THE REACTIVE DYEING
OF
CELLULOSIC FIBRES

by

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for the Degree of Doctor of Philosophy

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PREFACE

The present study is mainly directed at achieving high fixation efficiency of reactive dyes on cotton in order to solve the remaining problems with the use of this type of dyes, e.g. the necessity of using expensive and time-consuming wash off procedure and of using high concentration of electrolyte to exhaust the dyebath.

A number of ways to modify cotton have been sought to achieve the above objectives. Modification of cotton with a polyamide epichlorohydrin (PAE) resin and its derivatives was extensively studied; three simple pretreatment methods have been proposed and mechanistic implications are also discussed.

Light fastness of the dyeings produced on cotton modified with polymeric compounds was compared to that achieved on cotton modified with low molecular weight compounds. It is concluded that reduction of light fastness of reactive dyeings always occurs on the former polymer modified substrate whilst there is no such problem with the dyeings on the latter substrate.

Modification of cotton with a specially synthesized low molecular weight compound, 1,1-dimethyl-3-hydroxyl-1-azetidinium chloride (DMAC), and a commercially available compound, Glytac A, were carried out and the dyeability of the subsequent substrate was studied. The practical importance of these methods and the mechanism of covalent bond formation when using reactive dyes on these substrate are discussed.

A systematic study of introducing different amino groups into cotton via reaction of cotton with N-methylol acrylamide followed by amination with different amines was undertaken and the dyeing behaviour of reactive dyes on the substrate produced was evaluated.

An unusual reaction was observed when further treating cotton which had been pre-esterified with chloropropionyl chloride (CPC) in an aqueous solution of amines. Amination under severe conditions led to substrates which are dyeable with reactive dyes with good fastness properties but amination under much milder conditions produced substrates which gave the subsequent dyeings of poor wash fastness.

A method to determine the chlorine content in CPC cotton by ion-exchange chromatography is discussed.

An alternative way to achieve dye-fibre covalent bonding was proposed: cotton was activated first and then dyed with alkyl-amino dyes. The ways of cotton activation, the methods to prepare alkyl-amino dyes and activation agents are discussed. This approach not only imparts high efficiency to the fibre-dye reaction but also avoids the problem of dye hydrolysis.

The present study has thus far produced six papers which have been published during the course of this project. The Journal names and the other details about the publications were given as follows:

[1] S.M. Burkinshaw, X.P. Lei and D.M. Lewis, J.S.D.C., 105(1989) 391-398.

[2] D.M. Lewis and X.P. Lei, Text. Chem. and Col., 21(1989) 23-29.

[3] S.M. Burkinshaw, X.P. Lei, D.M. Lewis, J.R. Easten, B. Parton and D.A.S. Phillips, J.S.D.C., 106(1990) 307-315.

[4] X.P. Lei and D.M. Lewis, J.S.D.C., 106(1990)352-356.

[5] D.M. Lewis and X.P. Lei, J.S.D.C., 107(1991)102-109.

[6] X.P. Lei and D.M. Lewis, Dyes and Pigments, in press.

To my mother.....

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CHAPTER I

I INTRODUCTION

1.1 Chemistry of Cellulose

1.1.1 Sources of cellulose

Cellulose is the most abundant of all naturally occurring organic polymers. Since it constitutes the main structural material of land plants, thousands of millions of tonnes are produced by photosynthesis throughout the world every year [1]. Recent reports based on spectroscopic evidence even suggest that cellulose exists in interstellar space [2]. In addition, the possibility that industrial cellulose may be produced by bacteria instead of by plants is now real, although still somewhat remote [3]. With the development of scientific research, more new sources of cellulose may be found before long [4]. For the time being, however, the main sources of cellulose for industry are still the traditional vegetable ones. Table 1.1.1 shows the cellulose content of some plant materials [5,6].

Table 1-1-1 cellulose content of plant materials

plant materials	cellulose (%)
Cotton	95-99
Ramie	80-90
Flax	82 (*)
Jute	65-75 (*)
Wood	45-50
Bark	20-30
Mosses	25-30
Bacteria	20-30

(*) these data are from reference [5].

The non-cellulosic matter in raw cotton consists mainly of wax (0.35-0.42%), pectic matter (0.53-0.68%) and mineral matter (0.12-0.25%)

[7]. The nitrogenous matter in cotton is very small, its quantity depending on the type of cotton and its origin[8], e.g. Egyptian cotton has an average nitrogen content of 0.3%, compared with 0.2% for American cotton.

1.1.2 Molecular structure of cellulose

The chemical structure of cellulose may most conveniently be described as a 1,4-ß-D-glucan, i.e. a condensation polymer of ß-D-glucopyranose with 1,4-glycosidic bonds.

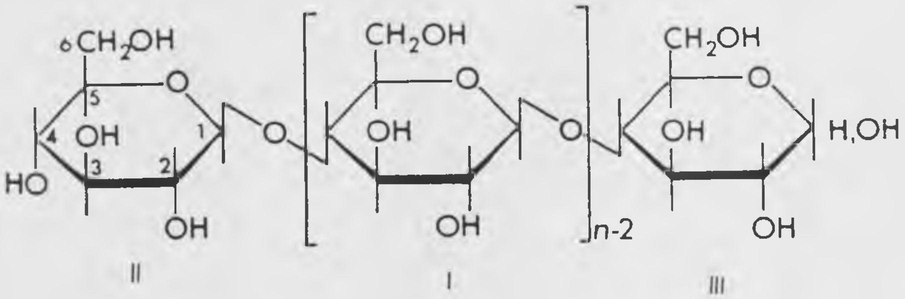
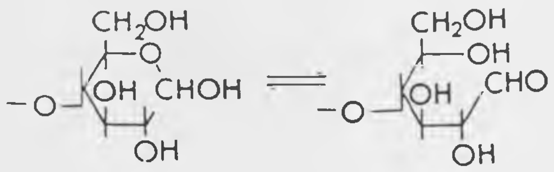


Figure 1-1-1

The essential features of the polymer chain are the main sequence of intermediate units(I), the non-reducing end group(II), the reducing end group(III) and the glycosidic linkages. The intermediate chain units possess one primary and two secondary alcohol groups each. The reducing end group (capable of reducing Fehling's solution or ammoniacal silver nitrate) is a cyclic hemiacetal which exhibits the characteristics of both an alcohol and an aldehyde under appropriate conditions(Scheme 1-1-1).



Scheme 1-1-1

Noteworthy contributions to the establishment of the above cellulose structure have been made by the following workers:

i) Irvine and Hirst [9] prepared cellulose triacetate in more than 99% yield from cotton, which they then subjected to methanolysis. This yielded an equilibrium mixture of α- and β-methylglucosides with the proper optical rotation and melting point range. The mixture accounted for 95.5% of cellulose after the weight of the latter was corrected for moisture and ash. The furfural test for pentosans was negative and compounds other than methyl glucoside were not detected. This work was generally accepted as decisive proof that pure cellulose consisted exclusively of glucose residues.

ii) On subjecting cellulose to a methylation mixture of dimethylsulphate in sodium hydroxide, Howorth et al. [10] found that methylated cellulose could be produced, in which the methoxyl groups comprised about 45% of the total content. Further exhaustive methylation could not improve on this methoxy group yield. This indicated that the maximum degree of hydroxyl group methylation was three since the theoretical methoxyl content is 45.6% assuming there are three hydroxyl groups per ß-D-glucopyranose unit. In conjunction with the fact that the highest degree of cellulose substitution of obtained by acetylation and nitration is also three, this demonstrates that cellulose contains an average of three hydroxyl groups per glucosidic residue.

iii) Using studies of osazone formation, Denham and Woodhouse [11] showed that the C2 position in the hydrolysate of trimethylcellulose, i.e. trimethylglucose, must be blocked by a methoxyl group. Ruff and Ollendorff [12] used methylated lactose to demonstrate that on hydrolysis. one of the products had methoxyl groups in the second and third position. Following this, Irvine and Hirst [13] had no difficulty in deducing that the other methoxyl group had occupied the terminal or sixth position and consequently, the methylated glucose was the 2,3,6-isomer.

iv) Skraup and König [14] showed cellobiose octaacetate to be resistant towards yeast maltase. Since yeast maltase readily hydrolyses the ß-linkage in maltase, the above fact indicated that the disaccharide linkage in cellobiose must be of a ß-configuration. If methylation of cellobiose is carried out to yield the heptamethyl derivative which is subsquently hydrolysed, equimolar amounts of 2,3,4,6-tetramethylglucose and 2,3,6-trimethylglucose are produced. This demonstrates that the linkage in cellobiose must be either (1⟶4) or (1⟶5). Confirmation that the linkage was (1⟶4) and that cellobiose was in fact 4-O-ß-D-glucopyranose-ß-D-glucose, was obtained from studies of the hydrolysis products of methylated cellobionic acid [15].

1.1.3 Degree of polymerisation of cellulose

The degree of polymerisation of cellulose (DP) varies with its source, and is usually expressed as an average number of anhydroglucose units per chain molecule, since a wide distribution is always found in any particular sample. In unpurified native cellulose it may well exceed 10000 [16], but purification involving treatment with alkali usually reduce this to about 1000-2000. Furthermore the hemiacetal end groups are converted to carboxylic acid groups. Thus purified native cellulose is usually lacking in reducing power. Regenerated celluloses have DPs of about 250-300 and may contain small numbers of aldehyde, ketone and carboxylic acid groups, introduced during manufacture. Chemically they are nearly identical with native cellulose and differences between the two types arise mainly in their supramolocular structure. Polynosic fibres have higher DPs (about 500-700) than other forms of regenerated cellulose.

1.1.4 Supramolecular structure of cellulose

Cellulose is a highly crystalline material and, in its native form, consists of crystalline fibrils of varying degrees of complexity and of indeterminate length. These fibrils are constituted in the fibre in such a way that they may be interspersed with material in which the chain molecules are less well ordered than in a crystal. The same molecular chain may occur in crystalline and non-crystalline parts of a fibre, along different portions of its length.

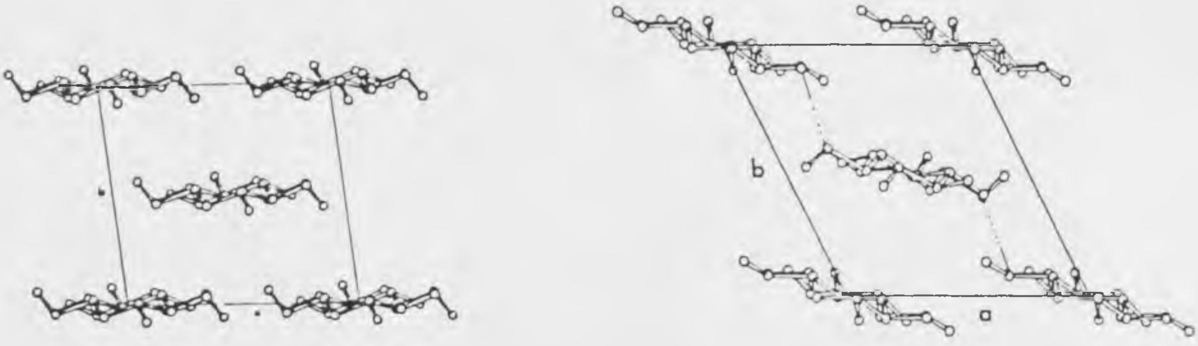
Cellulose exists in at least five polymorphic forms[17]. As far as the present work is concerned, cellulose I and cellulose II are the most important and will be discussed here. Cellulose I is the form found in nature and cellulose II (namely 'hydrate cellulose') is the thermodynamically stable form produced when cellulose is regenerated from solution or is subjected in the solid state to the process of mercerisation. Table 1-1-2 shows some important parameters of the unit cell of these two kinds of celluloses.

Table 1-1-2 Important parameters of the unit cell

parameters	cellulose I	cellulose II
crystal type	monoclinic	monoclinic
average dimension:		
a	0.82	0.81
b	0.79	0.91
c(fibre axis)	1.035	1.035
γ	97°	117°

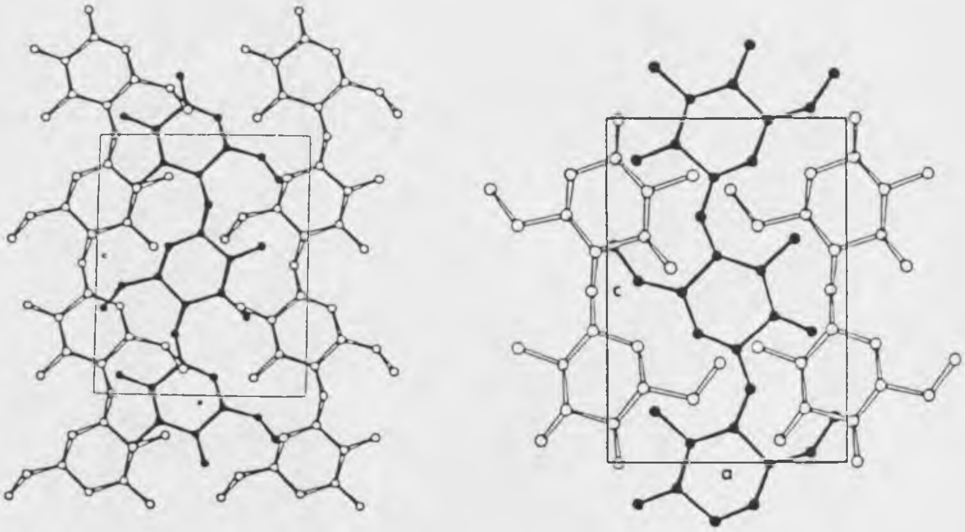
Figure 1-1-2(a) shows the cross-section of the cells of cellulose I in the *ab* plane(looking along the fibre axis). The 'centre' and 'corner' chains are parallel to one another with the centre chains staggered by approximately 0.25c(0.26 nm) with respect to the corner chains (Figure 1-1-3(a)). Adjacent chains are held together in a system of hydrogen-bonded sheets in the *ac* planes as shown in Figure 1-1-4, alternate sheets being staggered with respect to each other in accordance with the arrangement indicated in Figure 1-1-3(a); thus there are two interpenetrating sets of sheets, one comprising the corner chains and the other the centre chains. Since the surfaces of the rings are hydrophobic, the sheets of chains are held together in that direction by Van der Waals forces [18].

The cross-section of the unit cell of cellulose II in the *ab* plane is shown in Figure 1-1-2(b). The chain arrangement differs from that in cellulose I in three respects. One is that the planes of the glucose rings are inclined at a small angle to the *ac* plane, another is that the centre chains are oriented antiparallel to the corner chains and still staggered with respect to the corner chain in the *c* direction, in the same way as in cellulose I (Figure 1-1-3(b)). Hydrogen-bonding systems are also different in the case of cellulose II; not only are there hydrogen bonds in the *ac* planes between parallel corner chains and between parallel centre chains but there are also hydrogen bonds between antiparallel corner and centre chains [18].



(a) (b)

Figure 1-1-2. Unit cell of (a) cellulose I and (b) cellulose II, looking along the fibre axis



(a) (b)

Figure 1-1-3. (a) parallel-chain model of cellulose I perpendicular to the ac plane (b) antiparallel-chain model of cellulose II perpendicular to the ac plane [17]

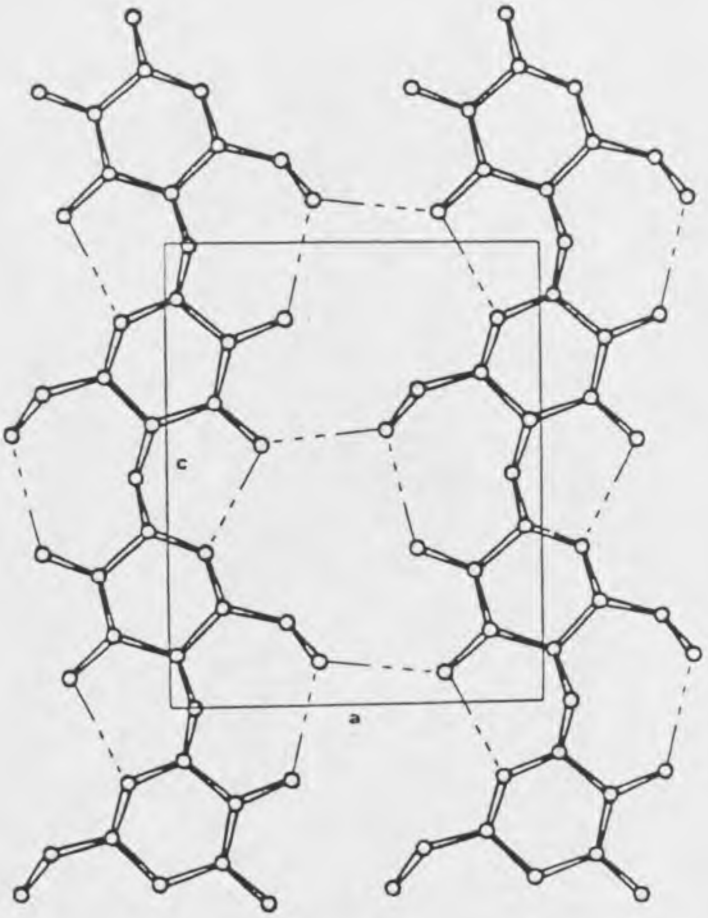


Figure 1-1-4. Hydrogen bonding network in cellulose I [17]

The basic structural entities beyond the unit cell are the elementary fibril and the microfibril. The reported dimensions for these basic units varies considerably. Warwicker et al. [19] summarized the measurements reported up to 1966 and most recent measurements have simply served to more or less confirm these previous size estimates [20,21]. It appears that the elementary fibril is about 3.5 nm (2-6 nm) wide. Larger microfibrils are either continuous structures or aggregations of elementary fibrils with dimensions ranging up to 3.5-10 nm thick and 10-30 nm wide depending on the source of cellulose. There can also be interfibrillar spaces of width 1.2-5 nm with water present in the wet state and of about 1 nm in the dry [22].

Cotton may be regarded as being composed of structural units termed fibrils, which are essentially crystalline and built up from the close association of a number of identical unit cells of cellulose I (native cotton) [1,3]. The crystalline regions form the bulk of the fibrils, the disordered regions being confined to the surface of the fibrils and to very short regions along their length. Accessibility and reactivity [23] are therefore explained by a system of voids bounded by fibrillar surfaces.

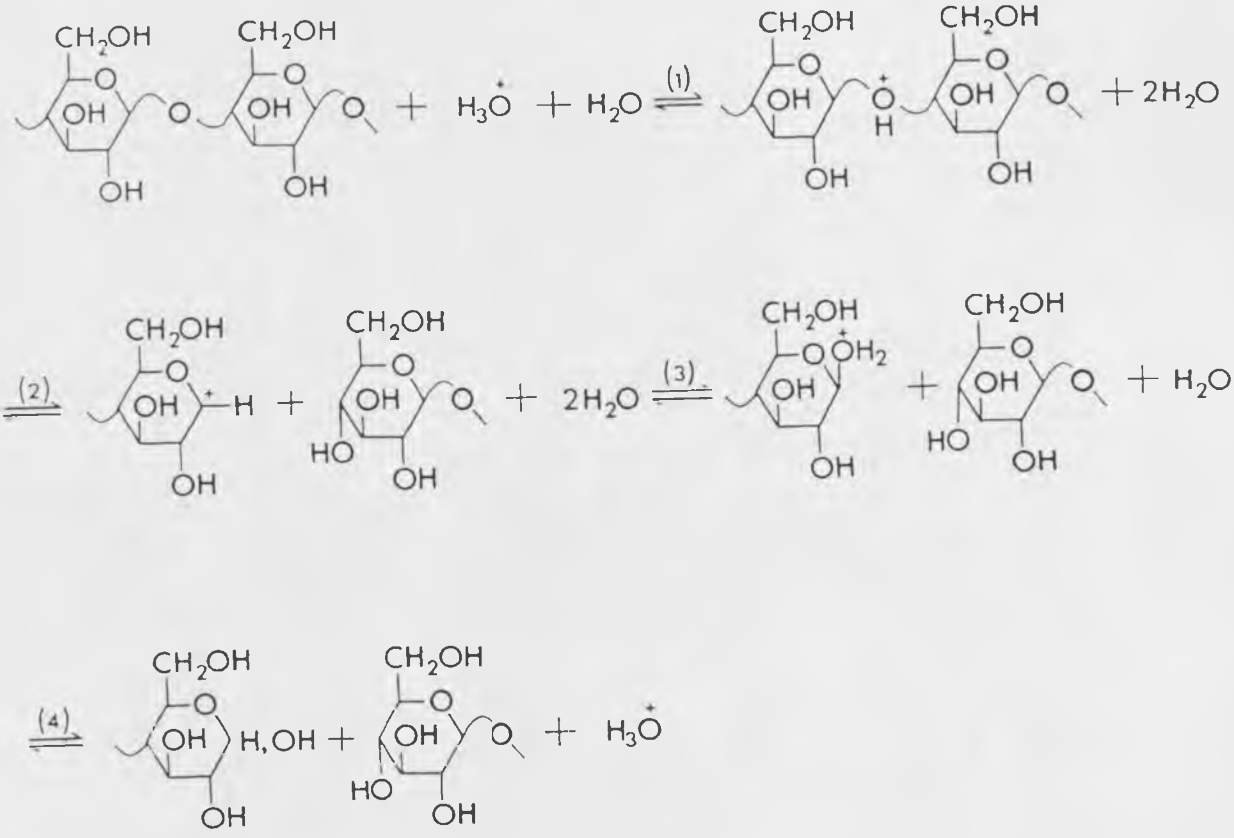
1.1.5 Typical reactions of cellulose

In its reactions, cellulose is usually attacked in one or several of three ways: i) the glucosidic linkage is attacked by hydrolysis and some other degradation reactions; ii) the very reactive hydroxyl groups may be oxidised or substituted in various ways; iii) the C-H bond or other low-energy bonds may be broken. Of particular importance to the present discussion are the degradation and substitution reactions of cellulose.

1.1.5.1 Degradation reactions

From a chemical point of view the complete degradation of cellulose results in its conversion to carbon dioxide and water. Any intermediate stage in this process may be described as partial degradation, and it is the very early stages of degradation which are important in the textile field. The types of degradation to be considered here are those produced by acids, alkalis and oxidising agents.

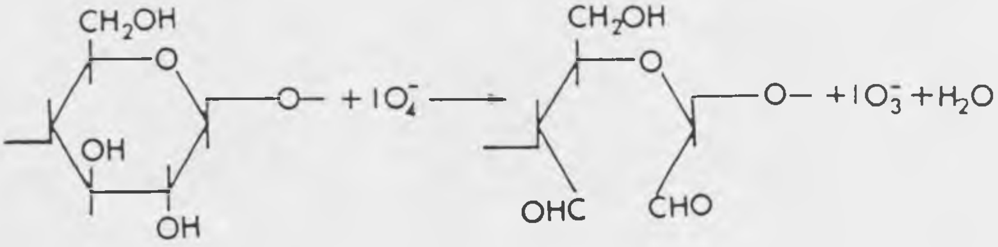
Cellulose is sensitive to acids. The degradation of cellulose by aqueous acids consists in the hydrogen-ion catalysted hydrolysis of the glucosidic linkages according to scheme 1-1-2 [24].



Scheme 1-1-2

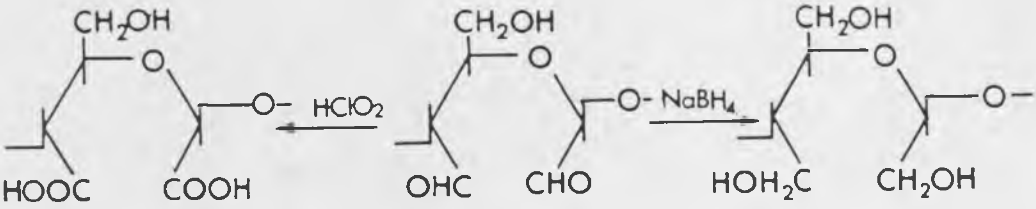
Acidic hydrolysis of cellulose leads to reduction in strength and ultimate loss of fibre structure. Products formed are referred to as 'hydrocelluloses'. Since hydrolysis of cellulose will break the main chain, releasing reducing and non-reducing groups, the extent of hydrolytic degradation is determined by the 'copper number', which represents a quantitative measure of the reducing power of the hydrocelluloses.

Both the alcohol groups in the intermediate units and the end groups of cellulose can be oxidised by a variety of oxidising agents. Treatment of cellulose fibres with oxidising agents in acidic, neutral or alkaline conditions almost invariably leads to a reduction in tensile strength. Products of cellulose oxidation are normally referred to as 'oxycelluloses' even though such materials may differ widely in their properties. One particular oxidation reaction that is important to the present work is the oxidation of cellulose by sodium metaperiodate ($NaIO_4$) which is widely used in carbohydrate chemistry. It was first applied to cellulose by Jackson and Hudson [25] and by Davidson [26]. The reaction is best carried out at a pH value between 2 and 5 according to the scheme 1-1-3:



Scheme 1-1-3

Periodate oxycelluloses are extremely sensitive to degradation by dilute alkalies due to the presence of the aldehyde groups, which allow the ß-hydroxycarbonyl elimination to occur [27]. When the aldehyde groups are oxidised with chlorous acid to carboxyl groups [28,29] or reduced with sodium borohydride to primary alcohol groups [30], stability to alkali is restored.



Scheme 1-1-4

The extent of oxidative damage is assessed by the absorption of the basic dye, Methylene blue, which gives a measure of the acidic groups present, as well as by the copper number which measures the reducing property.

The glucosidic linkage is stable to alkalies, but due to the presence of aldehyde groups, cellulose can be slowly attacked by hot alkali leading to degradation of the fibre by the ß-alkoxycarbonyl elimination mechanism [27]. The chemical degradation of cellulose in alkaline solutions has been studied in great detail by several workers [31-33] and their findings suggest that oxygen exercises a profound effect in such reactions.

1.1.5.2 Substitution reactions

The intermediate chain unit of cellulose contains three hydroxyl groups capable of participating in substitution reactions. The degree of substitution (DS) of a cellulose derivative is the fraction of hydroxyl groups that have reacted, and can therefore have any value between 0 and 3.

It is generally accepted that the primary alcohol group in position C6 is considerably more reactive than the secondary groups at C2 and C3, but relative rates differ from one reaction to another. The overall relative reactivity of the three hydroxyl groups under heterogeneous conditions is determined by the combined effect of three factors: their inherent chemical reactivity, steric effects arising from the size of the entering group and steric effects arising from the supramolocular structure of the cellulose. In most reactions the reactivity decreases in the order C6 > C2 > C3.

Cellulose can be esterified with most inorganic and organic acids by methods analogous to those used for simple alcohols, this reaction giving many important products. Apart from the three important derivatives, i.e. acetates and xanthates, which already have practical application, a number of other esters have also been prepared. For example, esterification with phosphoric acid leads to the production of flameproof cellulose [34-36] and the reaction of cellulose with urea produces a carbamate [37].

The etherification of cellulose can be brought about in several ways [38]. Most common is the reaction of alkali cellulose with a reactive alkyl, especially a halide, to form a salt and the cellulose ether, as in the case of the preparation of methyl [39] and benzyl cellulose [40]. Other reaction of this type include the addition of ethylene oxide and its derivatives and of activated olefins. Examples of the latter reactions include hydroxyethylation [41] and cyanoethylation [42] of cellulose.

1.2 Chemistry of Fibre-reactive Dyes for Cellulose Fibres

1.2.1 General

Prior to the development of reactive dyes all methods of dyeing cellulosic fibres to the highest standards of wet-fastness depended on converting water soluble substances into relatively insoluble compounds within the fibre. These processes were always accompanied by a measure of difficulty in application [43]. Work by Rattee and Stevens in 1953 led to the development of the first successful method of applying reactive halo-s-triazinyl dyes to cellulose so as to form covalent bonds under practical dyeing conditions [44].

Cellulose consists of poly-1,4-D-glucopyranose and may therefore be regarded as a polyhydric alcohol capable of undergoing most of the general reactions of alcohols. Under alkaline conditions the hydroxyl groups in cellulose are partially ionised and thus can act as nucleophilic sites in Schotten-Baumann type reactions with acylating agents or with unsaturated trigonal aliphatic carbon atoms. These two approaches have been the ones most extensively investigated in the chemistry of fibre-reactive dyes.

Many reactive systems may be used to produce cellulose derivatives on the above basis. However, in the production of reactive dyes, apart from the chemistry of the dye-fibre reaction, many other factors have to be taken into account, for example:

---any reactive system selected as a basis for a reactive dye range must be capable of being economically incorporated into chromophores.

---the reactive system must give an efficient dye-fibre fixation ratio following application under a wide variety of conditions.

---the dye containing the labile group must be stable when stored as dry powder and preferably show stability in liquid form.

---the dye-fibre bond, once formed, should show sufficient stability during washing and storage of the dyed articles, since wet fastness depends entirely on this factor.

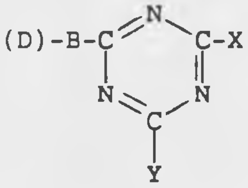
---the system selected must be free from patent restrictions, health hazards, etc.

The very large number of possible reactive systems covered in over 1000 patents granted to the different dye manufacturers has been reduced to a few commercially utilised dye ranges, as a consequence of technical-commercial considerations. They may be classified into two main groups which will be discussed separately:

1.2.2 Dyes undergoing nucleophilic substitution reactions

The reaction of this class of dyes with cellulose proceeds via a bi-molecular nucleophilic substitution mechanism (SN2), whereby a suitable leaving group is displaced from the dye by an attacking nucleophilic group present in the fibre. The majority of the reactive groups in this category are derived from halogen -containing nitrogen heterocycles of aromatic character, which owing to the electronegativity of the N-atoms, cause electron deficiency at the adjacent C-atoms, thus rendering them susceptible to attack by nucleophilic reagents [45,46].

The dyes of this type can be exemplified by the s-triazine reactive system. The general formulae of this reactive systems can be written as follows:



where B = bridging groups for insulating the chromophoric system from the dye-fibre bond system, thus preventing a change in hue.

X = leaving groups which may be Cl, F, etc.

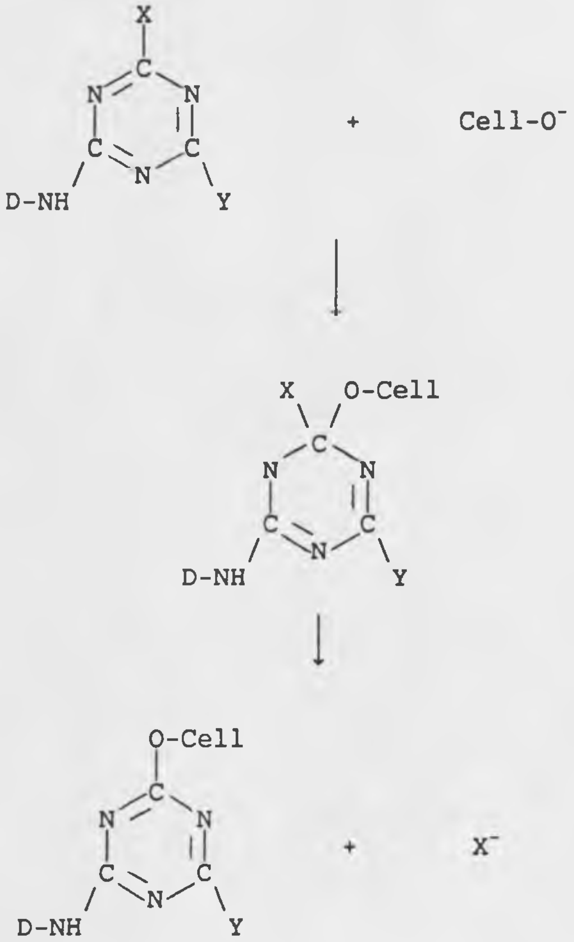
Y = activating/inactivating groups which may be Cl, OCH_3, NHR, etc.

(D)= chromophore

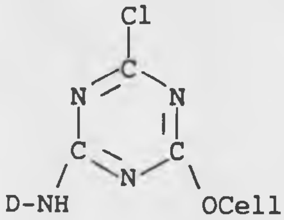
The mechanism of the reaction between the cellulose fibre and this type of dye can be illustrated as in scheme 1-2-1.

The cellulose glucosidic hydroxyl groups become ionised under mildly alkaline conditions. It is thus the highly nucleophilic cellulosate anion which attacks the electron deficient C-atoms in the heterocyclic ring to form a δ-complex [47] from which the chlorine atom is expelled, leaving the cellulose covalently bonded to the dye via the s-triazine ring.

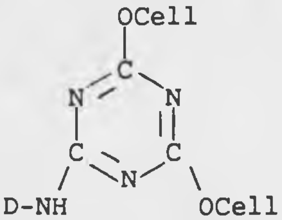
When both X and Y are chlorines the reactive group is the dichloro-s-triazinyl system which is employed commercially in the Procion MX (ICI) reactive dyes. In the case of this reactive system, under suitable conditions both chlorine atoms may be replaced but the second is displaced less readily than the first. During nucleophilic substitution there are competitive reactions. Hydroxyl groups in water can also react resulting in the inactivation of the reactive groups(i.e. hydrolysis of the dyes). The products of dyeing cellulosic fibre with dichloro-s-triazinyl dyes are, therefore, much more complicated than that described above. As far as the dye-fibre bond is concerned, the following three structures can be obtained [48]:



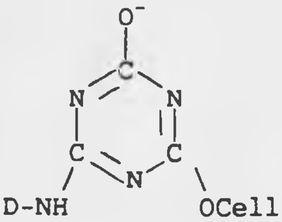
Scheme 1-2-1



Type 1



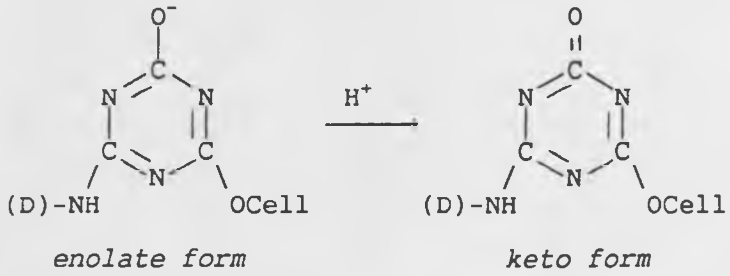
Type 2



Type 3

The form obtained depends on the application conditions, Type 3 being obtained under alkaline or severe conditions; Type 2 under less severe conditions and Type 1 under still less severe conditions. The alkaline stability of the dye-fibre bond increases in the order: Type 1 < Type 2 < Type 3 [48], but, in practical terms, there is no effective difference in fastness between Type 2 and Type 3, since the first stage of alkaline attack is to convert the Type 2 to Type 3 dyeing.

Acid hydrolysis of dye-fibre bonds appears to involve ester hydrolysis in which the bridging oxygen becomes protonated and thus subject to nucleophilic attack by water [48]. Since the oxygen atom is attached to a heterocyclic ring containing powerful electronic influences, the chemical nature of the dye-fibre system influences its resistance to acid hydrolysis. Under acid conditions, the type 3 system character changes according to the following scheme:



Scheme 1-2-2

The carbonyl group in the latter keto form is likely to reduce considerably the over-all electronegativity of the ring system, making protonation of the bridging oxygen easier than in other cases; acid bleeding may therefore occur on cotton goods dyed with dichloro-s-triazine reactive dyes.

Storage stability of the dry powder of dichloro-s-triazine dye is not very good. This is due to the fact that the reaction in scheme 1.2.1 is autocatalytic [49]. The liberated halide acid causes quaternisation of a triazine ring nitrogen atom, thereby increasing its electrophilic character and hence accelerating the dye hydrolysis by water from the atmosphere.

Altering the substituents (B, X or Y) attached to the triazine ring affects the reactivity in the nucleophilic exchange. Electron-attracting groups increase reactivity but electron-donating groups decrease it. Replacement of one chlorine atom in the Procion MX dyes by an amine produces the commercially important Cibacron (CIBA), Basilen E (BASF), Procion H and Procion HE (ICI) dyes. These monochloro-s-triazine dyes must be applied at higher temperatures (60-80°C) to achieve dye-fibre bonding. This lower reactivity permits the use of chromophoric systems with higher intrinsic substantivity for the fibre and the use of reactive dyes for printing, dichlorotriazinyl dyes being too unstable to meet the printer's demand to store expensive printing pastes.

By replacing chlorine in the monochloro-s-triazine dye with fluorine the monofloro-s-triazine, Cibacron F (CIBA), dyes are obtained [50]. Since fluorine has higher electro- negativity than chlorine, the Cibacron F dyes exhibit high reactivity and can be used for cold-dyeing, while still give the same dye-fibre bonding system as monochloro-s-triazinyl dyes.

The dye-fibre bonds formed when using monochlorotriazinyl dyes are less stable under alkaline conditions than those formed between dichlorotriazinyl dyes and cellulose, since the amino group is more strongly electron releasing than the cellulosyl group and therefore the 4-position in the dye-fibre compound is more reactive [43].

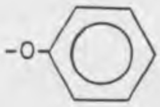
The reactivity of reactive groups is also affected by the numbers of hetero-atoms in the aromatic ring. The diazine unit exploited in some commercial reactive ranges is less reactive than the corresponding triazine, because only two electro- negative nitrogen atoms are present in this heterocyclic system. The reactivity of the 1,3-diazinyl reactive system can be increased by introducing strong electronegative leaving groups into the heterocyclic ring. Sandoz and Ciba-Geigy have used the trichloro-pyrimidine reactive system to produce the Drimaren Z and Cibacron T-E dyes respectively, Bayer have produced two ranges of dyes based on difluorochloropyrimidine (Levafix E-A) and methylsulphonochloromethylpyrimidine (Levafix P) reactive systems [51].

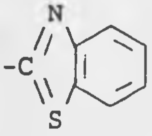
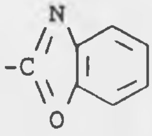
The pyrimidine ring system gives rise to much less dye association in solution than does the triazine ring and therefore dyes containing this residue generally show better solubility and lower substantivity. By appropriate selection of chromophoric systems, however, the substantivity of this type of dyes can be improved [43].

Due to the lower degree of activation produced by the diazine ring as compared with the triazine ring, the alkaline stability of the dye-fibre bond of pyrimidinyl dyes is higher than for the corresponding triazinyl compounds. However since the 5-chloro substituent in the pyrimidine ring does not take part in dye-fibre bonding its presence on the dyed fibre can lead to instability when laundering in the presence of hydrogen peroxide. This effect has been attributed to the nucleophilic attack on the 5-chloro position by the highly nucleophilic OOH^- anion leading to disruption of the dye-fibre bond [52].

The alternative approach via the use of the 2,3-dichloro- quinoxaline system offers significant advantages over the pyrimidine system from the point of view of increasing the reactivity of dyes. Bayer have exploited this reactive system in their Levafix E range of dyes which show high reactivity and satisfactory substantivity [43]. The dye stability in alkaline solutions is, however, not very good and is inadequate for printing applications.

Leaving groups play a very important role in determining the reactivity of reactive groups. Apart from chlorine and fluorine atoms, various alternative electro-negative groups have been the subject of patent specifications. e.g. $-SO^{-}_{3}Na^{+}$, $-S-SO^{-}_{3}Na^{+}$, -SH, $-N^{+}R_{3}$, -SCN,


,

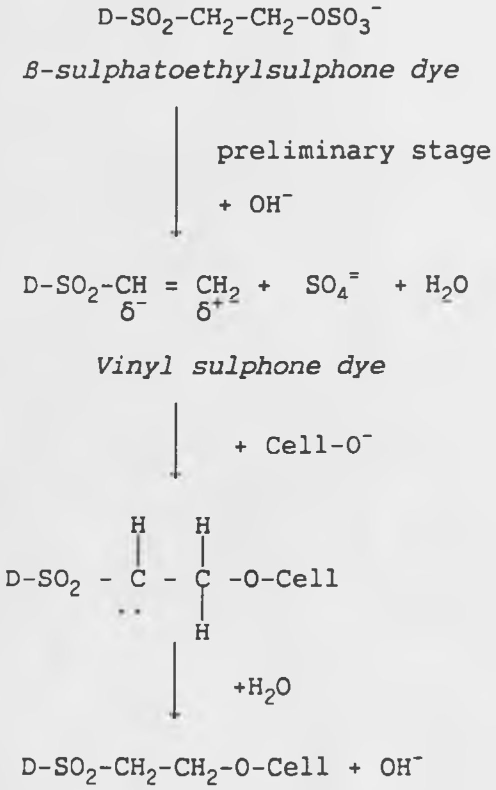

and

.

The quaternary alkylammonium groups ($-N^{+}R_{3}$) are of special interest. Not only are such groups more electronegative than halogen substituents, so that dyes of very high reactivity are obtained, but they also enable certain tertiary amines to be used as dyebath catalysts [53].

Nippon Kayaku has produced a range of reactive dyes, the Kayacelon React dyes, by modifying the monochlorotriazinyl dyes with nicotinic acid [54]. These dyes can react with cellulose under neutral pH conditions at high temperatures (100-130°C) to give a high fixation efficiency [55].

1.2.3. Dyes undergoing nucleophilic addition reaction

The mechanism of reaction of this group of dyes is basically different from that of the types considered hitherto. In all instances 1,2-trans-addition of a compound HB to a polarised double bond is involved. Activation of the double bond results from the presence of a strongly electron-attracting substituent and this type of reaction may thus be classified formally within the general scope of the Michael addition reaction [56]. The mechanism may be exemplified by the Remazol dyes (FH) which are sold as the ß-sulphato-ethylsulphone derivatives. Under alkaline conditions this group undergoes ß-elimination to form the fibre reactive vinyl sulphone residue (scheme 1-2-3):



$$D\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}OSO_3^-$$

β-sulphatoethylsulphone dye

$$\xrightarrow[+\ OH^-]{\text{preliminary stage}}$$

$$D\text{-}SO_2\text{-}\underset{\delta^-}{CH} = \underset{\delta^+}{CH_2} + SO_4^= + H_2O$$

Vinyl sulphone dye

$$\xrightarrow{+\ \text{Cell-O}^-}$$

$$D\text{-}SO_2 - \underset{\cdot\cdot}{\overset{H}{C}} - \underset{H}{\overset{H}{C}}\ \text{-O-Cell}$$

$$\xrightarrow{+H_2O}$$

$$D\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}Cell + OH^-$$

Scheme 1-2-3

As with all reactive dyes the dyes are initially applied as direct dyes under neutral or very weakly acidic conditions in the presence of electrolyte; on rendering the dyebath alkaline, the protective group ($-SO_4^-$) is eliminated leaving the reactive vinylsulphone group. Addition to the fibre is initiated by a nucleophilic attack at the terminal positive carbon atom of the polarised double bond.

An important and characteristic difference between this group of dyes and the group of heterocyclic ring derivatives is the fact that the latter dyes react with the fibre via substitution reactions which proceed, under dyeing conditions, practically irreversibly, whereas the former dyes follow addition reactions which are reversible. With the latter group, hydrolysis of the dye-fibre bond leads directly to the hydrolysed dye (Figure 1-2-1), but with the former, the original active vinyl dye, still capable of reaction with the fibre (Figure 1-2-2) may be formed along with the hydroxyethyl sulphone.

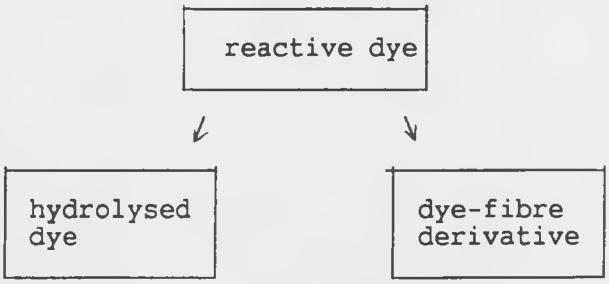


Figure 1-2-1 Nucleophilic Substitution

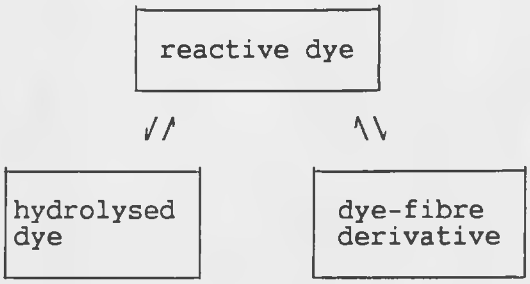


Figure 1-2-2 Nucleophilic Addition

The dye-fibre bonds obtained using vinylsulphone reactive dyes are less stable to alkaline conditions than those obtained using triazine and pyrimidine based dyes. Stability can be improved by substituting the activating O=S=O group with groups of lower electronegative character, e.g. sulphonamide ($-NHSO_2-$), amido (-NHCO-), etc [57,58].

Table 1-2-1 summarizes the most important reactive groups which are currently used in commercial reactive dyes introduced by various dyestuff manufacturers.

Table 1-2-2 gives an indication of the relative reactivity of the dyes listed in table 1-2-3 [59] and Table 1-2-3 shows the stability of dye-fibre bonds formed by these dyes in various media [60]. The reactivity of the Kayacelon React dyes is not mentioned in the table, but from reference [55] it can be seen that this dye has a slightly higher reactivity than the vinylsulphone reactive dyes or the difluorochloropyrimidine types, and exhibits a slightly lower reactivity than the dichlorotriazine or dichloroquinoxaline reactive dyes.

The requirement to improve selectivity and fixation of reactive dyes has led to the production of bireactive dyes. These include three types:

Type 1 $\boxed{\text{Chromophore}} - R_1 - R_2$

Type 2 $R_1 - \boxed{\text{Chromophore}} - R_2$

Type 3 $\boxed{\text{Chromophore}} - R_1 - R_2 - \boxed{\text{Chromophore}}$

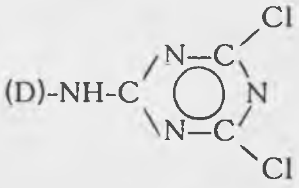
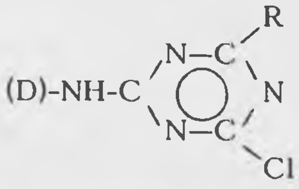
R_1 and R_2 can be either two identical (bireactive dyes) or different reactive groups (heterobireactive dyes). For example, the most important products in the Procion SP and HE (ICI), Cibacron E (Ciba-Geigy) and Basilen E (BASF) ranges contain bimonochloro-triazine groups of type 3; There are some bivinyl sulphone and mixed monochlorotriazine/vinyl sulphone dyes of type 1 and 2 in the Remazol range (Hoechst); Sumifix Supra (Sumitomo) and selected dyes from the Cibacron F (Ciba-Geigy) ranges are mixed monochlorotriazine/vinyl sulphone dyes of type 1 and bifluorotriazine dyes of type 2 respectively; some dyes in the Cibacron C range contain bivinyl sulphone (type 2) and mixed fluorotriazine/vinyl sulphone (type 1) dyes.

The presence of the second reactive group not only improves the fixation but also the reproducibility of the shade, washing -off properties and the levelness of dyeings.

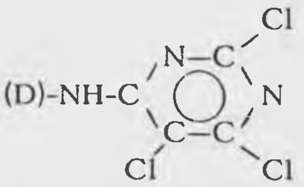
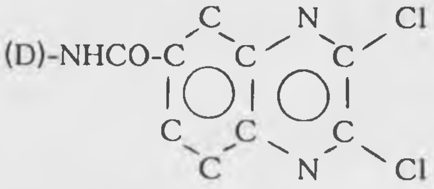
Since the stability of the dye-fibre bond from monochloro- triazinyl dyes is not very good under acidic conditions and that of vinyl sulphone dyes is poor under alkaline conditions, the combination of these two different reactive systems in one dye molecule largely reduces the specific weaknesses of each type of reactive group

There are, however, some limitations of bireactive dyes, which include their higher manufacturing cost compared to similar monoreactive ones as well as the reduced diffusion properties due to the bulkiness of the dye molecules.

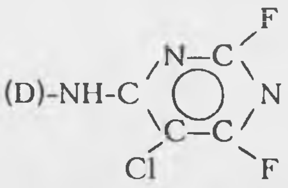
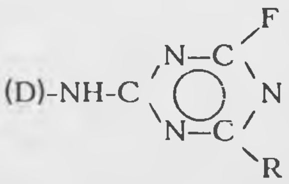
Table 1-2-1. The important reactive groups in current commercial reactive dyes

Released	Reactive group	Current manufacturer commercial name		Fixation mechanism	Reactivity 5-1 (high-low)	Uses(preferred)
1956	 dichlorotriazine (DCT)	ICI BASF	Procion MX Basilen M etc	SN2	5	-exhaust(40°C) -pad-batch
1957	 monochlorotriazine (MCT)	ICI BASF SANDOZ CIBA-GEIGY	Procion H,HE,SP Basilen E, P Drimaren P Cibacron Cibacron E	SN2	2	-exhaust (80° -pad-batch- pad-steam -pad-thermofix -printing (1 phase)

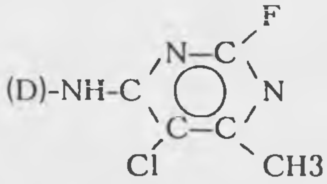
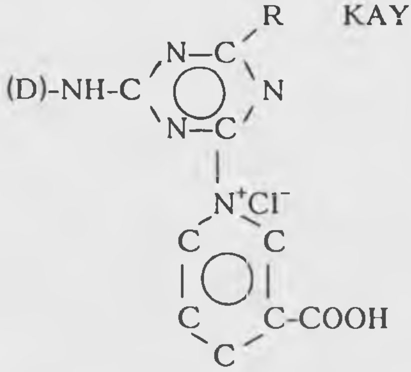
Continue table 1-2-1.

1957	(D)-$SO_2CH_2CH_2OSO_3H$ sulphatoethyl-sulphone (VS)	HOECHST SUMI-TOMO	Remazol Sumifix etc.	A	3	-pad-batch -pad-dry-pad-steam -exhaust(60°C) -printing (2 phase)
1960	 trichloropyrimidine (TCP)	SANDOZ CIBA-GEIGY	Drimaren Z,X Cibacron T-E	SN2	1	-exhaust (80°C)
1961	 dichloroquinoxaline (DCQ)	BAYER	Levafix E	SN2	4	-exhaust -pad-steam -pad-batch

Continue table 1-2-1.

1971 1972	 difluorochloropyrimidine (DFCP)	BAYER SANDOZ	Levafix E-A Drimaren K,R	SN2	4	-exhaust (40°C) -pad-batch
1978	 monofluorotriazine (MFT)	CIBA-GEIGY BAYER	Cibacron F Levafix E-N	SN2	2	-exhaust (80°C) -pad-dry- -pad-steam -pad-thermofix -printing (1 phase)

continue table 1-2-1.

1981	 fluorochloromethyl pyrimidine	BAYER	Levafix PN	SN2	2	-printing (1 phase) -pad-thermofix
1984	 m-carboxylpyridinium-triazine	NIPPON-KAYAKU	Kayacelon-React	SN2	4	-exhaust neutral (100-130°C)

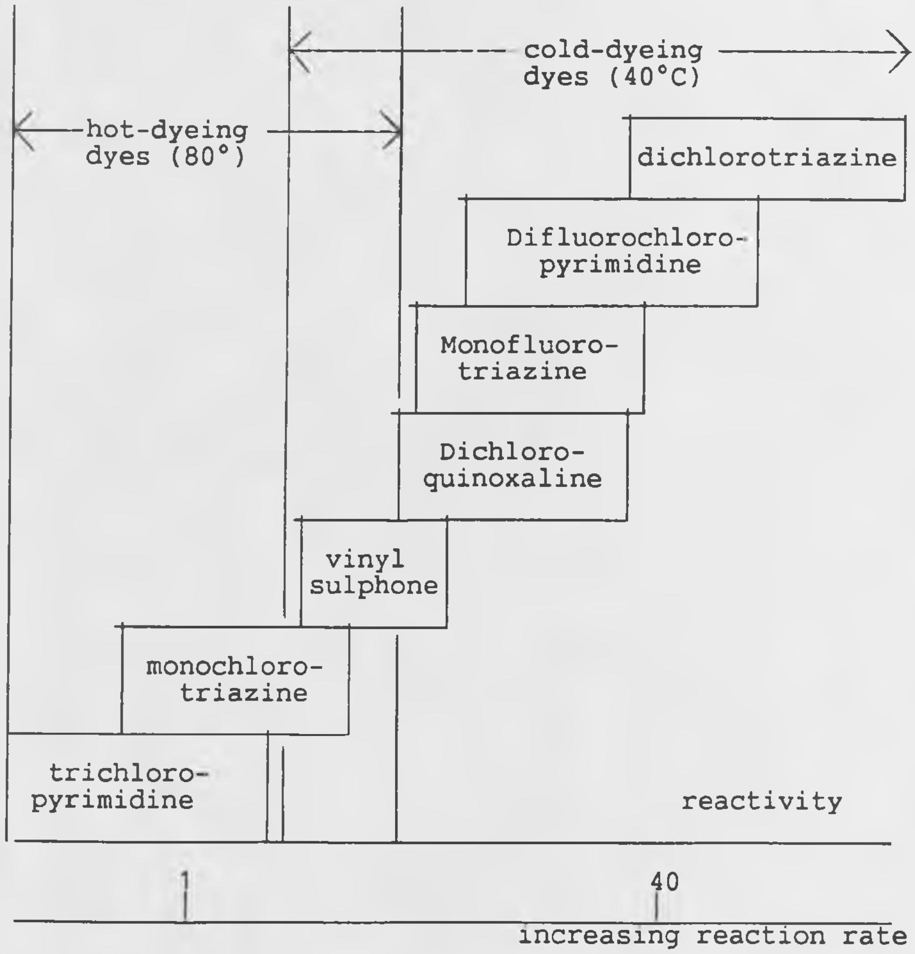


Table 1-2-2 The relative reactivity of some commercial reactive dyes [59]

Table 1-2-3 Dye-fibre bond stabilities of commercial reactive dyes

Stability of dye/fibre bond	Tendency
in alkaline media	MCT, MFT, DFCP better than VS, DCQ.
in acid media	VS better than DFCP, MFT, MCT, DCQ.
in perborate-containing media	MCT, MFT, VS better than DFCP, DCQ.
in chlorine-containing media (1-5 ppm)	MCT, MFT, VS better than DFCP, DCQ

Where: MCT = monochloro-triazine;
MFT = monofluoro-triazine;
DFCP= difluorochloro-pyrimidine;
VS = vinyl sulphone;
DCQ = dichloro-quinoxaline.

1.3 Reasons for Carrying out This Study

1.3.1 Problems associated with the use of reactive dyes

Of the dyes currently applied for dyeing cellulosic fibres, the reactive dyes show the greatest growth potential; this is attributed to their almost unrestricted shade range coupled with their excellent wet fastness properties. There are, however, certain environmental problems which may increasingly arise from the use of reactive dyes (or for that matter most other cellulosic fibre dye classes). These arise from the necessity to use high salt concentrations (40-100g/l) and only moderate efficiency of dye usage since dye fixation varies between 50% and 90% depending on application method, depth of shade and dye type. Additionally, the discharge of some reactive dyes into aqueous effluent may fall into the category of organic halogen discharges which are carefully monitored in some countries (AOX legislation; AOX is a measure of total Adsorbable Organo-Halogen).

The electrolyte used in dyeing reactive dyes on 100% cellulosic materials is usually sodium chloride but when dyeing cellulose/ polyester mixtures it is necessary to use sodium sulphate since during the normal high temperature (120-130°C) dyeing step required to fix the disperse dye on the polyester component, sodium chloride solutions would attack the stainless steel dyeing vessel. High concentrations of both sodium chloride and sodium sulphate are undesirable in aqueous effluent but sulphate discharge may be even more suspect, since it attacks concrete pipes and also increases the undesirable accumulation of sulphate ions in water courses.

Using high concentrations of electrolyte not only produces environmental problems but also contributes to the time consuming, energy intensive and expensive washing-off procedure following application of reactive dyes on cellulose fibre, since dilution of electrolyte concentration is necessary to reduce the substantivity of unfixed reactive dye; the latter must be effectively removed otherwise poor wet fastness properties will be apparent.

When dyeing polyester/cotton blends, disperse dyes are used for the polyester component and reactive dyes usually used for the cotton component. The fixation step when dyeing cotton with reactive dyes has to be carried out under alkaline conditions which adversely affects many disperse dyes; thus either a two-bath or a one-bath, two-step dyeing procedure must be adopted. Obviously, the processing time used in such methods is long (6-8 hours) and also the dyeing procedure is complicated. If the dyeing of the cotton component could be carried out under neutral pH conditions, then a one-bath, one step dyeing method for the polyester/cotton blend would be achievable [55].

1.3.2 The proposed resolution of the problems

The above considerations indicate that the ideal reactive dyeing process for cellulosic fibres would be to exhaust the dye under neutral to slightly acidic conditions and then to fix it by simply raising the dyebath to the boil. Such processes in fact exist for applying reactive dyes to wool fibres [61] and it is therefore worthwhile to consider the differences between the two fibres.

All reactive dyes are sulphonated (2-6 sulphonate groups per dye molecule) and are thus dissolved in aqueous solution at pH values above 1.0 - 1.5 as negatively charged anions. The cellulose fibre is unstable under strongly acidic conditions and should be dyed above pH 4.0 to preserve its physical properties; under these conditions the surface of the fibre is more or less negatively charged due to the presence of ionized carboxylic acid groups. As the dyebath pH rises above 7.0 the fibre becomes even more negatively charged due to ionization of the hydroxyl groups [62].

Anionic dyes thus have to overcome a significant adverse charge barrier before they are adsorbed by the cellulosic fibre. Large concentrations of salt serve to screen these negative charges and also decrease their magnitude by reducing the degree of ionization of fibre carboxylic acid residues [63].

In the case of wool dyeing the overall surface charge under acidic conditions is positive due to the presence of protonated amino groups. Thus dyeing with sulphonated anionic dyes proceeds relatively readily in the absence of salt even under weakly acidic conditions. There are also significant concentrations of non-polar, hydrophobic residues in the wool fibre which undoubtedly contribute markedly to wool's substantivity for water soluble dyes [64,65] - such residues are notably lacking in cellulose.

From the above considerations it would seem that cellulose modified by the introduction of primary , secondary or tertiary amino groups would be dyeable with sulphonated dyes under mildly acidic conditions (i.e. sufficient acid to significantly protonate the amino group to form a cation) in the absence of electrolyte. If the fibre were to be modified by the incorporation of fully quaternised cationic amino residues then we might expect high substantivity for anionic dyes regardless of the dyebath pH. Such a modified cellulose may be schematically represented as in figure 1-3-1.

Depending on the basicity of the amino groups and the pH of the solution, under mildly acidic or alkaline conditions the species shown in figure 1-3-2 would be present.

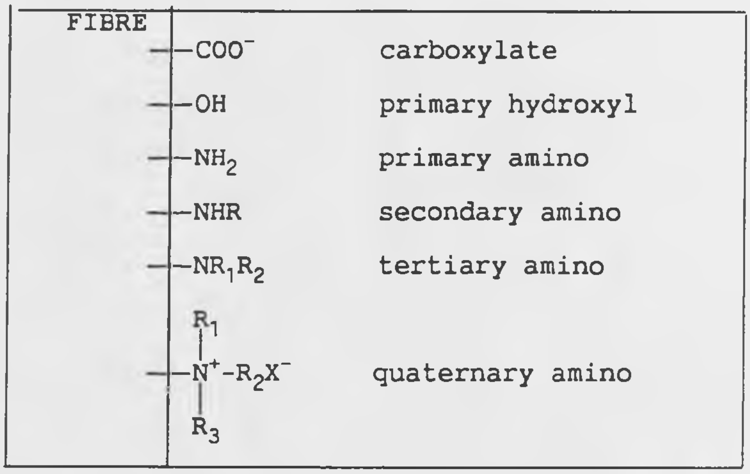


Figure 1-3-1 Illustration of the species in a modified cellulose

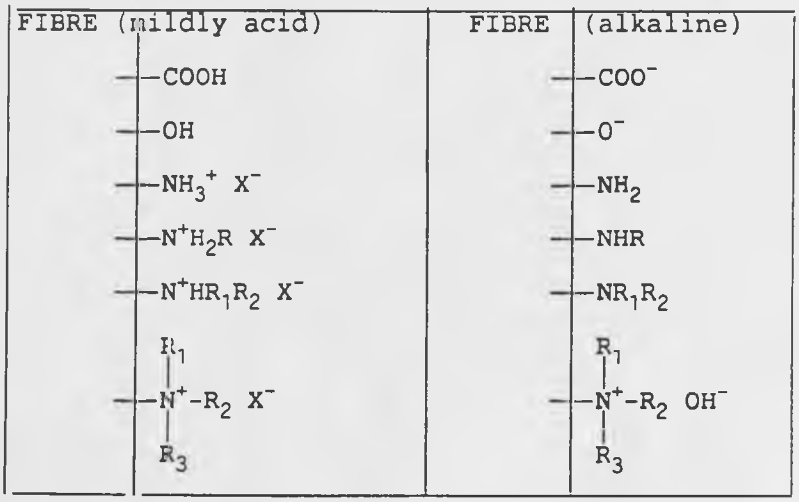


Figure 1-3-2 Illustration of the species in a modified cellulose under different pH conditions

The important nucleophilic sites which could be involved in reaction with reactive dyes are:

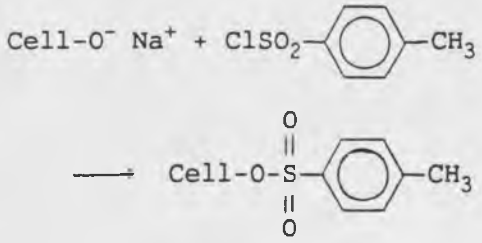
$-O^-$, $-NH_2$, $-NHR_1$, and $-NR_1R_2$.

It is clear that under neutral or weakly acidic dyebath conditions only the latter three amine derivatives would be involved in nucleophilic substitution or addition reactions. Even under alkaline fixing conditions one would expect the strong amine nucleophiles to predominate in the reaction with reactive dyes.

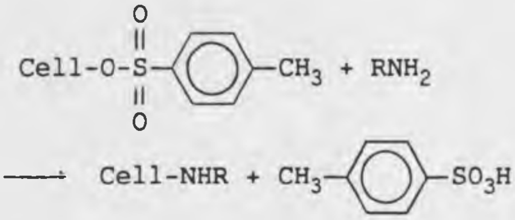
1.4. Previous Studies on Cellulose Modification

1.4.1. Modification of cellulose with low molecular weight compounds

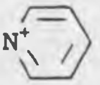
One of the first attempts to 'aminate' cellulose to improve its dyeing properties was by Karrer and Wehrli [66] in 1926. These workers first produced the p-toluene sulphonate ester of cellulose by the reaction of p-toluene sulphonyl chloride with alkali cellulose. The ester was then reacted either with ammonia or substituted aliphatic amines to give a variety of amino celluloses (scheme 1-3-1 and 1-3-2).



Scheme 1-3-1



Scheme 1-3-2

Karrer and Wehrli noted that the aminated celluloses could be readily dyed with acid dyes in the presence of 10-20% Glaubers salt, 1-4% acetic acid and raising the bath to the boil; very high levels of bath exhaustion were reported. Interestingly, the pyridine modified cellulose (possibly Cell- X^-) was noted as giving the most brilliant dyeings with the highest wash fastness.

A number of patents and publications [67-70] have since considered the modification of cellulose with amines. One particularly well researched technique [68,70] utilizes the reaction of 2-amino-ethyl-sulphate with cellulose to introduce amino ethyl groups according to scheme 1-3-3. This reaction is in fact an over-simplification; three products, O-(2 aminoethyl) -cellulose, ethanolamine and polyamine polymers being formed [70]. The polyethylene imine is covalently bonded to the cellulose, according to scheme 1-3-4.

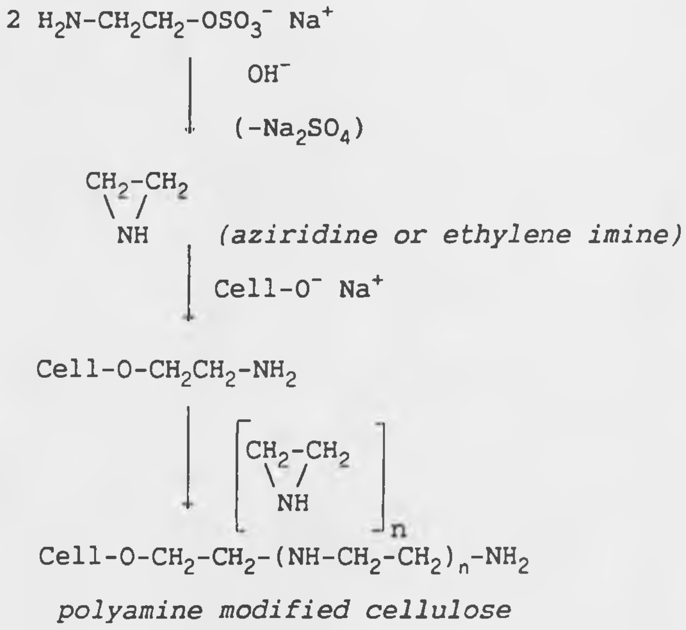
$$\text{Cell-OH} + \text{NaOH} + H_2N\text{-}CH_2CH_2\text{-}OSO_3^-\ Na^+$$

$$\Big\downarrow\ [140°C]\ (10\text{-}15\ \text{minutes})$$

$$\text{Cell-O-}CH_2CH_2\text{-}NH_2 + Na_2SO_4 + H_2O$$

O-(2-aminoethyl)-cellulose

Scheme 1-3-3

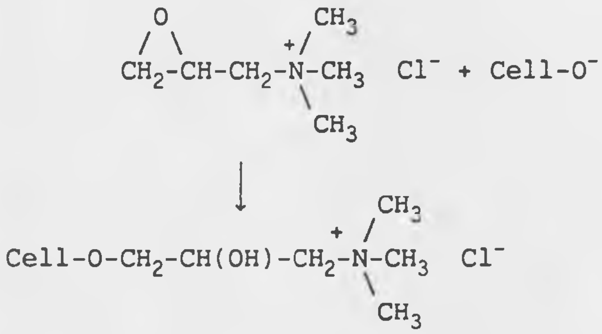


Scheme 1-3-4

Reeves and Guthrie [69] reported on dyeing tests carried out by the Dupont Company and D.E. Gamble on this modified cellulose; they noted that the aminized cotton has a noticeable increased substantivity for direct, vat, sulphur and azoic dyes than either mercerised or untreated cotton. The light and wash fastness properties of dyeings were also slightly better on the modified cellulose. Gamble also observed that dyeing of the aminized cotton with cotton dyes requires shorter time and lower temperatures than normal and also little or no salt to exhaust the bath.

Einsele [72] studied the dyeing of this modified cellulose with monochloro-s-triazine reactive dyes and observed that good uptake and fixation was achieved under slightly acidic or neutral conditions in the absence of salt.

Much work has been carried out to covalently bind fully quaternised amino groups to cellulose [73-77]. One of the most well known water soluble, reactive quaternary products was sold by Protex as Glytac A [74,75]. This product is glycidyl-trimethyl ammonium chloride and reacts with cellulose under alkaline conditions according to the following scheme:



Scheme 1-3-5

Bayer [76] also marketed a similar product, Levogen RS, which was glycidyl-N-methyl-morpholinium chloride.

When used for cellulose pretreatments this type of product greatly increases the substantivity of both direct and reactive dyes for the fibre. Light fastness of both dye classes was unaffected by these treatments and in the case of direct dyes wet fastness was substantially improved.

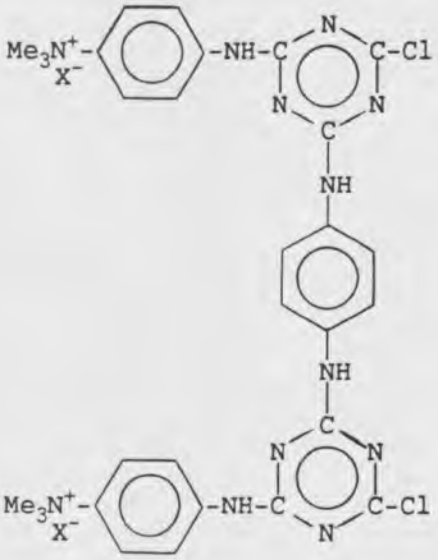
Rippon [77] showed that these products could be employed as a pretreatment to improve levelness when dyeing cotton fabrics containing significant quantities of immature or dead cotton.

Dyeing studies [78] on the prequaternised cellulose produced by the pad-dry-bake (150°C) application of 1-trimethyl-ammonium-2-hydroxy-3-chloro-propane chloride (precursor to glycidyl-trimethyl-ammonium chloride) and sodium hydroxide, showed that selected direct dyes could be applied without salt giving adequate yields and dyeings which were resistant to ISO3 wash testing. Reactive dyes also showed high exhaustion without salt and were apparently bound covalently to the modified substrate, even when dyeing under neutral pH conditions [79].

Evans et. al. [80] critically compared these epoxy based pretreatments and made the following observations:

> pretreatments with reactive quaternary compounds give promising improvements in wet fastness without adversely affecting light fastness.
>
> the main problem with pretreatments which greatly enhance the substantivity of the fibre for anionic dyes is that the dyer must achieve adequate uniformity of the pretreatment agent itself.
>
> pretreatments should be fibre substantive thus allowing the dyer to apply the reactive compounds by long liquor exhaustion techniques -neither of the epoxy derivatives mentioned above are sufficiently substantive and have therefore to be applied by padding techniques.
>
> significant migration of these agents occurred during baking giving rise to surface dyeings on the outside of yarns if the agents were fixed by pad-batch techniques they modified the fibre evenly; however on subsequent dyeing, the substantivity of the anionic dye for the cationic sites in the fibre is so high that ring dyeing of individual fibres occurs.

To overcome some of the latter deficiencies, Evans et. al [80] prepared the following type of water soluble, fibre substantive, reactive pretreatment agent:



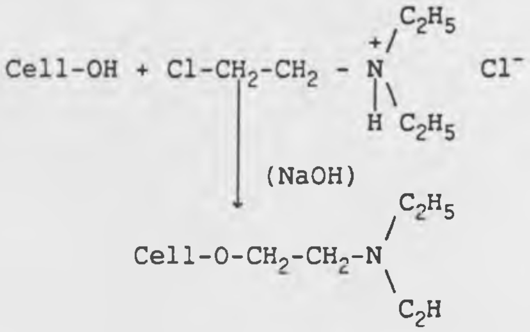
This type of agent was found to have significant substantivity for the fibre and could be applied under neutral pH conditions in the absence of salt. Under alkaline conditions optimum substantivity was observed (pH 12, 40-60°C).

Subsequent reactive dyeing of the above modified cellulose showed the following differences compared with untreated cotton dyeings.

significant changes in hue; most dyeings were duller although those produced from CI Reactive Reds 5 and 8 were brighter.

tendency to ring dyeing on the modified cellulose.
better colour yields and dye fixation on the modified cellulose.

Tertiary amino groups have been incorporated into cellulose using ß-chloroethyl-diethylamino hydrochloride [80] according to the following scheme:



$$\mathrm{Cell{-}OH} + \mathrm{Cl{-}CH_2{-}CH_2{-}\overset{+}{N}(H)(C_2H_5)(C_2H_5)\ Cl^-} \xrightarrow{(NaOH)} \mathrm{Cell{-}O{-}CH_2{-}CH_2{-}N(C_2H_5)(C_2H)}$$

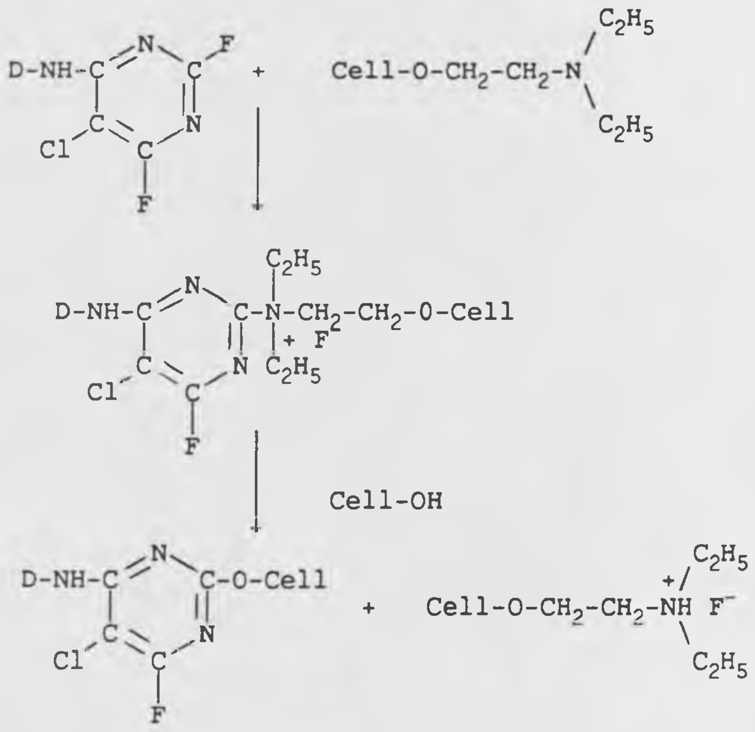
Scheme 1-3-6

The dyeing properties of this modified cellulose were examined by El Alfy et.al.[82] who showed that it exhibited excellent substantivity for reactive dyes from dye baths set at pH 7. In the case of a Drimarene K dye, a 2,4-difluoro-5- chloro-pyrimidine (FCP) type of reactive dye, the adsorbed dye was surprisingly covalently bonded to the substrate and this phenomena was attributed by El Alfy et. al to the ability of the fixed tertiary amino group to catalyse the reaction of the reactive dye with the cellulose primary hydroxyl groups. Dawson [83] has described the catalytic action of selected tertiary amines in the reactive dyeing of cellulose with monochlorotriazine dyes.

The proposed reaction for the 2,4-difluoro-5-chloro- pyrimidine type of reactive dye with the modified cellulose, may thus be written as scheme 1-3-7:

1.4.2 Modification of cellulose with polymeric compounds

Courtaulds and Sandoz [84] have developed a cationic polymer pretreatment of cellulose which is known as the Sandene process. The resin employed is Sandene 8425 which is highly cationic in character and highly substantive to cellulose under alkaline conditions. Cellulose treated with this polymer (about 5% o.w.f) is highly cationic, exhibits increased neutral substantivity for anionic dyes and also reacts with reactive dyes under neutral to weakly acid conditions.



Scheme 1-3-7

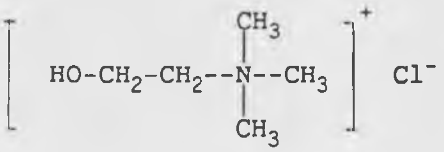
Disadvantages of the procedure include a reduction in light fastness of some azo chromophores and a flattening or dulling in shade. Since untreated cellulose will not dye under the same neutral to weakly acid conditions as the Sandene pretreated fibre, Courtaulds have developed differential dyeing fabrics from mixtures of treated and untreated fibres or yarns - the so-called Depertex process.

Thomas et. al [85] have pretreated linen with Sandene prior to blending with wool, to give a blend fabric which could be dyed in a one bath operation with selected reactive dyes at pH 5-6.

Rippon [77] has investigated the effect of pretreating cellulose fabrics with chitosan. Chitosan is a long chain unbranched polymer prepared from chitin (poly-N-acetyl- D-glucosamine) by partial deacetylation with hot alkali. Its structure is thus analogous to cellulose in which the hydroxyl groups in the 2 position of the glucose ring may have been replaced by either acetyl amino or amino groups. The hydrolysis of c.a. 80% of the acetyl amino groups leads to a polycationic polymer soluble in dilute acids. Rippon demonstrated that cellulose pretreated with this polymer showed greatly increased substantivity for direct dyes; he did not, however, study the dyeing of this modified substrate with reactive dyes.

Nikolaides [86] found that pretreatment of cotton with Chitosan increased both the rate and extent of uptake of mono- and di-chlorotriazine dyes and FCP reactive dyes when dyeing was carried out under neutral pH conditions and in the absence of salt.

Harper et al [87] produced an easy care cationic cotton fabric by use of a crosslinking agent and choline chloride:



$$\left[HO-CH_2-CH_2--\overset{CH_3}{\underset{CH_3}{N}}--CH_3 \right]^+ Cl^-$$

The fabric was found to be of enhanced dyeability. In many instances it is dyed to a much greater depth than the cotton control. Light fastness of dyeings on this fabric is lowered to some extent, but the dyeings obtained with reactive dyes under acidic conditions had somewhat better light fastness than those obtained under alkaline conditions.

CHAPTER II

II EXPERIMENTAL

2.1. Materials

2.1.1. Cotton

Bleached and unmercerised plain weave cotton fabric was used throughout the work.

2.1.2. Dyes and auxiliaries

All dyes and auxiliaries used were of commercial grade and were supplied gratis by the appropriate manufacturers.

2.1.3. Chemicals

Hercosett 125 (Hercules Powder Corp) was supplied as a 12.5% solids aqueous solution of a reactive polyamide-epichlorohydrin polymer, glycidyl trimethylammonium chloride-Glytac A (Protex) was supplied as a pure solid, and N-methylol-acrylamide (Allied Colloids Limited) was supplied as a 45% aqueous solution.

All other laboratory chemicals used in this project are summarised in Table 2.1.1.

2.2 Fibre Modification

2.2.1 Treatment of cotton with a polyamide-epichlorohydrin (PAE) reactive resin

Cotton fabric was impregnated using the padding liquor trough formed between the bowls and side plates of a Benninger laboratory mangle. The pad liquor contained different amounts of Hercosett 125 and 10 g/l of

Sandozin NIE (non-ionic surfactant). The pressure on the mangle was adjusted to give 80% wet pick-up. The samples were then dried at 100°C for 3 min. using a Werner Mathis AG Steamer/Baker Unit.

Table 2-1-1: The grade of chemicals used in this project

Chemicals	Grade
mercuric oxide,	Analar reagent
potassium sulphate,	"
sodium thiosulphate,	"
sulphuric acid 98% w/w	laboratory reagent
hydrochloric acid 36% w/w	"
thiourea	Analar reagent
sodium hydroxide	"
sodium thiosulphate	"
sulphuric acid (98% w/w)	laboratory reagent
sodium hydrosulphide	"
hydrochloric acid (36% w/w)	"
sodium dihydrogen phosphate	"
disodium hydrogen phosphate	"
citric acid	"
dimethylamine (40%)	"
epichlorohydrin	"
ammonia(d=0.880 g/cm^3)	"
methylamine (25-30%)	"
trimethylamine (25-30%)	"
ethanolamine	Analar reagent
ethylenediamine	"
chloro-propionyl chloride	"
dimethylformamide(DMF)	"
pyridine	"

2.2.2 Treatment of cotton with a PAE/thiourea mixture

Apart from the fact that thiourea was included in the pad-liquor, the cotton preparation method was exactly the same as in 2.2.1.

In several cases, further treatment of PAE treated cotton was carried out using two different procedures:

i) Pad-batch(cold):

Cotton samples were padded as in 2.2.1 with the pad-liquor containing the required reagents, batched (sealed in polythene) and washed off in running cold water after the required batching time. The samples were then dried.

ii) Batchwise

Samples were treated with an aqueous solution of the required reagent at a liquor ratio of 20:1 at the boil for 1 hour. The samples were then dried.

In each case, the Hercosett 125 concentration used in the pad-liquor was 200 g/l, sufficient to give 2% Hercosett solids on the weight of fabric when padding to 80% wet pick-up.

2.2.3 Preparation of PAE/ethylenediamine (EDA) treated cotton

Cotton fabric was impregnated with a pad-liquor containing Hercosett 125 (200 g/l), Sandozin NIE (10 g/l) (non-ionic surfactant) and different amounts of ethylenediamine; the pH of the liquor was adjusted to 7 with formic acid. The general cotton preparation conditions were the same as those employed in 2.2.1.

2.2.4 Reaction of cotton with 1,1-dimethyl-3-hydroxy-azetidinium chloride (DMAC)

Cotton fabric was impregnated with the required amount of DMAC using the Benninger laboratory mangle, adjusted to give 80% wet pick-up. The samples were then dried at 100°C for 3 mins and baked at different temperatures for different times.

Some samples of this treated fabric were immediately dyed whilst others were washed thoroughly with water before dyeing.

2.2.5 Reaction of cotton with glycidyl trimethylammonium chloride (Glytac A treated cotton)

Cotton fabric was wetted and padded in the same manner as in 2.2.1. The pad-liquor contained 40 g/l of Glytac A and different concentrations of sodium hydroxide. The wetted and padded (80% pick-up) fabric was then treated at 120°C for 5 minutes using a Werner Mathis AG Steamer/Baker Unit.

2.2.6 Reaction of cotton with N-methylol acrylamide (NMA treated cotton)

Cotton fabric was immersed in a solution containing 110 g/l of N-methylol-acrylamide (45% aqueous solution) and 10 g/l of $ZnCl_2$ and padded to 80% wet pick-up. The wet fabric was pre-dried at 100°C for 2 mins and then baked at 150°C for 5 mins, rinsed thoroughly in tap water and air dried.

2.2.7 Aminization of NMA treated cotton

Following the procedure in 2.2.6, the NMA cotton was further treated in an aqueous solution containing 10 g/l of NaH_2PO_4 and 'V' ml/l of the amine (table 2-1-2); the treatment was carried out at the boil for 60 mins in 120 ml sealed stainless steel dyepots, housed on a rotadyer (John Jeffreys) laboratory dyeing machine at a liquor to goods ratio of 20:1. The samples were then rinsed thoroughly in tap water and air dried.

Pad-batch was used as an alternative method of amination in the case of ethanolamine. In this case a pad-liquor containing 50 ml/l ethanolamine was used, the NMA-fabric was padded to 80% wet pick-up and the sample was batched for 24 hours at room temperature. Thorough rinsing completed the process.

Table 2-1-2: conditions for amination of NMA cotton

amine	V (ml/l)
ammonia (0.880)	30
methylamine (25-30%)	20
dimethylamine (40%)	18
trimethylamine(25-30%)	20
ethanolamine(99%)	2.5

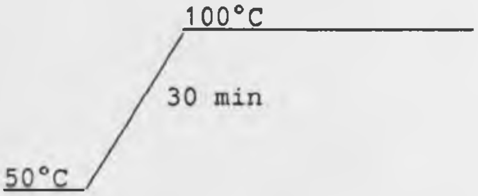
2.2.8 Acylation of cotton with chloropropionyl chloride (CPC cotton)

Cotton fabric was treated in a solution containing 10%(v/v) of chloro-propionyl chloride and 90%(v/v) of DMF at a liquor to goods ratio of 30:1; the treatment was carried out in a glass reactor with continuous stirring, housed in a water bath at a given temperature for 2 hours; the fabric was then rinsed thoroughly in tap water and dried in the open air.

Alternatively. the treatment was also carried out in a Pyrex glass dyepot housed on a Rotadyer (John Jeffreys) laboratory dyeing machine at the temperature required for 2 hours at a liquor to goods ratio of 30:1.

2.2.9 Amination of CPC treated cotton

The CPC cotton was further treated in an aqueous solution containing 10 g/l of NaH_2PO_4 and 'V' ml of amine; the treatment was carried out in 500 ml sealed stainless steel dyepots housed on a rotadyer (John Jeffreys) laboratory dyeing machine at a liquor to goods of 20:1. The oil bath was heated according to the following scheme:



the samples were then rinsed thoroughly in tap water and dried in the open air. The specific conditions for the treatment with each amine are listed in table 2-1-3.

Table 2-1-3: conditions for amination of CPC cotton

amine	V (ml/l)	t (mins)
ammonia (0.880)	150	120
methylamine (25-30%)	175	60
dimethylamine (40%)	125	60
trimethylamine(25-30%)	175	180

2.2.10 Treatment of cotton with a reactive cationic compound (3-carboxyl-1-[4-{4-[4-chloro-6-(3-trimethylammonioanilino)-1,3,5-triazin-2-ylamino]anilino}-6-(3-trimethylammonio-anilino)-1,3,5-triazin-2-yl]=pyridinium trichloride) (Compound I) (see page 60 for structure)

Cotton fabric was treated in a solution containing different concentrations of Compound I and buffer (to give the required pH value) using 100 ml. sealed stainless steel dyepots housed on a Rotadyer (John Jeffreys) laboratory dyeing machine, at a liquor to goods ratio of 20:1 . Treatment was commenced at 50°C, the temperature was raised to the boil over 30 mins and then continued at the boil for a further 60 mins. The fabric was then taken out and rinsed.

2.2.11 Treatment of cotton with the reactive cationic compound 2,4-dichloro-6-(2-pyridinium ethyl amino)-s-triazine chloride (Compound II) (see page 63 for structure)

Cotton fabric was wetted and padded in a similar manner as in 2.2.1. with a pad-liquor containing 60 g/l of Compound II, 10 g/l of Sandozin NIE, 40 g/l of sodium bicarbonate, 20 g/l of sodium carbonate and 120 g/l of Urea. The wetted and padded (80% pick-up) fabric was then batched (sealed in polythene) at room temperature for 24 hours; after batching the fabric was washed thoroughly in running water.

2.3 Dyeing Methods

All dyeings were carried out in 100 ml. sealed stainless steel dyepots housed on a Rotadyer (John Jeffreys) laboratory dyeing machine, at a liquor to goods ratio of 20:1. Dyeing of modified cotton was commenced at 50°C, the temperature was raised to the boil over 25 mins (2°C/min) and dyeing was continued at the boil for a further 60 mins. Untreated cotton was dyed both by the dye manufacturer's recommended method for the particular reactive dye selected and for comparison, by the novel method employed for the modified cottons.

The dyeing of NMA treated cotton with the aliphatic amino-containing dyes was carried out at the boil for 60 minutes under different pH conditions.

The dyed samples were rinsed thoroughly in tap water and cut into two equal portions. One of these portions was soaped in a solution containing 5 g/l of Sandozin NIE(S) and 2g/l of sodium carbonate at the boil for 15 mins (liquor ratio 50:1)---such a severe alkaline soaping process is sufficient to desorb all sulphonated dyes from cotton unless a covalent bond exists between the dye and nucleophilic sites in the fibre.

2.4 Measurements of Dye Exhaustion and Fixation

2.4.1 Exhaustion

The uptake of dye by both pretreated and untreated 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 (λmax) of the dye using a UV-visible Spectrophotometer (PHILLIPS PYE Unicam PU8600). Dyebath exhaustion was calculated using the following equation:

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

A0, A1--- Absorbance of dye solution before and after the process respectively.

2.4.2 Fixation

Measurement of the extent of 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, LR=10:1). This stripping treatment was carried out repeatedly using fresh aqueous pyridine solutions until no further dye was removed, The Kubelka Munck K/S values of the stripped, dyed samples were then measured at λmax using an I.C.S. Micromatch colour measurement system. Assuming K/S was proportional to dye concentration on the fibre the extent of fixation of dye could be calculated using the following equations:

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

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

C1,C2 ---- K/S values of dyed samples before and after
stripping respectively

The fixation value (T%) essentially represents the overall efficiency of the reactive dyeing process and the fixation value (F%) is probably the most useful since as it represents the amount of exhausted (or adsorbed) dye which is fixed covalently, then it gives a direct indication of the amount of dye which has to be removed by a soaping off process to achieve maximum wet fastness properties.

2.5 FTIR Analysis

2.5.1 FTIR analysis of fabric materials

2.5.1.1 IR/Microscopy

IR Microscopy examination of some of the PAE treated and untreated cotton was carried out using a PU 9800(Philips) FTIR Spectrometer. A piece of cotton fabric was taken and a single strand removed using tweezers and a scalpel. This fibre was placed under the stereo Spectra Physics IR microscope and the fibres of this strand teased out using tweezers and a single fibre (approximately 1 cm long) removed. This single fibre was carefully laid flat and flattened using a roller (alternatively pressing the fibre between two polished KBr windows should give the same effect). The pressed fibre was taken and suspended on a microscope sample stage plate using sellotape. The sample was placed on the IR microscope sample stage and focused on the sample using visible light. Once a suitable area of the fibre was located, the area was isolated using the variable apertures and the infrared spectrum recorded.

The microscope had its own dedicated Mercury Cadmium Telluride (MCT-A) detector (range 7000-750 cm-1) and the data collection parameters used were 250 scans at 8cm-1 resolution using a fast mirror speed and normal apodisation.

2.5.1.2 IR/diffuse reflectance

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. The operation procedure involves cutting an approximately 8 mm square of fabric and placing it on a bed of KBr powder before recording a spectrum. The standard data collection parameters are as follows:

> Resolution = 4 cm-1; detector = DTGS; No. of scans = 100;
> scan range = 4000 - 400 cm-1; gain = 1; mirror velocity = normal;
> apodisation = normal.

The following is a brief overview of the theory of diffuse reflectance spectroscopy for solid samples. When incident infrared radiation falls onto a sample surface, one of several processes can occur: it can be absorbed, it can be reflected from the surface of the sample (so called specular reflectance), or it can penetrate the sample before being scattered (figure 2-1-1). This latter effect is known as diffuse reflectance, and it is this radiation that the technique of diffuse reflectance infrared spectrometry (DRIFFTS) measures. This technique is applicable to most solids especially to these solids with rough surfaces, involves little or no sample preparation, and avoids the unnecessary complications of absorption due to solvents or mulling agents.

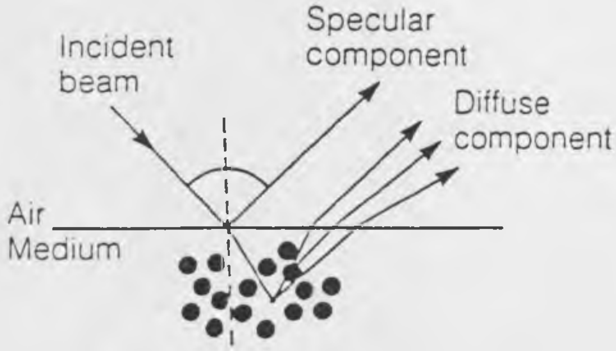


Figure 2-1-1 Illustration of diffuse reflectence infrared spectrometry

2.5.1.2 IR/attenuated total internal reflectance (ATR)

Attenuated total internal reflectance (ATR) has been established as a method of choice for the analysis of samples which are either too thick or too strongly absorbing to analyse by transmission techniques without complicated sample preparation. The theory of this technique involves the phenomenon of internal reflection reported for infrared spectroscopy in 1959. It was observed that if certain conditions were met, infrared radiation entering a prism (ATR crystal) made of a high-refractive-index infrared material would be totally internally reflected. This internal reflectance creates a wave, called the evanescent wave, which extends beyond the surface of the crystal into the sample held in intimate contact with the crystal. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will interact with the sample and a spectrum is obtained. Because the evanescent wave decays very rapidly with distance from the surface, it is important to have the sample in intimate contact with the crystal.

In the present study, IR analysis of both treated and untreated cotton was carried out using the Perkin Elmer 1740 Infrared Fourier Transform

Spectrometer using a vertical ATR attachment to obtain IR spectra. Two pieces of fabric which have been cut into the same size as that of the crystal were placed on either side of the crystal, ensuring that good surface contact is made between the sample and crystal. The standard data collection parameters were as follows:

Resolution = 4 cm-1; detector = DTGS; No. of scans = 100;
scan range = 4000 - 400 cm-1; gain = 4; mirror velocity = normal;
apodisation = normal.
ATR crystal: KRS5 (Spectra Tech)

2.5.2 FTIR analysis of solids,solutions and liquids

i) Solids

FTIR analyses of Procion Red H8BN (ICI) (CI Reactive Red 58), the alkyl amino dye and all other solids prepared during this study were carried out using the Perkin Elmer 1740 Fourier Transform Infrared Spectrometer and the diffuse reflectance attachment. Samples were prepared by mixing 1 mg of sample in 200 mg of potassium bromide (KBr).

ii) solutions and liquids

FTIR analysis of liquid 1,1-dimethyl-3-hydroxy-azetidinium chloride (DMAC) was carried out using the same spectrometer with the contact sampler. The contact sampler is a horizontal internal reflectance accessory (ATR) designed to simplify the FTIR analysis of powders, pastes, gels, semi-solids, films and liquids. With a horizontal "face-up" sampling surface, it allows convenient sample handling of virtually all materials. Figure 2-1-2 shows a simplified diagram for the contact sampler. In this diagram, the sampling surface is the top surface of the crystal. IR radiation from the spectrometer is directed up to the bevelled, input face of the ATR crystal. It then reflects through the crystal, passing "into" the sample a small finite distance with each reflection along the top surface. At the output end of the crystal, the beam is directed down to a reflecting surface and back into the normal beam path of the spectrometer. The contact sampler is available with a choice of two different sampling plates (the flat sampling plate version for solid samples and the trough sampling plate version for liquids). In the present analysis, the trough sampling plate version was chosen. The liquid sample was simply poured onto the trough without further sample preparation. The spectra were obtained using the following standard data collection parameters:

Resolution = 4 cm-1; detector = DTGS; No. of scans = 100;
scan range = 4000 - 400 cm-1; gain = 4; mirror velocity = normal;
apodization = normal.
ATR crystal: ZnSe (Spectra Tech).

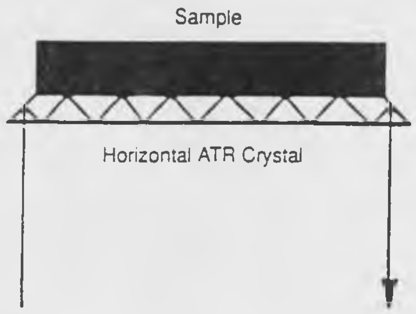


Figure 2-1-2 Simplified diagram for the contact sampler

2.6 Chromatographic Analysis

2.6.1 HPLC analysis of dyes

The purity of the aliphatic amino dyes was checked either on a Perkin-Elmer Series 10 Liquid Chromatograph or a Varian VISTA Series 5000 liquid Chromatograph using a Hypersil C8 column. This commercially available column is made through the reaction of alkyl C8 trichlorosilane ($C_8H_{17}SiCl_3$) with silanol groups on the surface of the silica particle to bond the functional group ($-O-Si-C_8H_{17}$) to the silica support. Detection was with a variable wavelength UV-VIS detector at the wavelength of maximum absorbance of the dye. The mobile phase used in this analysis was a mixture of water/methanol; it also contained 0.001 mole of tetrabutylammonium bromide as an ion-pairing reagent, 0.5 ml/l of 20% (w/w) acetic acid and 0.5 ml/l of 5% (w/w) of potassium hydroxide as a buffer. Specific HPLC running conditions for each dye were as follows:

Red dyes (CI Reactive Red 58 and its amine modified form):
Flow: 1.0 ml/min, Detector wavelength setting: 550 nm,
Eluent composition: water/methanol = 50/50.
Blue dye (CI Reactive Blue 5 and its amine modified form):
Flow: 1.0 ml/min, Detector wavelength setting: 600 nm,
Eluent composition: water/methanol = 48/52.
Yellow dye (CI Reactive Yellow 81 and its amine modified form):
Flow: 1.0 ml/min, Detector wavelength setting: 410 nm,
Eluent composition: water/methanol = 42/58.

2.6.2 Determination of CPC fixation on cotton by Ion Chromatography

The extent of CPC cotton esterification was measured both by fabric weight gain (2.8.2) and Ion Chromatography. In the latter case, a Varian 2510 HPLC pump, a PRP-X100 IC Anion column and a Varian CM-2 Conductivity Monitor were used. The mobile phase used in this analysis consisted of 2 mmol/l of phthalic acid, 10% of acetone (pH 5, conductivity approx. 180 µS/cm). The flow rate for this analysis was 7.5 ml/min and the volume for each injection was 10 µl.

Ion chromatographic separations occur by ion exchange on stationary phases with charged functional groups. The corresponding counter ions are located in the vicinity of the functional groups and can be exchanged with other ions of the same charge in the mobile phase. For every ion, the exchange process is characterized by a corresponding ion exchange equilibrium, which determines the distribution between the mobile and stationary phase, for example in the present case (anion exchangers):

$$E^-_{stat} + A^-_{mob} \rightleftharpoons A^-_{stat} + E^-_{mob}$$

$$K_A = \frac{[A^-]_{stat} \quad [E^-]_{mob}}{[A^-]_{mob} \quad [E^-]_{stat}}$$

where, A: sample anion,

E: eluent anion (counter ion).

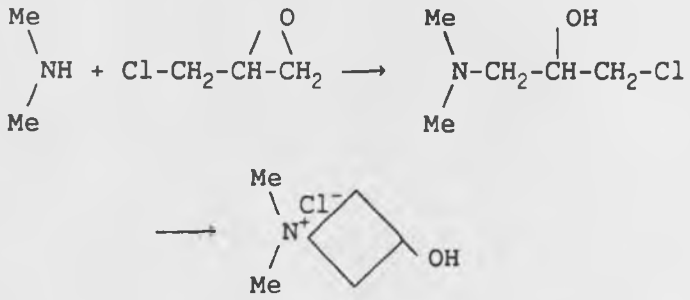
The various ionic components of a sample can thus be separated on the basis of their different affinities for the stationary phase of the ion exchanger (different equilibrium constants K).

The PRP-X100 IC anion column employs a copolymer of styrene and divinylbenzene as the support; the anion exchanging groups are obtained by chloromethylation of this copolymer followed by amination.

2.7 Synthesis

2.7.1 Synthesis of 1,1-dimethyl-3-hydroxy-azetidinium chloride(DMAC)

DMAC was prepared in a similar manner to the method proposed by Gaertner (88) who started with diethylamine to make 1,1-diethyl-3-hydroxy-azetidinium chloride. Dimethylamine (1M) was cooled to 0-5°C and epichlorohydrin (1M) slowly dripped in over 20 minutes, The reaction mixture was stirred for 2 hours at 0-5°C and then left to warm to 20°C for 16 hours. The liquid product was found to be completely water soluble. The following reaction scheme is appropriate:



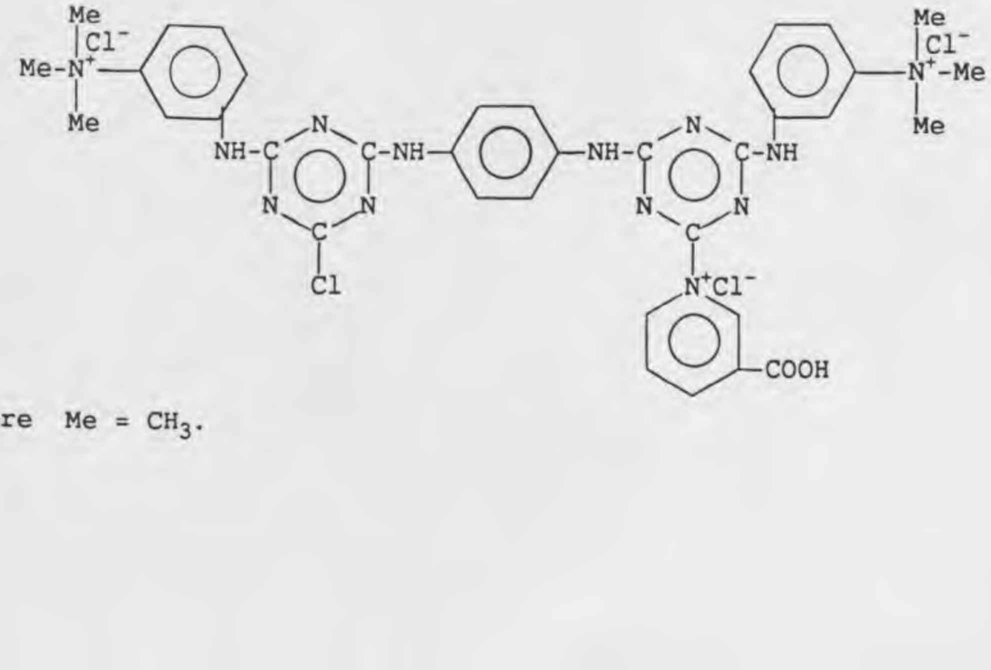
Scheme 2-7-1

where Me = CH_3.

2.7.2 Synthesis of 1,1-diethyl-3-hydroxy-azetidinim chloride (DEAC) and 1,1-diethylol-3-hydroxy-azetidinium chloride (DEOAC)

Apart from using diethylamine instead of dimethylamine, the method used for preparation of DEAC and DEOAC was exactly the same as in section 2.7.1.

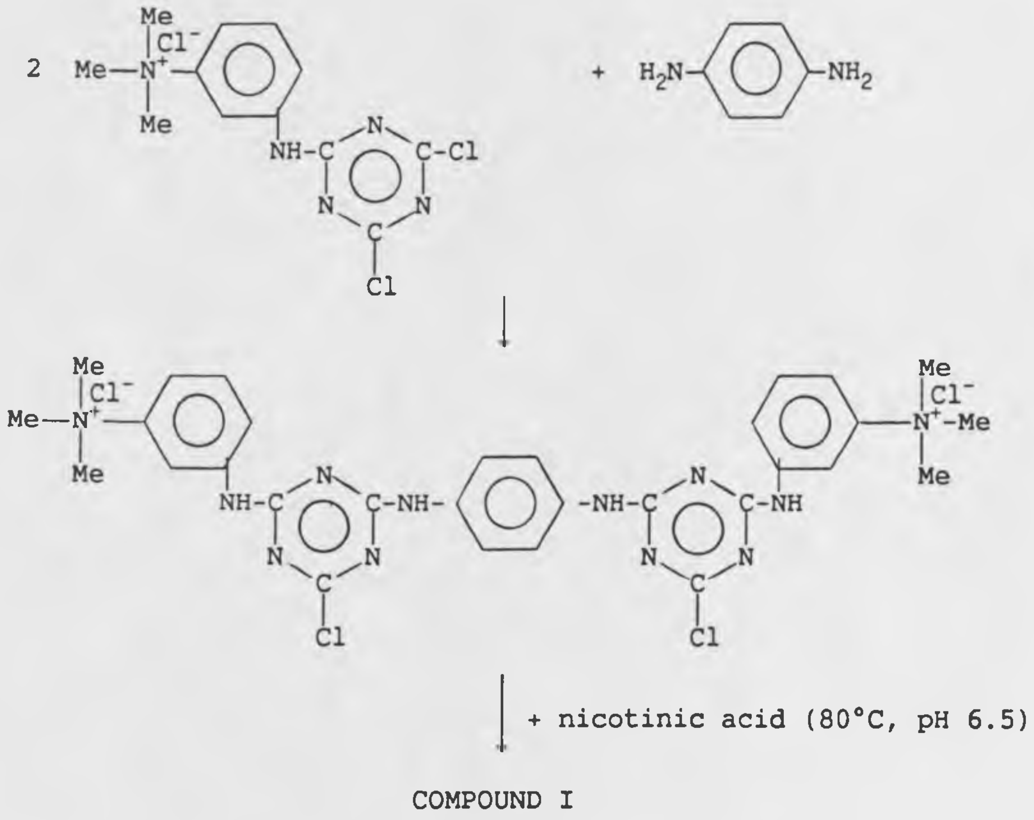
2.7.3 Synthesis of (3-carboxyl-1-[4-{4-[4-chloro-6-(3-trimethylammonio-anilino)-1,3,5-triazin-2-ylamino]anilino}-6-(3-trimethylammonio-anilino)-1,3,5-triazin-2-yl]=pyridinium trichloride)(Compound I)



where Me = CH_3.

A solution of 2,4-dichloro-6-(3'-trimethylammoniumanilino)-s-triazine chloride(1.97 g, 0.005 mole) in distilled water(70 ml) was stirred at 30-35°C and *p*-phenylenediamine (0.27 g, 0.0025 mole) was added. Immediately after this addition, the pH was maintained at 5-6 by adding 2M aqueous solution of KOH as required. The reaction was followed using a special dichloro-s-triazine detection test (to a drop of the reaction mixture on a piece of filter paper, add a few drops of 25% pyridine aqueous solution and a few drops of 2M KOH; a yellow colour appears spontaneously if dichloro-s-triazine is present). After the reaction was completed, nicotinic acid (0.31 g, 0.0025 mole) was added to the reactor and the temperature was raised to 80°C while maintaining the pH at 6.5-7. The reaction was run under these conditions for two hours and the product was then precipitated with acetone, filtered off and washed with acetone (yield 2.1 g).

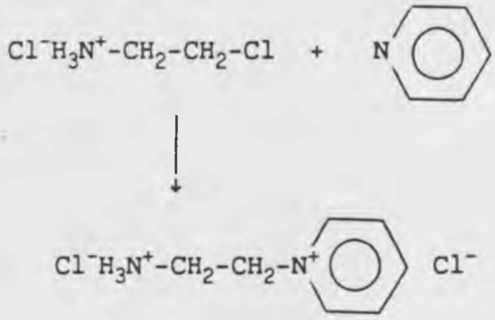
The reaction may be written as scheme 2-7-2.



Scheme 2-7-2

2.7.3 Synthesis of N-(2-aminoethyl) pyridinium chloride hydrochloride

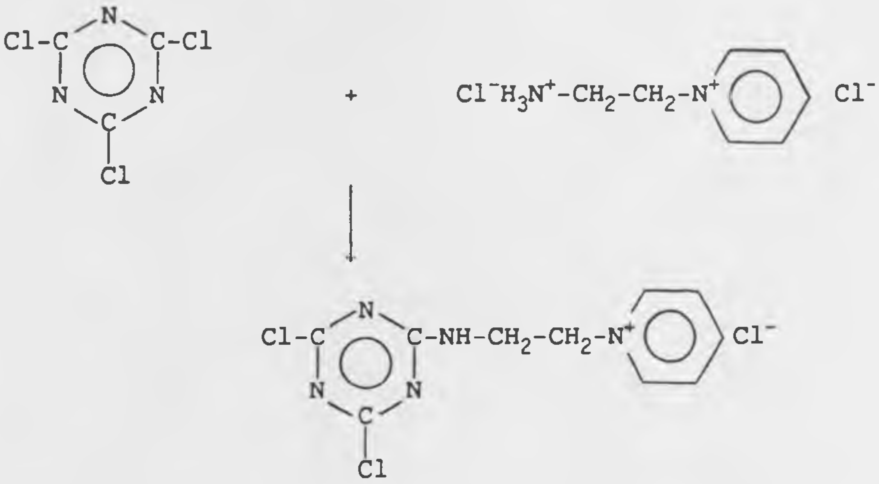
An aqueous solution (75 ml) containing 2-chloro-ethylamine hydrochloride (21 g) was mixed with pyridine (62.5 ml) and heated under reflux for two hours. The two-phase mixture was extracted with ether (three portions, each 100 ml), the aqueous layer acidified to pH 2 with concentrated hydrochloric acid and evaporated leaving a straw-coloured oil which slowly solidified to a white solid. This was stirred with isopropanol, filtered off and dried to give N-(2-aminoethyl) pyridinium chloride hydrochloride (29.74g). The reaction scheme may be written as follows:



Scheme 2-7-3

2.7.4 Synthesis of 2,4- dichloro-6-(2-pyridinoethylamino)-s-triazine chloride (Compound II)

A solution of cyanuric chloride (18.4 g, 0.1 mole) in acetone (100 ml) was added to a stirred mixture of ice (100 g) and water (100 ml); a solution of N-(2-aminoethyl) pyridinium chloride hydrochloride (19.5 g, 0.1 mole), which had been adjusted previously to pH 7 using 2M KOH as required, was run into the suspension over 10 min. Following this addition, the pH was maintained slightly above 4, and finally, when pH fluctuation ceased, raised to 6.5 by adding 2M KOH as required, the temperature being kept below 5°C throughout. The mixture was then left in the fridge overnight and the precipitate was filtered off, washed with acetone and dried in vacuo (32.5 g).

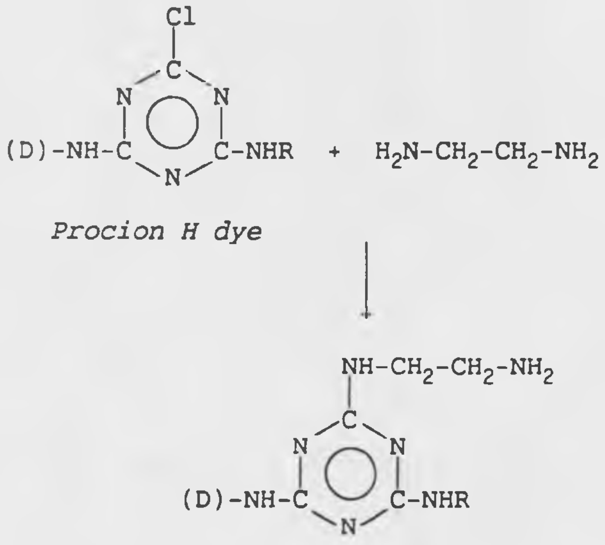


Scheme 2-7-4

2.7.5 Synthesis of alkyl-amino dyes

50 ml of 50% (v/v) ethylenediamine aqueous solution was stirred and heated to the boil on a magnetic stirrer-heater unit; 50 ml of 5% aqueous Procion Red H8BN(ICI) (monochlorotriazine reactive dye) dye solution was added dropwise over 15 mins. The mixture was then stirred and refluxed for another 2 hours. The product was salted out, filtered off, washed with a solution of 200 g/l salt and dried at 60°C. This reaction may be written as scheme as scheme 2-7-5.

The synthesis of the blue alkyl-amino dye (from Procion Blue P-RG, CI Reactive Blue 5), yellow alkyl-amino dye (from Procion Yellow H-E3G, CI Reactive Yellow 81) and another red one (from Procion Red H-E3B, CI Reactive Red 120) was carried out in the same manner as the above.



Scheme 3-7-5

where (D) = sulphonated chromophore.

2.8 Fixation of Colourless Chemicals on Cotton

2.8.1 Total nitrogen determination

The total nitrogen content of the treated fibre was measured according to ASTM standard D1013-81 [89] (standard test method for total nitrogen in resins and plastics). The detailed operation procedure was as follows:

10 g of fabric samples, which had been cut into small pieces (about 1 cm^2) and weighed to the nearest 1 mg, were transferred to a Kjeldahl flask. 0.7 g of HgO, 10 g of K_2SO_4, and 60 ml of H_2SO_4 (sp gr 1.84) were then added to the flask, the contents of the flask were thoroughly mixed and heated slowly at first until the frothing subsided. Temperature was increased until the acid boiled briskly, and the digestion continued for 2 h after the solution became colourless or nearly so.

After allowing the flask to cool, about 500 ml of water and a few boiling aids to prevent bumping were added. A mixture containing 30 ml of $Na_2S_2O_4$ solution (80 g/l) and 85 ml of NaOH solution (760 g/l) was prepared and poured slowly down the side of the flask so that it did not mix at once with the acid solution. The flask was immediately connected to the bulb and condenser, and the contents of the flask were mixed thoroughly.

The solution was distilled into 50 ml of 0.5 N HCl, making certain that the connecting tube from the condenser extends below the surface of the acid in the receiver. The distillation was continued until the ammonia had been collected in the receiver in about 300 ml of distillate.

5 to 7 drops of methyl red indicator solution were added to the distillate and the excess acid in the distillate was titrated with 0.5 N NaOH solution.

A blank determination was made, following the same procedure and using the same amounts of all reagents.

The percentage of nitrogen was then calculated as follows:

$$\text{Nitrogen \%} = [((B-V)N\ 0.014)/S] * 100]$$

where:

B = millilitres of NaOH solution required for titration of the blank,

V = millilitres of NaOH solution required for titration of the specimen,

N = normality of the NaOH solution, and

S = grams of specimen used.

2.8.2 Weight gain

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

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

W1, W2----weights of samples before and after treatment respectively.

2.8.3 UV absorbance

2.8.3.1 Determination of fixation of 2,4- dichloro-6-(2-pyridiniumethylamino)-s-triazine chloride on cotton

Cotton fabric was cut into rectangles each of which had a weight of exactly 1.00 gram. The rectangular pieces were impregnated using the Benninger laboratory mangle. The pad liquor contained 60 g/l of 2,4-dichloro-6-(2-pyridiniumethylamino)-s-triazine chloride, 40 g/l of sodium bicarbonate, 20 g/l of sodium carbonate, 120 g/l of urea and 10 g/l of Sandozin NIE. The pressure on the mangle was adjusted to give 95% pickup. The samples were then sealed with polythene film and batched for the required period. The sample was then taken out and rinsed with distilled water 10 times (using 100 ml of distilled water each time). The rinse water was then collected in a 1000 ml volumetric flask and made up to the mark with distilled water. The UV absorbance of the solution was then measured at the wavelength of maximum absorption (λmax = 229 nm) of the compound using a UV-visible Spectrophotometer (PHILLIPS PYE Unicam PU8600). The fixation of the compound was calculated using the following equation:

$$\text{Fixation} = 100(1-Ai/A0)\%$$

A0, Ai--- UV absorbance of the solution collected from 0 hr and i hr respectively.

2.8.3.2 Determination of fixation of DMAC and Glytac A on cotton

The determination of the fixation of these two compounds on cotton were carried out in the same manner as in 2.8.3.1. In some cases, the diluted aqueous extract solution was collected from the samples which were treated using a pad thermasol method.

2.9 Textile Testing

Fabrics were tested according to BS, AATCC and ASTM standard procedures. Specific tests used were: BS C04-1978, colour fastness to washing; BS B02-1978 colour fastness to light: Xenon arc, continuous light; AATCC test method 66-1984, wrinkle recovery of fabrics: recovery angle method; ASTM: D-1682(1975) breaking strength and elongation of textile Fabrics(1R method).

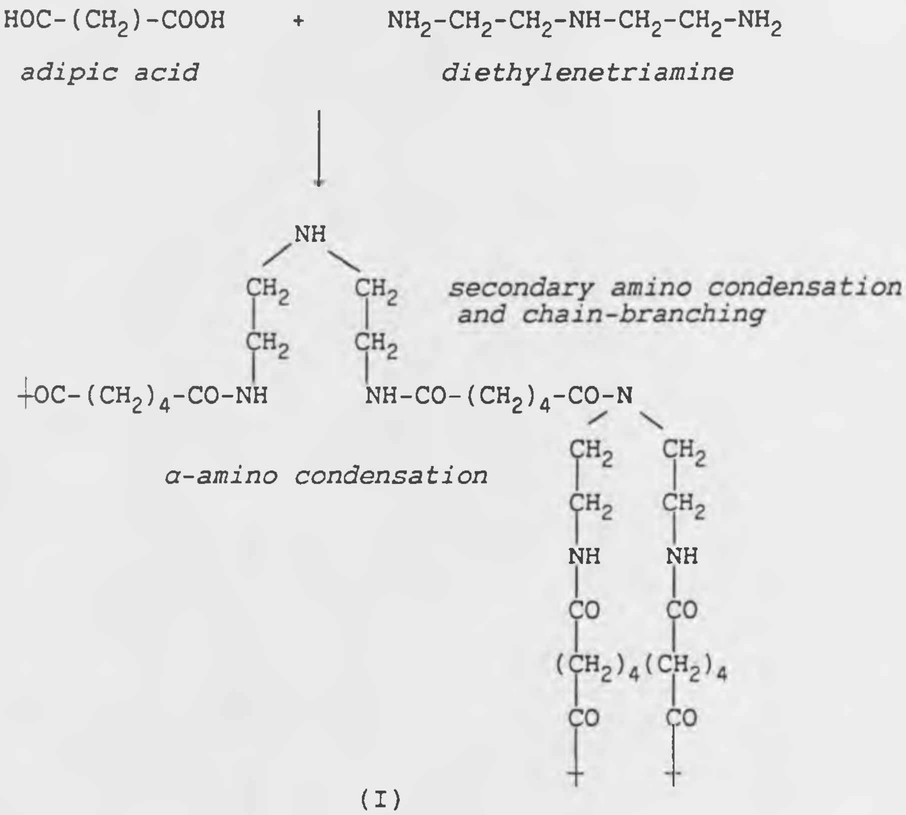
CHAPTER III

III MODIFICATION OF COTTON WITH POLYAMIDE-EPICHLOROHYDRIN (PAE) RESIN AND ITS DERIVATIVES

3.1. Pretreating Cotton with PAE Resin

3.1.1. Chemistry of PAE resin

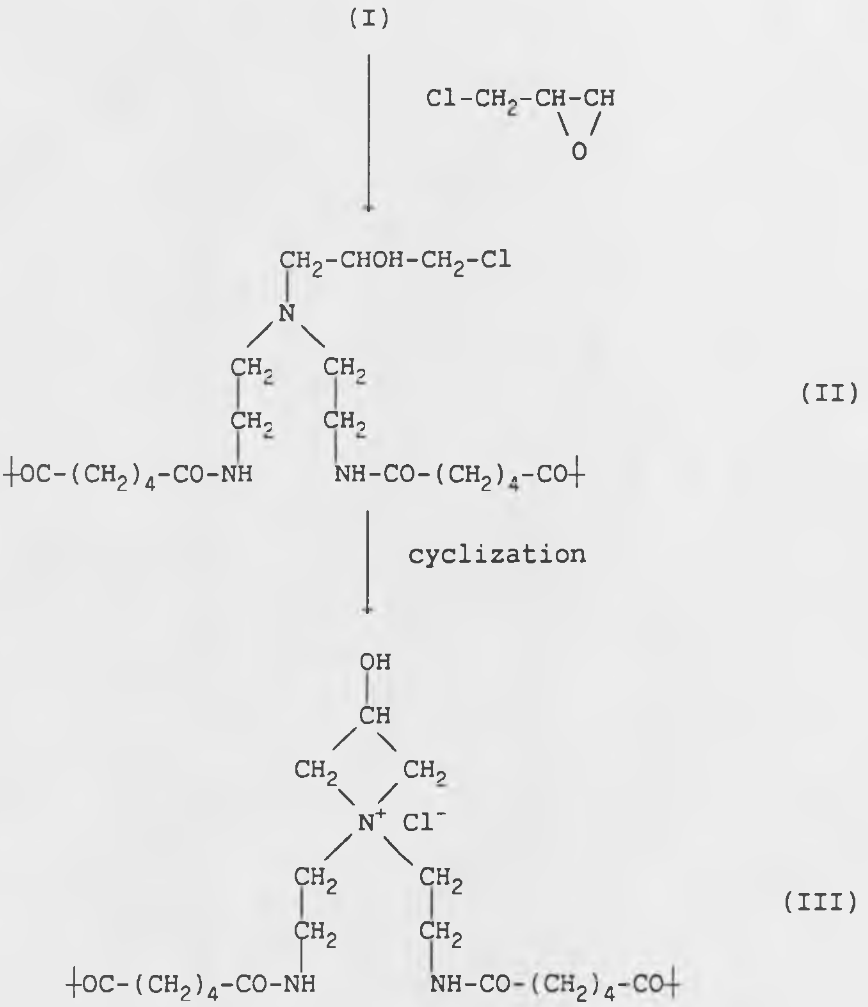
The preparation of polyamide epichlorohydrin resin involves three seperate reactions [90, 91]. The polyaminamide is firstly obtained through the reaction of adipic acid with diethylenetriamine (scheme 3-1-1):



(I)

Scheme 3-1-1

This water-soluble branched polyaminamide is then reacted with epichlorohydrin in the presence of a weak base and the product formed cyclized to produce a fully quaternized polymer (scheme 3-1-2):



Scheme 3-1-2

A study [92] on the chemistry of the above preparation using ^{15}N-NMR and ^{13}C-NMR has shown that alkylation of (I) by epichlorohydrin is 30-40 times faster than cyclization of (II), whilst cyclization is approximately 300-400 times faster than hydrolysis of the azetidinium ring in compound (III).

At room temperature under acidic conditions ($pH < 5$) PAE resin is quite stable due to the low rate of hydrolysis, however, at higher temperature the stability of this polymer becomes poor. This was shown by heating 20% (by weight) aqueous solutions of (III); insoluble gels were formed within

5-10 min.. The reason for this is that unreacted secondary amino groups and ionized OH groups of the side chain undergo crosslinking by attacking the highly electrophilic azetidinium rings. It is, however, most likely that the highly nucleophilic secondary amino groups are most involved in crosslinking.

3.1.1. Theoretical considerations of cotton modification to improve its reactive dyeability

The efficiency of the reaction between dye and substrate in a reactive dyeing system depends on a few factors including the reactivity of the dye, the reactivity of the substrate and the substantivity of the dye for the substrate. It therefore appears necessary to theoretically analyse the reactive system, to get a clear picture regarding which factors should be altered when carrying out cotton modification to improve the reactive dyeability of the fibre.

Danckwert's equation [93] for a diffusing reacting substance gives:

$$dQ/dt=[D]_F\ (Dk'_f)^{1/2} \qquad (3.1)$$

where dQ/dt = rate of sorption of reactive dye per unit area of surface, which can be equated to the rate of fixation or covalent bond formation (since the material is considered to be infinitely thick and all the dye which enters will be fixed);

$[D]_F$ = equilibrium concentration of dye at the surface of the material;

D = diffusion coefficient of dye in the material;

k'_f = first-order or pseudo-first-order reaction constant for the reaction between dye and substrate;

and since there are two competing reactions taking place in the dye bath, the efficiency of dye fixation(E) is given by equation (3.2) [94].

$$E = \frac{\text{rate of dye fixation}}{\text{rate of dye hydrolysis}}$$

$$\left(\frac{S}{L}\right)\left(\frac{[D]_F}{[D]_S}\right)\left\{\left(\frac{D}{k'_H}\right)\left(\frac{R_F[\text{cell-O}^-]}{[OH^-]}\right)\right\}^{1/2} \tag{3.2}$$

where S = the surface area of the substrate;

L = the liquor ratio;

$[D]_F/[D]_S$ = substantivity ratio of the dye;

R_F = the ratio of the bimolecular rate constants (i.e. fixation/ hydrolysis), (R_F is a constant for a given dye over a wide range of alkaline pH values);

$[\text{cell-O}^-]/[OH^-]$ = the ratio of cellulosate anion and hydroxyl anion concentrations;

k'_H= first-order or pseudo-first-order reaction constant for the reaction between dye and water.

For a given dye and given dyeing conditions, S,L,D and k_H' can each be considered to be constant, and so equation (3.2) can be re-written in the form of equation (3.3):

$$E = \left(\frac{S}{L}\right)\left(\frac{D}{k'_H}\right)^{1/2}\left(\frac{[D]_F}{[D]_S}\right)\left\{\left(\frac{R_F[\mathrm{cell}\text{-}O^-]}{[OH^-]}\right)\right\}^{1/2} \qquad (3.3)$$

$$= A * [\text{the substantivity ratio of the dye}] * [\text{the reactivity of the substrate}]$$

where $A = (S/L)(D/k'_H)^{1/2}$ = constant.

From equation(3.3), it can be seen that for a given dyeing system, there are two factors which affect the efficiency of dye fixation, namely the substantivity of the dye for the substrate and the reactivity of the substrate. In conventional dyeing methods, these two factors are controlled by adding a large amount of electrolyte (e.g. common salt or sodium sulphate) and alkali to the dye bath which leads to the problems previously mentioned.

In the case of cotton modification to improve reactive dyeability, the two factors discussed above should also be born in mind. Ideally, modification should introduce functional groups into the cotton which not only improve the substantivity of the reactive dye for the cotton but also possess reactivity towards reactive dyes or, alternatively, provide a catalyst system which can promote the reaction between the cellulosic fibre and the reactive dye.

It has been shown by earlier workers[73,75,80,96,97] that the introduction of cationic groups into cellulosic fibres can increase the substantivity of anionic dyes for the fibre. However, there have been few modifications thus far which introduce reactive functional groups.

From its chemistry, a commercial polymer, Hercosett 125 (Hercules Powder Corp.), was considered to possess the ability to impart to cotton increased substantivity and reactivity towards reactive dyes. Hercosett 125 contains azetidinium groups[91] which on drying may react with nucleophilic sites in cotton or in the polymer itself thus fixing the polymer to the substrate; furthermore, Bates showed that after drying the resin on paper, only a limited amount of crosslinking was required to immobilise the polymer, some 65-70% of unreacted azetidinium groups remaining [95]. Thus because of the cationic nature of these residual azetidinium groups and the presence of unmodified highly nucleophilic secondary and tertiary amino groups, pretreatment of cotton with Hercosett 125 offers the opportunity for increasing both the substantivity and the reactivity of cotton towards reactive dyes under neutral or acidic conditions.

Cellulose when modified with this reactive polyamide epichlorohydrin resin thus has a reactive surface which may be represented as containing the reactive and nucleophilic sites illustrated in figure 3-1-1. Under the conditions subsequently employed to apply the PAE resin to the cotton the formation of resin - fibre covalent bonds is regarded as highly unlikely.

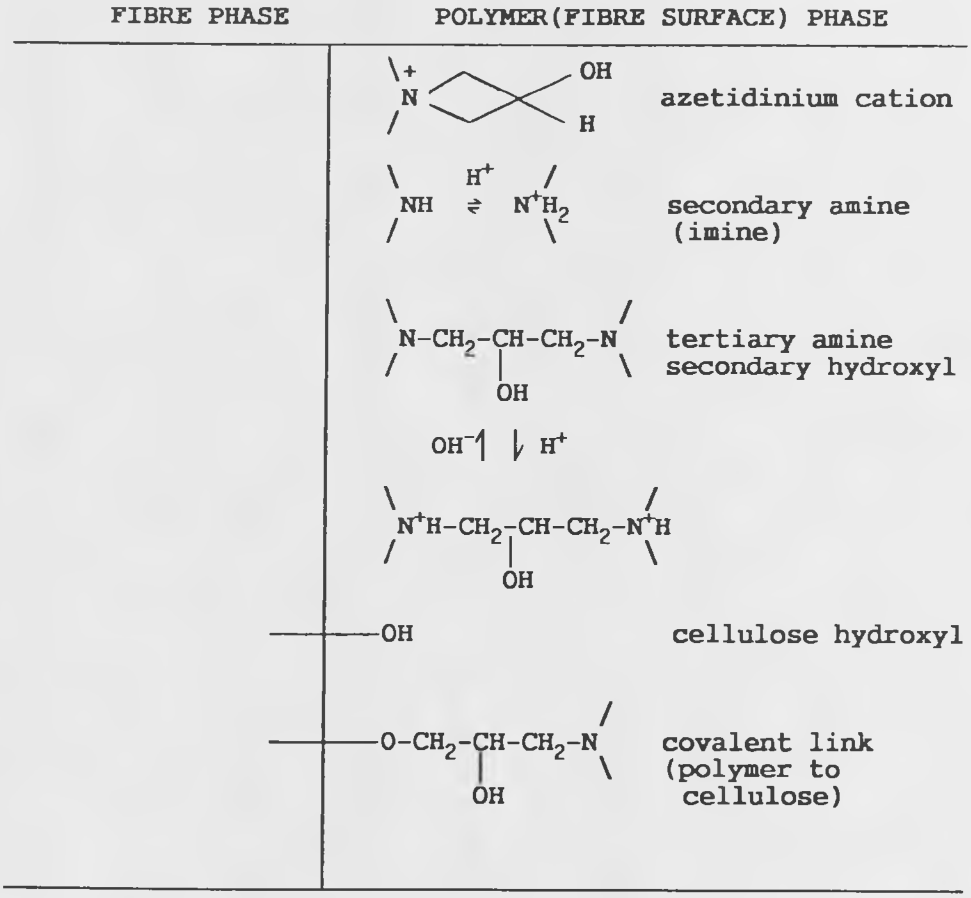


Figure 3-1-1.: Illustration of reactive surface of Hercosett treated cotton

3.1.2. Detection of PAE resin on treated cotton

FTIR analysis was carried out using the IR plan microscope on treated and untreated single cotton fibre and the IR Spectra obtained are shown in figures 3-1-2 and 3-1-3. Figure 3-1-4 shows the spectrum obtained by subtracting figure 3-1-3 from figure 3-1-2. Strong absorbance bands at 1550 and 1650 cm-1 correlate well with previous data obtained by Cockett and Lewis [98] for Hercosett resin precipitated from solution with acetone.

3.1.3. Effect of PAE pretreatment on the rate of uptake and fixation of reactive dyes on cotton

Cotton was pretreated by padding and drying with a solution containing Hercosett 125 (2% owf)(200g/l of 12.5% aqueous Hercosett solution) and Sandozin NIE(10g/l). The treated and untreated cotton samples were dyed separately with Verofix Red FBL(2% owf.) at pH 7, 80°C for different time periods.

Figures 3-1-5 and 3-1-6 show the rate of dye uptake and fixation of Verofix Red FBL on both treated and untreated cotton. It is clear that pretreatment with Hercosett 125 markedly increases both the rate and final extent (ie. after 60 mins) of dye uptake and fixation under the neutral conditions used.

3.1.4. Effect of PAE resin concentration on dye exhaustion and fixation

Various amounts of PAE resin (0 - 300 g/l in the pad liquor) were applied to cotton fabric by the pad-dry procedure and the treated fabric dyed with Verofix Red FBL (2% owf).

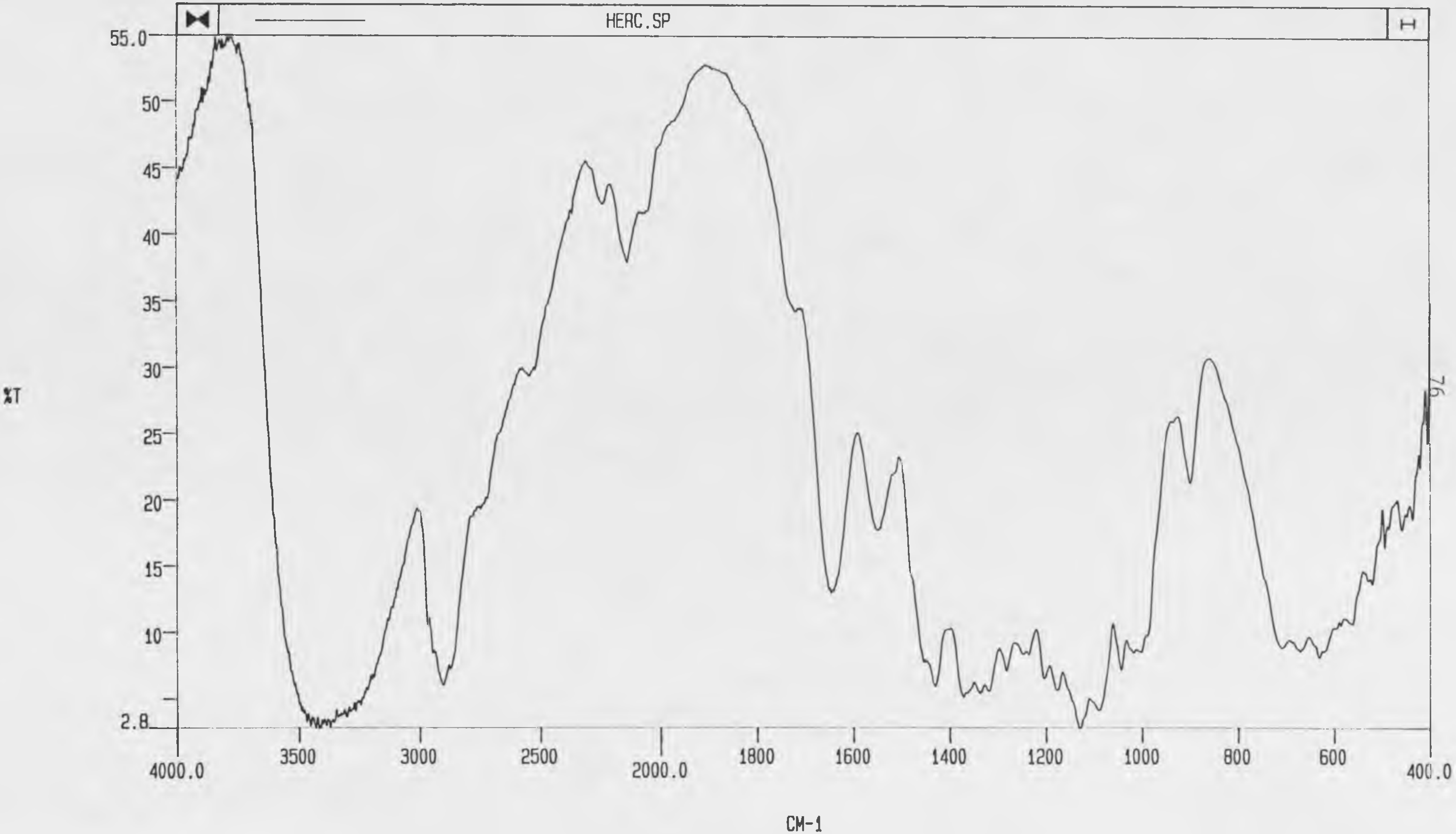


Figure 3-1-2 Infrared spectrum of Hercosett (PAE) treated cotton

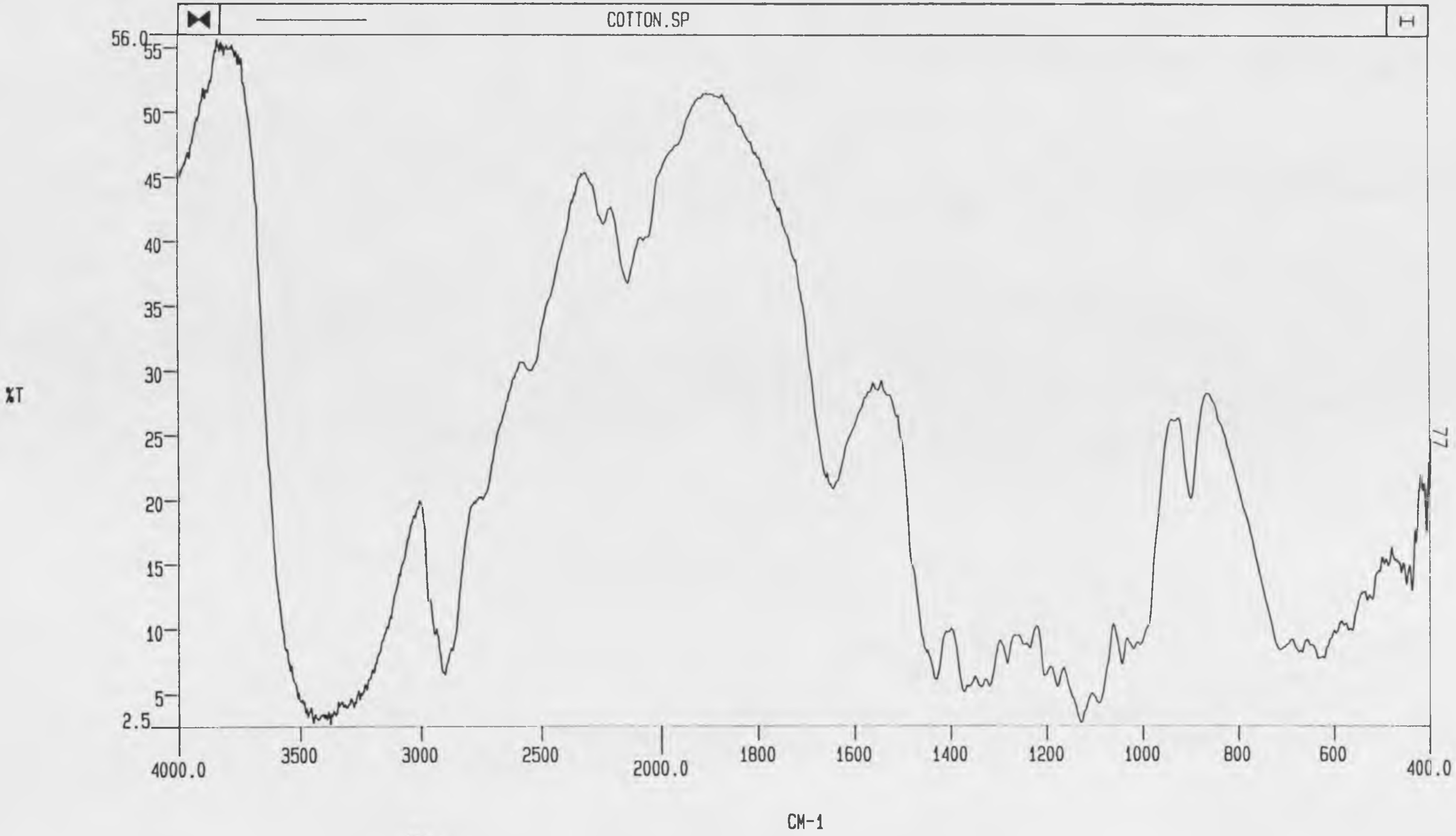


Figure 3-1-3 Infrared spectrum of untreated cotton

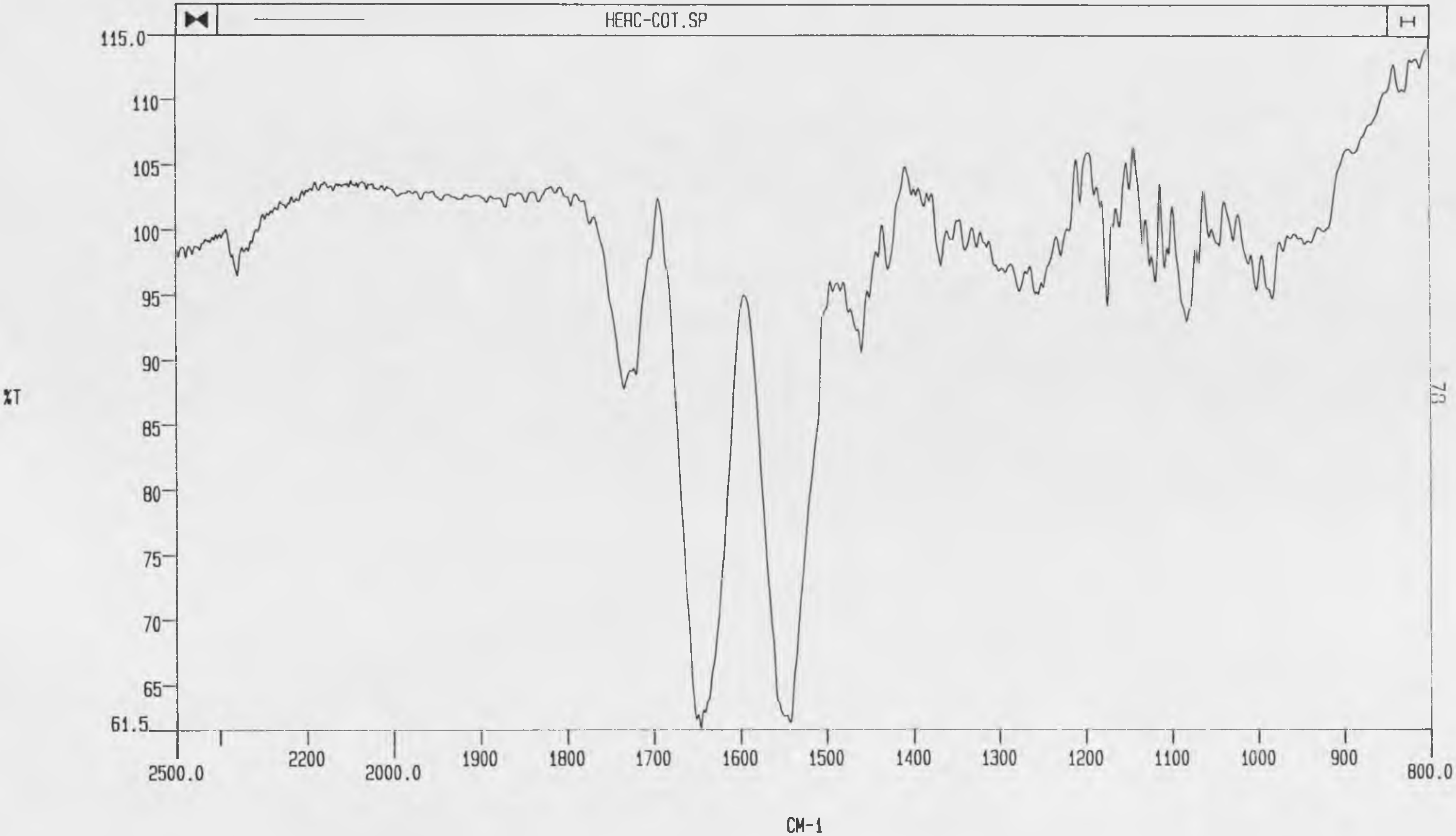
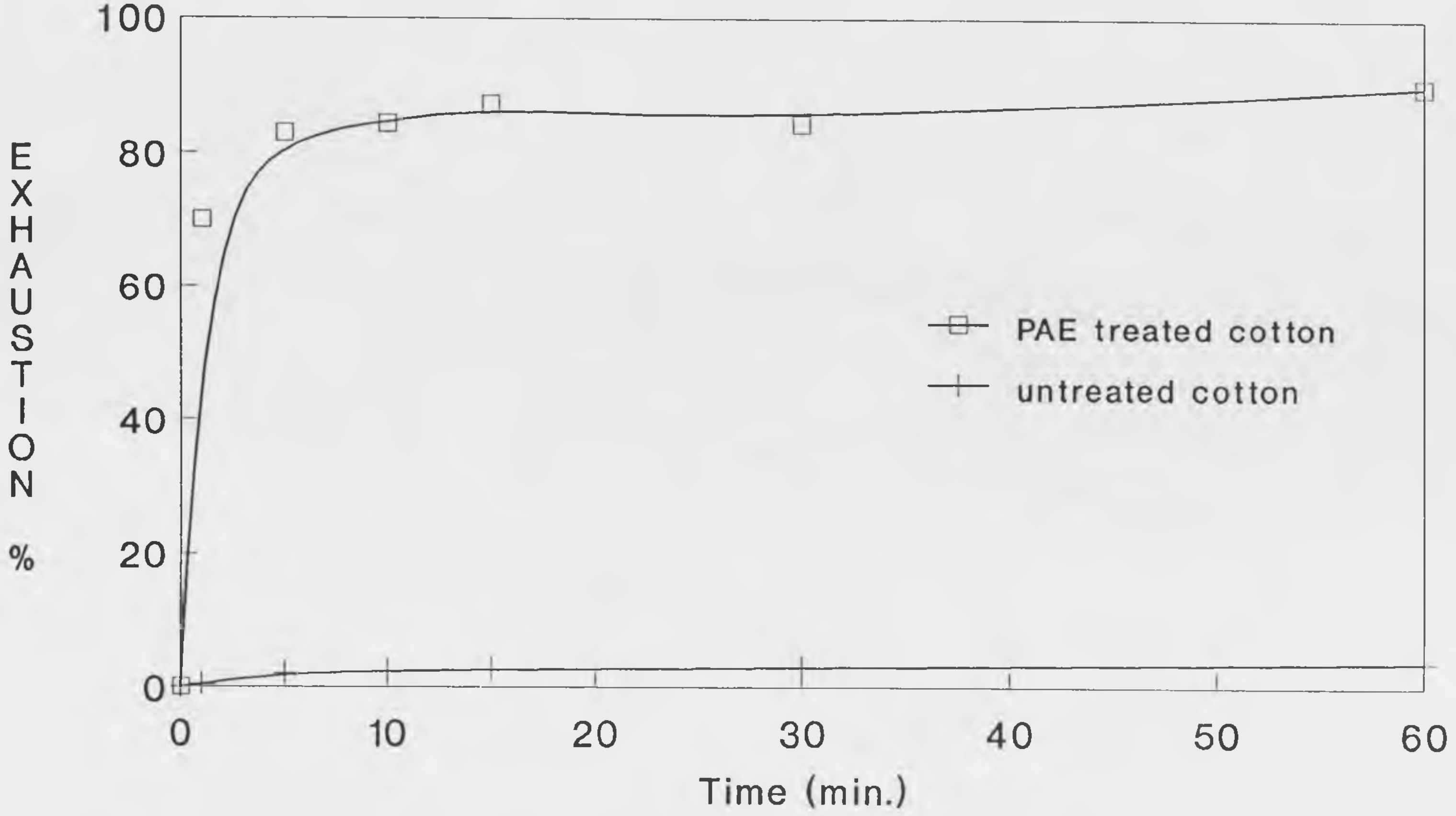


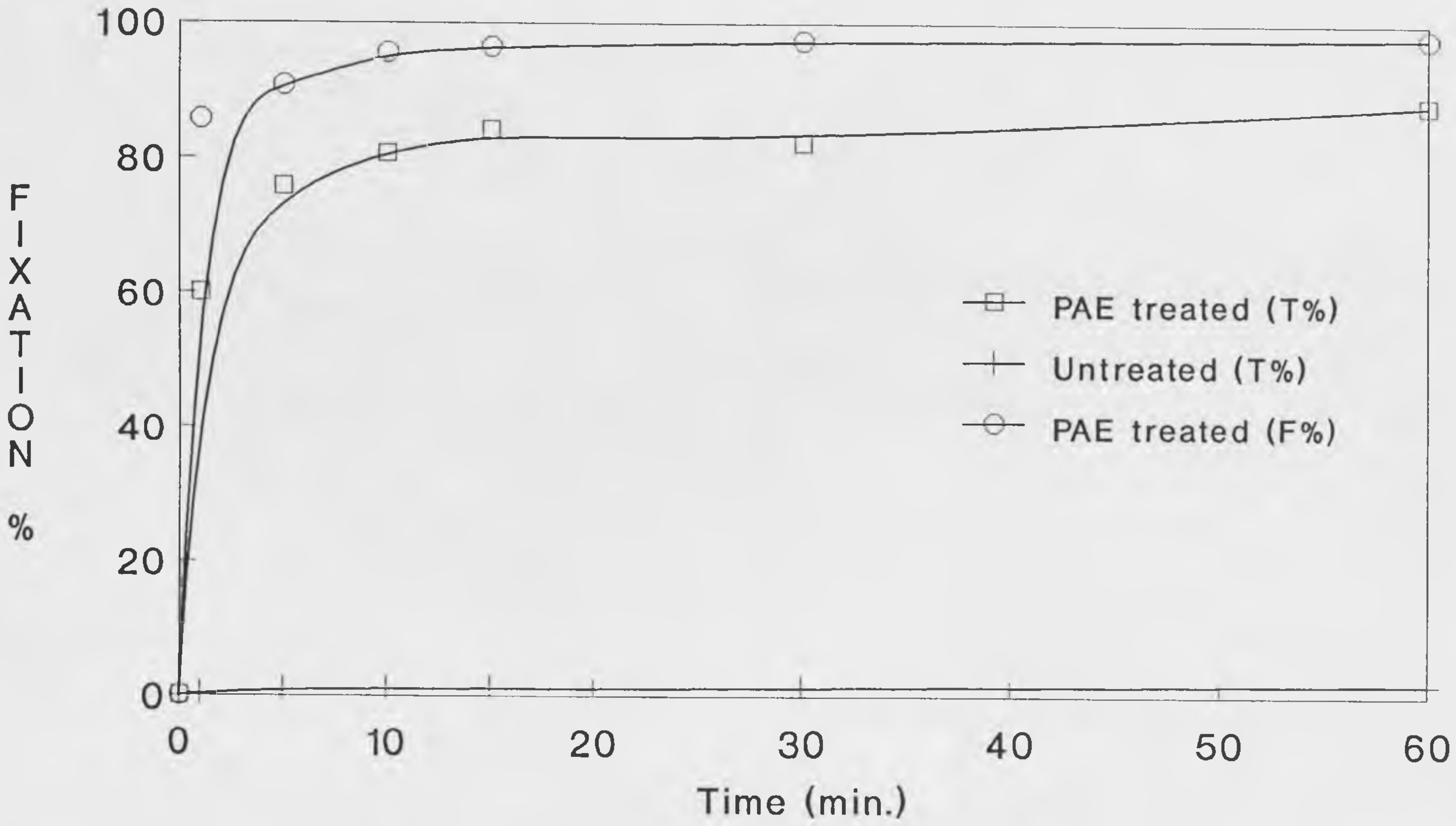
Figure 3-1-4 Infrared spectrum by subtracting cotton from Hercosett (PAE) treated cotton

Figure 3-1-5



Exhaustion rate of Verafix red FBL on PAE treated anf untreated cotton

Figure 3-1-6



Fixation rate of Verofix Red FBL on
PAE treated and untreated cotton

The dye bath was heated according to the following scheme:

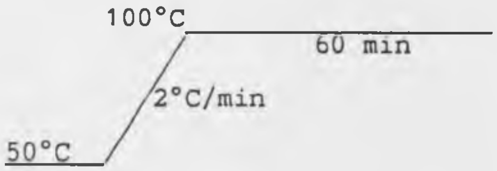


Figure 3-1-7 shows that at a level of 2% owf. Hercosett solids (ie. 200g/l of Hercosett 125), both dye exhaustion and fixation have almost reached their maximum values. Taking account of economic factors, little advantage would be given by using Hercosett concentrations in excess of this particular level.

3.1.5. Effect of dye bath pH on exhaustion and fixation of a reactive dye on treated cotton

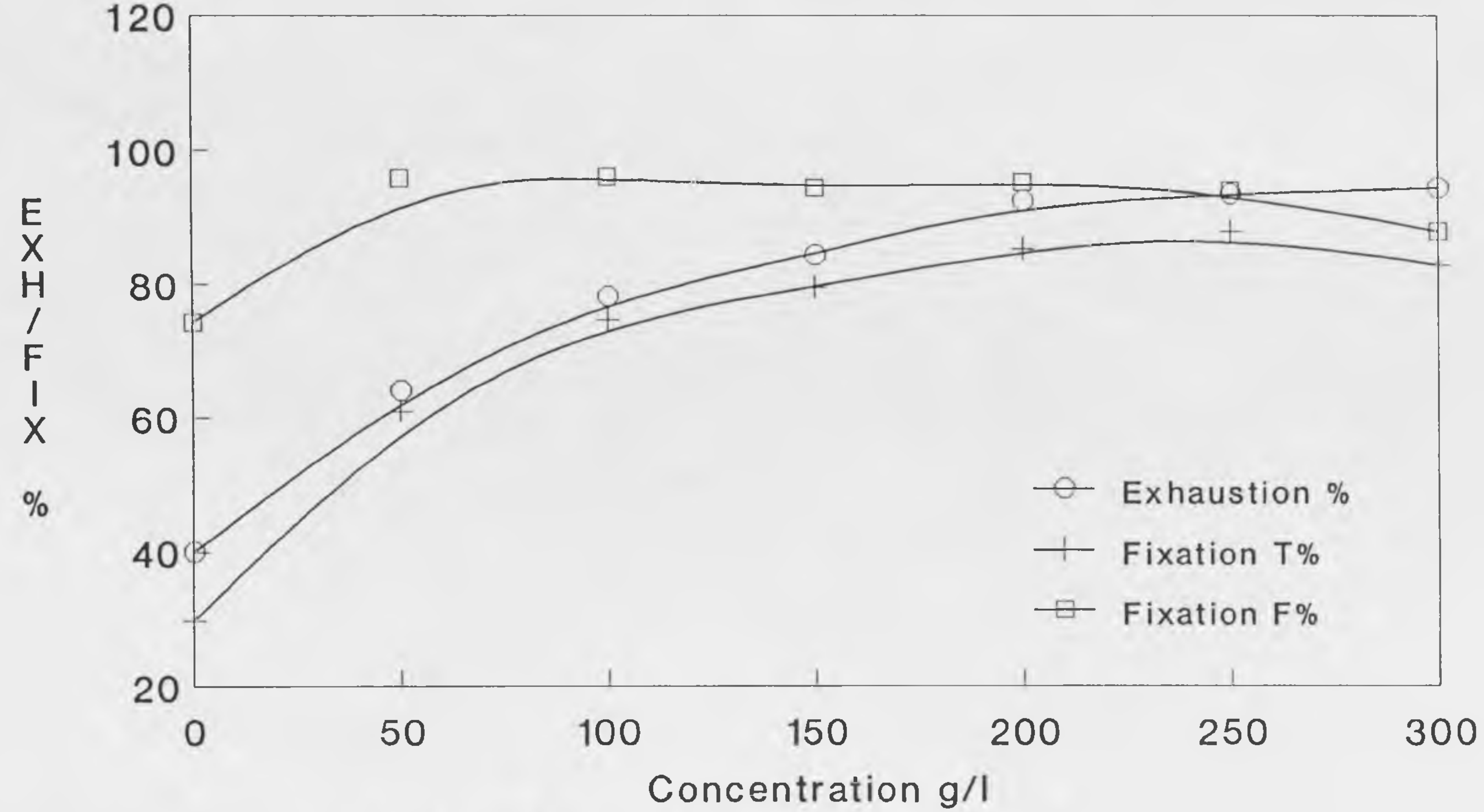
The following question should be asked: what is the optimum pH value for dyeing the treated cotton? Since it would be desirable to dye polyester/cotton blends under slightly acidic conditions by a one-bath-one-step procedure, the investigation was first carried out in the pH range of pH 6-8, the results are shown in table 3-1-1.

Table 3-1-1: Exhaustion and fixation from dye baths of different pH

pH	exhaustion	fixation	
	(%)	(T%)	(F%)
6	88	69	78
7	78	73	94
8	66	65	98

2% owf. Verofix Red FBL dyeing at 100°C for 60 mins.

Figure 3-1-7



Effect of PAE resin concentration in pad liquor on dye exhaustion and fixation

Table 3-1-1 shows that dye exhaustion increased with decreasing pH value and dye fixation reaches a maximum at pH 7. This can be attributed to the fact that besides azetidinium groups, Hercosett also contains secondary and tertiary amino groups. These amino groups absorb more protons at low pH values than at high pH values and, therefore, the cotton fibre surface is more positively charged under acidic conditions. As a result, the substantivity of the anionic reactive dye increases with decreasing application pH and so does dye exhaustion; on the other hand, because the nature of the dye-fibre reaction is nucleophilic substitution, the reactivity of the treated cotton decreases with decreasing application pH since the protonated amino group does not take part in such reactions. Since the fixation extent depends on both the substantivity and reactivity between dye and substrate, there is an optimum degree of fixation at a certain pH value; in this case, it is pH 7.

3.1.6. The suitability of Hercosett pretreatment for different types of reactive dyes

The study was extended to five different types of reactive dyes. With the exception of the Procion MX (ICI) range of dyes which were applied at 40°C for 60 mins, all other reactive dyes were applied using the neutral dyeing procedure previously recommended. Table 3-1-2 shows that difluorochloropyrimidine, and also dichlorotriazine reactive dyes exhibit high fixation values on the treated cotton; furthermore, monochlorotriazine (with the exception of Procion Turquoise H-A), monofluorotriazine and dichloroquinoxaline dyes give very low fixation values on the treated cotton.

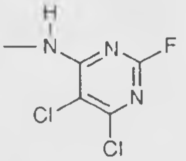
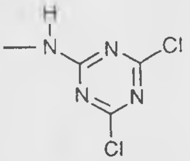
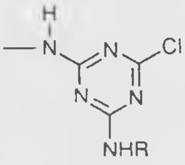
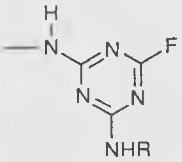
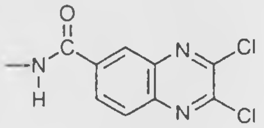
It thus appears that those dyes of high reactivity yield high fixation values whereas dyes of low reactivity yield low fixation values. The apparent exception of Procion Turquoise H-A is worth further consideration; it is our opinion that this large molecular weight, sulphonated copper phthalocyanine dye forms an extremely insoluble ionic complex with the Hercosett resin which can not be easily redissolved even under hot alkaline conditions.

3.1.7. Investigation of the reasons for low fixation of low reactivity dyes

As far as the fastness of reactive dyes on the modified cotton was concerned, the stability of both the cotton-polymer linkage and the polymer-dye or cotton-dye linkage must be equally taken into consideration. An initial study investigated the wet fastness of the Hercosett resin on cotton. Hercosett treated cotton was 'presoaped' before dyeing using a solution containing 5g/l Sandozin NIE (Sandoz) and 2 g/l sodium carbonate at the boil for 15 mins; the 'presoaped' sample was allowed to dry in the air and then dyed using Procion HE and MX (ICI) dyes. The results (table 3-1-3) shows that either Hercosett was removed by the 'pre-soap' treatment or the polymer secondary or tertiary amino groups underwent further crosslinking during the 'pre-soap', thus reducing the number of nucleophilic sites available for reaction with the dye. Further evidence that both explanations are correct was obtained from the determination of total nitrogen (table 3-1-4). Table 3-1-4 shows that the decrease in total nitrogen (therefore, Hercosett) was about 26%. It is thus quite certain that the low fixation of dyes of low reactivity is, at least partly, due to the fact that some of the Hercosett is incompletely fixed on the cotton.

The high fixation of the dyes of high reactivity, such as difluorochloropyrimidine and dichlorotriazine dyes, on the treated cotton can be explained as follows:

Table 3-1-2: Exhaustion and fixation of different reactive dyes on the treated cotton

dye name	reactive group	exhaustion	fixation	
		(%)	(T%)	(F%)
Levafix Blue E-3GLA		90.0	80.0	88.9
" Br. Red E-BA		91.0	73.2	80.4
" Turquoise Blue E-BA		92.0	67.2	73.0
Drimarene Blue K-2RL		89.0	81.7	91.8
Drimalan Red F-2BL		84.0	74.0	88.1
Procion Red MX-5B		92.5	57.2	61.8
" Blue MX-R		96.5	82.0	84.9
" Yellow MX-8G		82.7	75.3	91.1
Procion Yellow H-A		76.6	14.3	61.8
" Rubine BS		82.0	52.0	63.4
" Br. Red H8BS		79.6	30.1	37.8
" Green H-E4BD		93.0	40.0	43.0
" Turquoise H-A		96.6	69.6	72.0
" Red H-E3B		91.1	33.8	37.1
" Yellow H-E4R		91.2	47.3	51.8
Cibacron Red F-B		68.0	44.8	65.9
Levafix Br.Yellow E3D		80.0	66.9	83.6

Hercosett is fixed to cotton mainly by means of self- crosslinking. Since the reactive side chains of the polymer partially lose mobility when water is removed, crosslinking is incomplete in some parts of the resin film. However, because Hercosett has a large molecular structure, it is not extracted from cotton under neutral dyeing conditions, but during the dyeing, highly reactive and bifunctional dyes react with Hercosett on cotton surface forming further crosslinks and reducing the solubility of the resin; as a result, both dye and Hercosett are firmly fixed to the cotton. Also during boiling further self crosslinking may occur due to promotion of the reaction of the azetidinium cation with secondary amino residues.

Table 3-1-3: The K/S values of different modified cotton fabrics soaped before and after dyeing with reactive dyes

Treatment before dyeing	Procion Red H-E3B		Procion BlueMX-2R	
	as dyed	dyeing soaped off	as dyed	dyeing soaped off
None	13.918	8.529	19.691	16.344
'Pre-soap'	4.940	1.884	6.099	5.280

dyeing was carried out as described in (III)

Table 3-1-4: Total nitrogen(%) of different treated samples

samples	total nitrogen (%)	
	original data	average
without 'pre-soap'	0.255, 0.235	0.245
with 'pre-soap'	0.167, 0.196	0.181

3.1.8. The quality of Hercosett treated and dyed cotton

Colour fastness properties of reactive dyes on this treated cotton are shown in tables 3-1-5 and 3-1-6, It is clear from both tables that the wash fastness is excellent whereas the light fastness is unsatisfactory, being significantly lowered by the polymer pretreatment.

Table 3-1-5: Wash fastness(CO4) of Procion MX dyes on treated and untreated cotton after soaping

dyes	untreated			treated		
	E	V	C	E	V	C
Blue MX-2R	5	5	5	5	5	5
Yellow MX-8G	5	5	5	5	5	5
Orange MX-2R	5	5	5	5	5	5
Red MX-G	5	5	5	5	5	5

E----Effect on pattern
V----Viscose adjacent
C----Cotton adjacent

Table 3-1-6: Light fastness of Procion MX dyes on treated and untreated cotton after soaping

dyes	untreated	treated
Blue MX-2R	4 - 5	3
Yellow MX-8G	5 - 6	3 - 4
Orange MX-2R	5	3
Red MX-G	4 - 5	3

From microscopic investigation of the cross-sections of the treated and dyed cotton, it was observed that only those fibres on the surface of individual yarns were coloured while the fibres in the centre of such yarns remained colourless (figure 3-1-8,(a)). Particular attention was given to the dyed fibres on the yarn surface (figure 3-1-8,(b)) which showed that good colouration was achieved with these fibres. This indicates that under neutral pH conditions, reactive dyes can only form covalent bonds with Hercosett being unable to react with cellulose. The nucleophilicity of amino groups is very high under these conditions whilst the nucleophilic cellulosate anion will not be present in sufficient concentration at these pH values.

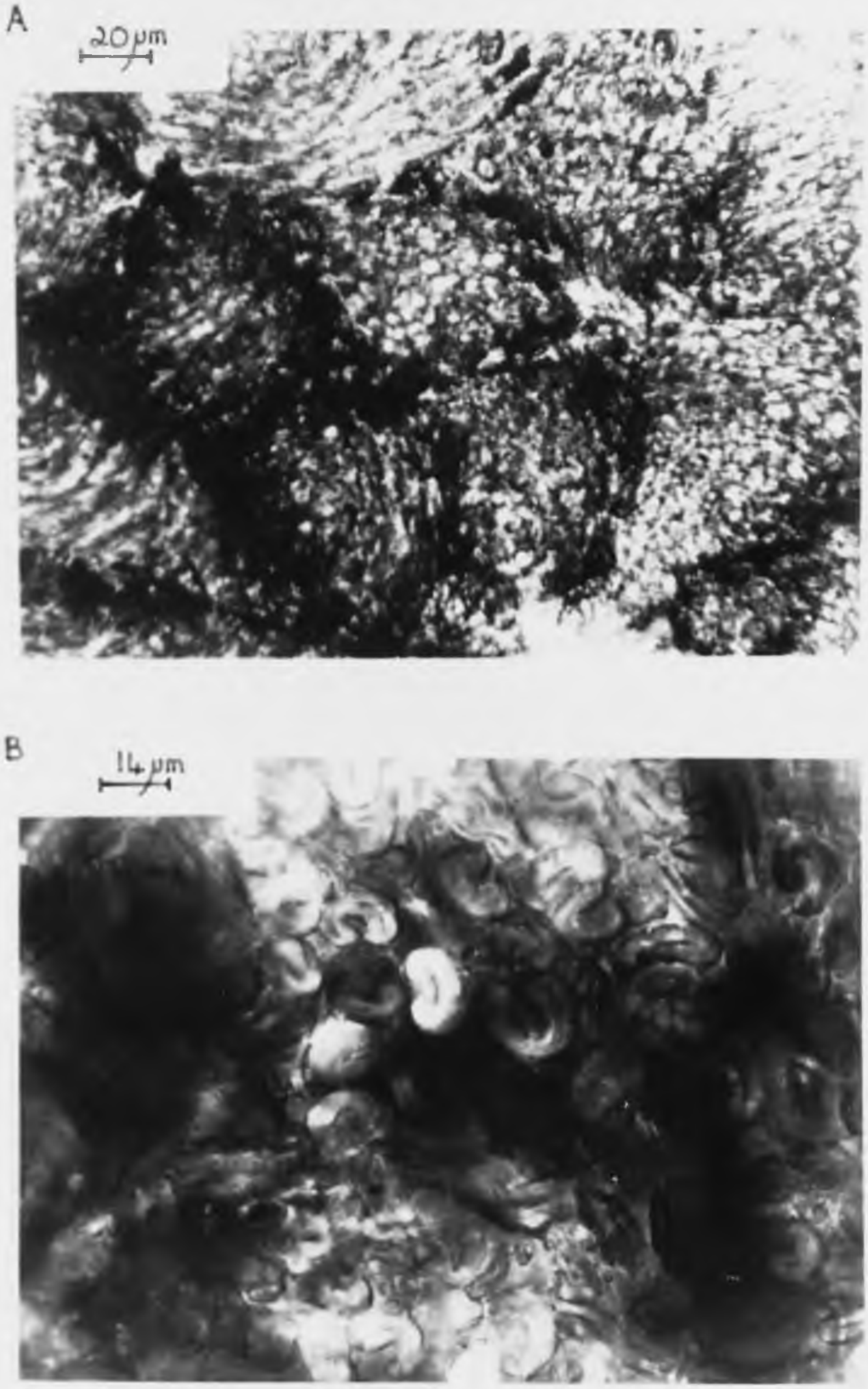


Figure 3-1-8 Cross-sections of Hercosett(PAE) treated cotton overdyed (a)---33 times, (b)---132 times.

The surface colouration also explains the low light fastness of treated and dyed fabric. Further work could possibly be directed towards the achievement of a better distribution of Hercosett within cotton. However this is unlikely since the molecular weight distribution of the polymer, as determined by Guise et al [99], indicated the presence of 60% of high molecular weight species formed by crosslinking reactions of both functional groups of one epichlorohydrin molecule with two polyaminamide chains. These species are believed to be unable to penetrate the fibre.

Strength properties of treated and untreated cotton are reported in table 3-1-7. Comparison between these two fabrics makes it clear that the pretreatment with Hercosett does not affect breaking strength and elongation, whilst the wrinkle recovery properties are slightly improved.

Table 3-1-7: The comparison of strength properties between treated and untreated cotton

properties		untreated	treated
Breaking strength (Kg)	warp	30.81 ± 1.42	29.66 ± 0.86
	fill	31.09 ± 0.93	31.26 ± 1.22
Elongation (%)	warp	9.97 ± 0.37	10.69 ± 0.38
	fill	17.52 ± 0.67	21.43 ± 1.00
W.R.A.(degree)	warp	62.00 ± 9.37	74.10 ± 5.22
	fill	68.50 ± 3.77	72.20 ± 4.53

3.1.9. summary of section 3.1.

Cotton can be modified by pretreating with Hercosett 125 (PAE). The modified cotton can be easily dyed under neutral pH conditions in the absence of salt using reactive dyes of high reactivity giving high fixation efficiency and good dyeing quality.

Pretreatment is carried out by padding with a solution containing 200g/l of Hercosett 125 and 10g/l of Sandozin NIE without adjustment of the pH. This treated cotton may be dyed optimally at pH 7 in the absence of electrolyte.

This pretreatment demonstrates the necessity to introduce functional amino groups which increase both the substantivity and reactivity of cotton, thus achieving reactive dye application under mild conditions.

3.2. Pretreating Cotton with PAE Resin and its Thiol and Thiourea Derivatives

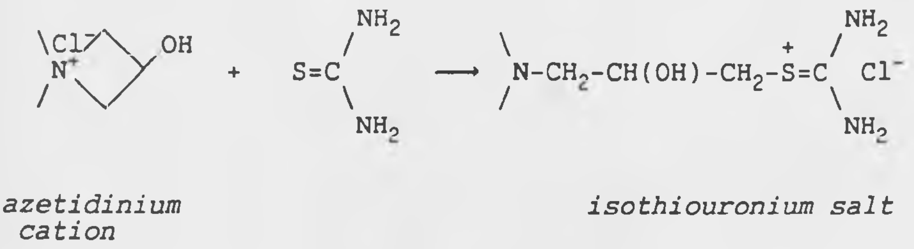
3.2.1. Introduction

In section 3.1., cotton which had been pretreated with an aqueous solution of polyamide-epichlorohydrin (PAE) resin was shown to be dyeable with reactive dyes under neutral conditions without salt. These dyeings were found to be bright and the colour yield of moderate depth dyeings was generally higher than that of corresponding dyeings produced by conventional methods on untreated cotton using salt and alkali. The wash fastness properties of dyeings produced with highly reactive dyes on the treated cotton were excellent and the physical properties of the treated cotton were identical to those of untreated fabrics. Problems observed with this system, included the lower fixation values obtained when applying dyes of low reactivity to the pretreated cotton and a significant drop (ca. 1-2 points) in light fastness of dyeings, in comparison to dyeings on untreated cotton produced by conventional methods. Therefore the main purpose of this study is to overcome these deficiencies.

The earlier work showed that, the reactive azetidinium cations present in the resin, compete with the reactive groups of reactive dyes during the dyeing process for the highly nucleophilic secondary amino sites in the resin. Thus a possible reason for the observed lower neutral fixation of low reactivity dyes is that they lose out in this competition reaction. If this hypothesis is correct it would appear necessary to introduce an increased number of highly nucleophilic sites into the resin treated cotton, so that better fixation of both high and low reactivity dyes might be achieved.

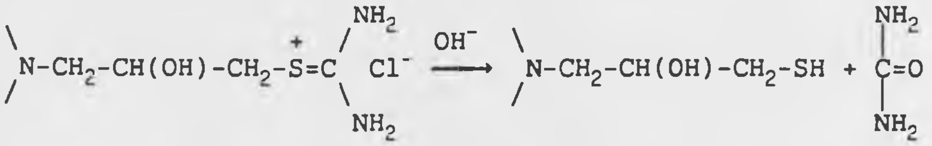
The chemistry of the azetidinium cation [88] indicates that it can react by means of ring opening with strong nucleophiles such as amines and thiols under mild conditions. Since only a small proportion of the azetidinium cations is needed for crosslinking reaction to immobilise the resin on cotton [95], the remainder might be employed to introduce either isothiouronium salt or Bunte salt or thiol residues as described in the following schemes:

Isothiouronium salt formation:



Scheme 3-2-1

Cotton fabric was therefore pretreated with an aqueous solution containing PAE resin plus thiourea and dried. The formation of isothiouronium salts in the fibre surface, would not initially decrease the total number of cationic sites in the resin but may subsequently increase the concentration of strongly nucleophilic centres in this substrate, because of the decomposition of the isothiouronium salt to nucleophilic thiol residues during the dyeing process:



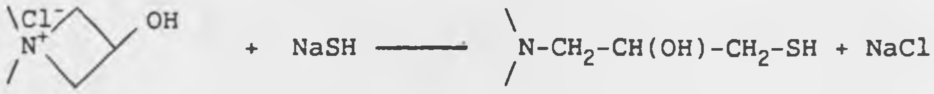
$$\rangle N\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}\overset{+}{S}{=}C(NH_2)_2\ Cl^- \xrightarrow{OH^-} \rangle N\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}SH + (NH_2)_2C{=}O$$

Scheme 3-2-2

The earlier observed reduction in light fastness of dyeings may be related to the strong tendency to ring dyeing and the pronounced hydrophilic character of the cationic polymers. Oxidative fading of azo dyes in their hydrazone form is a common mechanism [100] and one can readily envisage the accelerating role of water in this system due to hydroperoxide formation during photo-oxidation. Some reducing groups were therefore introduced into the resin finished cotton with the hope of scavenging any hydroperoxides and thus improving the light fastness of the dyeings.

Introduction of thiol groups:

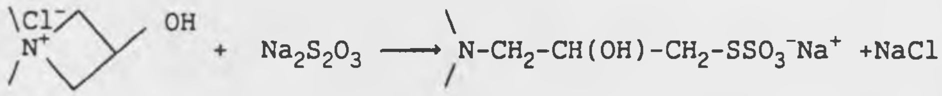
Thiol groups may be introduced as a result of ring opening of the azetidinium groups with sodium hydrosulphide:



Scheme 3-2-3

Introduction of S-thiosulphate (Bunte Salt) residues:

Sodium thiosulphate reacts with the azetidinium cation in PAE resins [98] according to the following scheme:



Scheme 3-2-4

3.2.2. Effect of adding thiourea to the PAE pad-liquor on dye fixation

The pad liquor for the PAE pretreatment was prepared containing 200 g/l Hercosett 125 and 10 g/l Sandozin NIE (Sandoz); the pad liquor for the combined PAE/thiourea pretreatment additionally contained 10 g/l thiourea. Both pretreatments were carried out using a simple pad-dry procedure without further baking and washing-off. The colour yield and fixation of dyeings on both treated cotton fabrics are shown in table 3-2-1.

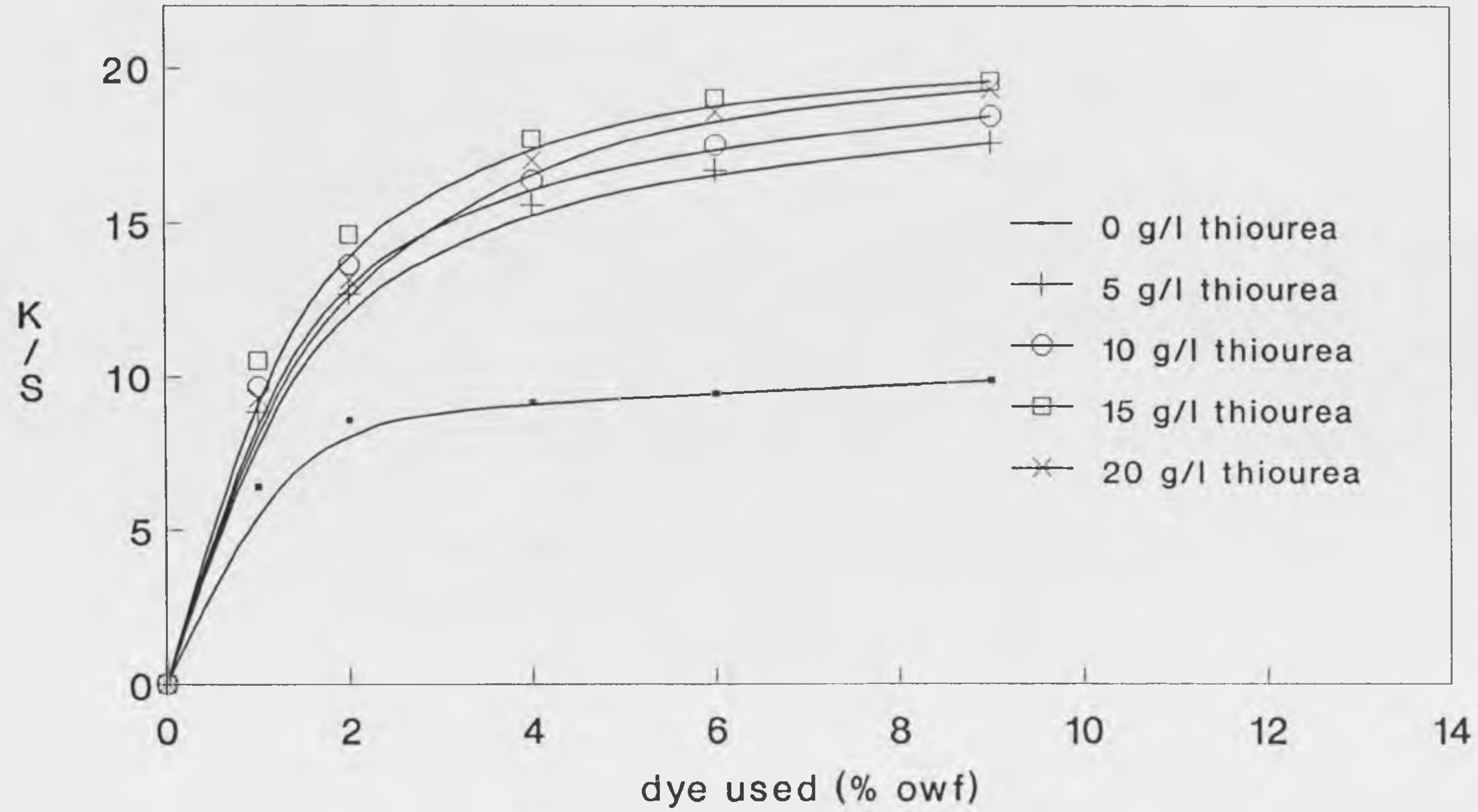
It can be seen from table 3-2-1 that if thiourea is included in the PAE pad liquor, the fixation of the above types of reactive dyes on the treated cotton is markedly improved. Table 3-2-1 also shows that, in the case of the PAE/thiourea pretreatment, raising the dyeing temperature from 60°C to 100°C does not have a pronounced effect on colour yield and fixation values obtained for the highly reactive Procion MX dye (ICI), which suggests that the reaction between the dichlorotriazine reactive dyes and the nucleophilic sites in the resin is rather facile.

3.2.4. Effect of thiourea pad-liquor concentration on dye fixation

The thiourea concentration in the PAE pad-liquor was varied from 0-15 g/l and the thus prepared cotton fabrics were then dyed (2% owf) at pH 5 (1 hour, 100°C) in the absence of electrolyte. Tables 3-2-2 and 3-2-3 show that the optimum thiourea concentration in the pad-liquor to give the best colour yields varies from dye to dye.

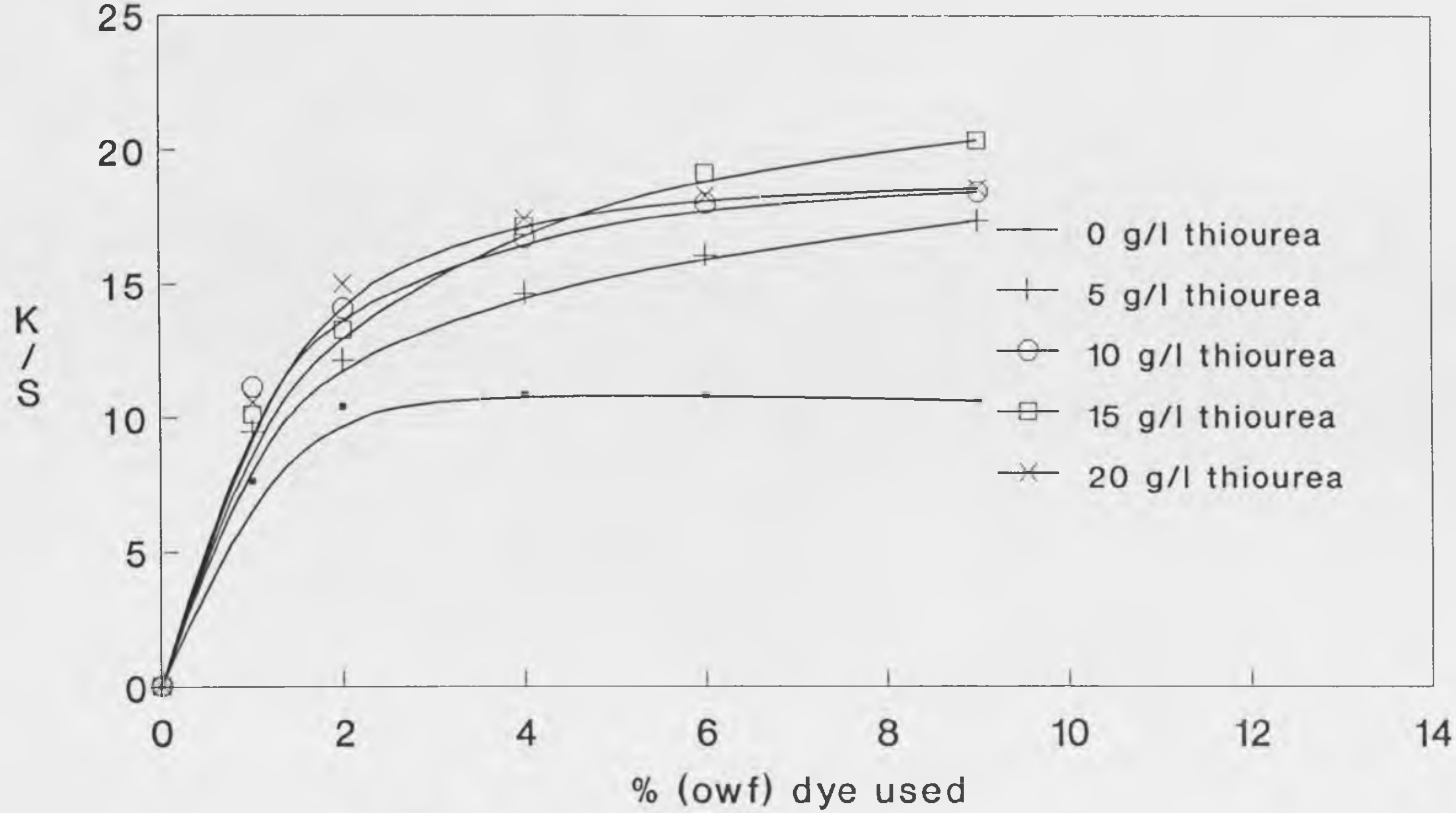
Further work was therefore carried out using a variety of reactive dyes at different depths of shade ranging from 0-10% owf and the results are shown in figures 3-2-1 and 3-2-2. These curves suggest that a pad liquor containing 15 g/l of thiourea gives optimum colour yield when applying reactive dyes at depth of shades between 0-10% owf.

Figure 3-2-1



Build up of Procion Red MX-5B (ICI) on a variety of substrates (2% owf PAE)

Figure 3-2-2



Build up of Procion Orange MX-2R on a variety of substrates (2% owf PAE)

Table 3-2-1. Colour yield and fixation of dyeings (pH 5, without electrolyte) on various pretreated cotton fabrics

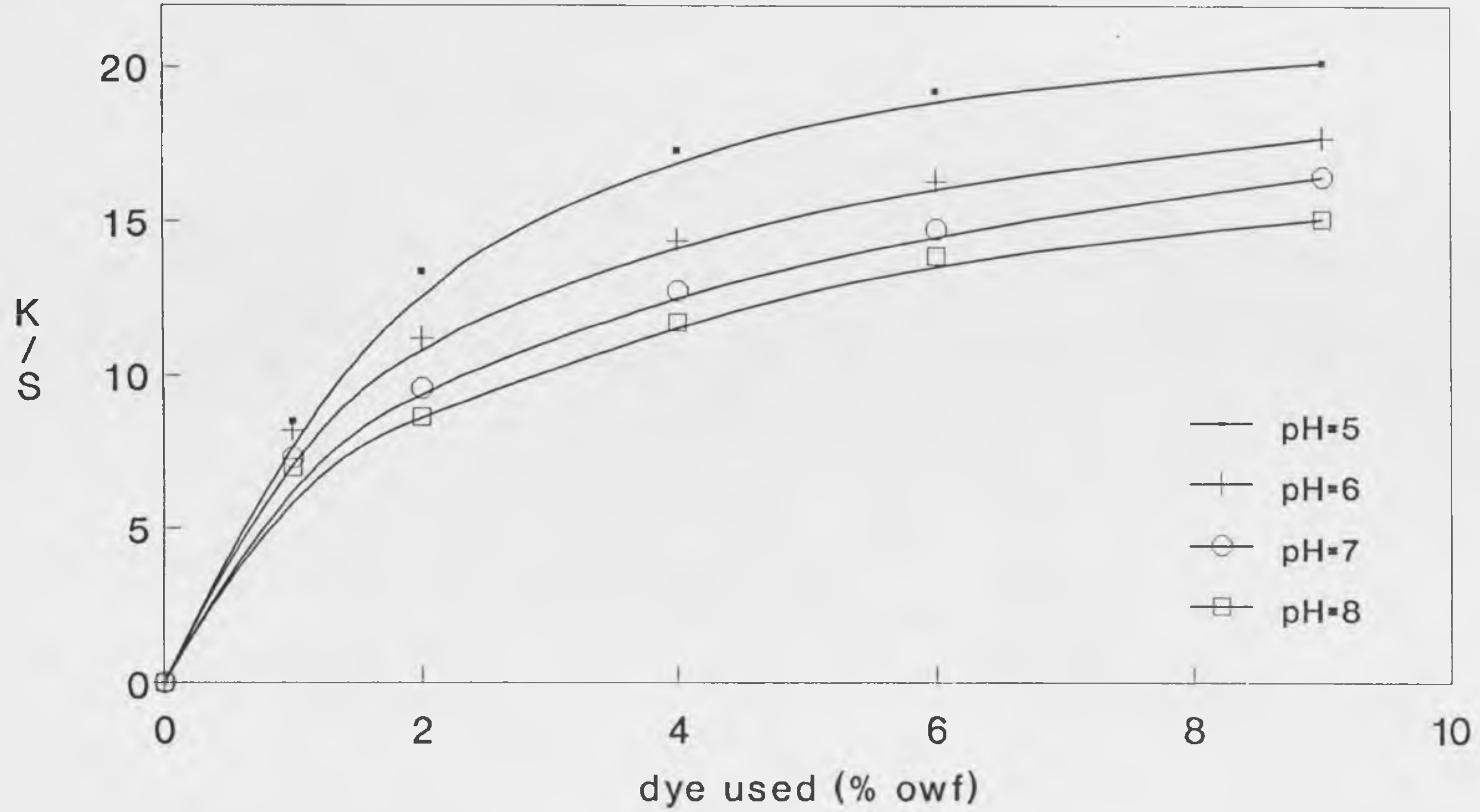
Treatment	colour yield(K/S)		E%	F%
	before soaping	after soaping		
	[a]Procion Red H-EXL (ICI) (2% owf)			
PAE	22.23	11.76	95	51
PAE/Thiourea	19.31	17.25	83	89
	[b]Levafix Red E-BA (Bayer) (2% owf)			
PAE	15.82	11.42	83	72
PAE/Thiourea	17.09	16.20	90	95
	[b] Procion Red MX-G (ICI) (2% owf)			
PAE	16.37	11.34	73	69
PAE/Thiourea	20.85	18.94	93	91
	Dye as above - dyed at 60°C			
PAE	17.95	9.04	79	50
PAE/Thiourea	18.83	18.25	84	97

[a] *low reactivity bis-monochloro-s-triazine derivative.*
[b] *high reactivity dichloro-s-triazine derivative.*

3.2.5. Effect of dyebath pH on colour yield and fixation of dyeings on the PAE/thiourea treated cotton

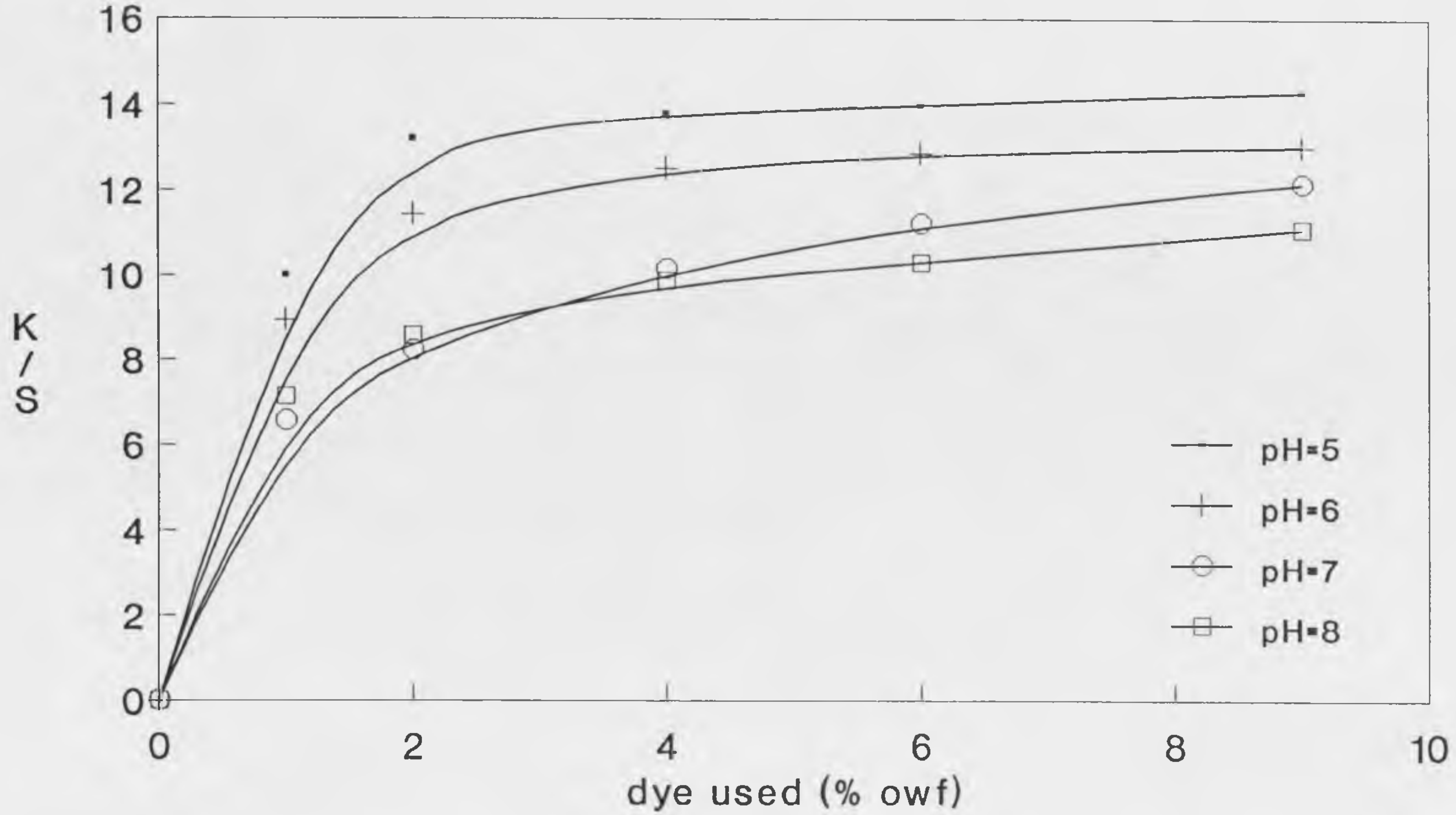
The build-up obtained from dyeings produced at different dye bath pH values was studied for Procion Red MX-5B (ICI) and Procion Red H-E3B (ICI) on the PAE/thiourea (10 g/l) treated cotton. The results are shown in figures 3-2-3 and 3-2-4. Although the build up curves are quite different, each dye shows the same trend of decreasing colour yield with increasing pH. Since dyeing cotton below pH 5 would risk fibre damage, dyeing below this pH value was not studied.

Figure 3-2-3



Effect of dyebath pH on the build up of
Procion Red MX-5B on PAE/thiourea cotton

Figure 3-2-4



Effect of dyebath pH on the build up of Procion Red H-E3B on PAE/thiourea cotton

Table 3-2-2. Colour yield and fixation of dyeings on cotton pretreated with PAE and different amounts of thiourea

Thiourea in pad-liquor (g/l)	Colour Yield(K/S) before soaping	Colour Yield(K/S) after soaping	E%	F%
	[a] Procion Red H-E3B (ICI) (2% owf)			
0	21.20	9.57	92	45
2.5	18.96	9.55	82	50
5.0	18.92	10.60	82	56
7.5	20.57	16.55	89	80
10.0	19.97	17.06	87	85
12.5	18.80	12.25	82	65
15.0	19.50	14.02	85	72
	[b] Procion Blue MX-2R (ICI) (2% owf)			
0.0	16.79	14.13	92	84
2.5	15.61	12.28	86	77
5.0	14.40	11.67	80	81
7.5	17.96	17.71	94	99
10.0	19.82	15.75	96	79

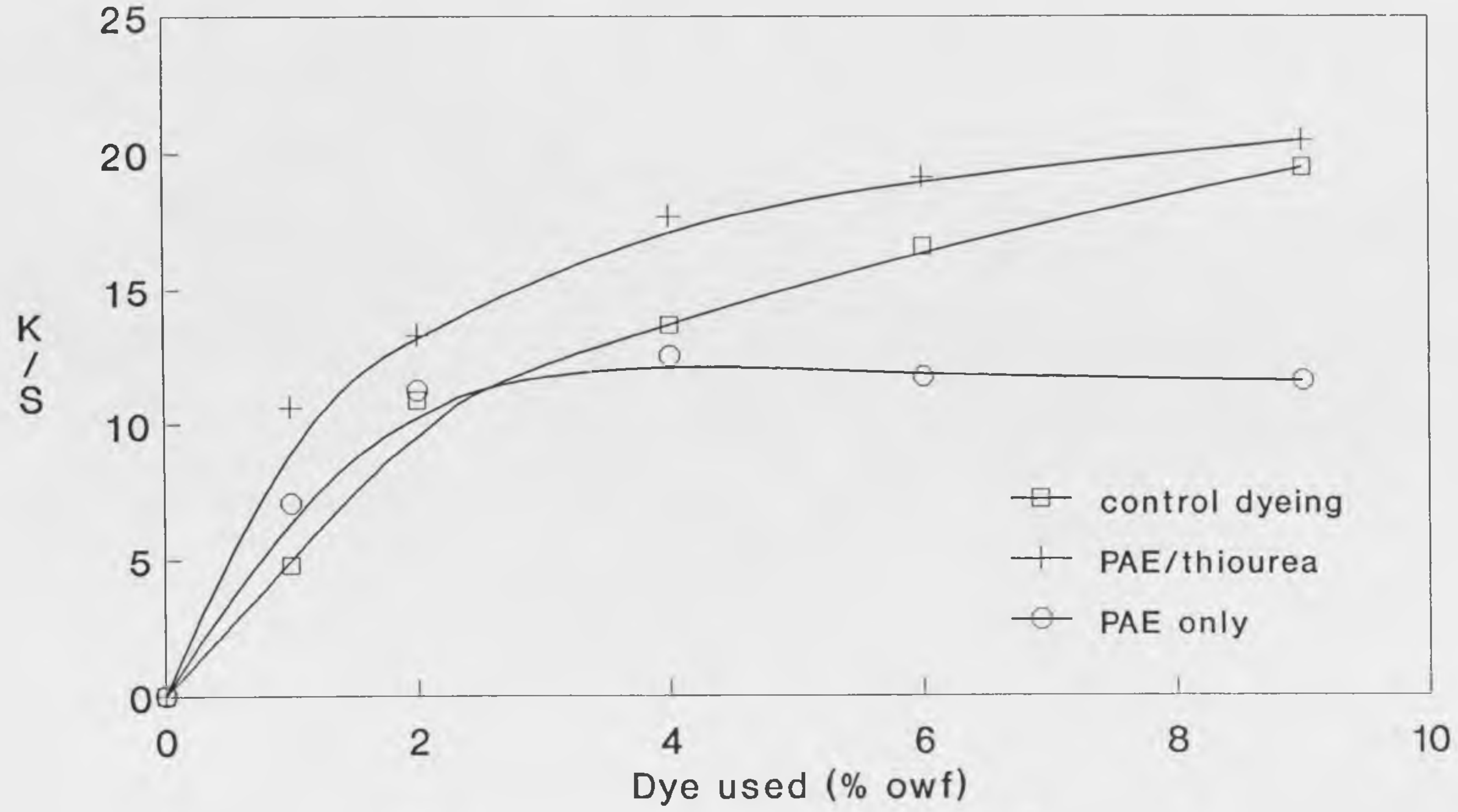
[a],[b] *see footnotes of table 3-2-1.*

The observation that the best colour yields were obtained under mildly acidic conditions confirms that the mechanism of dye absorption relies on electrostatic interactions between the anionic dye and protonated secondary amino groups in the resin. Possible contributions from cationic isothiouronium residues should not be neglected.

3.2.6. Build up properties of reactive dyes on PAE/thiourea treated cotton

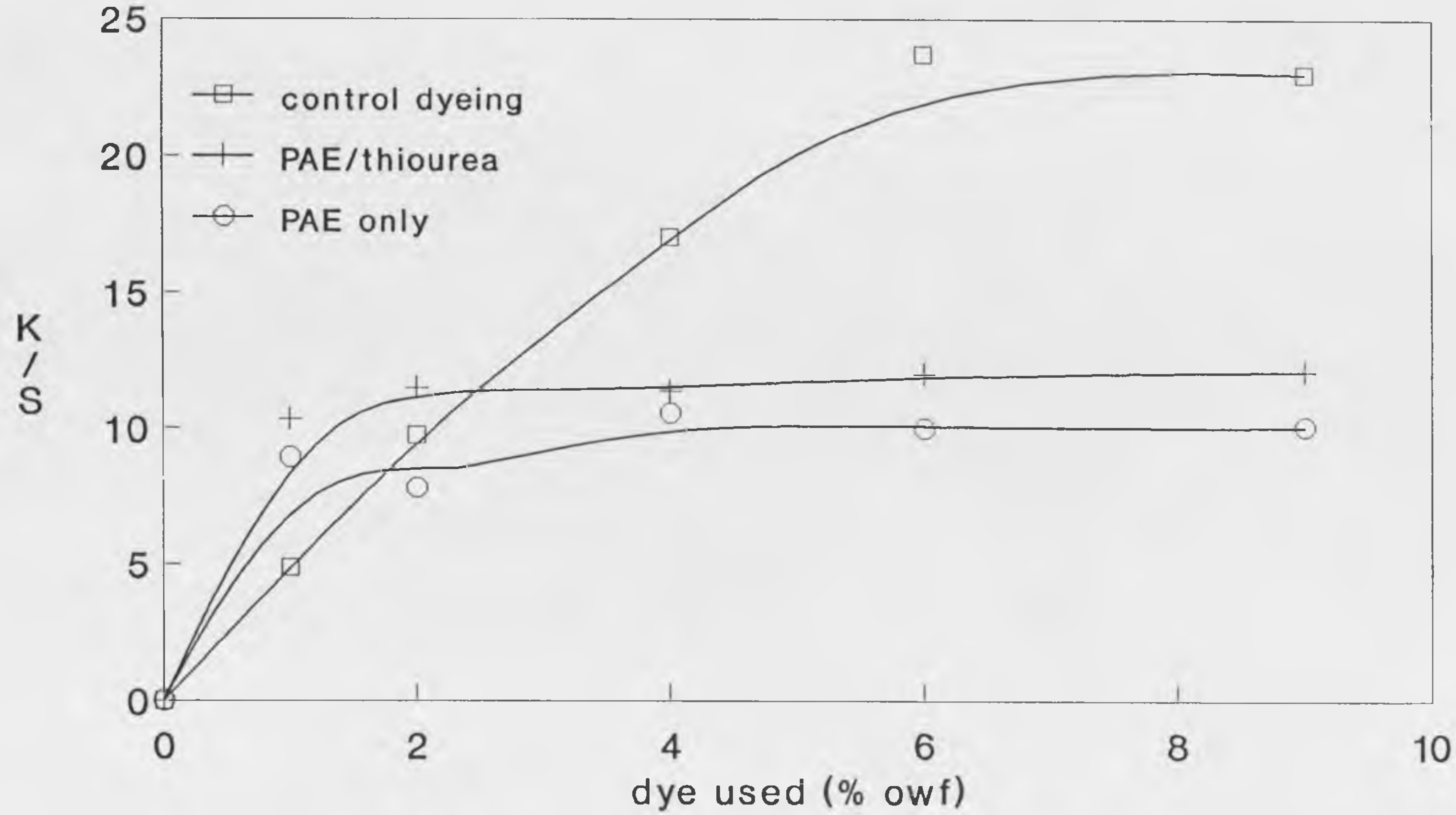
The colour yields of dyeings on untreated and treated cotton fabrics at different depths of shade were measured and the results are shown in figures 3-2-5, 3-2-6, 3-2-7 and 3-2-8. It appears that using highly reactive Procion MX dyes (ICI), optimum build up was achieved on the

Figure 3-2-5



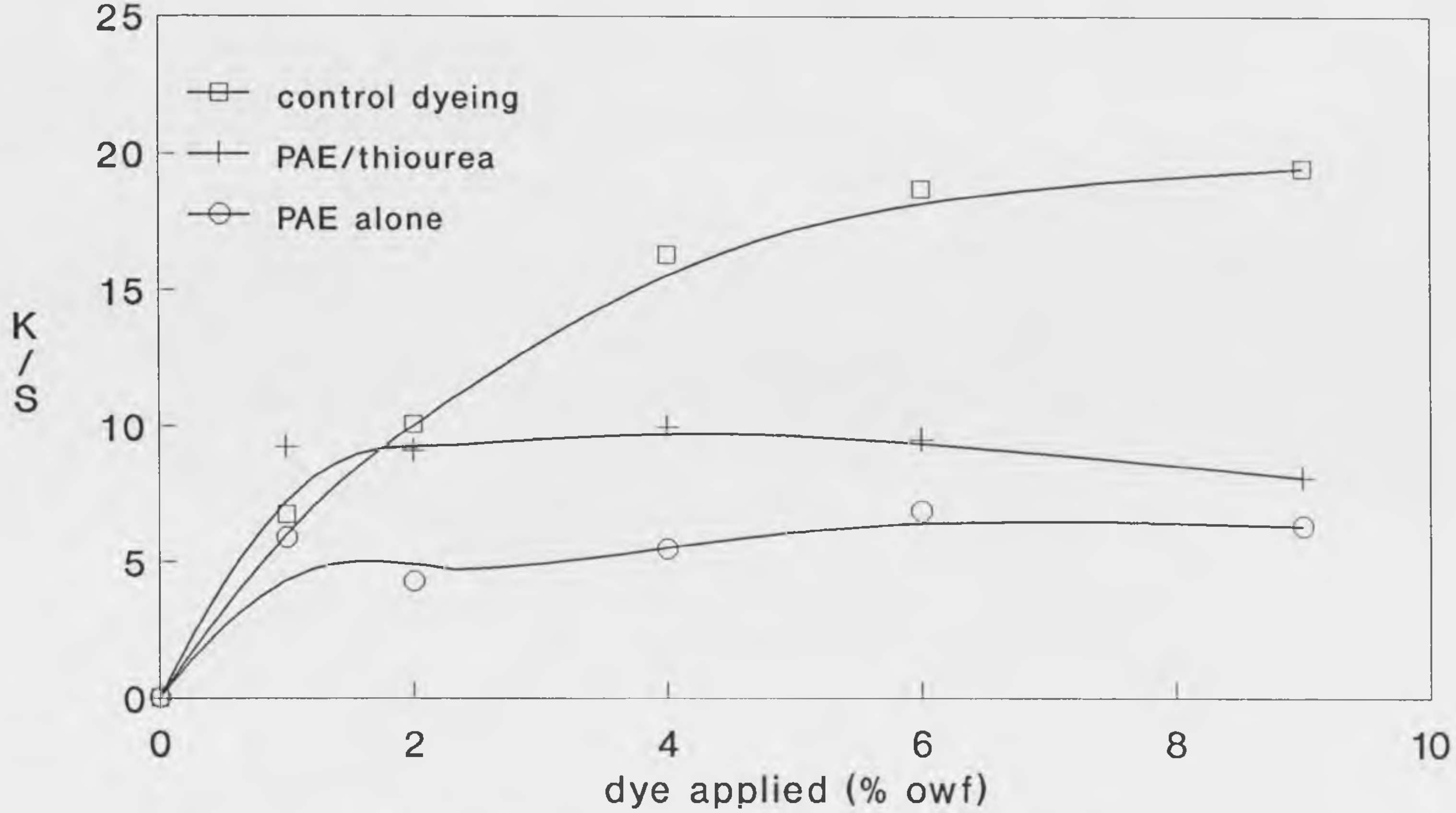
Build up of Procion Red MX-5B (ICI) on a variety of substrates

Figure 3-2-6



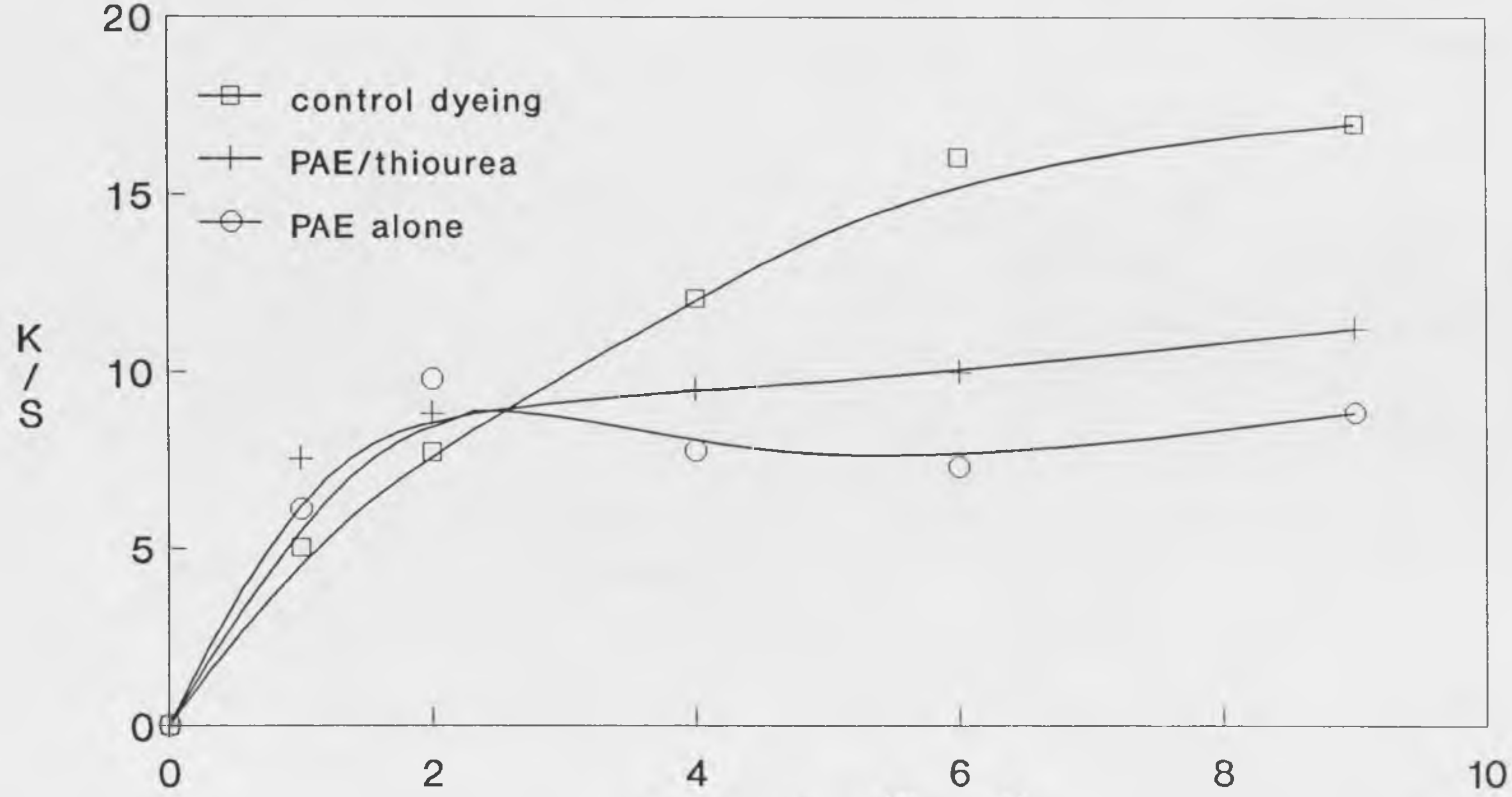
Build up of Procion Brill. Red H-EXL (ICI) a variety of substrates

Figure 3-2-7



Build up of Cibacron Red FR on a variety of substrates

Figure 3-2-8



Build up of Remazol Red RB (Hoechst)
on a variety of substrates

PAE/thiourea (10 g/l) treated cotton when compared with the build up obtained on PAE treated cotton and on untreated cotton dyed using conventional dyeing methods. In the case of the lower reactivity Procion H-E dyes (ICI), Cibacron F dyes (Ciba-Geigy) and Remazol Red RB (Hoechst), good colour yield and dye fixation were only obtained providing the depth of shade was below 2% owf; in the case of depths greater than this level the build up on untreated cotton dyed by the conventional method was the highest although the build up on the PAE/thiourea treated cotton remained greater than that on cotton treated with PAE alone. With low reactivity dyes there is clearly a problem of site saturation when dyeing either PAE or PAE/thiourea modified cotton.

Table 3-2-3 . Colour yield and fixation of dyeings on the PAE/ thiourea treated cotton - pad liquor containing different amounts of thiourea

Thiourea in pad-liquor (g/l)	colour yield(K/S)		E%	F%
	before soaping	after soaping		
	[b] Procion Orange MX-2R (ICI) (2% owf)			
8.0	16.90	15.20	83	90
9.0	16.68	15.52	81	93
10.0	16.65	16.19	81	97
11.0	16.62	16.52	80	99
12.0	16.68	16.31	81	97
	[a] Procion Yellow H-E4R (ICI) (2% owf)			
8.0	13.52	10.54	74	78
9.0	12.60	11.07	69	87
10.0	13.03	12.23	72	94
11.0	13.22	12.16	73	92
12.0	13.32	12.40	73	92
	[a] Procion Blue H-EGN (ICI) (2% owf)			
8.0	15.56	11.30	94	72
9.0	15.50	11.62	93	75
10.0	15.72	13.24	95	84
11.0	15.55	12.96	94	83
12.0	15.72	13.30	95	85

[a,b] *see footnotes of table 3-2-1.*

3.2.7. The dyeing quality of PAE/thiourea treated and dyed cotton

Colour fastness properties of reactive dyes on both treated and untreated cotton are shown in tables 3-2-4 and 3-2-5, It is evident from both tables that the wash fastness is excellent but the light fastness is again significantly lowered by the pretreatment.

Table 3-2-4: Wash fastness(C04) of Procion MX dyes(ICI) on PAE/thiourea (10 g/l) treated and untreated cotton after soaping

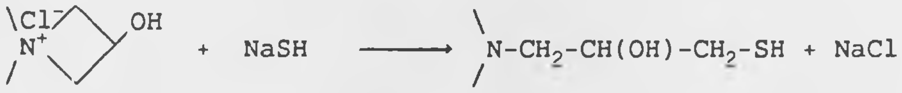
Procion dye (2 % owf)	untreated			treated		
	E	V	C	E	V	C
Blue MX-2R	5	5	5	5	5	5
Yellow MX-8G	5	5	5	5	5	5
Orange MX-2R	5	5	5	5	5	5
Red MX-G	5	5	5	5	5	5

E----Effect on pattern
V----Viscose adjacent
C----Cotton adjacent

Table 3-2-5: Light fastness of Procion MX dyes on PAE/ thiourea (10 g/l) treated and untreated cotton after soaping

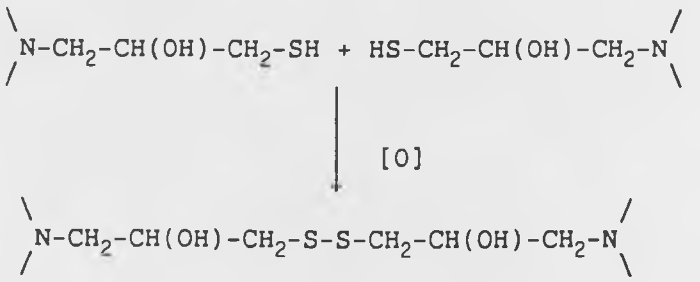
Procion dye (2 % owf)	untreated	treated
Blue MX-2R	4 - 5	3
Yellow MX-8G	5 - 6	3 - 4
Orange MX-2R	5	3
Red MX-G	4 - 5	3

Attempts to overcome the problem of poor light fastness were first made by introducing thiol groups into PAE modified cotton. This was done by aftertreating PAE treated cotton with 40 g/l aqueous sodium hydrosulphide (NaSH) using a cold pad-batch procedure. The reaction scheme proposed may be described as follows:



Scheme 3-2-5

The dyeing properties and light fastness of dyeings (2% owf) on this treated cotton are shown in table 3-2-6. The results surprisingly shows that after NaSH treatment, the colour yield and fixation values of the three types of dyes are more or less lowered, even when dyeing in the presence of 80 g/l of sodium chloride in comparison with dyeings on the PAE treated cotton. Since there is no doubt that the thiol group can readily react with monochlorotriazine dyes under neutral or slightly acidic conditions [101], it is likely that further crosslinking of the thiol terminated polymer has taken place prior to dyeing giving non-reactive residues. The following air oxidation reaction to give the disulphide may occur during drying the thiol treated fabric:



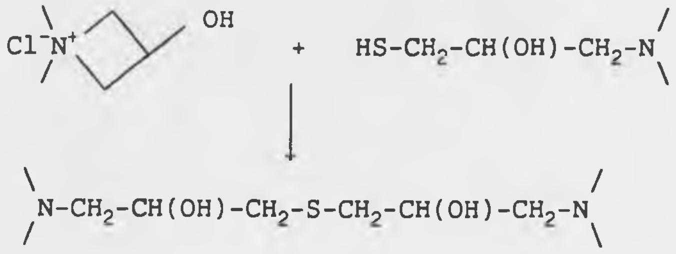
$$\begin{array}{c}
\backslash N\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}SH + HS\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}N/ \\
\Big\downarrow [O] \\
\backslash N\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}N/
\end{array}$$

Scheme 3-2-6

Table 3-2-6. Colour yield and light fastness of treated and dyed fabrics

Treatment	dyeing pH	salt added (g/l)	K/S before soap	K/S after soap	E%	F%	light fastness
			Procion Red MX-G (ICI)				
PAE	7	0	15.27	13.94	68	91	3
PAE/Thiol	5	0	12.41	8.37	55	67	3
	7	0	3.25	1.87	14	57	3
	7	80	9.94	8.09	44	81	3
			Procion Red H-E3B (ICI)				
PAE	7	0	13.92	8.53	60	61	3
PAE/Thiol	5	0	14.54	5.03	63	35	3
	7	0	5.88	2.30	26	39	3
	7	80	13.58	8.41	59	62	3
			Procion Red H-EXL (ICI)				
PAE	7	0	14.18	8.67	57	61	3
PAE/Thiol	5	0	12.16	1.21	49	9	3
	7	0	1.71	0.74	7	43	3
	7	80	8.05	2.99	32	37	3

However it is more likely that the highly nucleophilic thiol residues will react rapidly with azetidinium residues to give a thioether crosslink:-



Scheme 3-2-7

The formation of the disulphide or thioether crosslinks reduces the number of nucleophilic sites available for subsequent reaction with the reactive dye. Under neutral or slightly acidic dyeing conditions, the above type of disulphide bond is non-reactive towards reactive dyes and is stable, unlike the disulphide in wool cystine [102] which hydrolyses readily to the nucleophilic thiol, due to its activation by the neighbouring peptide carbonyl group.

The reduction in reactivity of this substrate for reactive dyes cannot simply be explained by the above reactions. During the treatment with NaSH there must be a significant drop in the number of nucleophilic secondary amino groups due to their reaction with azetidinium cations under the alkaline conditions employed.

From Table 3-2-6, it can also be seen that the attempted introduction of reducing (thiol or disulfide) groups does not improve the light fastness of reactive dyeings on the PAE treated cotton.

Attempts to solve the problem of poor light fastness via the introduction of Bunte Salt groups into the PAE treated cotton also failed. The fact that the presence of reducing groups in the dyed substrate does not improve its light fastness indicates that the mechanism of fading is photoreductive (103,104) or the reason for poor light fastness of dyeings on this substrate must be related to the poor fibre penetration and surface distribution of the dyes. Pretreatment of cotton with polymer finishes which are substantive and reactive towards reactive dyes gives rise to poor dye distribution mainly in the form of ring dyeing. It may therefore be predicted that pretreatment with amino functional lower molecular weight compounds will give dyeings of better penetration and light fastness since these agents will penetrate individual fibres during the pretreatment procedure.

Microscopic analysis of cross-sections of the resin treated and dyed cotton indicated that only those fibres on the surface of individual yarns were coloured while the fibres in the centre of such yarns remained colourless (figure 3-2-9,(a)). Particular attention was given to the dyed areas on the yarn surface (figure 3-2-9,(b)) which showed good dye distribution - it may well be that it is surface deposited polymer which is attracting dye. This unlevelness within the yarn can be attributed to the fact that PAE and its derivatives have very low substantivity for cotton; thus during drying after padding, PAE resin and its derivatives migrate to the yarn surfaces.

Strength properties of treated and untreated cotton are reported in table 3-2-7. A comparison between the two fabrics makes it clear that pretreatment with PAE/thiourea does not affect breaking strength and elongation, whilst the recovery properties are slightly improved.

Table 3-2-7. The comparison of strength properties between treated and untreated cotton

properties		untreated	treated
Breaking strength (Kg)	warp	30.81±1.42	29.56±0.99
	weft	31.09±0.93	30.56±1.10
Elongation (%)	warp	9.97±0.37	11.30±0.51
	weft	17.52±0.67	22.56±1.08
W.R.A.(degree)	warp	62.00±9.37	76.10±3.56
	weft	68.50±3.77	75.50±3.69

3.2.8. Mechanism proposed to explain the nature of the PAE/Thiourea pretreatment

As described previously, the improvement of dye fixation brought about by addition of thiourea to the PAE pad liquor is due to the formation

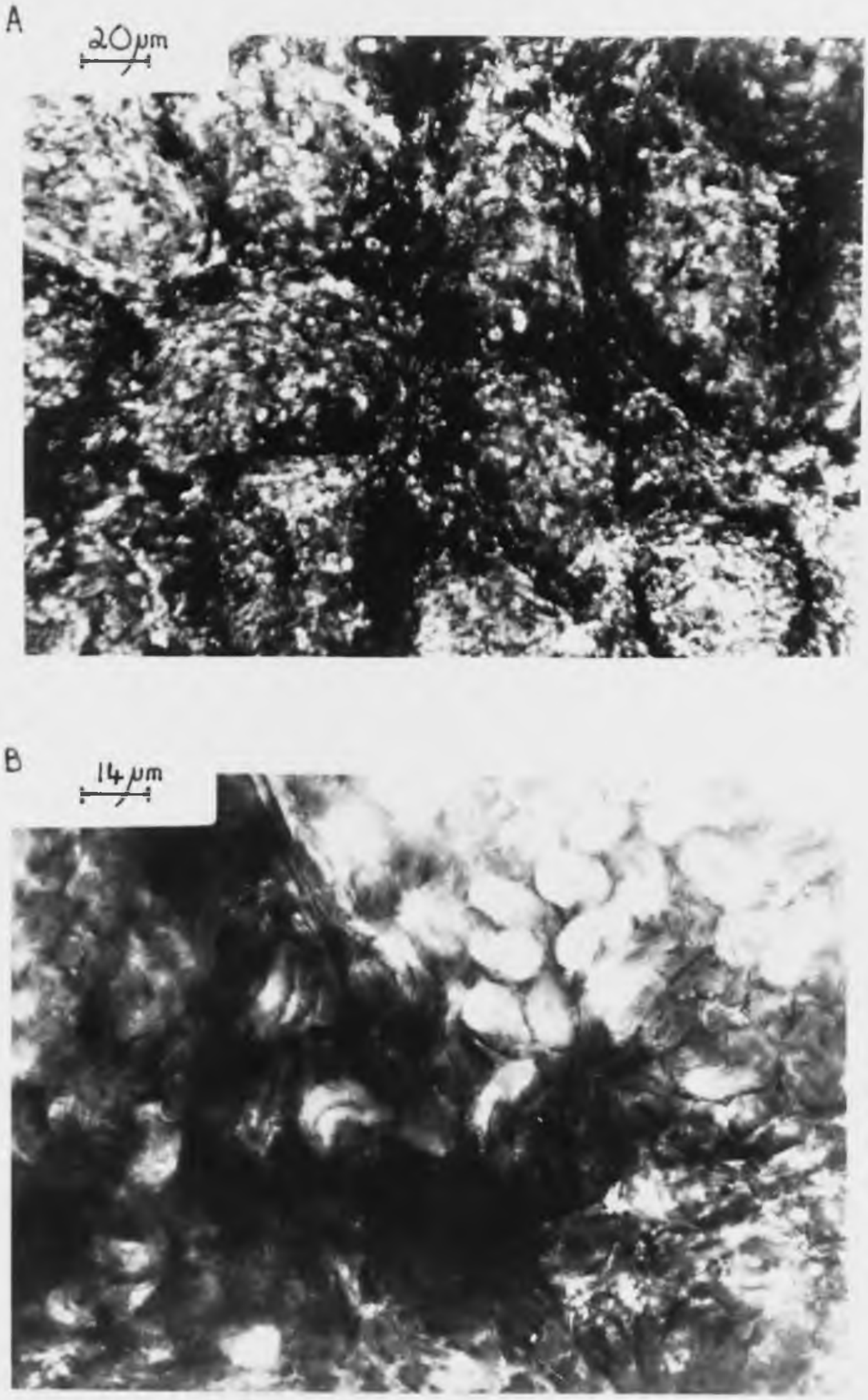


Figure 3-2-9 Cross-sections of PAE/thiourea treated cotton overdyed (a)---33 times, (b)---132 times.

of isothiouronium salt residues which not only impart a strongly cationic character to the substrate but also supplies highly nucleophilic thiol groups during the dyeing process, due to hydrolytic decomposition of the isothiouronium salt at elevated temperatures.

Evidence for the presence of isothiouronium salt residues in the PAE/thiourea treated cotton was obtained from FTIR spectroscopy. Figure 3-2-10 shows the Diffuse Reflectance IR spectrum of the PAE/thiourea treated cotton from which the spectrum of the PAE treated cotton has been subtracted. A broad, moderate N-H stretching band approximately in the 3100 cm-1 region and a strong band in the 1667 cm-1 region indicate the presence of $-N^{+}H_3$; a further strong absorbance in the region of 2058 cm-1 suggests the presence of ammonium cations in the form of the hydrochloride salt. These spectra support the contention that isothiouronium salt residues are present in the PAE/thiourea treated cotton.

In order to explain the marked difference in the build up curves for dyes of high and low reactivity on PAE treated cotton, two hypotheses were considered:

(i) The resin itself is incompletely insolubilised and partially dissolves into the dyebath during the actual dyeing process; high reactivity dyes somehow immobilize the resin possibly by cross linking reactions and prevent the above dissolution which is, of course, accompanied by a loss in nucleophilic sites. This hypothesis is unlikely to hold since the work of Bates (95) showed that the complete insolubilisation of PAE resin on paper required the formation of only one or two crosslinks by the reaction of the azetidinium cation with reactive secondary amino groups.

(ii) The dye sites in the resin treated cotton are secondary amino groups of high nucleophilicity. During the dyeing process it may

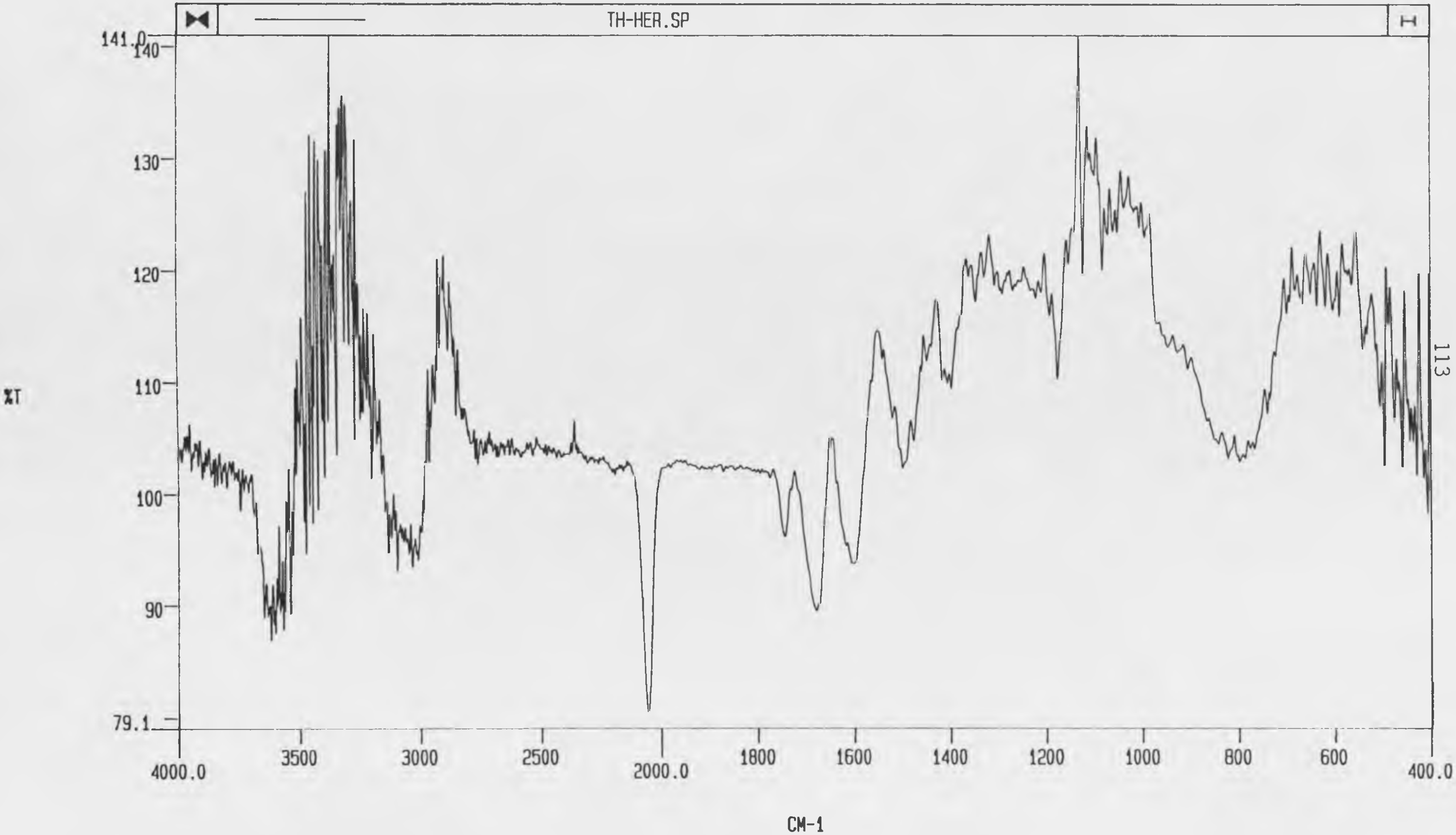
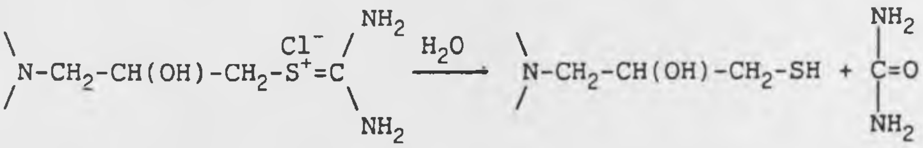


Figure 3-2-10 Infrared spectrum by subtracting PAE treated cotton from PAE/thiourea treated cotton

be expected that these will react in a competitive manner with residual azetidinium cations and thus become unavailable for reaction with reactive dye. Providing reactive dyes of higher reactivity than the azetidinium cation are employed then good build up properties would be achieved. If this hypothesis were true then the assumption would have to be made that even in the case of PAE/thiourea treatments, a significant number of reactive azetidinium cations are available in the pretreated cotton, ie. that reaction with thiourea is incomplete. Figure 3-2-11 shows the effect of pre-boiling the treated cotton before dyeing; colour yield are significantly reduced for dyeings on both PAE and PAE/thiourea treated cotton. Total nitrogen determination on both pretreated cottons (table 3-2-8) indicates that a small amount of resin is lost from the PAE pretreated cotton (about 15 %) but there are much larger nitrogen losses for the PAE/thiourea system. This may be explained by the following reaction:

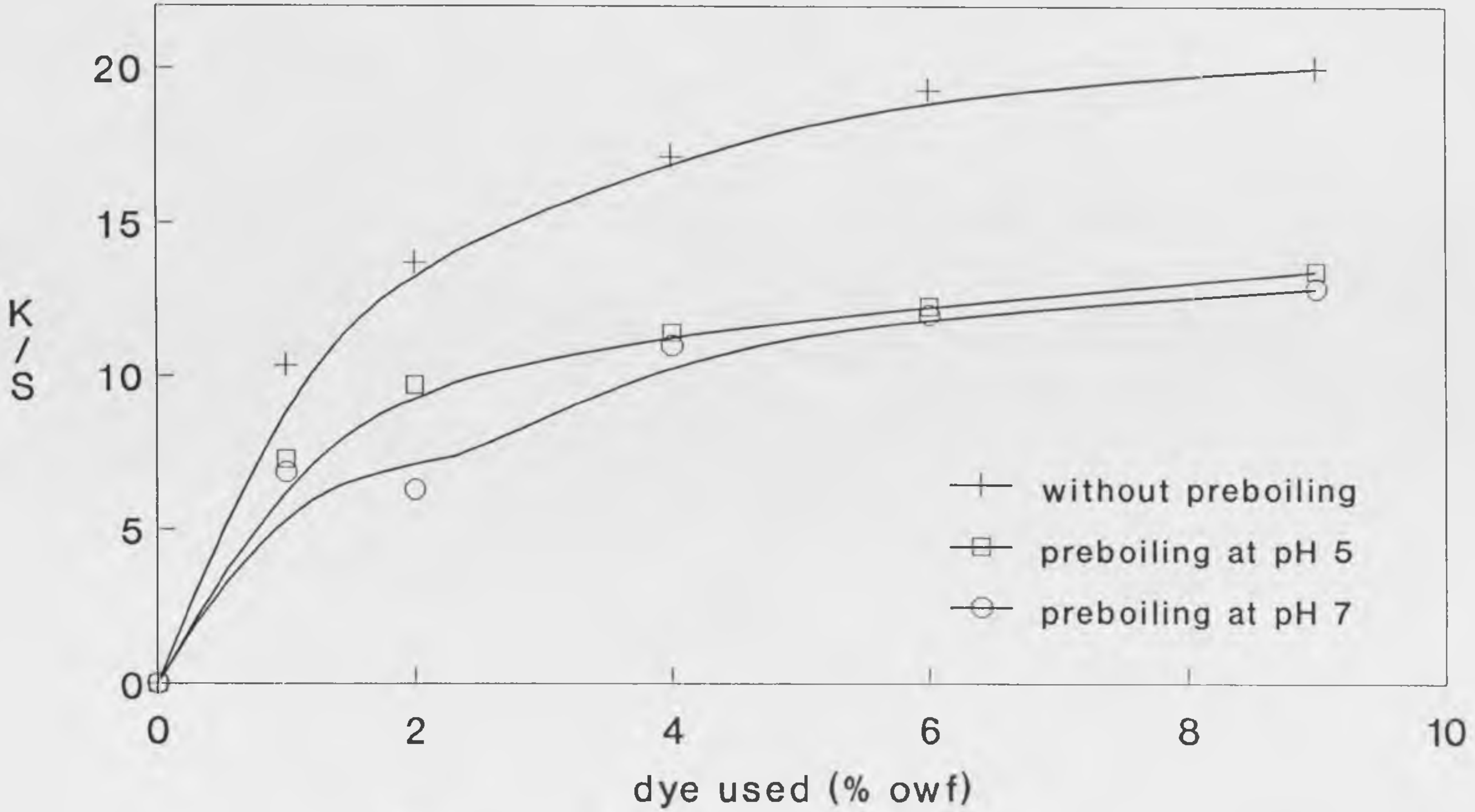


$$>N-CH_2-CH(OH)-CH_2-S^+=C(NH_2)_2\ Cl^- \xrightarrow{H_2O} >N-CH_2-CH(OH)-CH_2-SH + NH_2-C(=O)-NH_2$$

Scheme 3-2-8

The urea liberated in the hydrolysis is soluble thus accounting for the large total nitrogen loss.

Figure 3-2-11



Effect of preboiling substrates before dyeing on build up of Procion Red MX-5B

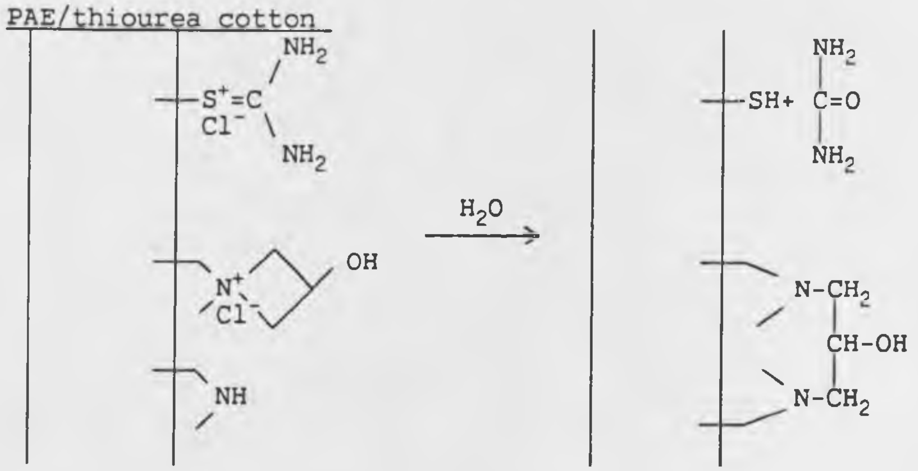
Table 3-2-8. Total nitrogen content of the different pretreated cotton

treatment	Total Nitrogen (%) PAE treated	Total Nitrogen (%) PAE/Thiourea treated
no	0.3141	0.6265
pre-boil*	0.2616	0.3010
pre-soap+	0.2450	0.2590

** treated cotton was preboiled at pH 5 for 60 minutes.*

+ treated cotton was presoaped in a solution containing 5 g/l Sandozin NIE and 2 g/l sodium carbonate at the boil for 15 minutes.

Although it is difficult to be absolutely certain of the reasons for the reductions in colour yields on preboiling the resin treated cotton it appears as though the following reactions will occur:



Scheme 3-2-9

Any free thiol groups produced during preboiling will also react rapidly with azetidinium cations to give the thioether crosslink. These reactions involve therefore a loss in the number of highly cationic residues (isothiouronium salts and azetidinium cations) and, additionally, a reduction in nucleophilic sites. The above factors thus account for the marked reduction in substantivity for and fixation of reactive dyes on the preboiled samples as shown in figure 3-2-11.

3.2.9. Summary of Section 3.2.

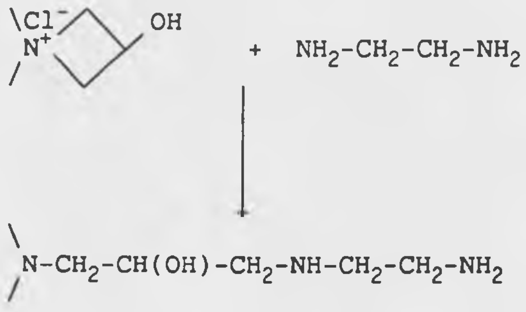
Pretreatment of cotton with PAE/Thiourea markedly improves the reactive dyeability of this fibre when compared to the earlier results achieved on PAE modified cotton. Dyeing can be carried out under neutral pH conditions in the absence of salt to give good colour yields and good dye fixation. The wash fastness of dyeings and mechanical properties of the treated cotton are excellent but the light fastness of dyeings was lowered by this pretreatment.

The improvement of the dyeability of PAE treated cotton secured by the addition of thiourea to the PAE pad liquor is believed to be due to the formation of isothiouronium salt residues in the substrate following reaction of thiourea with the azetidinium cation. This reaction results in removal of a significant number of azetidinium residues thus reducing the frequency of their subsequent crosslinking reactions with highly nucleophilic secondary amino groups.

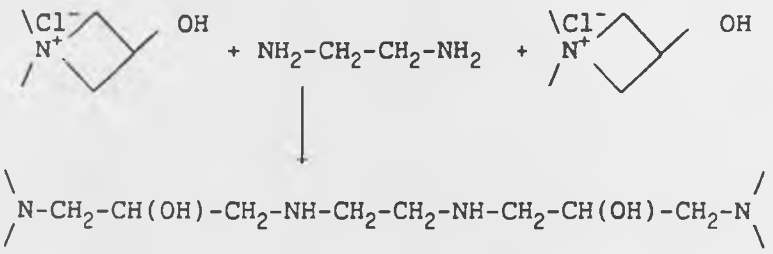
3.3. Pretreating Cotton with a Mixture of PAE Resin and Ethylene Diamine

3.3.1. Introduction

In section 3.2., reactive polyamide - epichlorohydrin (PAE) resin and thiourea mixtures were used to pretreat cotton instead of PAE alone, in order to overcome deficiencies of the PAE pretreatment when using reactive dyes of low reactivity. A significant improvement in colour yield and dye fixation was achieved with an addition of only 10-15 g/l of thiourea to the PAE pad-liquor. However, in medium to dark shades, obvious differences in colour yield could still be observed between dyeings obtained using high reactivity dyes and those using low reactivity dyes. In this study, increased amounts of amino groups were introduced in the substrate with the aim of achieving efficient dyeing with dyes of low reactivity. Amino groups were introduced by pretreating cotton with an aqueous solution of PAE resin and ethylene diamine (EDA). During this application procedure, some of the azetidinium cations in the resin react with this diamine to form primary, secondary and tertiary amino groups according to the following scheme:



Scheme 3-3-1



Scheme 3-3-2

The products may be much more complicated than shown above since the following PAE derivatives could also be present in the substrate after application:

$P{-}NH{-}CH_2{-}CH_2{-}N(P)_2$ and $(P)_2N{-}CH_2{-}CH_2{-}N(P)_2$

Scheme 3-3-3

where P is PAE resin.

The proposed advantages of using ethylene diamine in the pretreatment are as follows:

i) It promotes the crosslinking of the PAE resin since EDA is a tetra functional compound; possible desorption of a small proportion of PAE resin from the substrate during the dyeing process may thus be prevented, improving the efficiency of the pretreatment.

ii) It improves reactivity of the treated substrate towards reactive dyes due to the fact that an increased number of highly nucleophilic amino groups are made available for reaction with the dyes.

iii) It increases the substantivity of the treated substrate for anionic dyes; under slightly acidic conditions the amino groups are protonated thus providing plenty of cationic sites for the anionic dye.

Dyeings of high fixation values with both high reactivity and low reactivity dyes should therefore be achievable on the PAE/EDA treated substrate.

3.3.2. Infra-red study of PAE/EDA treated cotton

It is necessary to confirm that the number of amino groups have increased after the addition of EDA to the PAE pad liquor. This was done with the help of diffuse reflectance FTIR; the instrument's computing facility will subtract the spectrum obtained on the PAE treated cotton from the one obtained on the PAE/EDA treated cotton. Figures 3-3-1 and 3-3-2 show the spectra of PAE alone and PAE/EDA treated cotton respectively; in both cases, the spectrum of untreated cotton has been subtracted. Figure 3-3-3 is the spectrum obtained by subtracting figure 3-3-1 from figure 3-3-2. The strong absorbance at 1591 cm-1 indicates the presence of an increased number of amino groups in the substrate following EDA addition to the PAE pad liquor.

3.3.3. Selection of application pH

Since the primary amino groups in EDA are very nucleophilic and there is a large excess of available amino groups in the PAE/EDA pretreatment compared to the PAE only pretreatment, it may be possible for crosslinking reactions to take place at any stage before the drying procedure. These should be prevented since they would bring about poor

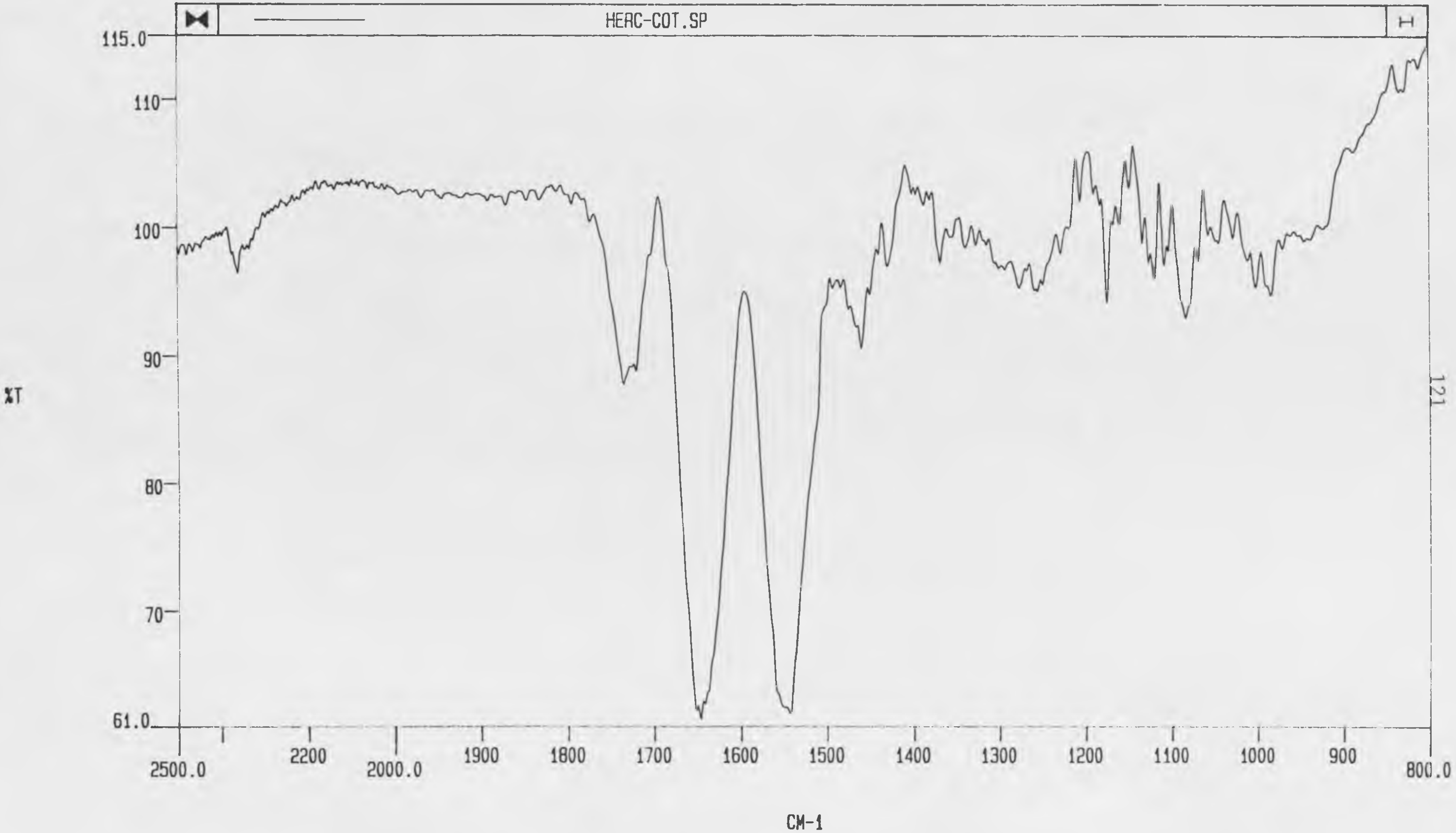


Figure 3-3-1 Infrared spectrum by subtracting cotton from PAE treated cotton

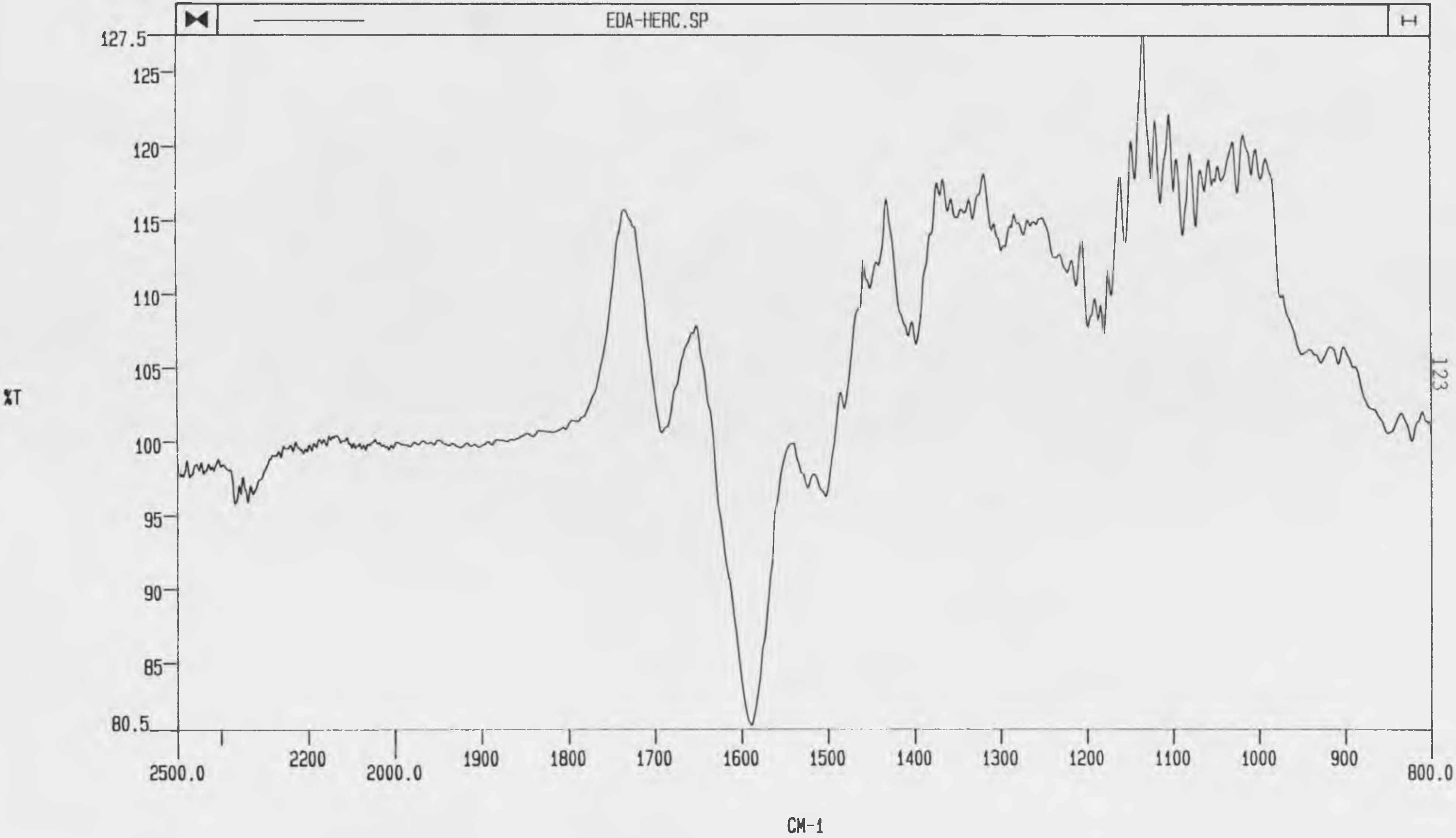


Figure 3-3-3 Infrared spectrum by subtracting PAE treated cotton from PAE/EDA treated cotton

fixation of the resin on the cotton and hence poor dyeability. The nucleophilicity of the ethylene diamine amino groups can be controlled by varying the application pH.

Experiments were therefore carried out by varying application pH between 5-11; the treated cotton was then dyed at pH 5 with 2% owf of the low reactivity dye, Procion Red HE-3B (ICI). The subsequent results are shown in table 3-3-1. These show that the colour yield of the dyeings was constantly high until the application pH approached pH 11. These results can be explained as follows: when the liquor is below pH 11, some of the amino groups in both the PAE resin and in the ethylene diamine are protonated and thus can not easily react with the azetidinium groups present in the PAE resin at room temperature. Resin crosslinking reactions therefore mainly take place during the drying procedure. However, above pH 11 the amino groups are mainly deprotonated and crosslinking reactions may occur before the drying stage especially at high EDA concentration due to the high nucleophilicity of the amino groups. These conditions would bring about a reduction in the amount of the PAE resin fixed to the cotton.

Table 3-3-1. Colour yield obtained on the substrates prepared at different pad liquor pH values

pH	K/S		E%	F%
	before soap	after soap		
5.0	20.06	20.03	91	95
7.4	22.37	20.74	97	93
8.7	21.99	20.53	96	93
10.8	19.36	18.65	88	96

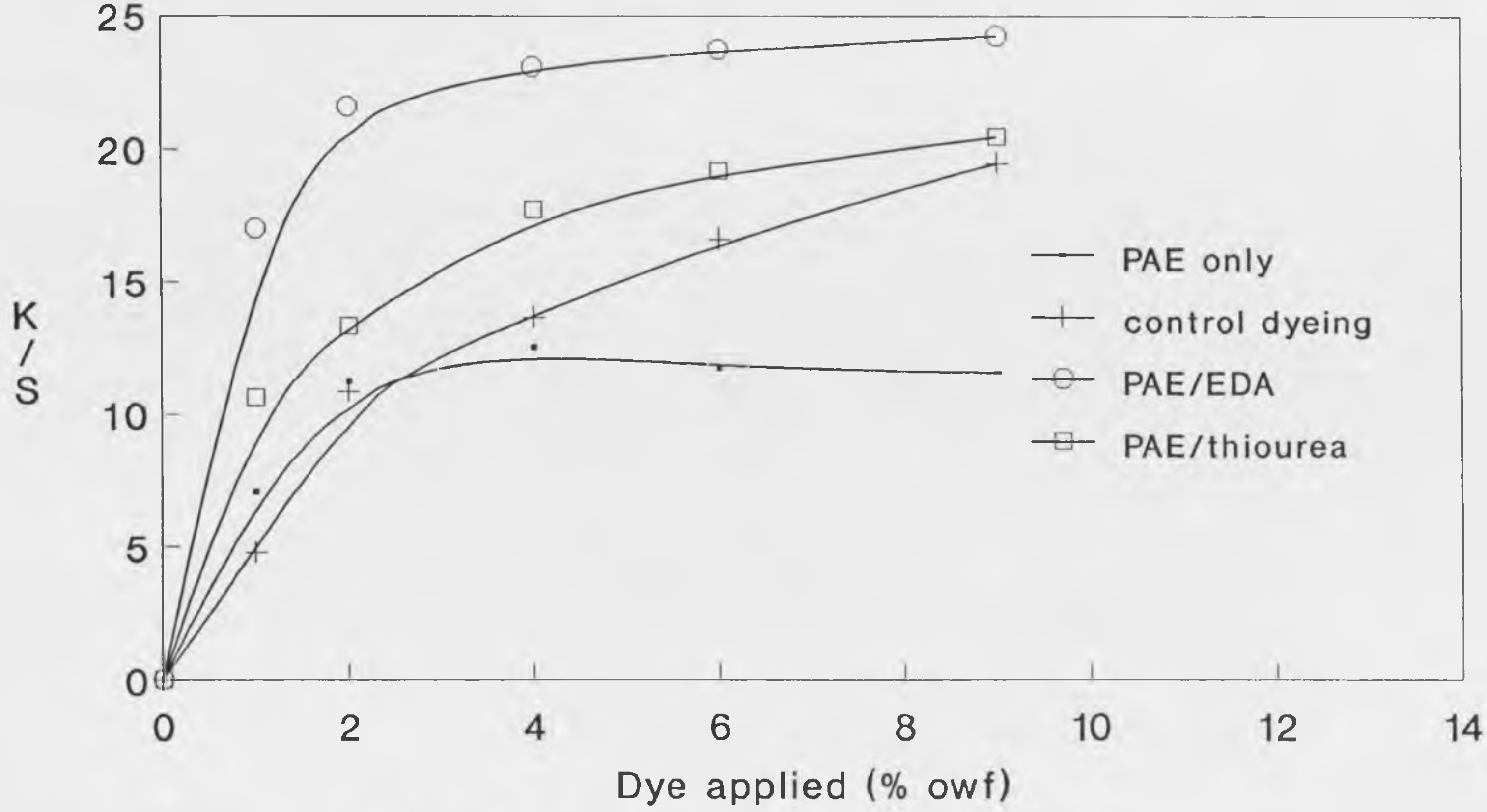
3.3.4. Effect of EDA concentration in the PAE pad liquor

Application of PAE resin and EDA were carried out at pH 8 with different EDA concentrations; pH 8 was achieved by adding formic acid to the PAE/EDA pad liquor. Table 3-3-2 shows the effect of EDA concentration on the exhaustion and fixation of subsequent dyeings. The results indicate that similar exhaustion and fixation values were obtained with concentrations of ethylene diamine ranging from 5ml/l to 20 ml/l. However, when full depths of shade(i.e. over 4 % owf) are considered, 10 g/l of ethylene diamine seems to be necessary to give adequate dye exhaustion and fixation.

3.3.5. Dyeing properties of reactive dyes on PAE/EDA treated cotton

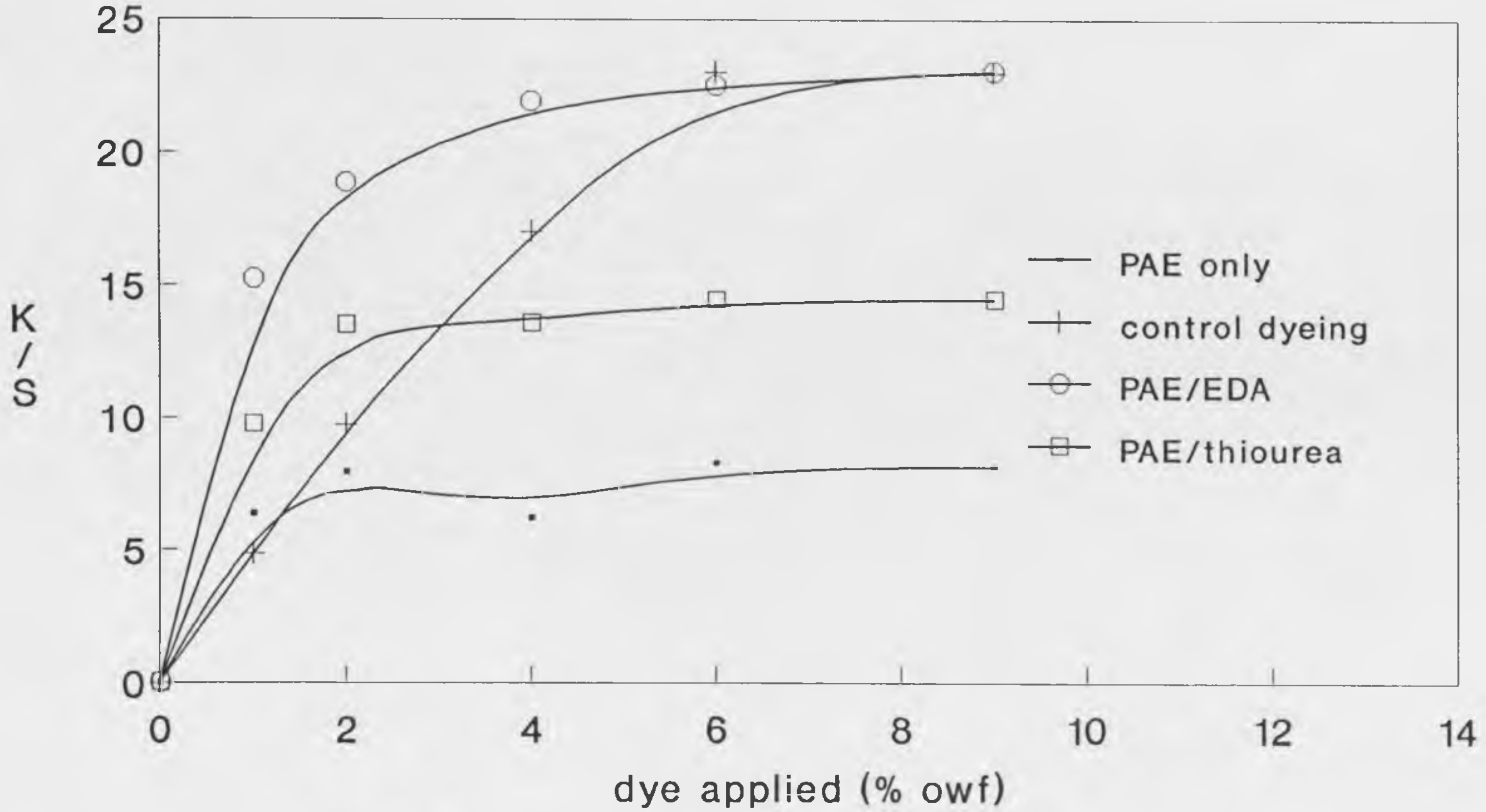
Procion Red HE-3B (ICI) and Procion Red MX-5B (ICI) were selected as being representative of both low and high reactivity dyes; 10 ml/l of ethylene diamine and 200 g/l Hercosett 125 were used to prepare the PAE/EDA pad liquor to treat the substrate. The dyeings were carried out at pH 5 in the absence of salt following the procedure described in the experimental section. The build up profiles of both dyes on this substrate are shown in figures 3-3-4 and 3-3-5. These graphs indicate that the build up properties of the two dyes on PAE/EDA treated cotton are excellent, being much better than those achieved on PAE/thiourea and PAE treated cottons. The reasons for this effect are believed to be twofold. Firstly the PAE/EDA pretreatment promotes more effective cross-linking of the resin to the cotton, unlike the situation previously reported for PAE/thiourea and PAE only treated cotton, in which a small proportion of the resin could be extracted during the dyeing process. Secondly the reactive azetidinium residues which in the earlier case competed with the reactive dye for amino nucleophiles have been greatly modified through reaction with EDA; this reaction will thus provide a large excess of nucleophilic amino sites. These mechanisms are supported

Figure 3-3-4



Build up of Procion Red MX-5B (ICI) on a variety of substrates

Figure 3-3-5



Build up of Procion Red H-E3B (ICI) on a variety of substrates by the fact that with PAE/EDA pretreatments presoaping before dyeing has no effect on colour yields (table 3-3-3).

Table 3-3-2. Exhaustion and fixation of Procion Red HE-3B (ICI) on substrates prepared using different EDA concentration

EDA conc. (ml/l)	K/S		E%	F%
	before soap	after soap		
	1 % owf dye used			
5.0	15.72	14.56	97	93
10.0	15.50	15.21	98	98
15.0	15.15	14.69	97	95
20.0	15.06	14.48	96	96
	2 % owf dye used			
5.0	20.50	18.28	93	89
10.0	20.04	18.83	95	94
15.0	19.62	18.48	95	94
20.0	19.69	18.95	94	96
	4 % owf dye used			
5.0	23.51	20.90	82	89
10.0	23.12	21.91	88	95
15.0	22.74	21.24	91	93
20.0	22.46	21.81	89	97
	6 % owf dye used			
5.0	24.10	21.73	64	90
10.0	24.30	22.52	71	93
15.0	24.62	22.91	75	93
20.0	24.39	22.32	73	92

* *All dyeings were carried out at pH 5.*

Table 3-3-3. Colour yield and fixation of dyes on both PAE/EDA pretreated and PAE/EDA pretreated then presoaped cotton

Presoaping	K/S before soap	K/S after soap	F%
	Procion Red HE-3B		
no	20.04	18.83	94
yes	20.80	19.87	96
	Procion Red MX-5B		
no	18.08	17.19	95
yes	19.04	17.93	92

It has also been found that PAE/EDA pretreatment is efficient not only when using Procion HE and MX dyes but also when using other types of reactive dyes under slightly acidic to neutral pH conditions (table 3-3-4).

The washing fastness and light fastness of Procion HE and Procion MX dyes on both PAE/EDA treated and untreated cotton are shown in tables 3-3-5 and 3-3-6. Obviously the washing fastness is excellent but the light fastness is again down by 1-2 points compared to dyeings produced by the conventional dyeing method on untreated cotton.

Table 3-3-4. Colour yield and fixation of various dyes on PAE/EDA pretreated cotton

dyes(2% owf)	K/S before soap	K/S after soap	E%	F%
Procion Red H-8BN(ICI)	19.78	17.90	98	91
Procion Red HE-3B(ICI)	20.56	19.52	97	95
Procion Red MX-5B(ICI)	18.08	17.19	93	95
Remazol Yellow R(FH)	13.92	10.19	89	73
Cibacron Red F-B(CG)	18.46	14.19	91	77
Levafix Br. Red E-BA(BY)	16.54	13.78	99	83
Drimalan Red F-2BL(Sz)	16.87	16.58	98	98

Table 3-3-5: Wash fastness(CO4) of Procion dyes on PAE/EDA (10 ml/l) treated and untreated cotton after soaping

Provion dye (2 % owf)	untreated			treated		
	E	V	C	E	V	C
Red MX-5B	5	5	5	5	5	5
Blue MX-2R	5	5	5	5	5	5
Red HE-3B	5	5	5	5	5	5
Red H8BN	5	5	5	5	5	5

E----Effect on pattern
V----Viscose adjacent
C----Cotton adjacent

Table 3-3-6: Light fastness of Procion dyes on PAE/EDA (10 ml/l) treated and untreated cotton after soaping

Procion dye (2 % owf)	untreated	treated
Red MX-5B	4 - 5	3
Blue MX-2R	5 - 6	3 - 4
Red HE-3B	5	3
Red H8BN	4 - 5	3

3.3.6. Summary of Section 3.3.

Polyamide-epichlorohydrin resins may be applied to cotton with the addition of ethylene diamine to give a substrate which is dyeable with reactive dyes under weakly acidic conditions without the necessity to add electrolyte. Fixation is achieved simply by raising the dyebath to the boil.

Dyeings produced were bright, level and of very high wash fastness. In the case of H-acid based reds some bluing of the shade was noted; this effect was also observed when these dyes were applied to wool indicating that reaction with amino groups is responsible.

In many cases the light fastness was reduced by 1-2 points. This is seen as the biggest disadvantage of the process.

The high level of dye uptake and fixation makes this process of possible interest to dyers and printers since better colour yields than normal are achievable especially at lower concentrations. Higher fixation is also noted (often of the order of 95%) thus simplifying washing off procedures and reducing the environmental problems of colour in the waste water.

CHAPTER IV

IV MODIFICATION OF COTTON WITH LOW MOLECULAR WEIGHT COMPOUNDS TO OBTAIN IMPROVED DYEING WITH CONVENTIONAL REACTIVE DYES

4.1. Pretreating Cotton with 1,1-Dimethyl-3-Hydroxyl-Azetidinium Chloride (DMAC)

4.1.1. Introduction

When cotton was modified with polymeric compounds, poor light fastness of subsequent reactive dyeings always resulted. In order to obtain dyeings on modified cotton with good light fastness, a low molecular weight compound, dimethyl-azetidinium-chloride (DMAC), was prepared and used to pretreat cotton. This compound has similar characteristics to Hercosett in that it is water soluble, cationic due to the azetidinium group and through this group capable of reaction with nucleophilic cellulosate anions.

The preparation of DMAC is described in the experimental section. The FTIR spectrum of this compound is shown in figure 4-1-1. In the spectrum, the peak at 3386 cm-1 is from absorption caused by O-H stretch vibrations and the broadness of this peak is due to hydrogen bonding. The peak at 1231 cm-1 is attributed to the C-N stretch absorption and the deformation vibrations of C-H and O-H bonds are possibly responsible for the peaks appearing at 1478 cm-1 and 1365 cm-1 respectively.

4.1.2. Light fastness of dyeings on the low molecular weight compounds on treated cotton

Cotton fabric was pretreated with different concentrations of DMAC using a pad-dry-bake method. The pretreated cotton was dyed at pH 7 using 2% owf Procion Brilliant Red HEGL (low reactivity, bis-mono-chlorotriazine derivative). The light fastness of dyeings on this substrate with the reactive dyes was tested and a comparison also made with the

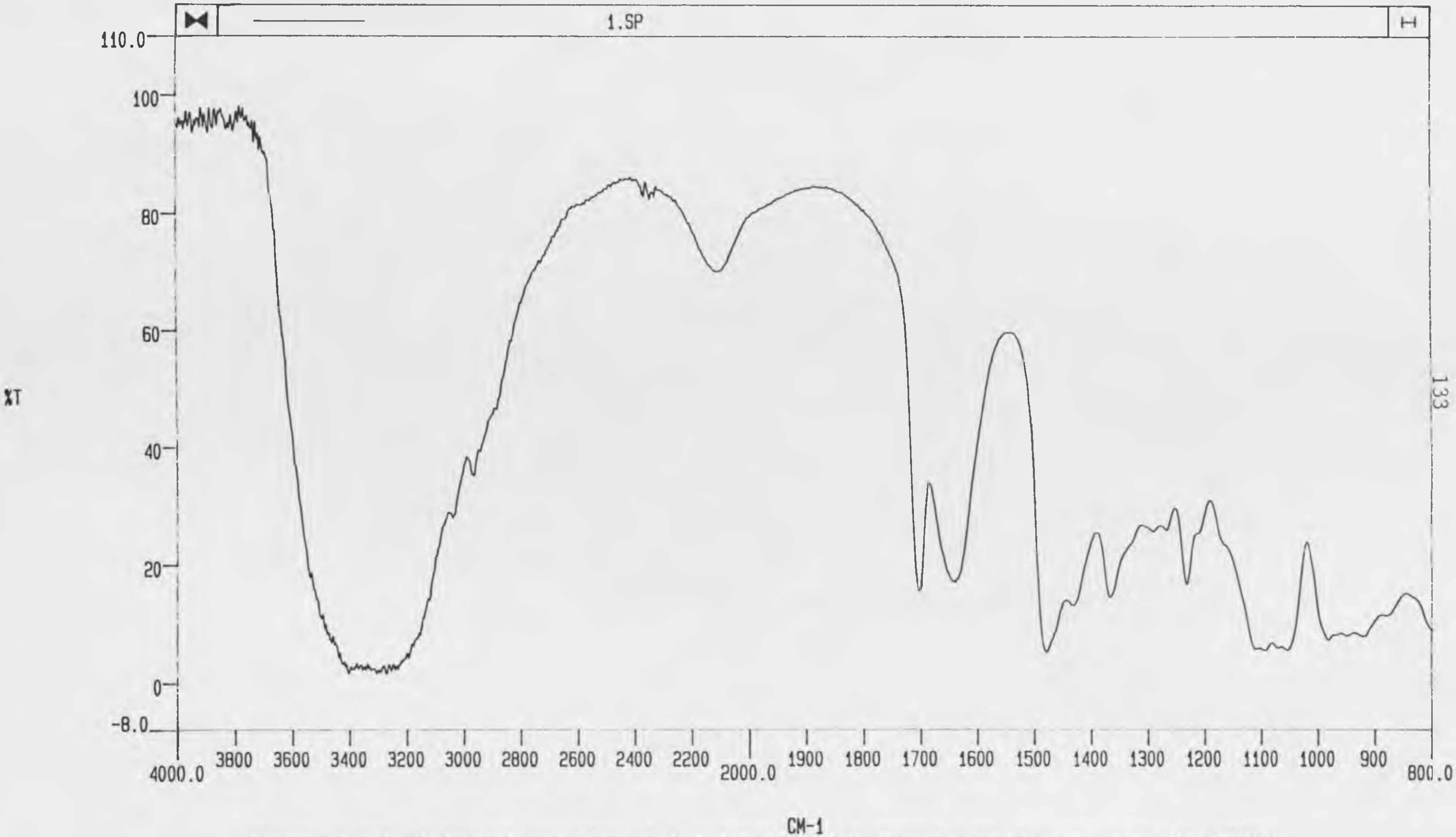


Figure 4-4-1 Infrared spectrum of 1,1-dimethyl-3-hydroxyl-azetidinium chloride (DMAC)

corresponding dyeings on both Hercosett treated cotton and untreated cotton dyed using the conventional method; Table 4-1-1 shows the light fastness results achieved.

Table 4-1-1 Light fastness of dyed fabrics (2% owf Procion Brill. Red HEGL)

dyeing method	light fastness
Hercosett	3
DMAC	5
Conventional	5

4.1.3. Application conditions for DMAC on cotton

4.1.3.1. Effect of DMAC concentration in the pad-liquor on the dyeing properties of the modified cotton.

Table 4-1-2 shows the colour yields obtained with increasing DMAC concentration. These results indicate that 40g/l of DMAC in the padding liquor is the minimum concentration required to give adequate dye uptake; however dye fixation increases further at higher DMAC concentration.

Table 4-1-2 Colour yield of DMAC treated and dyed cotton fabrics (2% owf Procion Brill.Red HEGL)

concentration of DMA-AC (g/l)	K/S			
	before soap	after soap	E%	F%
80	18.561	12.165	98	66
60	18.792	10.740	98	57
40	18.453	9.733	98	53
20	13.732	6.357	72	46
conventional dyeing	14.815	12.165	85	82

4.1.3.2. Effect of baking conditions

Tables 4-1-3 and 4-1-4 shows that after predrying padded fabric for 3 mins, optimum colour yields were obtained by baking the fabric at 200°C for 1 minute without washing-off prior to dyeing.

Table 4-1-3 Dye colour yield according to baking conditions (2% owf Procion Brill. Red HEGL)

Conc. of DMAC (g/l)	Temp. (°C)	Baking time (mins)	K/S before soap	K/S after soap	E%	F%
80	200	1	18.562	12.165	98	66
	150	2	15.369	11.115	81	72
	(no baking)		10.161	6.401	53	63
60	200	1	18.792	10.740	98	57
	150	2	13.974	5.704	73	41
40	200	1	18.453	9.733	98	53
	150	2	14.815	5.383	98	36

Table 4-1-4 Effect of washing-off (prior to dyeing) on colour yield

Washing-off after baking	K/S before soap	K/S after soap	E%	F%
no	18.483	9.733	98	53
yes	14.502	9.351	76	64

40 g/l of DMAC, 2% owf Procion Brilliant Red HEGL were used in this experiment.

4.1.3.3. Effect of presence of alkali in padding liquor on dye fixation

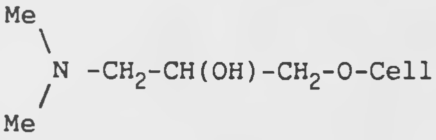
Application of DMAC in the presence of strong alkali was also examined (table 4-1-5).

Table 4-1-5 Effect of NaOH in the DMAC (40g/l) padding liquor on subsequent dye fixation

conc. of NaOH (g/l)	K/S before soap	K/S after soap	E%	F%
0	11.660	5.664	66	49
4	12.234	11.612	71	95

2% owf of Levafix Brilliant Red E-BA (medium reactivity, 2,4-difluoro-5-chloro pyrimidine derivative) was used.

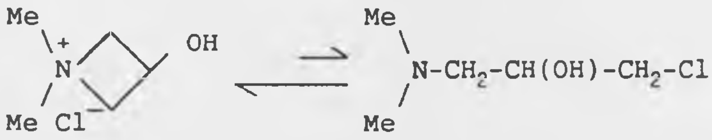
From the results obtained, it is clear that the presence of a strong alkali in the padding liquor is essential for sufficient covalent bond formation between DMAC and cellulose. The behaviour of DMAC treatments when applied to cellulose by baking under neutral conditions can be explained by both reaction with cellulose to form



$$\mathrm{Me_2N{-}CH_2{-}CH(OH){-}CH_2{-}O{-}Cell}$$

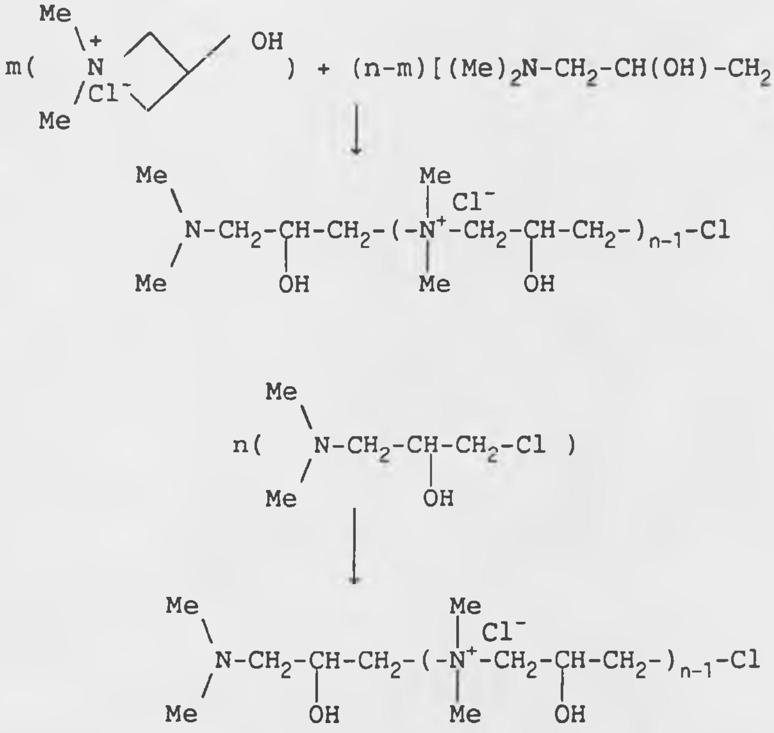
and possibly by the formation of medium molecular weight oligomers which are still able to penetrate the fibre.

The equilibrium between DMAC and 1-N,N-dimethylamino-2-hydroxy-3-chloropropane could be described:



Scheme 4-1-1

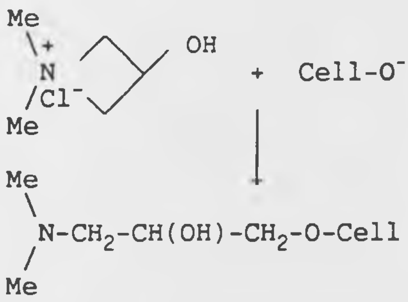
Since the tertiary amino group is a fairly strong nucleophile, it may react with the azetidinium cation or the γ-chloro group to form DMAC oligomers:



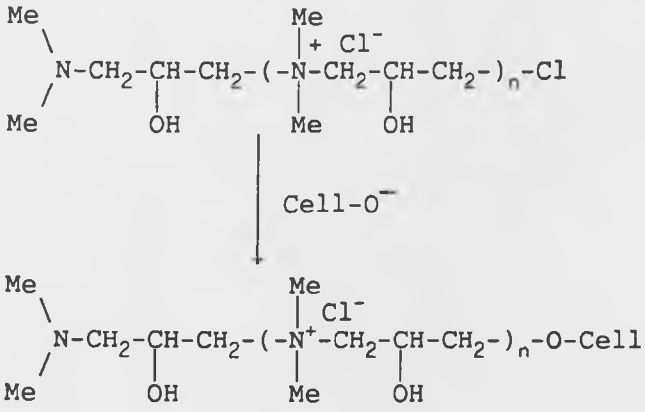
Scheme 4-1-2

The strongly cationic character and relatively large molecular weight of these oligomers makes them substantive to cotton by means of both molecular interactions and ionic bond formation. Such treatments can not be removed under neutral conditions but significant removal occurs under alkaline conditions explaining the only moderate reactive dye fixation values achieved when DMAC was applied under neutral conditions.

When DMAC was applied in the presence of strong alkalis such as NaOH, apart from the possible formation of oligomers, the reaction between DMAC or its oligomers and cellulose is promoted due to the increased nucleophilicity of the cellulose. DMAC and its oligomers are thus covalently bonded and cannot therefore be removed even under alkaline soaping conditions:



Scheme 4-1-3



$$Me_2N-CH_2-CH(OH)-CH_2-(-N^+(Me)_2-CH_2-CH(OH)-CH_2-)_n-Cl\ Cl^- \xrightarrow{Cell-O^-} Me_2N-CH_2-CH(OH)-CH_2-(-N^+(Me)_2-CH_2-CH(OH)-CH_2-)_n-O-Cell\ Cl^-$$

Scheme 4-1-4

Since reactive dyes cannot react with cellulose under neutral conditions, the good fixation of reactive dyeings on DMAC treated cotton produced under neutral dyeing conditions must be due to the presence of tertiary amine nucleophiles and possibly increased deprotonation of hydroxyl groups in the vicinity of basic tertiary and quaternary nitrogen atoms; such effects would lead to the formation of highly nucleophilic cellulosate residues which readily form covalent bonds with the reactive dye even under the above neutral to slightly acidic conditions.

4.1.4. Effect of pH when dyeing DMAC treated cotton with reactive dyes

Table 4-1-6. shows that the colour yields on DMAC treated cotton are slightly higher when it is dyed with highly reactive dyes under neutral conditions than under slightly acidic conditions. This is because the cationic groups in the substrate impart sufficient substantivity at pH 5-7, but the colour yields are slightly higher under neutral conditions since the reactivity of the substrate is higher (increased concentration of the nucleophilic cellulosate anion).

Figure 4-1-2 shows the effect of dyeing pH on colour yield in more detail using the FCP dye Levafix Brilliant Red E-BA (2% owf)(By).

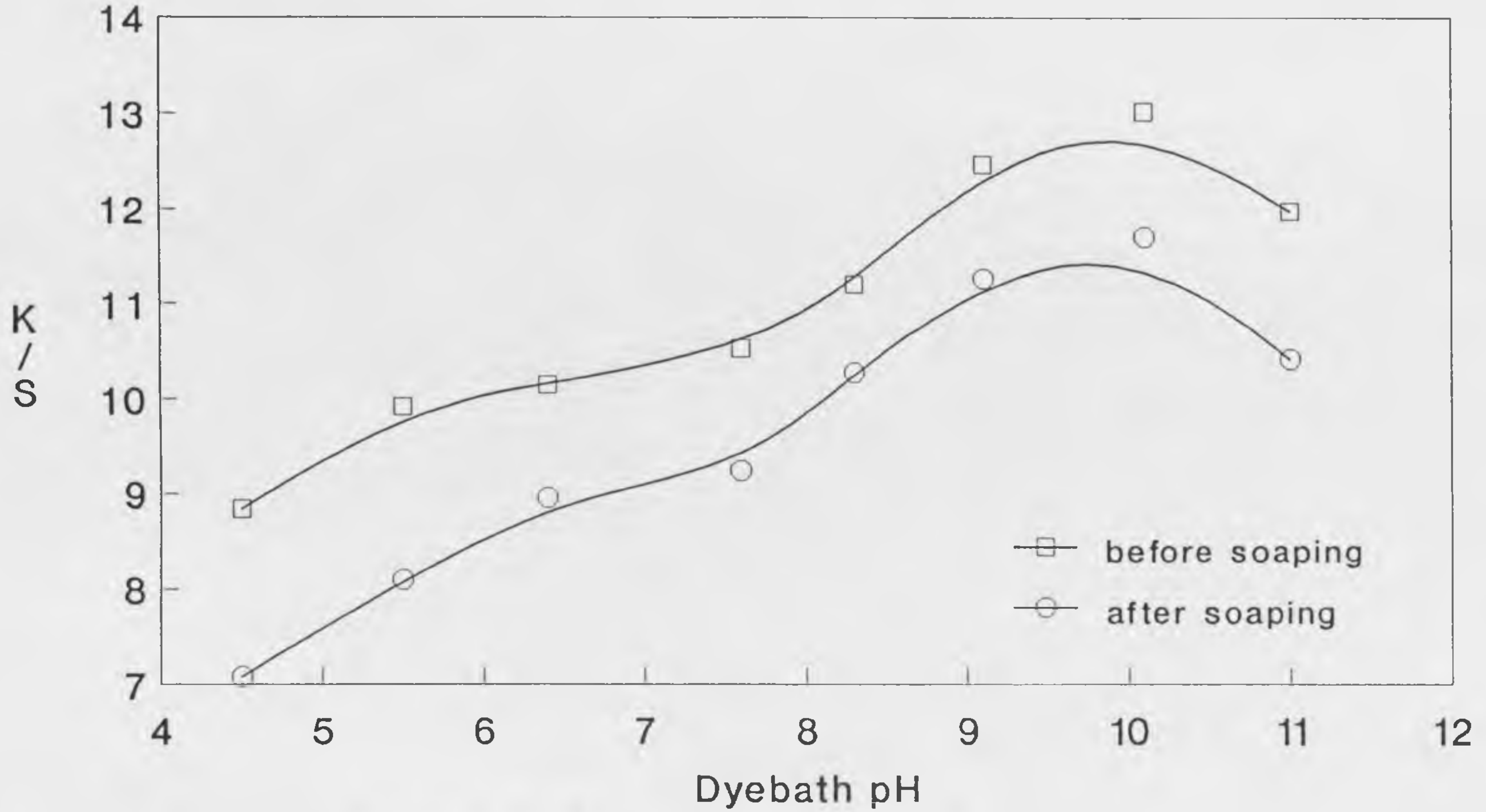
Table 4-1-6 Effect of dyeing pH on colour yield of dyeings on DMAC (40g/l DMAC, 4g/l NaOH) treated cotton

	K/S			
pH	before soap	after soap	E%	F%
5	11.17	10.99	74	98
7	12.77	12.63	85	99

2% owf of Procion Red MX-G (ICI)was used.

A study of this figure indicates high dye substantivity even under mildly alkaline conditions; however aliphatic tertiary amine residues could still be protonated at these pH values (pKa values of aliphatic tertiary amines are typically 9-10.)

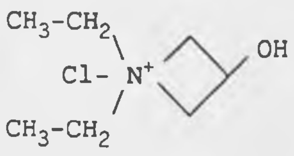
Figure 4-1-2



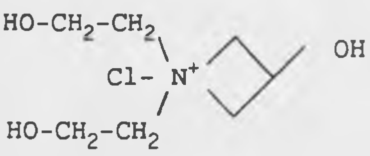
Colour yield of dyeing of Procion Red MX-G on DMAC cotton vs dyebath pH

4.1.5. Effect of pretreating cotton with compounds analogous to DMAC on its dyeability

Two analogous compounds to DMAC, 1,1-diethyl-3-hydroxyl-azetidinium chloride (DEAC) and 1,1-diethylol-3-hydroxyl-azetidinium chloride (DEOAC), were also prepared and used to modify cotton.



DEAC



DEOAC

These two compounds were applied by padding cotton with a pad liquor containing 40 g/l of the compound, 4 g/l of NaOH and 10 g/l of Sandozin NIE. The impregnated fabric was then dried at 100°C for 3 minutes and baked at 200°C for 1 minute. Dyeing of this treated cotton with a difluoromonochloro pyrimidine reactive dye (Levafix Red E-BA) was carried out under neutral pH conditions and at the boil for 1 hour without addition of electrolyte. Colour yield and fixation values achieved on the substrates are shown in table 4-1-7. It can be seen that the colour yield and fixation values of dyeings on the DEAC and DEOAC treated cotton are much lower compared with those on DMAC treated cotton. This may be attributed to the fact that the steric hindrance produced by the longer alkyl side chains in the DEAC and DEOAC azetidinium groups interfere with their reaction with the cellulosate anion.

Table 4-1-7 comparison of dyeability of DMAC treated cotton with its analogues

compound name	concn used (g/l)	K/S before soap	K/S after soap	E%	F%
DMAC	40	11.07	10.26	70	93
DEAC	40	5.23	4.10	33	78
DEOAC	40	4.56	2.58	28	56

4.1.6. Comparison of DMAC treatments with Glytac A treatments and conventional dyeing

Glytac A (Protex) is a commercial compound sold as a solid material (glycidyl-trimethyl-ammonium chloride), it reacts with cellulose via the reactive epoxy group according to the scheme described in the introduction (scheme 1-3-5).

A comparison was therefore made between DMAC and Glytac A treatments in order to evaluate the practical importance of the DMAC treatment. The results are shown in table 4-1-8 which shows: i) Almost the same dyeing behaviour was achieved when using either DMAC pretreatment or Glytac A pretreatment; this indicates that DMAC pretreatment may be an alternative practical method for achieving neutral reactive dyeing of cellulose with high dye fixation; ii) increased colour yields were obtained when using DMAC and Glytac A pretreatments when compared with the conventional dyeing method; iii) bound nitrogen contents were similar for both treatments.

These results indicate that modification of cellulose leading to attachment of tertiary or quaternary amino groups by covalent bonding gives a substrate which may be dyed with reactive dyes at pH 7 without salt addition; fixation of the dye on the fibre is extremely high and hence lengthy soaping off processes at the boil are not required.

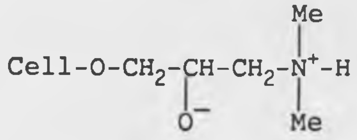
Table 4-1-8 Colour yield of dyeings on DMAC and Glytac A treated cotton

reagent	total nitrogen (%)	dye (2% owf, pH 7, 100°C)	K/S before soap	K/S after soap	E%	F%
Glytac A (40g/l)	0.108	Procion Red MX-G	12.838	11.775	85	92
		Levafix Br.Red E-BA	10.754	10.722	68	99
DMAC (40g/l)	0.150	Procion Red MX-G	12.766	12.625	85	99
		Levafix Br.Red E-BA	11.037	10.256	70	93
Conventional dyeing		Procion Red MX-G	4.245	3.477	40	83
		Levafix Br.Red E-BA	10.561	9.583	71	90

Both DMAC and Glytac A pad-liquors contained 4g/l NaOH. Baking conditions for DMA-AC were 200°C, 1 minute and for Glytac A 120°C, 3 minutes

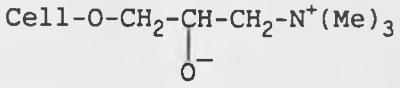
The reason for the high fixation values achieved on the above modified substrates under such mild conditions is worthy of further thought. It is likely that the secondary hydroxy group, in the 2-position of the propane side chain, is ionised at a much lower pH value than the cellulose hydroxyl groups and is thus highly nucleophilic even at pH 7. Schematically the following species could be responsible for the high neutral reactivity:

i)



$\text{Cell-O-CH}_2\text{-}\underset{\text{O}^-}{\text{CH}}\text{-CH}_2\text{-}\overset{\text{Me}}{\underset{\text{Me}}{\text{N}^+}}\text{-H}$

ii)



$\text{Cell-O-CH}_2\text{-}\underset{\text{O}^-}{\text{CH}}\text{-CH}_2\text{-N}^+(\text{Me})_3$

4.1.7. Summary of section 4.1.

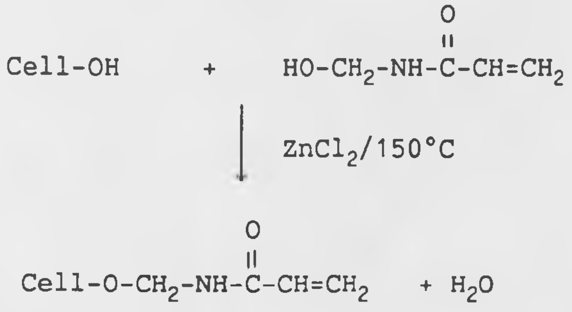
The improved substantivity and fixation of reactive dyeings under neutral conditions has been achieved when cotton was pretreated with DMAC. Light fastness of dyeings on this small molecular weight compound treated cotton is as good as that on untreated cotton dyed with reactive dyes using conventional dyeing methods. The improved neutral fixation has been suggested to occur as a result of increased cellulose hydroxyl ionization due to the proximity of strongly basic groups.

4.2. Amination of Cotton through Pretreatment with N-Methylol Acrylamide (NMA)

4.2.1. Introduction

Chapter 3 and section 4.1. have considered a number of different fibre pretreatments which allow reactive dyeing to be performed under neutral to slightly acidic conditions in the absence of electrolyte. All of these pretreatments introduced cationic residues in the form of quaternary, tertiary and secondary amino residues.

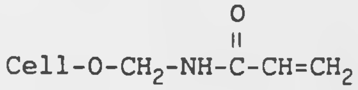
To investigate systematically the effect of attaching a variety of amines to the cellulose fibre by a simple pre-treatment it was decided to modify the cotton with N-methylol-acrylamide (NMA). This reagent is a versatile, commercially available crosslinking agent formerly employed in the Deering Milliken's Visa process for producing durable press cellulosic fabrics [105,106]. Cotton will react with NMA in the presence of a Lewis acid catalyst according to scheme 4-2-1.



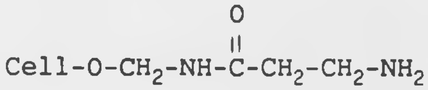
$$\text{Cell-OH} + \text{HO-CH}_2\text{-NH-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-CH=CH}_2 \xrightarrow{\text{ZnCl}_2/150°\text{C}} \text{Cell-O-CH}_2\text{-NH-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-CH=CH}_2 + \text{H}_2\text{O}$$

Scheme 4-2-1

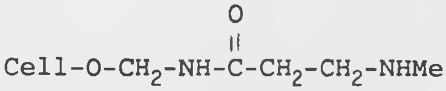
Using the pendant double bond as a site for Michael addition a number of modified celluloses could, in principle, be readily prepared. This section thus considers the preparation and reactive dyeing properties of the following six cellulose derivatives (I-VI):

I 

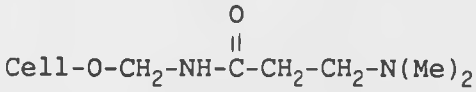
$\mathrm{Cell\text{-}O\text{-}CH_2\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH{=}CH_2}$

II 

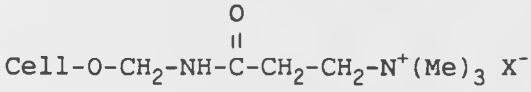
$\mathrm{Cell\text{-}O\text{-}CH_2\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}NH_2}$

III 

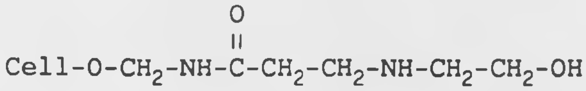
$\mathrm{Cell\text{-}O\text{-}CH_2\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}NHMe}$

IV 

$\mathrm{Cell\text{-}O\text{-}CH_2\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}N(Me)_2}$

V 

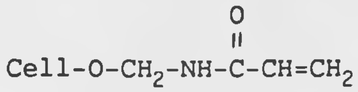
$\mathrm{Cell\text{-}O\text{-}CH_2\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}N^{+}(Me)_3\ X^{-}}$

VI 

$\mathrm{Cell\text{-}O\text{-}CH_2\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}OH}$

4.2.2. FTIR study of treated and untreated cotton fabrics

Figure 4-2-1 shows the FTIR spectrum of NMA cotton from which the spectrum of untreated cotton has been subtracted. The two strong absorbances at 1671 cm-1 and 1543 cm-1 indicates the presence of monosubstituted amide groups in the substrate, a medium absorbance at 1626 cm-1 is due to the presence of pendant double bonds from the N-methylol-acrylamide reaction. Thus following pretreatment with NMA, the cellulosic fibre is modified:



$\mathrm{Cell\text{-}O\text{-}CH_2\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH{=}CH_2}$

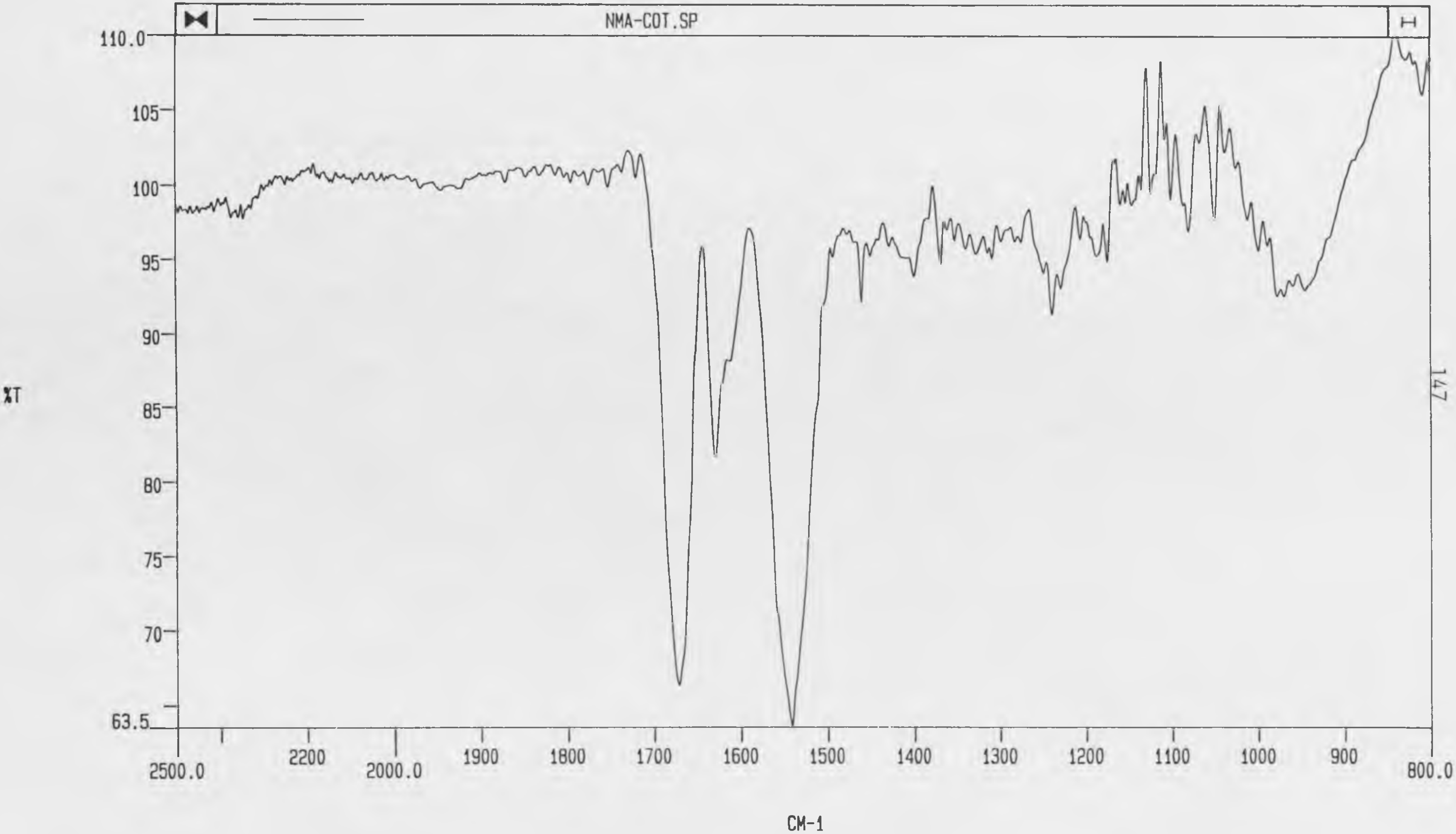


Figure 4-2-1 Infrared spectrum by subtracting cotton from N-methylol acrylamide (NMA) treated cotton

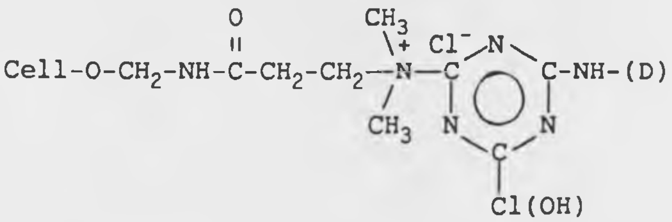
Figures 4-2-2, 4-2-3, 4-2-4, 4-2-5, 4-2-6 and 4-2-7 show the spectra of the substrates obtained by aminization of NMA cotton with ammonia, methylamine, dimethylamine, trimethyl amine and ethanolamine respectively. The disappearance of the absorbance at 1626 cm-1 indicates that the amines add readily to the double bond.

4.2.3. Dyeing properties of different aminized cottons

Table 4-2-1 shows the colour yield and fixation values of reactive dyeings on different aminized substrates. It can be seen clearly that introduction of primary and secondary amino groups by treating NMA cotton with ammonia and methylamine (or ethanolamine) respectively gives rise to dyeings with good colour yield and high fixation values. This is clearly due to the introduction of primary and secondary amino groups which improve both the substantivity of the dye for the substrate and the reactivity of the substrate.

It was also found that the presence of tertiary amino groups in the substrate improved dye exhaustion but did not improve dye fixation under weakly acidic conditions. Under these conditions a significant number of tertiary amine sites are protonated thus offering a cationic site for the anionic dye explaining the observed high substantivity.

Tertiary amino groups would react with the dyes to form the following derivative:



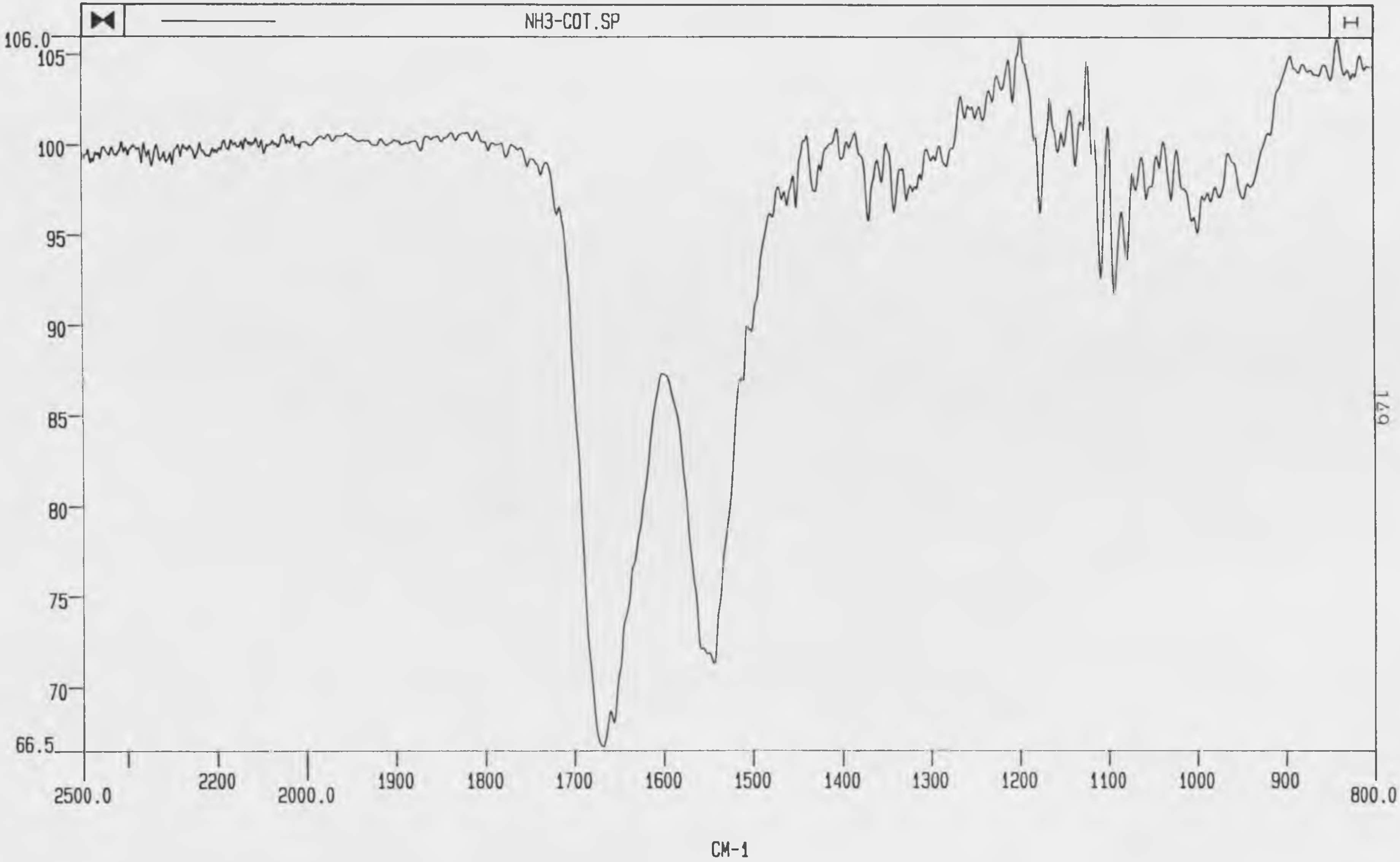


Figure 4-2-2 Infrared spectrum by subtracting cotton from NMA/ammonia treated cotton

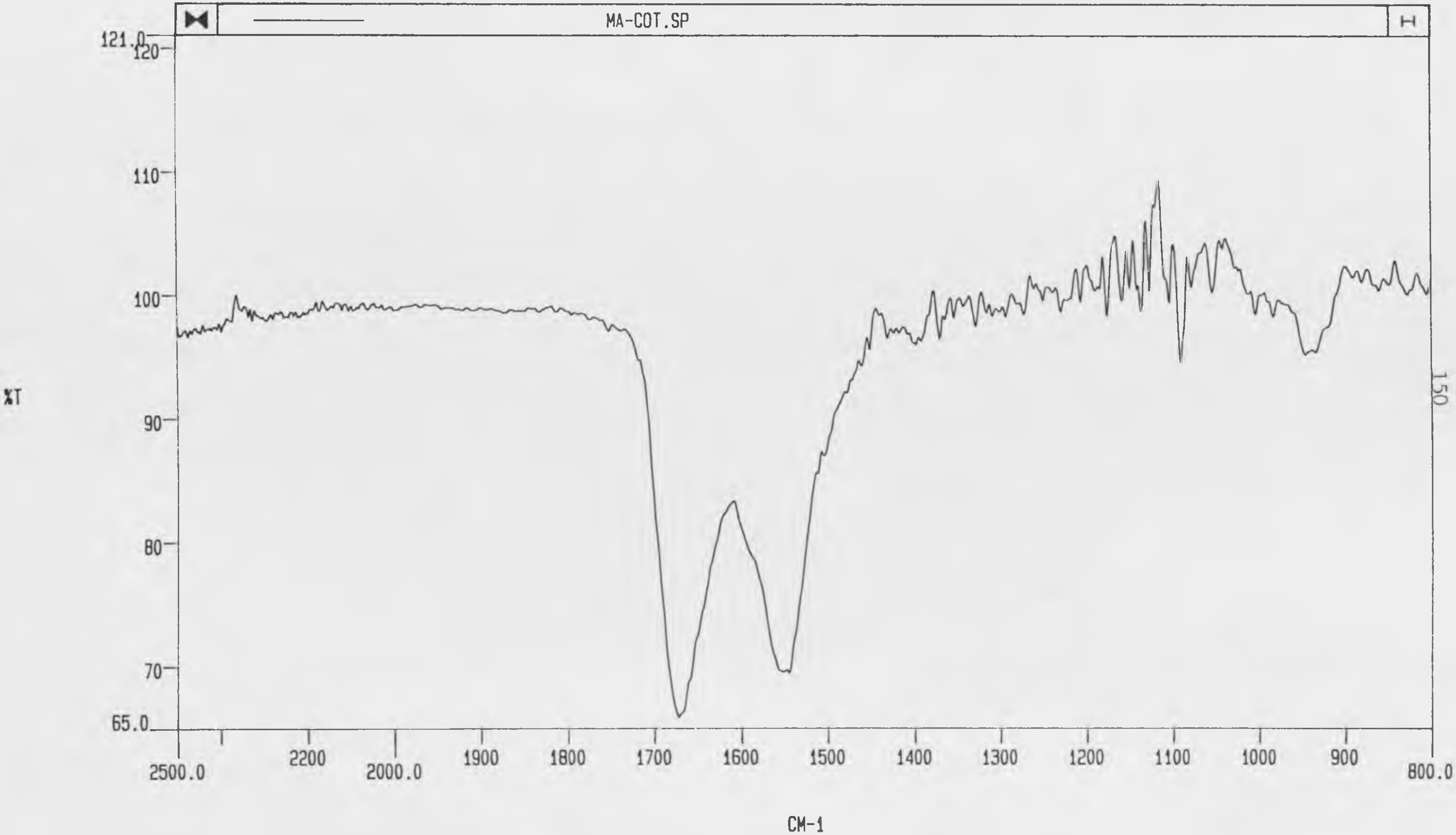


Figure 4-2-3 Infrared spectrum by subtracting cotton from NMA/methylamine treated cotton

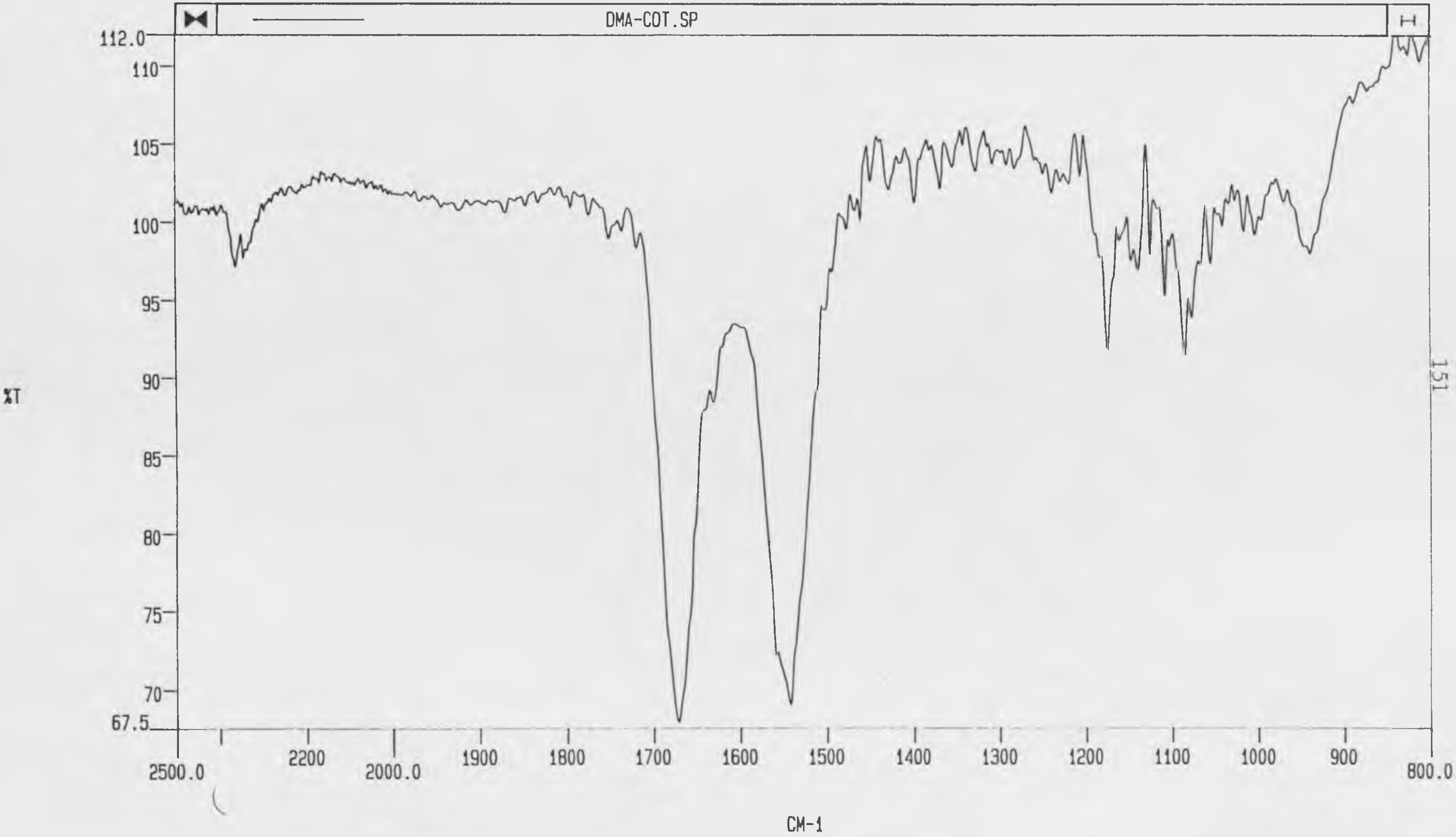


Figure 4-2-4 Infrared spectrum by subtracting cotton from NMA/dimethylamine treated cotton

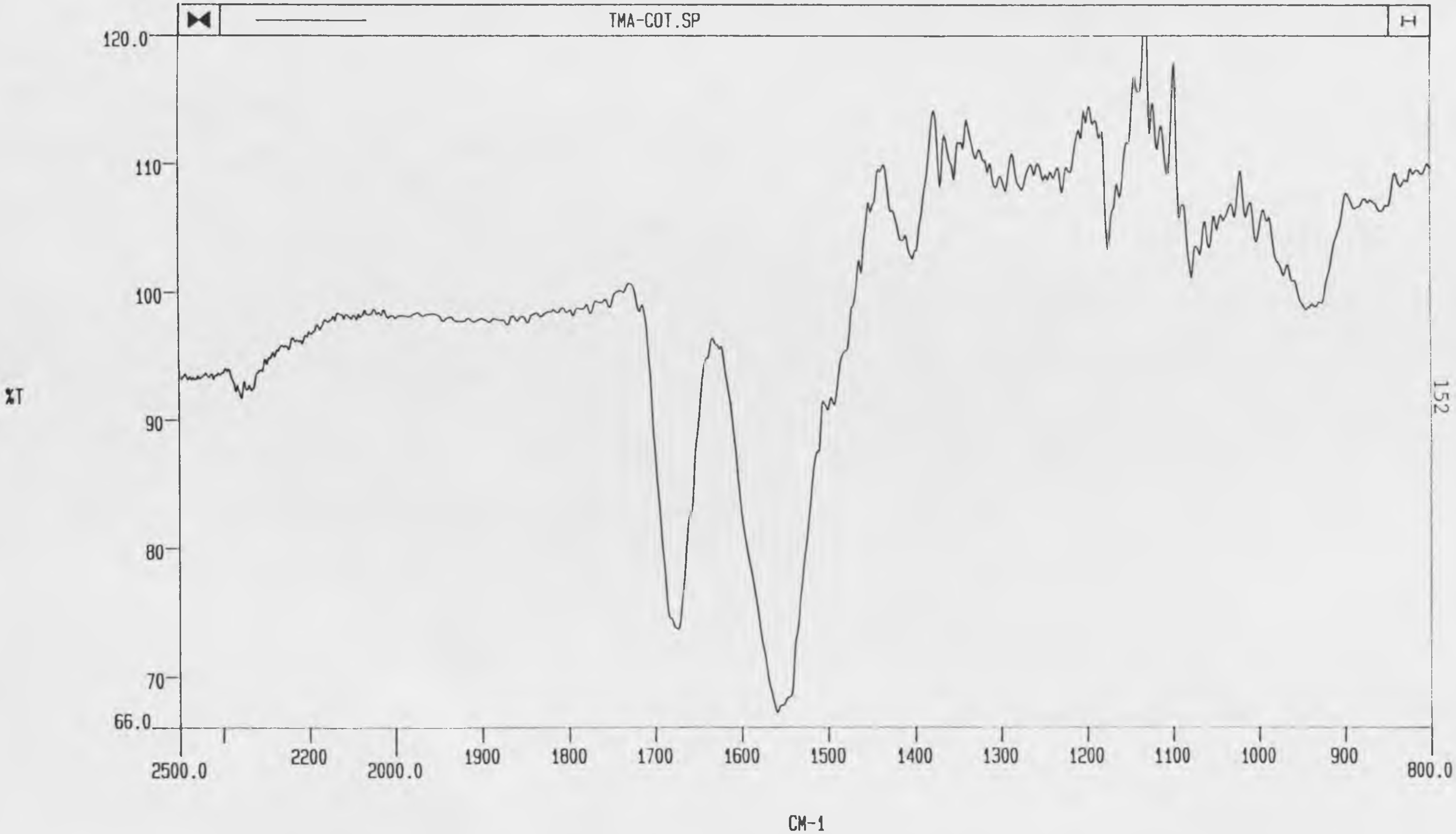


Figure 4-2-5 Infrared spectrum by subtracting cotton from NMA/trimethylamine treated cotton

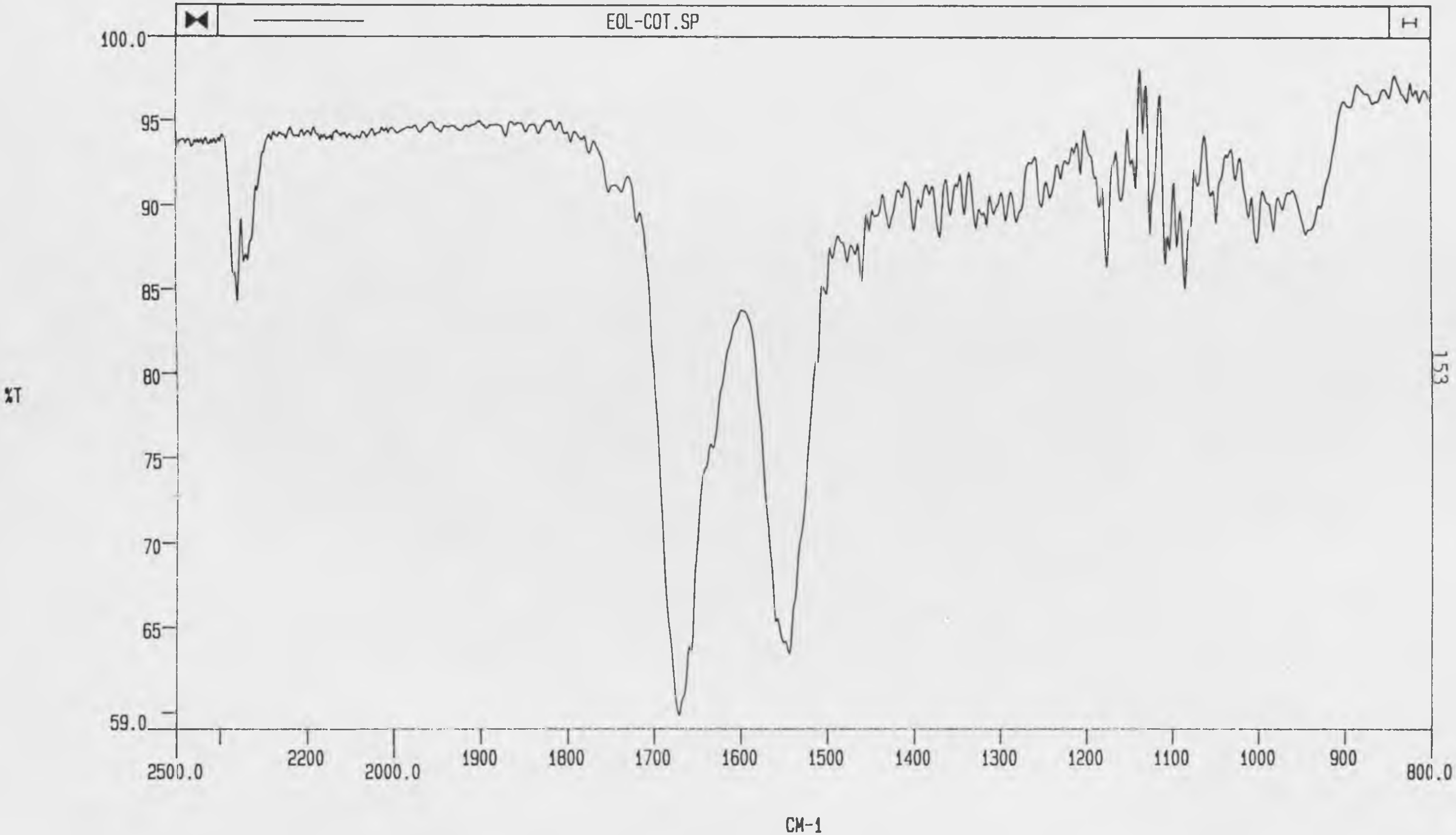


Figure 4-2-6 FTIR spectrum by subtracting cotton from NMA/ethanolamine (batchwise) treated cotton

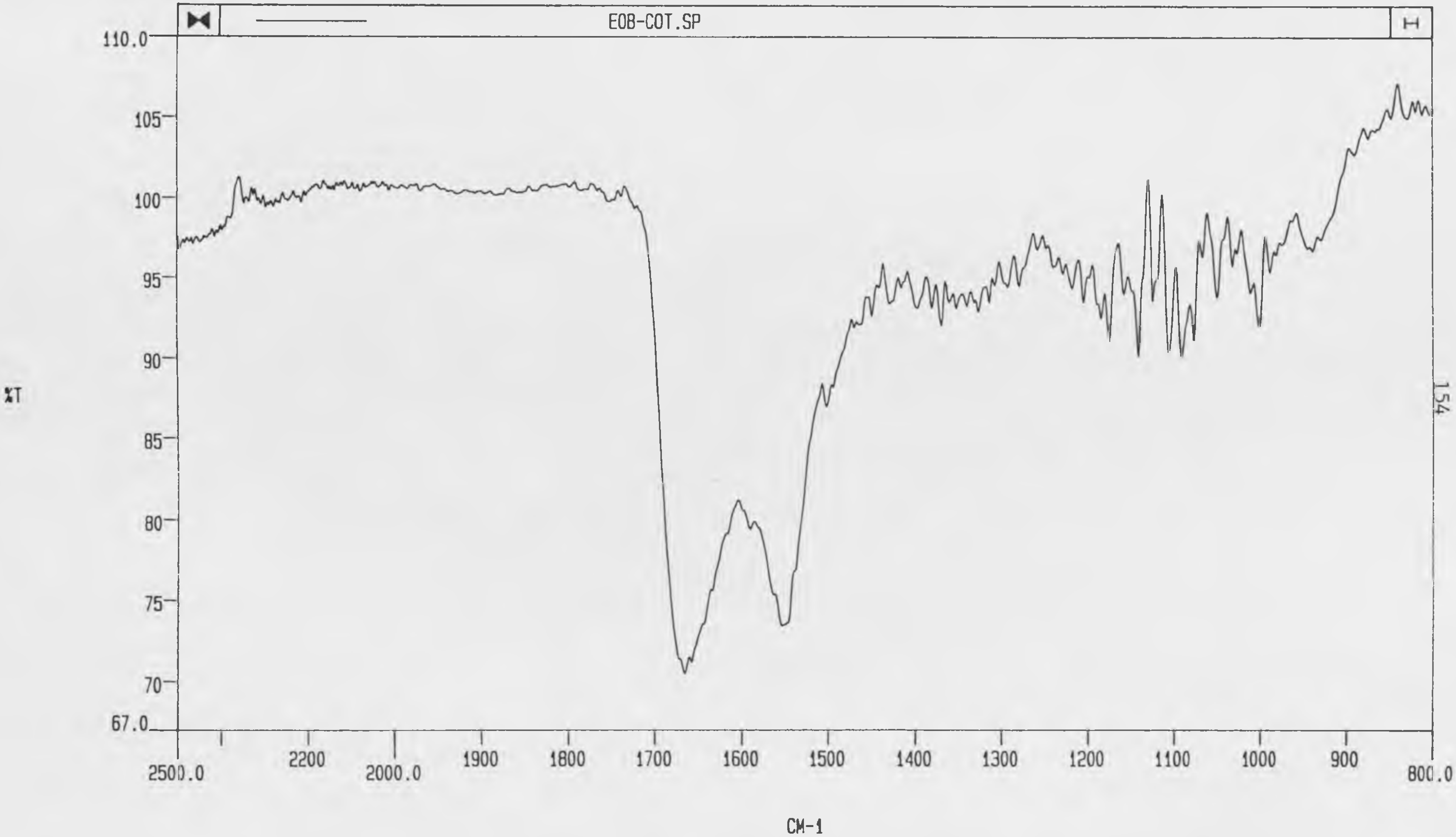
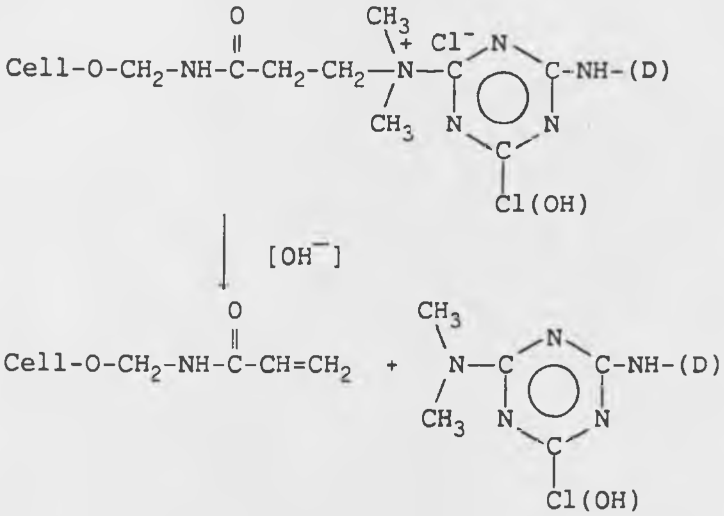


Figure 4-2-7 FTIR spectrum by subtracting cotton from NMA/ethanolamine (pad-batch) treated cotton

Since the onium group is strongly electron-withdrawing and thus a very good leaving group, its elimination occurs readily during alkaline soaping thus accounting for the low fixation values on substrate IV. This effect is described in scheme 4-2-2.

Table 4-2-1 also shows that under weakly acidic conditions the colour yield and fixation of dyeings on the substrate containing the fully quaternised amino groups are fairly good. This was attributed to the easier deprotonation of cellulose hydroxyl groups in the vicinity of the cationic groups and to the increased substantivity of the anionic dye for the cationic site.



Scheme 4-2-2

Comparing the results for dyeing the pretreated cotton with those from the conventional dyeing of untreated cotton, it can be seen that in some cases the colour strength of dyeings obtained on the former is significantly stronger(>100%) than for the dyeings on untreated cotton, indicating that large savings in dye usage may be made.

Table 4-2-1 Colour yield and fixation of Procion Red MX-G (ICI,CI Reactive Red 5)(2% owf) on different substrates

Substrate Type	colour yield		E%	F%
	before soap	after soap		
II (ammonia)	13.77	13.64	91	99
III(methylamine)	14.64	14.45	93	99
IV (dimethylamine)	15.60	1.94	94	12
V (trimethylamine)	10.32	8.93	85	87
VI (ethanolamine)	12.61	11.52	91	91
UT (conventional dyeing) (4% owf of dye)	14.31	14.10	71	98

Table 4-2-1 demonstrates that best results were obtained by using ammonia, ethanolamine and methylamine as the reactive amines to add on the NMA cotton. For practical purposes, the first two may be more important. Ammonia may be applied by a batchwise method, it is cheap and practically acceptable, especially at lower concentrations. Table 4-2-2 shows that the ammonia concentration can be reduced from 30 ml/l to 10 ml/l without affecting colour yield and fixation. This concentration value could be used under mill conditions without any problems.

Table 4-2-2 Effect of ammonia concentration in the amine pretreatment on colour yield and fixation of Procion Red MX-G(ICI,CI Reactive Red 5)(2% owf)

conc. (ml/l)	colour yield		E%	F%
	before soap	after soap		
10	13.72	13.34	91	97
30	13.77	13.64	91	99

It is convenient to carry out the amine pretreatment step by a pad-dry-bake procedure followed by pad-batch aminization rather than pad-dry-bake followed by batchwise amine treatment. In the pad-batch procedure, ammonia can not be used at the higher concentrations required. Ethanolamine is a safe compound and has no smell even at high concentration. Table 4-2-3 shows the results obtained when ethanolamine is used in the different pretreatment procedures; pad-batch application gives the best results in terms of maximum colour yield of subsequent reactive dyeings.

Table 4-2-3 Colour yield and fixation of Procion Red MX-G (ICI, 2% owf) on NMA/ethanolamine cotton

application procedure	colour yield		E%	F%
	before soap	after soap		
batchwise(2.5 ml/l)	12.61	11.52	90	91
pad-batch(50 ml/l)	18.54	16.81	97	91

4.2.4. Conditions for dyeing aminized cotton with reactive dyes

Table 4-2-4 shows that adding electrolyte to the dyebath has no effect on the dyeability of reactive dyes on the NMA/amine treated cotton, indicating that the NMA/amine cotton behaves much more like wool when dyeing with anionic reactive dyes.

Table 4-2-4 Colour yield and fixation of Procion Red MX-G (ICI, 2% owf) on NMA/NH_3 cotton

salt added (g/l)	colour yield		E%	F%
	before soap	after soap		
0	13.77	13.64	91	99
20	13.30	13.18	91	99

The effect of dyebath pH on the dyeability of amino-containing substrates is shown in table 4-2-5. In this study, the substrate used was NMA/ethanolamine cotton obtained by the pad-batch application of ethanolamine to NMA cotton. The results show that colour yield values decrease slightly with increasing pH. This can be explained by the increased protonation of the secondary amino groups at the lower pH values, increasing the substantivity for anionic dyes.

Table 4-2-5 Colour yield and fixation of Procion Red MX-G (ICI, 2% owf) on NMA/ethanolamine cotton

pH	colour yield		E%	F%
	before soap	after soap		
5	17.26	16.81	96	97
6	16.94	16.67	95	98
7	14.99	14.35	94	96

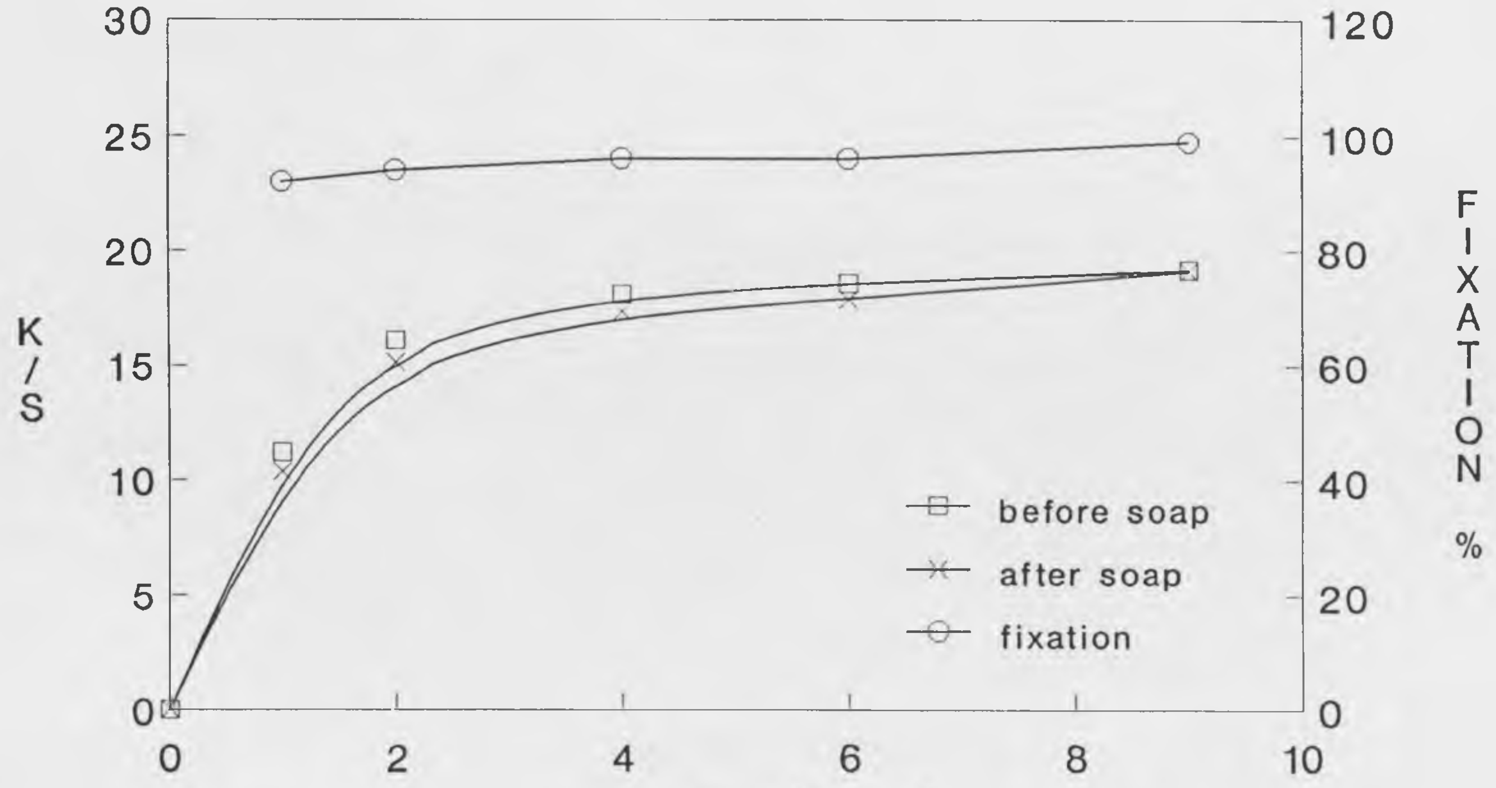
4.2.5. The build up of reactive dyes on NMA/amine treated cotton

Reactive dyes build up very well on the NMA/amine treated cotton (figures 4-2-8 and 4-2-9), indicating that in the case of the NMA/ethanolamine pretreatments sufficient reactive dye sites are supplied, whereas the NMA/ammonia procedure is much less effective.

4.2.6. The quality of reactive dyeings on the NMA/amine treated cotton

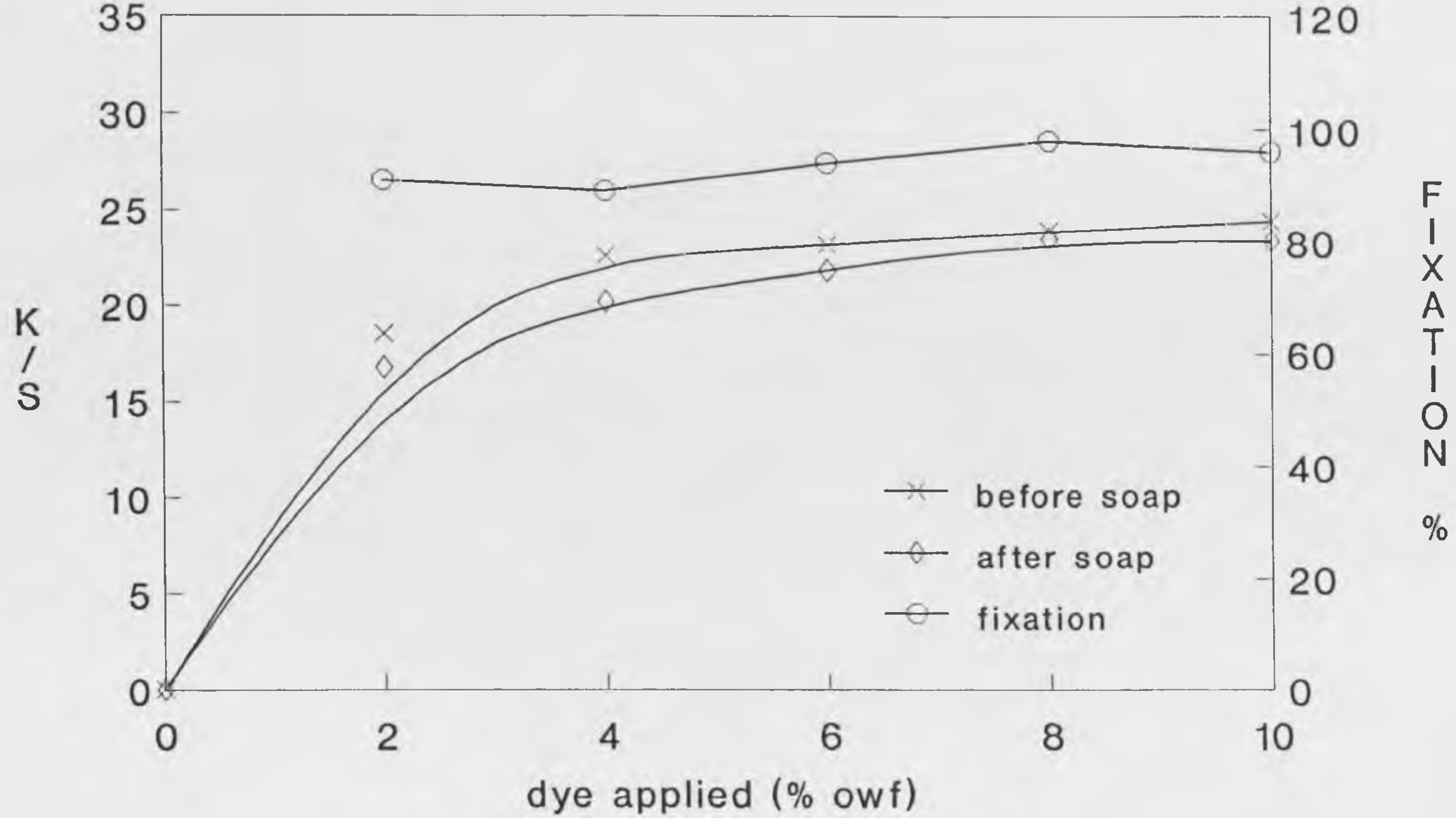
The wash fastness of dyeings on this treated cotton was excellent, change of shade, staining of adjacent fabrics being assessed as 5 in the C04 wash test. Physical appearance and levelness was also very good. Light fastness testing showed a small drop of 0.5-1 point compared with a conventional dyeing of Procion Red MX-G. Cross-sections examined by microscopy showed the dyeings obtained by this pretreatment method were

Figure 4-2-8



Build up of Procion Red MX-G (ICI) on NMA/ammonia treated cotton

Figure 4-2-9



Build up of Procion red MX-G (ICI) on NMA/ethanolamine (pad-batch) cotton well penetrated (figures 4-2-10 and 4-2-11).

Apart from C.I. Reactive Red 5 other classes of reactive dyes, commercially available for dyeing cotton, give promising effects on this pretreated cotton (Table 4-2-6).

Table 4-2-6 colour yield and fixation values of a variety of reactive dyes on NMA/ethanolamine (pad-batch) cotton

dye used (2% owf)	colour yield		E%	F%
	before soap	after soap		
[a]Procion Red H8BN	16.85	16.25	94	96
[a]Procion Red HE-7B	10.61	9.75	95	92
[a]Procion Red HE-3B	12.94	12.69	97	98
[a]Procion Red MX-8B	14.29	14.17	97	99
[a]Procion Red HE-GL	15.26	14.47	96	95
[a]Procion Red HE-XL	17.18	16.56	95	96
[b]Remazol Red FB	13.85	12.21	99	88
[c]Sumifix Supra Red 3BF	8.96	8.68	99	97
[d]Kayacelon React Red CN-3B	7.59	5.46	88	72
[e]Cibacron Red FB	11.34	9.48	98	84
[f]Levafix Red E-BA	12.18	11.22	99	92

[a] - ICI, [b] - Hoechst, [c] - Sumitomo, [d] - Nippon Kyaku,
[e] - Ciba-Geigy, [f] - Bayer.

4.2.7. summary of section 4.2.

Cotton may readily be modified by pretreatment with N-methylol acrylamide to introduce pendant activated double bonds. Amino residues were then incorporated by further reaction of this modified substrate with various types of amines.

Excellent dyeings, coupled with a very high degree of fixation, of reactive dyes of any types have been obtained on the aminized cotton in which primary or secondary amino groups have been introduced. The dyeing was performed in the absence of electrolyte at pH 5-7 by simply raising to the boil and running at this temperature for 1 hour.

Figure 4-2-10 Cross-section of dyeings obtained by dyeing NMA/ethanolamine (batchwise) treated cotton with Procion Red MX-G (ICI) at pH 5 without salt

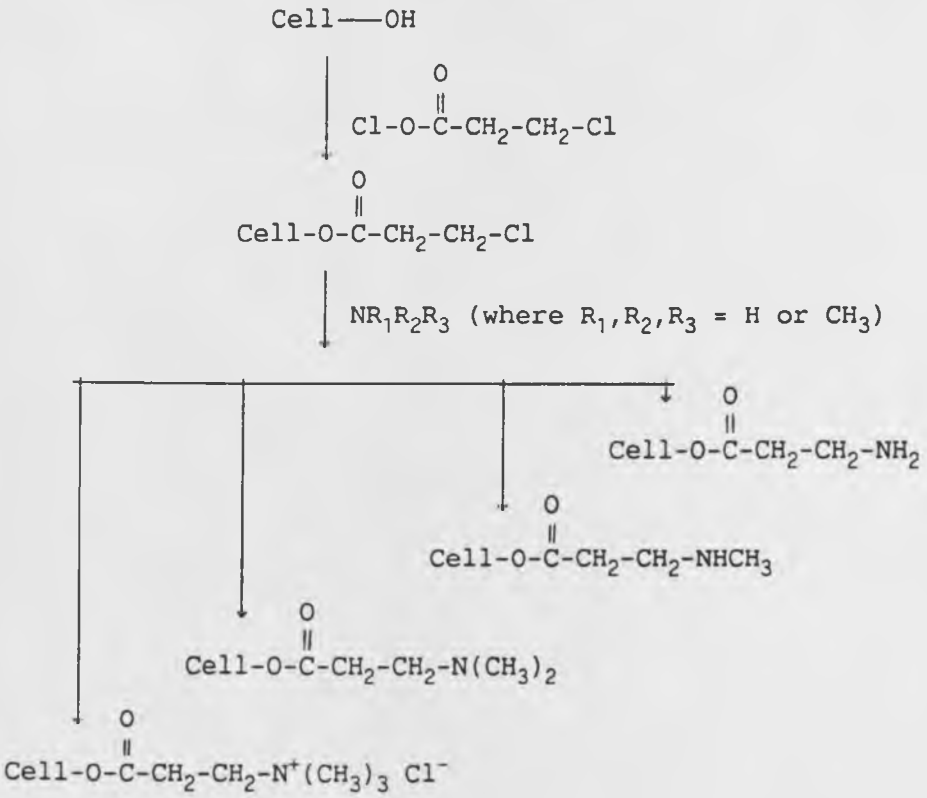
Figure 4-2-11 Cross-section of dyeings obtained using Procion Red MX-G (ICI) on untreated cotton by conventional dyeing method

4.3. Amination of Cotton Following Esterification with Chloro-propionyl Chloride (CPC)

4.3.1. Introduction

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 ß-chloro groups by different amines (ammonia, methylamine, dimethylamine and trimethylamine). It was the aim of this study to give further support to the previous theoretical analysis in section 3.1.2., as well as to clarify the type of 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 the following scheme:

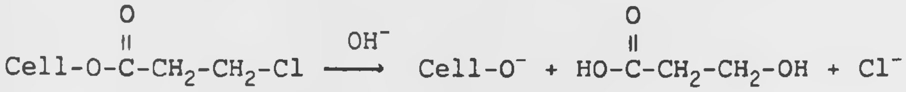


Scheme 4-3-1

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

4.3.2. 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 [107]. 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 following hydrolysis scheme:



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

Scheme 4-3-2

For quantitative measurement when using this instrumentation, it is necessary to use an internal standard to avoid errors. In the present case, both OH^- and K^+ give a single peak which may be employed as a constant internal standard. Figure 4-3-1 shows the chromatogram obtained by injection of the residual solution collected after the hydrolysis had been carried out for 3 hours, the peak which comes out after 0.29 minute is that from OH^- and K^+ and the chloride ion gives a peak at 1.30 minutes.

Figure 4-3-1 IC chromatogram of the residual solution collected after 3 hour hydrolysis of chloro propionic acid in aqueous alkaline solution

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:

$$[RCL] = \frac{\text{Area of Chloride Peak}}{\text{Area of } (OH^- + K^+) \text{ Peak}} * 1000$$

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 chloro-propionic acid(0.5%) in 5g/l KOH aqueous solution for 0 and 5 hours respectively and by treating CPC cotton under the same conditions at a liquor to goods ratio of 20:1 for 3 hours. The collected data and the [RCL] values are given in table 4-3-1. 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 4-3-2 gives the results:

Table 4-3-1 Reproducibility of Relative Cl^- concentration

No.	Duration of treatment	Area of (OH^-+K^+) peak	Area of Cl^- peak	RCL
1*	5	2,008,753	664,641	330.8
2*	5	2,021,406	667,821	330.4
3*	5	2,006,333	661,145	329.5
4*	0	1,982,776	137,400	69.3
5*	0	2,011,202	139,351	69.3
6+	3	2,093,371	290,483	138.8
7+	3	2,089,561	290,856	139.2
8+	3	2,096,375	293,510	140.0

* solution treatment.
\+ fabric treatment.

Table 4-3-2 the change of [RCL] with treatment time

Time (hours)	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

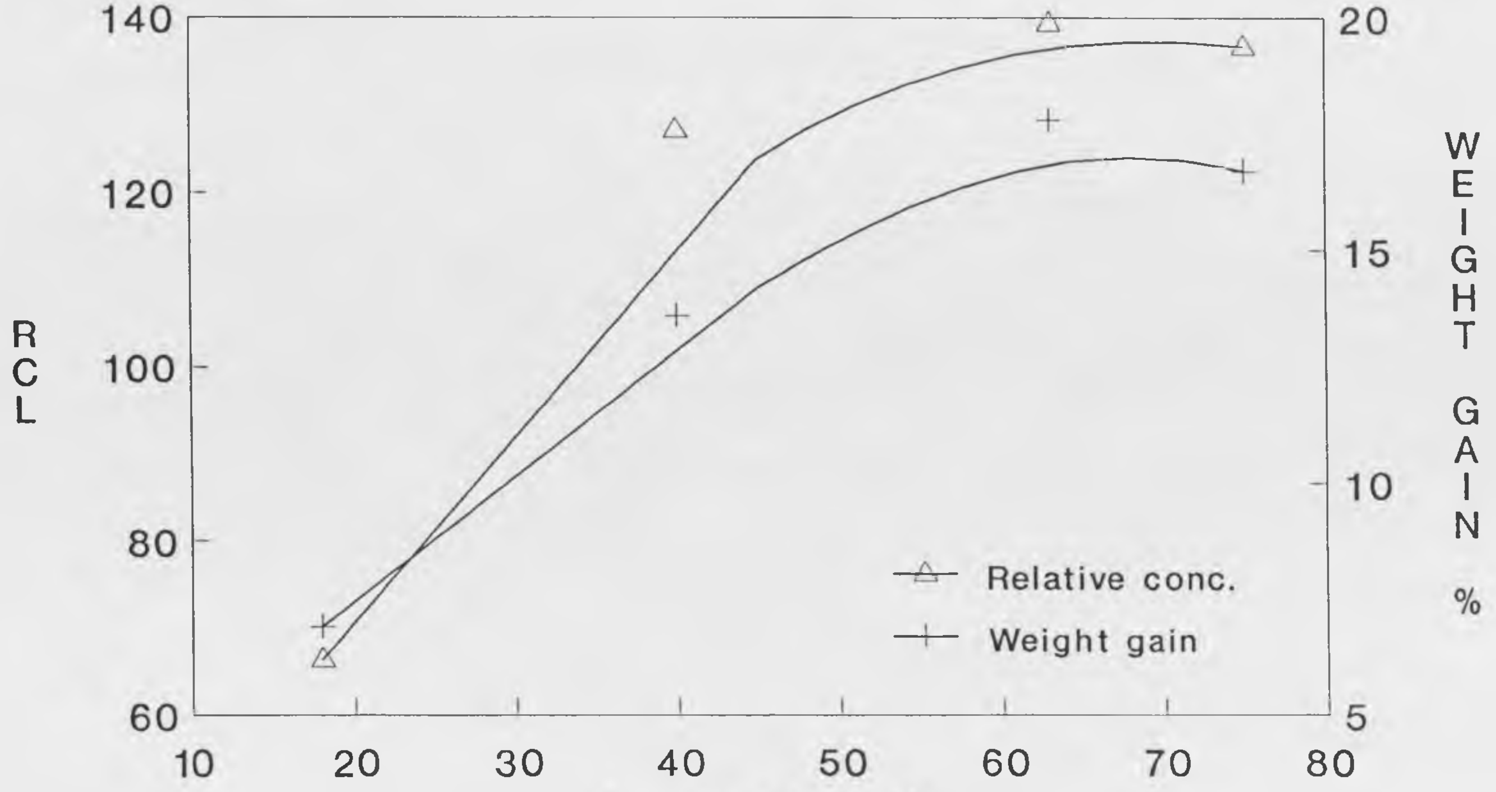
The data in table 4-3-2 suggests that treatment of CPC cotton under the above-mentioned conditions for 3 hours would lead to complete hydrolysis of all C-Cl bonds. These conditions were therefore used for all the latter studies.

4.3.3. Effect of temperature on CPC-cellulose ester yield

During the reaction of cellulose with chloropropionyl chloride, the reaction temperature was kept as low as possible so that a suitable amount of CPC-cellulose ester could be 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 figure 4-3-2. It can be seen from figure 4-3-2 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.

The formation of CPC-cellulose ester was confirmed by the diffuse reflectance FTIR spectra of both untreated and CPC treated cotton. Figure 4-3-3 and 4-3-4 show the spectra of both fabrics and figure 4-3-5 is the

Figure 4-3-2



temperature(C)

Effect of temperature on the yield of cotton-CPC ester

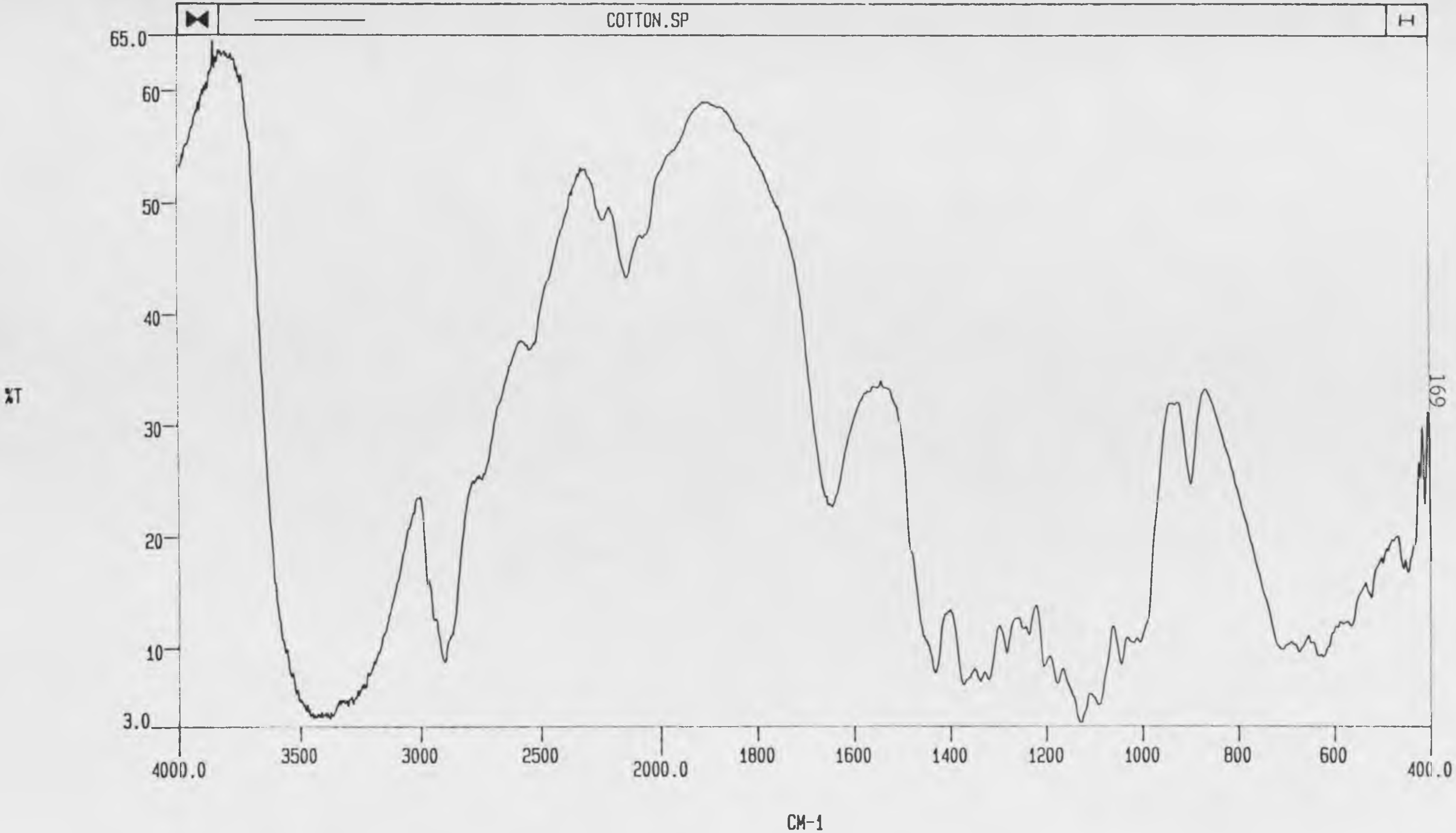


Figure 4-3-3 Infrared spectrum of untreated cotton

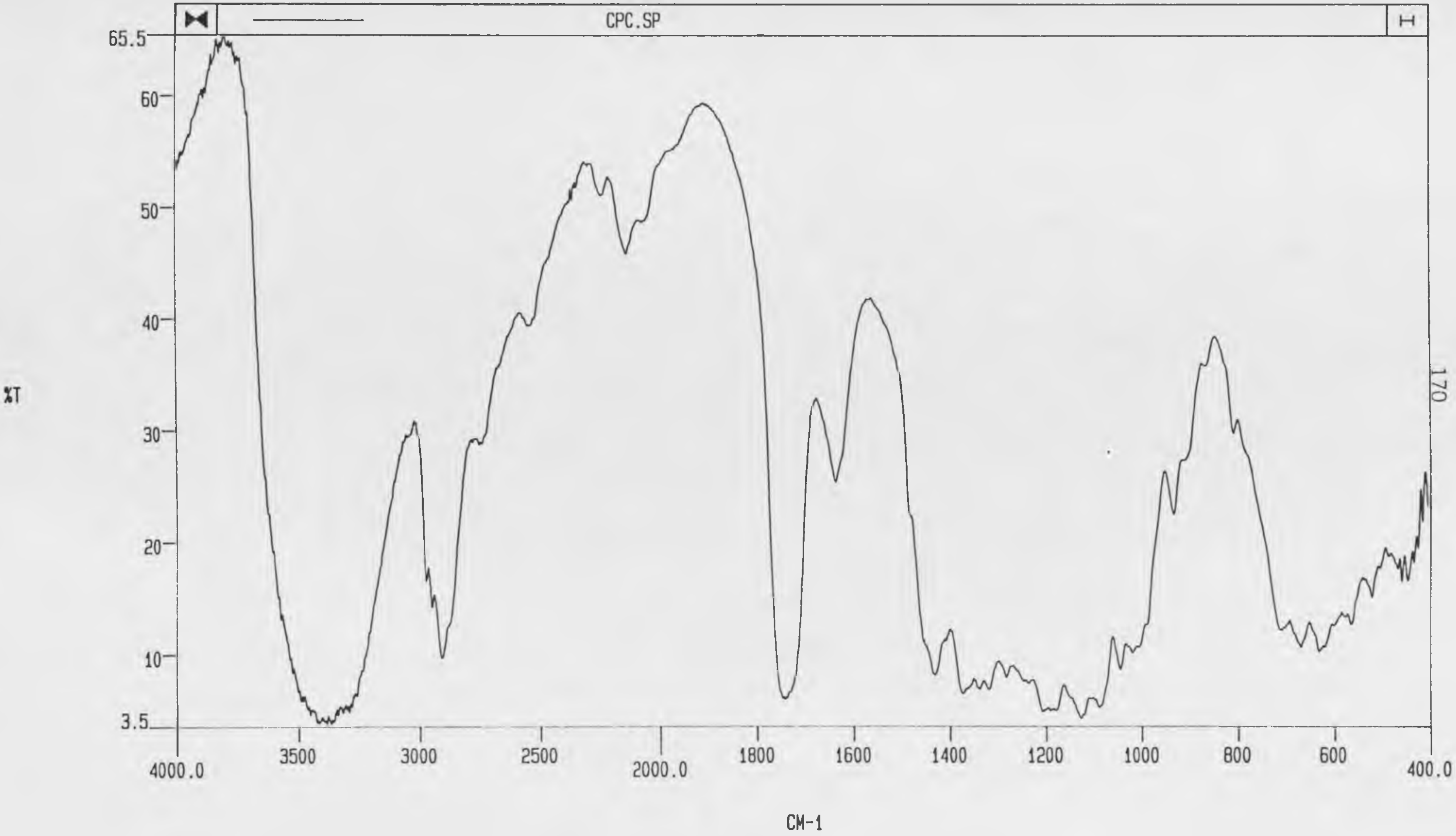


Figure 4-3-4 FTIR spectrum of CPC treated cotton

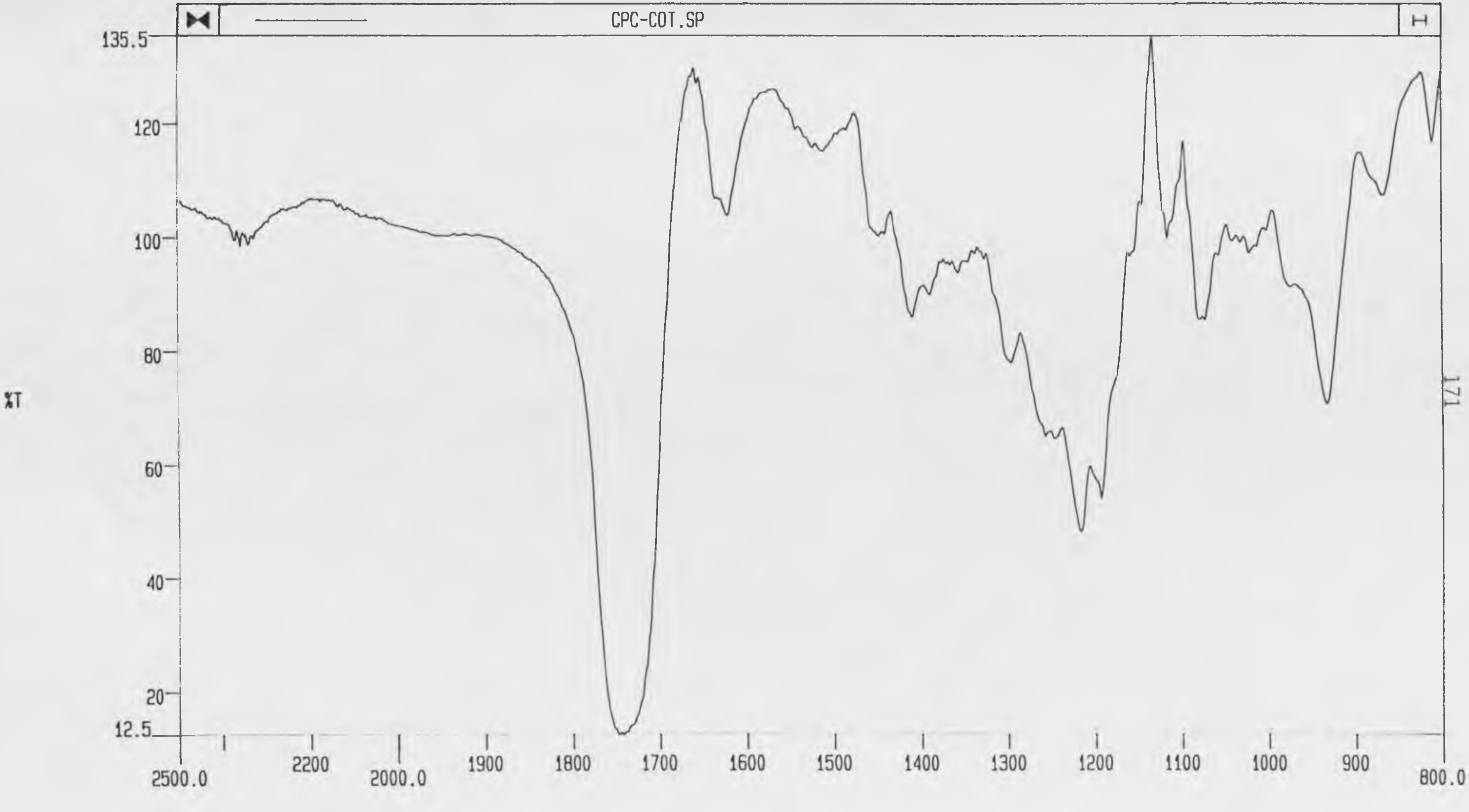


Figure 4-3-5 Infrared spectrum obtained by subtracting cotton from CPC treated cotton

spectrum obtained by computer subtraction of figure 4-3-3 from figure 4-3-4. A strong absorbance attributable to the ester bond is apparent at 1746 cm-1 and some evidence exists for the carbon-chlorine bound at 790 cm-1.

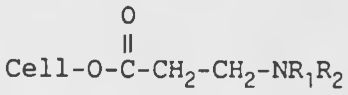
4.3.4. Substrate properties produced by the CPC/amine treatment

Two phenomena were observed following investigation of CPC/amine treated cotton:

i) Neutral dyeings, without salt, of Procion Red MX-G (CI Reactive Red 5 - ICI) on CPC/amine treated cotton are very fast being resistant to alkaline soaping (table 4-3-3). This was surprising if one assumes the ester linkage remained intact during the amination.

ii) CPC cotton gave a strong i.r. absorbance at about 1740 cm-1 indicating the presence of ester bonds in this substrate (figure 4-3-5), but this peak disappeared after the substrate was further treated with boiling aqueous amine solutions under the conditions described in the experimental section (figure 4-3-6).

It is suggested from the above observations that the substrate obtained after amination under the above boiling conditions is <u>not</u>



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

but rather has the following structure:

$$\text{Cell-NR}_1\text{R}_2 \qquad \text{(I)}$$

where R_1, R_2 may be either H or $-CH_3$.

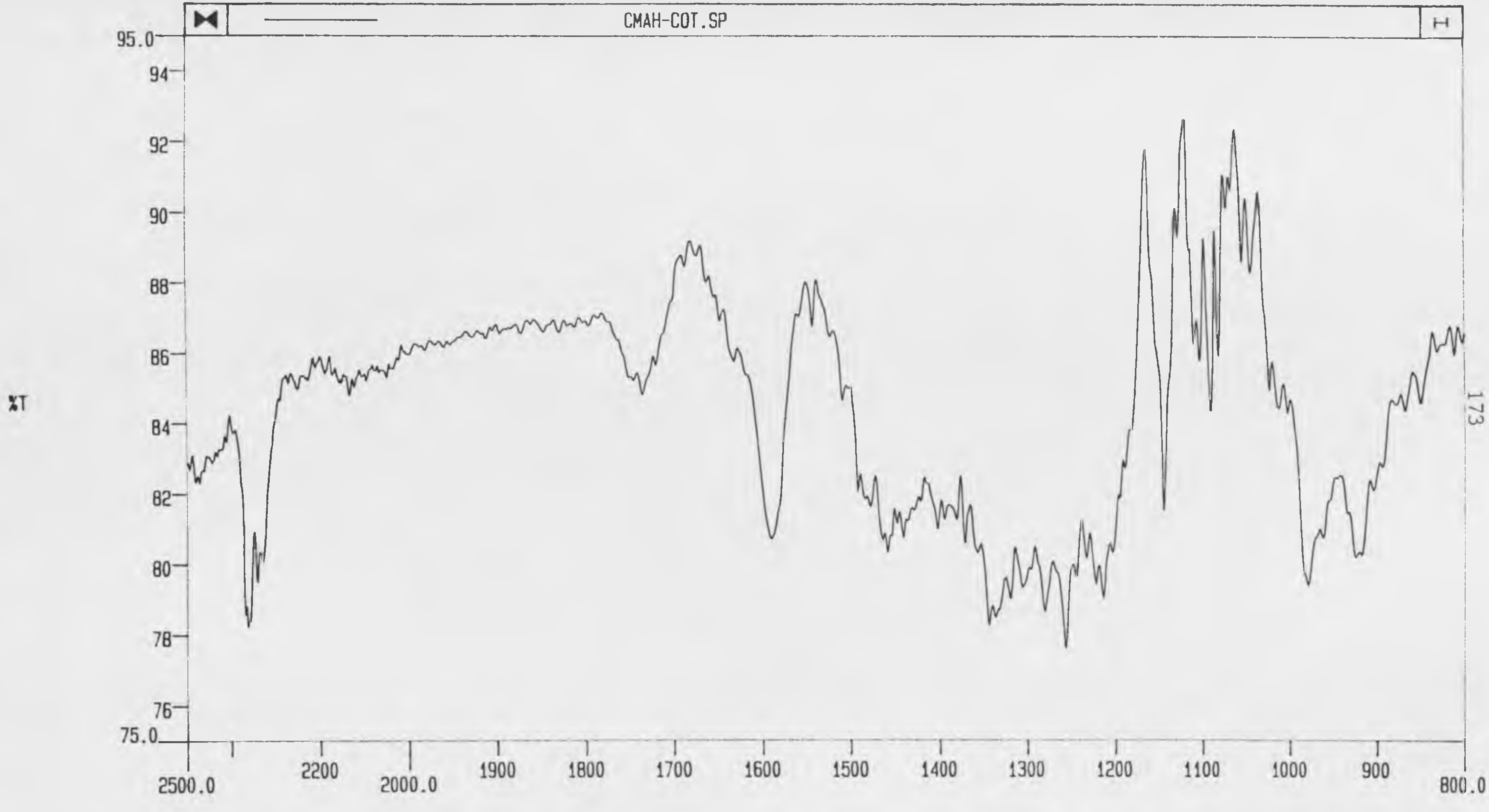
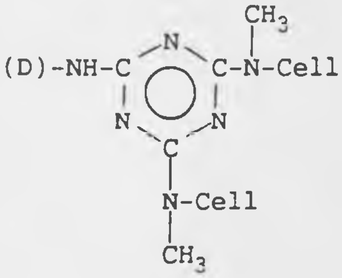
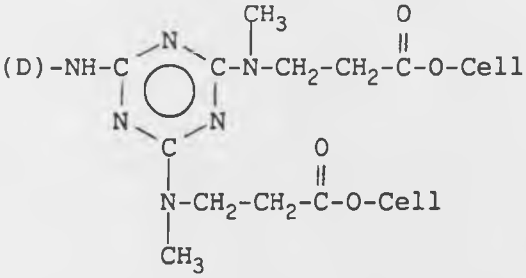


Figure 4-3-6 Infrared spectrum by subtracting cotton from substrate I (methylamine reaction with CPC treated cotton at the boil)

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

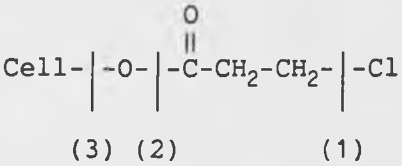


rather than



No coloration could be produced when dyeing chloropropionated cotton which had not been aminated under the same conditions as those used for dyeing CPC/amine treated cotton, thus excluding the possibility that the fast dyeings obtained on the latter substrate might be due to a modification derived, somehow, from the CPC treatment procedure.

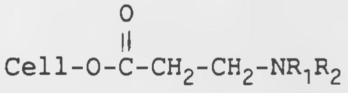
CPC cotton has the following structure:



$$\text{Cell-}\underset{(3)}{|}\text{-O-}\underset{(2)}{|}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-CH}_2\text{-CH}_2\text{-}\underset{(1)}{|}\text{-Cl}$$

(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:



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

(III)

This substrate would still give a strong i.r. ester absorbance at about 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/l of 25-30% methylamine aqueous solution and at 50°C for 1 hour). Figure 4-3-7 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 this substrate (III) were found to show poor alkaline wet fastness (table 4-3-3); this was expected since the ester bonds would not be stable under alkaline conditions.

Table 4-3-3 colour yield of dyeings on different substrates (methylamine 25-30% was used for amination)

	amination conditions		colour yield	
substrate code	amine conc. (g/l)	temp. (°C)	before soap	after soap (pH 10.5)
I	175	100	12.63	11.95
III	10	50	19.72	8.72

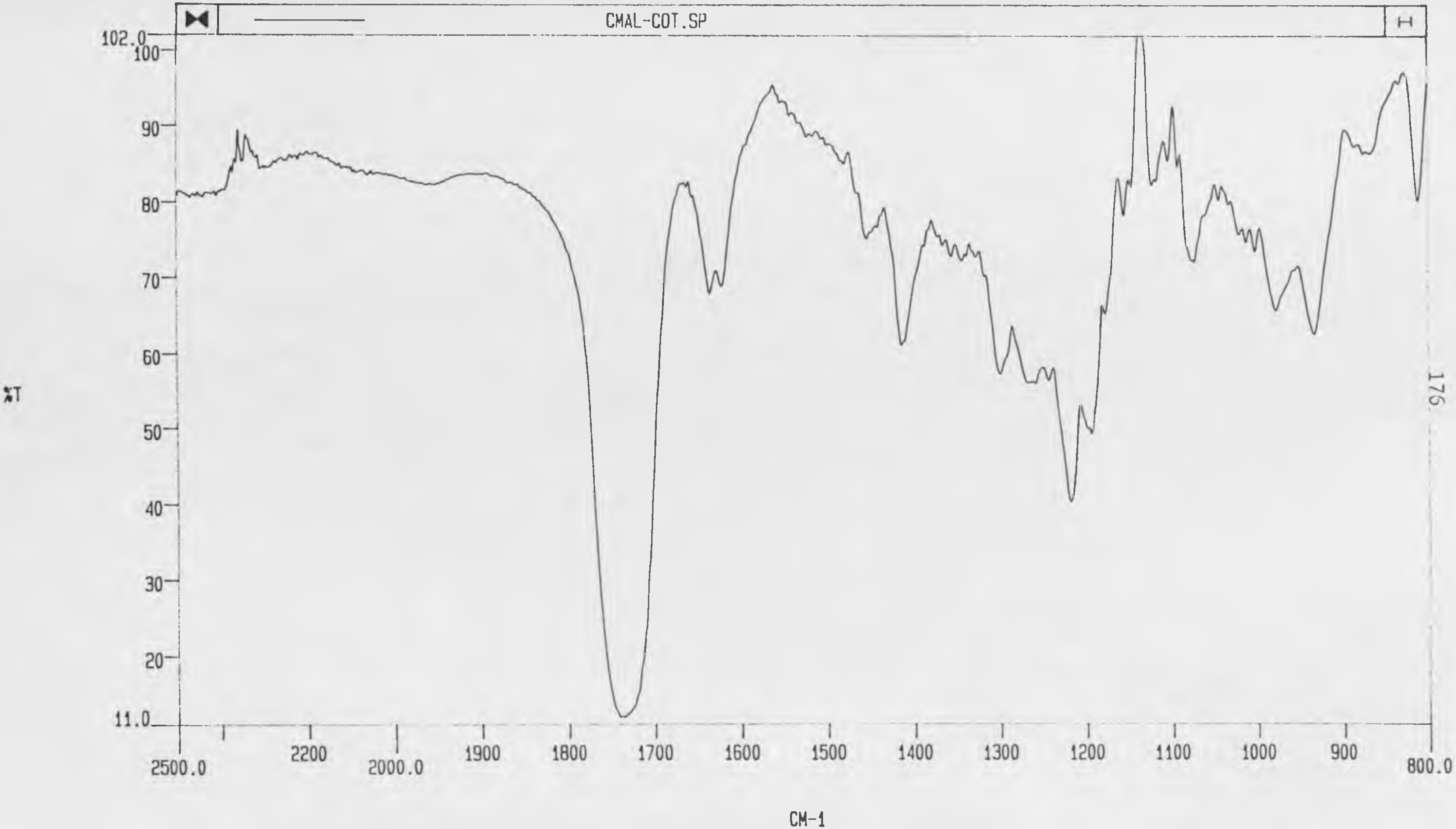


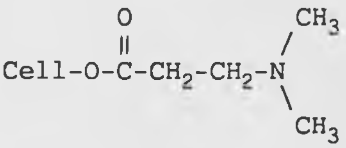
Figure 4-3-7 Infrared spectrum by subtracting cotton from substrate III (methylamine reaction with CPC treated cotton under mild conditions)

Furthermore, when the above modified substrates (I and III) were treated with an aqueous solution containing 20 g/l of sodium carbonate at a liquor to good ratio of 20:1, at the boil for 1 hour and then dyed with Procion Red MX-G under the same dyeing conditions (pH 5, no salt), the one aminized under severe conditions (substrate I) still gave a good colour yield whilst the other exhibited no coloration (table 4-3-4), indicating that the ester bond had been hydrolysed (confirmed by FTIR).

Table 4-3-4 colour yield of dyeings on different substrates ethylamine 25-30% was used for amination) following alkaline hydrolysis treatment.

substrate code	amination conditions		colour yield	
	amine conc. (g/l)	temp. (°C)	before soap	after soap (pH10.5)
I	175	100	11.03	10.57
III	10	50	0.21	0.19

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/l of 40% aqueous dimethylamine solution, 50°C, 1 hour) the following substrate was obtained (FTIR spectrum confirms ester bond still intact):



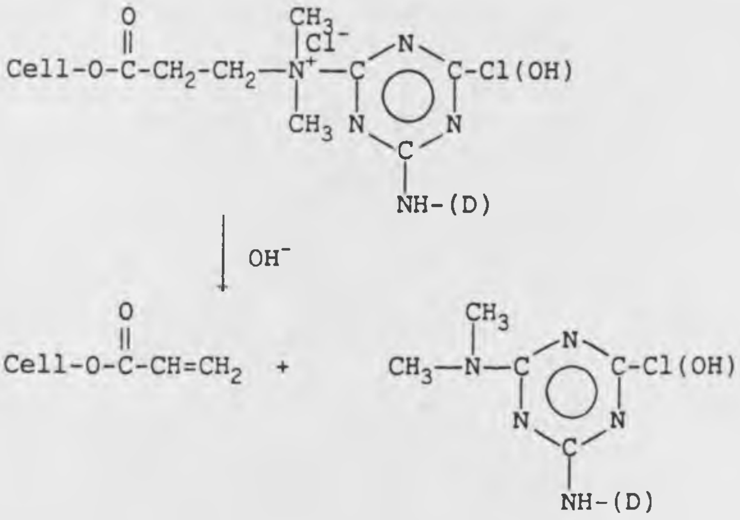
$$\mathrm{Cell{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_2{-}N(CH_3)_2}$$

(IV)

Dyeings of Procion Red MX-G on this substrate were readily decolourized by alkaline soaping because of ß-elimination and ester hydrolysis reactions. The ß-elimination reaction proposed is shown in scheme 4-3-3.

This type of ß-elimination was previously observed when studying the dyeing behaviour of N-methylol acrylamide/ dimethylamine treated cotton (section 4.2.3). Other literature has also discussed this type of reaction [108]. 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 4-3-5).

If cleavage 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.



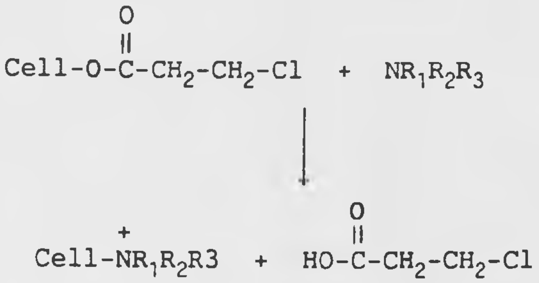
Scheme 4-3-3

Table 4-3-5 colour yield of dyeings on different substrates (dimethylamine 40% was used for amination)

substrate code	amination conditions		colour yield	
	amine conc. (g/l)	temp. (°C)	before soap	after soap (pH 10.5)
I	125	100	10.31	8.39
III	10	50	14.72	1.40

One might think that aldehyde groups in cellulose could react with amines thus introducing some amino groups. This possibility has also been excluded since the treatment of cotton with methylamine under the same conditions as those described in the experimental section led to no coloration when dyeing with Procion Red MX-G under the prescribed conditions.

The above discussion indicates that the only possible cleavage site would be position (3) and the substrate produced would be type (I). Karrer and Wehrli [66] produced type (I) amino celluloses by means of tosylation of cotton with toluene-4-sulphonyl chloride followed by a further treatment with amines. The present system must therefore follow a similar mechanism to that proposed by Karrer and Wehrli. We thus propose the following scheme:



$$\mathrm{Cell{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}Cl} + \mathrm{NR_1R_2R_3} \longrightarrow \mathrm{Cell{-}\overset{+}{N}R_1R_2R3} + \mathrm{HO{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}Cl}$$

Scheme 4-3-4

4.3.5. 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 4-3-6).

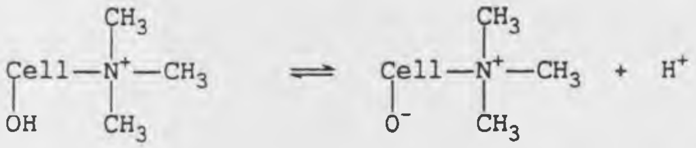
table 4-3-6 Nitrogen contents and dye exhaustion/fixation values on different substrates (Procion Red MX-G, 2% owf)

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

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 2-1-3) and the total nitrogen values (table 4-3-6).

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 4-3-6).

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 the cellulose hydroxyl group.



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

4.3.6. summary of section 4.3.

Cotton may be effectively esterified with chloropropionyl chloride to give a reactive substrate which can undergo further reactions with a variety of amines. Thus a series of primary, secondary, tertiary and quaternary amino residues were incorporated covalently into the fibre. These modified amino celluloses were examined as suitable substrates for neutral to slightly acidic dyeing of reactive dyes in the absence of electrolyte.

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 substrate exhibited excellent alkaline stability. Evidence has been obtained that attachment of the amino groups involves nucleophilic displacement of either chloropropionic acid or its ß-elimination form, acrylic acid, from the pre-esterified substrate.

CHAPTER 5

V DYEING ACTIVATED CELLULOSE WITH ALKYL AMINO DYES

5.1 Introduction

Fixation efficiency of reactive dyes on substrates containing aliphatic amino groups is much higher than that on unmodified cotton. This has been demonstrated not only by reactive dyeing of wool but also by dyeing aminized cotton with reactive dyes. The reason for this is that the reaction of reactive dyes with aliphatic amino groups is much more selective than the reaction of reactive dyes with the hydroxyl groups in cellulose, when compared with the competing hydrolysis reaction of the dyes during the dyeing process.

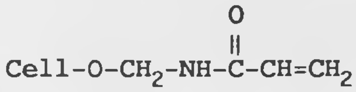
However even though highly efficient reactive sites are available conventional reactive dyes will always be partly hydrolysed during the dyeing process, which invariably gives rise to a reduction in the efficiency of reaction with the substrate. It would therefore be a good idea to first introduce reactive groups into cellulose fibre and then to dye with alkyl-amino dyes. Dyes of this type would never be hydrolysed and thus high fixation efficiency could therefore be achieved using this method; any hydrolysis would occur on the reactive groups initially introduced into the cellulose and provided an excess of these groups were present such a side reaction would be unimportant in terms of final colour yield.

Pretreatment of cotton to introduce reactive groups such as activated double bonds (or other reactive groups) is clearly necessary when using alkyl-amino dyes. The cost of producing a dye is much higher than the cost of producing a small molecular weight reactive compound for cotton pretreatment; hence if 100% of the dye applied is utilized by fixation to the substrate, not only can total application cost be reduced but environmental problems may be avoided.

5.2. Dyeing N-Methylol-Acrylamide (NMA) Treated Cotton with Alkyl-amino Dyes

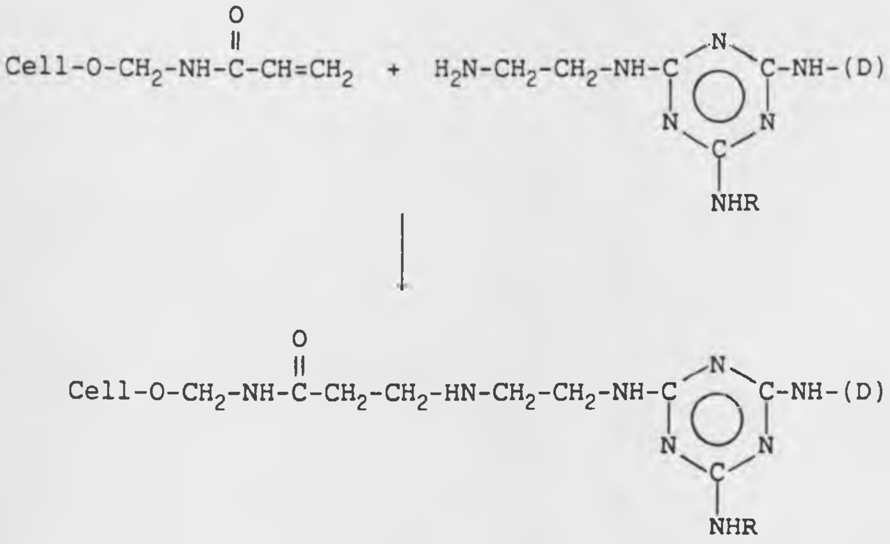
5.2.1. Substrate

In this study, N-methylol-acrylamide (NMA) was employed as a cotton activating reagent. The preparation procedure to produce NMA cotton was described in Chapter II; FTIR analysis and the nature of this substrate was discussed in section 4.2. of chapter IV. After activation, the substrate has the following formula:



$$\mathrm{Cell{-}O{-}CH_2{-}NH{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH_2}$$

When dyed with alkyl-amino dyes, the activated double bond would react with the aliphatic amino groups of the dyes to form a covalent dye-fibre bond:



scheme 5-2-1

5.2.2. Preparation and analysis of alkyl-amino dyes

The alkyl-amino dyes were prepared by modifying monochloro-triazine reactive dyes with ethylenediamine. The preparation procedure was described in Chapter 2 in detail.

The purity of the prepared dyes was assessed by ion-pair HPLC (figure 5-2-1). The shorter retention time of the modified form (dye A) compared with the original form (dye B) indicates that the former is more basic than the latter. Figures 5-2-2 and 5-2-3 show the FTIR spectra of both the alkyl-amino dye and its original form. The strong increase in the peak at 1600 cm-1 confirms the introduction of amino groups by this reaction.

5.2.3. Dye application

The alkyl-amino dye was first applied by a pad-batch method. The NMA cotton was impregnated in a dye liquor containing 20 g/l of the dye and 20 g/l of sodium carbonate and batched for 24 hours; soaping and washing off completed the process. Table 5-2-1 shows the results obtained both on NMA cotton and untreated cotton. The fixation of the dye on NMA cotton was found to be very high whilst that on untreated cotton was almost zero.

Table 5-2-1 Colour yield and fixation of an alkyl-amino dye on different substrates

substrate	colour yield(1.6% shade)			F%
	after dyeing	after rinse	after soap	
NMA cotton	12.25	11.71	11.55	94
cotton	10.01	---	0.18	2

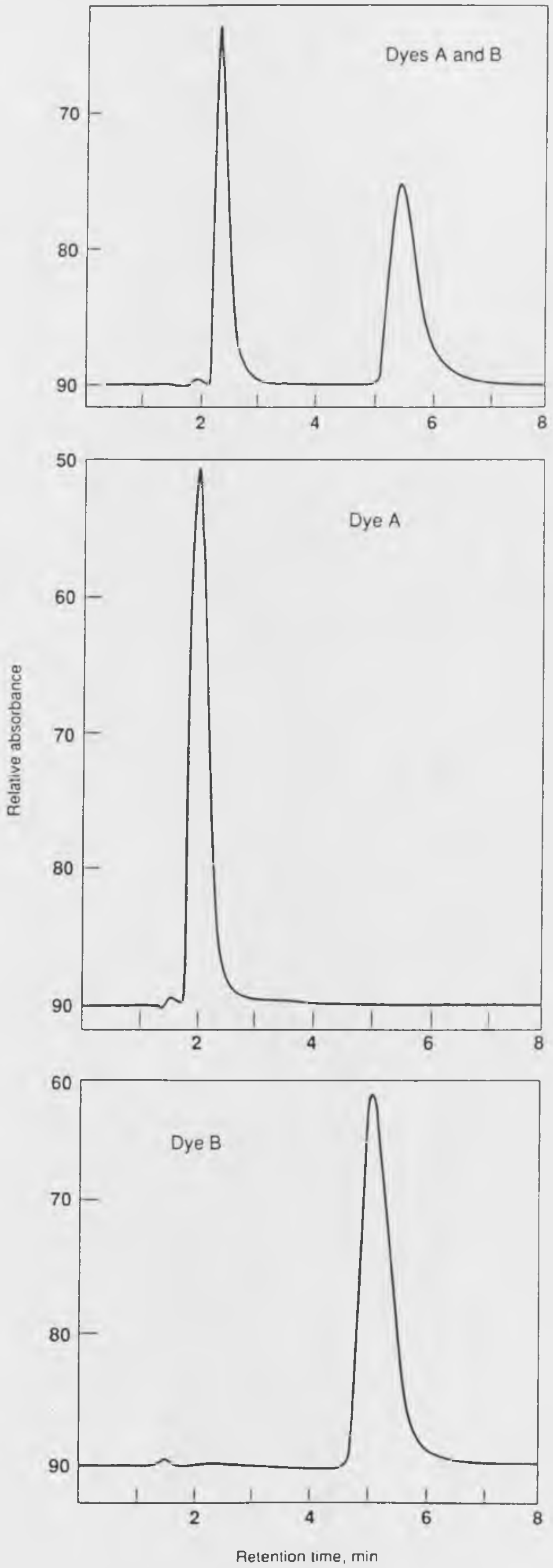


Figure 5-2-1 HPLC printouts of Procion Red H8BN (ICI) (dye B), an alkyl-amino dye (dye A) and their mixture (retention time, dye A 2.0 mins, dye B 5.1 mins).

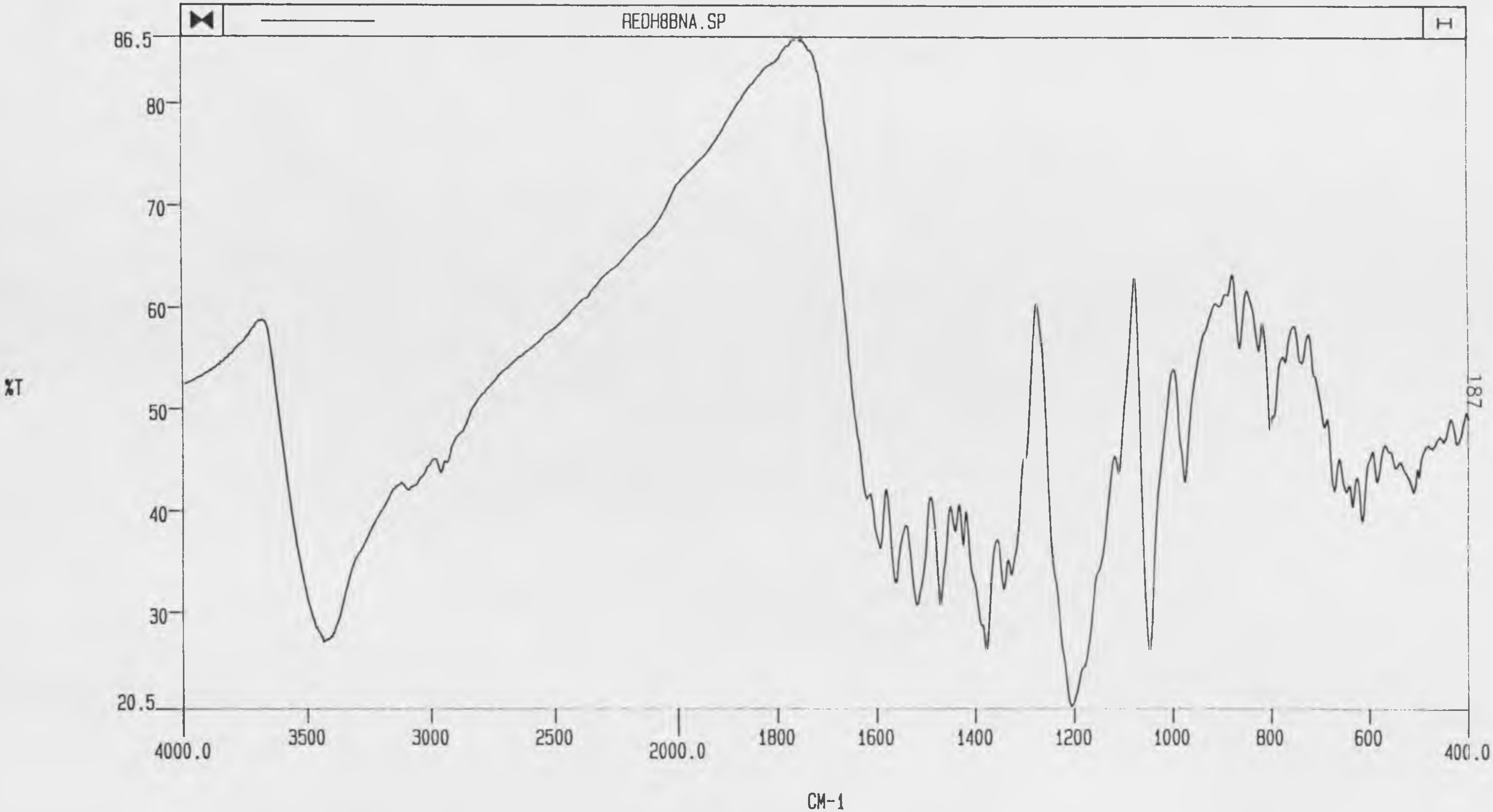


Figure 5-2-2 Infrared spectrum of an alkyl-amino dye prepared from Procion Red H8BN (ICI)

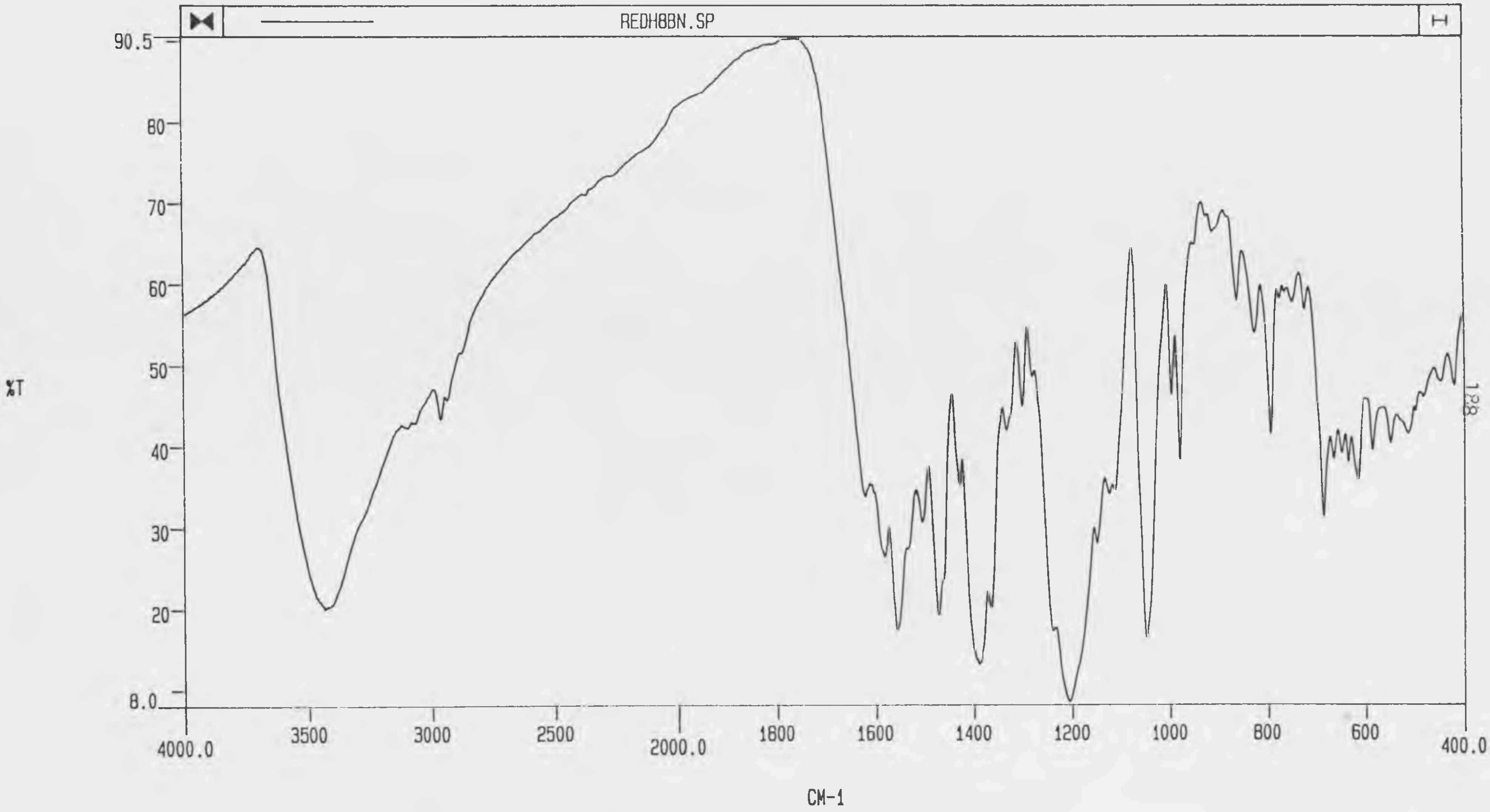


Figure 5-2-3 FTIR spectrum of Procion Red H8BN (ICI)

Application of the alkyl-amino dye by batchwise methods has also been studied. Table 5-2-2 gives the results. It appears to be necessary to dye the NMA cotton under alkaline conditions with salt. The necessity for alkali in the dyebath is due to the formation of the following zwitter-ionic structure under slightly acid or neutral pH conditions :

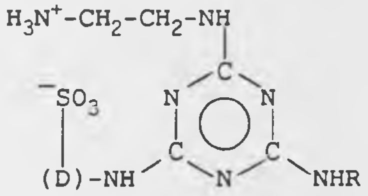


Table 5-2-2 Colour yield and fixation of an alkyl-amino dye (2% owf) on NMA cotton

pH	buffer used	NaCl (g/l)	colour yield before soap	colour yield after soap	F%
10.5	Na_2CO_3	80	13.72	13.60	99
10.5	Na_2CO_3	0	9.57	9.31	97
10.0	Na_2HPO_4/NaOH	80	15.91	15.14	95
10.0	Na_2HPO_4/NaOH	0	7.12	6.37	89
8.0	NaH_2PO_4/NaOH	80	15.57	13.85	89
8.0	NaH_2PO_4/NaOH	0	12.75	11.43	90
5.0	NaH_2PO_4	80	8.72	4.60	53
5.0	NaH_2PO_4	0	4.59	2.37	52

Thus the nucleophilicity of the amino group is reduced under acidic or neutral conditions. Since there are no cationic sites in NMA cotton, it was therefore necessary to use electrolyte to exhaust the dyebath at or above pH 10. At pH 8, however, a surprising effect was noted in that the dye exhaustion and fixation in the absence of salt was quite good; it was postulated that above pH 8 the rapid increase in cellulosate anion concentration diminishes exhaustion of the anionic dye necessitating salt additions to suppress the negative charge at the fibre surface.

5.2.4. Build up of an alkyl-amino dye on NMA cotton

Figure 5-2-4 shows the build up properties of both the alkyl-amino dye on the NMA cotton (dyed at pH 10.5 with 80 g/l salt, 1 hour at the boil) and the original unmodified dye on untreated cotton applied by the conventional dyeing method. Comparing these two dyeing methods, it can be seen that much higher fixation is achieved on the NMA cotton dyed with the alkyl-amino dye. It may be expected that using this new method, a relatively short duration wash-off would be required to remove unfixed dye, greatly reducing the cost of this procedure.

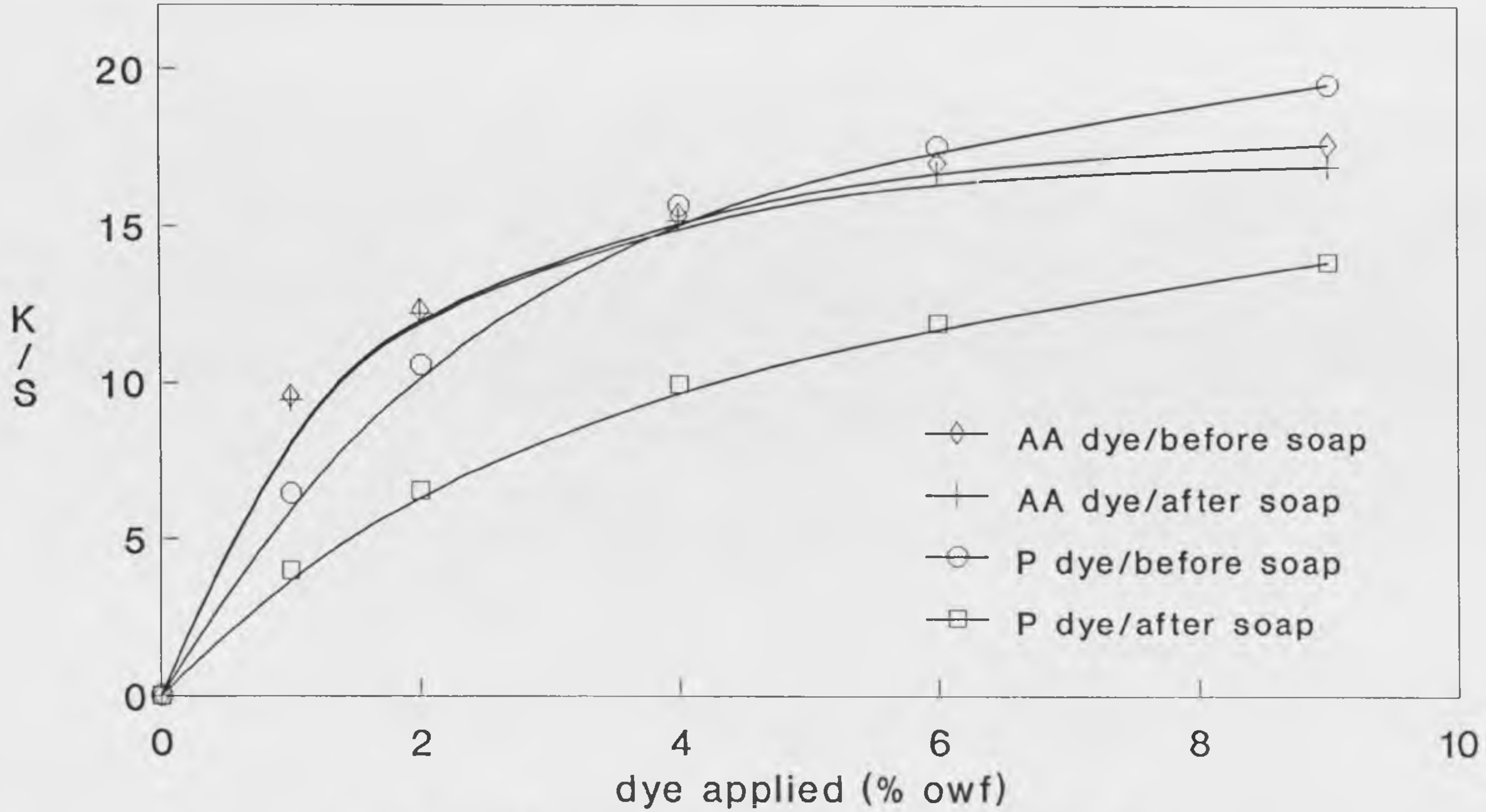
5.2.5. Dyeing quality

Washing fastness and light fastness of the dyeings obtained when dyeing NMA cotton with the alkyl-amino dye are very good. The dyeings were also found to be very level. Cross-sections examined by microscopy showed that the dye was well penetrated through the fibres (figure 5-2-5).

5.2.6. Summary of section 5.2.

It is possible to take cellulose modified only with N-methylol-acrylamide and to dye with dyes containing pendant aliphatic amino residues. In this case it is necessary to dye in the presence of electrolyte under alkaline conditions but very high colour yields are obtained thanks to the elimination of the hydrolytic side reactions normally associated with reactive dyeing. Such alkyl-amino dyes can be readily prepared from all commercial ranges of reactive dyes.

Figure 5-2-4



Build up of Procion Red H8BN & an alkyl-amino dye on NMA cotton

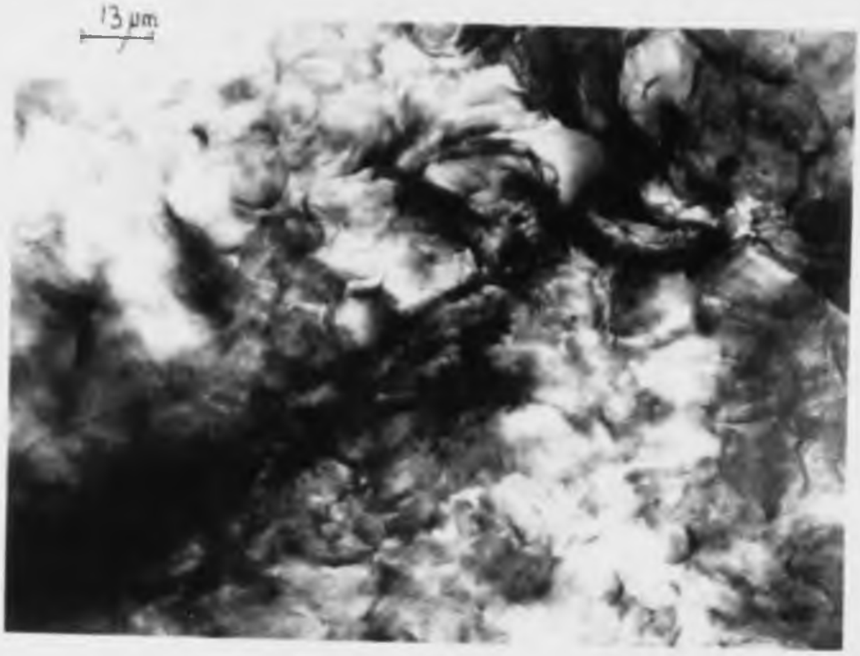


Figure 5.2.5 Cross-section of a dyeing produced by using an alkyl-amino dye on NMA treated cotton

5.3. Activation of Cotton with a Cationic Reactive Monochloro-s-triazine Based Compound (Compound I)

5.3.1. Introduction

Activation of cotton by pretreating this fibre with N-methylol acrylamide produced a substrate which is dyeable with alkyl-amino dyes to give dyeings of good quality. The disadvantage of this activation method is that NMA may not be a safe compound for large scale mill use, since during its application and also during the use of the textile produced, the release of free formaldehyde will occur, which will cause problems. It is the intention of this section to search for an alternative chemical to replace NMA.

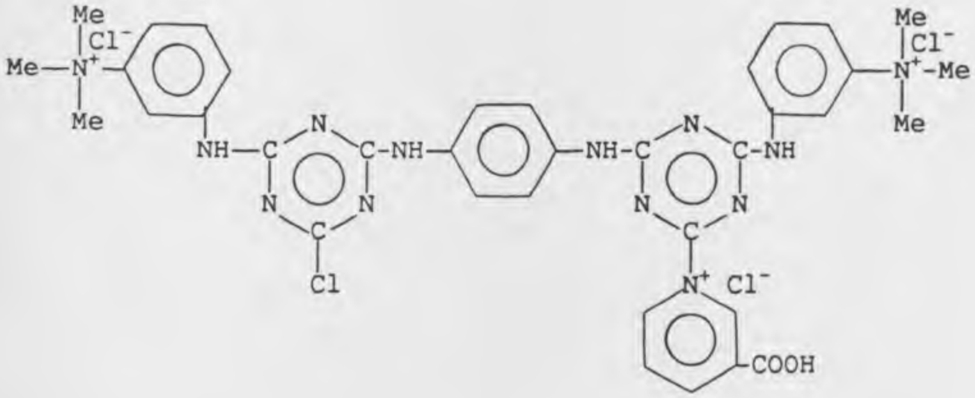
It is evident that the compound to be sought for activating cotton must have the following properties:

i) It must possess at least two reactive groups of different reactivities since after reaction with cellulose, there must be some free reactive groups remaining which will react with alkyl-amino dyes during the dyeing process.

ii) It should not polymerize itself during application to cotton, as the pretreatment of cotton with polymeric compounds produces dyeings of reduced light fastness.

iii) Ideally the compound should contain some cationic groups in order to increase the substantivity of anionic dyes for the modified substrate hence avoiding the use of electrolyte.

The first compound prepared was 3-carboxyl-1-[4-{4-[4-chloro-6-(3-trimethylammonioanilino)-1,3,5-triazin-2-ylamino]anilino}-6-(3-trimethylammonioanilino)-1,3,5-triazin-2-yl]=pyridinium trichloride (compound I), which has the following structure (Me = CH_3):



Compound I

Under neutral pH conditions the quaternary nicotinic acid reactive group in this compound can react with cellulose to form a covalent bond whilst the monochloro-s-triazine group is rather stable, being available for further reaction with alkyl-amino dyes. In addition, compound I is fibre substantive in the absence of electrolyte and can thus be applied by a batchwise procedure to achieve even pretreatment. Since a number of cationic groups are present in the compound the substantivity of anionic dyes for the modified substrate is also improved after activation.

5.3.2. Preparation of Compound I.

Compound I was prepared according to the reaction scheme 5-3-1. It is a brownish solid which dissolves easily in water and precipitates from aqueous solution when anionic surfactant was added, indicating its strong cationic character.

Figure 5-3-1 shows the FTIR spectrum of this compound. The peak at 3441 cm-1 corresponds to the N-H stretching absorption of secondary amines; the absorbance at 3126 cm-1 is due to the ring C-H stretch of the aromatic rings; the broad band at 2361 cm-1 may be attributed to the

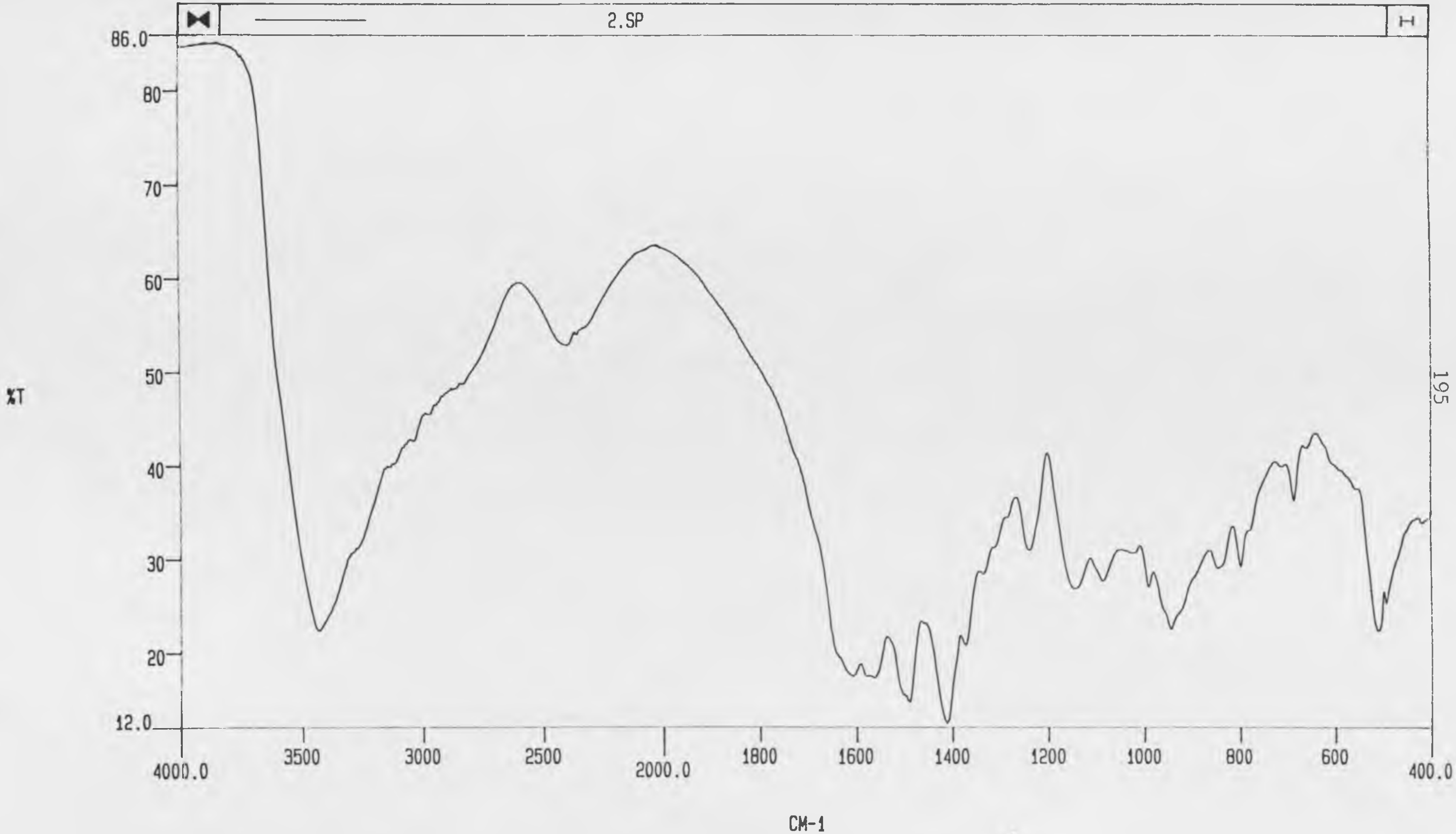
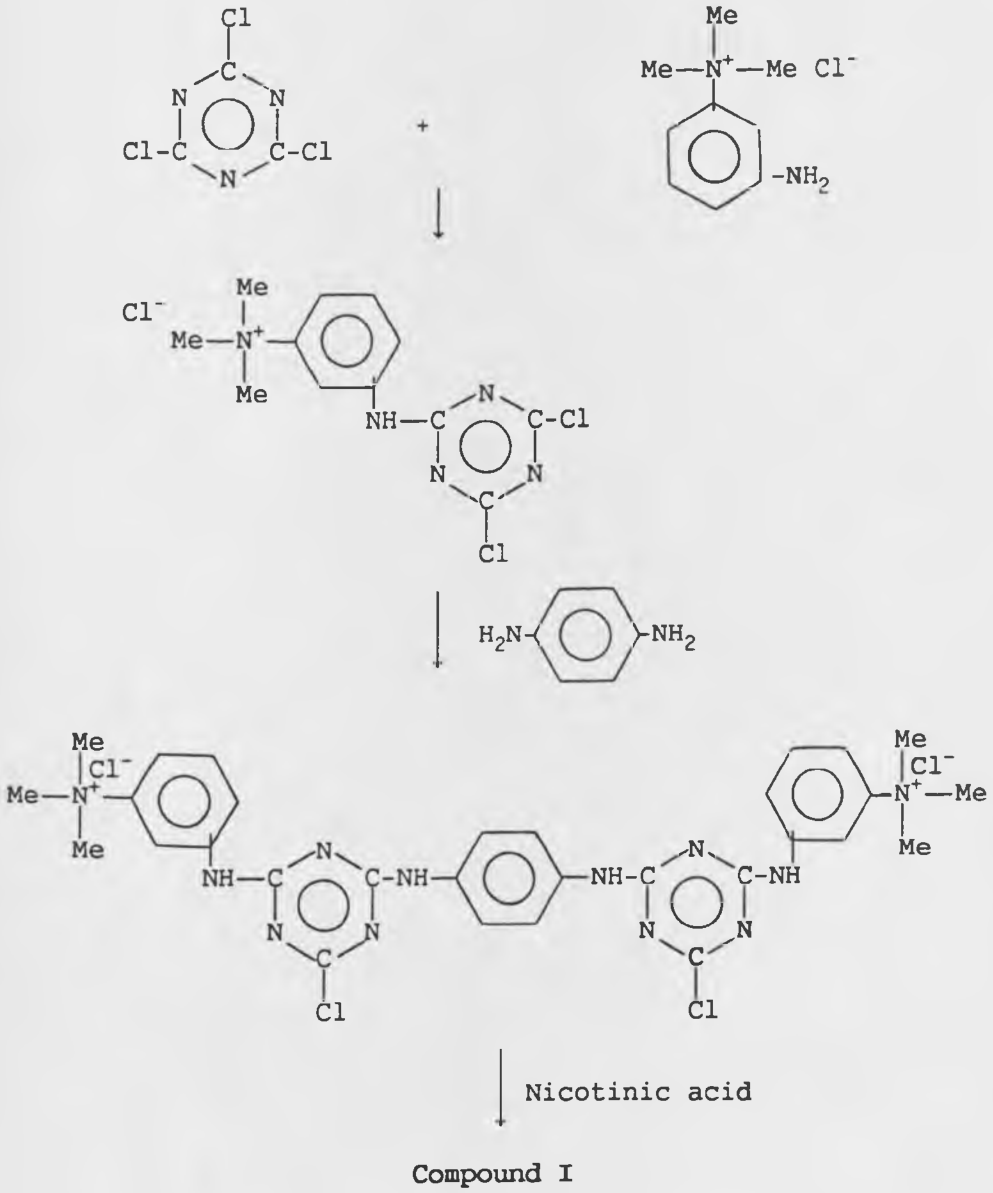


Figure 5-3-1 Infrared spectrum of compound I

strongly hydrogen bonded OH stretch absorption from the nicotinic acid group; the peaks near 1600 cm-1 are from the C=N stretch in the triazine ring and the one at 1370 cm-1 is due to the C-N stretch of aromatic amines; the peak at 992 cm-1 may be the absorbance of the quaternary amino groups whilst the peak at 799 cm-1 is the absorption from the C-Cl stretch of the monochloro-s-triazine.



scheme 5-3-1

where Me = CH_3.

Figure 5-3-2 shows the U.V. spectrum of Compound I. CHN analysis was not carried out for Compound I due to the length of time required for purification. This was not considered to be necessary, as only an unpurified compound was required for application to the cotton fibre.

5.3.3. Substrate Preparation and its Dyeing Properties

5.3.3.1. Effect of agent concentration on dyeability of the subsequent substrate

Cotton was pretreated with different concentrations of Compound I by a batchwise method under neutral pH conditions at a liquor to goods ratio of 20:1; the pretreatment commenced at 50°C and the temperature was then raised to the boil over 25 mins and the bath maintained at the boil for a further 60 mins. The substrate obtained was dyed using 2% (owf) of an alkyl-amino dye (made from Procion Red H8BN) at pH 9 using the procedure described in the experimental chapter. Table 5-3-1 shows the results obtained. It can be seen that reasonable fixation values were achieved only when the pretreatment was carried out at an agent concentration of 8% (owf).

Table 5-3-1. Effect of agent concentration on colour yield and fixation of subsequent dyeings (2% owf dye was used)

Agent conc. (% owf)	Exhaustion of agent %	colour yield before soap	colour yield after soap	E%	F%
2	91	10.97	6.64	75	61
4	88	12.72	9.05	90	71
8	69	13.55	11.24	95	83

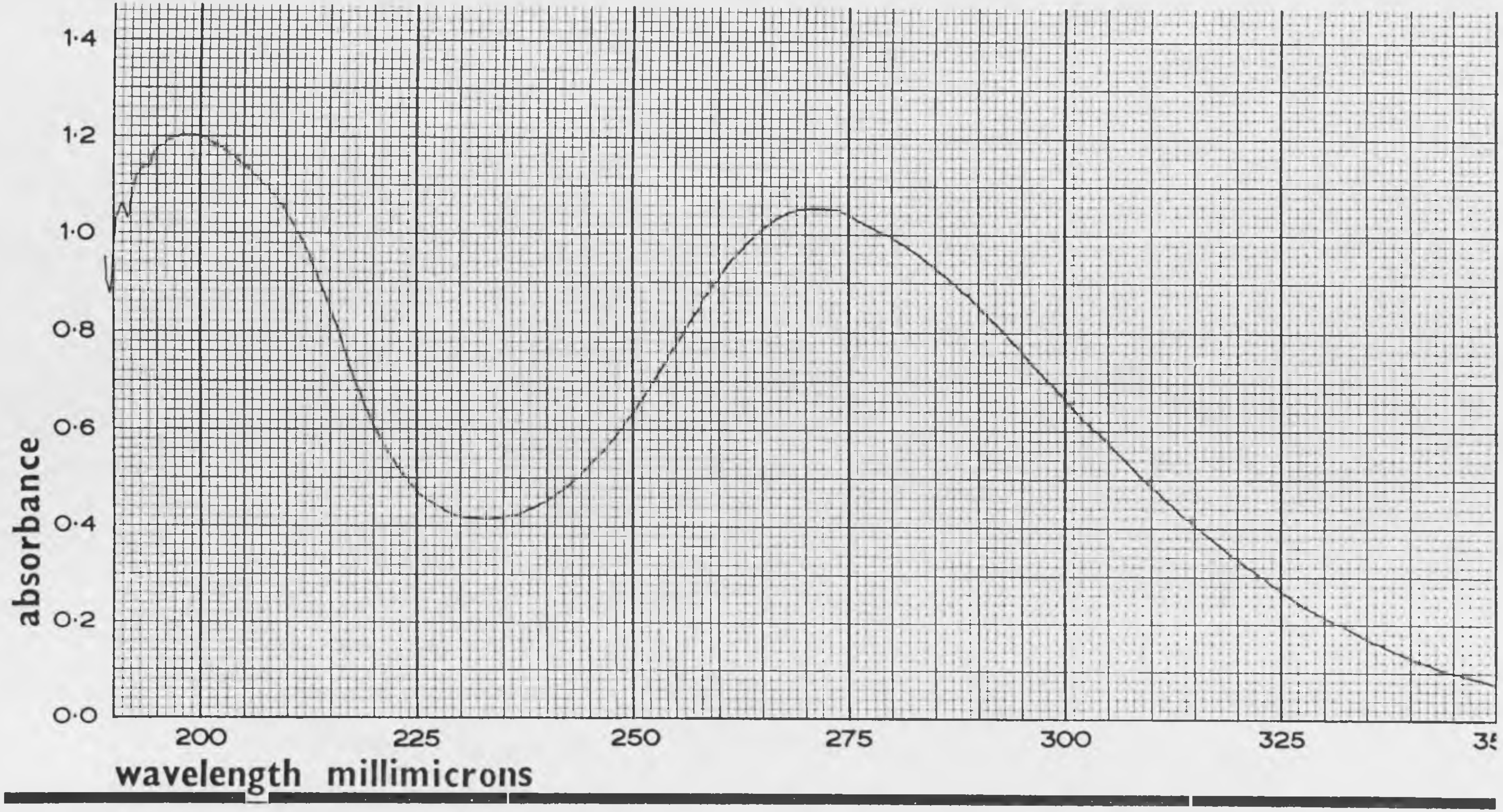


Figure 5-3-2 UV spectrum of compound I

5.3.3.2. Effect of pretreatment pH on dyeability of the subsequent substrate

Previous work has shown that when a quaternary amino group was used as a leaving group for triazine based reactive dyes, dyeing of cellulose fibre can be carried out under neutral pH conditions [55]. In the present case, in order to protect the monochloro-s-triazine reactive group from reaction before the dyeing process, the pretreatment pH cannot be too high; therefore only pH 7 and 8 were employed. The results in table 5-3-2 show that applying compound I at pH 7 gave subsequent dyeings of better colour yields and fixation value.

Table 5-3-2 Effect of pretreatment pH on colour yield and fixation of subsequent dyeings (4% owf of agent and 2% owf of dye were used)

pH	exhaustion of agent	colour yield		E%	F%
		before soap	after soap		
7		11.50	7.93	84	69
8		11.07	6.54	82	59

5.3.3.3. selection of dyebath pH

The substrate obtained by pretreating cotton using 4% owf of compound I at pH 7 was used for this experiment. The results shown in table 5-3-3 illustrates that pH 9 is the most suitable pH value for subsequent dyeing with alkyl-amino dye. When the pH is lower than this particular value, the nucleophilicity of the alkyl-amino dye is low due to the formation of the zwitter-ionic structure (section 5.2.3.). When the dyeing pH is higher than 9, the hydrolysis of the mono-chlorotriazine reactive groups in the substrate becomes significant thus reducing the colour yield and fixation values of the dyeings produced.

Table 5-3-3 Effect of dyebath pH on colour yield and fixation of the subsequent dyeings (4% owf of pretreatment agent and 2% owf of dye were used)

pH	colour yield		E%	F%
	before soap	after soap		
7	12.33	8.55	90	69
9	12.72	9.05	90	71
11	11.44	8.60	84	75

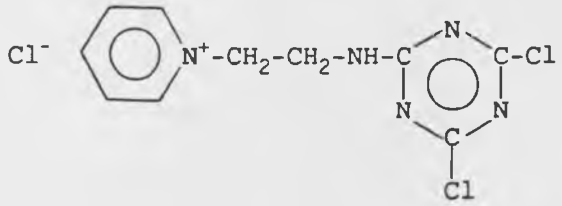
5.3.4. Dyeing quality

Since the substrate produced by this activation method turns out to have a brownish colour, dyeings obtained on this substrate were observed to be rather dull. Unless a colourless compound and thus a colourless substrate could be produced, any further testing on the dyeings would be meaningless.

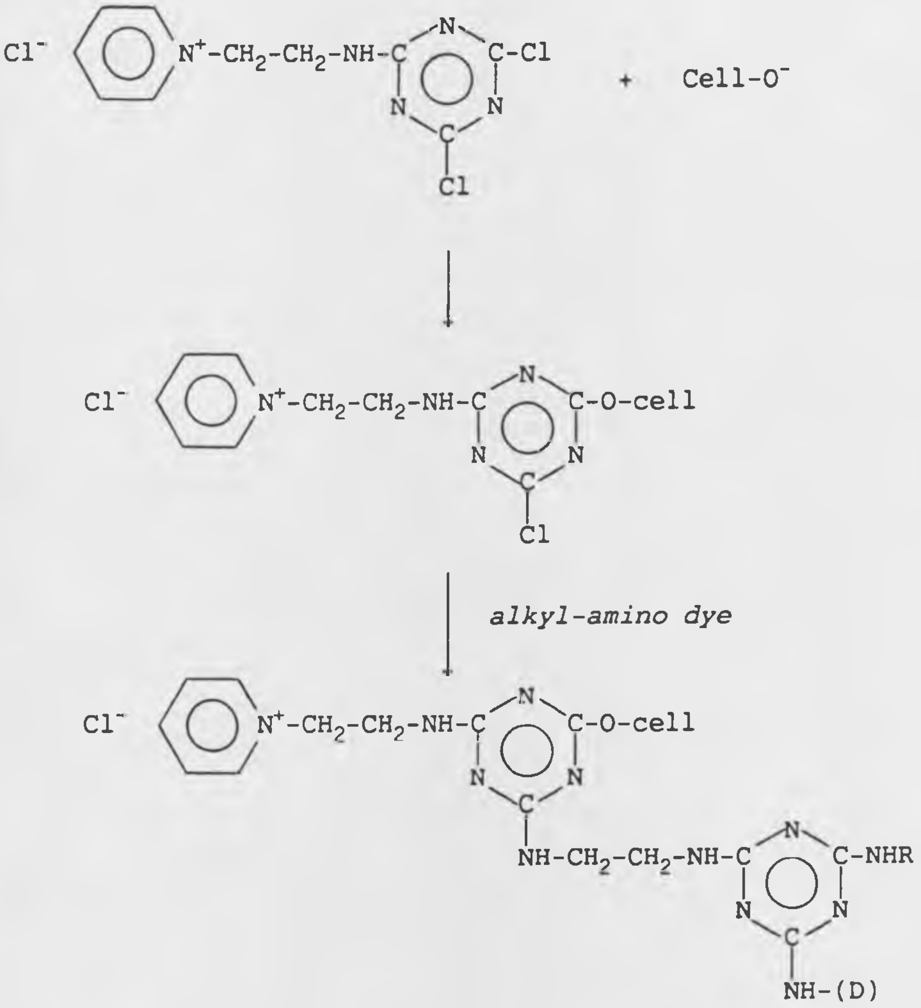
5.4. Activation of Cotton with Cationic Reactive Dichloro-s-triazine Based Compound (Compound II)

5.4.1. Introduction

2,4-dichloro-6-(2-pyridinoethylamino)-s-triazine chloride (Compound II) was prepared and used for activating cotton. The compound has the following structure:



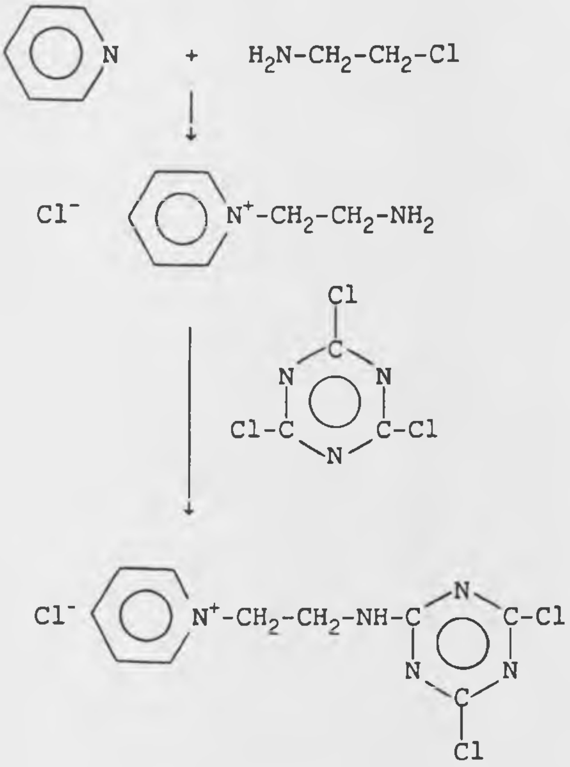
In the above compound, one chlorine atom is easily substituted being activated towards nucleophilic attack by the presence of another strongly electron-drawing chlorine atom in the heterocycle; thus the above compound may be applied under mild alkaline conditions to achieve a covalent bond with cellulose. After replacement of one chlorine atom the other one is more resistant to nucleophilic attack and is less able to react with cellulose under the above conditions. Thus many monochloro-s-triazine reactive groups remain following the pretreatment and are available for further reaction with alkyl-amino dyes. The following reaction schemes describe the pretreatment and subsequent dyeing processes:



Scheme 5-4-1

5.4.2. Preparation and analysis of Compound II

The preparation of Compound II is illustrated as follows (details are given in chapter 2):



Scheme 5-4-2

Figure 5-4-1 shows the FTIR spectrum of compound II. The peaks at 3386 cm-1 and 3057 cm-1 are the absorptions caused by N-H stretch and C-H stretch respectively; the peak at 1635 cm-1 is attributed to the N-H stretch from the pyridinium cation; a strong band at 1614 cm-1 corresponds to C=N stretch of the aromatic heterocycle; the C-H stretch of the aliphatic chain gives a peak at 1136 cm-1 and the presence of chlorine atoms in the triazine ring (C-Cl) is confirmed by an absorption at 778 cm-1.

Figure 5-4-2 gives the U.V. spectrum of compound II. CHN analysis was not carried out due to the difficulty of the compound purification.

5.4.3. Substrate preparation and its dyeing properties

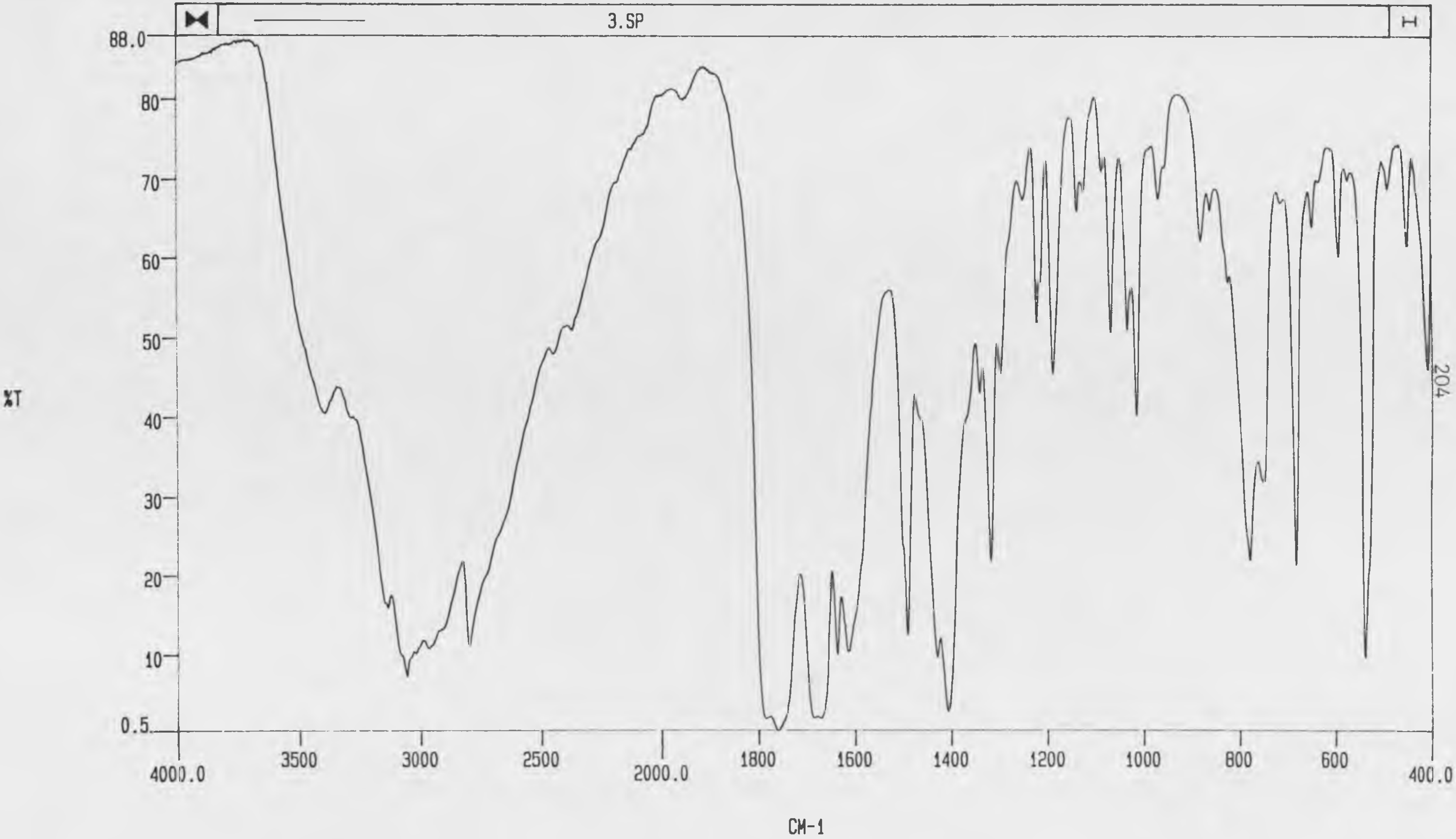


Figure 5-4-1 Infrared spectrum of compound II

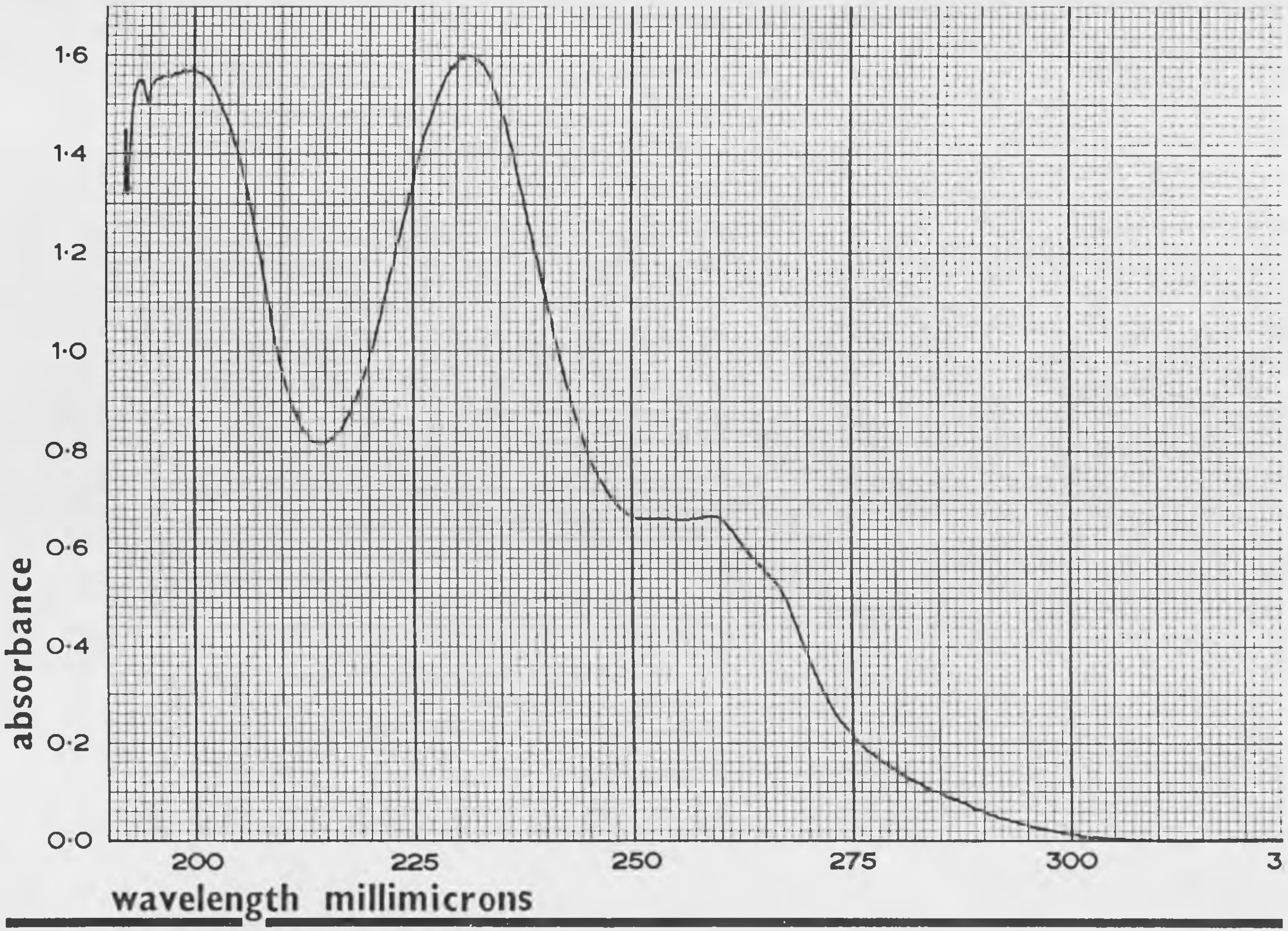


Figure 5-4-2 UV spectrum of compound II

5.4.3.1. Application of compound II by batchwise method

Experiments to apply Compound II using a batchwise method were first carried out under different pH conditions. Cotton was pretreated in a liquor containing 6% (owf) of compound II and buffer (sodium dihydrogen phosphate and disodium hydrogen phosphate) at a liquor to good ratio of 20:1; the pretreatment was commenced at 50°C, the temperature was raised to the boil over 25 mins and maintained at the boil for a further 60 mins. The substrates produced were dyed at the boil in the absence of electrolytes with alkyl-amino dyes (2% owf) at pH 9. Colour yields and fixation values of the dyeings are shown in table 5-4-1. Poor colour yields and fixation values may be due to the low substantivity of Compound II for cellulose during the above pretreatment process; salt was not added during this pretreatment process as it was thought that significant substantivity would be imported by the presence of the cationic group in the reactive molecule --- since cellulose is negatively charged the ionic interactions would be significant.

Table 5-4-1 Colour yield and fixation of an alkyl-amino dye on a variety of Compound II treated substrates (2% owf dye was used)

Pretreatment pH	Colour yield		E%	F%
	before soap	after soap		
7.7	7.27	3.75	50	52
8.2	8.59	4.92	55	57
8.6	7.48	3.85	51	51
9.1	8.17	5.41	53	66

The above results indicate that this method of pretreatment is inefficient; to achieve adequate subsequent dye substantivity and fixation more cationic and monochloro-s-triazine residues would need to be incorporated in the fibre.

5.4.3.2. Application of compound II by a pad-batch(cold) method

Compound II was applied to cotton by a pad-batch (cold) procedure; two concentrations of compound II were applied using the following two pad-liquor compositions:

liquor 1. 20.0 g/l of compound II,
13.3 g/l of sodium bicarbonate,
6.7 g/l of sodium carbonate,
10.0 g/l of Sandozin NIE.

liquor 2. 60.0 g/l of compound II,
40.0 g/l of sodium bicarbonate,
20.0 g/l of sodium carbonate,
10.0 g/l of Sandozin NIE,
120 g/l of urea.

Cotton fabric was padded with the above liquors to give 90% wet pick-up and batched at room temperature for 24 hours. The batched fabric was rinsed and thus the activated cotton was dyed at pH 9 with either an alkyl-monoamino dye (made from Procion Red H8BN) or an alkyl-bisamino dye (made from Procion Red H-E3B), at the boil in the absence of electrolyte. Colour yield and fixation values are shown in table 5-4-2; the results indicate that using 60 g/l of compound II in the pad liquor seems to be essential to give desirable dyeing properties to the subsequent modified substrate. Table 5-4-2 also indicates that it may be necessary to add 120 g/l of urea to the pad liquor when 60 g/l of compound II was used, since at such a high concentration of reactive agent in the presence of electrolyte (60 g/l), this reactive agent is incompletely dissolved in the pad-liquor.

Table 5-4-2 Colour yield and fixation values of alkyl-amino dyes on different substrates (2% owf dye was used)

Conc. of agent (g/l) in pad-liquor	urea (g/l)	colour yield before soap	colour yield after soap	E%	F%
		alkyl-monoamino dye			
20	0	11.30	8.60	80	76
60	0	13.82	12.18	92	88
60	120	14.35	13.53	95	94
		alkyl-bisamino dye			
60	0	12.64	12.16	96	96
60	120	13.59	12.54	97	92

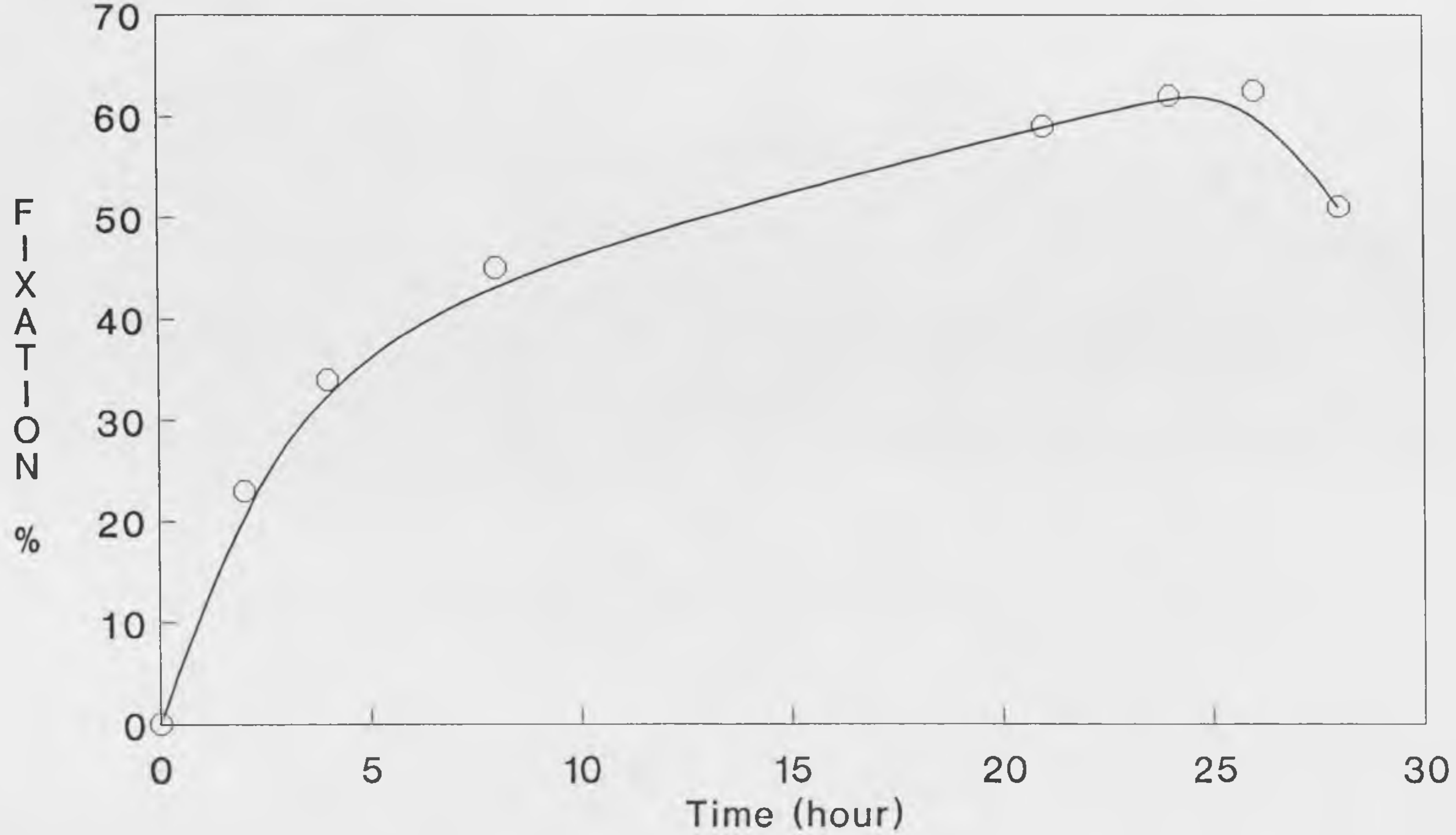
5.4.3.3. Influence of batching time

When pretreating cotton with Compound II, the influence of batching time was investigated by sampling the fabric at intervals and measuring the fixation value of compound II on each sample. Figure 5-4-3 shows the effect of batching time on subsequent dyeing and suggests that optimum fixation can be achieved on batching about 24 hours. In order to confirm this conclusion, the fabrics were dyed under the above mentioned conditions and K/S values (colour yield) were measured and plotted against batching time (figure 5-4-4). It was shown clearly by both curves that the fixation values of the compound in the pretreatment process correlate well with the colour yields of the subsequent dyeings.

5.4.4. dyeing quality

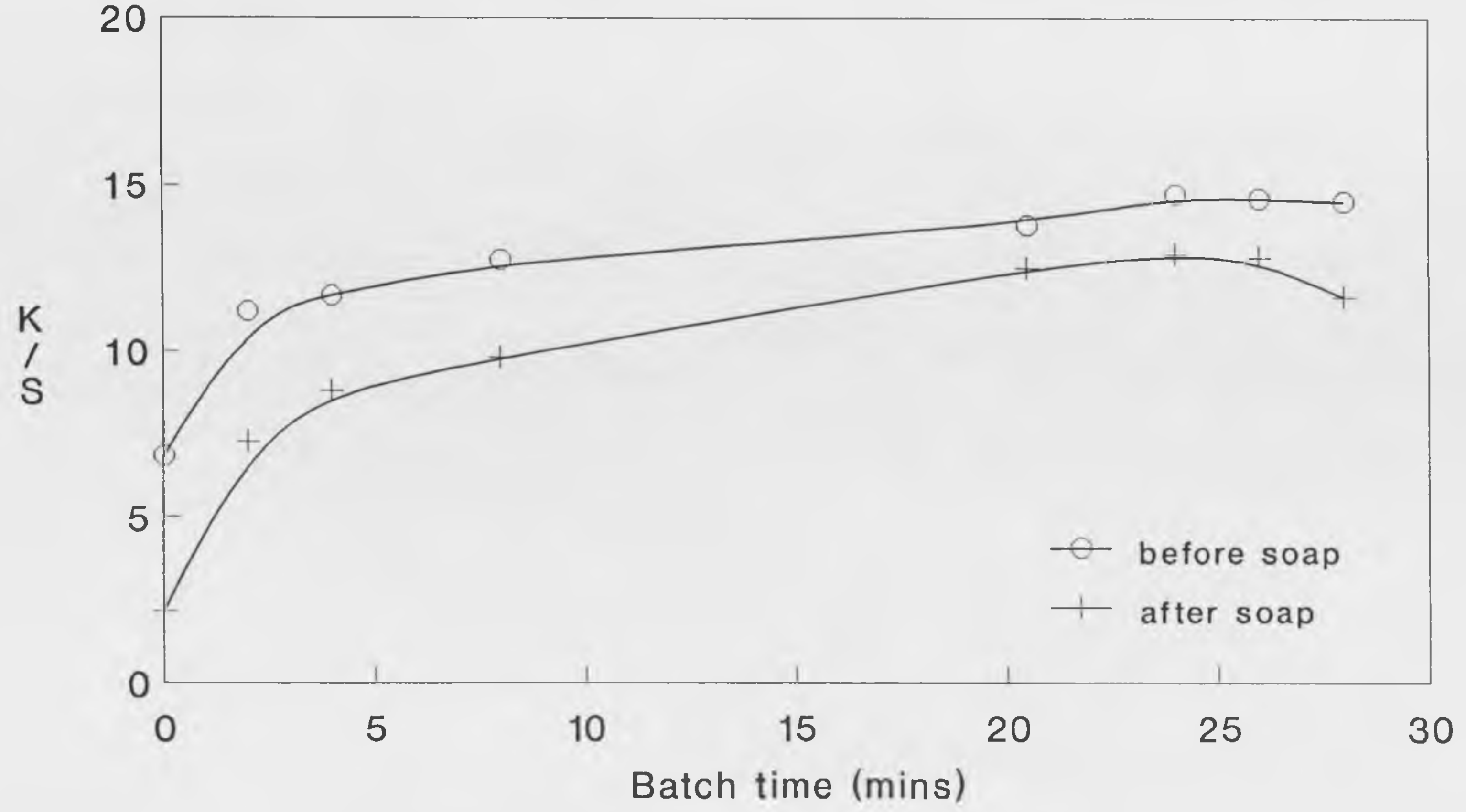
Dyeings of alkyl-amino dyes on Compound II pretreated cotton were found to be very good. Brilliant colours were always produced of the same hue as the parent reactive dyes on untreated cotton. Wet fastness and light

Figure 5-4-3



Fixation of Compound II on cotton

Figure 5-4-4



Effect of batch time on colour yield of the snbsequent dyeings fastness were at the same level as that of the conventional reactive dyes on untreated cotton.

CHAPTER VI

When 10 ml/l of ethylene diamine were added to the PAE pad-liquor, the substrate produced can be dyed with any type of reactive dyes under pH 5-7 conditions at the boil, in the absence of electrolyte, to produce dyeings of excellent wet fastness; the fixation values of reactive dyes on this substrate approached 100%.

iii) It was also found that pretreatment with polymeric compounds reduced the light fastness of subsequent dyeings, because of the surface deposition of polymer on individual fibres or yarns. This problem can be solved by using lower molecular weight compounds for fibre modification.

The substrate obtained by pretreating cotton with 1,1-dimethyl-3-hydroxy azetidinium chloride (DMAC) could be dyed under neutral conditions at the boil in the absence of electrolyte to produce dyeings of good light fastness. This pretreatment method is comparable with a commercially available pretreatment method using Glytac A. The dyeing quality of the dyeings achieved by both methods is equally good, from the point of view of high neutral exhaustion and fixation in the absence of electrolyte.

Modified cotton was also produced by the incorporation of pendant double bonds which could then undergo amination. Cotton readily reacts with N-methylol acrylamide in the presence of a Lewis acid to give a substrate containing activated double bonds. When undergoing amination, different substrates could be obtained by using different amines. Using ammonia and methylamine, substrates containing primary and secondary amino groups were produced which have excellent dyeing properties when dyed with all types of conventional reactive dyes. If dimethylamine was used for amination, a substrate containing tertiary amino groups was obtained; dyeings of reactive dyes on this substrate have poor fixation values due to ready ß-elimination of a quaternary amino group in the ß-position of the propionyl structure. If trimethylamine was used, a substrate of increased substantivity but low reactivity towards reactive dyes was produced, giving subsequent dyeings of poor wash fastness.

iv) Cotton can be effectively esterified with chloropropionyl chloride to give a reactive substrate which can undergo further reactions with a variety of amines. A series of primary, secondary, tertiary and quaternary amino residues were thus 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 treated esterified substrate, nucleophilic displacement of either chloropropionic acid or its ß-elimination product, acrylic acid, occurs and the amino nucleophile is directly attached to the cellulose. This proposed reaction is supported by FTIR studies and analysis of reactive dyeing behaviour.

v) Covalent dye-fibre linkages may be achieved by activating cotton and then dyeing it with alkyl-amino dyes. The advantage of this system over the conventional dye method is that dye hydrolysis does not occur during the dyeing process and thus full use of the dye can be made. Furthermore, environmental problems with the use of conventional reactive dyes may be avoided due to the overall reduction in coloured effluent.

The water soluble alkyl-amino dyes can be readily produced by reaction of conventional monochloro-s-triazine reactive dyes with ethylene diamine.

The activated fibre (or reactive fibre) may be produced either by introduction of pendant activated double bonds or by incorporation of monochloro-s-triazine groups into the fibre.

Pendant activated double bonds can be readily introduced by modifying cotton with an aqueous solution of N-methylol acrylamide. The substrate produced can be dyed with alkyl-amino dyes under mild alkaline conditions at the boil in the absence of salt to give dyeings of excellent quality.

Monochloro-s-triazine reactive groups may be introduced by pretreating cotton with a prepared compound containing both monochloro-s-triazine and 3-carboxypyridinium-s-triazine reactive groups. The groups of the latter type can react with cellulose under neutral pH conditions whilst leaving the groups of the former type intact for further subsequent reaction with alkyl-amino dyes. Unfortunately, the dyeings produced on this pretreated cotton turns out to be dull as the compound used for activation of cotton had a brownish colour.

A cationic dichloro-s-triazine reactive compound was prepared and used for the above purpose. When applied on cotton under mildly alkaline conditions one of the chlorine atoms in the triazine ring will be displaced by cellulosate anion to form a covalent bond with the fibre; once this happened the remaining chlorine atom has lower reactivity but is available for further reaction with the more nucleophilic alkyl-amino dyes. Using this method, the dyeings produced are not only bright but also have good fastness properties.

APPENDICES

Modification of cotton to improve its dyeability. Part 1 – pretreating cotton with reactive polyamide–epichlorohydrin resin

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Pretreatment of cotton with the polyamide–epichlorohydrin resin Hercosett 125 produces a fibre that may be dyed with selected reactive dyes under neutral pH conditions in the absence of salt and with high fixation efficiency. The physical and mechanical properties of the modified cotton, the colour fastness of the reactive dyeings and mechanistic implications are also discussed.

INTRODUCTION

Cellulosic fibres and their blends are often dyed using reactive dyes, especially when dyeings of high wash fastness are required. However, many problems arise from the use of these dyes, for example:

(a) High sodium chloride or sodium sulphate concentrations (up to 100 g/l) are required, which pose environmental problems

(b) Dye–fibre reaction is relatively inefficient, which, in some cases, results in only 50–60% of the applied dye being covalently bonded to the substrate

(c) To remove unfixed dye, time-consuming, energy-intensive and expensive washing-off procedures are required

(d) Unfixed reactive dye and/or hydrolysed dye may pose an environmental hazard; in some countries the discharge of organohalogens is controlled, and certain reactive dyes fall into this category.

The achievement of high dye fixation in a non-polluting dyeing procedure would therefore be of great benefit.

When dyeing polyester/cotton blends disperse dyes are used for the polyester component, and reactive dyes are usually used for the cotton component. Since the fixation step when dyeing cotton with reactive dyes has to be carried out under alkaline conditions, which adversely affect many disperse dyes, either a two-bath or one-bath/two-step dyeing procedure must be adopted. Obviously the processing time used in such methods is long and also the dyeing procedure is complicated. If the dyeing of the cotton component could be carried out under neutral pH conditions, then a one-bath/one-step dyeing method for the polyester/cotton blend would be achievable.

A number of processes have been proposed to increase the neutral substantivity of anionic dyes for cellulose by introducing new cationic sites. In the early 1950s aminised cotton was produced by means of reaction between cellulose and either β-chloroethylamine or β-aminoethylsulphuric acid [1], and this was found to be a very effective method of increasing the dyeability of cotton with anionic dyes [2].

Producing cationic cotton is an important method for improving the substantivity of cotton for anionic dyes [3–7]. A very popular chemical approach was based on the chemical reaction of cellulose epoxides or epoxide precursors [3–6]. The best known reagent, glycidyl trimethylammonium chloride, better known as Glytac-A, is now regarded as somewhat difficult to handle in a textile finishing operation. Introduction of a sulphonium salt structure into cotton represents a further way to improve affinity of cotton for anionic dyes [8,9]. Recently a commercial compound, Sandene, has been claimed by Sandoz and Courtaulds to improve the dyeability of cotton with reactive dyes; this polymer is simply applied by batchwise exhaustion under alkaline conditions [10]. Although these methods produce modified cotton with altered dyeing characteristics, many problems still remain to be solved with each of them.

In this study a theoretical analysis has been made of the factors that should be considered when carrying out cellulose modification. A commercial polyamide-epichlorohydrin polymer solution, Hercosett 125 (Hercules Powder Corpn), was used to modify cotton in order both to confirm theoretical predictions and to produce a modified cellulose that can be dyed with reactive dyes in the absence of salt and under neutral conditions.

Hercosett 125 is a reactive polymer prepared by the initial condensation of adipic acid with diethylenetriamine followed by reaction and partial cross-linking with epichlorohydrin [11]. The resin is sparingly soluble in water and stable up to 6 months at pH 4–5 as a 12.5% aqueous solution. N.m.r. studies [12] have shown that the reactive group in this polymer is the azetidinium cation (Figure 1), rather than the γ-chlorohydrin or epoxide residue.

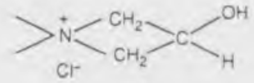


Figure 1 – Azetidinium cation

THEORETICAL CONSIDERATIONS

By applying Danckwert's equation [13]:

$$dQ/dt = [D]_f (D k'_f)^{1/2} \qquad (1)$$

where dQ/dt = rate of sorption of reactive dye per unit area of surface, which can be equated to the rate of fixation (since the material is considered to be infinitely thick and all the dye that enters will be fixed)

$[D]_f$ = equilibrium concentration of dye at the surface of the material

D = diffusion coefficient of dye in the material

k'_f = first-order or pseudo-first-order reaction constant for the reaction between dye and substrate,

and since there are two competing reactions taking place in the dyebath, the efficiency of dye fixation (*E*) is given by Eqn 2 [14] (in which *E* is the quotient of fixation rate and rate of hydrolysis):

$$E = \frac{S}{L}\,\frac{[D]_f}{[D]_s}\left(\frac{D}{k'_H}\,R_f\,\frac{[\mathrm{CellO^-}]}{[\mathrm{OH^-}]}\right)^{1/2} \qquad (2)$$

where S = surface area of the substrate

L = liquor ratio

$[D]_f/[D]_s$ = substantivity ratio of the dye

R_f = ratio of the bimolecular rate constants (i.e. fixation/hydrolysis) and is a constant for a given dye over a wide range of alkaline pH values

$[\mathrm{CellO^-}]/[\mathrm{OH^-}]$ = ratio of cellulosate anion and hydroxyl anion concentrations

k'_H = first-order or pseudo-first-order reaction constant for the reaction between dye and water.

For a given dye and given dyeing conditions *S*, *L*, *D* and *k'* can each be considered to be constant, and so Eqn 2 can be rewritten in the form of Eqn 3 (in which *E* is the product of the dye's substantivity ratio, the reactivity of the substrate and the constant *A*):

$$E = A\,\frac{[D]_f}{[D]_s}\left(R_f\,\frac{[\mathrm{CellO^-}]}{[\mathrm{OH^-}]}\right)^{1/2} \qquad (3)$$

where $A = (S/L)(D/k'_H)^{1/2}$

From Eqn 3 it can be seen that, for a given dyeing system, there are two factors which affect the efficiency of fixation, namely the substantivity of the dye for the substrate and the reactivity of the substrate. In conventional dyeing methods these two factors are controlled by adding a large amount of electrolyte (e.g. common salt or sodium sulphate) and alkali to the dyebath, which leads to the problems previously mentioned.

In the case of cotton modification the two factors discussed above should also be borne in mind. Ideally modification should introduce functional groups into the cotton that not only improve substantivity of the reactive dye for the cotton but also possess reactivity towards reactive dyes, or alternatively provide a catalyst system which can promote the reaction between the cellulosic fibre and the reactive dye.

It has been shown by earlier workers [3–10] that the introduction of cationic groups into cellulosic fibres can increase the substantivity of anionic dyes for the fibre. However, there have been few modifications thus far that introduce reactive functional groups.

We considered that the commercial polymer Hercosett 125 possessed the ability to impart increased substantivity to cotton and improved reactivity towards reactive dyes. Hercosett 125 contains azetidinium groups [12], which on drying may react with nucleophilic sites in cotton or in the polymer itself thus fixing the polymer to the substrate. Furthermore, Bates has showed that, after drying the resin on paper, only a limited amount of cross-linking was required to immobilise the polymer, some 65–70% of unreacted azetidinium groups remaining [15]. Thus, because of the cationic nature of these residual azetidinium groups and the presence of unmodified highly nucleophilic secondary and tertiary amino groups, pretreatment of cotton with Hercosett 125 offers the opportunity for increasing both the substantivity and the reactivity of cotton towards reactive dyes under neutral or acidic conditions.

Cellulose when modified with this reactive polyamide–epichlorohydrin resin thus has a reactive surface that may be represented as containing the reactive and nucleophilic sites illustrated in Figure 2.

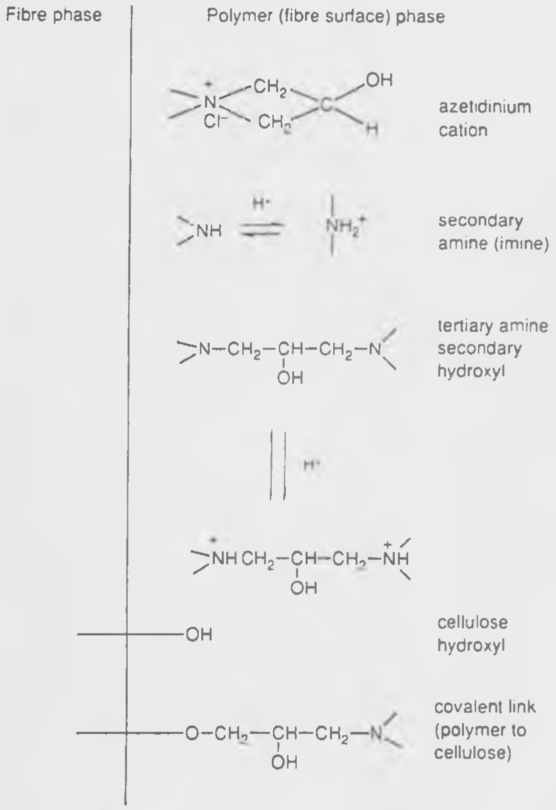


Figure 2 – Illustration of reactive surface of Hercosett-treated cotton

EXPERIMENTAL

Materials

Cotton

Bleached and unmercerised cotton fabric was used throughout the work.

Polymer

Hercosett 125, supplied as an aqueous solution containing 12.5% solids, was used.

Dyes and auxiliaries

All dyes and auxiliaries used were of commercial grade.

Chemicals

– Mercuric oxide	BDH reagent
– Potassium sulphate	Analar reagent
– Sodium hydroxide	laboratory reagent
– Sodium thiosulphate	Analar reagent
– Sulphuric acid (98%)	laboratory reagent
– Hydrochloric acid (36%)	laboratory reagent.

Application of polymer and additives

Cotton fabric was impregnated using the padding liquor trough formed between the bowls and side plates of a Benninger laboratory mangle. The pressure on the mangle was adjusted to give 80% pick-up. After predrying, the samples were then dried for 3 min at 100°C using a Werner Mathis AG steamer/baker unit.

Dyeing of untreated and treated cotton

All dyeings were carried out in 100 ml sealed stainless steel dye pots housed on a Rotadyer (John Jeffreys) laboratory dyeing machine at a liquor ratio of 20:1. Dyeing was begun at 50°C, the temperature was raised to the boil over 25 min at 2 degC/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/l Sandozin NIE (S) and 2 g/l sodium carbonate at the boil for 15 min at a liquor ratio of 50:1.

Measurements

Exhaustion

The uptake of dye by both pretreated and untreated 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 u.v.–visible spectrophotometer (Philips Pye Unicam PU8600). Percentage dyebath exhaustion, *S*, was calculated using Eqn 4:

$$S = 100(1 - A_2/A_1) \quad (4)$$

where A_1 = absorbance of dye solution before the process
A_2 = absorbance of dye solution after the process.

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 at 100°C and a liquor ratio of 10:1. This stripping treatment was carried out repeatedly using fresh aqueous pyridine solutions until no further dye was removed. The *K/S* values of the stripped dyed samples were then measured using an ICS Micromatch colour measurement system, from which the extent of fixation of dye was calculated using Eqns 5 and 6:

$$T = S(C_2/C_1) \quad (5)$$

$$F = 100(C_2/C_1) \quad (6)$$

where T = total dye fixed, %
C_1 = *K/S* value of dyed sample before stripping
C_2 = *K/S* value of dyed sample after stripping
F = degree of fixation of absorbed dye, %.

Total nitrogen determination

The total nitrogen content of the treated fibre was measured according to ASTM Standard D10113-81 [16] (standard test method for total nitrogen in resins and plastics).

Infra-red analysis

Infra-red (i.r.) microscopic examination of treated and untreated cotton was carried out using a Philips PU 9800 f.t.i.r. spectrometer. A single strand was removed from a cotton fabric with tweezers and a scalpel, then placed under the stereoscopic Spectra Physics i.r. microscope; the fibres were teased out and a single fibre (approx. 1 cm long) removed. This single fibre was carefully laid out and flattened using a roller (pressing the fibre between two polished potassium bromide windows should give the same effect). The pressed fibre was taken and suspended on a microscope sample stage plate using adhesive tape before placing on the i.r. microscope sample stage, focusing being carried out under visible light. Once a suitable area of the fibre had been located, the area was isolated using the variable apertures and the i.r. spectrum was recorded.

The microscope had its own dedicated mercury cadmium telluride (MCT-A) detector (range 7000–750 cm^{-1}) and the data collection parameters used were 250 scans at 8 cm^{-1} resolution at a fast mirror speed and normal apodisation.

Textile testing

Fabrics were tested according to BS, AATCC and ASTM procedures. Specific tests used were: BS C04 (1978) – colour fastness to washing, BS B02 (1978) – colour fastness to light (xenon arc continuous light), AATCC test method 66 (1984) – wrinkle recovery of fabrics: recovery angle method and ASTM D-1682 (1975) – breaking strength and elongation of textile fabrics (1R method).

RESULTS AND DISCUSSION

Detection of Hercosett on treated cotton

I.r. analysis was carried out on the treated and untreated cotton and the spectra of both fibres are shown in Figures 3 and 4. Figure 5 shows the spectrum obtained by subtracting the trace in Figure 4 from that in Figure 3. Strong absorbance bands at 1550 and 1650 cm^{-1} correlate well with previous data obtained by Cockett and Lewis [17] for Hercosett resin precipitated from solution with acetone.

Effect of Hercosett pretreatment on the rate of uptake and fixation of reactive dyes on cotton

Cotton was pretreated using a solution containing Her-

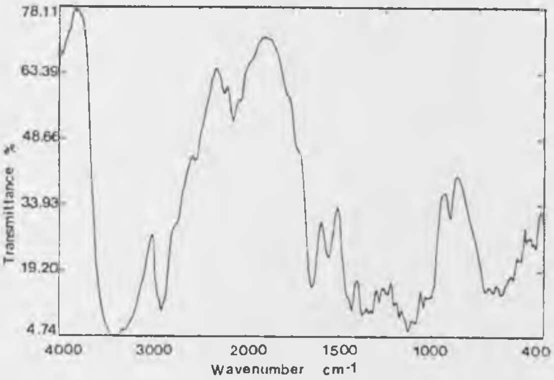


Figure 3 – I.r. spectrum of Hercosett-treated cotton

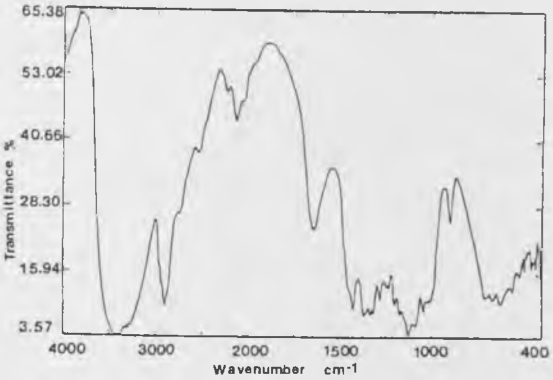


Figure 4 – I.r. spectrum of untreated cotton

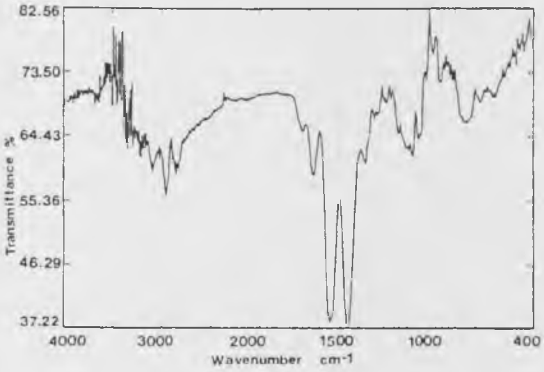


Figure 5 – I.r. spectrum obtained by subtracting spectrum of untreated cotton from that of Hercosett-treated cotton (Figures 3 and 4)

cosett (2% o.w.f.) (200 g/l of 12.5% aqueous Hercosett solution) and Sandozin NIE (10 g/l). The treated and untreated cotton samples were dyed separately with Verofix Red FBL (BAY, C.I. Reactive Red 158) (2% o.w.f.) at pH 7 and 80°C for different periods of time.

Figures 6 and 7 show the rate of dye uptake and fixation of Verofix Red FBL on both treated and untreated cotton. It is clear that pretreatment with Hercosett 125 markedly increases both the rate and final extent (i.e. after 60 min) of dye uptake and fixation under the neutral conditions used.

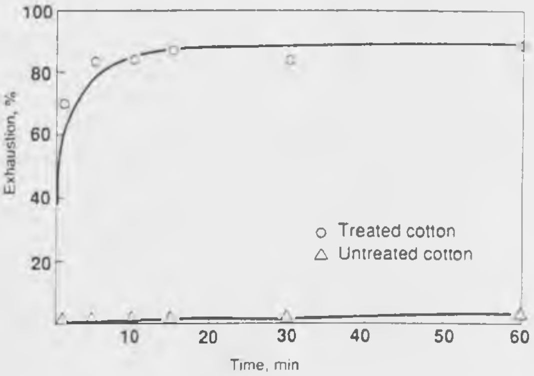


Figure 6 – Exhaustion rate of treated and untreated cotton

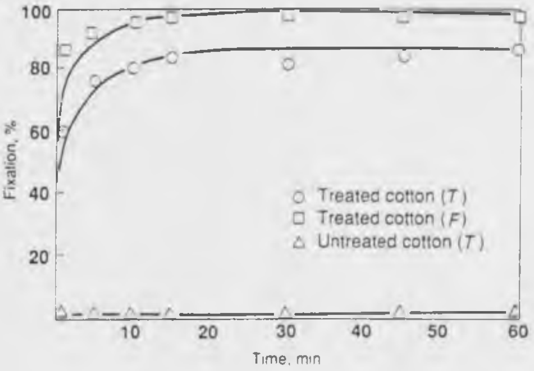


Figure 7 – Fixation rate of treated and untreated cotton

Effect of Hercosett concentration in pad liquor on dye exhaustion and fixation

The dyebath was heated to 100°C at 2 degC/min and maintained at this temperature for 60 min. Figure 8 shows that at a level of 2% o.w.f. Hercosett solids both dye exhaustion and fixation have almost reached their maximum values. Taking account of economic factors, little advantage would be gained by using Hercosett concentrations in excess of this particular level.

Effect of dyebath pH on exhaustion and fixation of a reactive dye on treated cotton

It is important to know the optimum pH value for dyeing the treated cotton. Since it would be desirable to dye polyester/cotton blends under slightly acidic conditions by a one-bath/one-step procedure, the investigation was first carried out in the pH range 6–8 and the results are given in Table 1, which shows that the dye exhaustion increased with decreasing pH, with dye fixation reaching a maximum at pH 7. This can be attributed to the fact that, besides azetidinium groups, Hercosett also contains secondary and tertiary amino groups that absorb more protons at lower pH values, and therefore the cotton fibre

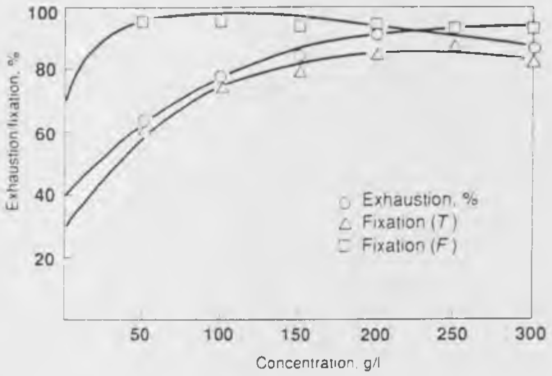


Figure 8 – Effect of Hercosett concentration on exhaustion and fixation

TABLE 1

Exhaustion and fixation from dyebaths of different pH

	Exhaustion	Fixation (%)	
pH	(%)	*T*	*F*
6	88	69	78
7	78	73	94
8	66	65	98

Verofix Red FBL dyeing for 60 min at 100°C at 2% o.w.f.

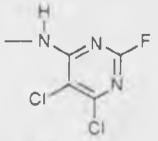
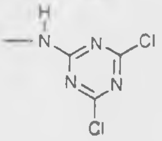
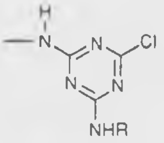
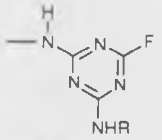
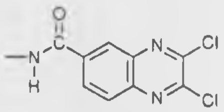
surface is more positively charged under acidic conditions. As a result, the substantivity of the anionic reactive dye increases with decreasing application pH and so does dye exhaustion; on the other hand, because the nature of the dye–fibre reaction is one of nucleophilic substitution, the reactivity of the treated cotton decreases with decreasing application pH. Since the extent of fixation depends on both the substantivity and the reactivity between dye and substrate, there is an optimum degree of fixation at a certain pH value: in this case it is at pH 7.

The suitability of Hercosett pretreatment for different types of reactive dyes

The study was extended to five different types of reactive

TABLE 2

Dyes used in the present study

Dye	Manuf.	C.I. generic name	Reactive group
Levafix Blue E-3GLA Levafix Brilliant Red E-BA Levafix Turquoise Blue E-BA Drimarene Blue K-2RL Drimalan Red F-2BL	BAY BAY BAY S S	C.I. Reactive Blue 113 C.I. Reactive Red 124 C.I. Reactive Blue 116 C.I. Reactive Blue 209 C.I. Reactive Red 100	
Procion Red MX-5B Procion Blue MX-R Procion Yellow MX-8G	ICI ICI ICI	C.I. Reactive Red 2 C.I. Reactive Blue 4 C.I. Reactive Yellow 86	
Procion Yellow H-A Procion Rubine BS Procion Brilliant Red H8BS Procion Green H-E4BD Procion Turquoise H-A Procion Red H-E3B Procion Yellow H-E4R	ICI ICI ICI ICI ICI ICI ICI	C.I. Reactive Yellow 3 C.I. Reactive Red 32 C.I. Reactive Red 58 C.I. Reactive Green 19 C.I. Reactive Blue 71 C.I. Reactive Red 120 C.I. Reactive Yellow 84	
Cibacron Red F-B	CGY	C.I. Reactive Red 184	
Levafix Brilliant Yellow E3D	BAY	C.I. Reactive Yellow 25	

dyes (Table 2). With the exception of the Procion MX (ICI) range of dyes which were applied for 60 min at 40°C, all other reactive dyes were applied using the procedure previously recommended. Table 3 shows that difluorochloropyrimidine and dichlorotriazine reactive dyes exhibit high fixation values on the treated cotton. Furthermore, monochlorotriazine (with the exception of Procion Turquoise H-A), monofluorotriazine and dichloroquinoxaline dyes give very low fixation values on the treated cotton.

It thus appears that those dyes of high reactivity yield high fixation values and vice versa. The apparent exception of Procion Turquoise H-A is worth further consideration; it is our opinion that this dye forms an insoluble ionic complex with Hercosett resin that can not easily redissolve, even under hot alkaline conditions.

TABLE 3

Exhaustion and fixation of different reactive dyes on the treated cotton

Dye	Exhaustion (%)	Fixation T	Fixation F
Levafix Blue E-3GLA	90.0	80.0	88.9
Levafix Brilliant Red E-BA	91.0	73.2	80.4
Levafix Turquoise Blue E-BA	92.0	67.2	73.0
Drimarene Blue K-2RL	89.0	81.7	91.8
Drimarene Red F-2BL	84.0	74.0	88.1
Procion Red MX-5B	92.5	57.2	61.8
Procion Blue MX-R	96.5	82.0	84.9
Procion Yellow MX-8G	82.7	75.3	91.1
Procion Yellow H-A	76.6	14.3	61.8
Procion Rubine BS	82.0	52.0	63.4
Procion Brilliant Red H8BS	79.6	30.1	37.8
Procion Green H-E4BD	93.0	40.0	43.0
Procion Turquoise H-A	96.6	69.6	72.0
Procion Red H-E3B	91.1	33.8	37.1
Procion Yellow H-E4R	91.2	47.3	51.8
Cibacron Red F-B	68.0	44.8	65.9
Levafix Brilliant Yellow E3D	80.0	66.9	83.6

TABLE 4

***K/S* values of different modified cotton fabrics soaped before and after dyeing with reactive dyes**

Treatment before dyeing	Procion Red H-E3B As dyed	Procion Red H-E3B Dyeing soaped off	Procion Blue MX-2R As dyed	Procion Blue MX-2R Dyeing soaped off
None	13.91	8.52	19.69	16.34
'Pre-soap'	4.94	1.88	6.09	5.28

Investigation of the reasons for low fixation of low reactivity dyes

The stability of both the cotton–polymer linkage and the polymer–dye or cotton–dye linkage are equally important when considering the fastness of the dyes on modified cotton. An investigation was carried out into the fastness of the Hercosett resin on cotton. Hercosett-treated cotton was 'pre-soaped' before dyeing with a solution containing 5 g/l Sandozin NIE and 2 g/l sodium carbonate for 15 min at the boil. The sample was then allowed to dry in the open air and dyed with Procion H-E and MX dyes by heating the bath to 100°C at 2 degC/min and maintaining it at this temperature for 60 min. The results are given in Table 4, which shows that either Hercosett was removed by the 'pre-soap' treatment or the polymer's secondary or tertiary amino groups underwent further cross-linking during the 'pre-soap', thus reducing the number of nucleophilic sites. Table 5 gives further evidence that both explanations are correct. The decrease in total nitrogen (and therefore Hercosett) was about 26%. It is thus quite certain that low fixation of dyes of low reactivity is, at least partly, due to the fact that some of the Hercosett is incompletely fixed on the cotton.

The high fixation of the dyes of high reactivity, such as difluorochloropyrimidine and dichlorotriazine dyes, on the treated cotton can be explained as follows. Hercosett is fixed to cotton mainly by means of cross-linking. Since the reactive side chains of the polymer partially lose mobility when water is removed, cross-linking is incomplete in some parts of the resin film. However, because Hercosett has a large molecular structure, it is not extracted from cotton under neutral dyeing conditions, but during the dyeing highly reactive and bifunctional dyes react with Hercosett on the cotton surface forming further cross-links and reducing the solubility of the resin. As a result, both dye and Hercosett are firmly fixed to the cotton. Alternatively the differences between high and low reactivity dyes may be that during the dyeing process the reactive groups compete with the azetidinium cations for the available highly nucleophilic imino sites in the resin. Dyes of low reactivity thus lose out and do not fix well.

The quality of Hercosett-treated and dyed cotton

Colour fastness properties of reactive dyes on this treated cotton are shown in Tables 6 and 7. It is clear from both

TABLE 5

Total percentage nitrogen content of different treated samples

Sample	Total nitrogen (%) Original data	Total nitrogen (%) Average
Without 'pre-soap'	0.255, 0.235	0.245
With 'pre-soap'	0.167, 0.196	0.181

TABLE 6

Wash fastness (C04) of Procion MX dyes on treated and untreated cotton after soaping

	Untreated			Treated		
Dye	E	V	C	E	V	C
Blue MX-2R	5	5	5	5	5	5
Yellow MX-8G	5	5	5	5	5	5
Orange MX-2R	5	5	5	5	5	5
Red MX-G	5	5	5	5	5	5

E – effect on pattern
V – viscose adjacent
C – cotton adjacent

TABLE 7

Light fastness of Procion MX dyes on treated and untreated cotton after soaping

Dye	Untreated	Treated
Blue MX-2R	4–5	3
Yellow MX-8G	5–6	3–4
Orange MX-2R	5	3
Red MX-G	4–5	3

tables that the wash fastness is excellent whereas the light fastness is unsatisfactory, being significantly lowered by the polymer pretreatment.

From microscopic investigation of the cross-sections of the treated and dyed cotton, it was observed that only those fibres on the surface of individual yarns were coloured while the fibres in the centre of such yarns remained colourless (Figure 9(a)). Particular attention was given to the dyed fibres on the yarn surface (Figure 9(b)), which showed that no ring dyeing occurred with these fibres. This can be attributed to the fact that Hercosett has very low substantivity for cotton, so that during drying after padding Hercosett migrates to the yarn surface. It is also clear that under neutral pH conditions reactive dyes can only form covalent bonds with Hercosett, and are thus unable to react with cellulose. The nucleophilicity of amino groups is very high under these conditions whilst the nucleophilic cellulosate anion will not be present in sufficient concentration at these pH values.

The surface coloration also explains the low light fastness of treated and dyed fabric. Further work should therefore be directed towards the achievement of a better distribution of Hercosett within cotton by increasing its substantivity.

Strength properties of treated and untreated cotton are reported in Table 8. Comparison between these two fabrics makes it clear that the pretreatment with Hercosett does not affect breaking strength and elongation, whilst the recovery properties are slightly improved.

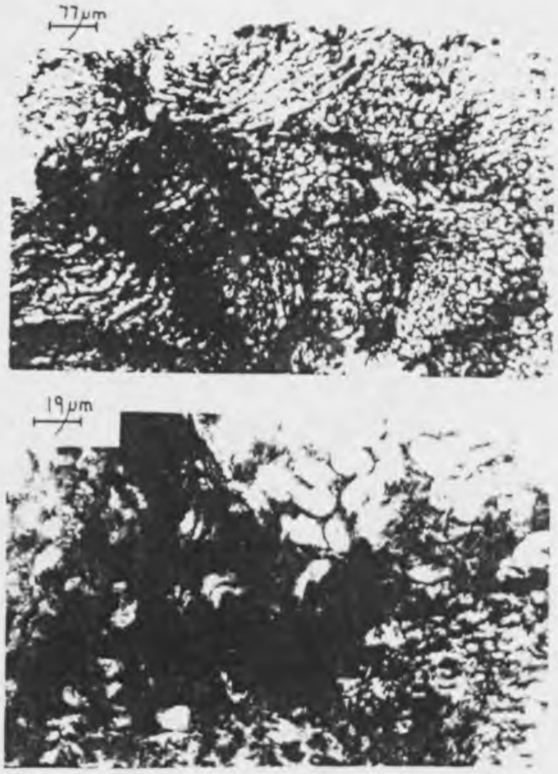


Figure 9 – Cross-sections of Hercosett-treated cotton overdyed several times (top 33 times, bottom 132 times)

TABLE 8

Comparison of strength properties between treated and untreated cotton

Property		Untreated	Treated
Breaking strength (kg)	warp	30.81±1.42	29.66±0.86
	weft	31.09±0.93	31.26±1.22
Elongation (%)	warp	9.97±0.37	10.69±0.38
	weft	17.52±0.67	21.43±1.00
WRA (degree)	warp	62.00±9.37	74.10±5.22
	weft	68.50±3.77	72.20±4.53

CONCLUSION

Cotton can be modified by pretreating with Hercosett 125. The modified cotton can be easily dyed under neutral pH conditions in the absence of salt using reactive dyes of high reactivity, giving high fixation efficiency and good dyeing quality.

Pretreatment is carried out by padding with a solution containing 200 g/l Hercosett 125 and 10 g/l Sandozin NIE without adjustment of pH. This treated cotton may be dyed at pH 7 in the absence of electrolyte.

This pretreatment demonstrates the necessity of introducing functional amino groups which increase both the substantivity and reactivity of cotton, thus achieving reactive dye application under mild conditions.

This work will be extended to study the effect of such resin treatments on the dyeing properties of cotton/polyester blend fabrics.

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Reactive Dyes

Improved Cellulose Dyeability by Chemical Modification of the Fiber

By DAVID M. LEWIS and XIAOPING LEI, Department of Colour Chemistry and Dyeing, University of Leeds, United Kingdom

Of the dyes currently employed for dyeing cellulose fibers, the reactive dyes show the greatest growth potential. The reasons for the popularity of this dye class can be attributed to their almost unrestricted shade range coupled with their excellent wetfastness properties.

There are however certain environmental problems which may arise from the use of reactive dyes—or for that matter most other cellulosic dye classes. The problems occur from using high salt concentrations (40-100 g/L) and only moderate efficiency of dye usage since dye fixation varies from 50-90% depending on application method, depth of shade and dye type. Additionally the discharge of some reactive dyes in aqueous effluents may fall in the category of organic halogen discharges. AOX is a measure of total adsorbable organo-halogen which is carefully monitored in some countries.

The electrolyte used in dyeing reactive dyes on 100% cellulosic materials is usually sodium chloride. When dyeing cellulose/polyester mixtures it is necessary to use sodium sulfate since during the normal high temperature (120-130C) dyeing step required to fix the disperse dye on the polyester component, sodium chloride solutions would attack the stainless steel dyeing vessel. High concentrations of both sodium chloride and sodium sulfate are undesirable in aqueous effluents. Sulfate discharge may be even more suspect since it attacks concrete pipes and also increases the accumulation of sulfate ions which is associated with an increase in total acidity of streams, lakes and rivers.

The above considerations indicate that the ideal reactive dyeing process for cellulose fibers would be to exhaust the dye under neutral to slightly acidic conditions then fix it by simply raising to the boil. Such processes in fact exist for dyeing reactive dyes on wool fibers (*1*). It is therefore worthwhile to consider the differences between the two fibers.

All reactive dyes are sulfonated (2-circa 6 sulfonate groups per dye molecule) and are thus dissolved in aqueous solution at pH values above circa 1.0-1.5 in the form of negatively charged anions. The cellulose fiber is unstable under strongly acidic conditions and should be dyed above pH 4.0 to preserve its physical properties. Under these conditions the surface of the fiber is more or less negatively charged due to the presence of ionized carboxylic acid groups. As the dyebath pH rises above 7.0 the fiber becomes more negatively charged due to the ionization of the hydroxyl groups (*2*).

Anionic dyes thus have to overcome a significant adverse charge barrier before they are adsorbed by the cellulose fiber. Large concentrations of salt serve to screen the negative charges and also decrease the magnitude by reducing the degree of ionization of fiber carboxylic acid residues (*3*).

In the case of wool dyeing the overall surface charge under acidic conditions is positive due to the presence of protonated amino groups. Thus dyeing with sulfonated anionic dyes proceeds relatively readily in the absence of salt even under weakly acidic conditions. There are also significant concentrations of nonpolar, hydrophobic residues in the wool fiber which undoubtedly contribute markedly to wool's substantivity for water soluble dyes (*4,5*). Such residues are notably lacking in cellulose.

From the above considerations it would seem that cellulose modified by the introduction of primary amino, secondary amino or tertiary amino groups would be dyeable with sulfonated dyes under mildly acidic conditions—i.e., sufficient acid to significantly protonate the amino group to form a cation—in the absence of electrolyte.

If the fiber were modified by the incorporation of fully quaternized cationic amino residues then a high substantivity for anionic dyes regardless of the dyebath pH might be expected.

Modification of Cellulose with Low Molecular Weight Compounds

A number of patents and publications (*6-9*) have considered the modification of cellulose with amines. One particularly well researched technique (*7,9*) utilizes the reaction of 2-aminoethylsulfate with cellulose to introduce aminoethyl groups according to the following reaction:

$$\text{Cell-OH} + \text{NaOH} + \text{H}_2\text{N-CH}_2\text{CH}_2\text{-OSO}_3^-\,\text{Na}^+ \xrightarrow{\text{(140C for 10-15 minutes)}} \text{Cell-O-CH}_2\text{CH}_2\text{-NH}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$

O-(2-aminoethyl)-cellulose

The above reaction is an over-simplification. Three products, O-(2 aminoethyl)-cellulose, ethanolamine and polyamine poly-

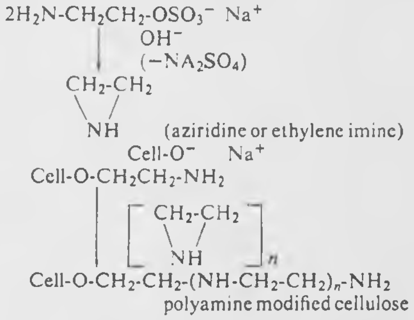
ABSTRACT

The chemical modification of cellulose has been examined from the viewpoint of improving existing procedures for reactive dyeing. It is important that such modifications should be capable of being applied in the mill environment; thus the reactants used should be water soluble and of low toxicity. The paper reviews much of the recent literature, and describes promising results achieved using pretreatments with derivatives of polyamide-epichlorohydrin resins and model fiber reactive amino compounds to impart improved reactive dyeing properties.

KEY TERMS

Cotton
Dyes
Dyeing
Modified Cellulose
Reactive Dyes

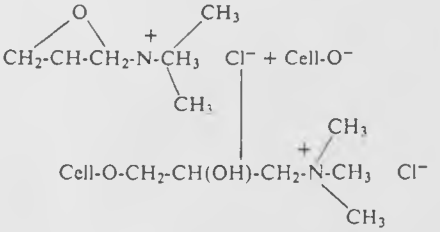
mers are formed (*10*). The polyethylene imine is covalently bonded to the cellulose, according to the following scheme:



Reeves and Guthrie (*8*) reported on dyeing tests carried out by the Du Pont Co. and Gamble on modified cellulose. They noted that the aminized cotton has a noticeable increased substantivity for direct, vat, sulfur and azoic dyes than either mercerized or untreated cotton. Light and washfastness was also slightly better on the modified cellulose. Gamble observed that dyeing of the aminized cotton with cotton dyes requires shorter time, lower temperatures than normal and little or no salt to exhaust the bath.

Einsele (*11*) studied the dyeing of modified cellulose with monochloro-*s*-triazine reactive dyes and observed that good uptake and fixation was produced under slight acidic or neutral conditions in the absence of salt.

Much work has been done to covalently bind fully quaternized amino groups to cellulose (*12-16*). One well known water soluble, reactive quaternary product was sold by Protex as Glytac A (*13*,14). This product is glycidyl-trimethyl ammonium chloride and reacts with cellulose under alkaline conditions according to the following scheme:



Bayer (*15*) marketed a similar product, Levogen RS, which was glycidyl-*N*-methyl morpholinium chloride. This type of product, used for cellulose pretreatments, greatly increases the substantivity of both direct and reactive dyes for the fiber. Lightfastness of both dye classes was unaffected by the treatments and in the case of direct dyes wetfastness was substantially improved.

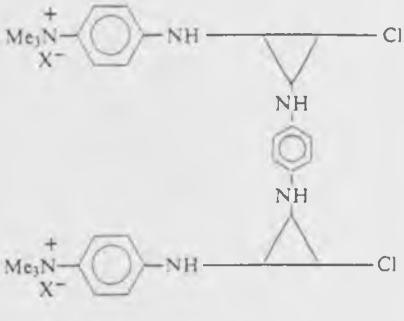
Rippon (*16*) showed that these products could be used as a pretreatment to improve levelness when dyeing cotton fabrics containing significant quantities of immature or dead cotton.

Dyeing studies (*17*) on the prequaternized cellulose produced by the pad-dry-bake (150C) application of 1-trimethyl-ammonium-2-hydroxy-3-chloropropane chloride (precursor to glycidyl-trimethyl ammonium chloride) and sodium hydroxide, showed that selected direct dyes could be applied without salt giving adequate yields and dyeings which were resistant to ISO3 wash testing. Reactive dyes also showed high exhaustion without salt and were apparently bound covalently to the modified substrate even when dyeing under neutral pH conditions (*18*).

Evans et al. (*19*) critically compared the epoxy based pretreatments and made the following observations:

- Pretreatments with reactive quaternary compounds give promising improvements in wetfastness without adversely affecting lightfastness.
- The main problem with pretreatments which greatly enhance the substantivity of the fiber for anionic dyes is that the dyer must achieve adequate uniformity of the pretreatment agent itself.
- Pretreatments should be fiber substantive thus allowing the dyer to apply the reactive compounds by long liquor exhaustion techniques. Neither of the epoxy derivatives mentioned are sufficiently substantive and have to be applied by padding techniques.
- Significant migration of the agents occurred during baking giving rise to surface dyeings on the outside of the yarns.
- If the agents were fixed by pad-batch techniques they modified the fiber evenly; however on subsequent dyeing the substantivity of the anionic dye for the cationic sites in the fiber was so large that ring dyeing of individual fibers occurred.

To overcome some of the latter deficiencies, Evans (*19*) prepared the following type water soluble, fiber substantive, reactive pretreatment agent:



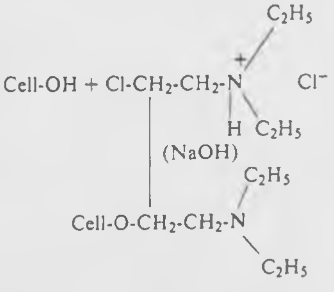
where △ = *s*-triazine

This type agent was found to have significant substantivity for the fiber and could be applied under neutral pH conditions in the absence of salt. Under alkaline conditions optimum substantivity was observed at pH 12 and 40-60C.

Subsequent reactive dyeing of the above modified cellulose showed the following differences compared with untreated cotton dyeings:

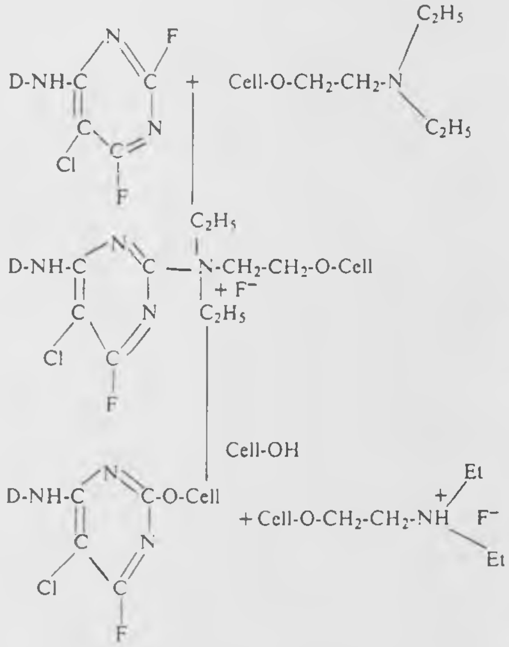
- Significant changes in hue. Most dyeings were duller although those produced from C.I. Reactive Reds 5 and 8 were brighter;
- Tendency to ring dyeing on the modified cellulose;
- Better color yields and dye fixation on the modified cellulose.

Tertiary amino groups have been incorporated in cellulose using *β*-chloroethyl-diethylamino hydrochloride (*20*) according to the following scheme:



The dyeing properties of this modified cellulose were examined by El Alfy et al. (*21*) who showed that it exhibited excellent substantivity for reactive dyes from dyebaths set at pH 7. In the case of a Drimarene K dye, a 2,4-difluoromonochloropyrimidine (FCP) type of reactive dye, the adsorbed dye was surprisingly covalently bonded to the substrate. The phenomena was attributed by El Alfy to the ability of the fixed tertiary amino group to catalyze the reaction of the reactive dye with the cellulose primary hydroxyl groups (*21*).

The proposed reaction for the 2,4-difluoromonochloropyrimidine type reactive dye with the modified cellulose can be written:



Modification of Cellulose with Polymeric Compounds

Courtaulds Co. and Sandoz Chemical Corp. (*23*) developed a cationic polymer pretreatment of cellulose known as the Sandene process. The resin used is Sandene 8425 which is highly cationic in character and highly substantive to cellulose under alkaline conditions. Cellulose treated with the polymer (about 5% owf) is highly cationic, exhibits increased neutral substantivity for anionic dyes and reacts with reactive dyes under neutral to weakly acid conditions. Disadvantages of the procedure include a reduction in lightfastness of some azo chromophores and a flattening or dulling in shade.

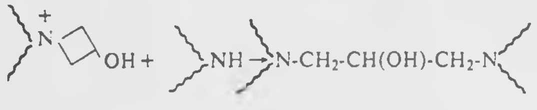
Since untreated cellulose will not dye under the same neutral to weakly acid conditions as the Sandene pretreated fiber, Courtaulds has developed differential dyeing fabrics from mixtures of treated and untreated fibers or yarns called the Depertex process.

Thomas et al. (*24*) pretreated linen with Sandene prior to blending with wool to give a blend fabric which could be dyed in a one bath operation with selected reactive dyes at pH 5-6.

Rippon (*16*) investigated the effect of pretreating cellulose fabrics with chitosan. Chitosan is a long chain unbranched polymer prepared from chitin (poly-*N*-acetyl-*D*-glucosamine) by partial deacetylation with hot alkali. Its structure is thus analogous to cellulose in which the hydroxyl groups in the second position of the glucose ring may have been replaced by either acetyl-amino or amino groups. The hydrolysis of approximately 80% of the acetyl-amino groups leads to a polycationic polymer soluble in dilute acids. Rippon demonstrated that cellulose pretreated with the polymer showed greatly increased substantivity for direct dyes. He did not, however, study dyeing the modified substrate with reactive dyes.

Burkinshaw et al. (*25*) studied the reactive dyeing of cellulose which was pretreated with a reactive polyamide-epichlorohydrin resin (Hercosett 125 by Hercules). They were able to show that the modified substrate could be dyed with highly reactive dyes without salt from dyebaths set at pH 7. Procion M dyes (ICI), which exhibit the highest reactivity, could be fixed by dyeing at 40C for 60 minutes whereas difluoromonochloropyrimidine dyes, Levafix EA (Bayer) or Drimarene R/K (Sandoz), gave good fixation after boiling for 60 minutes.

Fig. 1 shows the different nucleophilic groups present in the polymer modified substrate. The most likely nucleophilic group available for subsequent reaction with reactive dyes is the secondary amino (imino) group; however, there is a competing crosslinking reaction which will lead to a depletion of these reactive sites during the high temperature dyeing process, viz:



Where ~~~ represents polymer chain.

This competing reaction would explain the observed poor fixation of lower reactivity dyes such as monochloro or even monofluoro-*s*-triazines. The purpose of this paper is to clarify these observations.

Dyeings produced on the Hercosett 125 modified cellulose were extremely bright and the color yields of 2% owf dyeings were 50-100% higher than the corresponding dyeings produced by the conventional methods of dyeing reactive dyes on untreated cellulose using salt and alkali.

On further examination the dyeings on the polymer modified substrate were found to be ring dyed and exhibited a significant drop in lightfastness (1-2 points) especially in orange and red shades. This drop in lightfastness was noted previously with other cationic polymer pretreatments and may be related to the strong tendency to ring dyeing and the pronounced hydrophilic character of the cationic polymers. Oxidative fading of azo dyes in their hydrazone form is a common mechanism (*26*) and one can readily envisage the accelerating role of water in this system due to the formation of hydroperoxides on photo-oxidation.

This paper has extended the work on cellulose modification by studying pretreatments with reactive polymers and low molecular

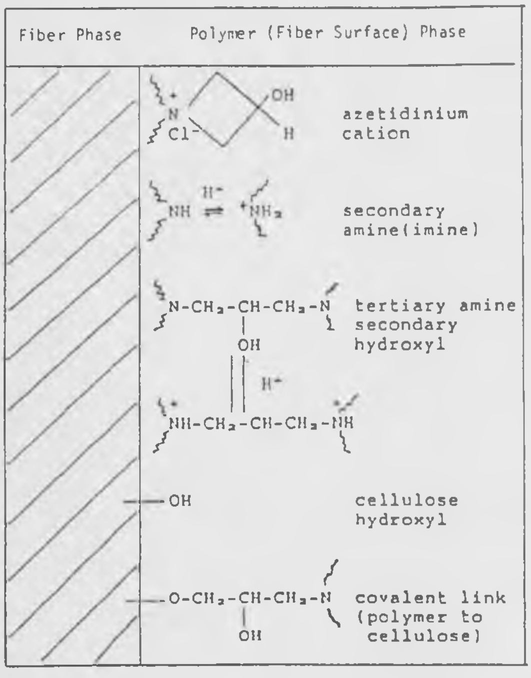


Fig. 1. Illustration of reactive surface of Hercosett treated cotton.

weight model compounds. Results are presented which confirm the lightfastness problems with polymeric pretreatment and the complete absence of this problem when pretreating with low molecular weight compounds.

Experimental

Materials

Cotton: Bleached and unmercerized cotton fabric was used throughout the work.

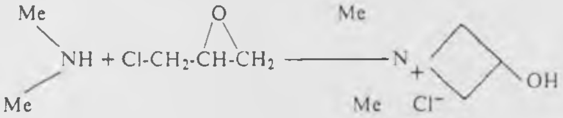
Polymer: Hercosett 125 (Hercules Powder Corp.), supplied as an aqueous solution containing 12.5% solids, was used.

Dyes and auxiliaries: All dyes and auxiliaries used were of commercial grade.

Chemicals: Sodium thiosulfate—Analar reagent grade; sodium hydroxide, sodium hydrosulfide, 40% dimethylamine aqueous solution and epichlorohydrin—all laboratory reagent grade; glycidyl trimethyl-ammoniumchloride-Glytac A (Protex).

Preparation of DMA-AC

DMA-AC (1,1-dimethyl-3-hydroxyazetidinium chloride) was prepared in a similar manner to the method proposed by Gaertner (*27*) who started with diethylamine. Dimethylamine (1M) was cooled to 0-5C and epichlorohydrin (1M) slowly dripped in over 20 minutes. The reaction was stirred for two hours at 0-5C then warmed to 20C for 16 hours. The liquid product was found to be completely water soluble. The following reaction scheme is appropriate:



Application of Polymers and Reactive Compounds

Pad-dry-bake: Cotton fabric was impregnated using the padding liquor trough formed between the bowls and side plates of a Benninger laboratory mangle, adjusted to give 80% wet pick-up. The samples were dried at 100C for three minutes using a Werner Mathis AG Steamer/Baker Unit. In some cases, a baking step (200C, one min) followed the drying procedure.

Pad-batch (cold): Samples were padded as above with the required reagent, batched up, sealed in polythene and washed in running water after the required batching time.

Dyeing Untreated and Treated Cotton

All dyeings were carried out in 100 mL sealed stainless steel dye pots housed on a Rotadyer (John Jeffreys) laboratory dyeing machine at a liquor to goods ratio of 20:1. Dyeing of modified cotton was commenced at 50C. The temperature was raised to the boil over 25 minutes (2C/min) and continued at the boil for a further 60 minutes. Untreated cotton was dyed both by the dye manufacturer's recommended method for the particular reactive dye selected and for comparison, by the method used for the modified cottons.

The dyed samples were rinsed thoroughly in tap water and cut in two equal portions. One portion was soaped in a solution containing 5 g/L of Sandozin NIE (Sandoz) and 2 g/L of sodium carbonate at the boil for 15 minutes in a 50:1 liquor ratio.

Measurement of Dye Fixation and Color Yield

The uptake of dye by both modified and unmodified cotton was determined by the usual spectrophotometric techniques. Dye fixation was determined by repeated extraction of the dyeings with boiling 25% aqueous pyridine solution (LR = 10:1) until no further color was removed. The Kubelka-Munk, *K/S*, values were obtained for the original and stripped dyeings using the ICS Micromatch color measurement system and fixation was calculated.

Table I. Color Yield of Dyed Fabric

	K/S			
Dyes[a]	Before Soap	After Soap	F	Lightfastness
Procion Red MX-G	15.274	13.944	91%	3
Procion Red HE3B	13.918	8.529	61	3
Procion Red H8BN	14.177	8.670	61	3

[a] 2% owf of dyes at pH 7.

Total Nitrogen Determination

The total nitrogen content of the treated fiber was measured according to ASTM SD1013-81; Standard Test Method for Total Nitrogen in Resins and Plastics (*28*).

Lightfastness Testing

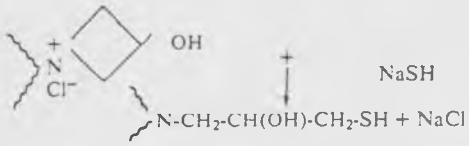
Lightfastness was determined using the Microscal Lamp. The degree of fading was assessed using the SDC blue scales.

Results and Discussion

Previous work (*25*) on cotton modified with Hercosett resin demonstrated that both high and low reactivity dyes show very high neutral substantivity for the modified substrate but only the former dyes exhibit high fixation (Table I). It is believed that the secondary amino nucleophiles in the resin modified cotton reacted too quickly with the residual reactive azetidinium groups in the resin making them unavailable for the lower reactivity dyes. It appears necessary to introduce additional reactive sites in cotton which are sufficiently nucleophilic to react with low reactivity dyes, thus allowing the modification to be used for all types of reactive dyes.

Oxidative fading of azo dyes in their hydrazone form could be the source of poor lightfastness on Hercosett treated cotton. The introduction of some reducing groups might improve the lightfastness of the dyeings on modified cotton.

Based on the above considerations, it was decided to introduce thiol groups, which are both strongly nucleophilic and reducing in the modified cotton according to the following scheme:



The above reaction was carried out by after-treating Hercosett treated cotton with an aqueous solution containing 40% of NaSH by a pad-batch (cold) method, batching for 16 hours and washing in cold water. According to Bates (*29*), when pretreating cellulose with aqueous Hercosett solution, about 60-70% of reactive azetidinium groups are left untreated after drying. These groups would react with NaSH to form thiol groups under the above conditions.

The Hercosett/NaSH treated cotton was dyed and color yield and lightfastness were measured. The results are shown in Table II.

Table II shows that after NaSH treatment, the fixation of Procion HE and H dyes was not improved. Since there is no doubt that thiol groups can readily react with monochlorotriazine dyes under neutral or slightly acidic conditions (*30*), it is likely that further reaction of the thiol terminated polymer takes place. The

Table II. Color Yield and Lightfastness of Treated and Dyed Fabrics

Dyes[a]	pH	Salt Added	K/S Before Soap	K/S After Soap	F	Lightfastness
Procion Red MX-G	5	0 g/L	12.407	8.369	67%	3
	7	0	3.248	1.873	57	3
	7	80	9.940	8.094	81	3
Procion Red HE3B	5	0	14.542	5.026	35	3
	7	0	5.881	2.304	39	3
	7	80	13.576	8.409	62	3
Procion Red H8BN	5	0	12.156	1.205	9	3
	7	0	1.708	0.744	43	3
	7	80	8.049	2.999	37	3

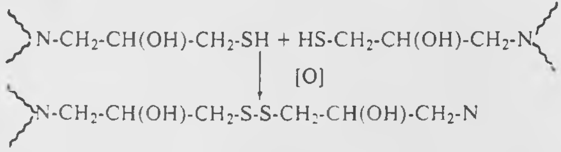
[a] 2% owf.

Table III. Lightfastness of Dyed Fabrics[a]

Dyeing Method	Lightfastness
Hercosett	3
DMA-AC	5
Conventional	5

[a] 2% owf Procion Brilliant Red HEGL.

following air oxidation reaction is highly probable during drying the thiol treated fabric:



$$>N\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}SH + HS\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}N< \xrightarrow{[O]} >N\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}N$$

The formation of the disulfide bond reduces the number of nucleophilic sites. In neutral or slightly acidic dyeing conditions, the above type of disulfide bond is nonreactive towards reactive dyes and is rather stable unlike the disulfide in wool crystine (*31*) which hydrolyses readily to the nucleophilic thiol due to its activation by the neighboring peptide carbonyl group.

Table II also shows that cationic azetidinium groups in Hercosett treated cotton play an important role in the uptake of reactive dyes. This can be seen by comparing the results of dyeings at pH 7 without salt (Tables I, II). After NaSH treatment, azetidinium groups form thiol groups or disulfide groups which lead to a significant reduction in substantivity due to the loss of the cationic sites.

Table II shows that the dyeing of the thiol modified substrate is sensitive to pH. The sharp increase in substantivity at pH 5 must be attributed to protonation of the secondary and tertiary amino groups in the polymer. The dye uptake at pH 5 without salt is almost the same as that at pH 7 in the presence of 80 g/L of salt. This result demonstrates an effective way to avoid the addition of high concentrations of electrolyte without reducing dye substantivity.

The introduction of reducing groups—thiol or disulfide groups—does not improve the lightfastness of reactive dyeings on Hercosett treated cotton. This indicates that the main reason for poor lightfastness of dyeings on the substrate must be related to the poor penetration and distribution of the dyes. Pretreatment with polymer finishes give rise to poor dye distribution more readily than pretreatment with lower molecular weight compounds since the former do not penetrate the individual fibers. If reactive dyes are mainly covalently bonded to the new reactive sites introduced, it would be necessary to use low molecular weight reactive compounds for pretreatment to achieve good dye penetration and hence dyeings of good lightfastness on the pretreated cellulose.

Effect of Pretreatment with Low Molecular Weight Compounds

In order to obtain dyeings on modified cotton with good lightfastness, a low molecular weight compound, dimethylazetidiniumchloride (DMA-AC), was prepared and used to pretreat cotton. The compound has similar characteristics to Hercosett in that it is water soluble, cationic due to the azetidinium group and capable of reaction with nucleophilic cellulosate anions. Application conditions for this compound were investigated and are described below.

Effect of DMA-AC Pad-Liquor Concentration on Color Yield

Cotton fabric was pretreated with different concentrations of DMA-AC using a pad-dry-bake method. The pretreated cotton was dyed at pH 7 using 2% owf Procion Brilliant Red HEGL. The lightfastness of dyeings on the substrate with the reactive dyes was tested and a comparison made with the corresponding dyeings on both Hercosett treated cotton and untreated cotton dyed using the conventional method. Table III shows the lightfastness results achieved.

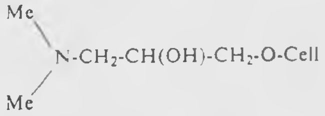
Table IV shows the color yields obtained with increasing DMA-AC concentrations. The results indicated that 40 g/L of DMA-AC in the padding liquor is the minimum concentration required to give adequate dye uptake. However dye fixation increases further at higher DMA-AC concentration.

Optimization of Baking Conditions

Tables V and VI show that after predrying padded fabric for three minutes, optimum color yields were obtained by baking the fabric at 200C for one minute without washing prior to dyeing.

Effect of Alkali in DMA-AC Padding Liquor

Application of DMA-AC in the presence of strong alkali was also examined (Table VII). Results show that the presence of a strong alkali in the padding liquor is essential for sufficient covalent bond formation between DMA-AC and cellulose. The behavior of DMA-AC treatments when applied to cellulose under neutral conditions can be explained both by reaction with cellulose to form:



$$(Me)_2N\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}O\text{-}Cell$$

and possibly by the formation of medium molecular weight oligomers which are still able to penetrate the fiber.

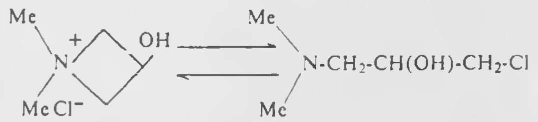
The equilibrium between DMA-AC and 1-*N*,*N*-dimethyl-

Table IV. Color Yield of DMA-AC Treated and Dyed Cotton Fabrics[a]

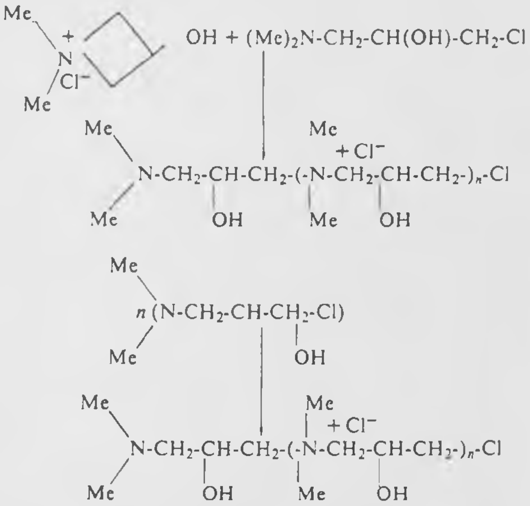
DMA-AC Conc	K/S Before Soap	K/S After Soap	F
80 g/L	18.561	12.165	66%
60	18.792	10.740	57
40	18.453	9.733	53
20	13.732	6.357	46
Conventional Dyeing	14.815	12.165	82

[a] 2% owf Procion Brilliant Red HEGL

amino-2-hydroxy-3-chloropropane could be described:



Since the tertiary amino group is a strong nucleophile, it can react with the azetidinium cation or the γ-chloro group to form DMA-AC oligomers:



The strongly cationic character and relatively large molecular weight of the oligomers makes them substantive to cotton by means of both molecular interactions and ionic bond formation. Such treatments cannot be removed under neutral condition but significant removal occurs under alkaline conditions explaining the only moderate reactive dye fixation values achieved.

Table V. Dye Color Yield According to Baking Conditions[a]

DMA-AC Conc	Temp	Baking Time	K/S Before Soap	K/S After Soap	F
80 g/L	200 C	1 min	18.562	12.165	66%
	150	2	15.369	11.115	72
	no baking		10.161	6.401	63
60	200	1	18.792	10.740	57
	150	2	13.974	5.704	41
40	200	1	18.453	9.733	53
	150	2	14.815	5.383	36

[a] 2% owf Procion Brilliant Red HEGL.

Table VI. Effect of Washing Prior to Dyeing on Color Yield[a]

Washing After Baking	K/S Before Soap	K/S After Soap	F
No	18.483	9.733	53%
Yes	14.502	9.351	64

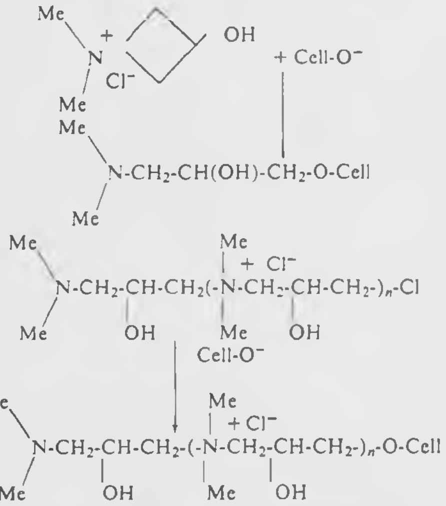
[a] 40 g/L of DMA-AC and 2% owf Procion Brilliant Red HEGL were used.

Table VII. Effect of NaOH in DMA-AC Padding Liquor on Subsequent Dye Fixation[a]

NaOH Conc	K/S Before Soap	K/S After Soap	F
0 g/L	11.660	5.664	49%
4	12.234	11.612	95

[a] 40 g/L of DMA-AC and 2% owf Levafix Brilliant Red E-BA were used.

When DMA-AC was applied in the presence of strong alkalies such as NaOH, apart from the possible formation of oligomers, the reaction between DMA-AC or its oligomers and cellulose was promoted due to the increased nucleophilicity of the cellulose. DMA-AC and its oligomers are thus covalently bonded and cannot be removed even under alkaline soaping conditions.



Since reactive dyes cannot react with cellulose under neutral conditions, the good fixation of reactive dyeings on DMA-AC treated cotton produced under neutral dyeing conditions must be due to the presence of tertiary amine nucleophiles and possibly increased deprotonation of hydroxyl groups in the vicinity of basic tertiary and quaternary nitrogen atoms. Such effects would lead to the formation of highly nucleophilic cellulosate residues which readily form covalent bonds with the reactive dye even under the above neutral to slightly acidic conditions.

Effect of pH when Dyeing DMA-AC Treated Cotton

Table VIII shows that the color yields on DMA-AC treated cotton are slightly higher when dyed with highly reactive dyes under neutral conditions than under slightly acidic conditions. This is because the cationic groups in the substrate impart sufficient substantivity at pH 5-7. The color yields are slightly higher under neutral conditions since the reactivity of the substrate is higher caused by an increased concentration of Cell-O⁻.

DMA-AC Treatments with Glytac A

Glytac A (Protex) is a commercial compound sold as an aqueous solution of glycidyl-trimethylammonium chloride. It reacts with cellulose via the reactive epoxy group according to the scheme described in the introduction.

A comparison was made between DMA-AC and Glytac A treatments to evaluate the practical importance of the DMA-AC

Table VIII. Effect of Dyeing pH on Color Yield of Dyeings on DMA-AC Treated Cotton[a]

pH	K/S Before Soap	K/S After Soap	F
5	11.172	10.989	98%
7	12.766	12.625	99

---

[a] 40 g/L DMA-AC, 4 g/L NaOH and 2% owf Procion Red MX-G were used.

Table IX. Color Yield of Dyeings on DMA-AC and Glytac A Treated Cotton[a]

Reagent	Total Nitrogen	Dye[b]	K/S Before Soap	K/S After Soap	F
Glytac A (40 g/L)	0 108%	Procion Red MX-G	12 838	11.775	92%
		Levafix Br.Red E-BA	10.754	10.722	99
DMA-AC (40 g/L)	0.150	Procion Red MX-G	12.766	12.625	99
		Levafix Br. Red E-BA	11.037	10.256	93
Conventional Dyeing		Procion Red MX-Levafix	4.245	3.477	83
		Br.Red E-BA	10.561	9.583	90

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[a] Both DMA-AC and Glytac A pad liquors contained 4 g/L NaOH. Baking conditions for DMA-AC were 200C, 1 minute and for Glytac A 120C, 3 minutes.[b] Dyes were 2% owf, pH 7 at 100C.

treatment. Results in Table IX show that almost the same dyeing behavior was achieved using either DMA-AC pretreatment or Glytac A pretreatment. This indicates that DMA-AC pretreatment is an alternative practical method for achieving neutral reactive dyeing of cellulose with high dye fixation. Much stronger color yield was obtained using both DMA-AC and Glytac A pretreatments compared with the conventional dyeing method.

The results indicate that modification of cellulose leading to attachment of tertiary or quaternary amino groups by covalent bonding gives a substrate which can be dyed with reactive dyes at pH 7 without salt addition. Fixation of dye on the fiber is extremely high and lengthy soaping processes at the boil are not required.

Conclusions

Cellulose has been modified by a variety of reactive compounds to covalently bind secondary amino, tertiary amino, quaternary amino, thiol or disulfide residues. In pretreatments with polymeric compounds, poor lightfastness of subsequent reactive dyeings was associated with ring dyeing. Pretreatments with lower molecular weight compounds did not exhibit this problem when dyed.

The improved substantivity and fixation of reactive dyeings on modified substrates even under neutral to slightly acidic conditions have been demonstrated. Improved neutral fixation of Hercosett pretreated cotton can be ascribed to the presence of highly nucleophilic secondary amino groups in the resin. In DMA-AC and Glytac A which introduce tertiary and quaternary amino groups, the improved neutral fixation has been suggested to occur as a result of increased cellulose hydroxyl ionization due to the proximity of strongly basic groups.

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PAPERS

Modification of cotton to improve its dyeability. Part 2 – pretreating cotton with a thiourea derivative of polyamide–epichlorohydrin resins

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A new method of pretreating cotton to improve its dyeability, using an aqueous solution containing polyamide–epichlorohydrin (PAE) resin and thiourea is introduced. The effect of dyebath pH on the colour yield, fixation and build-up of Procion HE, H and MX (ICI) dyes on the pretreated cotton, together with the quality of the dyeings obtained when using the new method and mechanistic implications, are discussed.

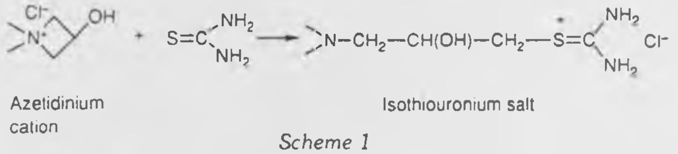
INTRODUCTION

In Part 1 of this series cotton that had been pretreated with an aqueous solution of polyamide–epichlorohydrin (PAE) resin was shown to be dyeable with reactive dyes under neutral conditions without salt [1]. These dyeings were found to be bright and the colour yield of medium-depth dyeings was generally higher than that of corresponding dyeings produced by conventional methods on untreated cotton using salt and alkali. The wash fastness properties of the dyeings on the treated cotton were excellent and the physical properties of the treated cotton were identical to those of untreated fabrics. Problems observed with this system included the lower fixation values obtained when applying dyes of low reactivity to the pretreated cotton and a significant drop (approx. 1–2 points) in the light fastness of dyeings, compared with dyeings on untreated cotton produced by conventional methods. Therefore the main purpose of this study is to overcome these deficiencies.

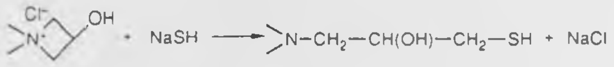
The earlier work showed that the reactive azetidinium cations present in the resin compete with the reactive groups of the reactive dyes during the dyeing process for the highly nucleophilic imino sites in the resin [1]. Thus the reason for the observed lower neutral fixation of low-reactivity dyes is that they lose out in this competitive reaction. It therefore appears necessary to introduce more highly nucleophilic sites into cotton so that better fixation of both high- and low-reactivity dyes might be achieved.

The chemistry of the azetidinium cation [2] indicates that it can react by means of ring opening with strong nucleophiles such as amines and thiols under mild conditions. Since only a few of the azetidinium cations are needed to immobilise the resin on cotton [3], the remainder might be employed to introduce either isothiouronium salt, Bunte salt or thiol residues as described in Schemes 1–3.

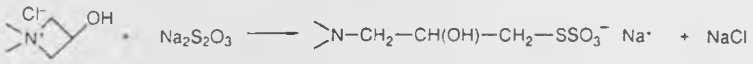
Cotton fabric was therefore pretreated with an aqueous solution containing PAE resin plus thiourea and dried. The formation of isothiouronium salts in the fibre surface would not initially decrease the total number of cationic sites in the resin but might subsequently increase the concentration of strongly nucleophilic centres in this substrate because of the decomposition of isothiouronium salt to thiol residues during the dyeing process (Scheme 4).



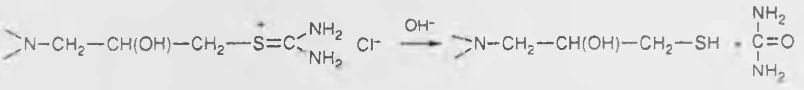
Scheme 1



Scheme 2



Scheme 3



Scheme 4

The reduction in light fastness of dyeings observed earlier might be related to the strong tendency to ring dyeing and the pronounced hydrophilic character of the cationic polymers. Oxidative fading of azo dyes in their hydrazone form is a common mechanism [4] and the accelerating role of water in this system due to hydroperoxide formation during photo-oxidation can be readily envisaged. Some reducing groups were therefore introduced into the resin-finished cotton with the hope of scavenging any hydroperoxides and thus improving the light fastness of the dyeings.

Introduction of thiol groups

Thiol groups may be introduced as a result of ring opening of the azetidinium groups with sodium hydrosulphide (Scheme 2).

Introduction of *S*-thiosulphate (Bunte salt) residues

Sodium thiosulphate reacts with the azetidinium cation in PAE resins [5] according to Scheme 3.

TABLE 1

Dyes used in the present study

Commercial name	Manufacturer	C.I. Reactive
Levafix Red E-BA	BAY	Red 124
Procion Blue H-EGN	ICI	Blue 198
Procion Blue MX-2R	ICI	
Procion Orange MX-2R	ICI	Orange 4
Procion Red H-E3B	ICI	Red 120
Procion Red H-EXL	ICI	Red 58
Procion Red MX-5B	ICI	Red 2
Procion Red MX-G	ICI	Red 5
Procion Yellow H-E4R	ICI	Yellow 84
Procion Yellow MX-8G	ICI	Yellow 86
Remazol Red RB	HOE	Red 198
Cibacron Red F-B	CGY	Red 184

EXPERIMENTAL

Materials

Bleached and unmercerised cotton fabric and Hercosett 125 (Hercules Powder Corpn), supplied as an aqueous solution containing 12.5% solids, were used throughout the work. All dyes and auxiliaries used were of commercial grade. The dyes for which results are reported are listed in Table 1. Thiourea, mercury(II) oxide, potassium sulphate, sodium hydroxide, sodium thiosulphate were all Analar reagent grade; sulphuric acid (98% by weight), sodium hydrosulphide and hydrochloric acid (36% by weight) were all laboratory reagent grade.

Application of polymer and additives

Cotton fabric was impregnated by padding through the liquor trough formed between the bowls and side-plates of a Benninger laboratory mangle; the pressure was adjusted to give 80% wet pick-up. The samples were then dried at 100°C for 3 min using a Werner Mathis steamer/baker unit.

In several cases further treatment of PAE-treated cotton was carried out using two different procedures.

Pad–batch(cold):

Samples were padded as above with the required reagent, batched (sealed in polythene) and washed-off in running water after the required batching time.

Batchwise

Samples were treated with an aqueous solution of the required reagent at a liquor ratio of 20:1 for 1 h at the boil.

Dyeing of untreated and treated cotton

All dyeings were carried out in 100 ml capacity sealed stainless steel dye pots housed on a Rotadyer (John Jeffreys) laboratory dyeing machine at a liquor ratio of 20:1. Dyeing of the modified cottons was begun at 50°C with the bath set at the required pH value (usually pH 5), the temperature was raised to the boil over 25 min (2 degC/min) and dyeing continued at the boil for a further 60 min. Untreated cotton was dyed both by the dye manufacturer's recommended method for the particular reactive dye selected (i.e. with salt and alkali) and (for comparison) by the novel method employed [1] for the modified cottons (i.e. no salt, no alkali).

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/l of the non-ionic surfactant Sandozin NIE (S) and 2 g/l sodium carbonate, at the boil for 15 min (liquor ratio 50:1).

Measurement of dye fixation and colour yield

The percentage uptake of dye (*E*) by both modified and unmodified cotton was determined using conventional spectrophotometric techniques. Dye fixation was determined by repeated extraction of the dyeings with boiling 25% aqueous pyridine solution (liquor ratio 10:1) until no further dye was removed. The Kubelka–Munk (*K/S*) values were obtained for the original and stripped dyeings using an ICS Micromatch colour measurement system, and the extent of dye fixation was thus calculated. Percentage fixation values given in this paper are determined as the percentage of exhausted dye fixed, using the definitions given previously [1]. This is represented by *F* and should not be confused with the value *T*, which represents the percentage of the original dye applied that is fixed.

Total nitrogen determination

The total nitrogen content of the treated fibre was measured according to ASTM standard D1013-81 [6] (standard test method for total nitrogen in resins and plastics).

Infra-red (i.r.) analysis

I.r. microscopic examination of both treated and untreated cotton was carried out using either a PU 9800 (Philips) FTIR spectrometer or a Perkin Elmer 1740 infra-red fourier transform spectrometer with the diffuse reflectance attachment.

Textile testing

Fabrics were tested according to BS, AATCC and ASTM standard procedures. Specific tests used were: BS C04:1978 colour fastness to washing; BS B02:1978 colour fastness to light (xenon arc, continuous light); AATCC test method 66-1984 wrinkle recovery of fabrics (recovery angle method); ASTM: D-1682(1975) breaking strength and elongation of textile fabrics (1R method).

RESULTS AND DISCUSSIONS

Effect of adding thiourea to the PAE pad liquor on dye fixation

The pad liquor for the PAE pretreatment was prepared containing 200 g/l Hercosett 125 and 10 g/l Sandozin NIE; the pad liquor for the combined PAE/thiourea pretreatment additionally contained 10 g/l thiourea. Both pretreatments were carried out using a simple pad–dry procedure without further baking and washing-off. The colour yield and fixation of dyeings on both treated cotton fabrics are given in Table 2. This also shows that if thiourea is included in the PAE pad liquor, the fixation of these types of reactive dyes on the treated cotton is markedly improved. Another factor that becomes clear is that, in the case of the PAE/thiourea pretreatment, raising the dyeing temperature from 60 to 100°C does not have a pronounced effect on the colour yield and fixation values obtained for the highly reactive Procion MX dye, which suggests that the reaction between the dichlorotriazine reactive dyes and the nucleophilic sites in the resin is rather facile.

Effect of thiourea pad liquor concentration on dye fixation

The thiourea concentration in the PAE pad liquor was varied from 0 to 15 g/l, and the cotton fabrics prepared in this way were then dyed (2% o.w.f.) at pH 5 (1 h, 100°C) in the absence of electrolyte. Tables 3 and 4 show that the thiourea concentration in the pad liquor to give the best colour yields varies from dye to dye. Further work was therefore carried out using a variety of reactive dyes at different depths of shade ranging from 0 to 10% o.w.f. and the results are shown in Figures 1 and 2. These curves suggest that 15 g/l thiourea gives optimum colour yields when applying reactive dyes at depth of shades up to 0–10% o.w.f.

TABLE 2

Colour yield and fixation of dyeings (pH 5-without electrolyte) on various pretreated cotton fabrics

	Colour yield (*K/S*)			
Treatment	Before soaping	After soaping	*E* (%)	*F* (%)
Procion Red H-EXL (2% o.w.f.)				
PAE	22.23	11.76	95	51
PAE/thiourea	19.31	17.25	83	89
Levafix Red E-BA (2% o.w.f.)				
PAE	15.82	11.42	83	72
PAE/thiourea	17.09	16.20	90	95
Procion Red MX-G (2% o.w.f.)				
PAE	16.37	11.34	73	69
PAE/thiourea	20.85	18.94	93	91
Procion Red MX-G (2% o.w.f.) dyed at 60°C				
PAE	17.95	9.04	79	50
PAE/thiourea	18.83	18.25	84	97

TABLE 3

Colour yield and fixation of dyeings on cotton pretreated with PAE and different amounts of thiourea

Thiourea in pad liquor (g/l)	Colour yield (*K/S*)			
	Before soaping	After soaping	*E* (%)	*F* (%)
Procion Red H-E3B (2% o.w.f.)				
0	21.20	9.57	92	45
2.5	18.96	9.55	82	50
5.0	18.92	10.60	82	56
7.5	20.57	16.55	89	80
10.0	19.97	17.06	87	85
12.5	18.80	12.25	82	65
15.0	19.50	14.02	85	72
Procion Blue MX-2R) (2% o.w.f.)				
0.0	16.79	14.13	92	84
2.5	15.61	12.28	86	77
5.0	14.40	11.67	80	81
7.5	17.96	17.71	94	99
10.0	19.82	15.75	96	79

Effect of dyebath pH on colour yield and fixation of dyeings on the PAE/thiourea-treated cotton

The build-up obtained from dyeings produced at different dyebath pH values was studied for Procion Red MX-5B and Procion Red H-E3B on the PAE/thiourea (10 g/l) treated cotton. The results are shown in Figures 3 and 4. Although the build-up curves are quite different, each dye shows the same trend to decreasing colour yield with increasing pH. Since there is a risk of damaging the cotton fibres below pH 5, dyeing below this pH value was not studied.

The observation that the best colour yields were obtained under mildly acidic conditions confirms that the mechanism of dye absorption relies on electrostatic interactions between the anionic dye and protonated secondary amino groups in the resin. Possible contributions from cationic isothiouronium residues should not be neglected.

Build-up properties of reactive dyes on PAE/thiourea-treated cotton

The colour yields of dyeings on untreated and treated cotton fabrics at different depths of shade were measured and the results are shown in Figures 5–8. It appears that by using Procion MX dyes optimum build-up was achieved on the

TABLE 4

Colour yield and fixation of dyeings on the PAE/thiourea-treated cotton – pad liquor containing different amounts of thiourea

Thiourea in pad liquor (g/l)	Colour yield (*K/S*) Before soaping	Colour yield (*K/S*) After soaping	*E* (%)	*F* (%)
Procion Orange MX-2R (2% o.w.f.)				
8.0	16.90	15.20	83	90
9.0	16.68	15.52	81	93
10.0	16.65	16.19	81	97
11.0	16.62	16.52	80	99
12.0	16.68	16.31	81	97
Procion Yellow H-E4R (2% o.w.f.)				
8.0	13.52	10.54	74	78
9.0	12.60	11.07	69	87
10.0	13.03	12.23	72	94
11.0	13.22	12.16	73	92
12.0	13.32	12.40	73	92
Procion Blue H-EGN (2% o.w.f.)				
8.0	15.56	11.30	94	72
9.0	15.50	11.62	93	75
10.0	15.72	13.24	95	84
11.0	15.55	12.96	94	83
12.0	15.72	13.30	95	85

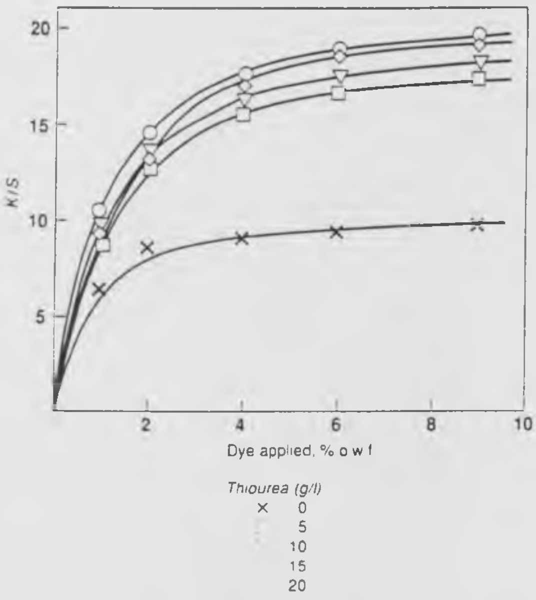


Figure 1 – Effect of thiourea concentration in pad liquor on the build-up of Procion Red MX-5B on a variety of substrates

PAE/thiourea (10 g/l) treated cotton, when compared with the build-up obtained on PAE-treated cotton and on untreated cotton dyed by conventional dyeing methods. In the case of Procion H-E dyes, Cibacron F dyes (CGY) and Remazol

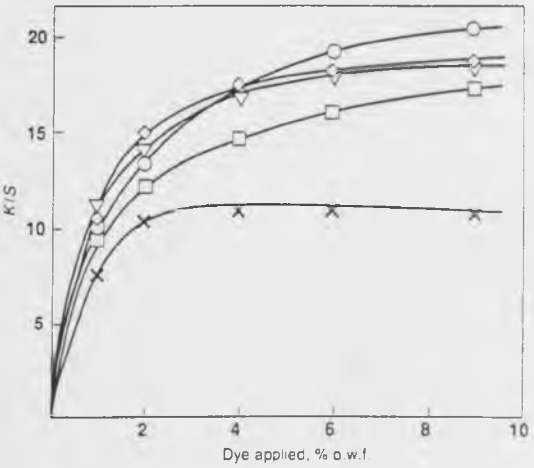


Figure 2 – Effect of thiourea concentration in pad liquor on the build-up of Procion Orange MX-2R on a variety of substrates (for key see Figure 1)

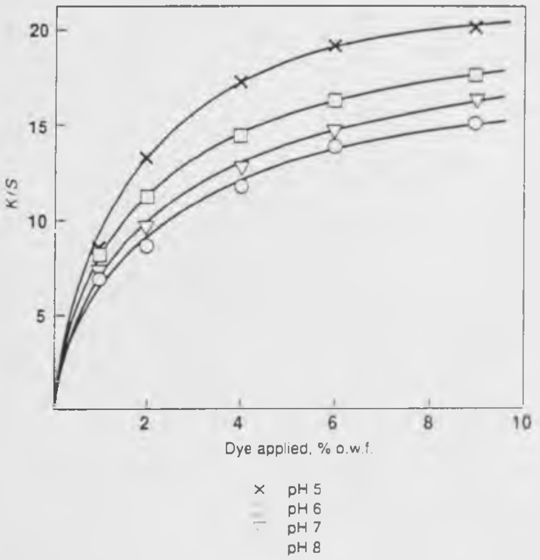


Figure 3 – Effect of dyebath pH on the build-up of Procion Red MX-5B

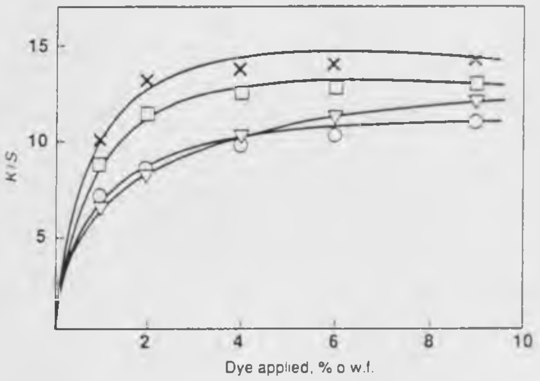


Figure 4 – Effect of dyebath pH on the build-up of Procion Red H-E3B (for key see Figure 3)

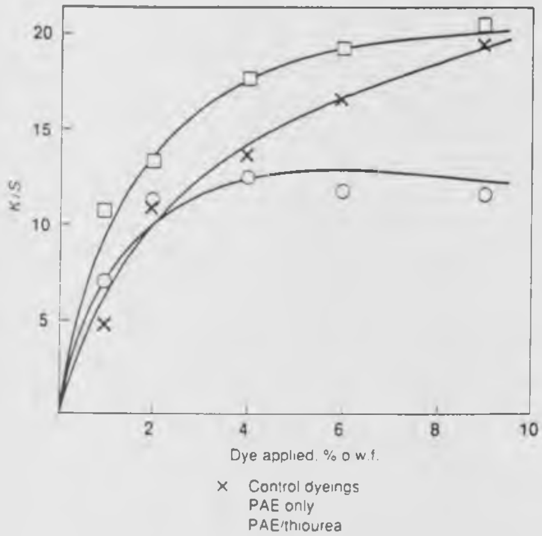


Figure 5 – Build-up of Procion Red MX-5B on a variety of substrates

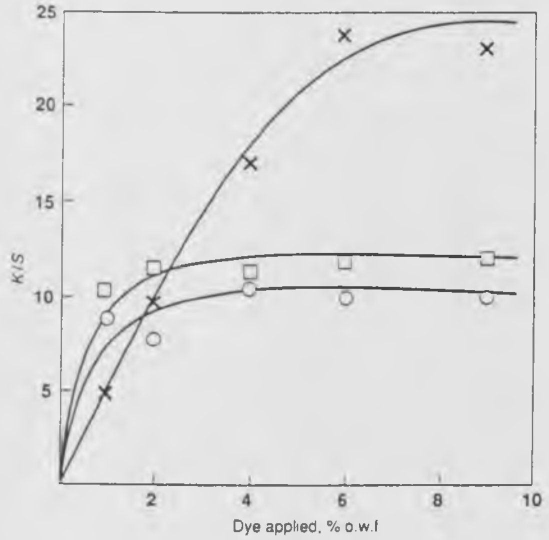


Figure 6 – Build-up of Procion Red H-EXL on a variety of substrates (for key see Figure 5)

Red RB (HOE), good colour yields and dye fixation were only obtained at depths of shade below 2% o.w.f.; at depths greater than this the build-up on untreated cotton dyed by the conventional method was the highest, although the build-up on the PAE/thiourea-treated cotton remained greater than that on cotton treated with PAE alone. With dyes of lower reactivity than Procion MX dyes there is clearly a problem of site saturation when dyeing either PAE- or PAE/thiourea-modified cotton.

Dyeing quality of PAE/thiourea-treated and dyed cotton

Colour fastness properties of reactive dyes on both treated and untreated cotton are shown in Tables 5 and 6, and it is evident from both tables that the wash fastness is excellent

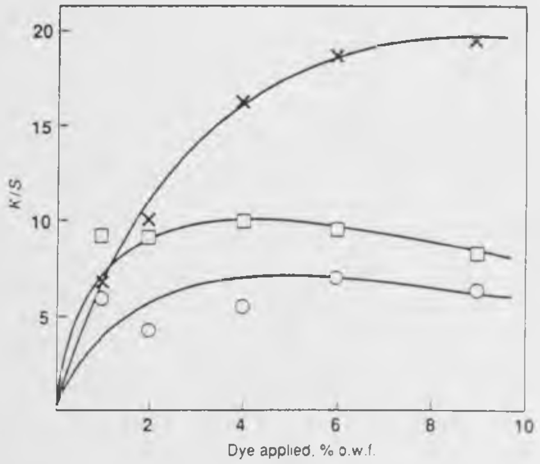


Figure 7 – Build-up of Cibacron Red FB on a variety of substrates (for key see Figure 5)

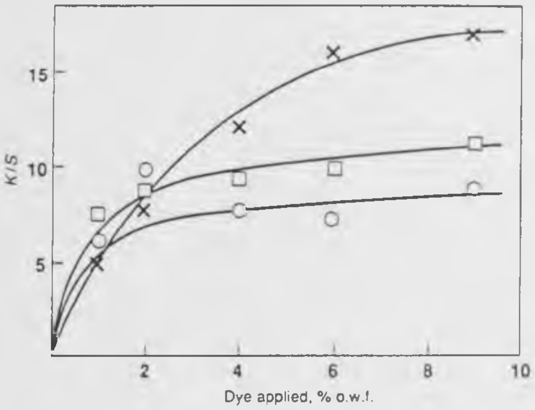


Figure 8 – Build-up of Remazol Red RB on a variety of substrates (for key see Figure 5)

TABLE 5

Wash fastness (C04) of Procion MX dyes on PAE/thiourea (10 g/l) treated and untreated cotton after soaping

Procion dye (2% o.w.f.)	Untreated			Treated		
	E	V	C	E	V	C
Blue MX-2R	5	5	5	5	5	5
Yellow MX-8G	5	5	5	5	5	5
Orange MX-2R	5	5	5	5	5	5
Red MX-G	5	5	5	5	5	5

E – Effect on pattern
V – Viscose adjacent
C – Cotton adjacent

TABLE 6

Light fastness of Procion MX dyes on PAE/thiourea (10 g/l) treated and untreated cotton after soaping

Procion dye (2% o.w.f.)	Untreated	Treated
Blue MX-2R	4–5	3
Yellow MX-8G	5–6	3–4
Orange MX-2R	5	3
Red MX-G	4–5	3

but the light fastness is again significantly lowered by the pretreatment.

Attempts to overcome the problem of poor light fastness were first made by introducing thiol groups into PAE-modified cotton. This was done by aftertreating PAE-treated cotton with 40 g/l aqueous sodium hydrosulphide (NaSH) using a cold pad–batch procedure. The dyeing properties and light fastness of dyeings (2% o.w.f.) on this treated cotton are quoted in Table 7. This surprisingly shows that after sodium hydrosulphide treatment the colour yield and fixation values of the three types of dyes are lowered to a greater or lesser extent, even when dyeing in the presence of 80 g/l salt in the dyebath, compared with dyeings on the PAE-treated cotton. Since there is no doubt that the thiol group can readily react with monochlorotriazine dyes under neutral or slightly acidic conditions [7], it is likely that further cross-linking of the thiol-terminated polymer has taken place to give non-reactive residues. The air oxidation reaction shown in Scheme 5 is possible during drying of the thiol treated fabric. However, it is more likely that the highly nucleophilic thiol residues will react rapidly with azetidinium residues to give a thioether cross- link (Scheme 6).

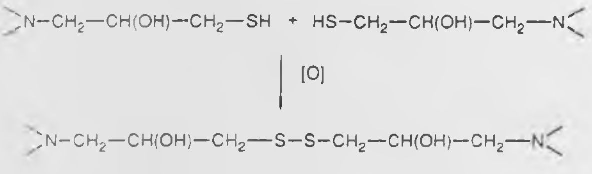
The formation of the disulphide or thioether cross-links reduces the number of nucleophilic sites available for subsequent reaction with the reactive dye. Under neutral or slightly acidic dyeing conditions, this type of disulphide bond is non-reactive towards reactive dyes and is stable, unlike the disulphide in wool cystine [8], which hydrolyses readily to the nucleophilic thiol owing to its activation by the neighbouring peptide carbonyl group. The reduction in reactivity of this substrate for reactive dyes cannot simply be explained by the above reactions. There must also be a significant drop in the number of nucleophilic secondary amino residues following treatment with sodium hydrosulphide; presumably the alkaline conditions promote reaction of these groups with the azetidinium cations. From Table 7 it can also be seen that the attempted introduction of reducing (thiol or disulphide) groups does not improve the light fastness of reactive dyeings on the PAE-treated cotton.

Attempts to solve the problem of poor light fastness via the introduction of reducing Bunte salt groups into the PAE-treated cotton also failed. The fact that the presence of reducing groups in the dyed substrate does not improve light fastness indicates that the mechanism of fading may be photoreductive [9,10]. Alternatively the reason for poor light fastness of dyeings on this substrate may be related to the poor penetration and distribution of the dyes. Pretreatment of cotton with polymer finishes that are substantive and reactive towards reactive dyes gives rise to poor dye distribution, mainly in the form of ring dyeing. It may therefore be predicted that pretreatment with lower molecular weight amino functional compounds will give dyeings of better penetration and light fastness, since these agents will penetrate individual fibres during pretreatment.

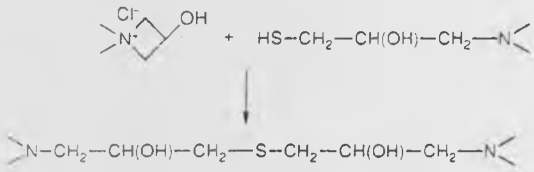
TABLE 7

Colour yield and light fastness of treated and dyed fabrics

Treatment	Dyeing pH	Salt added (g/l)	Colour yield (*K/S*) Before soaping	Colour yield (*K/S*) After soaping	*E* (%)	*F* (%)	Light fastness
Procion Red MX-G							
PAE	7	0	15.27	13.94	68	91	3
PAE/thiol	5	0	12.41	8.37	55	67	3
PAE/thiol	7	0	3.25	1.87	14	57	3
PAE/thiol	7	80	9.94	8.09	44	81	3
Procion Red H-E3B							
PAE	7	0	13.92	8.53	60	61	3
PAE/thiol	5	0	14.54	5.03	63	35	3
PAE/thiol	7	0	5.88	2.30	26	39	3
PAE/thiol	7	80	13.58	8.41	59	62	3
Procion Red H-EXL							
PAE	7	0	14.18	8.67	57	61	3
PAE/thiol	5	0	12.16	1.21	49	9	3
PAE/thiol	7	0	1.71	0.74	7	43	3
PAE/thiol	7	80	8.05	2.99	32	37	3

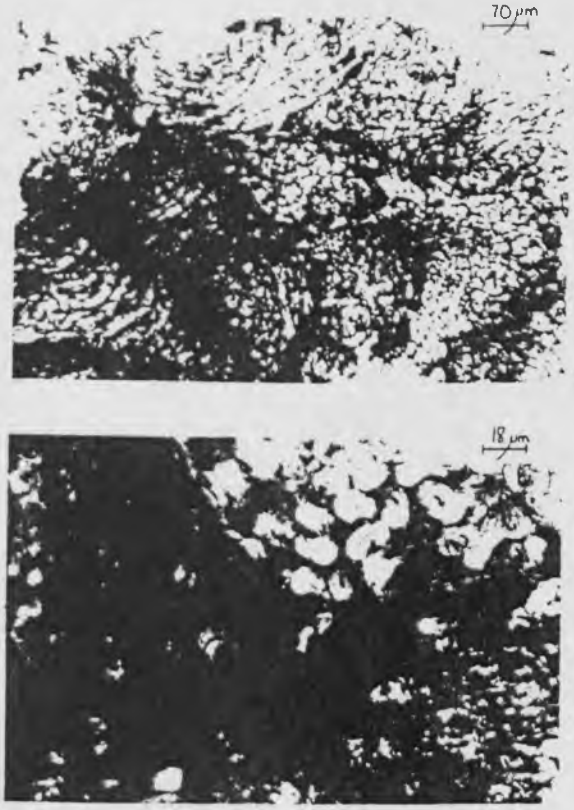


Scheme 5



Scheme 6

Microscopic analysis of cross-sections of the resin-treated and dyed cotton indicated that only those fibres on the surface of individual yarns were coloured, while the fibres in the centre of such yarns remained colourless (Figure 9(a)). Particular attention was given to the dyed areas on the yarn surface (Figure 9(b)) which showed good dye distribution; it may well be that it is superficially deposited polymer that is attracting dye. This unlevelness within the yarn can be attributed to the fact that PAE and its derivatives have very low substantivity for cotton: thus during drying after padding PAE resin and its derivatives migrate to the yarn surfaces.



(a) Bar = 70 µm
(b) Bar = 18 µm

Figure 9 – Cross-sections of PAE/thiourea-treated and dyed cotton

Strength properties of treated and untreated cotton are reported in Table 8. A comparison between the two fabrics makes it clear that pretreatment with PAE/thiourea does not affect breaking strength and elongation, whilst the wrinkle recovery properties are slightly improved.

TABLE 8

Comparison of strength properties between treated and untreated cotton

Property		Untreated	Treated
Breaking strength (kg)	warp	30.81±1.42	29.56±0.99
	weft	31.09±0.93	30.56±1.10
Elongation (%)	warp	9.97±0.37	11.30±0.51
	weft	17.52±0.67	22.56±1.08
WRA[a] (degree)	warp	62.00±9.37	76.10±3.56
	weft	68.50±3.77	75.50±3.69

(a) WRA – wrinkle recovery angle

Mechanism proposed to explain the nature of the PAE/thiourea pretreatment

As described in the introduction, the improvement of dye fixation brought about by addition of thiourea to the PAE pad liquor is due to the formation of isothiouronium salt residues. These not only impart a strongly cationic character to the substrate but also supply highly nucleophilic thiol groups during the dyeing process due to hydrolytic decomposition of the isothiouronium salt at elevated temperatures.

Evidence for the presence of isothiouronium salt residues in the PAE/thiourea-treated cotton was obtained from FTIR spectroscopy. Figure 10 shows the FTIR spectrum of the PAE/thiourea-treated cotton from which the spectrum of the PAE-treated cotton has been subtracted. A broad, moderate N–H stretching band approximately in the 3100 cm^{-1} region and a strong band in the 1667 cm^{-1} region indicate the presence of $-N^+H_3$, and a further strong absorbance in the region of 2058 cm^{-1} suggests the presence of ammonium cations in the form of the hydrochloride salt, which supports the contention that isothiouronium salt residues are present in the PAE/thiourea-treated cotton.

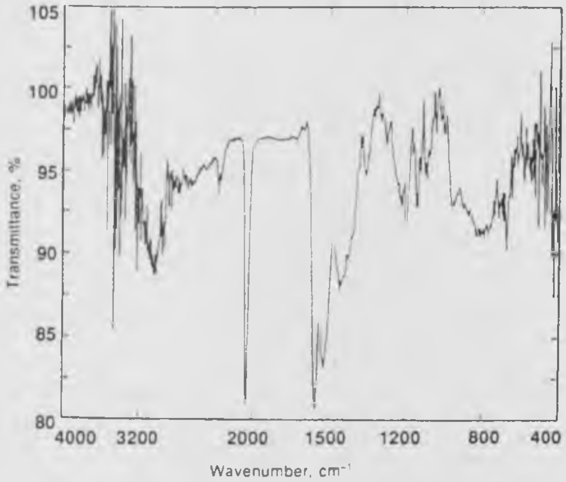


Figure 10 – *Infra red spectrum obtained by subtracting that of PAE-treated cotton from that of PAE/thiourea-treated cotton*

In order to explain the marked difference in the build-up curves for dyes of high and low reactivity, two hypotheses were considered, as follows.

(a) The resin itself is incompletely insolubilised and partially dissolves into the dyebath during the actual dyeing process; high-reactivity dyes somehow immobilise the resin, possibly by cross-linking reactions, and prevent the above dissolution which is, of course, accompanied by a loss in nucleophilic sites. This hypothesis is unlikely to hold since the work of Bates [3] showed that the complete insolubilisation of PAE resin on paper required the formation of only one or two cross-links by the reaction of the azetidinium cation with reactive secondary amino groups.

(b) The dye sites in the PAE resin-treated cotton are secondary amino groups of high nucleophilicity. During the dyeing process it may be expected that these will react in a competitive manner with residual azetidinium cations and thus become unavailable for reaction with reactive dye. Provided reactive dyes of higher reactivity than the azetidinium cation are employed then good build-up properties would be achieved. If this hypothesis were true then the assumption would have to be made that, even in the case of PAE/thiourea treatments, a significant number of reactive azetidinium cations are available in the pretreated cotton, i.e. that reaction with thiourea is incomplete. Figure 11 shows the effect of pre-boiling the treated cotton before dyeing; colour yields are significantly reduced for dyeings on both PAE- and PAE/thiourea-treated cotton. Total nitrogen determination on both pretreated cottons (Table 9) indicates that a small amount of resin is lost from the PAE-pretreated cotton (about 15%) but there are much larger nitrogen losses for the PAE/thiourea system. This may be explained by the following reaction shown in Scheme 7. The urea liberated in the hydrolysis is soluble, thus accounting for the large total nitrogen loss.

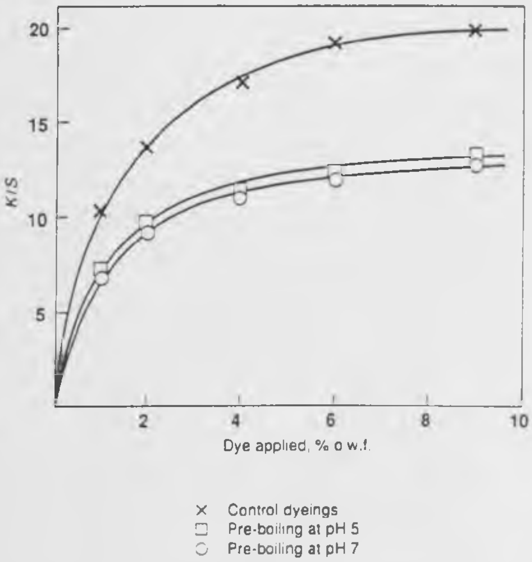


Figure 11 – *Effect of pre-boiling substrates before dyeing on the build-up of Procion Red MX-5B*

TABLE 9

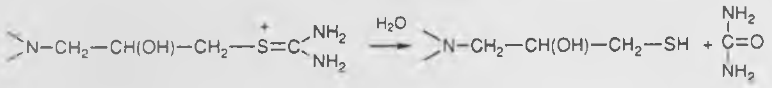
Total nitrogen content of the different pretreated cottons

	Total nitrogen (%)	
Treatment	PAE treated	PAE/thiolurea treated
None	0.314	0.627
Pre-boil[a]	0.262	0.301
Pre-soap[b]	0.245	0.259

(a) Treated cotton was pre-boiled for 60 min at pH 5

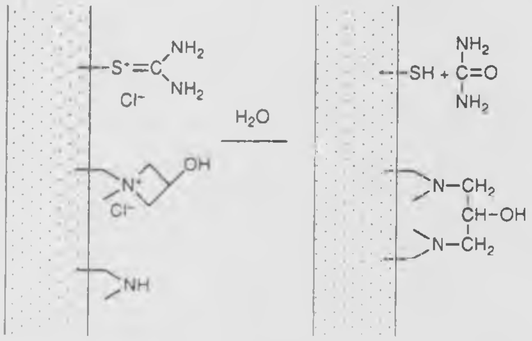
(b) Treated cotton was pre-soaped in a solution containing 5 g/l Sandozin NIE and 2 g/l sodium carbonate for 15 min at the boil

Although it is difficult to be absolutely certain of the reasons for the reductions in colour yields on pre-boiling, it appears as though the reactions shown in Scheme 8 occur. Any free thiol groups produced during pre-boiling will also react rapidly with azetidinium cations to give the thioether cross-link. These reactions therefore involve a loss in the number of highly cationic residues (isothiouronium salts and azetidinium cations) and, additionally, a reduction in nucleophilic sites. The above factors thus account for the marked reduction in substantivity for and fixation of reactive dyes on the pre-boiled samples, as shown in Figure 11.



$$>N-CH_2-CH(OH)-CH_2-\overset{+}{S}=C(NH_2)_2 \xrightarrow{H_2O} >N-CH_2-CH(OH)-CH_2-SH + H_2N-C(=O)-NH_2$$

Scheme 7



Scheme 8

CONCLUSIONS

Pretreatment of cotton with a polyamide–epichlorohydrin resin/thiourea mixture markedly improves the reactive dyeability of this fibre, when compared with the earlier results achieved on PAE-modified cotton. Dyeing can be carried out under neutral pH conditions in the absence of salt to give good colour yields and good dye fixation. The wash fastness of dyeings and mechanical properties of the treated cotton are excellent but the light fastness of dyeings was lowered by this pretreatment.

The improvement in the dyeability of PAE-treated cotton secured by the addition of thiourea to the PAE pad liquor is believed to be due to the formation of isothiouronium salt residues in the substrate following reaction of thiourea with the azetidinium cation. This reaction results in removal of a significant number of azetidinium residues, thus reducing the frequency of their subsequent cross-linking reactions with highly nucleophilic secondary amino groups.

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A review and assessment of numerical shade sorting methods

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The properties of current shade sorting geometries are evaluated on a mathematically generated, spherical population of normally distributed data points. The results compare well with those obtained from previously cited populations of textile production goods. The fixed-grid geometries (cubic, rhombic dodecahedral and truncated octahedral) are not as efficient in terms of the numbers and uniformity of shade sorting groups as the grid-free spherical clusters employed by Clemson Color Clustering (CCC).

INTRODUCTION

Shade sorting is the subdivision of populations of similarly coloured units that already occupy only a small volume of colour space, sometimes referred to as a microspace. Numerical shade sorting requires:

(a) Three-dimensional colorimetric coordinates for the population of samples to be sorted
(b) Three corresponding weighting factors with which the coordinates can be explicitly or implicitly scaled in order to generate a colorimetrically uniform microspace for the population
(c) A method of subdividing the microspace or shade sorting the population.

Each of these is discussed below.

Colorimetric coordinates

In principle there need be no restriction on which colorimetric coordinates are used to describe a color population. Several have been used quite effectively for shade sorting, including HunterLab, CIELAB and CIELCH [1–3]. However, the use of the lightness, chroma, and metric hue colour-difference coordinates of the CIELCH system, which is derived from CIELAB (1976) has recently received a major boost because of the rapidly increasing use of CMC(*l*:*c*) colour-difference equations [4]. This is the system that will be used here.

Any procedure for numerical shade sorting depends upon the accuracy of the underlying colorimetric data. If the instrumental colour measurements are unreliable or taken from non-representative samples, or if the colour differences calculated fail to agree with visual observations, they are of no practical value. Industrial data we have obtained and analysed has frequently exhibited one or more of these problems. The practitioner is advised to exercise caution.

Weighting factors

A new British Standard method [5] and a newer derivative AATCC Standard test method [6] both use the CMC(2:1) modification of CIELAB (1976) to derive weighting factors

PAPERS

Modification of cotton to improve its dyeability. Part 3 – polyamide–epichlorohydrin resins and their ethylenediamine reaction products

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The effect of pretreating cotton with a polyamide–epichlorohydrin resin and ethylenediamine is described. The treated substrate has enhanced substantivity for reactive dyes, which may be applied without electrolyte simply by setting the dyebath to pH 5 and raising the temperature to the boil. Dyed samples exhibit good brightness and very high wash fastness, but in many cases the light fastness is impaired.

INTRODUCTION

Part 2 in this series described the use of reactive polyamide-epichlorohydrin (PAE) resin and thiourea mixtures to pretreat cotton, in order to overcome deficiencies when pretreating with PAE alone, when using reactive dyes of low reactivity [1,2]. Significant improvements in colour yield and dye fixation were achieved with an addition of only 10–15 g/l thiourea to the PAE pad liquor. However, obvious differences in colour yield could still be observed between dyeings obtained using high-reactivity dyes and those using low-reactivity dyes [2]. In the present study increased amounts of amino groups have been introduced into the substrate with the hope of achieving efficient dyeing with dyes of low reactivity. Amino groups were introduced by pretreating cotton with an aqueous solution of PAE resin and ethylenediamine (EDA). During this application procedure some of the azetidinium cations reacted with this diamine to form primary, secondary and tertiary amino groups according to Scheme 1. However, the products may be much more complicated than shown since the PAE derivatives shown in Figure 1 could also be present in the substrate after application.

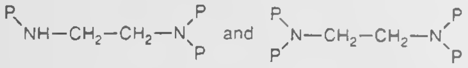


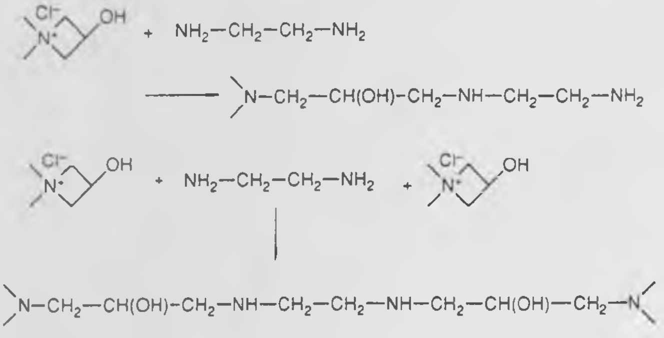
Figure 1 – Structure of PAE derivatives

The proposed advantages of using EDA in the pretreatment are as follows:

(a) It promotes the cross-linking of the PAE resin since EDA is a tetra-functional compound; possible desorption of a small proportion of PAE resin from the substrate during the dyeing process may thus be prevented, improving the efficiency of the pretreatment

(b) It improves reactivity of the treated substrate towards reactive dyes due to the fact that an increased number of highly nucleophilic amino groups are made available for reaction with the dyes

(c) It increases the substantivity of the treated substrate for anionic dyes; under slightly acidic conditions the amino groups are protonated, thus providing plenty of cationic sites.



Scheme 1

Dyeings of high fixation values with both high-reactivity and low-reactivity dyes should therefore be achievable on the PAE/EDA-treated substrate.

EXPERIMENTAL

Materials

Bleached and unmercerised cotton fabric was used throughout the work. The PAE polymer was Hercosett 125 (Hercules), supplied as an aqueous solution containing 12.5% solids. All the dyes (Table 1) and auxiliaries used were of commercial grade, while thiourea, EDA and formic acid were laboratory reagent grade.

TABLE 1

Dyes used in the present study

Dye	Manufacturer	C.I. Reactive
Procion Red H-8BN	ICI	Red 58
Procion Red HE-3B	ICI	Red 120
Procion Red MX-5B	ICI	Red 2
Remazol Yellow R	HOE	
Cibacron Red F-B	CGY	Red 184
Levafix Red E-BA	BAY	Red 124
Drimalan Red F-2BL	S	Red 100

Application of polymer and additives

Cotton fabric was impregnated by padding through the liquor trough formed between the bowls and side-plates of a Benninger laboratory mangle; the pressure was adjusted to give 80% wet pick-up. The samples were then dried for 3 min at 100°C using a Werner Mathis steamer/baker unit. The Hercosett 125 was always applied at a concentration (200 g/l) sufficient to give 2% resin solids on the weight of the fibre (o.w.f.).

Dyeing of untreated and treated cotton

All dyeings were carried out in 100 ml capacity sealed stainless steel dye pots housed on a Rotadyer (John Jeffreys) laboratory dyeing machine using a liquor ratio of 20:1. Dyeing of the modified cotton was commenced at 50°C with the bath set at the required pH value (usually pH 5), the temperature was raised to the boil over 25 min (2 degC/min) and dyeing continued at the boil for a further 60 min. Untreated cotton was dyed by following the dye manufacturer's recommended method for the particular reactive dye selected (i.e. with salt and alkali) and, for comparison, by the novel method employed for the modified cottons (i.e. no salt, no alkali) [1].

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/l Sandozin NIE (S) (non-ionic surfactant) and 2 g/l sodium carbonate, at the boil for 15 min (liquor ratio 50:1).

Measurement of dye fixation and colour yield

The percentage uptake of dye, *E*, by both modified and unmodified cotton was determined by means of conventional spectrophotometric techniques. Dye fixation was determined by repeated extraction of the dyeings with boiling 25% aqueous pyridine solution (liquor ratio 10:1) until no further colour was removed. The Kubelka–Munk *K/S* values were obtained for the original and stripped dyeings using an ICS Micromatch colour measurement system and the extent of dye fixation was thus calculated. Fixation values given in this paper were determined as the percentage of exhausted dye fixed, using the definitions given in Part 1 [1]. This is represented by the symbol *F* and should not be confused with the value *T*, which represents the percentage of the original dye applied that is fixed.

Infra-red analysis

Infra-red (i.r.) analysis of both treated and untreated cotton was carried out using the Perkin Elmer 1740 i.r. Fourier transform spectrometer using the diffuse attachment to obtain transmission i.r. spectra.

Textile testing

The dyeings obtained were tested according to British Standard procedures. Specific tests used were: BS C04(1978), colour fastness to washing, BS B02(1978), colour fastness to light (xenon arc, continuous light).

RESULTS AND DISCUSSION

Infra-red study of PAE/EDA-treated cotton

It was necessary to confirm that the number of amino groups had increased after the addition of EDA to the PAE pad liquor. This was done with the help of the f.t.i.r. instrument and its computing facility, which subtracts the spectrum obtained on the PAE-treated cotton from the one obtained on the PAE/EDA-treated cotton. Figures 2 and 3 show the spectra of cotton treated with PAE alone and with PAE/EDA cotton respectively; in both cases the spectrum of untreated cotton has been subtracted. Figure 4 is the spectrum obtained by subtracting the spectrum in Figure 2 from that in Figure 3. The strong absorbance occurring at 1591 cm^{-1} indicates the presence of an increased number of amino groups in the substrate following EDA addition to the PAE pad liquor.

Selection of application pH

Since the primary amino groups in EDA are very nucleophilic and there is a large excess of available amino groups

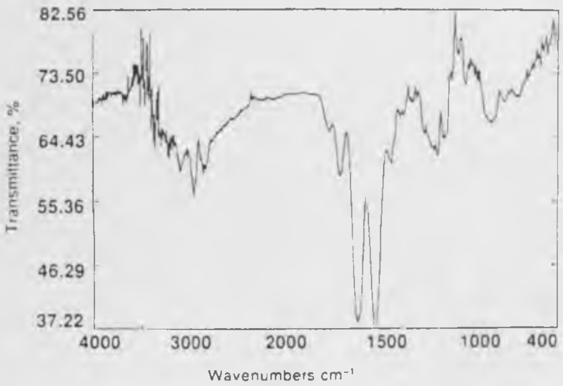


Figure 2 – F.t.i.r. spectrum obtained by subtracting spectrum of untreated cotton from that of PAE-treated cotton

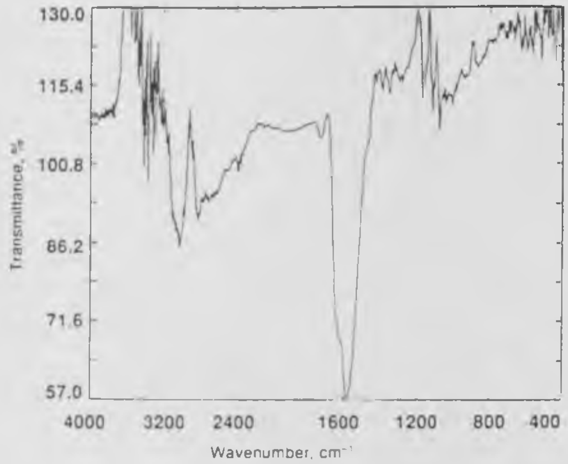


Figure 3 – F.t.i.r. spectrum obtained by subtracting spectrum of untreated cotton from that of PAE/EDA-treated cotton

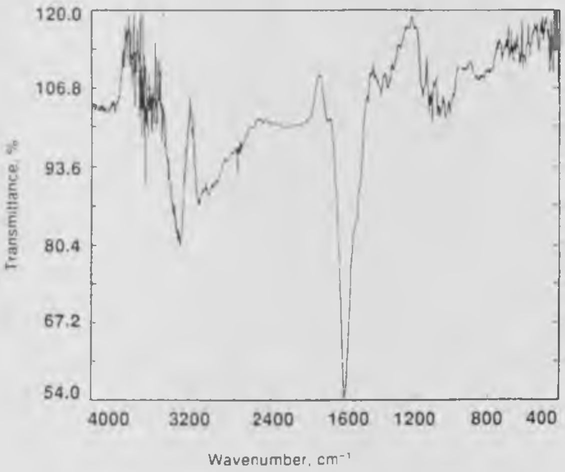


Figure 4 – F.t.i.r. spectrum obtained by subtracting spectrum of PAE-treated cotton from that of PAE/EDA-treated cotton

in the PAE/EDA pretreatment, compared with pretreatment with PAE alone, it may be possible for cross-linking reactions to take place at any stage before the drying procedure. These should be prevented since they would bring about poor fixation of the resin on the cotton, and hence poor dyeability. The nucleophilicity of the amino groups can be controlled by varying the application pH.

Experiments were therefore carried out by varying the application pH in the range 5–11; the treated cotton was then dyed at pH 5 with 2% o.w.f. Procion Red HE-3B (ICI). The results are presented in Table 2, which shows that the colour yield of the dyeings was not significantly affected until the application pH approached a value of 11. This might be because when the liquor is below pH 11, some of the amino groups in both the PAE resin and in the EDA are protonated and thus cannot easily react with the azetidinium groups present in the PAE resin at room temperature. Resin cross-linking reactions therefore mainly take place during the drying procedure. However, above pH 11 the amino groups are mainly deprotonated and cross-linking reactions may occur before the drying stage, especially at high EDA concentration, due to the high nucleophilicity of the amino groups. These conditions would bring about a reduction in fixation of the PAE resin on cotton.

TABLE 2

Colour yield obtained on the substrates prepared at different pad liquor pH values

	K/S			
pH	Before soaping	After soaping	*E* (%)	*F* (%)
5.0	20.06	20.03	91	95
7.4	22.37	20.74	97	93
8.7	21.99	20.53	96	93
10.8	19.36	18.65	88	96

Effect of EDA concentration in the PAE pad liquor

Application of PAE resin and EDA were carried out at pH 5 with different EDA concentrations; pH 5 was achieved by adding formic acid to the PAE/EDA pad liquor. Table 3 shows the effect of EDA concentration on the exhaustion and fixation of dyeings. The results indicate that similar exhaustion and fixation values were obtained with concentrations of ethylenediamine ranging from 5 to 20 ml/l.

TABLE 3

Exhaustion and fixation of Procion Red HE-3B$^{(a)}$ on substrates prepared using different EDA concentrations

	K/S			
Concn (ml/l)	Before soaping	After soaping	*E* (%)	*F* (%)
1% o.w.f. dye used				
5.0	15.72	14.56	97	93
10.0	15.50	15.21	98	98
15.0	15.15	14.69	97	95
20.0	15.06	14.48	96	96
2% o.w.f. dye used				
5.0	20.50	18.28	93	89
10.0	20.04	18.83	95	94
15.0	19.62	18.48	95	94
20.0	19.69	18.95	94	96
4% o.w.f. dye used				
5.0	23.51	20.90	82	89
10.0	23.12	21.91	88	95
15.0	22.74	21.24	91	93
20.0	22.46	21.81	89	97
6% o.w.f. dye used				
5.0	24.10	21.73	64	90
10.0	24.30	22.52	71	93
15.0	24.62	22.91	75	93
20.0	24.39	22.32	73	92

(a) All dyeings were carried out at pH 5

However, when full depths of shade (i.e. over 4% o.w.f.) are considered, 10 g/l ethylenediamine seems to be necessary to give adequate dye exhaustion and fixation.

Dyeing properties of reactive dyes on PAE/EDA-treated cotton

Procion Red HE-3B and Procion Red MX-5B (ICI) were selected as being representative of both low- and high-reactivity dyes respectively; 10 ml/l EDA and 200 g/l Hercosett 125 were used to prepare the PAE/EDA pad liquor to treat the substrate. The dyeings were carried out at pH 5 in the absence of salt following the procedure described in the experimental section. The build-up profiles of both dyes on this substrate are shown in Figures 5 and 6, which show that the build-up properties of the two dyes on PAE/EDA-treated cotton are excellent, being much better than those achieved on PAE/thiourea [2] and PAE [1] treated cotton. The reason for this effect is believed to be two-fold. Firstly the PAE/EDA pretreatment promotes more effective cross-linking of the resin to the cotton, unlike the situation previously reported for PAE/thiourea and for PAE-only treatments, in which a small proportion of the resin could be extracted during the dyeing process [1,2]. Secondly the reactive azetidinium residues, which in the earlier case [1] competed with the reactive dye for amino nucleophiles, have been greatly modified through reaction with EDA. This reaction will thus provide a large excess of nucleophilic amino sites. These mechanisms are supported by the fact that with PAE/EDA pretreatments pre-soaping before dyeing has no effect on colour yields (Table 4).

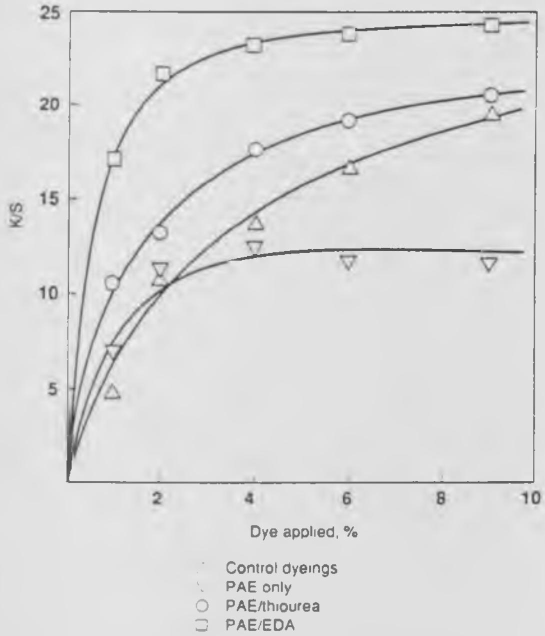


Figure 5 – Build-up of Procion Red MX-5B on a variety of substrates

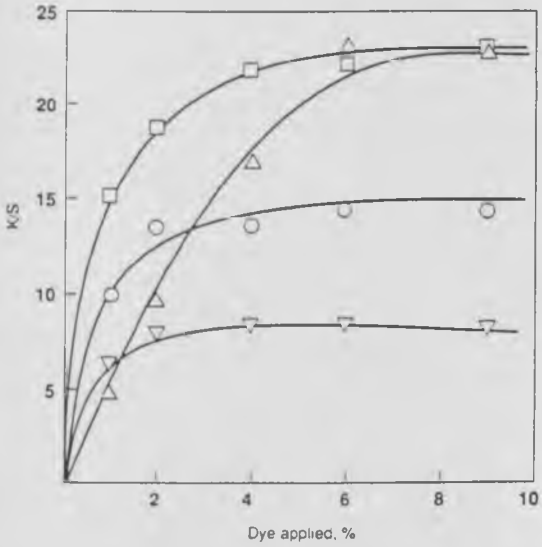


Figure 6 – Build-up of Procion Red H-E3B on a variety of substrates (for key see Figure 5)

TABLE 4

Colour yield and fixation of dyes on both PAE/EDA-pretreated and PAE/EDA-pretreated then pre-soaped cotton

	K/S		
Pre-soaping	Before soaping	After soaping	*F* (%)
Procion Red HE-3B			
No	20.04	18.83	94
Yes	20.80	19.87	96
Procion Red MX-5B			
No	18.08	17.19	95
Yes	19.04	17.93	92

It has also been found that PAE/EDA pretreatment is efficient not only when using Procion HE and MX dyes but also with other types of reactive dyes (Table 5).

TABLE 5

Colour yield and fixation of various dyes on PAE/EDA-pretreated cotton

	K/S		
Dye (2% o.w.f.)	Before soaping	After soaping	*F* (%)
Procion Red H-8BN	19.78	17.90	91
Procion Red HE-3B	20.56	19.52	95
Procion Red MX-5B	18.08	17.19	95
Remazol Yellow R	13.92	10.19	73
Cibacron Red F-B	18.46	14.19	77
Levafix Red E-BA	16.54	13.78	83
Drimalan Red F-2BL	16.87	16.58	98

The washing fastness and light fastness of Procion HE and Procion MX dyes on both PAE/EDA-treated and untreated cotton are shown in Tables 6 and 7. The washing fastness was found to be excellent but the light fastness was again down by 1–2 points compared with dyeings produced by the conventional dyeing method on untreated cotton.

TABLE 6

Wash fastness (C04) of Procion dyes on PAE/EDA (10 ml/l) treated and untreated cotton after soaping

Procion dye (2% o.w.f.)	Untreated			Treated		
	E	V	C	E	V	C
Red MX-5B	5	5	5	5	5	5
Blue MX-2R	5	5	5	5	5	5
Red HE-3B	5	5	5	5	5	5
Red H8BN	5	5	5	5	5	5

E – Effect on pattern
V – Viscose adjacent
C – Cotton adjacent

TABLE 7

Light fastness of Procion dyes on PAE/EDA (10 ml/l) treated and untreated cotton after soaping

Procion dye (2% o.w.f.)	Light fastness rating	
	Untreated	Treated
Red MX-5B	4–5	3
Blue MX-2R	5–6	3–4
Red HE-3B	5	3
Red H8BN	4–5	3

CONCLUSIONS

Polyamide–epichlorohydrin resins may be applied to cotton with the addition of ethylenediamine to give a substrate that is dyeable with reactive dyes under weakly acidic conditions without the necessity to add electrolyte. Fixation is achieved simply by raising the dyebath to the boil.

Dyeings produced were found to be bright, level and of very high wash fastness. In the case of H-acid-based reds some bluing of the shade was noted: this effect was also observed when these dyes were applied to wool, indicating that reaction with amino groups is responsible.

In many cases the light fastness was reduced by 1–2 points, which is seen as the biggest disadvantage of the process. However, the high level of dye uptake and fixation makes this process of interest to dyers and printers since better colour yields than normal are achievable, especially at lower concentrations. Higher fixation was also noted (often of the order of 95%) thus simplifying washing-off procedures and reducing the environmental problems of colour in the waste water.

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Accurate representation of the colour of physical samples on a cathode ray tube graphics monitor

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A colour graphics monitor has been calibrated using data obtained with a telespectroradiometer (TSR) by the method known as gamma correction. The accuracy of the calibration was checked by measuring standard surface colours with a spectrophotometer, displaying the colours on the monitor, and obtaining chromaticity and luminance readings for them with the TSR. Excellent correlation was achieved. Chromaticity coordinates have also been successfully predicted for screen colours.

INTRODUCTION

The use of computer-aided design (CAD) systems has increased rapidly in manufacturing industry recently. More often than not the visual display unit (VDU) employed in such a system consists of a colour cathode ray tube (CRT) similar to a colour television set. The product being designed may be anything from a warship to a toothbrush, and colour is usually incorporated simply to pick out different elements in the design or text. However, in certain cases it is desirable to display the colour of the product as accurately as possible.

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PAPERS

New methods for improving the dyeability of cellulose fibres with reactive dyes*

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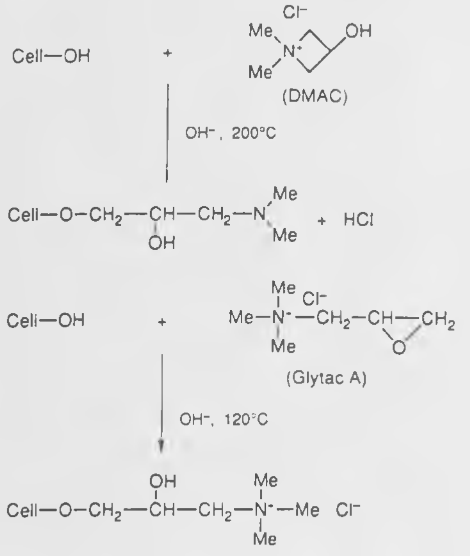
Cellulose fibres may be dyed with reactive dyes in the absence of added electrolyte under neutral to slightly acidic conditions provided the fibre is modified to include cationic sites. The effect of amine substitution has been examined in detail using the activated substrate prepared by the reaction of cotton with N-methylolacrylamide. Dyes containing pendant aliphatic amino groups were also prepared and their reactivity towards the pre-activated cotton substrate assessed.

INTRODUCTION

Reactive dyes are becoming increasingly popular for dyeing cellulosic fibres because of their wide shade range, ease of application and excellent wet fastness properties [1]. However, all current cellulose dyeing systems, including those featuring reactive dyes, pose certain environmental problems, which include the necessity to dye in the presence of a high concentration of electrolyte, discharge of coloured effluents and the presence of organohalogen residues. Therefore improvements have been sought in developing reactive dye systems of increased substantivity to diminish or eliminate the amount of electrolyte required [2] and in increasing the efficiency of the dye–fibre covalent bonding reaction, ideally to approach 100%.

Lewis *et al.* [2–4] have considered a number of different fibre pretreatments that allow reactive dyeing to be performed under neutral to slightly acidic conditions in the absence of electrolyte. All of these pretreatments introduced cationic agents in the form of quaternary, tertiary or secondary amino residues. One of the most convenient pretreatments was to apply a reactive polyamide–epichlorohydrin resin to the cellulosic fabrics by a pad–dry procedure [2,4]. Selected highly reactive dyes gave good colour yields and fixation simply by applying them from a bath set at pH 5 and raising the dyebath temperature to the boil. Unfortunately ring dyeing of the fibres and yarns was clearly evident and as a result light fastness was reduced by 1–2 points.

The problem of ring dyeing and low light fastness was resolved by using low molecular weight species to pretreat the cotton by a pad–Thermosol fixation technique [2,3]. Good results were achieved using *NN*-dimethylazetidinium chloride (DMAC) and glycidyltrimethyl ammonium chloride (Glytac A (Protex)). These reagents react with cotton according to Scheme 1. Both of these modified celluloses have excellent substantivity for reactive dyes from a bath set at pH 7 in the absence of electrolyte; equally importantly they require shorter washing-off procedures to remove unfixed dye because of the high level of fixation achieved.



Scheme 1

The reason for the high fixation values achieved on the above modified substrates under such mild conditions is worthy of further thought. It is likely that the secondary hydroxy group, in the 2-position of the propane side chain, is ionised at a much lower pH value than are the cellulose hydroxyl groups and is thus highly nucleophilic even at pH 7. The species shown in Figure 1 could be responsible for the high neutral reactivity.

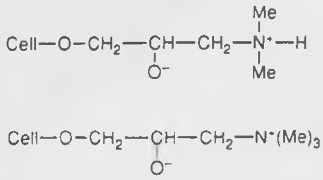


Figure 1 – Possible species responsible for high neutral reactivity in dyeing modified cellulose with reactive dye

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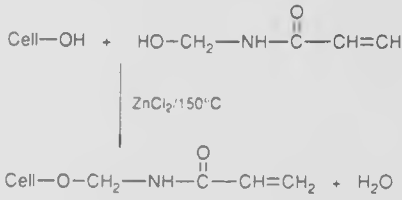
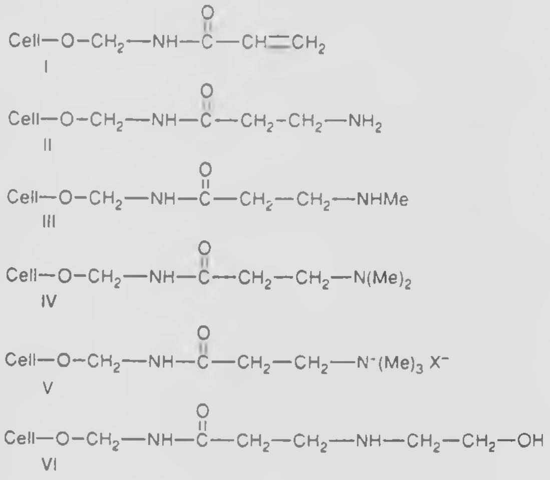
*This paper is based on a lecture given at the conference of the International Federation of Associations of Textile Chemists and Colourists (IFATCC), Lucerne, Switzerland, June 1990.

To investigate systematically the effect of attaching a variety of amines to the cellulose fibre by a simple pretreatment it was decided to modify the cotton with *N*-methylolacrylamide (NMA). This reagent is a versatile, commercially available cross-linking agent formerly employed in the Visa process for producing durable-press cellulosic fabrics [6,7]. Cotton will react with NMA in the presence of a Lewis acid catalyst according to Scheme 2. Using the pendant double bond as a site for Michael addition, a number of modified celluloses could, in principle, be readily prepared. This paper thus considers the preparation and reactive dyeing properties of the cellulose derivatives shown in Figure 2.



$$\mathrm{Cell{-}OH + HO{-}CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2 \xrightarrow{ZnCl_2/150^\circ C} Cell{-}O{-}CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2 + H_2O}$$

Scheme 2



$$\mathrm{Cell{-}O{-}CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2}\quad \mathrm{I}$$

$$\mathrm{Cell{-}O{-}CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}NH_2}\quad \mathrm{II}$$

$$\mathrm{Cell{-}O{-}CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}NHMe}\quad \mathrm{III}$$

$$\mathrm{Cell{-}O{-}CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}N(Me)_2}\quad \mathrm{IV}$$

$$\mathrm{Cell{-}O{-}CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}N^+(Me)_3\ X^-}\quad \mathrm{V}$$

$$\mathrm{Cell{-}O{-}CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}OH}\quad \mathrm{VI}$$

Figure 2 – Cellulose derivatives examined in the present study

Modified cellulose I may be looked on as 'reactive' cellulose and should prove a useful means of fixing dyes with pendant nucleophilic residues. Such nucleophilic dyes have been explored previously in the Basazol system developed by BASF. We have therefore prepared dyes of high nucleophilicity by the simple expedient of reacting existing reactive dyes with ethylenediamine. These dyes offer great advantages in the rapid dyeing of modified cellulose I, due to their complete resistance to hydrolysis and to the high efficiency of the dye-activated fibre reaction.

EXPERIMENTAL

Materials

Bleached and unmercerised cotton fabric was used throughout the work. All dyes and auxiliaries used were of commercial grade. The main dye used in the study was Procion Red MX-G (ICI, CI Reactive Red 5).

N-methylolacrylamide (Allied Colloids) was supplied as a 45% aqueous solution. Ammonia (sp. gr. 0.880), 25–30% aqueous methylamine, 40% aqueous dimethylamine and 25–30% aqueous trimethylamine were of laboratory-reagent grade. Thiourea, ethanolamine and ethylenediamine were analytical-grade materials.

N-methylolacrylamide-treated cotton (NMA cotton)

Cotton fabric was immersed in a solution containing 110 g/l *N*-methylolacrylamide (45% aq. solution) and 10 g/l zinc chloride and padded to 80% pick-up. The wet fabric was predried for 2 min at 100°C and then baked for 5 min at 150°C, rinsed thoroughly in tap water and air dried.

Amination of NMA cotton

The NMA cotton was further treated in an aqueous solution containing 10 g/l sodium dihydrogen phosphate and *V* ml/l amine (Table 1); the treatment was carried out at the boil for 60 min in 120 ml sealed stainless steel dye pots, housed on a Rotadyer (John Jeffreys) laboratory dyeing machine at a liquor ratio of 20:1. The samples were then rinsed thoroughly in tap water and air dried.

Pad–batch treatment was used as an alternative method of amination in the case of ethanolamine; a pad liquor containing 50 ml/l ethanolamine was used, the fabric was padded to 80% wet pick-up and the sample batched for 24 h at room temperature. Thorough rinsing completed the process.

TABLE 1

Conditions for amination of NMA cotton

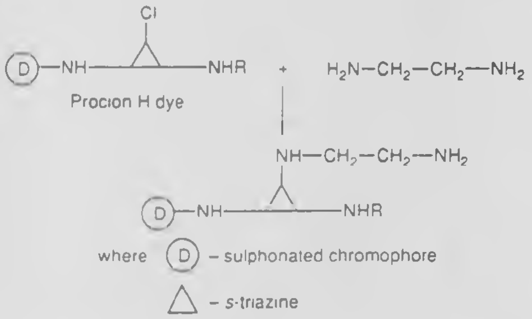
Amine	*V* (ml/l)
Ammonia (sp. gr. 0.880)	30
Methylamine (25–30%)	20
Dimethylamine (40%)	18
Trimethylamine(25–30%)	20
Ethanolamine(99%)	2.5

Synthesis of alkylamino dyes

A 50 ml portion of an aqueous solution of ethylenediamine (50% by vol.) was stirred and heated to the boil on a magnetic stirrer/heater unit; Procion Red H-8BN (ICI, CI Reactive Red 58) (50 ml of 5% aqueous dye solution) was added dropwise over 15 min. The mixture was then stirred and refluxed for another 2 h. The product was salted out, filtered and dried at 60°C. This reaction may be written as shown in Scheme 3.

Identification of alkylamino dye

The purity of the aliphatic amino dye was checked by h.p.l.c. on a Perkin–Elmer Series 10 liquid chromatograph using a Hypersil C8 column. The mobile phase used in this analysis was a water/methanol mixture (50/50 by vol.) which also contained 0.001 mol tetrabutylammonium bromide as an ion-pairing reagent, 0.5 ml/l acetic acid (20% by wt) and 0.5 ml/l potassium hydroxide (5% by wt).



Scheme 3

Fourier transform i.r. analyses of the reactive dye and the alkylamino dye were carried out using a Perkin–Elmer 1740 f.t.i.r. spectrometer. I.r. spectra of the dyes were obtained by mixing a 1 mg dye sample in 200 mg potassium bromide, forming into a disc in the normal way and then scanning in the spectrometer.

Dyeing of untreated and treated cotton

All dyeings of aminised cotton were carried out in 100 ml sealed stainless steel dye pots housed in a Rotadyer machine at a liquor ratio of 20:1. The dyebath was set at pH 5 in the absence of electrolyte. Dyeing was started at 50°C, the temperature raised to the boil over 25 min (2 degC/min) and dyeing continued at the boil for a further 60 min. For comparison, untreated cotton was dyed using the manufacturer's recommended method in the presence of 80 g/l sodium chloride.

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

Measurement of dye fixation

Measurement of the extent of reactive dye fixation 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 with fresh aqueous pyridine solutions until no further dye was removed. The Kubelka–Munk (K/S) values of the stripped and dyed samples were then measured using an ICS Micromatch colour measurement system from which the percentage fixation of dye (F) was calculated using Eqn 1:

$$F = \frac{C_2}{C_1} \quad 100 \qquad (1)$$

where C_1 and C_2 are the K/S values of dyed samples before and after stripping respectively.

Infra-red analysis

I.r. analysis of both treated and untreated cotton was carried out using the Perkin–Elmer 1740 spectrometer using the diffuse reflectance accessory; this device collects reflected radiation that has penetrated the fabric at the same time ignoring specular or non-absorbed radiation. Using the computing power of the instrument it is possible to store and subsequently subtract spectra, thus giving accurate information as to the state of chemical modification of the cotton.

Textile testing

The dyeings obtained were tested according to British Standard procedures. Specific tests used were: BS C04 (1978), colour fastness to washing, and BS B02 (1978), colour fastness to light (xenon arc, continuous light).

RESULTS AND DISCUSSION

Infra-red study of treated and untreated cotton fabrics

Figure 3 shows the f.t.i.r. spectrum of NMA cotton from which the spectrum of untreated cotton has been subtracted. The two strong absorbances at 1671 and 1543 cm^{-1} indicate the presence of monosubstituted amide groups in the substrate, while a medium absorbance at 1626 cm^{-1} is due to the presence of pendant double bonds from the *N*-methylolacrylamide reaction. Thus following pretreatment with NMA, the cellulosic fibre is modified as shown in Figure 4.

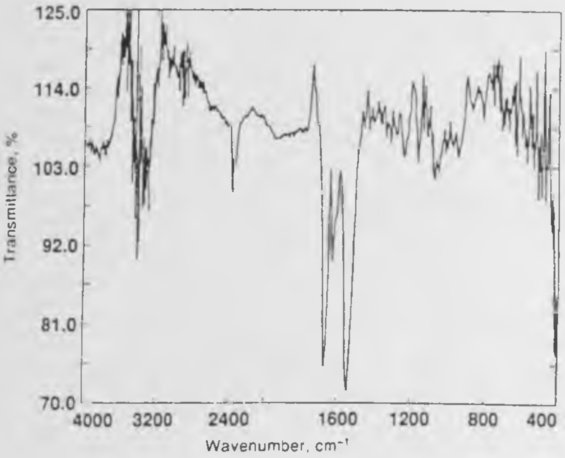
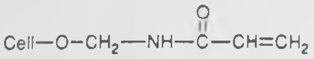


Figure 3 – F.t.i.r. spectrum obtained by subtracting spectrum of cotton from that of N-methylolacrylamide treated cotton (NMA cotton)



$$\text{Cell}-O-CH_2-NH-\overset{O}{\overset{\|}{C}}-CH=CH_2$$

Figure 4 – Modification of cellulosic fibre following NMA treatment

Figures 5–8 show the spectra of the substrates obtained by amination of NMA cotton with ammonia, methylamine, dimethylamine and ethanolamine (batchwise and semi-continuous application) respectively. The disappearance of the absorbance at 1626 cm^{-1} indicates that the amines readily add to the double bond. A similar spectrum for trimethylamine was obtained, indicating that the expected modification had occurred.

Dyeing properties of different aminised cotton fabrics

Table 2 shows the colour yield and fixation values of reactive dyeings on different aminised substrates. It can be seen that introduction of primary and secondary amino groups by treating NMA cotton with ammonia, methylamine and ethanolamine gives rise to dyeings with good colour yield

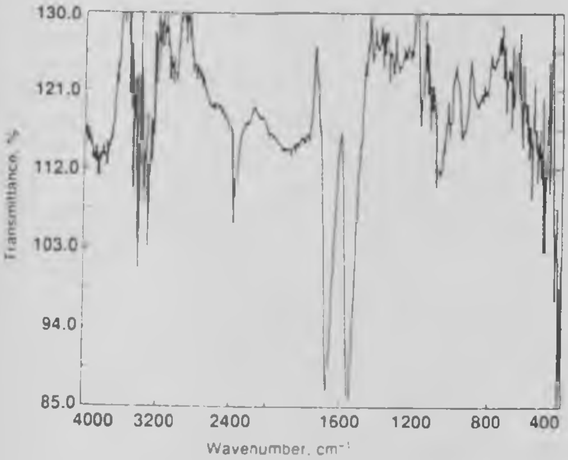


Figure 5 – F.t.i.r. spectrum obtained by subtracting spectrum of cotton from that of NMA/ammonia-treated cotton

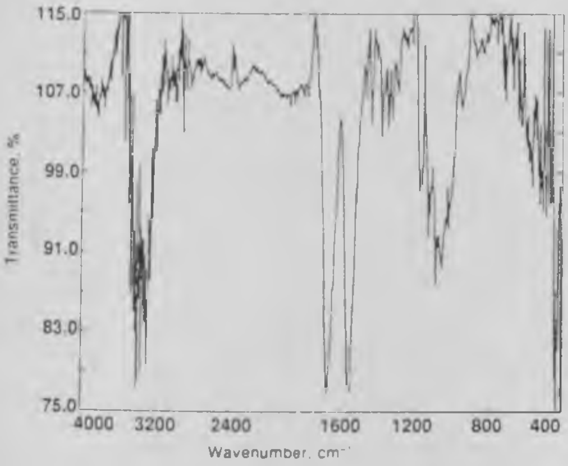


Figure 6 – F.t.i.r. spectrum obtained by subtracting spectrum of cotton from that of NMA/methylamine-treated cotton

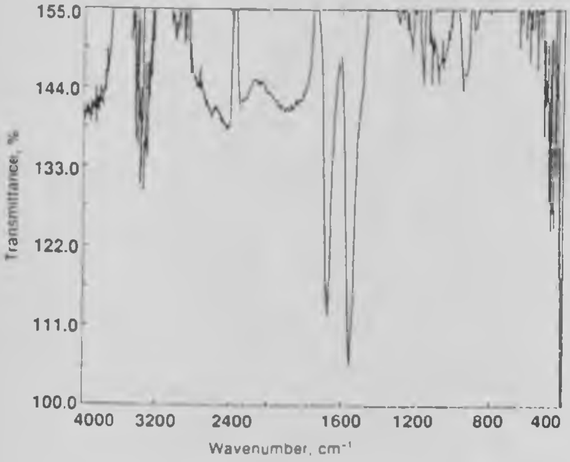


Figure 7 – F.t.i.r. spectrum obtained by subtracting spectrum of cotton from that of NMA/dimethylamine-treated cotton

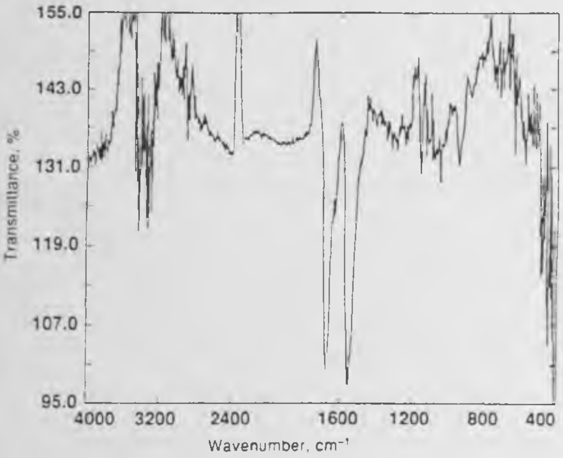


Figure 8 – F.t.i.r. spectrum obtained by subtracting spectrum of cotton from that of NMA/ethanolamine (pad–batch) treated cotton

TABLE 2

Colour yield and fixation of CI Reactive Red 5 (2% o.w.f.) on different substrates

	Colour yield		
Substrate	Before soaping	After soaping	*F* (%)
II (ammonia)	13.77	13.64	99
III (methylamine)	14.64	14.45	99
IV (dimethylamine)	15.60	1.94	12
V (trimethylamine)	10.32	8.93	87
VI (ethanolamine)	12.61	11.52	91
Untreated (conventional dyeing) (4% o.w.f. dye)	14.31	14.10	98

and high fixation values. This is clearly due to the introduction of primary and secondary amino groups, which improve both the substantivity of the dye for the substrate and the reactivity of the substrate.

It was also found that the presence of tertiary amino groups in the substrate improved dye exhaustion but did not improve dye fixation under weakly acidic conditions. Under these conditions a significant number of tertiary amine sites are protonated, thus offering a cationic site for the anionic dye and explaining the observed high substantivity. Tertiary amino groups would react with the dyes to form the derivative shown in Figure 9. Since the onium group is

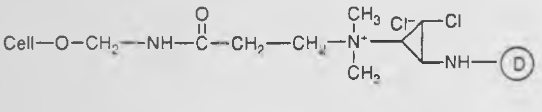
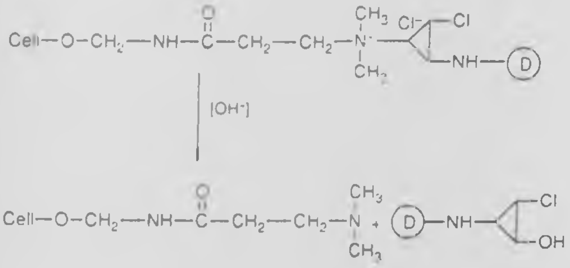


Figure 9 – Derivative formed by reaction of tertiary amino groups with reactive dye

strongly electron withdrawing, and also a very good leaving group, its elimination occurs readily during alkaline soaping. This accounts for the low fixation values observed on substrate IV (Scheme 4).



Scheme 4

Table 2 also shows that under weakly acidic conditions the colour yield and fixation of dyeings on the substrate containing the fully quaternised amino groups are fairly good. This was attributed to the easier deprotonation of cellulose hydroxy groups in the vicinity of the cationic groups and to the increased substantivity of the anionic dye for the cationic site.

Comparing the results for dyeing the pretreated cotton with those from the conventional dyeing of untreated cotton, it can be seen that in some cases the colour strength of dyeings obtained on the former is significantly greater (>100%) than on the dyeings on untreated cotton, indicating that large savings in dye consumption may be made.

Table 2 demonstrates that the best results were obtained by using ammonia, ethanolamine and methylamine as the reactive amines. For practical purposes, the first two will probably be the more important. Ammonia may be applied by a batchwise method and is cheap and practically acceptable especially at lower concentrations. Table 3 shows that the ammonia concentration can be reduced from 30 to 10 ml/l without affecting colour yield and fixation. The latter concentration could be used under mill conditions.

TABLE 3

Effect of ammonia concentration on colour yield and fixation of CI Reactive Red 5 (2% o.w.f.)

Concn (ml/l)	Colour yield Before soaping	 After soaping	*F* (%)
10	13.72	13.34	97
30	13.77	13.64	99

It is convenient to carry out the pretreatment by a pad–dry–bake procedure followed by pad–batch amination, rather than by pad–dry–bake followed by batchwise amine treatment. In the former procedure ammonia cannot be used at the higher concentrations required. Ethanolamine is a safe compound and has no smell even at high concentration. Table 4 shows the results obtained when ethanolamine is used in the different pretreatment procedures; pad–batch application gives the best results.

TABLE 4

Colour yield and fixation of CI Reactive Red 5 (2% o.w.f.) on NMA/ethanolamine-treated cotton

Amine application procedure	Colour yield Before soaping	 After soaping	*F* (%)
Batchwise (2.5 ml/l)	12.61	11.52	91
Pad–batch (50 ml/l)	18.54	16.81	91

Conditions for dyeing aminised cotton with reactive dyes

Table 5 shows that adding electrolyte to the dyebath has no effect on the dyeability of the NMA/amine-treated cotton with reactive dyes, indicating that the NMA/aminised cotton behaves much more like wool when dyeing with anionic reactive dyes.

The effect of dyebath pH on the dyeability of amino-containing substrates is shown in Table 6. In this study the substrate used was NMA/ethanolamine-treated cotton obtained via a pad–batch procedure. The results show that

TABLE 5

Colour yield and fixation of CI Reactive Red 5 (2% o.w.f.) on NMA/ammonia-treated cotton

Salt added (g/l)	Colour yield Before soaping	 After soaping	*F* (%)
0	13.77	13.64	99
20	13.30	13.18	99

TABLE 6

Colour yield and fixation of CI Reactive Red 5 (2% o.w.f.) on NMA/ethanolamine-treated cotton

pH	Colour yield Before soaping	 After soaping	*F* (%)
5	17.26	16.81	97
6	16.94	16.67	98
7	14.99	14.35	96

colour yield decreases with increasing pH. This can be explained by the increased protonation of the secondary amino groups at the lower pH values, increasing the substantivity for anionic dyes.

Build-up of reactive dyes on NMA/amine-treated cotton

Reactive dyes build up very well on the NMA/amine-treated cotton (Tables 7 and 8), indicating that the pretreatment efficiently supplies sufficient reactive dye sites.

TABLE 7

Build-up of CI Reactive Red 5 on NMA/ammonia-treated cotton

Dye used (% o.w.f.)	Colour yield Before soaping	 After soaping	F (%)
1	11.22	10.36	92
2	16.08	15.14	94
4	18.10	17.32	96
6	18.58	17.88	96
9	19.17	19.10	99

TABLE 8

Build-up of CI Reactive Red 5 on NMA/ethanolamine (pad–batch) treated cotton

Dye used (% o.w.f.)	Colour yield Before soaping	 After soaping	F (%)
2	18.54	16.81	91
4	22.60	20.20	89
6	23.17	21.84	94
8	23.89	23.52	98
10	24.39	23.40	96

Quality of reactive dyeings on the NMA/amine-treated cotton

The wash fastness of dyeings on this treated cotton was excellent, change of shade and staining of adjacent fabrics both being assessed as 5 in the C04 wash test. Physical appearance and levelness was also very good. Light fastness testing showed a small drop of up to one point compared with conventional dyeing. Cross-sections examined by microscopy showed the dyeings obtained by this pretreatment method were well penetrated.

Although the results outlined in this paper are based on CI Reactive Red 5, other reactive dyes commercially available for dyeing wool and cotton give promising effects on this pretreated cotton.

Dyeing NMA cotton with aliphatic amino-containing dyes

The work has been extended to study the dyeing of NMA cotton with alkylamino dyes. Conventional reactive dyes can be hydrolysed during the dyeing process, which invariably gives rise to a reduction in the efficiency of reaction with the substrate. However, if alkylamino dyes are applied to the NMA-pretreated substrate, the dye can never be hydrolysed and yet is still able to produce a covalent bond between the dye and fibre. This gives the possibility of approaching 100% dye fixation.

Pretreatment of cotton to introduce reactive groups such as activated double bonds is clearly necessary when using alkylamino dyes. The cost of producing a dye is much higher than that of producing a low molecular weight reactive compound for cotton pretreatment. Therefore if all the dye applied is subsequently fixed to the substrate, not only can total application cost be reduced, but environmental problems may also be avoided.

H.p.l.c. and f.t.i.r. analysis of dyes

The alkylamino dye was prepared by modifying CI Reactive Red 58 with ethylenediamine. The purity of the prepared dye was assessed by the ion-pairing h.p.l.c. technique (Figure 10). The shorter retention time of the modified form compared with that of the original form indicates that the former is more basic than the latter. Figures 11 and 12 show the f.t.i.r. spectra of both the alkylamino dye and its original form. The strong increase in peak height at 1600 cm^{-1} confirms the introduction of amino groups by this reaction.

Dye application

The alkylamino dye was first applied by a pad–batch method. The NMA cotton was impregnated in a dye liquor containing 20 g/l dye and 20 g/l sodium carbonate and batched for 24 h; soaping and washing-off completed the process. Table 9 shows the results obtained both on NMA and untreated cotton fabrics. The fixation of the dye on NMA cotton was found to be very high whilst that on untreated cotton was almost zero.

Application of the alkylamino dye by batchwise methods has also been studied: Table 10 gives the results. It appears to be necessary to dye the NMA cotton under alkaline conditions with salt. The necessity for alkali in the dyebath is due to the formation of a zwitterionic structure under slightly acid or neutral pH conditions (Figure 13). Thus the nucleophilicity of the amino group is reduced under acidic or neutral conditions. Since there are no cationic sites in NMA cotton, it was necessary to use electrolyte to exhaust the dyebath at or above pH 10. At pH 8, however, the dye exhaustion and fixation in the absence of salt were surprisingly found to be quite good. We postulate that above pH 8 the rapid increase in cellulosate anion concentration diminishes exhaustion of the dye, thereby necessitating salt additions.

Build-up of aliphatic amino-containing dye on NMA cotton

Figure 14 shows the build-up properties of both the alkylamino dye on the NMA cotton (dyed at pH 10.5 with 80 g/l salt, 1 h at the boil) and the original unmodified dye on untreated cotton applied by the conventional dyeing method. Comparing these two dyeing methods, it can be seen that much higher fixation is achieved on the NMA cotton dyed with the

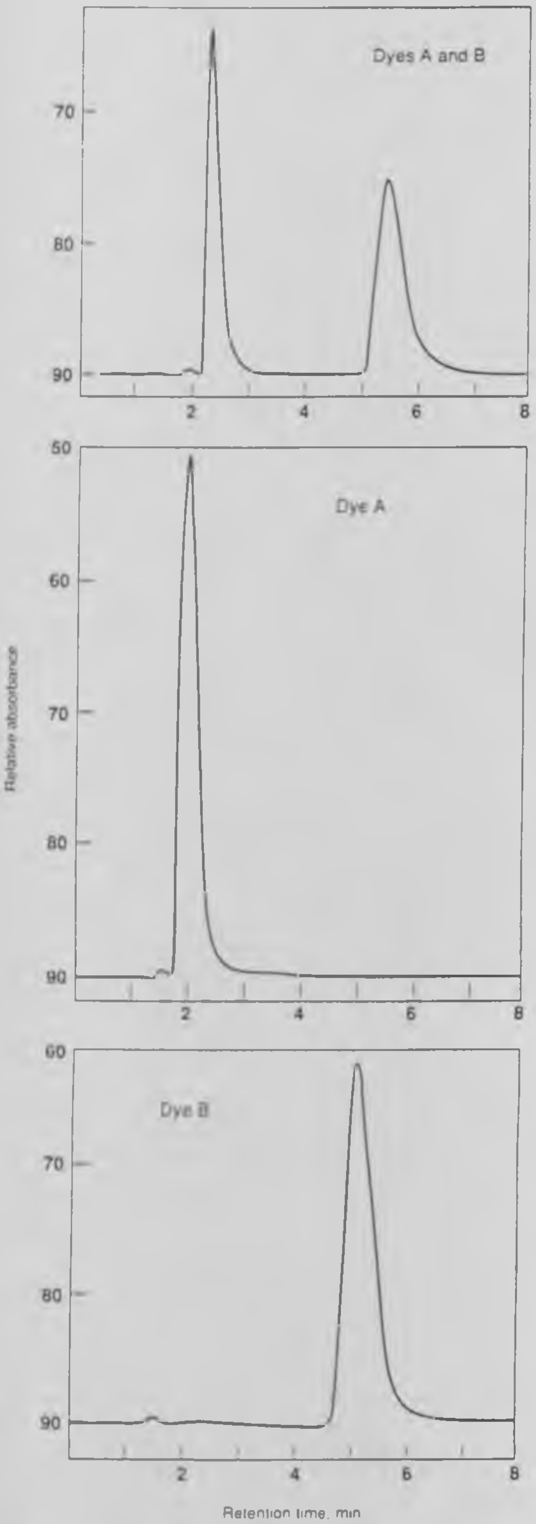


Figure 10 – H.p.l.c. print-outs of CI Reactive Red 58 (dye B), the alkylamino dye (dye A) and their mixture (retention times: dye A 2.0 min, dye B 5.1 min)

alkylamino dye. It may be expected that by using this new method a relatively short duration wash-off would be required to remove unfixed dye, greatly reducing the cost of this procedure.

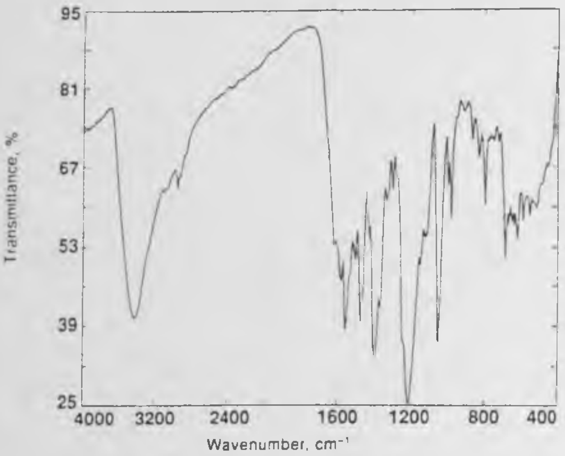


Figure 11 – F.t.i.r. spectrum of CI Reactive Red 58

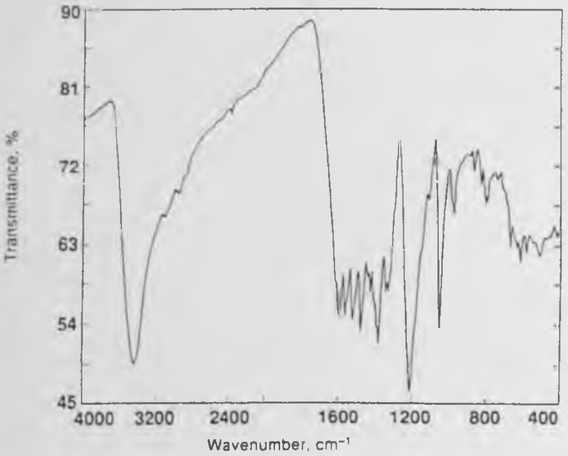


Figure 12 – F.t.i.r. spectrum of an alkylamino dye prepared from CI Reactive Red 58

TABLE 9

Colour yield and fixation of an aliphatic amino-containing dye on different substrates

	Colour yield (1.6% shade) after			
Substrate	Dyeing	Rinsing	Soaping	*F* (%)
NMA cotton	12.25	11.71	11.55	94
Untreatedcotton	10.01		0.18	2

Dyeing quality

Washing fastness and light fastness of the dyeings obtained when dyeing NMA cotton with the alkylamino dye were very good. The dyeings were also found to be very level. Cross-sections examined by microscopy showed that the dye was well penetrated through the fibres.

TABLE 10

Colour yield and fixation of an aliphatic amino-containing dye (2% o.w.f.) on NMA cotton

pH	Buffer	Sodium chloride (g/l)	Colour yield Before soaping	 After soaping	F (%)
10.5	Na_2CO_3	80	13.72	13.60	99
	Na_2CO_3	0	9.57	9.31	97
10.0	Na_2HPO_4/NaOH	80	15.91	15.14	95
	Na_2HPO_4/NaOH	0	7.12	6.37	89
8.0	NaH_2PO_4/NaOH	80	15.57	13.85	89
	NaH_2PO_4/NaOH	0	12.75	11.43	90
5.0	NaH_2PO_4	80	8.72	4.60	53
	NaH_2PO_4	0	4.59	2.37	52

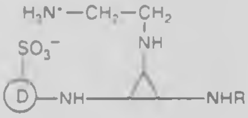


Figure 13 – Zwitterionic structure formed under slightly acid or neutral conditions when dyeing with alkylamino dye

CONCLUSIONS

Cotton may readily be modified by pretreatment with *N*-methylolacrylamide to introduce pendant activated double bonds. These have been exploited in two ways to improve the reactive dyeing of cotton.

Firstly, by introducing amino residues at these new sites excellent dyeings with reactive dyes can be achieved at pH 5–7 in the absence of electrolyte, coupled with a very high degree of fixation.

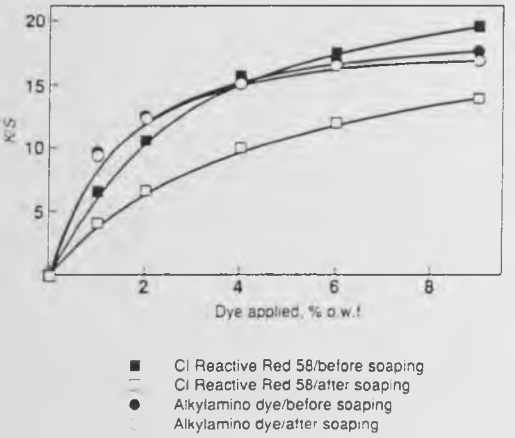


Figure 14 – Build-up of CI Reactive Red 58 on untreated cotton and of an alkylamino dye on NMA cotton

Secondly, it is possible to dye the cellulose modified only with *N*-methylolacrylamide with dyes containing pendant aliphatic amino residues. In this case it is necessary to dye in the presence of electrolyte under alkaline conditions but very high colour yields are obtained thanks to the elimination of the hydrolytic side reactions normally associated with reactive dyeing. Such amino-containing dyes can be readily prepared from all commercial ranges of reactive dyes.

* * *

We thank ICI Colours and Fine Chemicals (ICI Specialties) for their support and interest in this work.

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100 YEARS AGO

Extract from 'Some notes on causes which govern the formation of permanent and other dyes' by James Sharp, Journal, March 1891

If you take a solution of logwood in the form of hæmatïn, extracting the colour with pure distilled water and filtering, and then add a calculated quantity of peroxide of hydrogen, in a moment we have a solution that will not dye. Now, my own views are – and I am very glad we have so able an authority in the chair to correct me if I am mistaken – that the oxygen in the peroxide unites with the hydrogen and forms water. It is not a dehydrogenising process directly, but the two molecules go together and form water. I think that is probably the correct interpretation of the action; but if it is not, the object of these papers is to discuss errors and make them manifest, and to submit our views respectively to correction. I believe this action has not been pointed out by any authority before. If I am wrong, or may be proved to be wrong afterwards, all I can say is that I do not set myself to be an authority. I simply give you the result of practical, every-day experience. If that is not the reaction, tell me what is. That is the point I want to know.

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

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(This paper has been accepted by the journal of *Dyes and Pigments*)

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

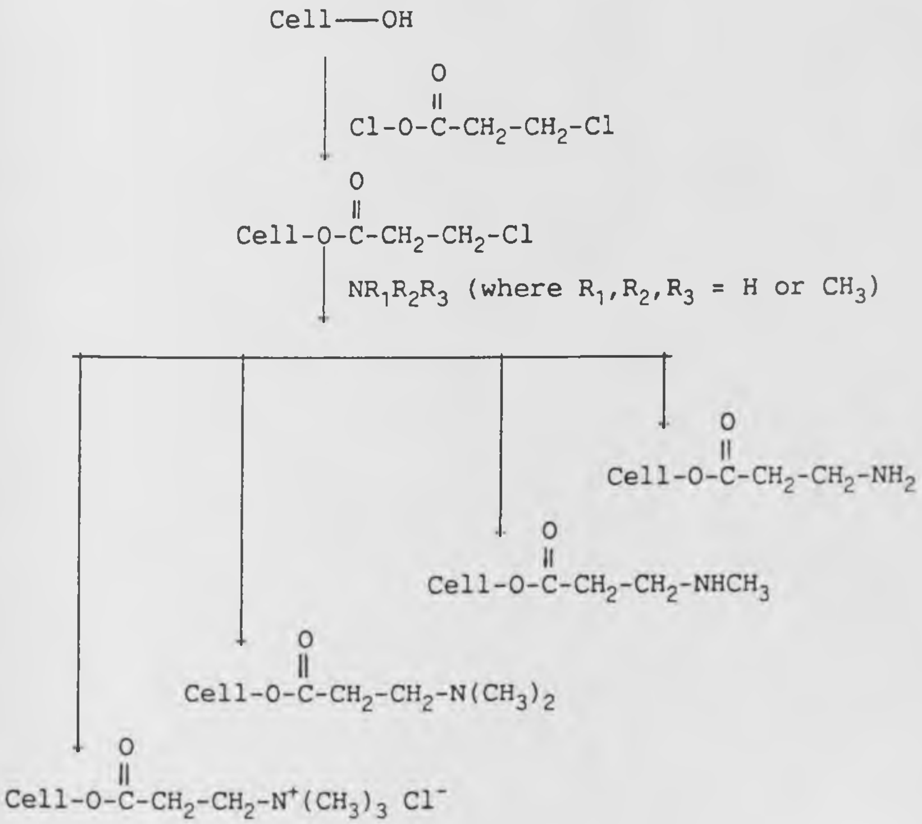
Processes for efficient dyeing cellulosic fibres with reactive dyes under neutral pH conditions in the absence of salt would exhibit the following advantages: i) higher fixation efficiency because of reduced reactive dye hydrolysis under neutral pH conditions; ii) polyester/ cotton blends could be dyed in a one-step, one-bath dyeing procedure using reactive and disperse dyes, thus saving time and energy; iii) 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 which are capable of increasing both the substantivity and the reactivity of reactive dyes.

The majority of reported chemical modifications which 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 ours[7] prepared a variety of cellulose derivatives using amine reactions with N-methylolacrylamide 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 ß-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 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 the following scheme:



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

I Materials

Cotton:
Bleached and unmercerised cotton fabrics were used throughout the work.

Dyes and auxiliaries:
All dyes and auxiliaries used were of commercial grade.

Chemicals:
Chloropropionyl chloride, 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=0.880),methyl amine (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.

II Acylation of cotton with chloropropionyl chloride(CPC cotton)

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

III Preparation of aminized cotton

The CPC cotton was further treated in an aqueous solution containing 10 g/l 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) laboratory dyeing machine at a liquor to goods ratio of 20:1.

Treatments were commenced at 50°C, raising to 100°C over 30 minutes, and maintaining for various times (t mins) 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/l)	t (mins)
ammonia (0.880)	150	120
methylamine (25-30%)	175	60
dimethylamine (40%)	125	60
trimethylamine(25-30%)	175	180

IV 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/l), 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 mins (2°C/min) and dyeing was continued at the boil for a further 60 mins.

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 5g/l of the non-ionic detergent Sandozin NIE(S) and 2g/l of sodium carbonate at the boil for 15 mins (liquor ratio 50:1).

V **Measurements**

i) 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 wave length of maximum absorption (λmax) of the dye using a UV-visible Spectrophotometer (PHILIPS PYE Unicam PU8600). Dyebath exhaustion was calculated using the following equation:

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

A0, A1--- Respective absorbance of dye solution before and after the dyeing process

ii) 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, LR=10:1). This stripping treatment was carried out repeatedly using fresh aqueous pyridine solutions until no further dye was removed, The K/S values of the stripped, dyed samples were then measured using the I.C.S. Micromatch colour measurement system from which the extent of fixation of dye was calculated using the following equations:

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

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

C1,C2 ----K/S values of dyed samples before and after stripping respectively

iii) Total nitrogen determination

The total nitrogen content of the treated fibre was measured according to ASTM standard D1013-81[12] (standard test method for total nitrogen in resins and plastics).

iv) 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 which measures to six decimal places. The weight gain was calculated using the following equation:

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

W1, W2----weights of samples before and after CPC treatment respectively.

v) 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.

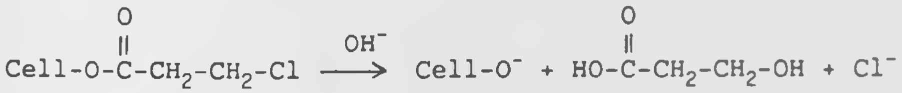
vi) Determination of CPC fixation on cotton by Ion-exchange Chromatography

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/l of phthalic acid, 10% of acetone (pH 5, conductivity approx. 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[8]. 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 following hydrolysis scheme:



$$\text{Cell-O-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-CH}_2\text{-CH}_2\text{-Cl} \xrightarrow{\text{OH}^-} \text{Cell-O}^- + \text{HO-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-CH}_2\text{-CH}_2\text{-OH} + \text{Cl}^-$$

Scheme 2

For quantitative measurement when using this instrumentation, it is necessary to use an internal standard to avoid errors. In the present case, both OH^- and K^+ give a single peak which 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:

$$[RCL] = \frac{\text{Area of Chloride Peak}}{\text{Area of } (OH^{-}+K^{+}) \text{ Peak}} * 1000$$

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 chloro-propionic acid(0.5%) in 5g/l KOH aqueous solution for 0 and 5 hours respectively and by treating CPC cotton under the same conditions at a liquor to goods ratio of 20:1 for 3 hours. 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:

Table 2 Reproducibility of Relative Cl^- concentration

No.	Duration of treatment	Area of (OH^-+K^+) peak	Area of Cl^- peak	RCL
1^*	5	2,008,753	664,641	330.8
2^*	5	2,021,406	667,821	330.4
3^*	5	2,006,333	661,145	329.5
4^*	0	1,982,776	137,400	69.3
5^*	0	2,011,202	139,351	69.3
6^+	3	2,093,371	290,483	138.8
7^+	3	2,089,561	290,856	139.2
8^+	3	2,096,375	293,510	140.0

* solution treatment.
$^+$ fabric treatment.

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

Table 3 the change of [RCL] with treatment time

Time (hours)	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

Effect of temperature on CPC-cellulose ester yield

During the reaction of cellulose with chloropropionyl chloride, the reaction temperature was kept as low as possible so that a suitable amount of CPC-cellulose ester could be 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 figure 1. It can be seen from figure 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.

The formation of CPC-cellulose ester was confirmed by the diffuse FTIR spectra of both untreated and CPC treated cotton. Figure 2 and 3 show the spectra of both fabrics and figure 4 is the spectrum obtained by computer subtraction of figure 2 from figure 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.

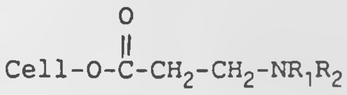
Substrate properties produced by the CPC/amine treatment

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

i) 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.

ii) CPC cotton gave a strong i.r. absorbance at about 1740 cm-1 indicating the presence of ester bonds in this substrate (figure 4), but this peak disappeared after the substrate was further treated with boiling aqueous methylamine solutions under the conditions described in the experimental section (figure 5). The other amines described in table 1 gave similar infrared 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



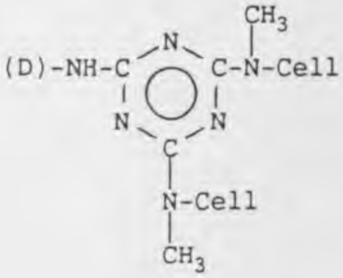
$$\text{Cell-O-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-CH}_2\text{-CH}_2\text{-NR}_1\text{R}_2$$

but rather has the following structure:

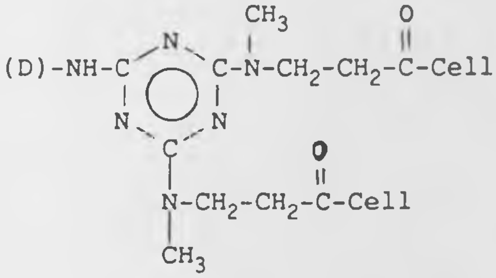
$$\text{Cell-NR}_1\text{R}_2 \qquad\qquad (I)$$

where R_1, 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):

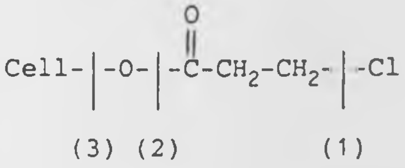


rather than



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.

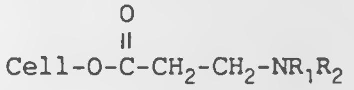
CPC cotton has the following structure:



$$\text{Cell-}\underset{(3)}{|}\text{-O-}\underset{(2)}{|}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}\underset{(1)}{|}\text{-Cl}$$

(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:



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

(III)

This substrate would still give a strong i.r. ester absorbance at about 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/l of 25-30% methylamine aqueous solution and at 50°C for 1 hour). 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 1740cm-1, new bands attributed to secondary amines appear at 1584 cm-1 and the carbon-chlorine band has disappeared. Dyeings with reactive dyes on this 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.

Table 4 colour yield of Procion Red MX-G (2% owf) dyeings on different substrates (methylamine 25-30% was used for amination)

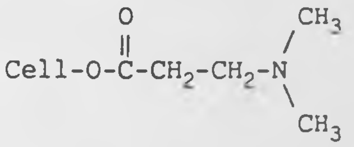
substrate code	amination conditions		colour yield	
	amine conc. (g/l)	temp. (°C)	before soap	after soap (pH 10.5)
I	175	100	12.63	11.95
III	10	50	19.72	8.72

Furthermore, when the above modified substrates (I and III) were treated with an aqueous solution containing 20 g/l of sodium carbonate at a liquor to good ratio of 20:1, at the boil for 1 hour and then dyed with Procion Red MX-G under the same dyeing conditions(pH 5, no salt), the one aminized under severe conditions (substrate 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).

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.

	amination conditions		colour yield	
substrate code	amine conc. (g/l)	temp. (°C)	before soap	after soap (pH 10.5)
I	175	100	11.03	10.57
III	10	50	0.21	0.19

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/l of 40% aqueous dimethylamine solution, 50°C, 1 hour) the following substrate was obtained (FTIR spectrum confirms ester bound still intact):

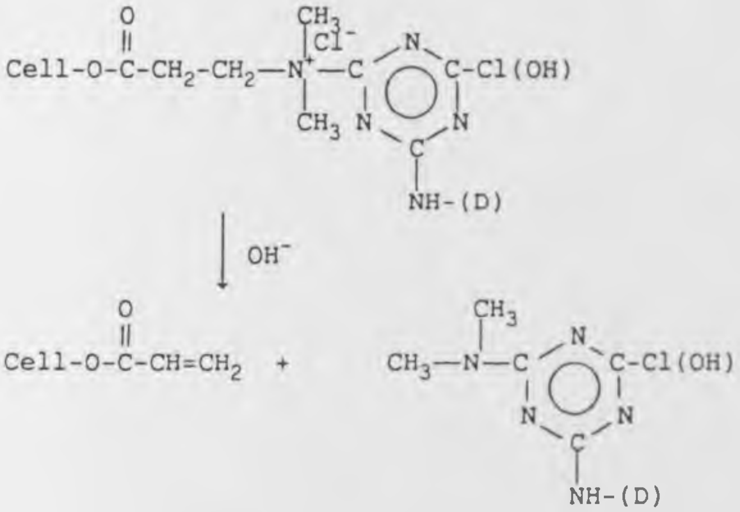


$$\mathrm{Cell{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}N}\begin{array}{l}\diagup CH_3\\ \diagdown CH_3\end{array}$$

(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-methylol acrylamide/ dimethylamine treated cotton[7]. Other literature has also discussed this type of reaction[9]. 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).



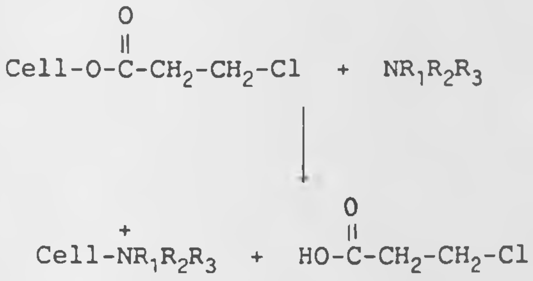
Scheme 3

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 amine conc. (g/l)	 temp. (°C)	colour yield before soap	 after soap (pH 10.5)
I	125	100	10.31	8.39
III	10	50	14.72	1.40

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.

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[10] 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. We thus propose the following scheme:



$$\mathrm{Cell{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}Cl} + \mathrm{NR_1R_2R_3} \longrightarrow \mathrm{Cell{-}\overset{+}{N}R_1R_2R_3} + \mathrm{HO{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}Cl}$$

scheme 4

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).

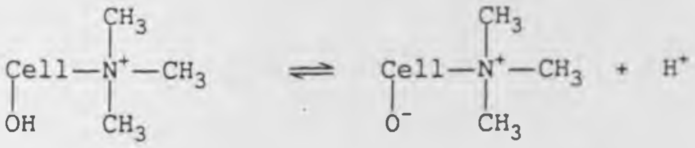
Table 7. Nitrogen contents and dye exhaustion/fixation values on different substrates (Procion Red MX-G, 2% owf)

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

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 the cellulose hydroxyl group.



$$\underset{\text{OH}}{\text{Cell}}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^+}}-\text{CH}_3 \rightleftharpoons \underset{\text{O}^-}{\text{Cell}}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^+}}-\text{CH}_3 + \text{H}^+$$

CONCLUSIONS

Cotton may be effectively esterified with chloropropionyl chloride to give a reactive substrate which 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 ß-elimination product, acrylic acid, occurs and 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:

secondary › tertiary › quaternary › primary

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

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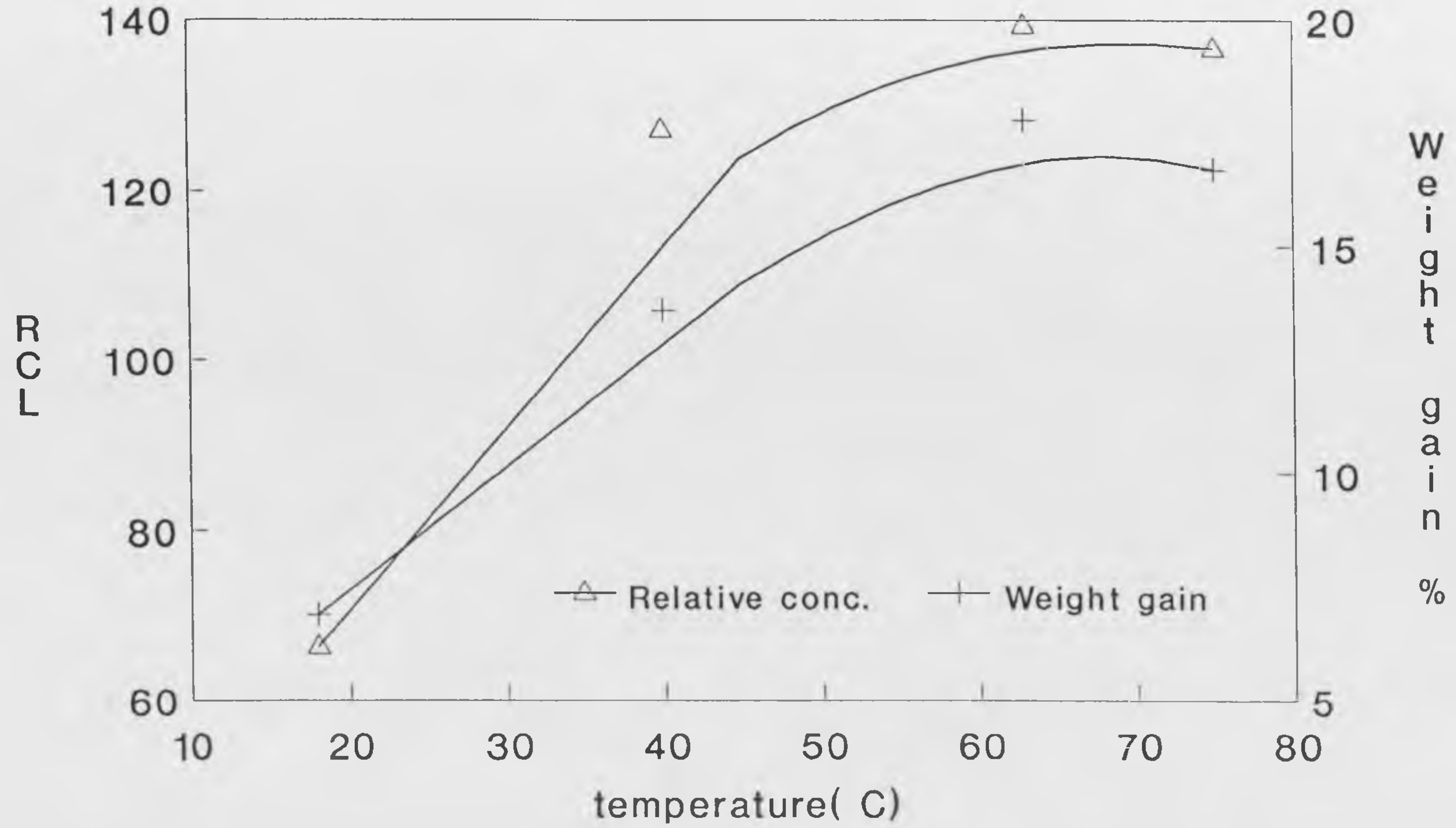
Figure 1



Effect of temperature on the yield of
CPC-cotton ester

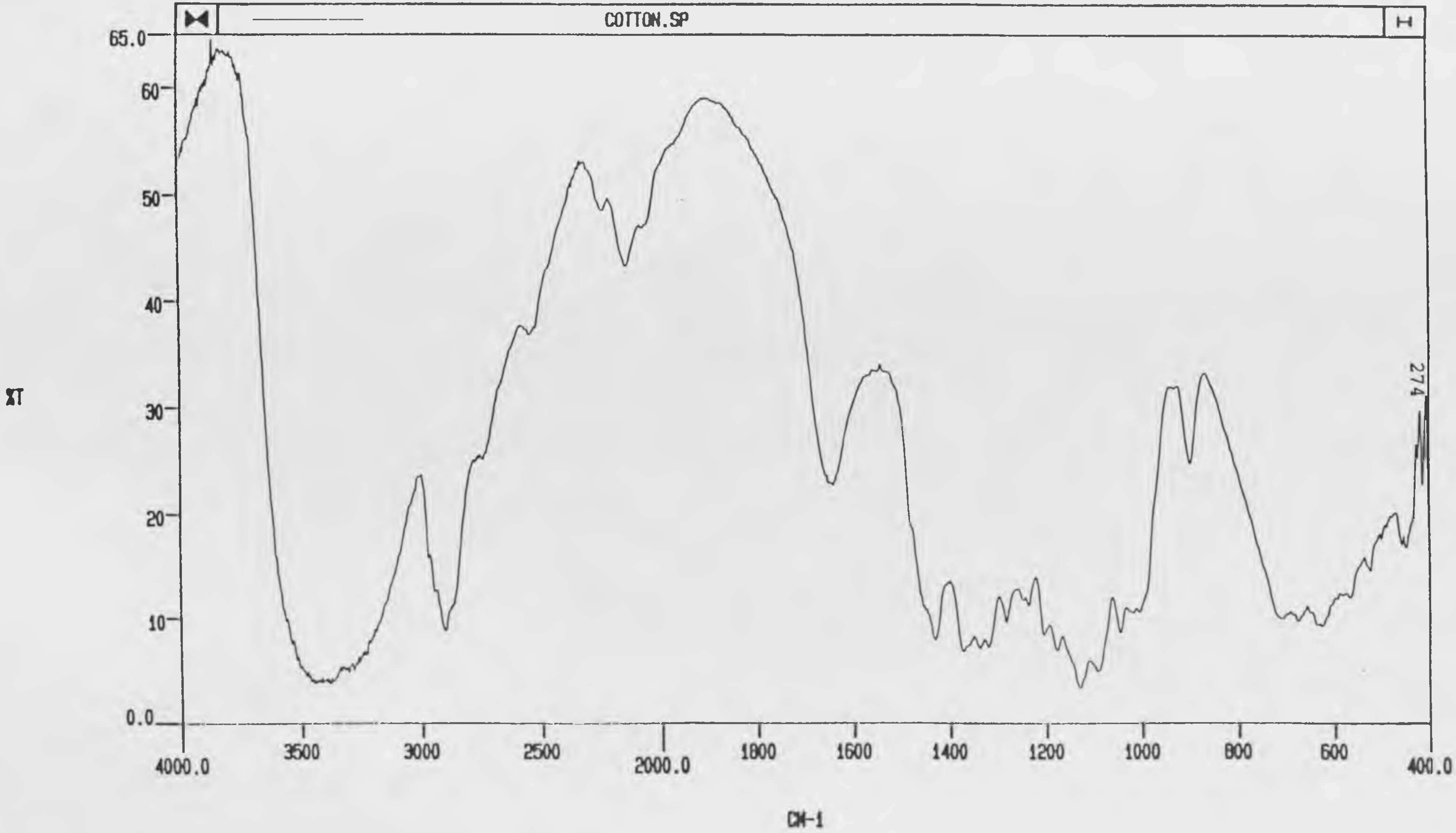


Figure 2. FTIR spectrum of untreated cotton

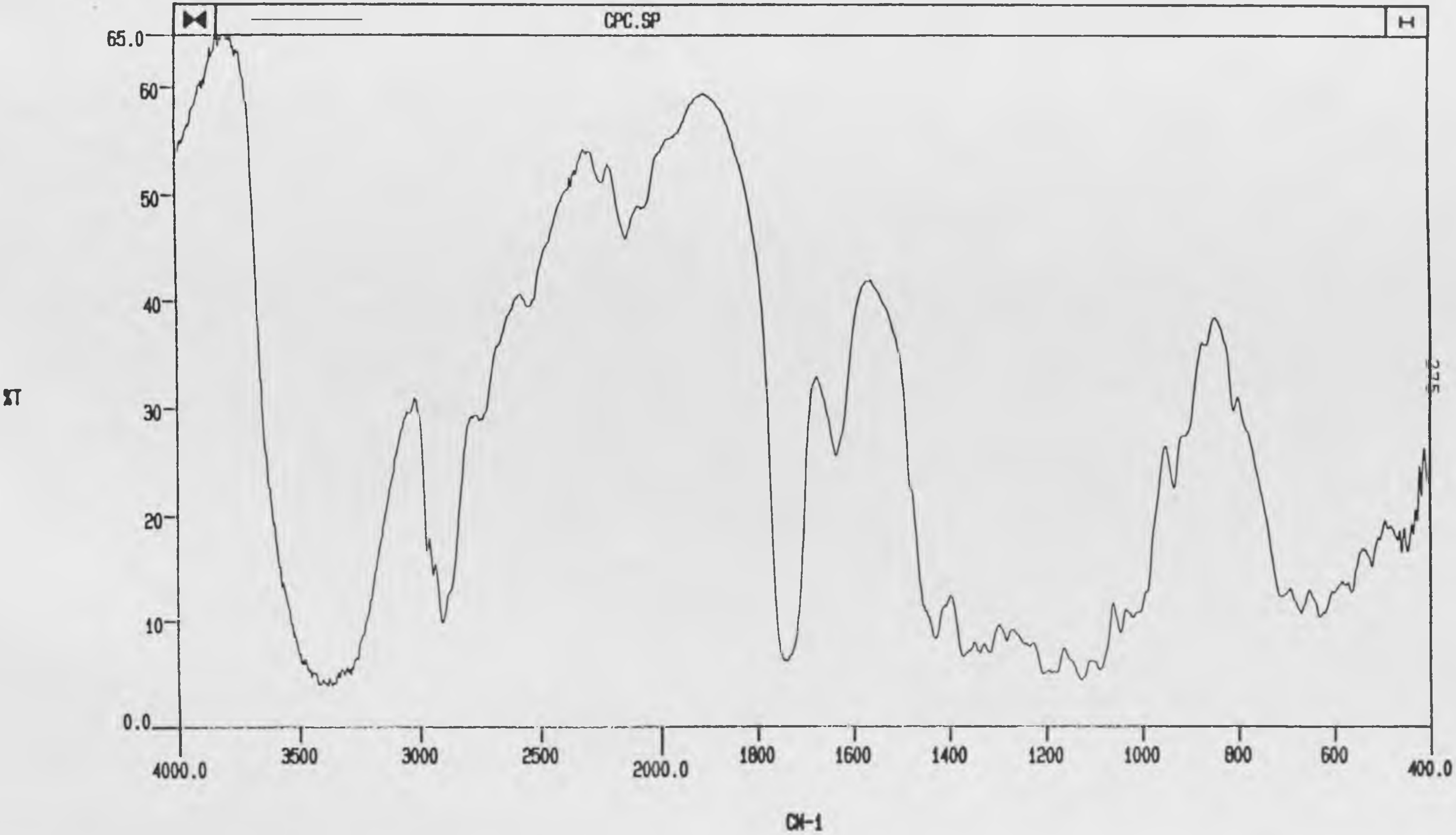


Figure 3. FTIR spectrum of CPC treated cotton

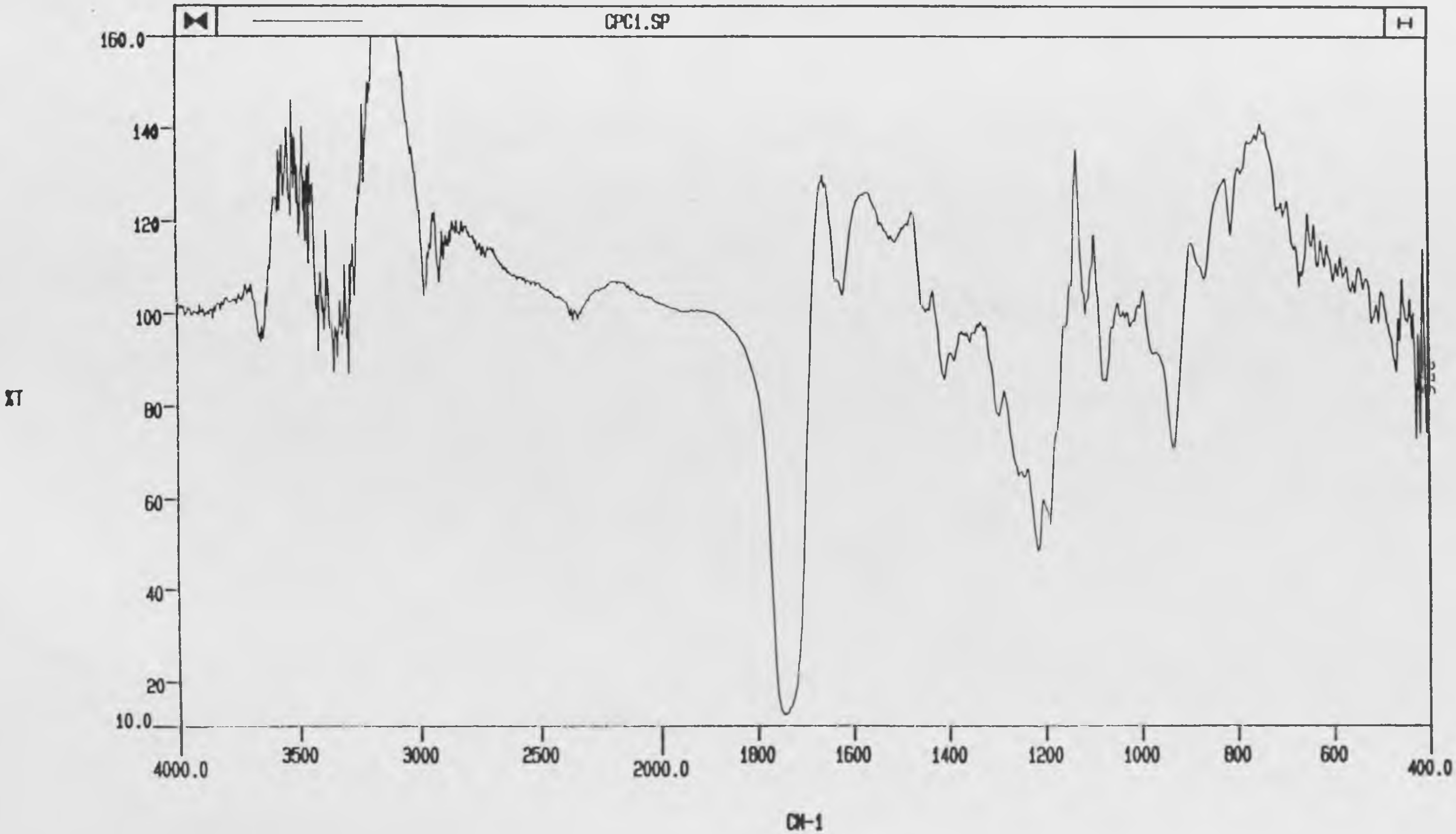


Figure 4. FTIR spectrum obtained by subtracting cotton from CPC treated cotton

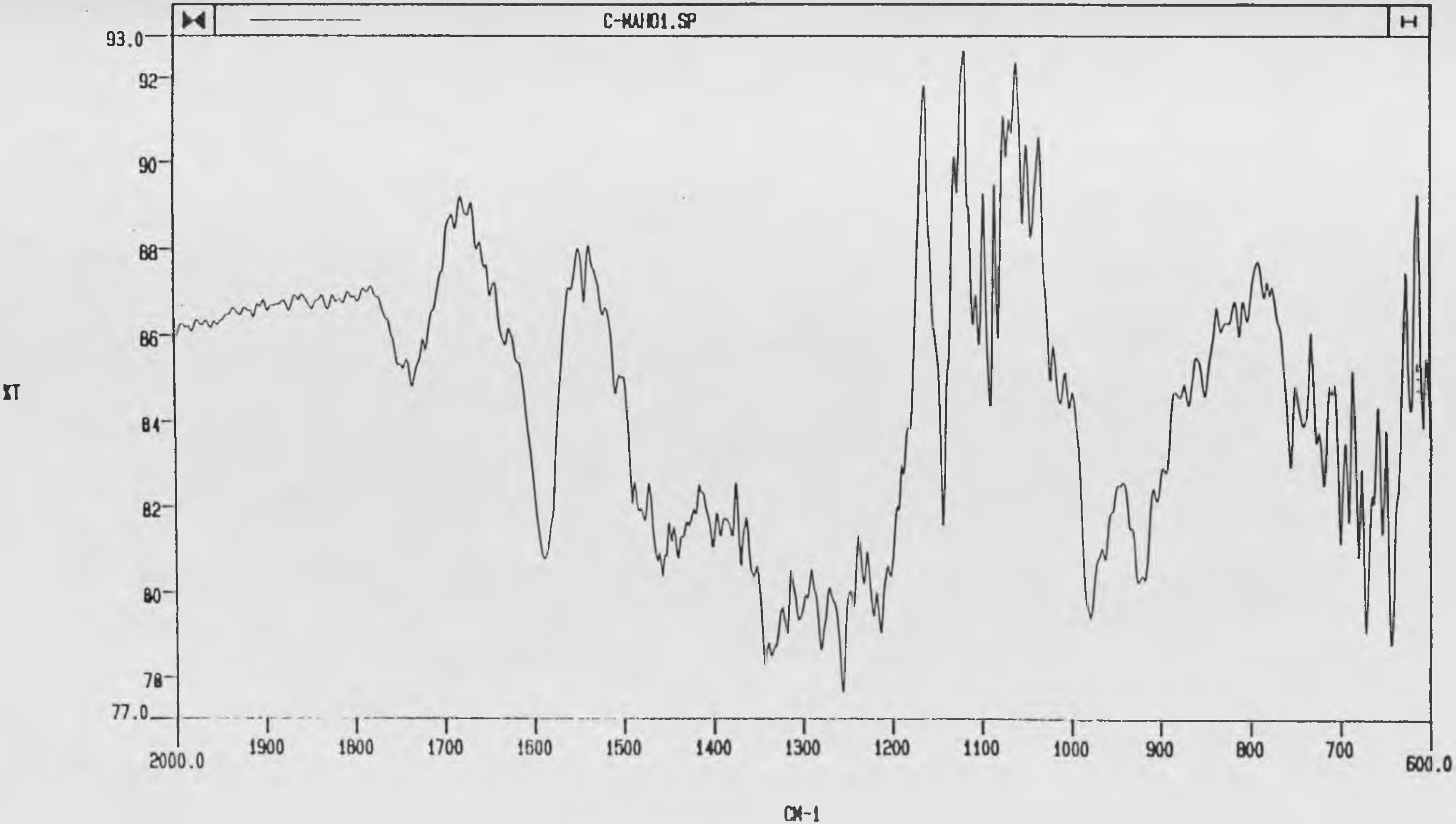


Figure 5. FTIR spectrum obtained by subtracting cotton from substrate I (methylamine reaction with CPC cotton at the boil)

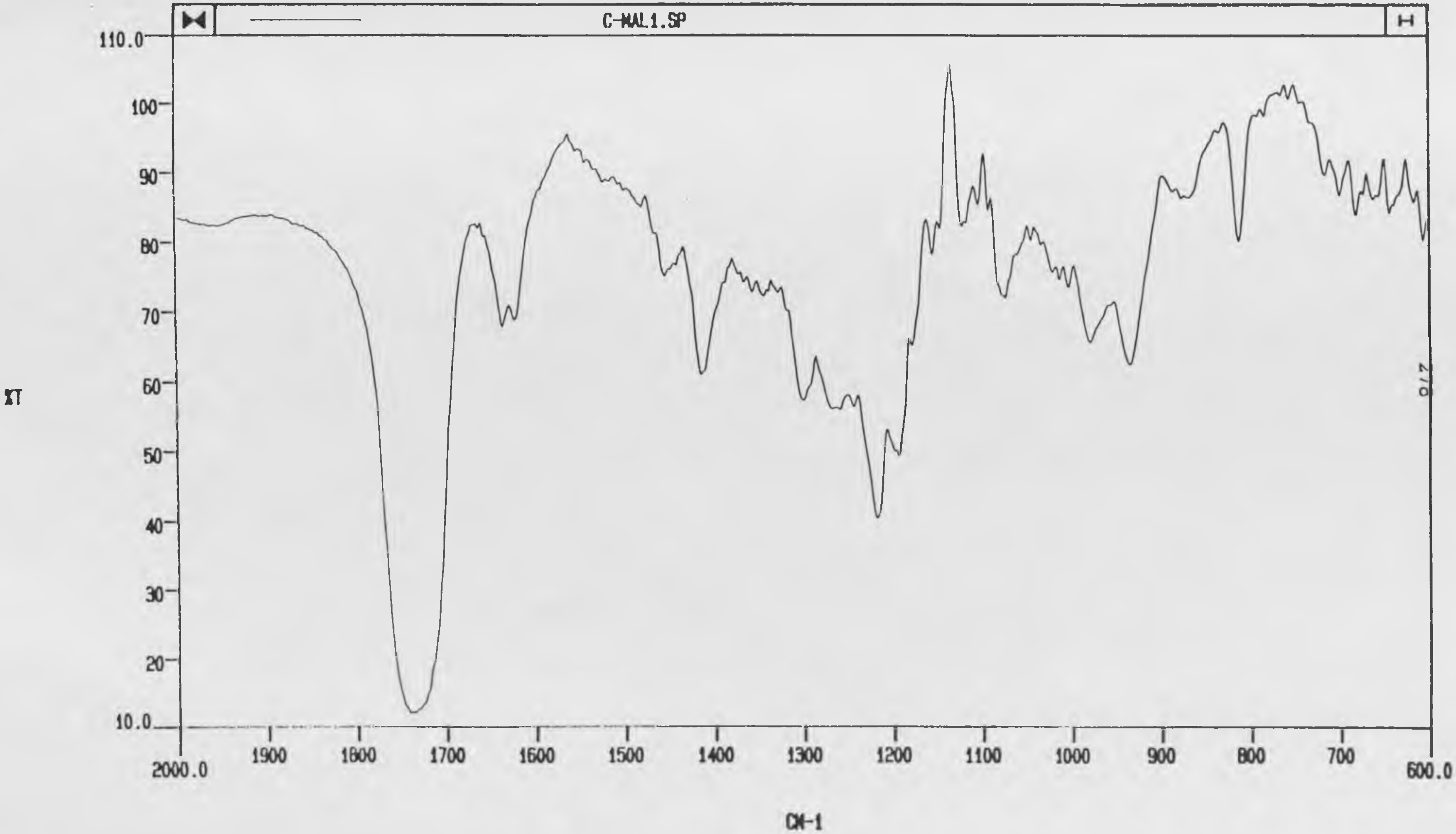


Figure 6. FTIR spectrum obtained by subtracting cotton from substrate III (methylamine reaction with CPC cotton under mild conditions)

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