolyte, was considered with regard to colour yield, fixation and exhaustion. The mechanistic implications and the quality of dyeings produced are discussed. Finally, a brief study into the dyeability of the modified cellulose with higher reactivity dyes and other non-reactive, anionic dyes is presented. © *1997 Elsevier Science Ltd*

Keywords: cotton modification, reactive dyes, nicotinoyl thioglycollate.

INTRODUCTION

There are many classes of dyes suitable for the dyeing of cotton. The required shade, fastness properties and cost of dyeing dictate dye class selection; the most versatile dye range meeting most criteria is the reactive dye class. During the application of reactive dyes, alkaline conditions are generally employed, since it is necessary to generate sufficient nucleophilic, cellulosate anions. However, it is under such conditions that there is an abundance of hydroxyl anions present and therefore hydrolysis is significant. Dye chemists have designed reactive dye molecules with two or more reactive groups to increase the chances of covalent dye–fibre bonding [1], but considerable dye wastage still occurs, particularly with heavy shades.

Highly coloured reactive dyebath discharge is not solely due to hydrolysed dye, since electrostatic repulsion by fixed sulphonated dye on the fibre can prevent further movement of reactive dye from the solution onto the fibre, especially in full shades [2].

High concentrations of electrolyte are necessary in reactive dyebaths to suppress the negative potential of the cellulose and essentially increase the substantivity of anionic, reactive dye towards the fibre. Thus, reactive dyes are far from ideal as they are difficult to exhaust from the dyebath and the dye–fibre fixation reaction is inefficient; the deeper the shade to be dyed the greater these problems.

Environmental concern over cotton reactive dyeing has drastically increased in recent years due to the consequences that arise from the above two factors. Discharges of high electrolyte concentrations are undesirable since increased salinity of the rivers affects the delicate biochemistry of aquatic life. Sodium chloride is an electrolyte commonly used in reactive dyeing but the alternative, sodium sulphate, is even more suspect. Sodium sulphate destructively attacks concrete pipes as a result of the formation of alumino–sulphato complexes that swell and crack concretes, especially those with a high alumina content [3]. Also, under anaerobic conditions, sulphate is converted to sulphide and results in the evolution of highly toxic, hydrogen sulphide gas. In addition, the generated sulphide dissolves moisture from exposed surfaces and is oxidised by sulphur oxidising bacteria to sulphuric acid, which then attacks the fabric of the sewer concrete walls and of iron material in manholes.

The incomplete utilisation of colour due to poor dye fixation increases the cost of dyeing with reactive dyes. Expensive, energy intensive wash-off procedures are required to remove unfixed dye remaining on the fibre; a direct consequence is lengthening of dyeing time and hence reduced productivity. The colour in the dye house effluent itself poses a major environmental problem. The UK has had about 600 complaints per annum concerning colour in rivers, some 300 of which are from the Severn Trent region [4]. The eventual consequence of exceeding consent limits is colour surcharges of £0.60–0.80 per cubic metre [5]. The special equipment required to remove dyes from effluent is expensive and the alternative colour surcharge attracts bad publicity as well as increasing the cost of dyeing.

As early as 1926 it was demonstrated that tosylated cellulose treated with amines gave enhanced uptake of anionic dyes [6]. A variety of cellulose modifications was examined more recently in an attempt to improve existing reactive dyeing procedures [7],[8]. Any new procedure which efficiently and evenly attaches an amino residue to cellulose promises improvement to the dyeability of cellulose and is worthy of exploration. In this study, the novel thioester, nicotinoyl thioglycollate, was prepared and its reactivity with

cotton evaluated. The thioester, nicotinoyl thioglycollate, should react with cellulosate nucleophiles, sodium thioglycollate being the leaving group (Scheme 1).

EXPERIMENTAL

Materials

Fabric

Scoured and bleached, fluorescent brightener-free, woven cotton was used throughout the work.

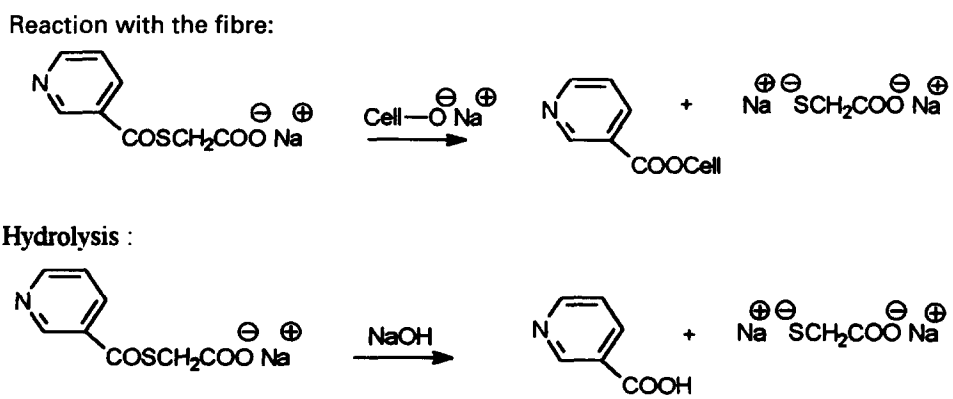
Chemicals

Thioglycollic acid was 97% material (Aldrich); nicotinoyl chloride hydrochloride was 98% material (Lancaster). All other chemicals were of laboratory reagent grade.

A commercial sample of the non-ionic surfactant Sandozin NIE (Clariant) was used for soaping-off procedures.

Dyes

All dyes were of commercial grade. The dye used in this study was Procion Red HE-3B, a bi-functional monochlorotriazine dye (Zeneca, C.I. Reactive Red 120). Other reactive dyes included Procion Blue MX-R, a dichlorotriazine dye (Zeneca, C.I. Reactive Blue 4) and Levafix Golden Yellow E-G, a dichloroquinoxaline dye (DyStar, C.I. Reactive Yellow 27). Non-reactive, anionic dyes included Acidol Brilliant Blue M 5GL (BASF, C.I. Acid Blue 163), Lanacron Olive SG (Ciba, C.I. Acid Green 73), Lanasyn Red S-NWJ (Clariant) and Acidol Green M-4GL (Ciba).



Scheme 1 Proposed NTG reaction with cotton in the presence of alkali.

Synthesis of nicotinoyl thioglycollate

The method developed by Barnes was used [9]. A solution of thioglycollic acid (5.0 ml, 7.4×10^{-2} mol) and water (5.0 ml) were stirred in a beaker immersed in an icebath until the temperature of the solution fell below 5°C. The solution was adjusted to pH 8.0 with 25% aq. sodium hydroxide. Nicotinoyl chloride hydrochloride (5.0 g, 2.9×10^{-2} mol) was added in eight portions and the reaction mixture was adjusted back to pH 8.0 after each addition with sodium carbonate. The reaction mixture was further stirred for 20 min.

Concentrated hydrochloric acid was then added to give a solution of pH 3.5 and a white precipitate of the zwitterion formed. This was filtered, washed with water (5×50 ml) and dried overnight to give an average crude product yield of 1.67 g (29%); reaction Scheme 2 is appropriate.

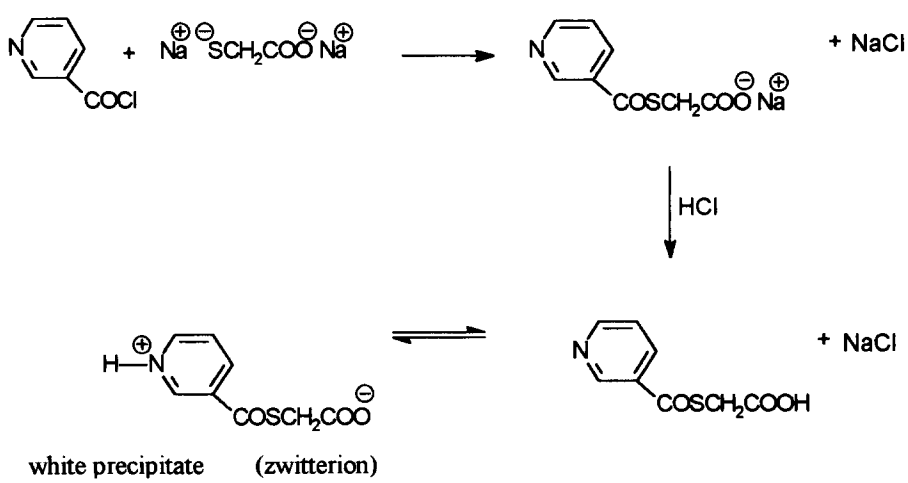
The solid was recrystallised from ethanol/water (50:50) and oven-dried overnight at 40°C.

The fine, white, powdery solid gave an average pure product yield of 1.29 g (23%) and a melting point of 181–182°C.

Microanalysis found: C, 48.8; H, 3.5; N, 7.0; S, 14.8%. $C_8H_7NSO_3$ requires: C, 48.7; H, 3.6; N, 7.1; S, 16.2%.

Infra-red analysis

FTIR analysis was carried out using the Perkin–Elmer 1740 Infra-red Fourier Transform spectrophotometer. Nicotinoyl thioglycollate was analysed in the



Scheme 2 Synthesis of nicotinoyl thioglycollate.

solid state by transmission through a KBr disc. The fabric samples were analysed by attenuated total internal reflectance using the thallium iodide composite crystal (KRS5).

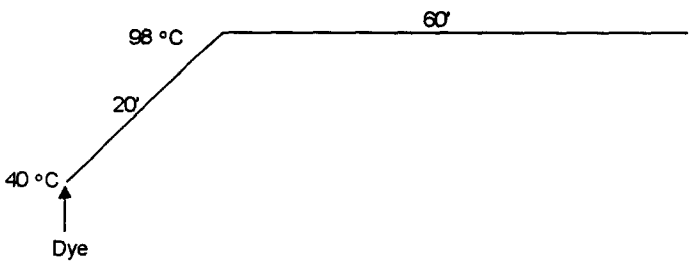
Application of NTG

Samples of cotton fabric were padded with an NTG solution (4% w/v) using the Ernst Benz pad mangle with the pressure set to give 85% wet pick-up. The samples were dried by passage through the Ernst Benz drier at 60°C for 3 min and then fixed by a thermosol treatment at 180°C for 60 s in a Werner Mathis AG baking unit. Finally, the modified cotton was rinsed thoroughly in warm water and left to dry overnight.

Dyeing procedures

All dyeings were carried out either in 300 ml sealed, stainless steel dyepots housed in a Zeltex Polycolor laboratory dyeing machine.

Dyeing procedure for NTG modified cotton
Dyeing (2% dye omf) was carried at a liquor ratio of 20:1. No addition of electrolyte was necessary.



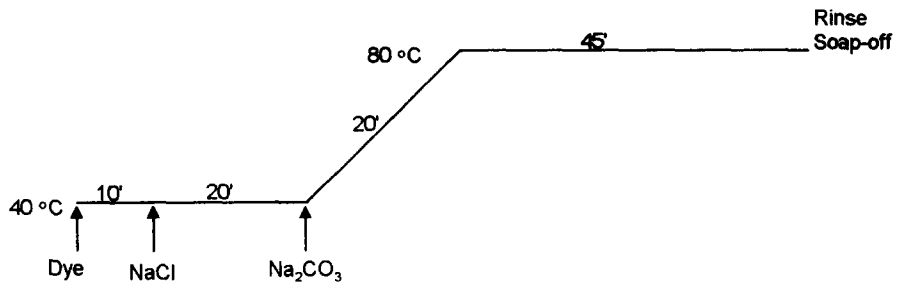
The dyed NTG fabric was rinsed in tap water and divided into two pieces. One of the fabric pieces was soaped-off at the boil in 2 g/l Sandozin NIE for 20 min and then thoroughly rinsed in tap water.

pH and temperature variables
Dyeings were carried out at 98°C with the dyebath set to pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.2. A citric acid/disodium hydrogen phosphate buffer system was used in each case, except the dyebath set to pH 9.2 which implemented a citric acid/sodium dihydrogen phosphate and sodium hydroxide buffer system.

Dyeings were carried out at 50 and 80°C with the dyebath set at pH 3.0, 4.0, 5.0 and 6.0. A citric acid/disodium hydrogen phosphate buffer system was used in each case.

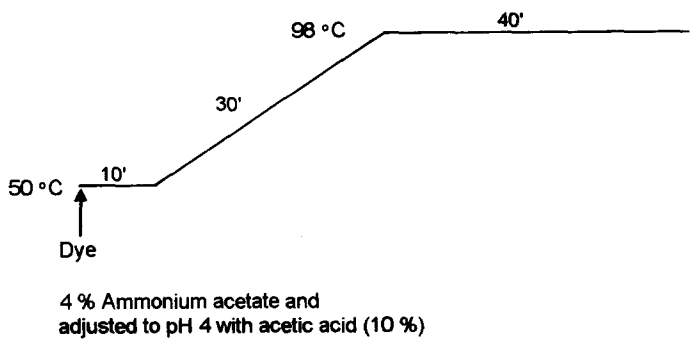
Dyeing procedures for untreated cotton

Procion Red HE-3B Dyeing (2% dye omf) was carried out at a liquor ratio of 20:1. The manufacturer's recommended dyeing procedure for Procion HE dyes was followed [10].



The dyed fabric was rinsed in tap water and divided into two pieces. One of the fabric pieces was soaped-off at the boil in 2 g/l Sandozin NIE for 20 min and then thoroughly rinsed in tap water.

Acidol Br. Blue M-5GL; Lanacron Olive SG; Lanasyn Red S-NWJ; Acidol Green M-4GL Cotton and wool fabric pieces were dyed (2% dye omf) at a liquor ratio of 50:1; the dyeing procedure was:



The dyed fabric samples were thoroughly rinsed in tap water

Determination of dye exhaustion and fixation

The optical densities of the dyebaths were measured at λ_{max} before and after the dyeing processes using a Kontron UV IKON 860 spectrophotometer.

Percentage exhaustion values (%E) of the dye on the fibre were calculated using eqn (1):

$$\%E = \frac{OD_1 - OD_2}{OD_1} \times 100 \tag{1}$$

where OD_1 and OD_2 are the optical densities of the dyebaths before and after the dyeing process, respectively.

The colour strength or colour yield of the dyed fabrics was determined by measuring the reflectance values (400–700 nm) and then calculating the Kubelka Munk K/S value at the highest absorption wavelength for each of the dyed samples. The degree of fixation of absorbed dye (%F) was calculated according to eqn (2):

$$\%F = \frac{(K/S)_2}{(K/S)_1} \times 100 \tag{2}$$

where $(K/S)_1$ is the colour yield of the dyeings before the soaping-off process and $(K/S)_2$ is the colour yield measured after soaping at the boil.

The total amount of original dye applied which is fixed (%T) was calculated according to eqn (3):

$$\%T = \frac{(K/S)_2}{(K/S)_1} \times \%E \tag{3}$$

Determination of NTG fixation on cotton according to time and temperature of thermosol treatment

The NTG cotton fabric was cut into 1 g pieces and baked in a Werner Mathis AG baker unit at 110, 150, 180, 200 and 220°C for 20, 40, 60, 90 and 120 s.

Each treated piece of fabric was shaken in warm, distilled, deionised water (50 cm^3) at 50°C for 1 min and the solution decanted; any excess liquor held in the samples was squeezed back into the extraction solution. The procedure was repeated a total of four times and the extraction solutions combined, allowed to cool and made up to 250 ml in a volumetric flask. The extracted fabric pieces were dried overnight in the open air and then weighed.

The UV absorption values of the extraction solutions were determined using a Kontron UV IKON 860 spectrophotometer at 270 nm (λ_{max} of nicotinoyl thioglycollate).

The percentage fixation (%F) of NTG on the cotton fabric was calculated using eqn (4):

$$\%F = \frac{OD_0 - OD_t}{OD_0} \times 100 \quad (4)$$

where OD_t and OD_0 are the optical densities of extraction solutions per gram mass of extracted NTG impregnated fabric samples, thermosolled and non-thermosolled, respectively.

Fastness testing

The fastness of the dyed samples to the ISO 3 wash test and the ISO B02 light test were determined using the standard methods [11].

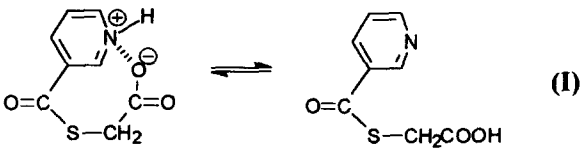
RESULTS AND DISCUSSION

Infra-red analysis of nicotinoyl thioglycollate and analogous compounds

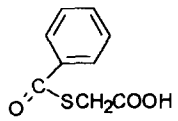
Figure 1 shows the FTIR spectrum of nicotinoyl thioglycollate (**I**). The strong peak at 1718 cm^{-1} indicates the presence of free carboxylic acid and the two peaks at 1595 and 1411 cm^{-1} indicate the presence of carboxylate groups. The strong peak at 1669 cm^{-1} is due to a thioester group. Differentiation between the groups was possible by comparing with published FTIR spectra of benzoyl thioglycollic acid (**II**) and sodium benzoyl thioglycollate (**III**) [12]. The FTIR spectrum of benzoyl thioglycollic acid (**II**) reveals a strong peak at 1710 cm^{-1} due to the free carboxylic acid groups, which is absent in the spectrum of sodium benzoyl thioglycollate but is replaced by two peaks at 1590 and 1400 cm^{-1} due to the ionised carboxylate. Both compounds **II** and **III** contain thioester groups, as strong peaks at 1665 cm^{-1} are detected.

Infra-red study of NTG modified cotton

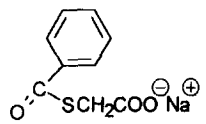
NTG solution (4% w/v) was applied to cotton by a pad–dry–thermosol procedure at various pad–liquor pH values. The presence of ester groups in the modified cotton was confirmed with the aid of FTIR. The attenuated total internal reflectance (ATR) technique was used; ATR is suitable for materials which contain strong absorbing groups. A pressure device which presses the fabric sample against the KRS5 crystal was used to give reproducible fibre–crystal contact. Care was taken to ensure the fabric sample covered the entire area of the crystal. The FTIR spectrum of unmodified cotton was subtracted from that of NTG treated cotton using Information Release Data Manager (IRDM) computer software from Perkin–Elmer.



(I)



(II)



(III)

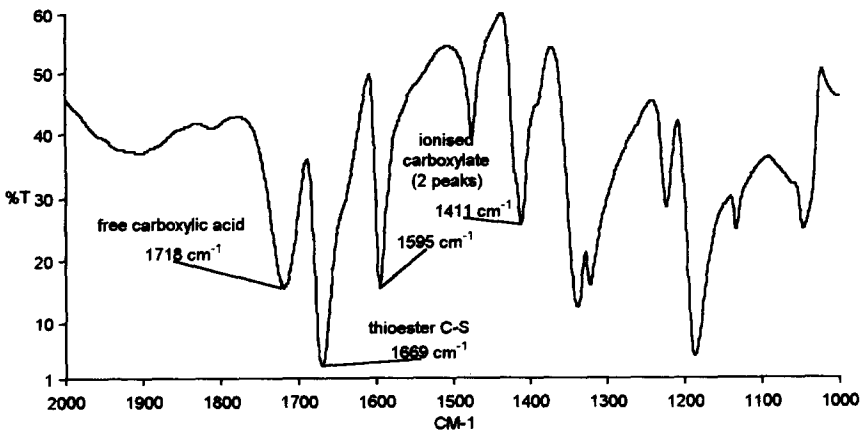


Fig. 1. FTIR spectrum of nicotinoyl thioglycollate (**I**).

Figure 2 shows the FTIR subtraction spectra of NTG cotton prepared at pH 7.4, 7.9, 9.5, 10.1 and 10.4, respectively. Peaks due to nicotinoyl–cellulose ester were observed at 1718 and 1284 cm^{-1}.

Peak 1. C=O stretching vibrations 1718 cm^{-1} (s).

Peak 2. C–O stretching vibrations 1284 cm^{-1} (s).

By relating the area of the ester peaks to the amount of NTG fixed on the cotton, the spectra provided a means of estimating NTG fixation on cotton. The IRDM software allowed manipulation of infra-red spectral data; the data command "Area" calculated the area of peaks 1 and 2 between specified wavenumbers. Peak area was used as a quantitative measure of ester concentration (Table 1).

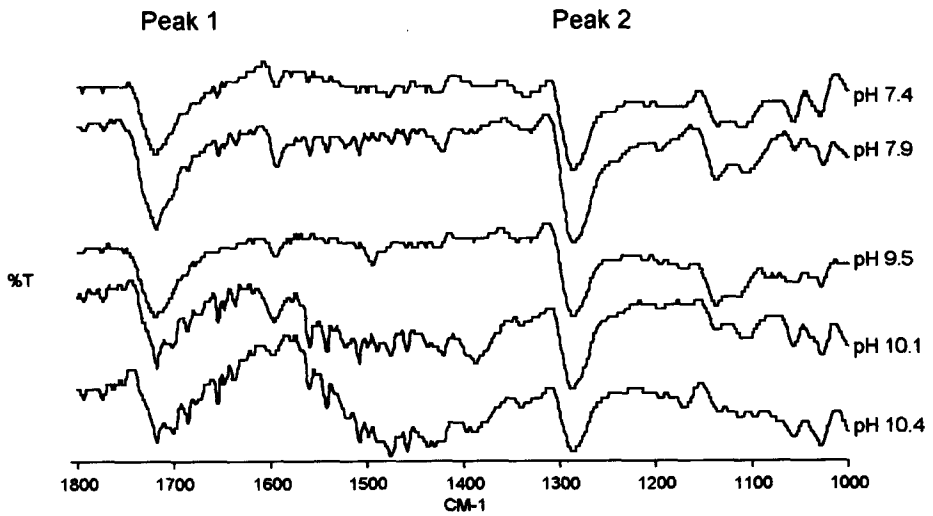


Fig. 2. FTIR spectra obtained by subtracting the spectrum of unmodified cotton from the spectra of NTG cotton, pretreated at various pH values (7.4–10.4).

TABLE 1
Peak Area Relating to the Ester Group in NTG Modified Cotton

NTG cotton spectra	*Area of peak 1 (1718 cm^{-1})*	*Area of peak 2 (1284 cm^{-1})*
pH 7.4	2.34	2.22
pH 7.9	4.85	3.93
pH 9.5	2.38	1.63
pH 10.1	1.88	1.46
pH 10.4	1.60	0.76

The greatest peak area and hence the highest NTG fixation was seen for the NTG pad liquor set at pH 7.9. NTG applications at higher pH values resulted in a reduction in NTG fixation. Hydrolysis of NTG was probably responsible for diminished NTG fixation at these higher pH values. Thus pH 8.0 was adopted as the optimum pH value for NTG application.

Effect of thermosol time and temperature on NTG fixation

Experiments were carried out at temperatures of 110, 150, 180, 200 and 220°C for thermosol times of 20, 40, 60, 90 and 120 s on cotton pretreated with NTG solution (4% w/v), pH 8.0.

The results are as shown in Fig. 3.

Figure 3 shows that the NTG fixation increases with increasing thermosol time, but after 90 s at 200°C and after 60 s at 220°C, the fixation slightly

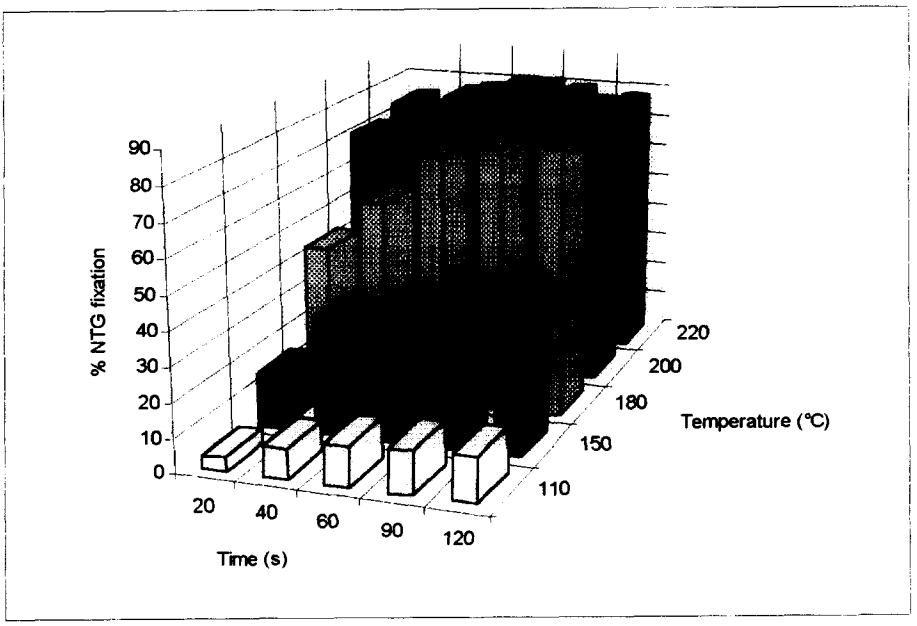


Fig. 3. 3D column chart showing the effect of thermosol time and temperature on NTG fixation (pH 8.0).

decreases. NTG fixation increases with increasing thermosol temperature, but fixation decreases at 200°C if thermosol times are 60 s or longer. The optimum combination of thermosol time and temperature is 90 s at 200°C.

The possibility of applying NTG to cotton by a pad–batch method at pH 8.0 was investigated. The NTG fixation after 24 h batching at room temperature was found to be 1%. Thus, pad–batch at this pH value is an unsatisfactory method to fix NTG to cotton.

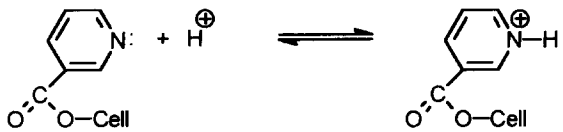
The effect of dyebath pH on colour yield and fixation

The mechanism for the reactive dyeing of NTG modified cotton in the absence of salt depends on two separate phenomena.

Exhaustion of reactive dye onto the modified cotton

Substantivity of the dye for the modified cotton is achieved by the presence of protonated tertiary amine attached via an ester bond to the cellulose. The pK_a value at 20°C for a nicotinic acid ester is 4.6; thus at 20°C and pH 4.6, 50% of the nicotinic acid ester is dissociated and 50% is in the unreactive, protonated form; as the temperature is raised dissociation also increases and thus the pK_a value is lowered. On raising to the boil, the extent to which the

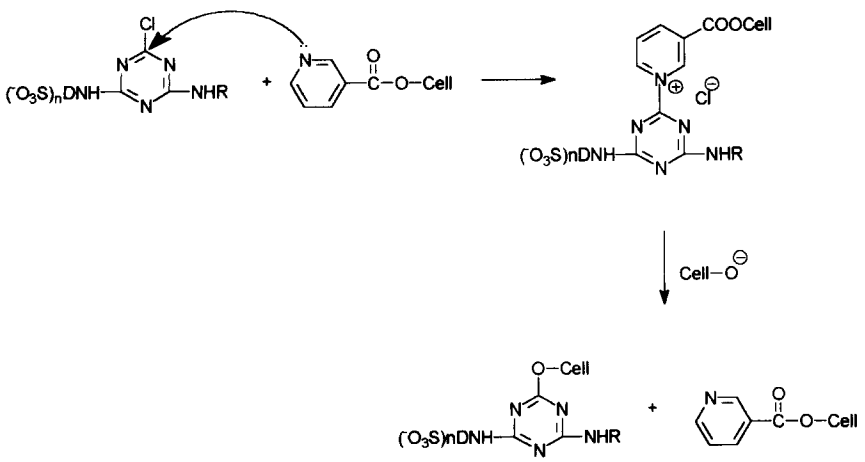
pK_a is lowered is uncertain, but analogy with other amines indicates a change of 1–2 pK_a units might be expected (Scheme 3).



Scheme 3 Ionic equilibrium for the bonded nicotinoyl ester of cellulose.

Covalent bonding

Even at pH 3.0, a significant number of tertiary amine groups are deprotonated and available for quaternization with MCT dyes. Under neutral or alkaline conditions this quaternized triazine is capable of further reaction with cellulosate anions. These reactions are shown in Scheme 4.



Scheme 4 Reaction of NTG treated cotton with MCT dye.

The NTG cotton was dyed at the boil with C.I. Reactive Red 120 (2% omf), varying the dyebath pH in the range 3.0–9.2. The results are shown in Table 2. All samples were 'soaped' at the boil after dyeing to determine the extent of covalent fixation.

Table 2 indicates that optimum dye uptake and fixation of the bi-functional MCT dye occurs at pH 3.0, since at this pH value the modified fibre is sufficiently protonated to provide good substantivity towards the anionic dye and yet covalent bonding is still possible, presumably through the unprotonated tertiary amine.

TABLE 2
Percentage Exhaustion (%*E*), Percentage Fixation of Absorbed Dye (%*F*) and Percentage Total Dye Fixed (%*T*) for Dyeings of C.I. Reactive Red 120 on the Modified Cotton at Various Dyebath pH Values

pH of dyebath	*%E*	*%F*	*%T*
3.0	87	75	65
4.0	47	68	32
5.0	36	69	25
6.0	21	68	14
7.0	15	64	10
8.0	12	55	7
9.2	12	51	6

The pH was not lowered below 3.0, as very acidic dyebaths at the boil are likely to cause adverse effects on the cellulose structure. Fixation values are significantly reduced when dyeing at pH 8.0 and above, probably due to hydrolysis of the ester bond linking the tertiary amine in the fibre and/or rapid hydrolysis of the quaternized triazinyl dye.

Comparison of the novel C.I. Reactive Red 120 dyeing method on NTG modified cotton with that of a conventional dyeing of C.I. Reactive Red 120 on untreated cotton

The modified cotton was dyed with C.I. Reactive Red 120 (2% omf) in a dyebath containing no electrolyte and buffered to pH 3.0. The dyeing was carried out at the boil for 1 h. The untreated cotton was dyed with C.I. Reactive Red 120 (2% omf) by the conventional dyeing method described by Zeneca for HE reactive dyes. Results are given in Tables 3 and 4.

The fixation, exhaustion and colour yield values for the novel dyeing method are similar to the values for the conventional dyeing. Dyeings on the modified cotton by the novel 'no salt' method gave higher colour yields than

TABLE 3
Comparison of Colour Yield (*K*/*S*), Percentage Exhaustion (%*E*), Percentage Fixation of Absorbed Dye (%*F*) and Percentage Total Dye Fixed (%*T*) for the Conventional and Novel Dyeing Methods with C.I. Reactive Red 120

Dyed sample	*Colour yield (K/S)*		*%E*	*%F*	*%T*
	Before soaping	*After soaping*			
Untreated cotton (conventional dyeing)	12.14	9.92	90	82	74
Modified cotton (novel dyeing)	16.26	12.18	87	75	65

TABLE 4
Results from ISO 3 Wash Fastness Tests on Conventional and Novel Dyeings with C.I. Reactive Red 120

Dyed sample	*Change in colour*	*Staining*	
		On cotton	*On wool*
Untreated cotton (conventional dyeing)	4/5	4/5	4/5
Modified cotton (novel dyeing)	4	3/4	4/5

the conventional method on untreated cotton, even though dyebath exhaustion values were similar; this indicates that in the former case more surface dyeing and fixation had occurred.

Wash fastness properties are slightly better for the conventional dyeing. Light fastness testing revealed the same fastness for novel and conventional dyeings.

The stability of the ester bond on cotton

The ester bond stability of the modified cotton was investigated by FTIR–ATR analysis of:

(i) NTG cotton dyed at the boil with C.I. Reactive Red 120 (2% omf), soaped-off and subjected to alkaline conditions, 5 g/l sodium carbonate at the boil for 20 min;

(ii) NTG cotton dyed with C.I. Reactive Red 120 (2% omf) and soaped-off;

(iii) NTG undyed cotton.

Difference spectra were obtained by subtracting the unmodified cotton spectrum from the spectra of (i), (ii) and (iii), and are reproduced in Fig. 4.

Clearly the ester peaks (1718 and 1284 cm^{-1}) are most intense in samples (iii) and (ii), but are absent in the alkali soaped sample (i).

Alkaline hydrolysis was responsible for the loss of the ester bond, but did not drastically affect the colour strength of the dyeing. It is therefore postulated that the quaternized triazine proposed in Scheme 4 is attacked by cellulosate nucleophiles, the tertiary amine behaves as a leaving group and a 'normal' dye–fibre bond is formed (reaction Scheme 4).

Effect of dyeing temperature

Experiments were carried out dyeing the NTG treated cotton with C.I. Reactive Red 120 (2% omf) and raising the temperature of the dyebath from 40 to 50°C (0.5°C/min) and 40 to 80°C (2°C/min). Dyeing was continued at 50 and 80°C for 1 h. Dyebaths were buffered to pH 3.0, 4.0, 5.0 and 6.0. The results are shown in Table 5.

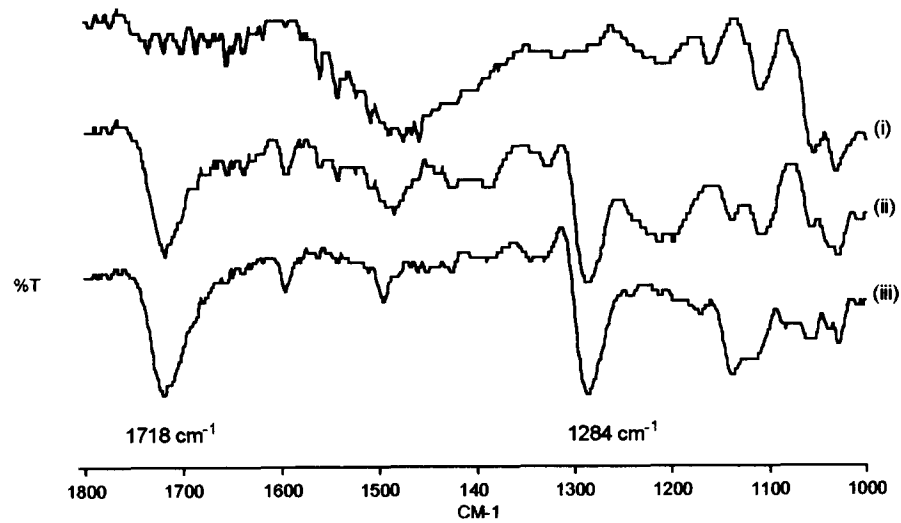


Fig. 4. FTIR spectra obtained by subtracting a spectrum of unmodified cotton from the spectra of NTG pretreated and soaped samples.

TABLE 5

Percentage Exhaustion (%*E*), Percentage Fixation of Absorbed Dye (%*F*) and Percentage Total Dye Fixed (%*T*) for Dyeings of C.I. Reactive Red 120 on the Modified Cotton at Various Dyebath Temperatures and pH Values

Dyeing temperature	*pH of dyebath*	*%E*	*%F*	*%T*
100°C	3.0	87	75	65
	4.0	47	68	32
	5.0	36	69	25
	6.0	21	68	14
80°C	3.0	86	86	74
	4.0	58	89	52
	5.0	40	79	32
	6.0	27	71	19
50°C	3.0	84	48	40
	4.0	55	46	25
	5.0	46	49	23
	6.0	38	46	17

Dyeing temperature combined with pH have an effect on exhaustion and fixation. When the pH is increased above pH 3.0 at 100°C, dyebath exhaustion rapidly decreases. This reduction in exhaustion with increasing pH is less dramatic at 80°C, and even more gradual at 50°C. It may be concluded that dye fixation is maximised by dyeing at 80°C, and significantly reduced by dyeing at 50°C.

TABLE 6

Percentage Exhaustion (%*E*), Percentage Fixation of Absorbed Dye (%*F*) and Percentage Total Dye Fixed (%*T*) for Dyeings of Higher Reactive Dyes on the Modified Cotton and Untreated Cotton (Dyebaths at pH 3.0)

Reactive dye	*Dyeing substrate*	*%E*	*%F*	*%T*
C.I. Reactive Blue 4	Modified cotton (dyebath 60°C)	96	53	51
	Modified cotton (dyebath 100°C)	95	22	21
C.I. Reactive Yellow 27	Modified cotton (dyebath 80°C)	94	15	14
	Modified cotton (dyebath 100°C)	95	21	20

TABLE 7

Colour Yield (*K*/*S*) for Selected Non-reactive, Anionic Dyes on the Modified Cotton, Untreated Cotton and Wool

Acid dye	*Dyeing substrate*	*Colour yield (K/S)*
Acid Blue 185	Modified cotton	20.80
	Untreated cotton	4.42
	Untreated wool	17.53
Acid Green 73	Modified cotton	15.14
	Untreated cotton	2.22
	Untreated wool	25.3
Lanasyn Red S-NWJ	Modified cotton	9.44
	Untreated cotton	1.59
	Untreated wool	18.24
Acidol Green M-4GL	Modified cotton	3.23
	Untreated cotton	0.51
	Untreated wool	17.53

TABLE 8

Results from ISO 3 Wash Fastness Testing of Dyeings on Modified Cotton

NTG cotton dyed	*Change in colour*	*Staining*	
		On cotton	*On wool*
C.I. Reactive Blue 4 (dyebath at 60°C)	3	3/4	4/5
C.I. Reactive Blue 4 (dyebath at 100°C)	3	4	4/5
C.I. Reactive Yellow 27 (dyebath at 80°C)	3/4	4	4/5
C.I. Reactive Yellow 27 (dyebath at 100°C)	3/4	4	4/5
C.I. Acid Blue 185	3	2	4
C.I. Acid Green 73	3	4/5	4
Lanasyn Red S-NWJ	2/3	4	3
Acidol Green M-4GL	2	3	3

It is apparent that by dyeing at 80°C and at pH 3.0, good exhaustion and fixation are achievable. Slight upward fluctuations in dyebath pH during dyeing must be avoided, otherwise the dyebath exhaustion and total dye fixed are adversely affected.

Dyeing NTG modified cotton with higher reactivity reactive dyes and non-reactive, anionic dyes for wool

C.I. Reactive Blue 4, a dichlorotriazine (DCT) reactive dye and C.I. Reactive Yellow 27, a dichloroquinoxaline reactive dye, both possess higher reactivity than C.I. Reactive Red 120. NTG pretreated cotton was dyed with C.I. Reactive Blue 4 (2% omf) and C.I. Reactive Yellow 27 (2% omf), at pH 3.0 for 1 h at the boil, as well as at 60°C for C.I. Reactive Blue 4 and 80°C for C.I. Reactive Yellow 27.

The modified cotton should be dyeable under acid conditions with anionic, premetallised dyes, as the fibre has essentially been chemically modified to contain amino residues, thus creating a fibre analogous to wool. NTG pretreated cotton was dyed (2% omf) with a selection of premetallised dyes at pH 3.0 for 1 h at the boil. In addition, untreated cotton and wool were dyed (2% omf) according to a typical dyeing method for 2:1 premetallised dyes on wool (Table 6).

The higher reactivity reactive dyes gave excellent exhaustion (approximately 95% in each case). However, once the dyed fabric was soaped, large amounts of unfixed dye were stripped off.

The asymmetrical monosulphonated 2:1 metal complex dyes, C.I. Acid Green 73 and Lanasyn Red S-NWJ, showed good colour strength on the modified cotton, but Acidol Green M-4GL, a symmetrical disulphonated 2:1 metal complex dye, did not perform as well. The best results were obtained with C.I. Acid Blue 185, a trisulphonated copper phthalocyanine dye. The colour yields of the non-reactive, anionic dyes on NTG cotton were lower than on wool, but much greater than on untreated cotton (Table 7). Wet fastness properties were, however, poor (Table 8).

CONCLUSIONS

Nicotinoyl thioglycollate reacts with cotton to form the nicotinoyl–cellulose ester at pH 8.0 by a pad–thermosol–rinse procedure. Optimum fixation conditions are 90 s at 200°C. NTG modified cotton is dyeable with C.I. Reactive Red 120 (a low reactivity MCT dye) in the absence of electrolyte. The dyebath should be adjusted to pH 3.0 and dyeing carried out at 80°C for 1 h.

Dyeing the nicotinoyl–cellulose ester with MCT dyes is successful at pH 3.0 at 80°C because the tertiary amino group is significantly protonated under these conditions; uptake of the anionic reactive dye is thus favoured initially by ionic interactions, but these are reinforced by reaction of the MCT dye with unprotonated nucleophilic, tertiary amine sites. It is thus proposed that, at pH 3.0, the dye is present mainly as a quaternized triazine dye, but on soaping ($pH \geq 7$) or alkaline washing, the quaternized triazine dye reacts readily with cellulosate anions to give the conventional dye–fibre bond.

The novel dyeings with C.I. Reactive Red 120 dyes were found to be bright, level and of good wash fastness. They possess similar light fastness to the conventional reactive dyeings.

Dyeing with higher reactivity reactive dyes was not so successful, probably due to the instability of the quaternized dyes. Selected non-reactive, anionic dyes showed some promise, although the wash fastness properties of the dyeings were disappointing.

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