Chemical Modification of Cotton to Enhance its Dyeability

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The candidate confirms that the work submitted is his own and that appropriate credit has been given where reference has been made to the work of others.

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Abstract

The dyeing of cotton can be problematic to the dyeing industry when dyeing with different dye classes because a significant amount of dyes find their way into effluents. Cotton dyed with different class of dyes suffers from washing-off, wash-fastness, light-fastness, rub-fastness and ring-dyeing problems. A method to increase the substantivity for the cotton fiber is to create a positive charge on the fiber. For this purpose the cotton fiber was pre-treated with cationising agents Servon XRK and NMM derivative. Servon XRK and NMM derivative were used as part of EU Frame Work V. Servon XRK (3-chloro-2-hydroxy-N, N, N-trimethyl-1-propanaminium chloride) and NMM derivative [4-(3-chloro-2-hydroxypropyl)-4-methylmorpholin-4-ium chloride)] were applied to cotton by pad-batch method. In this research vat dyes, acid dyes, azoic colourants and reactive dyes have been used.

The dyeings from vat dyes gave improved colour yield values when applied to the Servon XRK and NMM modified cotton fabrics as compared to the unmodified cotton fabrics. The dyeings from anthraquinone vat dyes (CI Vat Violet 1, CI Vat Red 13 and CI Vat Green 1) on modified (Servon XRK and NMM) cotton fabric absolutely did not lose any colour in wash-off liquor as the dyeings from anthraquinone vat dyes (CI Vat Violet 1, CI Vat Red 13 and CI Vat Green 1) on the unmodified cotton fabric gave a significant amount of colour in wash-off liquor. Vat dyes on the modified cotton fabric gave overall better dyeing results than on the unmodified cotton fabric.

Disulphonated acid dyes CI Acid Red 13 and CI Acid Red 17 gave better wash-fastness results than monosulphonated (CI Acid Red 88) and trisulphonated (CI Acid Red 18 and CI Acid Red 27). The light-fastness results were better for the dyeings from trisulphonated acid dyes than the monosulphonated and disulphonated acid dyes. The dyeings from CI Acid Blue 193 gave good dyeing results than the dyeings from CI Acid Violet 92. The overall dyeing results are better for the dyeings obtained by the application of Naphthol AS to the Servon XRK modified cotton fabric by pad-dry and pad-batch-dry methods followed by coupling than the corresponding dyeings on the unmodified cotton fabric.

Sumifix Supra Blue BRF and Sumifix Supra Red 3BF applied on the Servon XRK modified cotton fabric gave improved dyeing results than applying on unmodified cotton fabric. Reactive dyes co-applied with NMM have given overall better results than when applied without NMM.

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Abbreviations

CI	Colour Index
UV	Ultraviolet
ISO	International Standard Organisation
DP	Degree of Polymerisation
LR	Liquor to Ratio
o.m.f.	On the mass of fibre

Chapter 1

Introduction

1.1 Cellulose and cotton

1.1.1 Introduction

Cellulose (Latin word cellula, “little cell”) is a complex carbohydrate. In plants, cellulose is normally combined with woody, fatty or gummy substances. Photoinitiated biosynthesis results in the main product group of saccharides (particularly cellulose and starch) besides proteins, fats and oils. Payen suggested that the cell walls of a large number of plants were constructed of the same substrate to which he gave the name of cellulose [1]. His extensive work in this field has been reviewed [2-4].

1.1.2 Source of cellulose

Forests and cotton plantations are the main sources of cellulose used in industries producing paper, board, fibres or cellulose derivatives. On average, approximately 13 to 14 grams of cellulose is produced per day by every tree [5]. Cellulose is never found pure in nature. It is insoluble in all ordinary solvents and may be readily separated from the other constituents of plants. The cotton fibre is probably the purest natural source [6]. It is the seed hair of plants of the genus *Gossypium* [7, 8] which has many species.

The fibre length in different types of cotton varies from 25 to 60 mm. The highest quality and most valuable of the entire commercial cotton crop is grown on the Gulf coast of Florida, in

Barbados, and other adjacent islands where the climate is favourable. Table 1.1 represents the data for different cotton fibre length produced in various parts of the world [9].

Countries	**Average fibre length (mm)**
Egypt	38-44
United States	25-31
India and China	13-20

Table 1.1 Average cotton fibre length from different parts of the world

1.1.3 History of cotton

Although cotton is the most common textile fibre now in use, it was the last natural fibre to attain commercial importance. In the 5th century BC, the Greek historian Herodotus reported that among the valuable products in India, was the wild plant that bears fleece as its fruit. In the following century cotton was introduced from India to Greece by Alexander the Great. Although, the early Greeks and Romans used cotton for awnings and sails as well as for clothing; it was not adopted for widespread use in Europe until later centuries. In the New World, the Mexicans used cotton for weaving. Cotton textiles were found in West Indies and in South America by explorers in the 15th and 16th centuries. Cotton was cultivated by the early American colonists and after the introduction of the cotton gin, invented in 1793 by the American inventor Eli Whitney, cotton became the most important staple fibre in the world for quantity, economy, and utility [10].

1.1.4 Morphology of cotton

Cotton fibres show a bean-shaped appearance in cross-section, sometimes described as a bilateral structure which indicates that the density of packing of cellulose chains is not uniform across the fibre. Three main zones A, B and C (Figure 1.1) have been identified by means of enzymatic degradation [4]. The rate of degradation increases from A to B to C which is the order of decreasing density of packing between zones A and C. There appears to be limited areas (denoted by N) which are even more accessible than zone C [11].

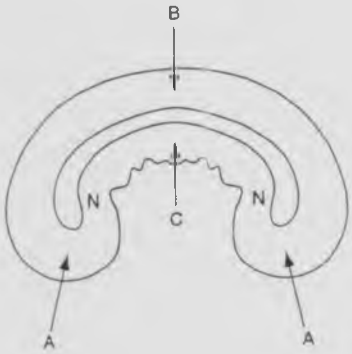


Figure 1.1 Bilateral structure of mature cotton (zones A, B, C and N differ in fibrillar packing density)

The seed hair of cotton consists of three parts as illustrated in Figure 1.2. When looking at a cotton-fibre cross-section, it shows a lumen or central canal (S_3), the secondary thickening (S_2) which is cellulose and the primary wall (S_1) or cuticle which forms a protective layer containing pectin, proteins, waxes and mineral matter. In the development of the secondary wall, cellulose is deposited in the form of fibrils. The fibrils in turn consist of micro fibrils which contain polymer chains that are well packed and almost identically oriented and thus are crystalline. The fibrils in the fibre are formed in layers which are associated with the day-night cycles experienced during growth. The fibrils are arranged spirally around the axis of the fibre, the direction of the spiral reverses from a left to right direction and vice versa, many times along the length of the fibre [12].

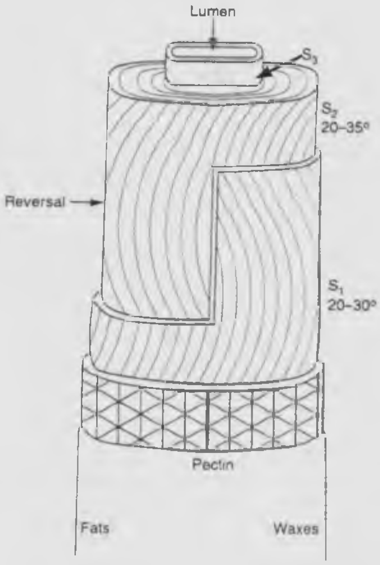


Figure 1.2 Morphological structure of the cotton fibre

1.1.5 Molecular structure of cellulose

Cellulose is composed of a large number of repeating units of 1,4-D-glucopyranose as shown in Figure 1.3.

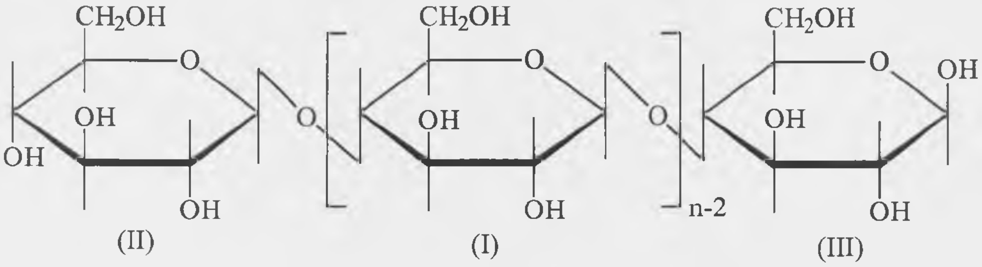


Figure 1.3 Molecular structure of cellulose

The distinguishing features of the polymer chain are the main sequence of repeating intermediate units (I), the non-reducing end group (II), the reducing end group (III) and the glycosidic linkage. Each intermediate unit contains three alcohol groups, two of which are secondary alcohols and one primary alcohol. The reducing end group is a cyclic hemiacetal, which shows the characteristics of both an alcohol and an aldehyde under appropriate conditions as shown in Figure 1.4.

Figure 1.4 Cyclic hemiacetal group showing both an alcohol and aldehyde characteristics

The cellulose triacetate was prepared in more than 99% yield from cotton [13]. The triacetate was then subjected to methanolysis; this resulted in the formation of an equilibrium mixture of α and β-glycoside, accounting for 95.5% of cellulose. The species formed other than methyl glycoside were not detected. This work was generally recognized as proof that cellulose contained exclusively of glucose residues.

The treatment of cellulose with dimethylsulphate in sodium hydroxide produced methylated cellulose [14], which contained approximately 45% of the total content. Further exhaustive methylation was not able to increase the methoxy content. This finding confirmed that the cellulose contains three hydroxyl groups per glucopyranose, since the theoretical content in such a case is 45.6%. Furthermore, the highest degree of cellulose substitution achieved by acetylation and nitration is also three; again this confirms that cellulose contains an average of three hydroxyl groups per glucosidic unit.

The studies of osazone formation [15] showed that the C-2 position in the hydrolysate of trimethyl cellulose, (trimethyl glucose), must be masked by a methyl group. The methylate lactose was also used to demonstrate this on hydrolysis [16]. One of the products contained methyloxyl groups in the second and third position. Following this work, the author [13] had no problem in determining that the methyloxyl group had taken the terminal or sixth position and consequently, the methylated glucose was the 2,3,6-isomer.

It was also shown [17] that cellobiose octaacetate to be resistant towards yeast maltase. Since yeast maltase readily hydrolyses the β-linkage in maltase, hence the above stated fact indicates that the disaccharide linkage in cellobiose must be of a β-configuration. If methylation of cellobiose is carried out to produce the heptamethyl derivative, which in turn was hydrolysed to yield equimolar amount of 2,3,4,6-tetramethyl glucose and 2,3,6-trimethyl glucose. This shows that the linkage was (1→4) or (1→5).

It was also confirmed that the linkage was (1→4), and that cellulose was in fact 4-O-β-D-glucopyranose-β-D-glucose (Figure 1.5), was obtained from studies of the hydrolysis products of methylated cellobionic acid [18].

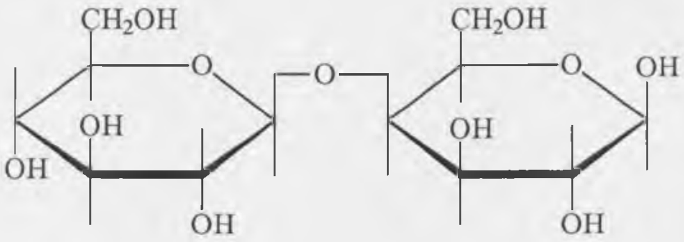


Figure1.5 Molecular structure of cellobiose

1.1.6 Degree of polymerisation of cellulose

The degree of polymerisation (DP) of cellulose 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. Native cellulose in its unpurified state may exceed 10,000 [19] but in a purified state involving treatment with alkali usually reduces this to about 1000-2000. Furthermore the hemiactal end groups are converted to carboxylic acid groups. Thus purified native cellulose is usually lacking in reducing power. Regenerated celluloses have DP of about 250-300 and may contain small numbers of aldehyde, ketone and carboxylic acid groups, introduced during manufacturing. Chemically they are nearly identical with native cellulose and differences between two types arise mainly in their supramolecular structure. Polynosic fibres have higher DP (about 500-700) than other forms of regenerated cellulose [7].

1.1.7 Supramolecular structure of cellulose

Native cellulose is a highly crystalline material which contains crystalline fibrils of varying degree of complexity and undetermined length. The fibrils are placed in the fibre in such a manner that they may be interspersed with material in which the chain molecules are not as well ordered as in the crystalline region. The same molecular chain may occur in both crystalline and non-crystalline regions of the fibre, along different portions of its length. The overall arrangement of chain molecules in a fibre, the supra molecular structure, may also be explained in two concepts; crystalline and fine structure. Several key features of the cotton cellulose molecule give rise to important structural and mechanical characteristics in the fibre itself [20].

- It is ribbon-like with an approximately rectangular cross-section.
- It is relatively flexible, through rotation about the bridging oxygen links between the glucose rings.
- It features a high concentration of hydroxyl groups along its edges.
- It has directionality.

The ability of hydroxyl groups to form secondary valence hydrogen bonds with one another is the cause of the high tendency of cellulose to organise into parallel arrangements of crystallites and fibrillar strands. Different orientations of the fibrils with respect to the fibre axis result in different allomorphic forms of cellulose. Cellulose I, the form found in nature and Cellulose II, the thermodynamically stable form produced when cellulose is regenerated are important ones for the textile industry. In Cellulose I the chain molecules are fully extended in the form of flat ribbons having the minimum possible thickness in the direction perpendicular to the mean plane of the rings [21]. Basically Cellulose I and Cellulose II are respectively parallel and antiparallel arrangements of fibrils giving rise to differences in some physico-chemical properties of cotton cellulose, e.g., natural cotton cellulose displays increased breaking strength in the wet state whilst the breaking strength of the regenerated cellulose fibre decreases in the wet state. Fibres have regions of differing degrees of molecular order and disorder as demonstrated in Figure 1.6. There is no distinctive boundary between the crystallite (ordered) and amorphous (disordered) regions. The amorphous content of cotton cellulose is found to vary from 30 to 70 %, regenerated cellulose having a higher amorphous content than natural cellulose. It is also considered that the higher order structures of the amorphous region of natural cotton and regenerated cellulose fibres are different from each other [22].

The disordered regions are important to facilitate dyeing, since the penetration of dyes and other chemical reagents is possible mainly through disordered regions. Molecules that are located at the surface of the crystallite areas are also accessible to chemical interactions and therefore size and distribution of crystallites play an important role in determining the accessibility of fibres. The morphology of a cotton fibre is illustrated in Figure 1.2. In addition to the form and structure of the fibre, the morphology of cellulose includes factors of fine structure such as fibrils and micelles, accessible and non-accessible regions [23].

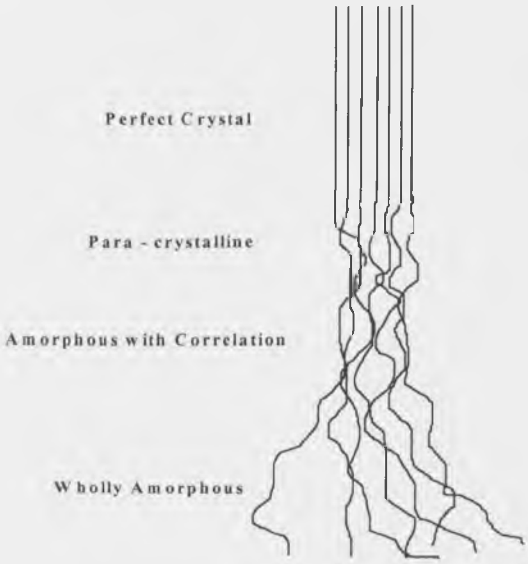


Figure 1.6 Relative degrees of order in the packing of chain molecules

Morphology changes account for the desirable technical properties of cotton after mercerisation e.g. increased absorbency, colour yield per unit of dye absorbed and lustre. They are due to total internal rearrangement of the natural cotton cellulose, into a different crystalline form, the end fibre having a circular cross-section. Viscose rayon or regenerated cellulose can be produced and handled with such a variety of processes that their morphology can change considerably according to their cross-section, wet modulus, crimp and lustre etc. [24].

All the different cellulosic fibres encountered in dyeing, including cotton, mercerised cotton, viscose rayon, linen, ramie, hemp and jute, have uniquely different morphologies derived from the same basic cellulose material. Thus, chemical behaviour of these fibres towards water and dyes will be similar but the overall behaviour will be determined by several variables depending on the morphological structure of the fibres such as characteristics of the outer and inner layers, the ratios of crystalline to amorphous cellulose and the size and distribution of the crystallite regions.

1.1.8 Degradation of cellulose

Cellulosic fibres are chemically stable which is very important from the industrial point of view. Six different degradative agents have been identified; acids, alkalis, oxidising agents, enzymes, heat and radiation [14]. When cellulose is treated with an alkali and then reacted with carbon disulphide, it dissolves; rayon and cellophane are useful cellulose products regenerated from such solutions. Cellulose acetates are spun into fine filaments for the manufacture of some fabrics and are also used for photographic safety film, as a substitute for glass, for the manufacture of safety glass and as a moulding material. Cellulose ethers are used in paper sizing adhesives, soaps and synthetic resins. With mixtures of nitric and sulphuric acids, cellulose forms a series of flammable and explosive compounds known as cellulose nitrates, or nitrocellulose. Pyroxylin, also called collodion cotton, is a nitrate used in various lacquers and plastics; another collodion, is used in medicine, photography, and the manufacture of artificial leather and some lacquers. Cellulose is sensitive to acids and the reaction under acidic conditions consists of hydrogen ion catalysed hydrolysis of the glucosidic linkages according to Figure 1.7 [25,26].

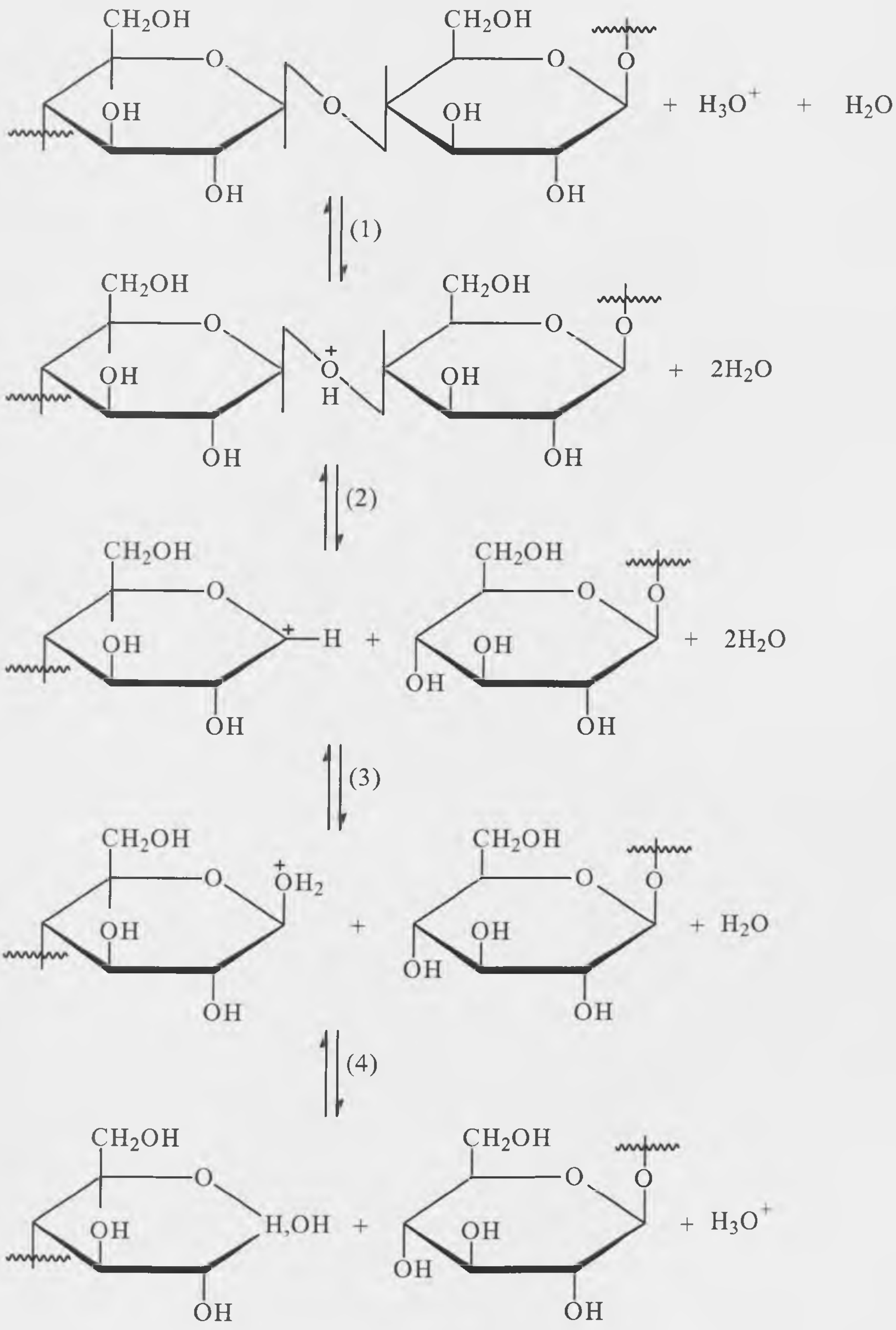


Figure 1.7 Acid degradation of glucosidic linkage

Acid hydrolysis of cotton cellulose results in reduction in strength and ultimate loss of fibre structure. Acid hydrolysis of cellulose results in the breakage of the main chain; producing 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 hydro-cellulose.

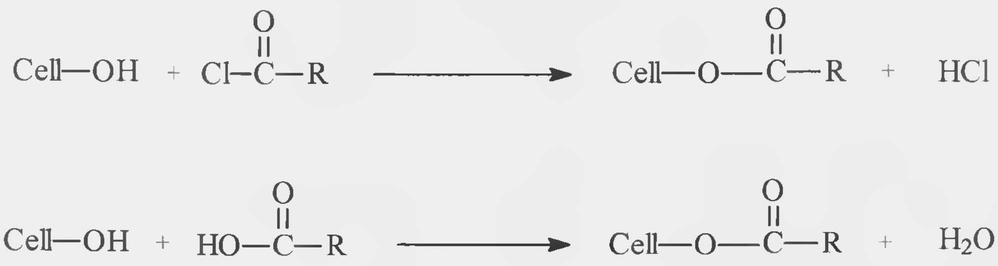
Cellulose can be heated for many hours at temperatures up to 120°C without any serious deleterious effects. In dry air at high temperatures, however, considerable de-polymerisation takes place which is accompanied by the formation of carbonyl and carboxyl groups in the solid material, the evolution of water, carbon monoxide, carbon dioxide and loss of tensile strength [27-29].

1.1.9 Cellulose substitution

The intermediate chain unit of cellulose contains three hydroxyl groups capable of participating in substitution reactions. The degree of substitution of any cellulose derivative is the fraction of hydroxyl groups in the glucose residue that have reacted and can therefore have any value between 0 and 3. It is generally accepted that primary alcohol groups 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:

- Inherent chemical reactivity.
- Steric effects arising from the size of the entering group.
- Steric effects arising from the supra-molecular structure of the cellulose.

Cellulose can be esterified with most inorganic and organic acids by methods similar to those employed for the simple alcohols, this reaction giving many important products such as acetates, xanthates and cellulose esters (Figure 1.8); other examples include esterification with phosphoric acid resulting in the formation of flameproof cellulose [30-32] and cellulose-carbamate on reaction of cellulose with urea [33].



$$\text{Cell—OH} + \text{Cl—}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{—R} \longrightarrow \text{Cell—O—}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{—R} + \text{HCl}$$

$$\text{Cell—OH} + \text{HO—}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{—R} \longrightarrow \text{Cell—O—}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{—R} + \text{H}_2\text{O}$$

Figure I.8 Reactions of cellulose to form cellulose esters

The etherification of cellulose can also be carried out in several ways [34]. The most common method is the reaction of alkali cellulose with a reactive alkyl derivative, such as an alkyl halide, to form a salt and the cellulose ether (illustrated in Figure 1.9 for methyl cellulose) [35] and benzyl-cellulose [36]. Ethylene oxide and its derivatives, in the presence of alkali also react with cellulose to give ethers; the examples of the latter reactions involve hydroxyethylation [37].

$$\text{Cell—OH} + \text{NaOH} + CH_3Cl \longrightarrow \text{Cell—O—}CH_3 + NaCl + H_2O$$

Figure 1.9 Formation of methyl-cellulose using methyl chloride

Activated olefinic compounds also react with cellulose under alkaline conditions to give cellulose other derivatives; cyanoethylation is typical of this reaction (Figure 1.10) [38].

$$\text{Cell—OH} + CH_2{=}CH{-}C{\equiv}N \xrightarrow{NaOH} \text{Cell—O—}CH_2{-}CH_2{-}C{\equiv}N$$

Figure 1.10 Formation of cyanoethyl-cellulose

1.1.10 Physical properties of cellulose

Simpler glycosides like glucose and sucrose are soluble in water and it is surprising that having so many hydroxyl groups, cellulose fibres do not dissolve in water. The oxygen or hydrogen of each hydroxyl group in cellulose could theoretically be solvated by hydrogen bonding with hydrogen and oxygen atoms of water but in reality this is not the case. Most of the hydroxyl groups in cellulose are bonded to one another into such a network of hydrogen bonds that, although water can interact with and break some of the cellulose-to-cellulose hydrogen bonds, not all such bonds are ever simultaneously accessible. The accessibility of hydrogen bonds to water and consequently to dyes dissolved in water, varies with the size and distribution of the crystalline (ordered) and amorphous (disordered) regions and the connecting regions of low order because of its small molecular size, water has access to areas the bigger molecules can not go. Nevell [21] has presented a detailed review about almost every aspect of the structure, properties and behaviour of cellulose.

1.2 Cotton in textiles

1.2.1 Trends in cotton production

Cotton is still a principal raw material for the world's textile industry with a market share of 45% but its dominated position has been seriously eroded by synthetic fibres but still cotton due to its fine properties is mostly liked as a major textile material. Cotton consumption world-wide is now at approximately 20,000,000 metric tonnes per annum and it is increasing every year (Figure 1.11) [39].

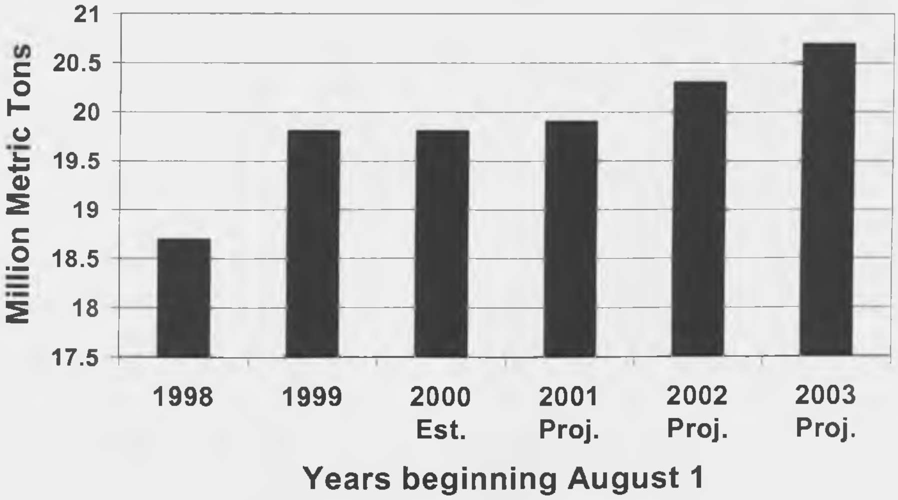


Figure 1.11 World-wide cotton consumption per annum

1.2.2 Cotton preparation

Before it is ready to be used as a textile fibre, cotton undergoes various processes. The first stage is the cultivation and harvesting of the cotton plant. The cotton fibres are removed from the seed husks during the ginning process and are graded depending upon their colour, staple length, fineness, strength and frictional characteristics. The cotton fibres are then blended together to yield fibres of optimum processing characteristics and user properties at the lowest possible cost. The fibre tufts are opened and separated during the carding process. During this process the husk and other impurities present are removed. Combing and drawing aligns the fibres and during a further drawing a slight twist is incorporated which aids the handling during spinning. During spinning, the fibre is further drawn and twisted to produce the final yarn.

The yarns produced are then sized during which the single fibres are bonded together to produce a more coherent material. During the sizing process, the fibres are treated with starch, modified starches or non-starch polymers. Sizing aids machine handling and helps to prevent the fibres becoming entangled in the looms or knitting machines.

Singeing is the passing of the fabric over a heat source to burn short fibres from the fabric surface. This can reduce pill formation and improve the uniformity of dyeings [40]. Desizing involves passing the fabric through a solution which promotes the solubilisation and removal of the sizes in the fabric. The fabric is then washed to rinse out the solubilised sizes. Starch is usually removed using an enzyme, polyvinyl alcohol and carboxy methyl cellulose are usually removed using a detergent and alkali. The purpose of scouring is to remove cotton waxes and other impurities such as pectin, hemi-cellulose and mineral salts from the fabric. This is usually achieved by the application of detergent and an alkali such as sodium hydroxide [41].

Bleaching is the whitening of the fabric and is achieved by solubilising and removing impurities from the fabric including natural and synthetic fats and waxes. The end goals of the bleaching process are to achieve a sufficiently high and uniform degree of whiteness which is stable to storage, a high and level absorption of water, dye and other chemicals by the fabric and the fabric should not be damaged to a great degree. Bleaching has traditionally been carried out using oxidising or reducing chemicals such as hypochlorite, chlorite, hydrogen peroxide and sulphur based reducing chemicals [42]. A recent development has been made for the bleaching of cotton fibres using ozone [43].

Mercerisation is the treatment of cotton with a strong alkaline solution, usually sodium hydroxide. Unlike desizing, scouring and bleaching, mercerisation is not a fibre purification process. Mercerisation causes swelling of the cotton fibres and changes the surface and crystalline structures of the cotton fibres. The end effect of mercerisation is increased lustre, increased absorption of dyes, water and alkali, increased tensile strength and improved dimensional stability [44]. A one-step process has been developed for the desizing, scouring, bleaching and mercerising of cotton fabrics [45].

1.3 Colour perception

Colour is a visual perception associated with the various wavelengths in the visible portion of the electromagnetic spectrum. In other words, it is a physical phenomenon of light and the function of the eye. White light is composed of many different colours. Each colour in the system corresponds to a different wavelength of light. Light with a wavelength of 700 nm is perceived as red and light of 400 nm is perceived as violet. The intermediate wavelengths are perceived as blue, green, yellow or orange moving from the wavelength of violet to that of red. We are able to see colours because our eyes contain three different colour receptors red, green and blue. When these receptors are stimulated, our eyes can perceive all colours and when these receptors are stimulated in pairs, we perceive yellow, cyan and magenta. As a sensation experienced by human beings and some animals, perception of colour is a complex neurophysiological process [46].

The methods used for colour specification today belongs to a technique known as *colorimetry* and consist of accurate scientific measurements based on the wavelengths of three *primary colours*. Other colours like orange, grey and brown result when some of the receptors are only partially stimulated. When colours result from combining lights of different wavelengths, the process is known as *additive colour mixing*. Colours arising from pigments involve *subtractive colour mixing*. When white light falls upon a coloured surface, some wavelengths are absorbed and others are reflected. We interpret the colour of the surface according to which wavelengths of light remain [47].

1.3.1 Textile dyeing

Dyeing is a process to colour material such as textiles in which the colouring material becomes the integral part of the fibre. There are different ways to dye the textiles. They can be dyed as piece dyeing, stock dyeing and yarn dyeing etc. Synthetic yarns can also be pre-coloured by incorporating pigments in the spinning solution before the filaments are extruded through the spinneret (solution or dope dyeing).

1.3.2 Cellulose during dyeing

The most important properties of cellulose according to dyeing point of view are hydrophilicity, accessibility to water, physical behaviour in aqueous solution and chemical reactivity. The important fact is that all the different cellulosic fibres encountered in dyeing, including cotton, mercerised cotton, viscose rayon, linen (from flax), ramie (from china grass), hamp and jute, have uniquely different physical organisations (morphology) of the same basic raw material: cellulose or Cell – OH. It means, although the overall chemical behaviour of these fibres towards water and dyes will be similar, properties such as the accessibility of the fibres to aqueous solutions of dye molecules will be governed to a large extent by several variables. These variables are the morphological characteristics of the fibres in both the outer and inner layers, the ratios of crystalline to amorphous cellulose and the size and the distribution of the crystalline regions.

1.4 Dyes for cotton

Cotton can be dyed with a range of different dye classes which are;

- **Direct dyes**
- **Reactive dyes**
- **Vat dyes**

- **Azoic colourants**
- **Sulphur dyes**

Cotton is such a versatile fibre that the choice of dye class, application method, shade and fastness properties, depends on the end-use of the material being dyed. Figure 1.12 shows the global market share for each dye class [48].

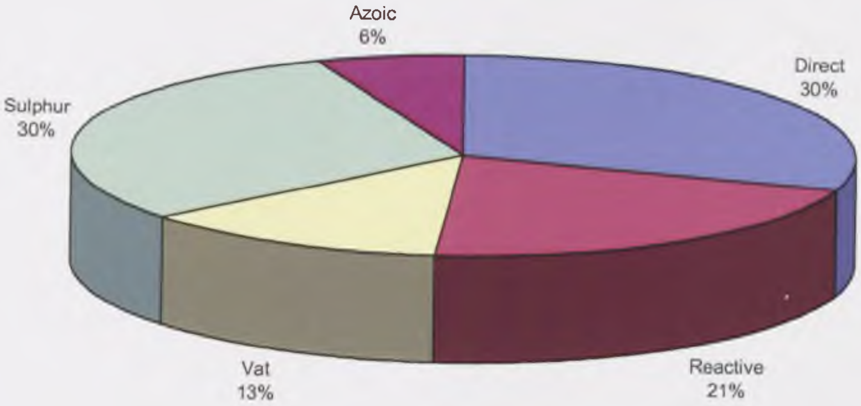


Figure 1.12 Global consumption of dyes for cellulosic fibres

1.4.1 Direct dyes

Direct dyes are anionic dyes with substantivity for cellulosic fibres, normally applied from an aqueous dyebath containing an electrolyte. Their most attractive feature is the essential simplicity of the dyeing process since no mordant is needed as before, but a separate aftertreatment to enhance wet-fastness is necessary for most direct dyeings [49]. Direct dyes are used in curtain fabrics, furnishings and carpets, where good light-fastness and moderate fastness to washing are usually adequate.

The first direct dye was Congo Red (CI Direct Red 28) as shown in Figure 1.13 and many other direct dyes followed. The majority are sulphonated azo compounds, very similar to acid dyes. More than 75% of all direct dyes are non-metallised azo structures and these are represented in every hue sector [50]. Examples of direct dyes are shown in Figures 1.13 – 1.14.

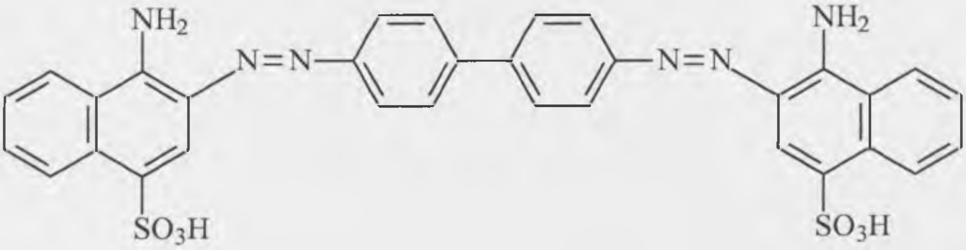


Figure 1.13 Chemical structure of CI Direct Red 28 (Congo Red)

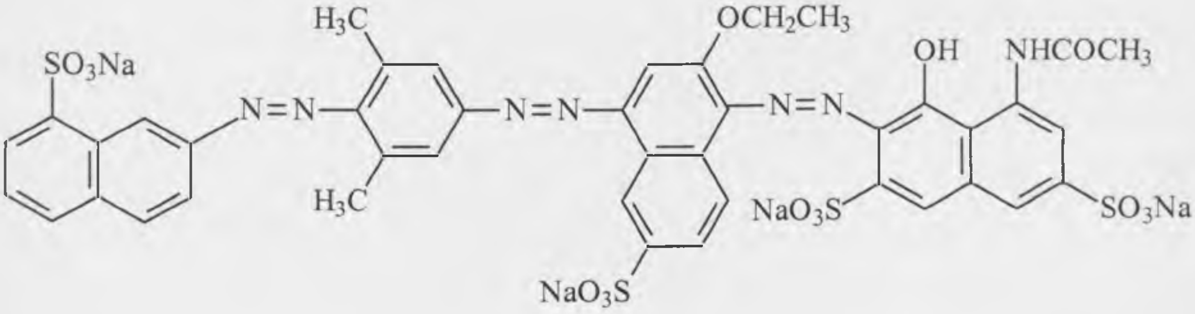


Figure 1.14 Chemical structure of CI Direct Green 33

Aftertreatments produce more complex dye molecules and hence bring about notable improvements in wet-fastness properties, but they add to the processing costs and may impair light-fastness/change in hue. The development of specialised aftertreating agents and cross-linking reactants for use with selected direct dyes of high light-fastness has reached new levels of sophistication, enabling direct dyes to compete more effectively with reactive dyes in meeting severe wet-fastness requirements [51-53].

1.4.2 Reactive dyes

Reactive dyes are one of the most successful classes of modern synthetic dyes. They are applied to wool, silk, nylon, cotton and regenerated cellulosic fibres. Cotton dyes such as direct dyes and sulphur dyes possess poor wet-fastness. However vat dyes show excellent all-round fastness properties but the range of shades is limited and they are expensive to produce. The success of the reactive dyes is due to their shade versatility, flexibility in application and the good fastness properties obtained.

Fibre reactive dyes contain one or more reactive groups, capable of reacting with the nucleophilic groups in a fibre to produce a covalent dye-fibre linkage [54]. Reactive dyes have the general structural requirements of a reactive group (R), a chromophore (C), a bridging group (B) and one or more solubilising group (S) [55], as shown in Figure 1.15.

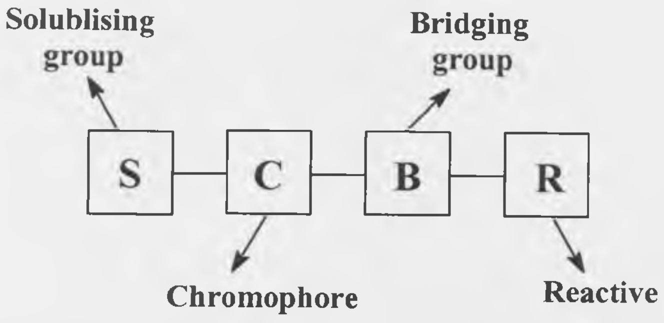


Figure 1.15 General structural requirements of a reactive dye

Reactive dyes are generally divided into two basic classes according to differences in the manner in which they bind to the cellulosic fibre. The first class (Figure 1.16) contains dyes that react by a nucleophilic substitution mechanism (Figure 1.17).

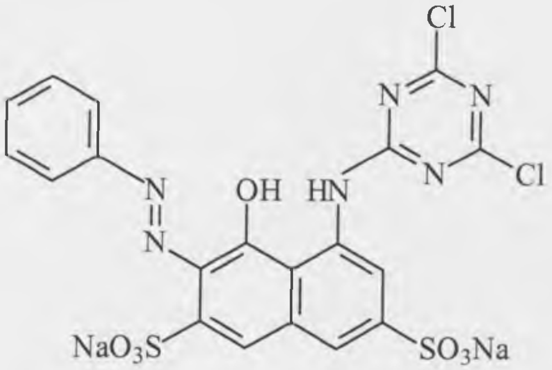


Figure 1.16 Chemical Structure of CI Reactive Red 2

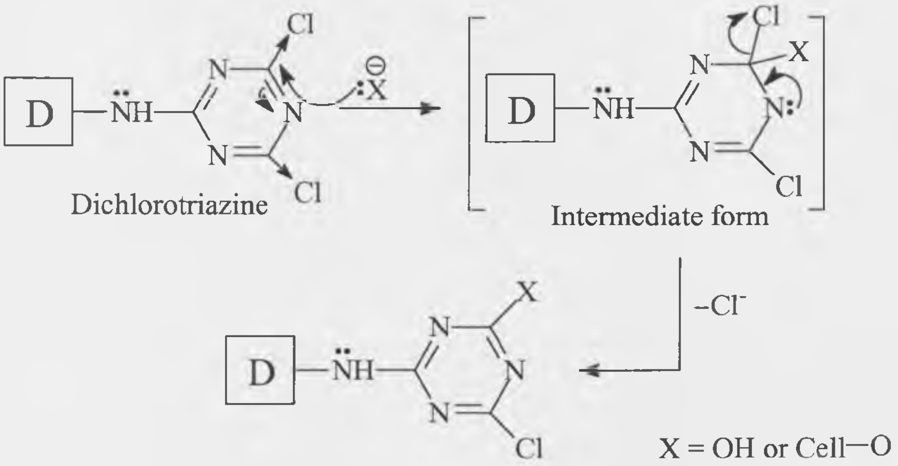


Figure 1.17 Nucleophilic substitution reaction occuring with cotton cellulose and hydroxyl anions

The second class (Figure 1.18) involves dyes that react with a cellulosic fibre by a nucleophilic addition reaction (Figure 1.19) via an activated carbon-carbon double bond in the dye. In the case of vinylsulphone dyes the unsaturated carbon-carbon double bond is only formed from an ester of hydroxyethylsulphone during the application; the most common precursor system used in dyes of this type is the sulphonic acid ester of β-hydroxyethylsulphone which eliminates to produce vinylsulphone residues during the dyeing process.

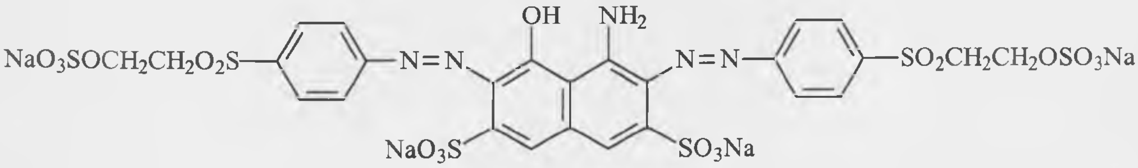


Figure 1.18 Chemical structure of CI Reactive Black 5

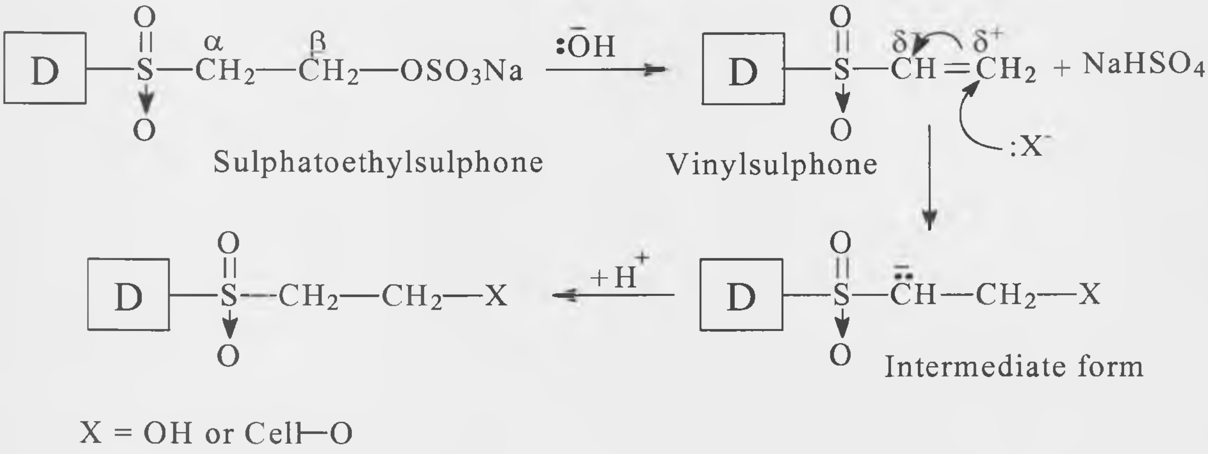


Figure 1.19 Nucleophilic addition reaction occurring with cotton cellulose and hydroxyl anions

Summifix Supra dyes can have both reactions of addition and nucleophilic. The general chemical structure of Summifix Supra dyes is shown in Figure 1.20.

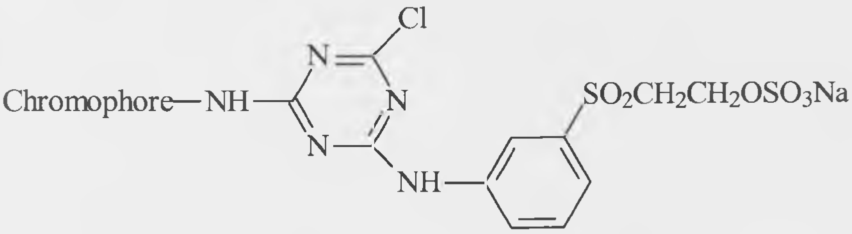
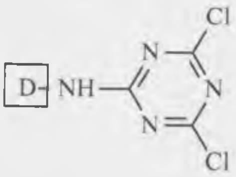
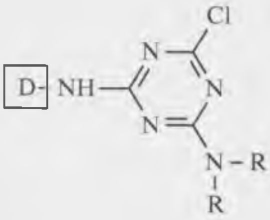
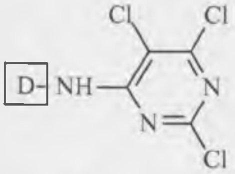
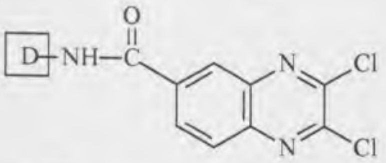
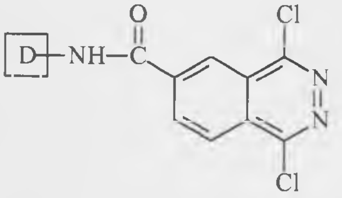
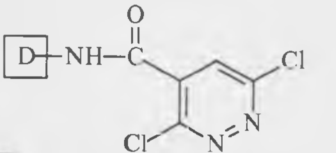
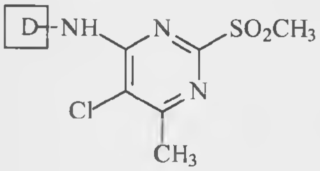
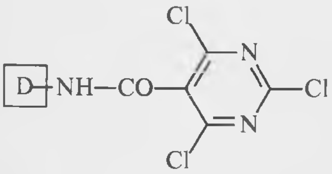
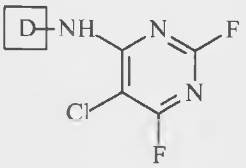


Figure 1.20 General structure of Sumifix Supra type dye containing MCT/SES reactive groups

Numerous reactive groups and systems of interest for dyeing and printing have been developed during the past 30 years [56-58]. Table 1.2 summarizes the different commercial reactive dyes for cellulosic fibre, with their reactive group, manufacturer's name and the year of their launch.

Reactive group	**Commercial name**	**Manufacturer**	**Year launched**	**Used for**
	Procion M	ICI	1956	Cellulose
	Procion H	ICI	1957	Cellulose
$\boxed{D}-SO_2-CH_2-CH_2-OSO_3H$	Remazol	Hoechst	1958	Cellulose
	Drimarene X	Sandoz	1959	Cellulose
	Levafix E	Bayer	1961	Cellulose
$\boxed{D}-NH-CO-CH_2-CH_2-OSO_3H$ $\boxed{D}-NH-CO-CH_2-CH_2-Cl$ $\boxed{D}-NH-CO-CH=CH_2$	Primazin	BASF	1961	Cellulose

	Elisiane	Francolor	1963	Cellulose
 $\boxed{D}$—NH—CO—CH$_2$–CH$_2$–SO$_2$R	Solidazol	Cassella	1964	Cellulose
$\boxed{D}$—NH—CO—CH=CH$_2$ (metal complex)	Procilan	ICI	1964	Wool
$\boxed{D}$—NH—CO—C(Br)=CH$_2$	Lanasol	Ciba	1966	Wool
	Levafix P	Bayer	1967	Cellulose
	Reactofil	Geigy	1968	Cellulose
	Verofix Levafix EA	Bayer	1970	Wool

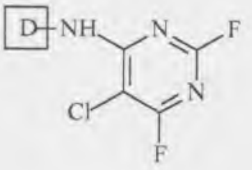
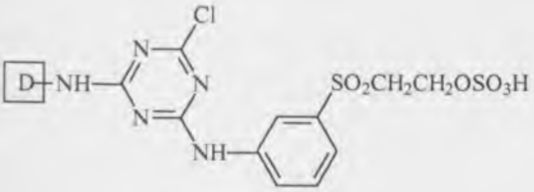
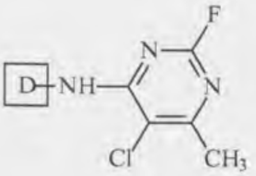
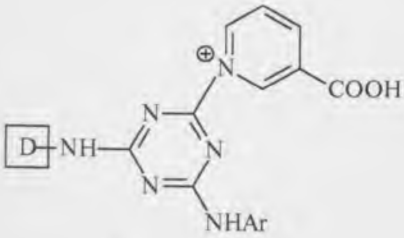
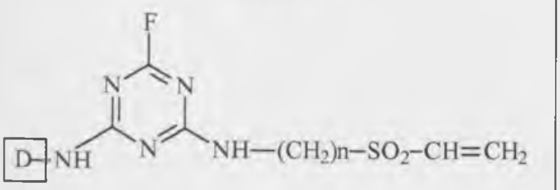
	Drimalan F Drimarene R and K	Sandoz Sandoz	1971 1971	Wool Cellulose
$\boxed{D}-PO(OH_2)$	Procion T	ICI	1977	Cellulose
	Sumifix Supra	Sumitomo	1980	Cellulose
	Levafix PN	Bayer	1981	Cellulose
	Kayacelon React	Nippon Kayaku	1984	Cellulose
	Cibacron C	CIBA	1988	Cellulose

Table 1.2 Major reactive groups of reactive dyes

The main advantages of reactive dyes are;

- Good light-fastness dyeings
- Give full range of colours on cotton and polyamide fibres
- Good fastness properties when dyed on cotton and polyamide fibres

Reactive dyes have some big drawbacks like;

- Hydrolysis of the dye giving coloured effluents
- Addition of electrolytes to increase their substantivity for cellulose
- Lengthy washing-off processes when applied to cellulosic fibres

1.4.3 Vat dyes

Chemically, vat dyes are one of two main classes which are derivatives of indigo and anthraquinone, the latter type being most popular. Vat dyes produce dyeings which display the highest overall fastness properties of all dyes used on cellulosic fibres. The water-insoluble dyes contain at least two, conjugated carbonyl groups ($-C=O$) that enable the dye to be converted, by means of reduction under alkaline conditions, to the corresponding water-soluble ionised leuco compound; it is in this form that the dye is adsorbed onto the fibre. Subsequent oxidation of the leuco derivative of the dye regenerates the parent, insoluble vat dye in the substrate; the dyeings are then soaped in order to develop the true hue and fastness. The dyeing cycle of vat dyes is shown in Figure 1.21.

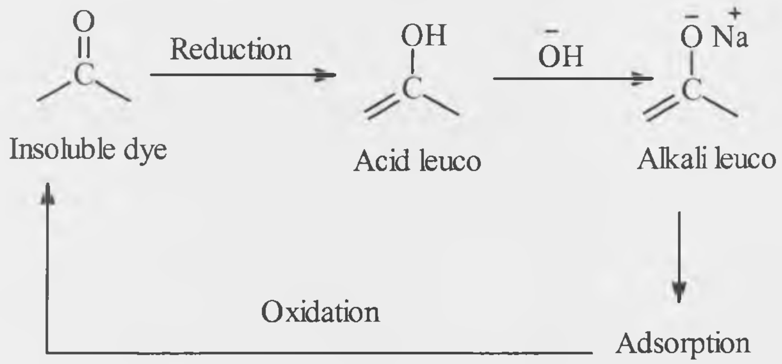


Figure 1.21 Dyeing cycle of vat dyes

Vat dyes are used predominantly for dyeing cellulosic fibres. Although the leuco dyes have also substantivity for wool and nylon, technical reasons (e.g. fibre damage when dyeing wool and the fastness properties on nylon) restrict their commercial significance for these fibres to the dyeing of nylon/cotton blends. The structures of vat dyes are shown in Figures 1.22 and 1.23. Different groups of vat dye structures have been illustrated in the literature, together with details of their preparation [59-68].

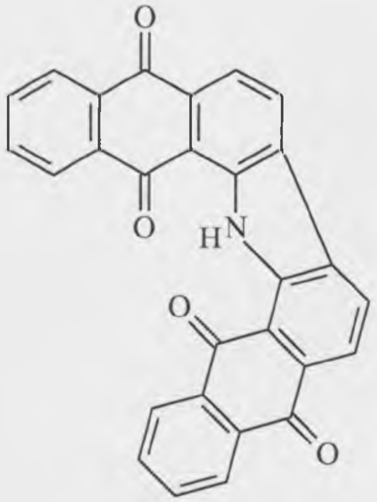


Figure 1.22 Chemical structure of CI Vat Yellow 28

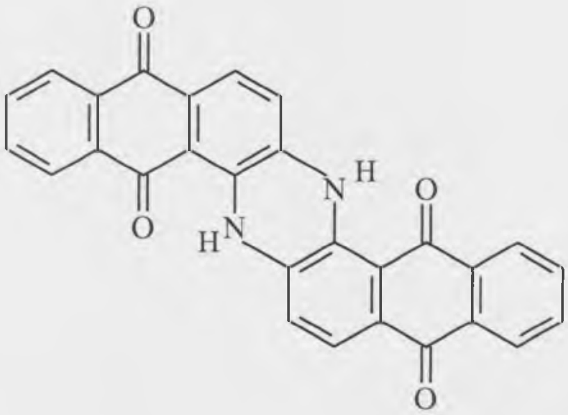


Figure 1.23 Chemical structure of CI Vat Blue 4

1.4.3.1 Reducing agents

The most important reducing agent in vat dyeing is sodium dithionite, generally referred to as hydrosulphite or hydros. Other reducing agents can only be used for special purposes, or have not yet been accepted in practice. The hydroxyalkylsulphinates is used in vat printing and for dyeing at temperatures above 100°C.

Thiourea dioxide is a strong reducing agent but in alkaline solutions it is just as sensitive to atmospheric oxygen as hydrosulphite. Although fresh prepared alkaline solutions of thiourea dioxide appear to be relatively stable, there is rapid formation of formamidinesulphinate. In this form, it is apparently even more readily oxidisable than hydrosulphite [69].

Sodium borohydride reacts too slowly for vat dyeing. From time to time, vatting processes using the readily biodegradable chemical hydroxyacetone have been proposed [70,71].

The properties of hydrosulphite are extremely important for the practical application of vat dyes. Its constitution as sodium dithionite ($Na_2S_2O_4$) has been known since the end of the 19th century but the erroneous designation hydrosulphite remains popular. The instability of the dithionite anion arises from the presence of the S – S linkage (Figure 1.24).

Sodium dithionite: $Na_2S_2O_4$

Structure of dithionite ion: $[O_2S - SO_2]^{2-}$

(a) Hydrolytic decomposition:

Neutral medium:

$$2Na_2S_2O_4 + H_2O \longrightarrow Na_2S_2O_3 + 2NaHSO_3$$

Alkaline medium

$$2Na_2S_2O_4 + 2NaOH \longrightarrow Na_2S_2O_3 + 2\,Na_2SO_3 + H_2O$$

(b) Reaction with atmospheric oxygen (alkaline medium):

$$Na_2S_2O_4 + 2NaOH + O_2 \longrightarrow Na_2SO_3 + Na_2SO_4 + H_2O$$

(c) Reaction with hydrogen peroxide (alkaline medium):

$$Na_2S_2O_4 + 3\,H_2O_2 + 2\,NaOH \longrightarrow 2\,Na_2SO_4 + 4H_2O$$

Figure 1.24 Reactions of sodium dithionite in neutral and alkaline media

In the anhydrous state the product is quite stable, but in contact with water it forms sodium thiosulphate and sodium bisulphite. The formation of acid products accelerates the decomposition, which proceeds exothermically and may result in spontaneous ignition. The same reactions occur in aqueous solution (without alkali) and both sulphur dioxide and sulphur have been identified as reaction products.

In the absence of air, hydrosulphite is extremely stable in alkaline solutions. Under these conditions it is more stable than hydroxyalkylsulphinates and the formamidinesulphinate that is formed from thiourea dioxide under alkaline conditions. It is only under extreme conditions that sodium dithionite forms the thiosulphate and sulphite as reaction products [72]; at high alkali concentrations and elevated temperatures some sulphide may also be produced [73]. Sodium dithionite is sensitive to atmospheric oxygen, an excess of dithionite must always be present. The amount of this excess depends on the application conditions, particularly on the influence of certain factors governing the rate of oxidation [74-76].

Vat dyes are applied to textile fibres in different ways;

1.4.3.2 Leuco dyeing

This is the oldest method of applying vat dyes to cellulosic fibres, the material being immersed in a solution of the leuco compound. Many dye makers have their own system of classifying their dyes. Vat dyes can be applied at temperatures of between 20 to 60 °C (the latter is perhaps most popular); higher temperatures (up to 115 °C can be used).

1.4.3.3 Prepigmentation method

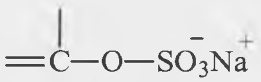
An aqueous dispersion of the unreduced vat dye is evenly distributed within the material and is subsequently reduced by stepwise addition of alkali and dithionite.

1.4.3.4 Semipigmentation method

The dispersed, unreduced dye, in the presence of reducing agent and alkali, is gradually converted to the leuco compound by means of a gradual increase in temperature. The rate of dyeing is thus controlled by the slow rate of reduction of dyes in the cold bath.

1.4.3.5 Solubilised vat dye powders

Vat dye makers have always been aware of how desireable it could be to have readily water soluble products, and for many years water soluble derivatives of vat dyes have formed a complete class of dyes unto themselves. They are called solubilised vat dyes. Such dyes are made by reacting vat-acid forms of some vat dyes to make the corresponding water soluble sodium salts of the sulphate esters. The functional group is shown in Figure 1.25.



$$=\overset{|}{C}-O-S\overset{-}{O_3}\overset{+}{Na}$$

Figure 1.25 Functional group of solubilised vat dye

From these water soluble anionic compounds, the original pigment can be restored by oxidation with acidified sodium nitrite [77].

1.4.3.6 Fastness properties of vat dyes

- Vat dyes give dyeings of higher fastness properties than other dye classes not only in use like wash-fastness and light-fastness but also to those factors important during fabric processing after yarn dyeing e.g. fastness to mercerising, soda boiling, chlorite and hypochlorite bleaching.

- If the dye is readily reducible, poor fastness ratings are obtained when the dyeing is washed at the boil in an alkaline medium. This applies to the flavaranthrones (e.g. CI Vat Yellow 1) and the pyranthrones (e.g. CI Vat Orange 9). This problem can be prevented by adding a mild oxidising agent, e.g. Ludigol.

- Indanthrones are sensitive to hypochlorite. In this case over-oxidation leads to the formation of azine groups and the dyeings become greener and duller. CI Vat Blue 4 is more prone to this problem than CI Vat Blue 6 [78].

1.4.4 Azoic colourants

Azoic components are used as to produce insoluble azo dye inside the fibre, usually on the textile fibre. Naphtols are usually used as for coupling components and azoic diazo components are primary amines or stabilized diazonium components which are called fast colour bases or fast colour salts. Azoic colourants provide bright shades of moderate to good wet-fastness and good light-fastness on cellulosic fibres. The first azoic colourant was discovered in 1880 by Thomas and Robert Holiday of Read, Holiday & Co., (Vacanceine Red) [79]. Cotton was impregnated with an alkaline solution of 2-naphthol and coupled with diazotised 2-naphthylamine.

In the past, green has presented a difficulty in the azoic range. Recently, however, some progress has been made by incorporating phthalocyanine. The presence of metallic atoms in the dye improved wet and light-fastness which can also be achieved by aftertreatment with a metallic salt.

1.4.4.1 CI Coupling components

Naphthols or Naphthol AS are insoluble in water and needed to be solublised form to apply to cellulose. They are applied as their sodium salts (naphtholates) dissolved in NaOH. In 1912 a new coupling component was introduced, the anilide of 3,2-hydroxynaphthoic acid by Winter, Laska and Zitcher, this was commercially introduced by Griesham Elektron Co. under the name of *Naphthol AS* (CI Coupling Component 2) [80] and is shown in Figure 1.26.

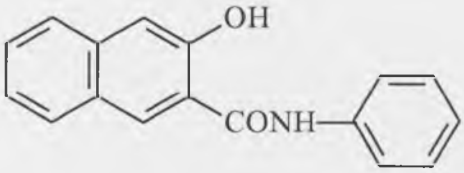


Figure 1.26 CI Coupling component 2

1.4.4.2 CI Diazo components

1. Fast Colour Bases (primary aromatic amines) which are diazotised to produce diazonium salts.

2. Fast Colour Salts which are stabilised diazonium salts in the form of:
    - Anti-diazotates, produced by the action of alkali on diazonium salt. On acidification, the antidiazotates generates the diazonium salt.

- Diazonium double salts by treatment of diazonium salt with zinc chloride
- Diazosulphonates ($Ar - N = N - SO_3Na$)

The normal procedure for azoic dyeings includes four major stags;

1. Application of Naphthols
2. Removal of access liquor from the surface
3. Development (Coupling)
4. Aftertreatment

The period of development depends on the coupling energy and rate of coupling of the diazo component, and is less dependent on the chemical constitution of the Naphthol. Fast colour bases and salts can be classified into four groups according to their coupling energies.

1.4.4.3 The advantages of azoic dyeing

- They are particular strong in the orange, red and Bordeaux sectors but the range also includes dark blue and black.
- Dyeings can be produced in certain bright full depths not always attainable with other classes of dyes.
- Materials can be dyed in many forms on various machines.
- Dyeings has excellent reproducibility.
- In general, the standard of fastness is high.

- Most combinations are dischargeable.
- They are economical viable.

1.4.4.4 The disadvantages of azoic dyeing

- Difficulties of handling the component chemicals under typical dyehouse conditions, particularly the diazotising of aryl amine fast bases.
- Complicated and time-consuming application procedures.
- The limitations of hue selection imposed by the need to avoid the cross-coupling that occurs if more than one azoic combination is applied.
- Rub-fastness properties of the dyeings are poor – moderate [78].

1.4.4.5 Stripping

Naphtholates, being alkali soluble, are readily stripped from undeveloped fabrics using boiling alkaline solutions. Azoic combinations can be chemically and irreversibly stripped with caustic, hydrosulphite, a dispersing agent and a little anthraquinone powder. The dye is destroyed by reductive cleavage of the azo group, and care has to be taken that the reduction products themselves do not stain the fabric.

The reducing agent in effect gives two hydrogen atoms to each of the nitrogen atoms in the azo chromophore $-N=N-$, to form two amino groups, $-NH_2 + H_2N-$. In the absence of a chromophore, the amines ($-NH_2$) formed are not heavily coloured but will often oxidize in the air to give coloured products if they are not removed quickly [81].

1.4.4.6 Fastness properties

At heavy depths, combinations can be selected which give dyeings offering good to excellent light-fastness and these azoic colours withstand washing even at the boil. However, at medium and pale depths light-fastness is markedly decreased. Many azoic pigments withstand chlorine bleaching, which can differentiate them from most sulphur dyes, but the blues are not outstanding in this respect. By contrast, fastness to peroxide bleaching can be less than satisfactory. The biggest single problem is the variable fastness to crocking, rubbing and solvent spotting.

Unfortunately all of the above properties are dependant on the extent to which the dyer has managed to keep the fibre surfaces free from pigmentry colour deposits; i.e., they depend upon the effectiveness of the colour application process itself as opposed to the properties of the colours.

Overall, the fastness properties of fabrics coloured with azoic combinations can be second only to those of vat dyeings, but the shade range and depth range for which this is the case, and where these products are most useful, is quite restricted. However, they are complementary to vat dyeings in that, for shade areas where vat dyeings are non-existent, azoic combinations are strong; i.e., in heavy scarlets, reds and Bordeaux [78].

1.4.5 Sulphur Dyes

Sulphur dyes are characterised by the presence of sulphur linkages in their molecule.

Generally, they are very complex and their true structure unknown. The first commercial sulphur dye marketed as Cachou de Laval (CI Sulphur Brown 1) [82] was prepared by Croissant and Bretonnier in 1873 by heating organic wastes such as sawdust with sodium polysulphide. In terms of quantity, sulphur dyes constitute the largest class of dyes used in cellulosics dyeing.

The dyes display moderate to good wet and light-fastness on cellulosic fibres; but their fastness to chlorine is very poor. Sulphur dyes are mostly used to black, brown, khaki, green and deep blue shades e.g. for work wear (overalls) and although the dyes cover a fair range of hues, there is no true red and other colours are in general duller than the corresponding ones produced with vat, reactive and azoic dyes but they are inexpensive. According to the *Colour Index* [38] sulphur dyes can be divided into four groups;

- CI Sulphur dyes (water insoluble)
- CI Leuco Sulphur dyes (water soluble)
- CI Solubilised Sulphur dyes (highly water soluble)
- CI Condense Sulphur dyes (now obsolete)

1.4.5.1 CI Sulphur dyes

These are water-insoluble dyes of low substantivity which need to be converted into soluble, substantive leuco compounds by treating them with reducing agent, sodium sulphide before being applied to the material and subsequently oxidising to regenerate the insoluble, parent sulphur dyes. The rate of dyeing is controlled by temperature rise and gradual addition of electrolyte (similar to direct dyes). The dyeing cycle of sulphur dyes is shown in Figure 1.27.

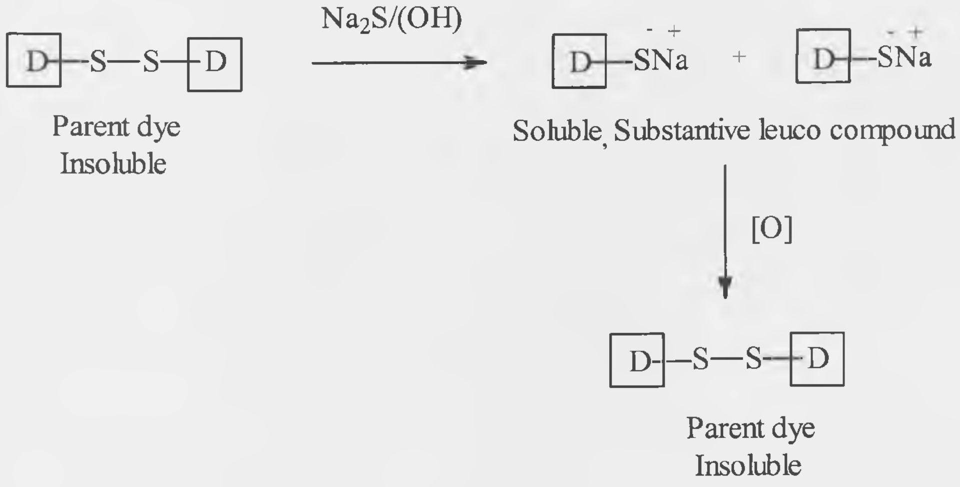


Figure 1.27 Dyeing cycle of sulphur dyes

1.4.5.2 CI Solubilised Sulphur dyes

These are highly water-soluble, thiosulphonic acid $(\mathrm{D{-}SSO_3^{-}Na^{+}})$ derivatives of sulphur dyes. They are non-substantive to the fibre but are converted into the substantive thiol form in the presence of alkali and reducing agent. After dyeing they are converted into the original insoluble sulphur dye in the fibre by oxidation (shown in Figure 1.28).

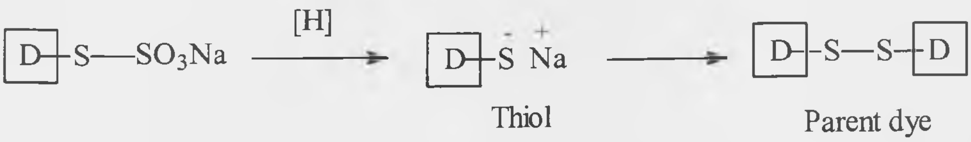


Figure 1.28 Dyeing reaction of sulphur dyes

1.5 Cellulose Modification

One of the major problems in the dyeing industry is pollution caused by unfixed dyes in effluents. Under strict legislation rules, dyeing industries have been pressurised to reduce unfixed dyes and salt concentration in effluents.

The increasing costs of energy, labour and chemicals have resulted in the dye house being one of the major areas in the textile industry from which increased efficiency is being sought. Combined with these factors there is urgent need to reduce the pollution of the environment from dye house effluents. It has been claimed that the loss of organic dyestuffs during processing in the textile industry is between 10 and 20%, resulting in a world-wide loss of about 94 000 tons annually. Approximately half of this dye finds its way into the environment. These factors have prompted research into the more efficient use of dyes. One area which has become the topic of research is the modification of cotton and cellulosic fibres to improve dye fixation and fastness.

1.5.1 Problems associated with dyeing cotton using reactive dyes

- Reactive dyes (except for a few neutral fixing dyes) need alkaline conditions for their covalent fixation with the fibre. Due to alkaline media, nucleophilic hydroxide ions compete with cellulosate anion for reaction with the dye. This results in formation of hydrolysed dye molecules which cannot react with the fibre and results in coloured dye effluents [83]. In addition, the build up of negative charge on surface of the dyed fibre due to covalent fixation of polysulfonated dye molecules, repels the dye molecules in solution preventing further uptake of dye. In some cases 40 – 50 % of the original dye is lost in the effluent. Increased awareness of environmental issues in the dyeing industry has been brought about by public concern and tougher legislation based on the "polluter pays" principle. Hence, an expensive aftertreatment is required to get rid of unfixed and/or hydrolysed dye from the dye effluent [84,85].

- To remove unfixed and/or hydrolysed fibre substantive dye, time consuming and energy intensive washing-off procedures are required.

- The presence of a high concentration of sodium sulphate or sodium chloride in dyebath is necessary to achieve adequate dye substantivity for the fibre. Since these salts are not consumed during dyeing, dye effluent results in an increased salinity in rivers which upsets the delicate balance of aquatic flora and fauna. Sodium sulphate increases the acidity of waterways and erodes concrete pipes [86]

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

Improving dye substantivity for cellulose will greatly reduce the need of electrolyte in the dyebath and will also improve dyebath exhaustion, hence reducing colour in the dyebath effluent. Increased dye substantivity can be achieved by chemical modification of cellulosic fibres.

1.5.2 Advantages and disadvantages of cotton modification

1.5.2.1 Advantages

1) Increased substantivity, exhaustion and fixation of the dyes on cotton.
2) No salt addition.
3) Reduced dye in effluents even with heavy shades.
4) Short soaping-off procedure.
5) Reduced effluent treatment cost.

1.5.2.2 Disadvantages

1) Reduced light-fastness with reactive dyes.
2) Fishy smell from fabrics treated with Servon XRK.
3) Increased cost due to additional modification step before dyeing.
4) Overall lengthy dyeing process.

1.5.3 Modification of cotton with low molecular weight amino compounds

Unlike cellulose, wool has a natural substantivity towards anionic dyes, especially under acidic conditions. Introduction of amine groups in the cellulose structure produces a fibre that may be considered to have similar dyeing characteristics as wool which can be dyed with reactive dyes at pH 5-7 without electrolyte, giving highly efficient reactive dyeings.

1.5.3.1 Amination of cotton through p-toluenesulphonyl chloride

In 1926 Karrer and Wehrli [87] tosylated cotton and then reacted this modified cotton with various amines to produce modified cotton. Figure 1.29 shows the tosylation of cotton with ρ-toluenesulphonyl chloride, followed by nucleophilic displacement of ρ-toluenesulphonic acid with ammonia to give cotton aminated with primary amino residues.

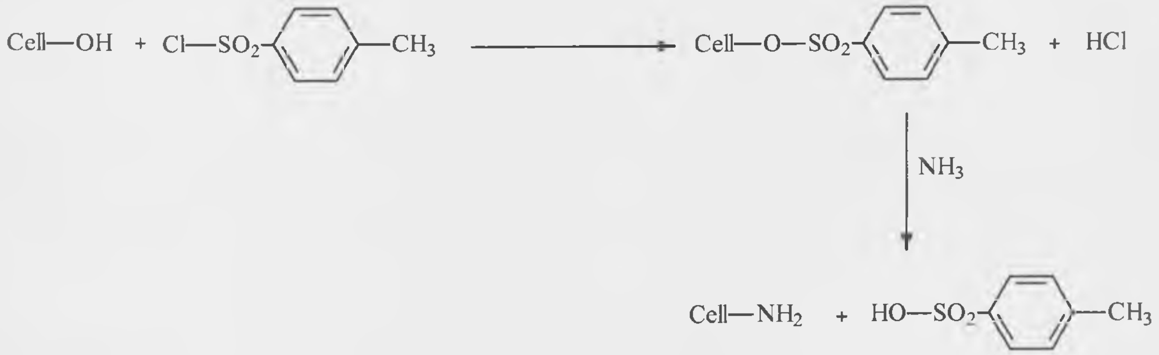


Figure 1.29 Tosylation of cotton and reaction of tosylated cotton with nucleophiles

Arrowsmith and Lewis [88] showed that these aminated cellulosic fibres could be dyed with reactive dyes from salt-free dyebaths. It has been also found that hydroxyethyl sulphone dyes would fix covalently on tosylated cotton (Figure 1.30).

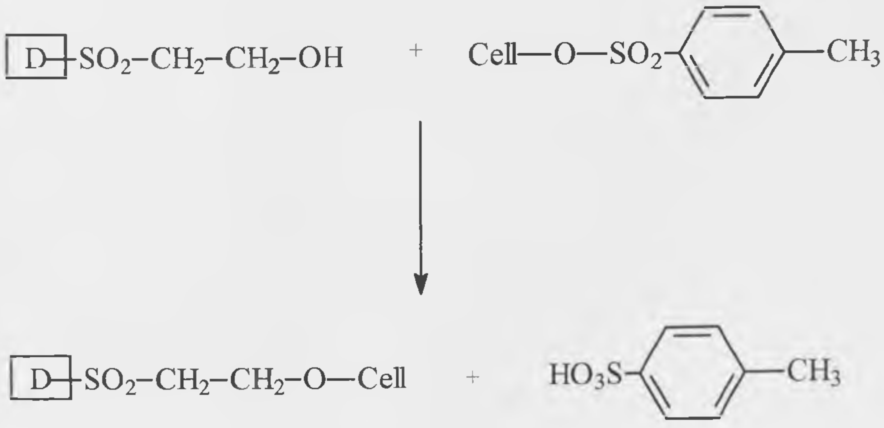
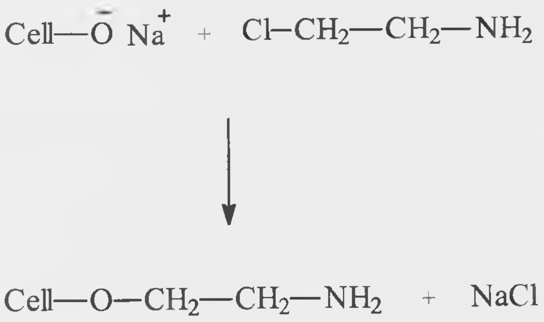


Figure 1.30 Reaction of hydroxyethyl sulphone dye with tosylated cotton

1.5.3.2 Amination of cotton through 2 – chloroethyl amine

Hartman [89] described the preparation of 2-aminoethylcellulose by reacting 2-chloroethylamine with alkaline cellulose as shown in Figure 1.31.



$$\text{Cell}-\overset{-}{\text{O}}\ \overset{+}{\text{Na}} + \text{Cl}-\text{CH}_2-\text{CH}_2-\text{NH}_2 \longrightarrow \text{Cell}-\text{O}-\text{CH}_2-\text{CH}_2-\text{NH}_2 + \text{NaCl}$$

Figure 1.31 Reaction of alkaline cellulose with 2 – chloroethylamine

1.5.3.3 Amination of cotton with sodium 2 – aminoethyl sulphate

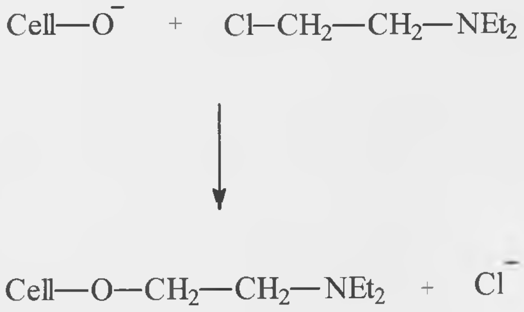
It was found that reaction of sodium 2-aminoethyl sulphate with cellulose was possible under alkaline conditions (Figure 1.32) and that this modified cellulosic fibre possessed increased affinity for direct dyes [90].

$$\text{Cell}-\text{OH} + \text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{OS}\overset{-}{\text{O}}_3\overset{+}{\text{Na}} \xrightarrow[15\ \text{min}]{130\ ^{\circ}\text{C}} \underset{\text{2-aminoethyl cellulose}}{\text{Cell}-\text{O}-\text{CH}_2\text{CH}_2\text{NH}_2} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$

Figure 1.32 Reaction of cellulose with sodium 2-aminoethyl sulphate

1.5.3.4 Amination of cotton through β-chloroethyldiethylamine

Diethylaminoethylcellulose (DEAE cellulose) has been prepared by reaction of cellulose with β – chloroethyldiethylamine (Figure 1.33) and this modified cellulosic fibre has exhibited increased uptake of acid, direct and reactive dyestuffs in subsequent dyeings [91].



$$\mathrm{Cell{-}O^{-}} + \mathrm{Cl{-}CH_2{-}CH_2{-}NEt_2}$$

$$\downarrow$$

$$\mathrm{Cell{-}O{-}CH_2{-}CH_2{-}NEt_2} + \mathrm{Cl^{-}}$$

Figure 1.33 Modification of cotton with β-chloroethyldiethylamine

1.5.3.5 Amination of cotton through esterification

Lewis and Lei [92] esterified cotton with chloropropionyl chloride (CPC) and then aminated the modified cotton by nucleophilic substitution of the chloro propionate residue with various amines to produce cotton fabrics containing primary, secondary, tertiary and quaternary amines where R1, R2, R3 = H or CH3 as shown in Figure 1.34.

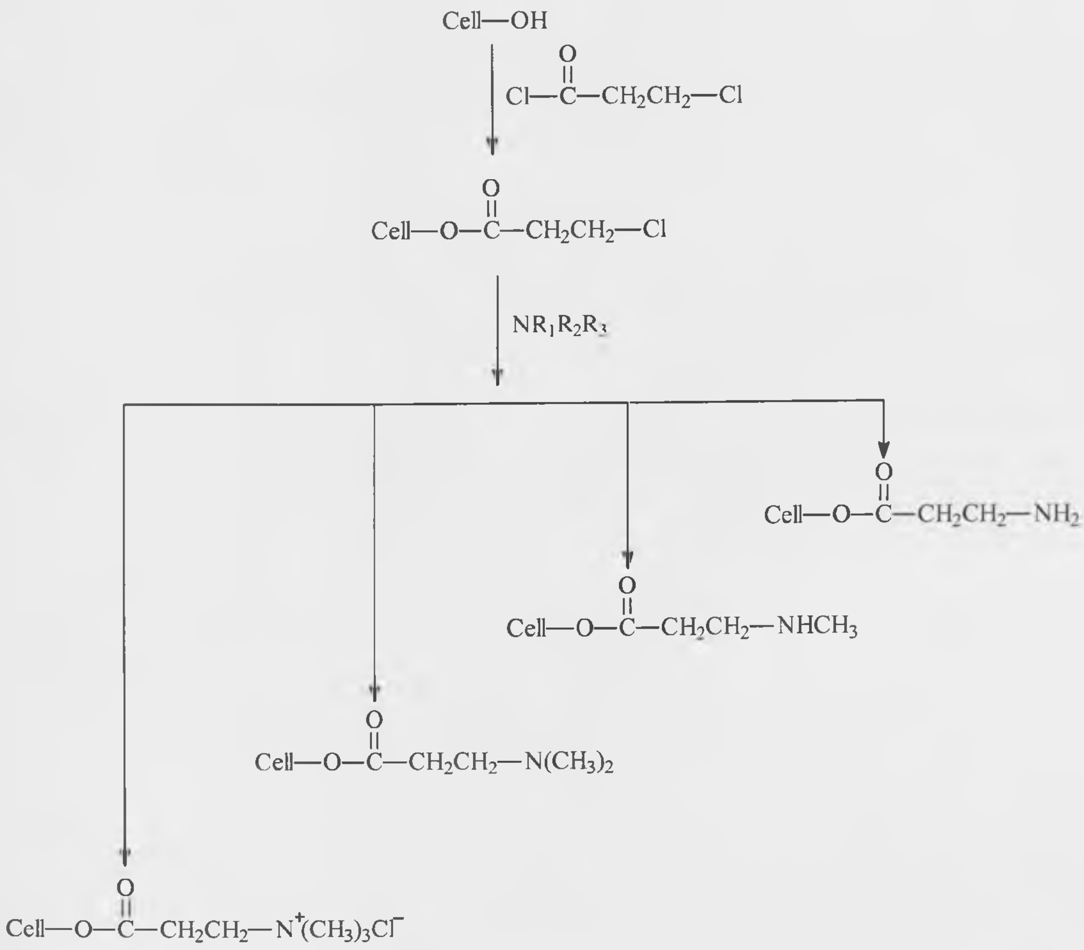
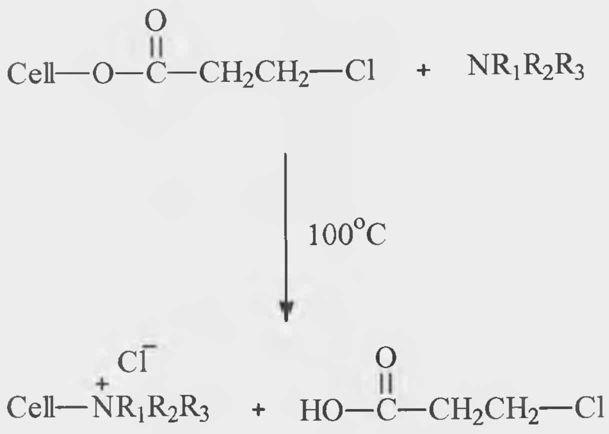


Figure 1.34 Reaction of cellulose with chloropropionyl chloride and subsequent amination reactions

Dyeing was carried out with reactive dyes under neutral to slightly acidic conditions in the absence of salt. The aminated cotton containing secondary amino residues (treatment with methylamine) gave the highest colour yields. When dyed with CI Reactive Red 5 (2% o.m.f., pH 5, at boil, no salt) the apparent amino residue efficiency, in terms of dyeuptake, was ranked as:

Secondary > tertiary > quaternary > primary



$$\mathrm{Cell{-}O{-}\overset{\overset{O}{\parallel}}{C}{-}CH_2CH_2{-}Cl} + \mathrm{NR_1R_2R_3} \xrightarrow{100^{\circ}C} \mathrm{Cell{-}\overset{+}{N}R_1R_2R_3\ \overset{-}{Cl}} + \mathrm{HO{-}\overset{\overset{O}{\parallel}}{C}{-}CH_2CH_2{-}Cl}$$

Figure 1.35 Substitution of cellulose propionate ester using amines

1.5.3.6 Amination of cotton through nicotinoyl thioglycollate

Lewis and McIlroy [93] synthesised nicotinoyl thioglycollate (NTG) and fixed it to cotton by a pad-thermofix process (Figure 1.36). Monochloro-s-triazine dyes gave excellent uptake in the absence of salt on this modified substrate and the best exhaustion and fixation values were obtained at pH 3.0 and at 80°C.

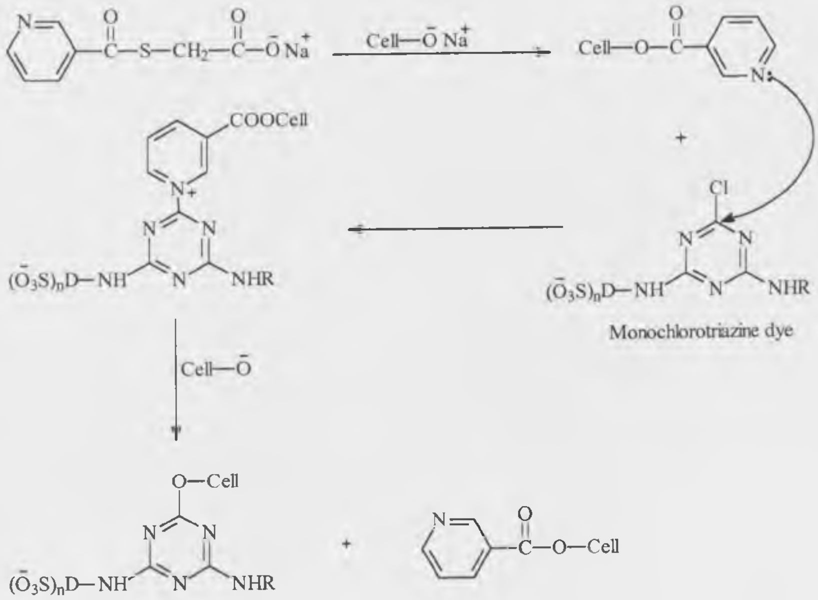
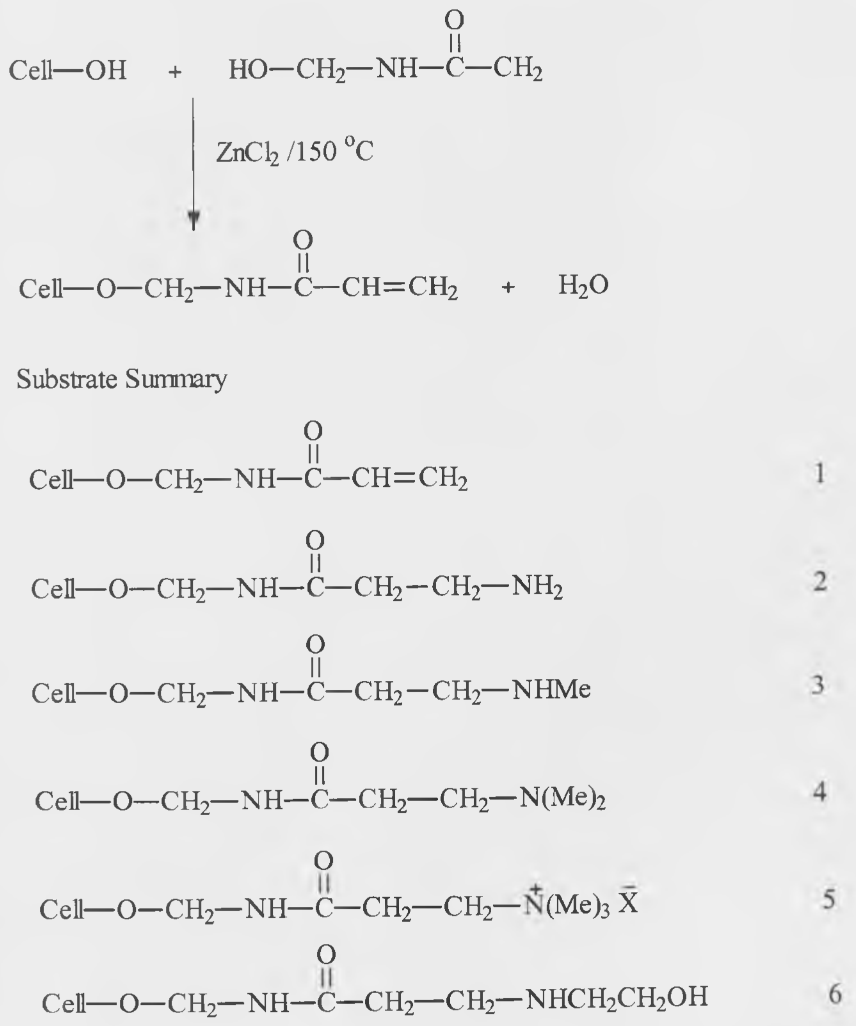


Figure 1.36 Reaction of cellulose with nicotinoyl thioglycollate

1.5.3.7 Amination of cotton through N-methylol type compounds

Lewis and Lei [94] modified cotton with N-methylolacrylamide (NMA) to investigate systematically the effect of attaching a variety of amines to the cellulose fibre by a simple pre-treatment. Cotton reacts with NMA in the presence of Lewis acid catalyst (Figure 1.37). Using the pendant double bond as a site for Michael addition with a variety of amines, a number of modified celluloses could be readily prepared.



$$\text{Cell—OH} + \text{HO—CH}_2\text{—NH—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—CH}_2 \xrightarrow{ZnCl_2\ /150\ ^{o}C} \text{Cell—O—CH}_2\text{—NH—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—CH=CH}_2 + H_2O$$

Substrate Summary

$$\text{Cell—O—CH}_2\text{—NH—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—CH=CH}_2 \qquad 1$$

$$\text{Cell—O—CH}_2\text{—NH—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—CH}_2\text{—CH}_2\text{—NH}_2 \qquad 2$$

$$\text{Cell—O—CH}_2\text{—NH—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—CH}_2\text{—CH}_2\text{—NHMe} \qquad 3$$

$$\text{Cell—O—CH}_2\text{—NH—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—CH}_2\text{—CH}_2\text{—N(Me)}_2 \qquad 4$$

$$\text{Cell—O—CH}_2\text{—NH—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—CH}_2\text{—CH}_2\text{—}\overset{+}{N}\text{(Me)}_3\ \overset{-}{X} \qquad 5$$

$$\text{Cell—O—CH}_2\text{—NH—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—CH}_2\text{—CH}_2\text{—NHCH}_2\text{CH}_2\text{OH} \qquad 6$$

Figure 1.37 Reaction of cellulose with N-methylolacrylamide

The amine-modified substrates were dyed with a dichloro-s-triazine reactive dye, CI Reactive Red 5 at pH 5; dyeings were produced in the absence of salt by raising the temperature to boil and boiling for an hour. Colour yield obtained on the modified substrates (ammonia and methylamine) is much greater than those achieved by the conventional dyeing method and dye fixation is higher (99%).

1.5.4 Modification of cotton through quaternary amino compounds

The pre-treatments increase the neutral substantivity of anionic dyes for cotton by introducing the new cationic sites. A quaternary, amino-epoxy derivative, glycidyltri-methylammonium chloride, was marketed by Protex as Glytac A, and its application chemistry (Figure 1.38) has been described by Rupin and co-workers, emphasising its use as a compound which offered enhanced dyeability of cotton with reactive and direct dyes [95,96]. The use of Glytac A was particularly useful in conjunction with direct dyes as it could be added to the dyebath without precipitation of the dye, to produce dyeings of higher tictorial strength and higher wash-fastness than conventional dyeing of direct dyes.

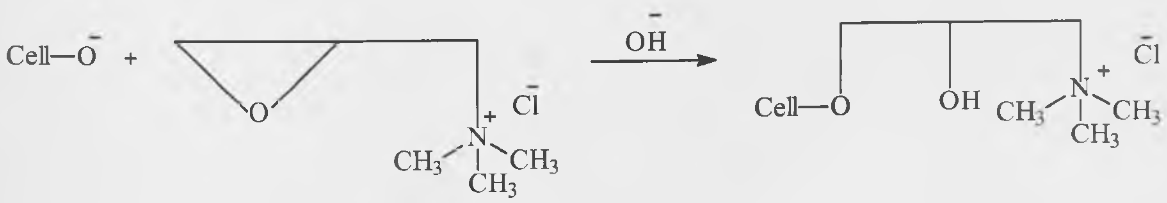


Figure 1.38 Reaction of cellulose with glycidyltri-methylammonium chloride

Cellulose may be treated with the less toxic chlorohydrin precursor of glycidyl-trimethylammonium chloride, since in the presence of sodium hydroxide 1-

trimethylammonium-2-hydroxy-3-chloropropane chloride is converted to the fibre-reactive epoxide form (Figure 1.39). Dyeing cotton pretreated with Glytac A in the absence of electrolyte with reactive dyes gave a high degree of covalent bonding under boiling, neutral dyebath conditions along with high dyebath exhaustion [97].

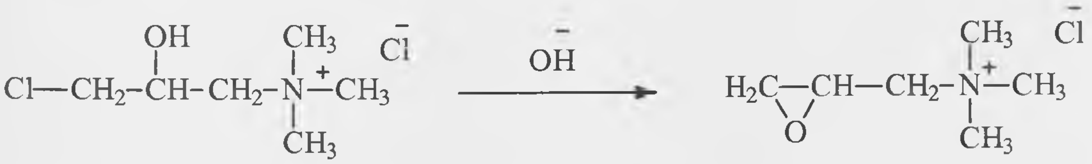


Figure 1.39 Conversion of 1-trimethylammonium-2-hydroxy-3-chloropropane chloride to its fibre-reactive epoxide form

The improved colour yield values of reactive dyes on the Glytac-treated fibre were attributed by Rupin [98] to the strong binding of the anionic sulphonated hydrolysed dye through electrostatic interaction with the fixed cationic sites. Dyeings on Glytac-treated cellulose are insensitive to removal in standard reactive dye identification tests. There was a partial decolouration of the reactive dyeings when the dyeings were treated with pyridine oxalate solution, indicating the existence of an ionically bonded portion. Therefore, when the modified cellulose is dyed, two species (I and II) may be formed (Figure 1.40). Maximum wash-fastness may only be expected from species II.

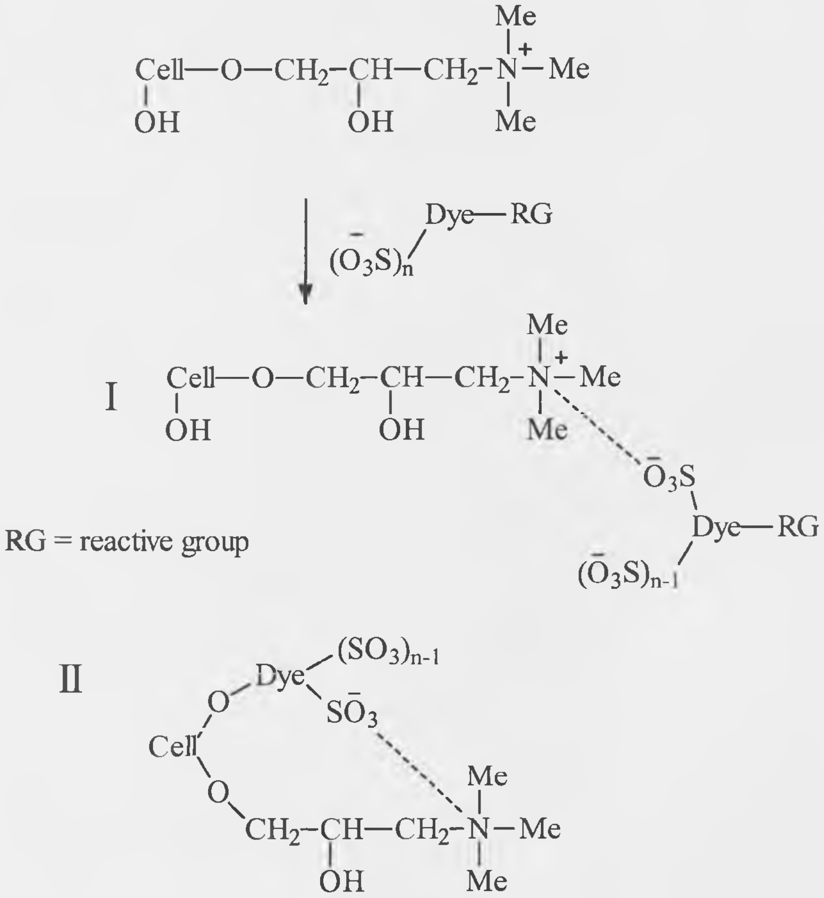


Figure 1.40 Application of reactive dyes to pre-cationised cotton

The normal soaping process does not remove the unfixed dye (species I) from the quaternised fibre properly, alkaline soaping will promote further fixation of unreacted, electrostatically bonded, reactive dye absorbed on the treated fibre to give species II.

Rupin [95] studied the stability of the epoxide to hydrolysis in aqueous solutions (Figure 1.41) at various temperatures and with various concentrations of alkali.

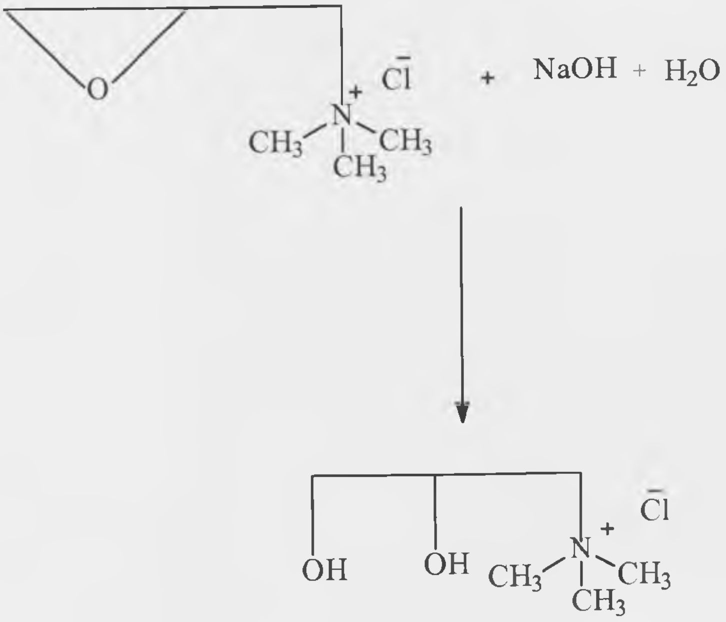


Figure 1.41 Alkaline hydrolysis of N,N,N-trimethyl (2-oxiranyl)methanaminium chloride

It was noticed that while the epoxide was stable in water at 20°C, increasing the temperature and/or pH resulted in increased hydrolysis of the epoxide group. Rupin also found that by cationising cellulose with N,N,N-trimethyl (2-oxiranyl) methanaminium chloride, either as a pre-treatment or during the dyeing stage, the uptake of reactive dyes by the modified cellulose was greater than on untreated cellulose and no loss of fastness to washing or light was observed. Rupin [99] confirmed these findings but also noted a dulling of shade in dyeings on cotton treated with N,N,N-trimethyl (2-oxiranyl) methanaminium chloride and a decrease in some fastness properties, particularly to washing with salt solutions.

Van Rensburg studied [100] that the modification of cellulosic fibres with N,N,N-trimethyl (2-oxiranyl) methanaminium chloride and subsequent cold pad-batch dyeing of the pre-treated cellulose. He concluded that when dyeing by this method using reactive dyes for cellulosic fibres, a N,N,N-trimethyl (2-oxiranyl) methanaminium chloride pre-treatment generally reduced dye fixation by about 20%. Furthermore, fastness to rubbing and alkaline perspiration tests were slightly reduced compared to control pad-batch dyeing on unmodified cotton.

Herbert, Barkhuysen and Van Rensburg [101] stated that cellulosic fibres pre-treated with N,N,N-trimethyl (2-oxiranyl) methanaminium chloride exhibited increased dye uptake and dye fixation; this resulted in the development of no salt and no alkali reactive dyeing processes for cotton. Fastness properties were not generally affected by this pre-treatment but some decrease in fastness to light, wet rubbing and alkaline perspiration was noted. The simultaneous application of a reactive dye and N,N,N-trimethyl(2-oxiranyl)methanaminium chloride to cellulosic fibres by a cold pad-batch process increased dye fixation by up to 30%. Again the treatment resulted in slightly reduced fastness properties, particularly fastness to light, compared with cotton dyed by a conventional reactive dyeing process. N,N,N-trimethyl (2-oxiranyl) methanaminium chloride was also applied to cotton after dyeing. This resulted in improved dye fixation but a decrease in fastness properties, particularly alkaline perspiration fastness. Fastness properties of dyed fabric were slightly better when the N,N,N-trimethyl (2-oxiranyl) methanaminium chloride was applied prior to dyeing rather than as an aftertreatment.

Hauser and Tabba [102] studied the effect of dye structure on the fixation of reactive dyes on cotton fabric modified using 3-chloro-2-hydroxy-N,N,N-trimethyl-1-propanaminium chloride and concluded that the structures of both the chromophore and the reactive system in the reactive dye molecule had an effect on dye fixation and that the improvement seen compared with un-modified cotton varied depending on the structure of the chromophore and reactive system.

Reaction of 4-(3-chloro-2-hydroxypropyl)-4-methylmorpholin-4-ium chloride with a stoichiometric amount of alkali such as NaOH produces 4-methyl-4-(2-oxiranylmethyl) morpholin-4-ium chloride (Figure 1.42).

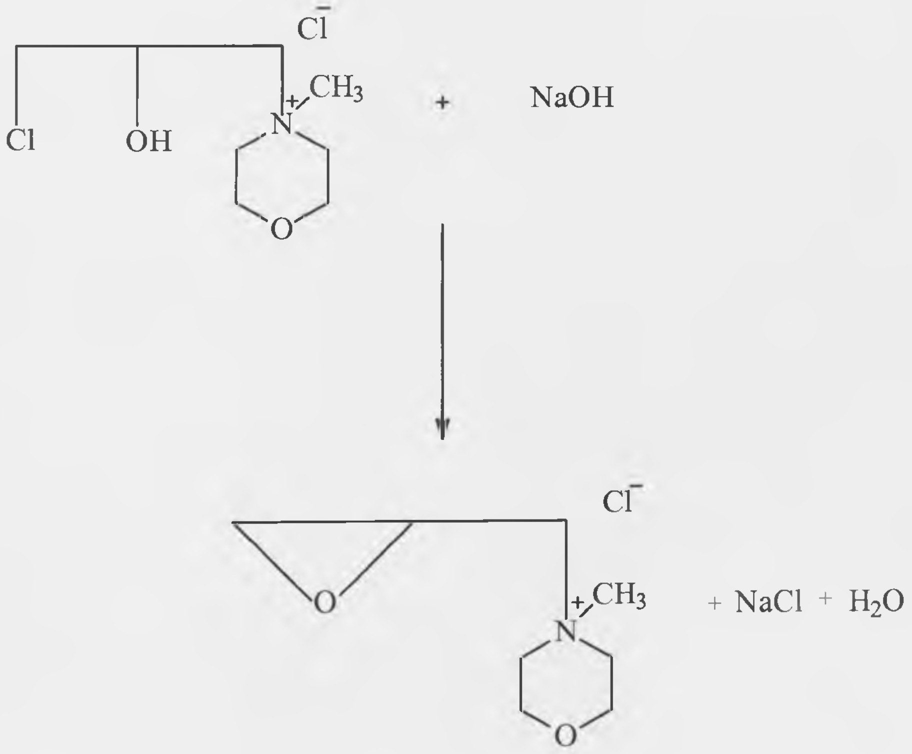


Figure 1.42 Reaction of 4-(3-chloro-2-hydroxypropyl)-4-methylmorpholin-4-ium chloride with alkali

4-methyl-4-(2-oxiranylmethyl)morpholin-4-ium chloride has been used to improve the dye uptake and fastness of direct dyeings on cotton [103]. 4-methyl-4-(2-oxiranylmethyl)morpholin-4-ium chloride was applied with alkali by pad-batch, pad-steam, pad-thermofix and print processes before, during and after dyeing with direct dyes. 4-methyl-4-(2-oxiranylmethyl)morpholin-4-ium chloride has also been used as a pre-treatment for cotton to improve the uptake of acid, vat and reactive dyes on the modified substrate [104]. 4-methyl-4-(2-oxiranylmethyl)morpholin-4-ium chloride was again applied with alkali by pad-batch, pad-steam, pad-thermofix and print processes and also without alkali by a pad-thermofix process. This pre-treatment improved the uptake of reactive dyes from a neutral, salt-free dyebath and increased fixation of said dyestuff on the modified cellulosic fibre.

1.5.5 Modification of cotton with amino polymers

1.5.5.1 Modification of cotton with sandene 8425

Sandene 8425, developed by Courtaulds Co. and Sandoz Chemical Corp., is a polyamino cationic resin. [105]. It is highly substantive to cellulose under alkaline conditions. Cellulose treated with this polymer (about 5% o.w.f.) exhibited increased substantivity for anionic dyes and reacted with reactive dyes under neutral to weakly acidic conditions. This process has resulted in the development of a single bath, single stage process for dyeing polyester/cellulosic blends. The disadvantage of this treatment is a reduction in light-fastness of some azo chromophores and dulling in shade.

1.5.5.2 Modification of cotton with chitosan

Rippon [106] studied the pre-treatment of cellulosic fibres using chitosan to decrease the speckling effect of immature and dead cotton in dyed cotton fabrics. Chitosan is an unbranched, long chain polymer derived from chitin by acid hydrolysis. The chemical structure of chitosan is similar to that of cellulose but with one of the secondary hydroxyl groups in each ring replaced by an amino group (Figure 1.43).

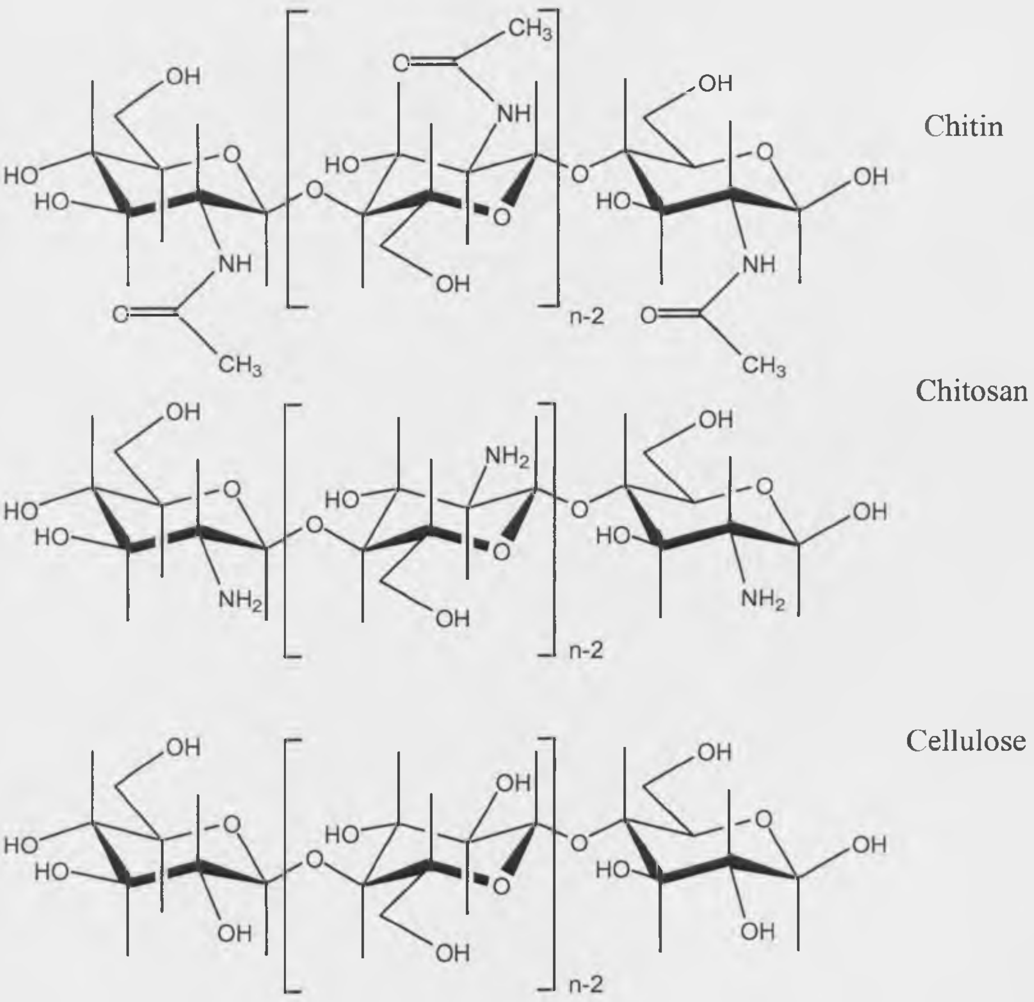


Figure 1.43 Chemical structures of chitin, chitosan and cellulose

Cotton pre-treated with chitosan showed improved substantivity for direct dyes and improved coverage of immature and dead cotton in the fabrics; however the pre-treatment decreased the wash and rub-fastness of the dyed fabrics. Because of this deleterious effect on fastness properties a further treatment was required using a fibre-reactive quaternary compound to achieve high fastness properties.

1.5.5.3 Modification of cotton with Hercosett 125

Burkinshaw, Lei and Lewis [107] used a commercial polyamide epichlorohydrin (PAE) polymer solution, Hercosett 125 (Hercules Powder Corpn.), to modify cotton that can be dyed with reactive dyes in the absence of salt and under neutral conditions. The reactive group in this polymer is the azetidinium cation as shown in Figure 1.44.

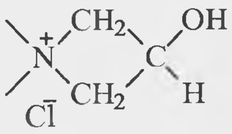


Figure 1.44 Azetidinium cation

Cellulose when modified with polyamide-epichlorohydrin (PAE) resin, produced a reactive surface that contained reactive and nucleophilic sites (Figure 1.45). Substantivity and fixation of dyes with Hercosett 125 treated cotton was found to be much higher than untreated cotton and the substantivity of the anionic reactive dyes increased with decreasing application pH. Dyes with high reactivity gave high fixation on Hercosett pre-treated cotton and the poor fixation of low reactive dyes was attributed to the comparatively higher reactivity of the azetedinium cation for the available highly nucleophilic sites in the resin. The light-fastness of the dyeings was also inferior.

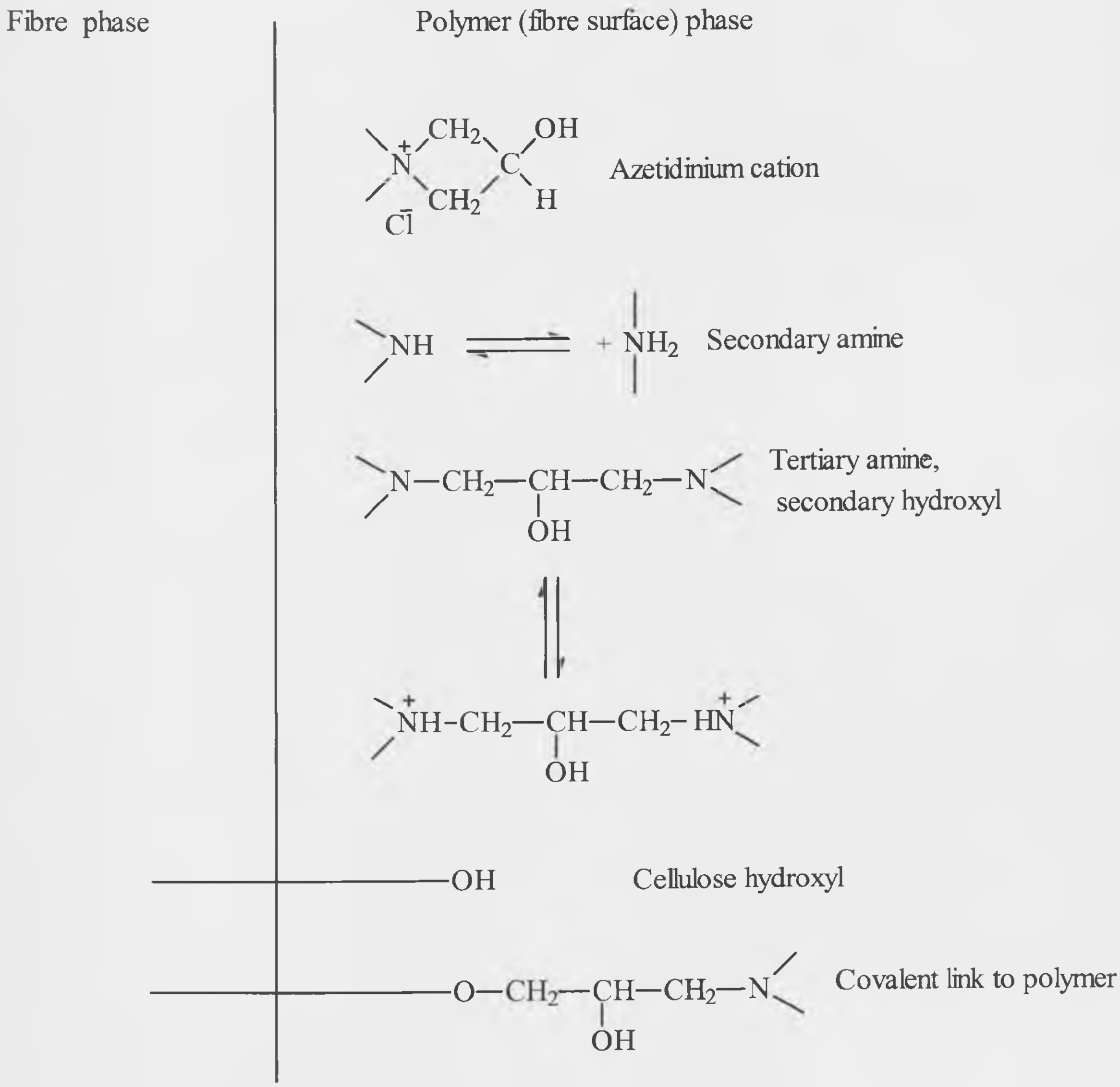
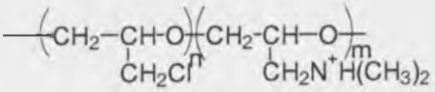


Figure 1.45 Reactive surface of Hercosett-treated cotton

Lewis et al. [108,109] included thiourea in aqueous solution of PAE resin in order to increase the fixation efficiency of low reactivity dyes and to increase light- fastness of the treated fabric. Thiourea addition improved the reactive dyeability of the treated fabric. However, the light-fastness remained poor. The addition of ethylene diamine instead of thiourea to the PAE resin bath produced similar results of increased dye build-up with lower light-fastness.

1.5.5.4 Modification of cotton with Polyepichlorohydrin-amine polymers

Polyepichlorohydrin-amine polymers with the likely structure in Figure 1.46 have been synthesised and examined by Wu and Chen [110]. Cotton pre-treated with this polymer shows increased dyeability for reactive dyeing and can be dyed without salt. Dyeings on treated cotton exhibited high wash-fastness but light-fastness was 1-2 points down compared to conventionally dyed material.



$$-\left(CH_2-\underset{CH_2Cl}{\underset{|}{C}H}-O\right)_n\left(CH_2-\underset{CH_2N^+H(CH_3)_2}{\underset{|}{C}H}-O\right)_m$$

Figure 1.46 Likely structure of polyepichlorohydrin-amine polymers

1.5.5.5 Modification of cotton with Polymer PL (ICI)

Polymer PL (ICI), a cationic acrylic copolymer, was applied to cotton fabric by a pad-dry method. It was reported [111] that, in addition to improve the dyeability of cellulosic fabrics with reactive dyes, this pre-treatment was not harmful to the light-fastness of dyeings and gave no dulling, giving shades of comparable hue to untreated samples dyed conventionally.

1.5.6 Modification of cotton to produce reactive fibres

Lewis and Lei [94] have shown that cotton can be modified using N-methylolacrylamide (NMA) and that reaction of this activated substrate with the nucleophilic alkylamino dyes is possible (Figure 1.47). The main advantage of this process is that because the dyes are not reactive no hydrolysis of the dye is possible; fixation of the dye on the fibre is thus efficient yielding dyed cellulosic substrates with high fastness to washing and light.

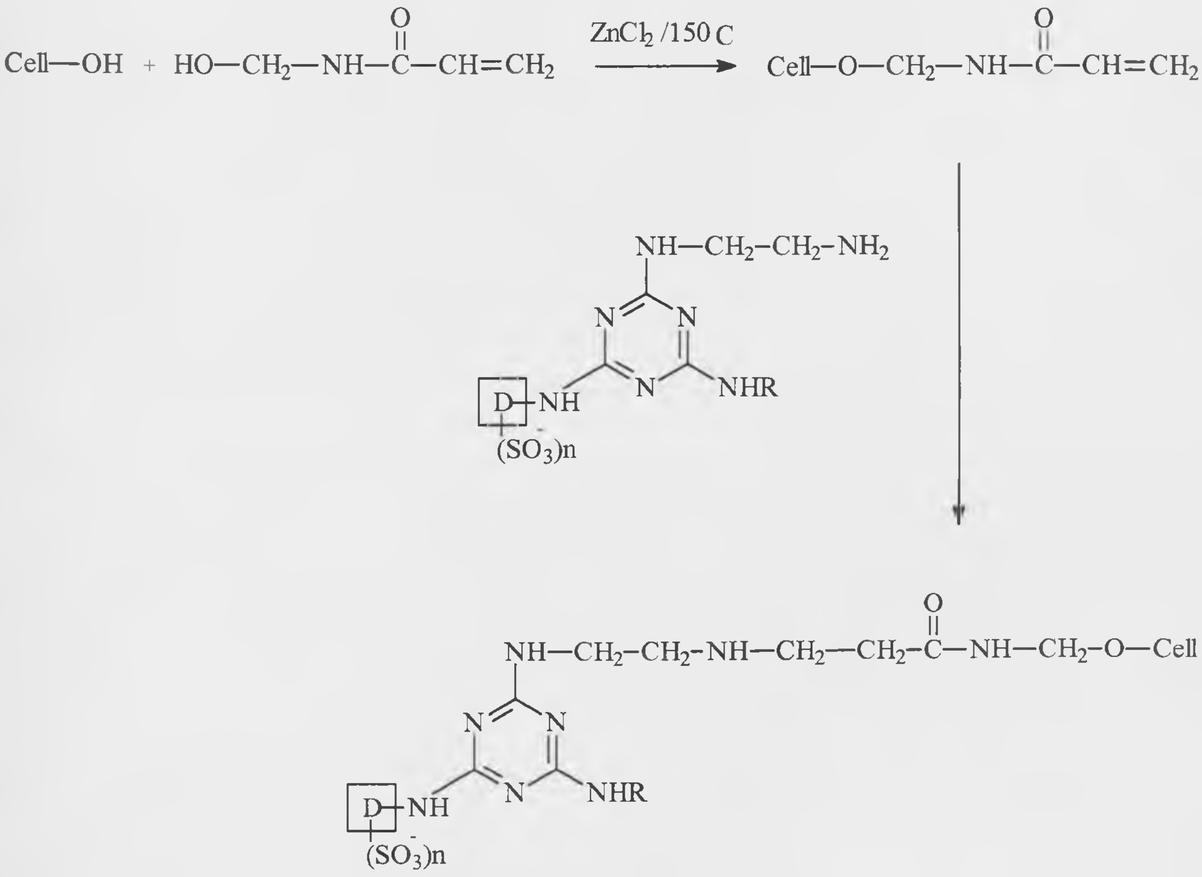


Figure 1.47 Modification of cellulose with N-methylolacrylamide and dyeing of the modified fibre with nucleophilic alkylamino dyes

When these reactive cellulosic fibres were dyed at depths of shade greater than 4% o.m.f. the build-up of dye fixed on the fibres tailed-off significantly. The biggest factor in this was thought to be fixed sulfonate anion build-up acting as a dye resist (Figure 1.48).

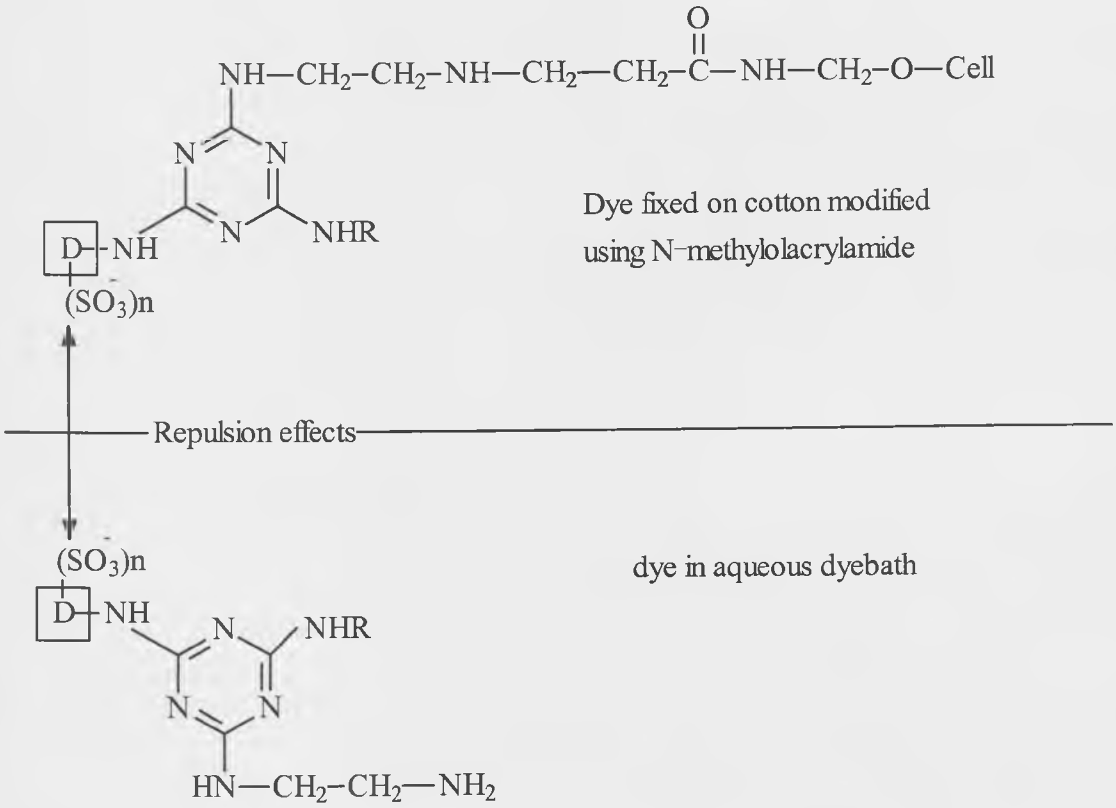


Figure 1.48 Fixed sulfonate anion build-up acting as a barrier to dyeing heavy shades on modified fibres

Lewis and Lei [112] studied the reaction of 2, 4-dichloro-6-(2-pyridinoethylamino)-s-triazine (DCPEAT) with cotton as shown in Figure 1.49. The modified fibre has monochloro-s-triazine residues which can react with amino-alkyl dyes without salt addition.

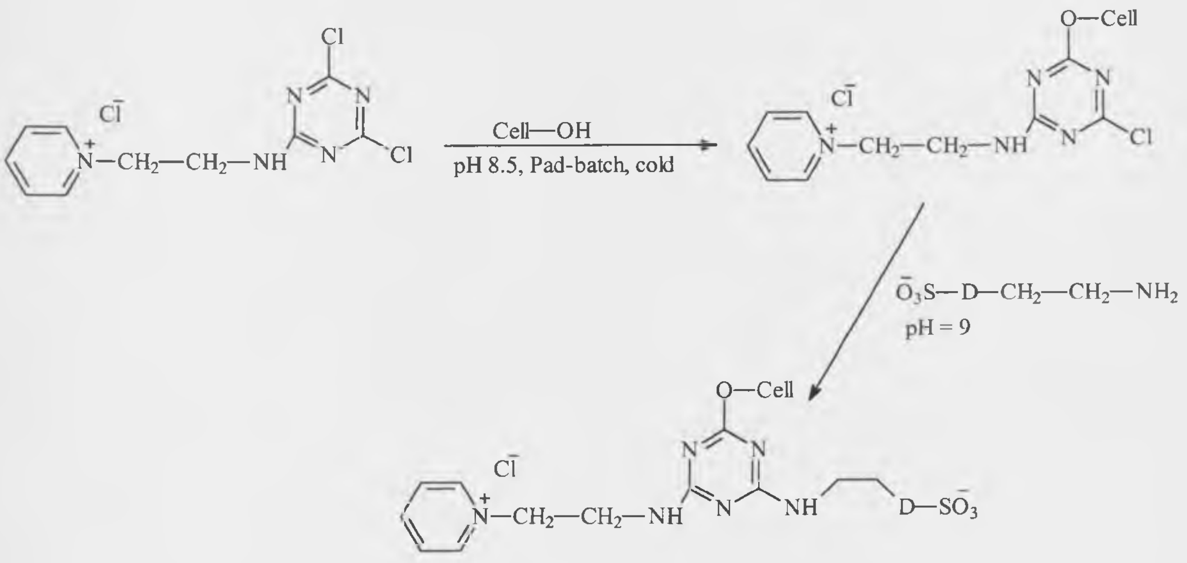


Figure 1.49 Modification of cellulose with 2, 4-dichloro-6-(2-pyridinoethylamino)-s-triazine (DCPEAT)

The advantage of this method over the conventional dyeing method is that dye hydrolysis does not occur during the dyeing process and thus full use of the dye can be made. Dyeing of aminoalkyl dyes on DCPEAT pre-treated cotton were found to be very good. Brilliant colours were always produced of similar hue to the parent reactive dyes on untreated cotton. Wet-fastness and light-fastness were at the same high level as that of conventional reactive dyes on untreated cotton.

1.5.7 Modification of cotton with cross-linking agents

Cross-linking agents were used to activate cellulosic fibres to react with dyes containing a suitable nucleophilic group, was first studied and commercialised in the late 1960s

[113-122]. BASF developed 1,3,5-triacroylamino-hexahydro-s-triazine (FAP) to use as a poly-functional crosslinking agent to fix nucleophilic Basazol dyes containing aminosulphonyl groups [113,114].

Lewis and Ho [123] investigated the optimum conditions for reaction between FAP and polyamide fibre; they showed that FAP-treated nylon could be reacted with amines to improve the subsequent dyeing of the treated nylon with reactive (nucleophilic) dyes.

Jabbar and Lewis [124] studied the cross-linking of 1,3,5-triacroylamino-hexahydro-s-triazine (FAP) with cellulosic fibres to fix reactive dyes. The FAP cross-linked cotton fabric was aminated with ammonia, ethanolamine, diethylenetriamine and cysteamine. The FAP cross-linked and subsequently aminated cotton fabrics were dyed (as illustrated in Figure 1.50) at pH 7.0 and 5.0. Exhaustion, fixation and colour yield values of dyeings were slightly better at pH 5.0 as compared to the dyeings at pH 7.0. This may be due to the protonation of the amine moiety on the fibre which would enhance the affinity of the fibre towards $—SO_3^-$ groups in the dye.

The dyeings of FAP cross-linked samples aminated with diethylenetriamine (DETA) with CI Reactive Red 2 (at 2% o.m.f.) gave very good colour yield, exhaustion and fixation (up to 94%) values because DETA is a trifunctional amine and has more sites available for cross-linking and subsequent dyeings. Cysteamine treated samples also exhibited good dye fixation (about 80%) as the thiol group has highly nucleophilic character and enhances the cysteamine fibre reaction. Ammonia and ethanolamine proved to be less effective as compared to the DETA and cysteamine but they still show much better dye fixation as compared to the untreated samples.

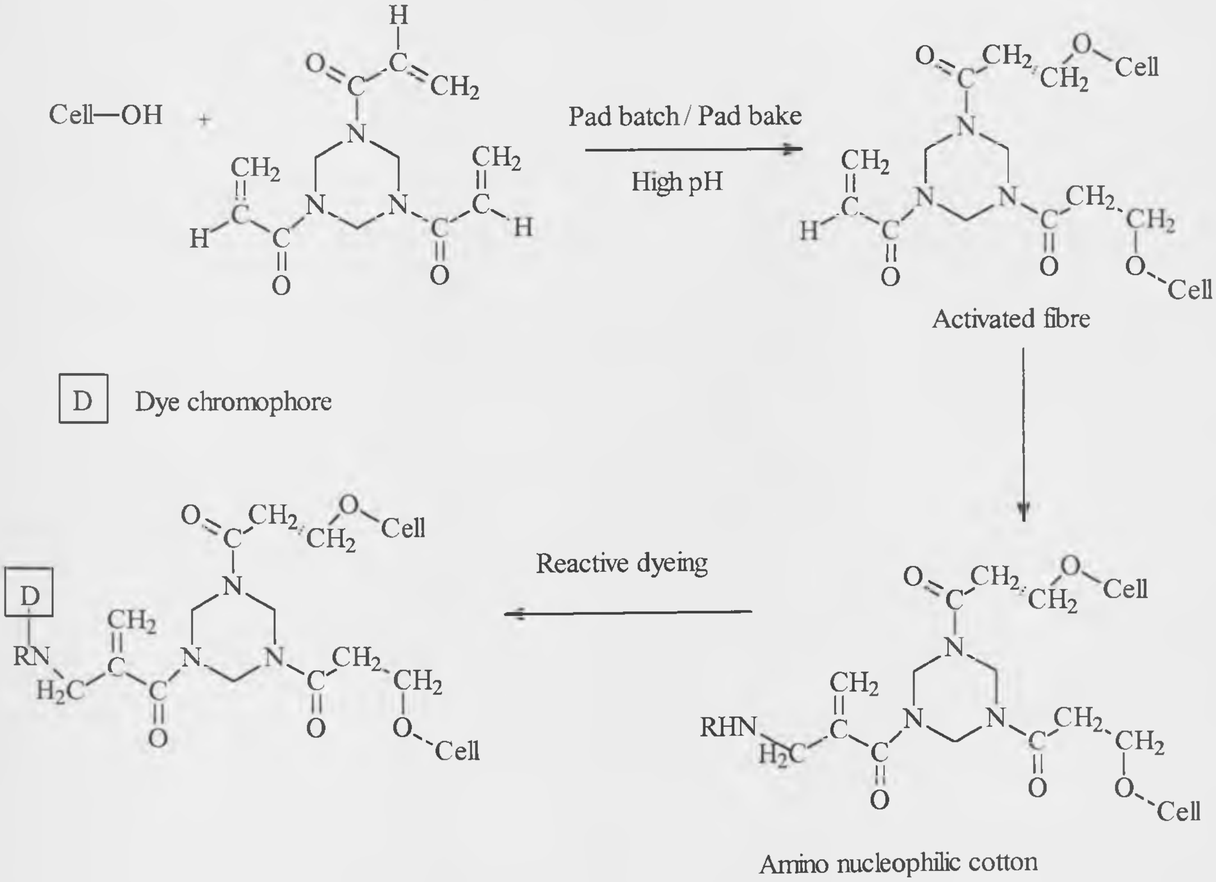


Figure 1.50 Reaction of FAP modified cellulose with amines and thus aminated cellulose with CI Reactive Red 2

N-methylol type crosslinking agents [125] such as dimethyloldihydroxyethylene urea (DMDHEU) or 1,3-bis(hydroxymethyl)-4,5-dihydroxy-2-imidazolidinone are applied to cotton after dyeing [126], as pre-treatment with these compounds generally makes cellulosic fibres undyeable.

Non-methylol type agents e.g. 4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone (DHDMI) as shown in Figure 1.51, shows some substantivity for reactive and direct dyes, especially low molecular mass direct dyes [127,128]. The acidic conditions employed in the dyebath resulted in the hydrolysis of the DHDMI finish and hence reduced its smooth-drying performance [129].

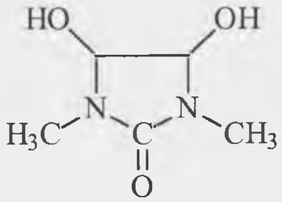


Figure 1.51 The structure of DHDMI (4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone)

Cotton treated with DMDHEU in combination with hydroxyalkylamines by thermal fixation (3 min, 150C, plus Lewis acid catalyst) gave substrates with high anionic dye substantivity, especially under acidic (pH 3.0 – 3.5) dyebath conditions (Figure 1.52) [130,131].

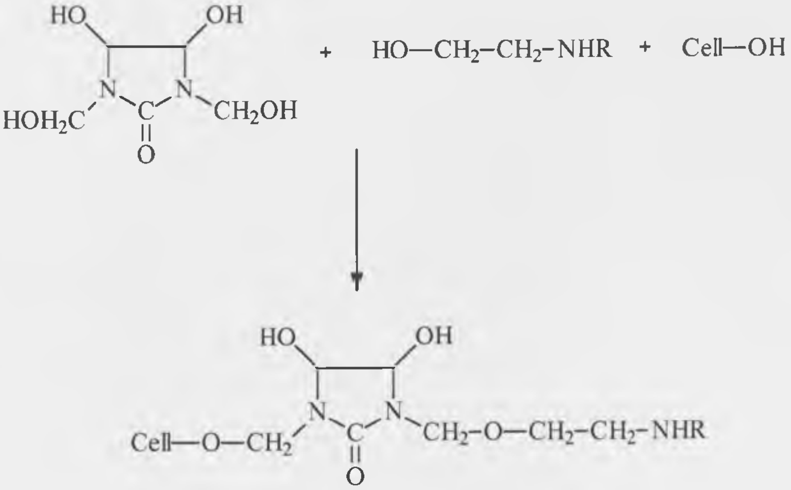


Figure 1.52 Reaction of cellulose with DMDHEU in combination with hydroxyalkylamine

The tetra-functional polycarboxylic acid crosslinking agent, butanetetracarboxylic acid (BTCA), in combination with hydroxyalkylamine additives, such as monoethanolamine (MEA), diethnolamine (DEA), triethanolamine (TEA) and tris(hydroxymethyl)amino-methane (THAM), were applied to cotton to determine if dyeable ester-crosslinked fabrics could be obtained [132]. Dyeing with acid, direct and reactive dyes was good to very good in most cases.

1.6 Acid dyes

In the *Colour Index* they are classified as 'Acid dyes' or 'Mordant dyes'. The name 'Acid dye' derives from the use of an acidic dyebath. Most pre-metallised and mordant dyes are acid dyes. In the case of mordant dyes, the dyeings are aftertreated with a suitable metal ion mordant, usually chromium. Infact, mordant dyes are often referred to as chrome dyes. The metal in pre-metallised dyes is incorporated into the dye molecule during the manufacturing process [133].

Acid dyes are classified by their dyeing behaviour and wet-fastness properties rather than chemical composition. Dyeing behaviour is determined by relative molecular mass (r.m.m.) and degree of sulphonation. The arbitrary classification is stated below [134];

- Level-dyeing or equalising acid dyes
- Fast acid, half-milling or perspiration-fast dyes
- Acid milling dyes

- Super-milling dyes

In this research non-metallised and pre-metallised dyes have been used.

1.6.1 Non-metallised acid dyes

These dyes can be applied to nylon in the pH range 3.0 to 7.0. The wet-fastness of these dyes on nylon varies from moderate to good and their light-fastness is generally in the blue scale range 5 to 6 [135].

These small relative molecular mass (Mr) dyes are applied to nylon at low pH values so that dye-fibre substantivity arises from ion-ion electrostatic forces operating between the amino end groups of the nylon which is protonated under acidic conditions and the anionic dye. Under these conditions the dyes display very good migration and levelling characteristics but low fastness. Dyes with higher molecular mass show greater substantivity for the fibre but the migrational properties are lower although a higher wet-fastness is achieved with these dyes.

These dyes have been divided into three sub-groups due to their varying application and fastness properties. Stevens [136] used a 1 to 3 grouping for classifying non-metallised acid dyes on nylon.

Group 1 Dyes with little affinity under neutral or weakly acidic conditions, but which exhaust under strong acidic conditions.

Group 2 The largest group of dyes that exhaust on to nylon within the pH range 3.0 to 5.0

Group 3 Dyes that exhibit a high affinity for nylon under neutral or weakly acidic conditions (pH 5.0 to 7.0).

The water solubility of these dyes is due to the presence of one or more sulphonic groups. These dyes belong to the azo chemical class which represents the largest class of dyes, providing an extremely large gamut of shades. The examples of these dyes are shown in Figures 1.53 – 1.55.

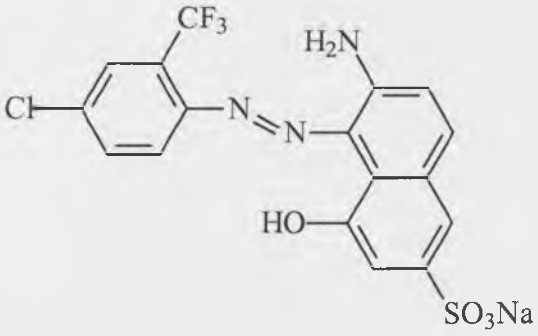


Figure 1.53 Erionyl Rubin GP (CI Acid Red 266, monoazo)

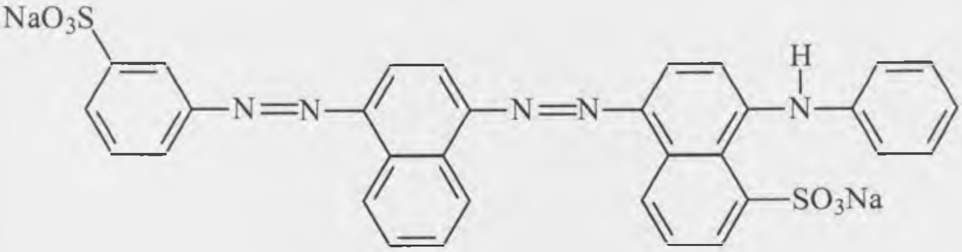


Figure 1.54 Erionyl Navy Blue R (CI Acid Blue 113, disazo)

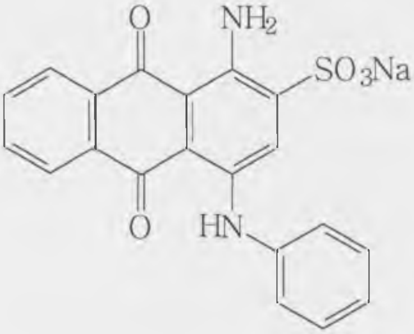


Figure 1.55 Tectilon Blue GRL (CI Acid Blue 25, anthraquinoe)

1.6.2 Pre-metallised acid dyes

These dyes are based upon mordant dyes, the difference is that metal-complex dyes have the mordanting metal incorporated within the dye molecule so do not require a separate mordanting stage. There are two classes of metal-complex dyes 1:1 metal complex and 1:2 metal complex dyes. As the name suggest, the metal complex dye comprises one metal atom (usually chromium) coordinated with one or two molecules of a dye ligand [81]. The structure CI Acid Blue 193 is shown in Figure 1.56.

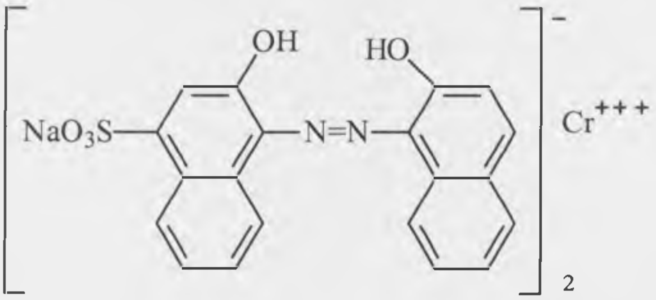


Figure 1.56 Chemical structure of CI Acid Blue 193

The 1:1 metal-complex dyes are applied under strongly acidic conditions for satisfactory migration to take place. These conditions can cause severe degradation of nylon fibres and this limits the use of these dyes for dyeing nylon. A few dye manufacturers have tried to overcome this problem by either using sulphamic acid in place of sulphuric acid or by including of a levelling agent to reduce fibre damage.

The 1:2 metal-complex dyes exhibit high saturation values and excellent compatibility in mixture shades, they have good wet-fastness and light-fastness properties. However, their ability to cover chemical variations within the fibre varies significantly and is dependant upon molecular size and substituent solubilising groups. The shade gamut of these dyes is restricted to dull shades and the class is deficient in bright blues and reds. There is a wide range of 1:2 metal-complex dyes available for nylon; different manufacturers ranges differ in optimum pH range but they are generally applied from a neutral to weakly acidic dyebath [137].

1.7 Aims and objectives

The dyeing of cellulosic fibres suffers from problems such as significant amount of colour loss in effluents, low substantivity of the cellulosic fibres for the anionic dyes, rub-fastness and lengthy washing-off processes. In this project, cotton has been chemically modified with Servon XRK (3-chloro-2-hydroxy-N, N, N-trimethyl-1-propanaminium chloride) and NMM derivative [4-(3-chloro-2-hydroxypropyl)-4-methylmorpholin-4-ium chloride)] by pad-batch method.

Vat, acid, azoic and reactive dyes have been used in this research. Vat dyes have been applied to the NMM and Servon XRK modified cotton fabrics and the dyeing results have been compared with the dyeings on the unmodified cotton fabric. The dyeing properties of non-metallised and pre-metallised acid dyes have been studied by applying them to the Servon XRK modified cotton fabric. The dyeings from pre-metallised acid dyes on Servon XRK modified cotton fabric have been studied by comparing with wool dyeings. Naphthol AS was applied by long liquor, pad-batch and pad-batch-dry method on the unmodified and Servon XRK modified cotton fabric, followed by coupling with Fast Red salt FRN. Naphthol AS was co-applied with Servon XRK to the unmodified cotton and its dyeing properties have been studied. Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF have been applied to the unmodified and the Servon XRK modified cotton fabric by the exhaustion method. A set of reactive dyes were also co-applied with NMM by cold pad-batch method and the dyeing results were compared with the dyeings from the given set of reactive dyes by applying them to the unmodified cotton fabric without NMM.

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Chapter 2

Experimental Techniques

2.1 Introduction

Measurement is a fundamental aspect of all branches of science and engineering and without accurate analytical systems; scientific research would be very difficult. Recently many advanced analytical methods and apparatus have been introduced to the chemical and dyeing research field which have strongly enhanced technological progress in this field. During this research, the analytical techniques used for identification and characterisation are ultra-violet and visible spectroscopy, spectra-flash and Light-microscopy.

2.2 Measurement of colour

It is a very important and crucial to measure accurately how much colour is on different fabrics. Colour measurement is a very sensitive measurement tool both for research and industrial marketing. The colour can be measured with Spectra flash using the Kubelka-Munk equation for solid samples or with UV/VIS Spectrophotometer for solutions.

2.2.1 Colour strength

The colour strength of a dye is a measure of its ability to impart colour to other materials. The light is absorbed in the visible range of the spectrum and can be expressed mathematically as a colour strength value of the dye. The relation between the dye concentration on the fibre and the light reflectance is expressed by the Kubelka- Munk equation;

$$K/S = (1-R)^2/2R \qquad (2.1)$$

Where;

K= absorption co-efficient

S = scattering co-efficient

R = Fractional reflectance

The value of R (Reflectance) at λ_{max} (maximum wavelength) is used to calculate the K/S value which is directly proportional to the dye concentration on the fibre. The sum of K/S value in the visible region of the spectrum is calculated the equation;

$$Fk = \sum_{\lambda=400}^{700} (K/S)_2[x_{10}(\lambda) + y_{10}(\lambda) + z_{10}(\lambda)] \qquad (2.2)$$

Where x10λ, y10λ and z10λ are the colour matching functions for the 10° observer at each wavelength measured (ISO 7724/1-1984) [1].

2.2.2 Measurement of dye fixation using fk values

After dyeing the fabric the fk values are measured before and after the soaping-off stage to calculate how much dye has fixed to the substrate. Fixation value is determined by using the equation;

$$\%F = (fk_1/fk_2).100 \qquad (2.3)$$

Where;

fk_1 = colour strength before soaping-off

fk_2 = colour strength after soaping-off

2.3 UV/Vis Spectroscopy

2.3.1 Elementary Theory

When a molecule absorbs radiation, its energy increases. This increase is equal to the photon absorbed and is expressed by the relationship:

$$E = h\nu = hc/\lambda \qquad (2.4)$$

Where h is Planks constant, ν and λ are the frequency and wavelength of radiation respectively and c is the velocity of light. The change in energy may be in the electronic, vibrational or rotational energy of the molecule. The pure rotation of a bond gives rise to absorption in the microwave region [2], molecular bond vibrations are associated with absorption in the microwave region and molecular bond vibrations are associated with absorption of energy from the infrared region. The electronic energy transitions normally give rise to absorption or emission in the ultraviolet and visible regions of the electromagnetic spectrum. An electronic energy level of a molecule under normal conditions is called its ground state and higher electronic levels represent the first and second excited states respectively. For each electronic level there are the ground and several possible excited vibrational states and similarly, for each vibrational level there are the ground and excited rotational levels.

Energy absorption usually causes the promotion of an electron, dependent on the energy difference between the two relevant orbitals which in turn depends on the type of electrons involved such as σ, π and n electrons.

For a molecule, according to the types of valence electrons forming single bonds are called σ electrons; the characteristic functions and charge densities of these electrons are rotationally symmetrical with respect to the valency axis. The electrons responsible for double bonds are called π electrons; the characteristic functions and charge densities of which have an oscillation nodal plan through the valency axis [3]. In unsaturated systems, π electrons predominantly determine the energy states of the electron sheaths which are excited by the absorption of visible or ultra-violet light. Unshared electrons or non-bonded electrons in molecules containing atoms like nitrogen, oxygen etc. usually called n electrons. Among these different types of electrons, the π electrons are very useful to the colourist. Since their absorption is usually in the 200-800 nm region.

Conjugation of double bonds causes an increase in the wavelength of absorption. Those substances containing one or more unsaturated linkages, which often confer colour to substances, are called chromophores [4] and generally absorb in the 200-800 nm region. The wavelength corresponding to the absorption maximum (λ_{max}) varies from chromophore to chromophore. The factors governing the λ_{max} of chromophores are the difference in the electronagetivities of elements forming the double bond and the relative ease in forming the double bond.

2.3.2 Absorption Intensity

From the practical point of view, there are two empirical laws which have been derived concerning absorption intensity. Individually these are known as Lambert s law and Beers law. However, it is common practice for them to be combined into the Beer-Lambert law which states that the absorbance (A) of a sample at a particular wavelength is proportional to the concentration (c) of a sample (in moles per litre) and the path length (1) of the light through the sample (in centimetres). Absorbance (A) is further defined as the ratio of incident light (I_0) to the intensity of transmitted light (I). Hence

$$A = \log_{10}(I_0/I) = \varepsilon cl \qquad (2.5)$$

Where the constant ε is called the molar extinction coefficient and is a measure of how strongly the compound absorbs at that wavelength [5]. In general, the more conjugated the chromophore, the more intense the absorption and hence higher the value of ε provided that the concentration of a sample is known. If the ε value for a compound is known at a given wavelength, measuring the absorbance at this wavelength permits the determination of the concentration of the sample.

2.3.3 The UV/Visible Instrument

A typical example of a UV spectrophotometer is shown schematically in Figure 2.1.

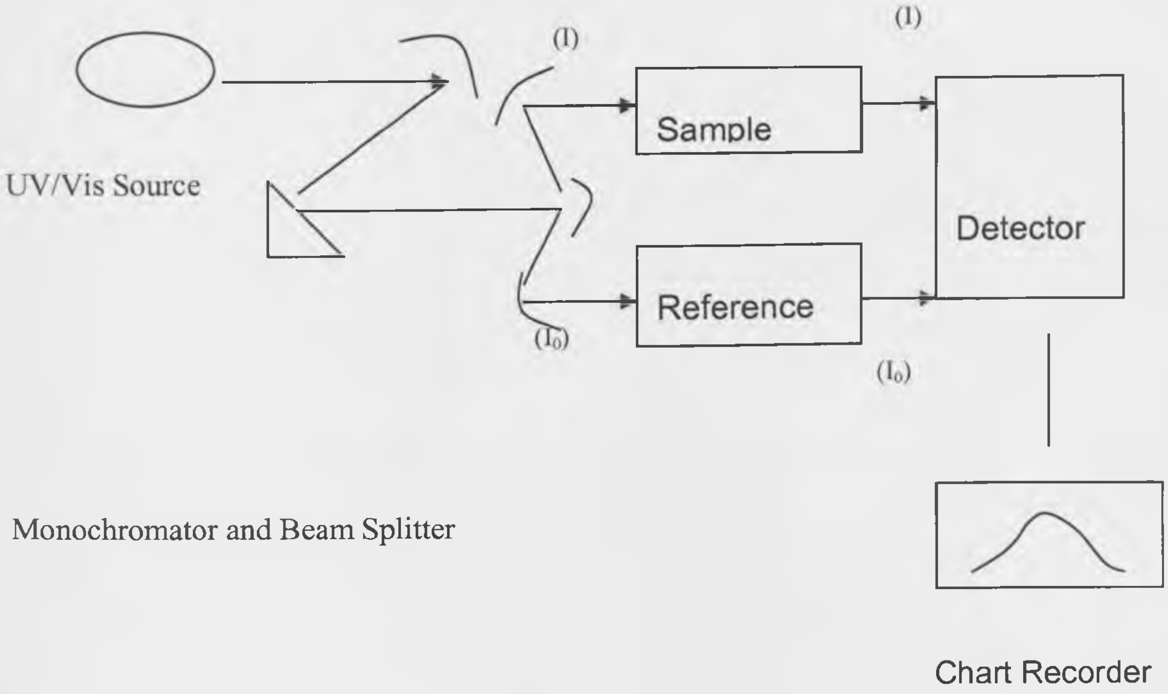

Figure 2.1 Schematic representation of a double beam ultraviolet spectrometer

The light from the source passes through a monochromator and is then further divided into two beams of equal intensity; one beam passing through a solution of the compound to be examined in the sample cell, and the other beam passing through the reference cell which contains pure solvent. After passing through the cells, the light arrives at the detector, which measures the ratio of the intensity of the reference beam (the incident intensity, I_0) to the intensity of the sample beam (the transmitted intensity I). The computer automatically manipulates the data obtained to produce a UV spectrum of absorbance (A) against wavelength (nm). If the wavelength of maximum absorbance is fixed, then the absorbance at this wavelength can be obtained [6].

2.3.4 Determination of dye concentration using Ultra-Violet and Visible spectroscopy

Information as to the rate and extent of exhaustion of dyes that occurs in a dye bath is important in practical dyeing. The amount of dye absorbed by a fibre is measured in terms of the difference between the initial and final bath concentrations of dye. Often the Beer-Lambert law is used to determine the concentration of dyes or other conjugated organic compounds in a dye bath by measurement of the absorbance (optical density) of the dye bath liquor at the wavelength of maximum absorbance (optical density) at λ_{max} of the dye or compound. Thus from the measurement of the absorbance (optical density) of the dye bath before and after dyeing, the total fixation efficiency can be calculated as;

$$\text{Total fixation efficiency} = \%E \times \%F/100 \qquad (2.6)$$

Where;

%E = Percentage exhaustion

The %E can be calculated by using spectrophotometer by calculating the optical densities of the solution before and after the dyeing.

$$\%E = ((OD_1 - OD_2)/OD_1)) \text{ X } 100 \qquad (2.7)$$

Where OD_1 and OD_2 are the optical densities of the dyeing solutions before and after the dyeing at λ_{max}.

The fixation of the dye is also calculated by calculating optical densities;

$$\%F = ((OD_1 - (OD_2 + OD_3)/OD_1)) \times 100 \qquad (2.8)$$

Where OD_1 is the optical density of the dyeing solution (λ_{max}) before dyeing and OD_2 is the optical density of exhausted dye bath (λ_{max}) and OD_3 is the optical density of wash off liquor (λ_{max}).

2.4 Colour fastness

Fastness is defined as the resistance to being removed; so colour fastness itself is defined as "the resistance of colour being removed from a substrate" [7]. This might be wash-fastness, light-fastness or rub-fastness etc. When the dye is not entirely fixed to the fibre, during washing it may come off and stain onto adjacent fabrics or it may not stain, but simply be washed away and stay in wash-off solution. In the case of rub-fastness, those dyes which are on the fibre surface may be rubbed with adjacent fabrics and the dye will stain the adjacent fabric.

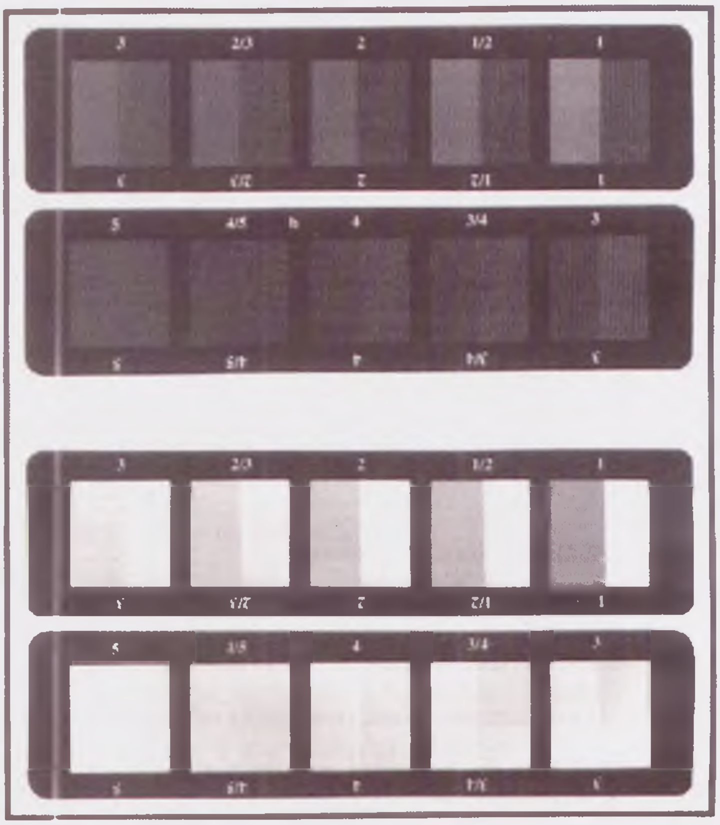

Figure 2.2 Grey scales: (Top) the scale used for assessing colour change of samples (Bottom) the scale used for assessing staining

Staining and shade change is measured by using the grey scales as shown in the Figure 2.2 [8].

2.4.1 Wash-fastness

Wash-fastness is very important test to analyse the wet-fastness of the dyes. Washing powders contain different types of detergents and different washing temperatures are recommended different fibres, therefore a variety of wash- fastness methods have been devised e.g. ISO2 and ISO3.

The washed fabric strip is compared with the unwashed fabric strip and grey scales are used to rate them. Also a multiple fibre strip is attached to the dyed strip before washing to check staining. After washing the multiple adjacent fibres strip is also assessed against the unwashed multiple fibres strip with grey scale to see whether the dye has stained. If there is any staining then it is assessed with grey scale.

2.4.2 Light-fastness

To predict the fading of a coloured material by the effect of light is very complex phenomena because it depends on many criteria e.g. colour strength, air temperature, humidity, surface temperature of the specimens, impurities in the coloured substrate, impurities in the atmosphere, light intensity of the source and the spectral quality. The blue wool standards are also subjected under the same conditions as the specimens to known light intensity. The fading difference between exposed and unexposed areas of the specimen to measure with grey scales. Both specimens and blue wool standards are partially covered. After a specified time of exposure they are checked to determine the fading of both specimens and wool standards. The specimens are faded equivalent to grade 4 on the grey scale for light fastness. Then the exposed and unexposed specimens are compared with the blue wool standards. The rating given is the number of the standard that exhibits the same degree of contrast.

It is quite difficult to carry out such type of tests in open day light because the set of conditions vary time to time and place to place. It would be easy and useful if these tests are done in artificial light source and conditions. Then the results will be consistent because all specimens and wool standards have been exposed under the same set of conditions. So for this purpose, the light of xenon arc is quite useful to replace day light.

2.5 Light Microscopy

In this research, light microscopy has been used to check the dye distribution (uniform dyeing) throughout the fibre following chemical modification with quaternary amines. The light microscopy of dyed fibre has been conducted by cutting dyed fibre into their cross-sections. There are four possible techniques for the preparation of cross-sections of the textile materials for light microscopy.

- The plate method
- The Hardy microtome
- Mechanical microtome sections
- The grinding method

In this research, the plate method technique has been used. The plate consists of a hard steel microscope slide through which holes approximately 0.75 mm diameter have been drilled. The fibre samples to be sectioned are pulled through one of the holes, the protruding ends cut flush with the smooth surfaces of the plate. The resulting section is examined with either transmitted or reflected light by placing the plate carefully on the microscope stage and locating the hole in which the fibre sections are held. The plate is used as a slide. Black oil paint may be rubbed over the section carefully to increase the contrast between the fibres and background in transmitted light examinations. This produces a black background against which the fibres appear bright, transmitting light by internal reflection [9].

2.6 References

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Chapter 3

Application of Vat Dyes to Unmodified and Modified Cotton

3.1 Introduction

Vat dyes applied to unmodified cotton give bright shades with excellent light-fastness properties but the main disadvantage of vat dyes is the poor rub-fastness of the dyeings produced because they are in a pigment form on the surface of the fabric. Modified cotton has positively charged end groups which can attract the negatively charged reduced dye molecules giving a greater up-take than on the unmodified cotton. This increased substantivity will enable the dye molecules to penetrate the fabric giving an increase in colour yield together with an increase in the rub-fastness. In this chapter the following dyeing characteristics have been analysed;

- Wash-off
- Colour yield
- Wash-fastness
- Light-fastness
- Rub-fastness
- Ring-dyeing

3.2 Experimental

3.2.1 Materials

3.2.1.1 Fabric

Three types of fabric were used in this research. Unmodified (scoured and bleached) cotton, cotton modified with cationising agents Servon XRK (XRK) and cotton modified with Servon NMM (N-methylmorpholine or NMM derivative). Servon XRK was supplied by Condea Servo (Netherlands). Scoured and bleached unmodified cotton was supplied by Whaleys (Bradford).

3.2.1.2 Other reagents

All other chemical reagents used in this research were laboratory-grade obtained from Aldrich.

3.2.1.3 Dyes

Four commercial vat dyes (anthraquinone and indigoid) were used namely CI Vat Violet 1, CI Vat Red 13, CI Vat Green 1 and CI Vat Blue 1 (indigoid) generously supplied by Dystar. Their chemical structures are shown in Figures 3.1 – 3.4.

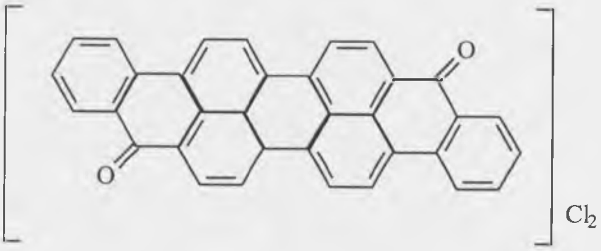


Figure 3.1 Structure of CI Vat Violet 1

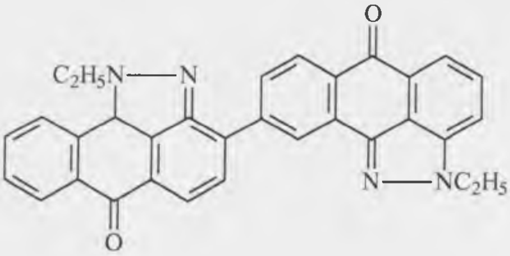


Figure 3.2 Structure of CI Vat Red 13

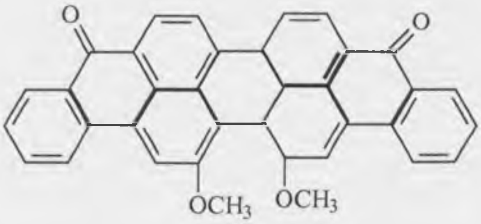


Figure 3.3 Structure of CI Vat Green 1

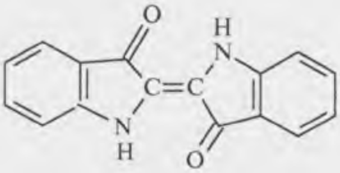


Figure 3.4 Structure of CI Vat Blue 1

3.2.2 Application of Servon XRK (3-chloro-2-hydroxy-N, N, N-trimethyl-1-propanaminium chloride) to cotton

3.2.2.1 Preparation of the padding solution

20 g of Servon XRK (65% w/w) [1]

20 g of 50% NaOH

2 g of Sandozin NIE

158 g of H_2O

This solution will give 6.5% Servon XRK o.m.f. when the fabrics are padded at 100% wet pick up.

Pad liquor:

20 g Servon XRK was diluted in 100 g distilled water; when equipment was ready for padding, 20 g NaOH was added drop-wise with stirring. Then 2 g of Sandozin NIE were added and stirred for a while. The remaining water was then added to make up to 200 g and again stirred for some time. The solution was then ready for padding. The conversion of Servon XRK to its epoxide form and its application to cotton is shown in Figure 3.5.

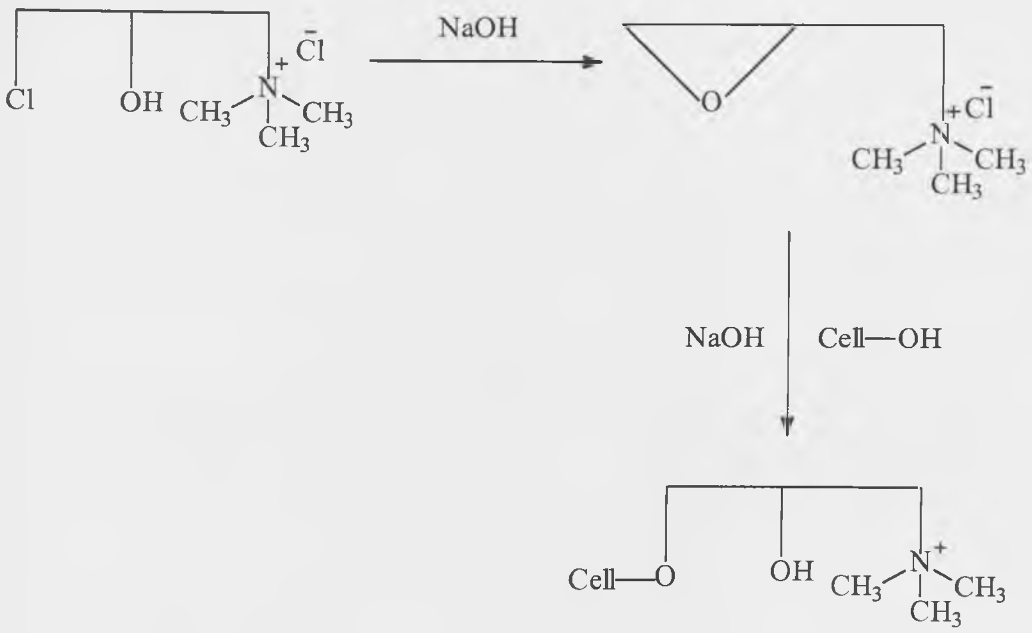


Figure 3.5 Application of Servon XRK 65 to cotton

3.2.2.2 Padding conditions

Padding should be done with bleached fabric to give 100% wet pick up. The nip pressure should be 1.1 bar with fabric speed of 0.5 m/min. By batching the fabric onto a tube and wrapping in cling film, water is excluded. Batching time will be 20 hours (overnight) at 22 °C.

3.2.2.3 Cold wash-off

After the batching process, cold washing was conducted in the jig dyeing machine for 20 minutes, changing the water after every five minutes in order to remove any unfixed quaternary amines.

3.2.2.4 Drying

The modified washed-off fabric was dried in a dryer, passing through it at a speed of 0.3 m/min at 100 °C.

3.2.3 Application of NMM derivative [4-(3-chloro-2-hydroxypropyl)-4-methylmorpholin-4-ium chloride)] to cotton

- A similar method to the above has been used for the application of the NMM derivative to cotton (3.2.2). Figure 3.6 shows the application of the NMM derivative to cotton [2].

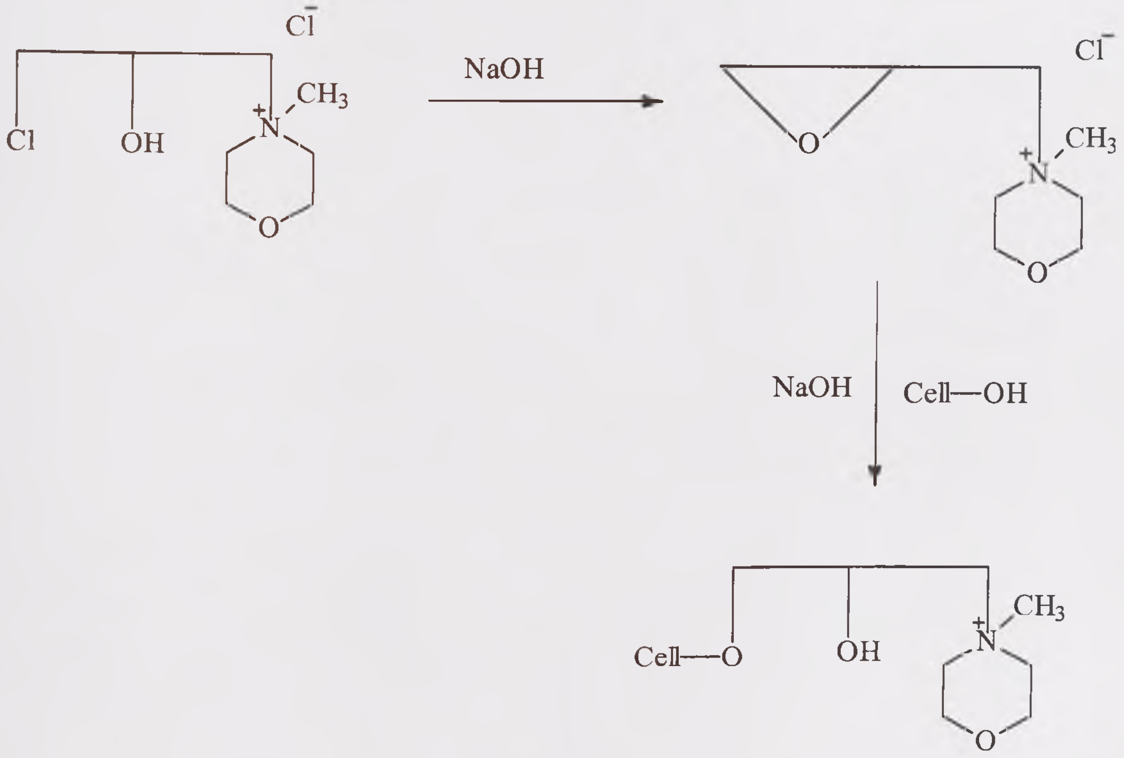


Figure 3.6 Application of the NMM derivative to cotton

3.2.4 Dyeing of vat dyes

Vat dyes are not applied to cotton like traditional direct or reactive dyestuffs because vat dyes are insoluble in water and in this state they have no substantivity for cotton. They need to be converted to the water soluble, reduced form before applying to produce substantivity between dye and cotton [3].

3.2.4.1 Dyeing profile

Figure 3.7 shows the dyeing profile for unmodified cotton, cotton modified with the NMM and cotton modified with the XRK.

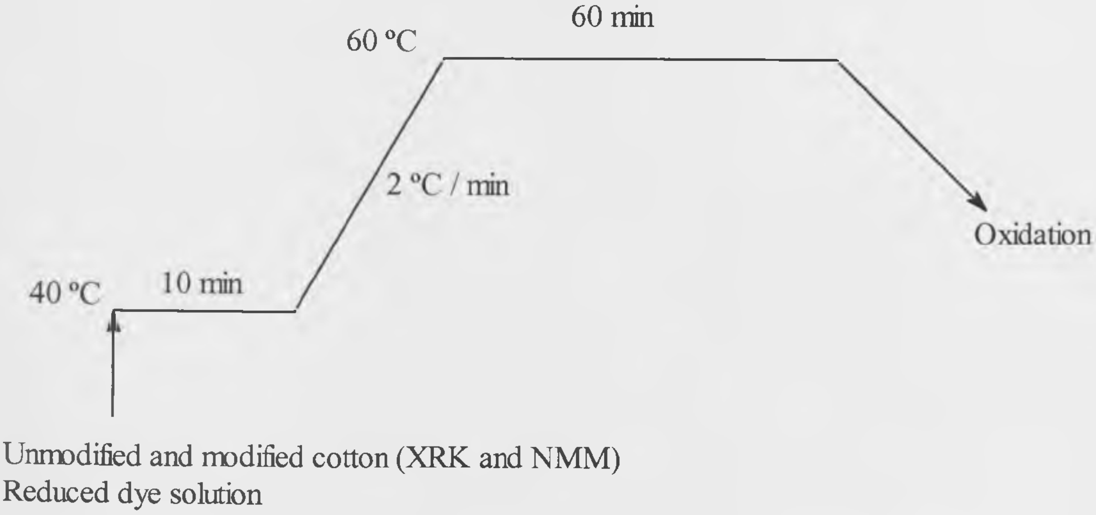


Figure 3.7 Profile for dyeing unmodified cotton and modified cotton fabrics at 60°C

3.2.4.2 Reduction of vat dyes

A dye stock solution 4% (w/w) conc. was prepared. 2 g of the original dye was reduced by using sodium hydrosulphite solution (4.5 g $Na_2S_2O_4$ in 25 g water); 8 g of sodium hydroxide (50% w/w) solution (4 g NaOH) was also used in the reducing solution. The dye was reduced at 50-60°C by stirring for 30 minutes [1].

3.2.4.3 Oxidation of vat dyes

After dyeing, the dyed fabric was oxidised to convert the dye back to its original form using hydrogen peroxide at pH 5 (H_2O_2) 4 ml/l using a liquor ratio 10:1. The reduction and oxidation of vat dyes is shown in Figure 3.8.

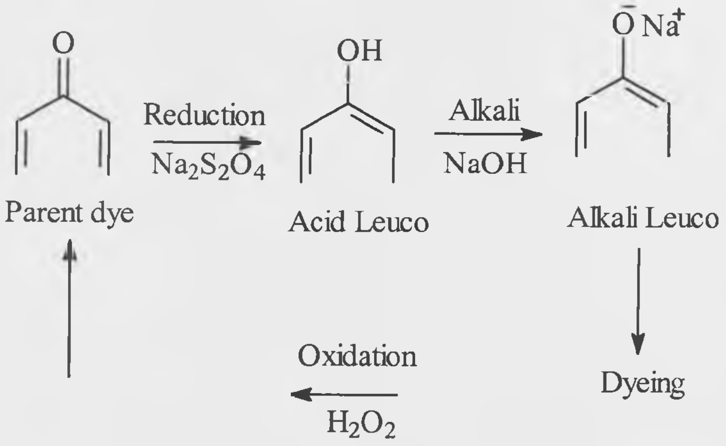


Figure 3.8 Reduction / oxidation cycle for vat dyes

3.2.4.4 Washing-off

Wash-off was conducted at 100°C for 15 minutes by using Sandozin NIE (2 g/l) solution.

L.R = 25:1

3.3 Results and discussion

3.3.1 Washing-off

The dyed fabric samples were washed-off and the liquors saved in sample bottles. The washed-off liquors in the sample bottles have been taken and their photographs are shown in Figures 3.9 – 3.16. In each photograph the wash-off sample bottles are shown from left to right, the wash-off solutions from unmodified cotton (a), from NMM modified cotton (b) and from XRK modified cotton (c).

(a) (b) (c)

Figure 3.9 Wash-off liquors for CI Vat Violet 1 at 2 % o.m.f.

In Figure 3.9;

(a) Unmodified cotton

(b) NMM modified cotton

(c) XRK modified cotton

(a) (b) (c)

Figure 3.10 Wash-off liquors for CI Vat Violet 1 at 4 % omf.

In Figure 3.10;

(a) Unmodified cotton

(b) NMM modified cotton

(c) XRK modified cotton

(a) (b) (c)

Figure 3.11 Wash-off liquors for CI Vat Red 13 at 2 % omf

In Figure 3.11;

(a) Unmodified cotton

(b) NMM modified cotton

(c) XRK modified cotton

(a) (b) (c)

Figure 3.12 Wash-off liquors for CI Vat Red 13 at 4 % omf

In Figure 3.12;

(a) Unmodified cotton

(b) NMM modified cotton

(c) XRK modified cotton

(a) (b) (c)

Figure 3.13 Wash-off liquors for CI Vat Green 1 at 2 % omf.

In Figure 3.13;

(a) Unmodified cotton

(b) NMM modified cotton

(c) XRK modified cotton

(a) (b) (c)

Figure 3.14 Wash-off liquors for CI Vat Green 1 at 4 % omf.

In Figure 3.14;

(a) Unmodified cotton

(b) NMM modified cotton

(c) XRK modified cotton

(a) (b) (c)

Figure 3.15 Wash-off liquors for CI Vat Blue 1 at 2 % omf.

In Figure 3.15;

(a) unmodified cotton

(b) NMM modified cotton

(c) XRK modified cotton

(a) (b) (c)

Figure 3.16 Wash-off liquors for CI Vat Blue 1 at 4 % omf.

In Figure 3.16;

(a) Unmodified cotton

(b) NMM modified cotton

(c) XRK modified cotton

Unmodified cotton dyed with anthraquinone vat dyes at 2% and 4% shade depths gives a significant amount of colour in the wash-off liquors but in the case of the reactive cation modified cotton (both the NMM and XRK); no colour is removed at both the shade depths of 2% and 4% omf. Anthraquinone vat dyes when absorbed on the modified cotton fabric are not removed from the dyed fabric during the wash-off because they are absorbed more efficiently inside the fibre due to the positive charges on the fibre attracting the negatively charged leuco (reduced) dye molecule in a very efficient manner.

The wash-off liquors of modified cotton fabric (XRK and NMM) dyed with CI Vat Blue 1 (indigo) at 2% shade depth does not show any colour in its wash-off liquor but CI Vat Blue

1 applied at 4% shade depth on modified cotton gives a little cloudy wash-off liquor after washing-off. CI Vat Blue 1 applied on unmodified cotton at 2% and 4% shade depths gave significant colour in the wash-off liquor because molecules of CI Vat Blue 1 being smaller in size are readily removed and remain in the wash-off solution or if they re-adsorb on the fabric cause rub-fastness problems.

3.3.2 Colour yield

Table 3.1 gives the colour yield values for the dyeings from CI Vat Violet 1, CI Vat Red 13, CI Vat Green 1 and CI Vat Blue 1 at 2% and 4% o.m.f. on unmodified, NMM modified and Servon XRK modified cotton fabrics.

Dyes used	% omf	fk Values		
		Unmodified cotton	NMM modified cotton	XRK modified cotton
CI Vat Violet 1	2 %	166.0	185.1	199.7
	4 %	229.5	262.6	286.1
CI Vat Red 13	2 %	228.2	237.1	253.6
	4 %	305.5	316.2	329.7
CI Vat Green 1	2 %	197.6	200.4	210.4
	4 %	304.2	313.8	324.0
CI Vat Blue 1	2 %	47.4	85.1	90.2
	4 %	66.1	130.6	134.9

Table 3.1 Colour yield values for the dyeings on the unmodified, NMM modified and Servon XRK modified cotton fabrics

The colour yield values for the dyeings from all the vat dyes used at 2% and 4% o.m.f. on NMM modified cotton fabric are higher than the colour yield values for the dyeings on unmodified cotton fabric. Also the colour yield values for the dyeings on Servon XRK modified cotton are much higher than the colour yield values for the dyeings on both the unmodified and the NMM modified cotton fabrics. This is attributed to the fact that the modified cottons (XRK and NMM) have much higher substantivity for vat dyes in their leuco form (reduced form) than the unmodified cotton. Also the cotton modified with Servon XRK shows higher substantivity than the NMM modified cotton for vat dyes; having higher colour yield values as given in Table 3.1.

3.3.3 Wash-fastness test

Wash-fastness is a crucial test to examine the wet fastness properties of the dyes applied to the fabric i.e. the quantity of dye remaining on the fabric under specific set of conditions. In this research the ISO2 wash-fastness test has been conducted [4].

Wash-fastness test (ISO2)

Tables 3.2-3.4 give the staining and the shade change results for the dyeings at 2% o.m.f. and Tables 3.5-3.7 give the staining and the shade change results for the dyeings from CI Vat Violet 1, CI Vat Red 13, CI Vat Green 1 and CI Vat Blue 1 at 4% o.m.f. on the unmodified, NMM modified and Servon XRK modified cotton fabrics.

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	Shade change
CI Vat Violet 1	5	5	4/5	5	5	5	4/5
CI Vat Red 13	5	5	4/5	5	5	5	4/5
CI Vat Green 1	5	5	4/5	5	5	5	4/5
CI Vat Blue 1	4/5	5	4	5	4/5	4/5	2/3

Table 3.2 Staining and the shade change results for the dyeings on the unmodified cotton fabric

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	Shade change
CI Vat Violet 1	5	5	5	5	5	5	5
CI Vat Red 13	5	5	5	5	5	5	5
CI Vat Green 1	5	5	5	5	5	5	5
CI Vat Blue 1	4/5	5	4/5	5	4/5	5	3

Table 3.3 Staining and the shade change results for the dyeings on the NMM modified cotton fabric

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	Shade change
CI Vat Violet 1	5	5	5	5	5	5	5
CI Vat Red 13	5	5	5	5	5	5	5
CI Vat Green 1	5	5	5	5	5	5	5
CI Vat Blue 1	5	5	4/5	5	4/5	5	3/4

Table 3.4 Staining and the shade change results for the dyeings on the Servon XRK modified cotton fabric

The dyeings from CI Vat Violet 1 on the unmodified cotton do not stain acetate, cotton, polyester, acrylic and wool adjacents in the wash test. There was slight staining on the nylon adjacent (4/5) and a shade change of 4/5 as given in Table 3.2. The dyeings from CI Vat Violet 1 on the NMM modified cotton and Servon XRK modified cotton fabrics do not give any staining on adjacent fabrics. For the dyeings from CI Vat Violet 1 on the modified (NMM and Servon XRK) cotton fabrics at 2% o.m.f. are excellent. The dyeings from CI Vat Violet 1 on the NMM and the Servon XRK modified cotton fabrics do not give any shade change as shown in Tables 3.3 and 3.4.

The dyeings from CI Vat Red 13 and CI Vat Green 1 give similar wash-fastness results to the dyeings from CI Vat Violet 1 on the unmodified and modified cotton fabrics.

After the ISO2 wash-fastness test, the dyeings from CI Vat Blue 1 stain on acetate, nylon, acrylic and wool adjacents but they do not stain on cotton and polyester adjacent fabrics in case of unmodified cotton fabric. Staining on acetate, acrylic and wool adjacent fabrics is rated as 4/5 and the staining on nylon adjacent is rated as 4 (Table 3.2). The wash-fastness results for the dyeings from CI Vat Blue 1 are slightly better on the cotton modified with NMM than on the unmodified cotton fabric as given in Table 3.3.

Staining on acetate, nylon and acrylic is rated as 4/5. The dyeings from CI Vat Blue 1 on the unmodified cotton fabric stain slightly on wool adjacent fabric (4/5). Staining on nylon adjacent is rated as 4/5 for the dyeings on the modified (NMM and Servon XRK) cotton fabrics which is 1/2 point better than on the unmodified cotton. The shade change result is rated as 2/3 for the dyeings from CI Vat Blue 1 on unmodified cotton fabric (Table 3.2) and the shade change result for the dyeings on the NMM modified cotton fabric and the Servon XRK modified cotton fabric is rated as 3 and 3/4 respectively as given in Tables 3.3 and 3.4.

The wash-fastness results for the dyeings from CI Vat Blue 1 at 2% o.m.f. on Servon XRK modified cotton are better than both the unmodified cotton and NMM modified cotton fabrics. Comparing the wash-fastness results for the dyeings from CI Vat Blue 1 on Servon XRK and NMM modified cotton fabrics, the Servon XRK modified cotton fabric gives less staining after the ISO2 wash-fastness test on acetate adjacent with an improvement of 1/2 a point; the staining on other adjacents are the same for both modified fabrics. The shade change result for the dyeings from CI Vat Blue 1 on Servon XRK modified cotton fabric is rated as 3/4 which is 1/2 point better than the shade change result for the dyeings from CI Vat Blue 1 on the NMM modified cotton fabric which is rated as 3 (Table 3.3).

The wash-fastness results for the dyeings from CI Vat Blue 1 on the Servon XRK modified cotton are better than the dyeings on the unmodified and NMM modified cotton fabrics. The dyeings from CI Vat Blue 1 on the Servon XRK modified cotton do not stain on acetate adjacent while the dyeings from CI Vat Blue 1 on NMM modified cotton give a staining on the acetate adjacent which is rated as 4/5. The staining results for the dyeings on the Servon XRK modified cotton are rated as 1/2 point better than the dyeings on the NMM modified cotton. The shade change result for the dyeings from CI Vat Blue 1 on the Servon XRK modified cotton is rated 3/4 which is 1/2 point better than the dyeings on the NMM modified cotton which is rated as 3. Further the shade change result for the dyeings on NMM modified cotton is 1/2 point better than the shade change result of the dyeings from CI Vat Blue 1 on the unmodified cotton which is rated as 2/3.

Overall the wash-fastness results for the dyeings from CI Vat Blue on the Servon XRK modified cotton are better than the dyeings from CI Vat Blue 1 on the NMM modified cotton and unmodified cotton fabrics.

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	Shade change
CI Vat Violet 1	5	5	4/5	5	5	5	4/5
CI Vat Red 13	5	5	4/5	5	5	5	4/5
CI Vat Green 1	5	5	4/5	5	5	5	4/5
CI Vat Blue 1	4/5	5	3	5	3	4/5	3/4

Table 3.5 Staining and the shade change results for the dyeings on the unmodified cotton fabric

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	Shade change
CI Vat Violet 1	5	5	4/5	5	5	5	4/5
CI Vat Red 13	5	5	4/5	5	5	5	5
CI Vat Green 1	5	5	5	5	5	5	5
CI Vat Blue 1	4/5	5	3/4	5	4	4/5	4

Table 3.6 Staining and shade change results for the dyeings on the cotton modified with NMM

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	Shade change
CI Vat Violet 1	5	5	4/5	5	5	5	4/5
CI Vat Red 13	5	5	5	5	5	5	5
CI Vat Green 1	5	5	5	5	5	5	5
CI Vat Blue 1	4/5	5	4	5	4/5	5	4

Table 3.7 Staining and the shade change results for the dyeings on the cotton modified with Servon XRK

After the wash-fastness test, the dyeings from CI Vat Violet 1 on the unmodified cotton did not stain on the acetate, cotton, polyester, acrylic and wool adjacent fabrics. The staining has been found on nylon adjacent which is rated as 4/5. The shade change result for the dyeings from CI Vat Violet 1 on the unmodified cotton is rated as 4/5 (Table 3.5). The dyeings from CI Vat Violet 1 on the NMM modified cotton fabric and the Servon XRK modified cotton fabrics give similar staining and shade change results as on the unmodified cotton fabric.

The dyeings from CI Vat Red 13 on the unmodified cotton after the wash-fastness test stain on the nylon adjacent (4/5). There is no staining on acetate, cotton, polyester, acrylic and wool adjacents. The shade change for the dyeings from CI Vat Red 13 on the unmodified cotton fabric is rated as 4/5 as given in Table 3.5. The dyeings from CI Vat Red 13 on the NMM modified cotton do not stain on acetate, cotton, polyester, acrylic and wool adjacent fabrics. There is slight staining on nylon adjacent (4/5). The shade change result for the dyeings from CI Vat Red 13 on the NMM modified cotton fabric is rated as 5 as given in Table 3.6. The dyeings from CI Vat Red 13 on the Servon XRK modified cotton do not stain on the multiple adjacent fabrics and there is no change in the shade for the dyeings as given in Table 3.7.

After the wash-fastness test, the dyeings from CI Vat Green 1 on the unmodified cotton fabric stain slightly on nylon adjacent (4/5) but there is no staining on the other adjacent fabrics. The shade change result for the dyeings from CI Vat Green 1 on the unmodified cotton fabric is rated as 4/5 (Table 3.5). There is no staining on the adjacent fabrics for the dyeings from CI Vat Green 1 on the NMM modified cotton. The shade change result for the dyeings from CI Vat Green 1 on the NMM modified cotton fabric is rated as 5 as given in Table 3.6. The dyeings from CI Vat Green 1 on the Servon XRK modified cotton gave similar wash-fastness results as the dyeings on the NMM modified cotton fabric with no staining on the adjacent fabrics. The shade change result for the dyeings from CI Vat Green 1 on the Servon XRK modified cotton is rated as 5 as given in Table 3..

The dyeings from CI Vat Blue 1 on the unmodified cotton fabric stain on acetate, nylon, acrylic and wool adjacents. There was no staining on cotton and polyester adjacent fabrics. The staining on acetate and wool is rated as 4/5 and staining on nylon and acrylic is significant which is rated as 3. The shade change for the dyeings from CI Vat Blue 1 on the unmodified cotton is rated as 3/4 (Table 3.5). The dyeings from CI Vat Blue 1 on the NMM modified cotton stain on acetate, nylon, acrylic and wool adjacents. The staining on acetate and wool adjacent fabrics is rated as (4/5). The staining on nylon and acrylic adjacent fabrics is rated as 3/4 and 4 respectively. There is no staining on cotton and polyester adjacents. The shade change results for the dyeings from CI Vat Blue 1 on the NMM modified cotton is rated as 4 as given in Table 3.6. The dyeings from CI Vat Blue 1 on the Servon XRK modified cotton on acetate, acrylic and nylon adjacents. The staining on acetate and acrylic adjacent fabrics is rated as 4/5. There is staining on nylon adjacent which is rated as 4. There is no staining on cotton, polyester and wool adjacent fabrics. The shade change result for the dyeings from CI Vat Blue 1 is rated as 4 as given in Table 3.7.

3.3.4 Light-fastness

Table 3.8 gives the light-fastness results for the dyeings from CI Vat Violet 1, CI Vat Red 13, CI Vat Green 1 and CI Vat Blue 1 on the unmodified, NMM modified and Servon XRK modified cotton fabrics.

Dyes used	Unmodified cotton		NMM modified cotton		XRK modified cotton	
	2 %	4 %	2 %	4 %	2 %	4 %
CI Vat Violet 1	5	5	5	5	5	5
CI Vat Red 13	5	5	5	5	5	5
CI Vat Green 1	5	5	5	5	5	5
CI Vat Blue 1	5	5	5	5	5	5

Table 3.8 Light-fastness results for the dyeings from the given set of vat dyes at 2% and 4% o.m.f.

Light-fastness results for the dyeings from CI Vat Violet 1, CI Vat Red 13, CI Vat Green 1 and CI Vat Blue 1 at 2% and 4% o.m.f. on the unmodified, NMM modified and Servon XRK modified cotton fabrics is rated as 5 as given in Table 3.8.

3.3.5 Rub-fastness

Vat dyes have overall good fastness properties but being in a pigment form on the dyed fabric they suffer from rubbing-fastness problems. Indigoid vat dyes being smaller molecules than anthraquinone vat dyes show poorer rub-fastness results having less forces of attraction with cellulosic fibres which cause rubbing problems.

Tables 3.9 and 3.10 give rub-fastness results for the dyeings on the unmodified, NMM modified and Servon XRK modified cotton fabrics. The colour yield is better (Table 3.1) with modified cotton in both cases of XRK and NMM but the rub-fastness results are the same in either case of unmodified and modified substrates.

Dyes used	Unmodified cotton		NMM modified cotton		XRK modified cotton	
	Dry	Wet	Dry	Wet	Dry	Wet
CI Vat Violet 1	4/5	3	4/5	3	4/5	3
CI Vat Red 13	4	2/3	4	2/3	4	2/3
CI Vat Green 1	4/5	2/3	4/5	2/3	4/5	2/3
CI Vat Blue 1	3/4	2/3	3	2	3	2

Table 3.9 Dry and wet rub-fastness results for the dyeings from the given set of vat dyes at 2% o.m.f.

The rub-fastness results for the dyeings from CI Vat Violet 1 are similar on the unmodified, NMM modified and Servon XRK modified cotton fabrics which is rated as 4/5 and 3 for dry and wet tests respectively. The dyeings from CI Vat Red 13 give staining in the dry rub test rated as 4 and in case of wet rub test, the staining is significant which is rated as 2/3. The dyeings from CI Vat Green 1 give similar rub-fastness results on the unmodified, NMM modified and Servon XRK modified cotton fabrics with stain ratings of 4/5 in the dry rub test and 2/3 in wet rub test as given in Table 3.9.

The dyeings from CI Vat Blue 1 stain significantly on the adjacent fabric which is rated as 3/4 and 2/3 in dry and wet tests respectively for unmodified cotton fabric. The staining results for the NMM modified and Servon XRK modified cotton fabrics are rated as 3 in the dry rub test and 2 for the wet rub test. The rub-fastness results for both the modified cotton fabrics are 1/2 point lower than on the unmodified cotton fabric as the colour yield values for the dyeings on the NMM modified and the Servon XRK modified cotton fabrics are higher than the colour yield values for the dyeings on the unmodified cotton fabric as given in Table 3.1.

Dyes used	Unmodified cotton		NMM modified cotton		XRK modified cotton	
	Dry	Wet	Dry	Wet	Dry	Wet
CI Vat Violet 1	4/5	2/3	4/5	2/3	4/5	2/3
CI Vat Red 13	4	2	4	2	4	2
CI Vat Green 1	4	2/3	4	2/3	4	2/3
CI Vat Blue 1	3/4	2	3	1/2	3	1/2

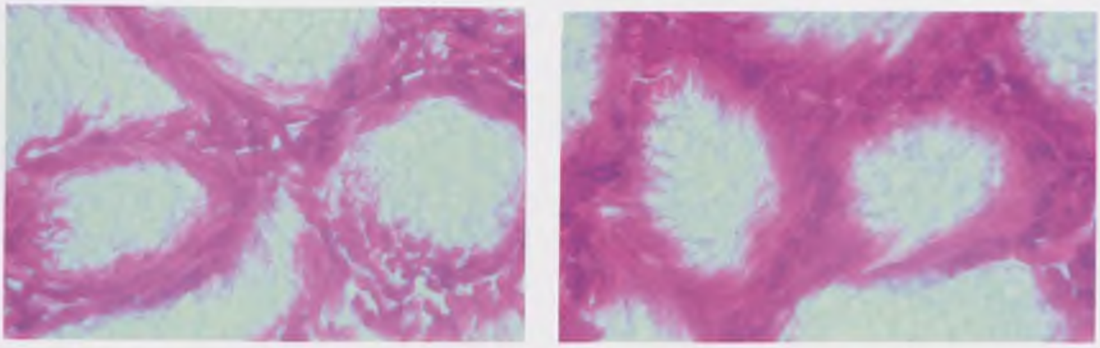
Table 3.10 Dry and wet rub-fastness results for the dyeings from the given set of vat dyes at 4% o.m.f.

After dry and wet rub-fastness tests, the dyeings from CI Vat Violet 1 at 4% o.m.f. on the unmodified, NMM modified and Servon XRK modified cotton fabrics give staining results rated as 4/5 for dry test and 2/3 for wet test. The rub-fastness results for the dyeings from CI Vat Red 13 on the unmodified, NMM modified and Servon XRK modified cotton fabrics are similar which are rated as 4 for the dry test and 2 for the wet test. The dyeings from CI Vat Green 1 again give the similar rub-fastness results on all the three substrates which are rated as 4 for the dry test and 2/3 for the wet test. It shows that rub-fastness results for anthraquinone vat dyes (CI Vat Violet 1, CI Vat Red 13 and CI Vat Green 1) on the NMM modified and Servon XRK modified cotton fabrics are improved when the colour yield values for the dyeings from anthraquinone vat dyes on both modified cotton fabrics are higher than on the unmodified cotton fabric.

The dyeings from CI Vat Blue 1 on the unmodified cotton come-off after rubbing and stain on the adjacent fabric which is rated as 3/4 in the dry rub test and 2 in the wet rub test. The rub-fastness results for the dyeings from CI Vat Blue 1 on both the modified cotton fabrics are similar for the dry rub test and the wet rub test which are 3 and 1/2 respectively. It shows as the colour yield values for the dyeings from CI Vat Blue 1 increase on the NMM modified and Servon XRK modified cotton fabric, the rub-fastness decreases up to 1/2 point in both the dry and wet rub test as compared to the dyeings on the unmodified cotton fabric.

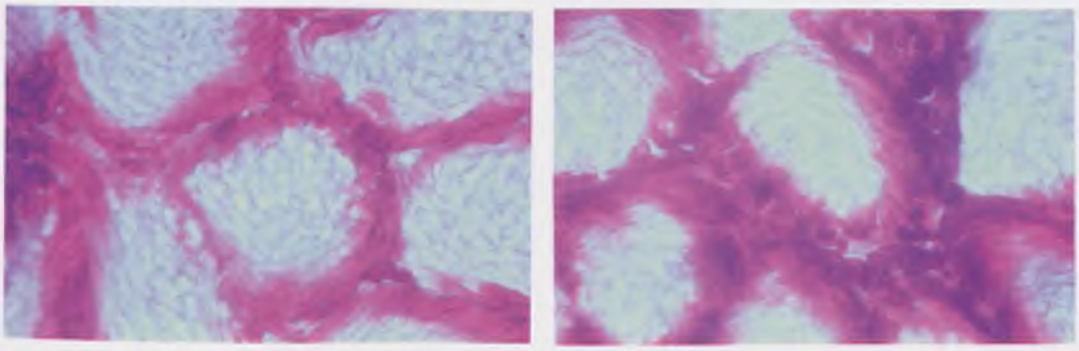
3.3.6 Microscopic images of yarn/fibre cross-sections

Figures 3.17 – 3.22 show the microscopic yarn/fibre cross-sectional images for the dyeings from CI Vat Violet 1 and CI Vat Red 13 at 2% and 4% o.m.f. on the unmodified cotton fabric, cotton modified with NMM and the cotton modified with Servon XRK [5].



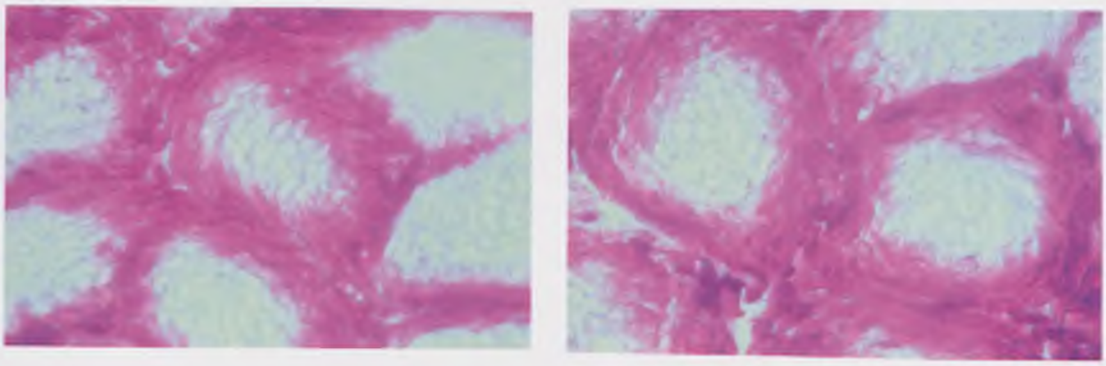
2% o.m.f. 4% o.m.f.

Figure 3.17 Microscopic images of yarn/fibre cross-sections for the dyeings from CI Vat Violet 1 on the unmodified cotton fabric at 2% and 4% o.m.f.



2% o.m.f. 4% o.m.f.

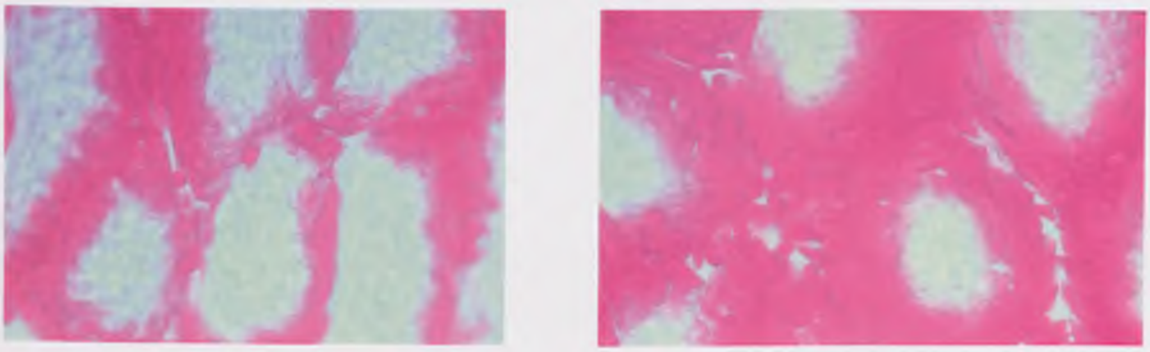
Figure 3.18 Microscopic images of fibre cross-sections for the dyeings from CI Vat Violet 1 on the NMM modified cotton fabric at 2% and 4% o.m.f.



2% o.m.f. 4% o.m.f.

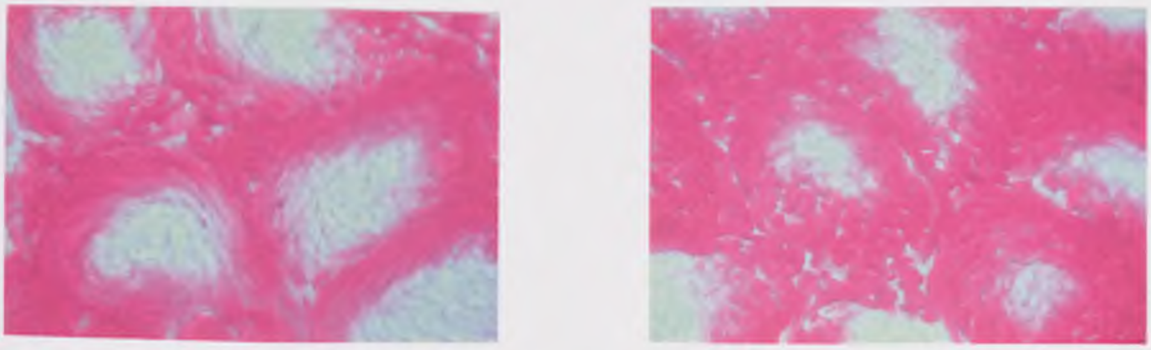
Figure 3.19 Microscopic images of fibre cross-sections for the dyeings from CI Vat Violet 1 on the Servon XRK modified cotton fabric at 2% and 4% o.m.f.

The dyeings from CI Vat Violet 1 on the unmodified cotton, the NMM cotton and the Servon XRK modified cotton fabrics at 2% and 4% o.m.f. gave significant ring dyeing as shown in Figures 3.17 – 3.19. There is no significant difference in the results of dye distribution inside the fibre between the unmodified and the modified (NMM and Servon XRK) cotton fabrics.



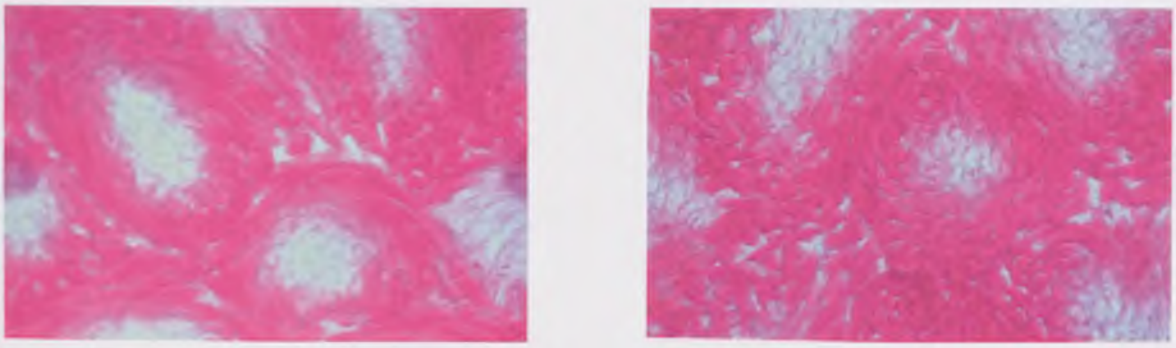
2% o.m.f. 4% o.m.f.

Figure 3.20 Microscopic images of fibre cross-sections for the dyeings from CI Vat Red 13 on the unmodified cotton fabric at 2% and 4% o.m.f.



2% o.m.f. 4% o.m.f.

Figure 3.21 Microscopic images of fibre cross-sections for the dyeings from CI Vat Red 13 on the NMM modified cotton fabric at 2% and 4% o.m.f.



2% o.m.f. 4% o.m.f.

Figure 3.22 Microscopic images of fibre cross-sections for the dyeings from CI Vat Red 13 on the Servon XRK modified cotton fabric at 2% and 4% o.m.f.

The dyeings from CI Vat Red 13 on NMM modified and Servon XRK modified cotton fabric at 2% and 4% o.m.f. give less ring-dyeing as compared to the ring-dyeing results from CI Vat Red 13 on the unmodified cotton fabric. It shows slightly better dye distribution for the dyeings on the modified (NMM and Servon XRK) cotton fabrics.

Further the dyeings on the Servon XRK modified cotton fabric give better dye distribution results as compared to the dyeings on the NMM modified cotton fabrics as shown in the Figures 3.21 and 3.22.

3.4 Conclusions

Vat dyes show a great potential for use on cationic modified cotton because of their good fastness properties except rub-fastness. Colour yield was greatly increased for the dyeings on the NMM modified and the Servon XRK modified cotton fabrics. Washing-off of the anthraquinone vat dyes applied to both the modified (NMM and Servon XRK) cotton fabrics is excellent since no colour comes-off by the soaping-off process. Soaping-off process in the case of anthraquinone vat dyes applied to the NMM modified and Servon XRK modified cotton fabrics can be eliminated. The wash-fastness results are better for the dyeings on the NMM modified and the Servon XRK modified cotton fabrics compared to the dyeings on the unmodified cotton fabric even though the modified (NMM and Servon XRK) cotton fabrics give deeper dyeings (Table 3.1).

The light-fastness results for the dyeings from CI Vat Violet 1, CI Vat Red 13, CI Vat Green 1 and CI Vat Blue 1 on the unmodified, NMM modified and Servon XRK modified cotton fabrics at 2% and 4% o.m.f. are very good. The dyeings from anthraquinone (CI Vat Violet 1, CI Vat Red 13 and CI Vat Green 1) vat dyes on the NMM and the Servon XRK modified cotton fabrics give similar rub-fastness results such as the dyeings on the unmodified cotton fabrics even though there is a significant increase in the colour yield values for the dyeings on the modified (NMM and Servon XRK) cotton fabrics. The dyeings from Indigo-based (CI Vat Blue 1) dye on the modified (NMM and Servon XRK) cotton fabrics give slightly poorer rub-fastness results. There is still a need to study the dyeing kinetics of the modified cotton fabrics to understand the phenomenon of ring-dyeing associated with vat dyes on such cellulosic substrates.

3.5 References

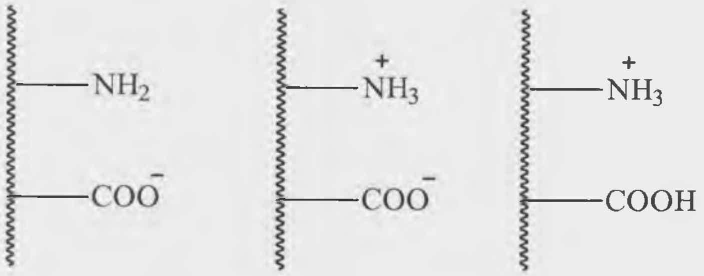
1. M Clark, PhD Thesis, University of Leeds, 2002.
2. P Grooby, PhD Thesis, University of Leeds, 2003.
3. J Shore, *Cellulosics Dyeing,* Ed., J Shore, Society of Dyers and Colourists, Bradford 1995.
4. *Methods for Colour Fastness of Textiles and Leather,* 5th edn., Society of Dyers and Colourists, Bradford 1990.
5. PH Greaves and BP Saville, *Microscopy of Textile Fibres,* Royal Microscopical Society 1995.

Chapter 4

Application of Acid Dyes to Cotton Modified With Servon XRK

4.1 Introduction

Generally acid dyes are used for dyeing polyamide fibres e.g. natural fibres like wool and man-made fibres like nylon. The sulphonate groups in these dyes can interact electrostatically with protonated amine end groups in the fibre especially if the carboxylate end groups are also protonated (reducing negative charge). The wool fibre on different pH values have bee shown in Figure 4.1.



> pH 9 (Average negative charge)   pH 4 – 9 (Average zero charge)   pH 4 (Average positive charge)

Figure 4.1 Ionic condition of wool fibres at different pH values

In this research, cotton has been chemically modified with Servon XRK to attach quaternary amine groups to the fibre which will have an electrostatic attraction for the negatively charged sites in sulphonated dye molecules. This will therefore allow the fibre to be dyed with anionic dyes. Low to medium molecular weight anionic dyes do not have substantivity for cotton (cellulose) but modified cotton carrying positive charges will attract the negatively charged sites of such dye molecules.

4.2 Non-metallised acid dyes

4.2.1 Experimental

4.2.1.1 Materials

Fabric

Servon XRK (6.5% o.m.f.) modified cotton fabric was used to conduct dyeings with CI Acid Red 88, CI Acid Red 13, CI Acid Red 17, CI Acid Red 18 and CI Acid Red 27.

Other reagents

All other chemical reagents used in this research were laboratory-grade obtained from Aldrich.

Dyes

Five commercial non-metallised acid dyes were used and were kindly supplied by DyStar as laboratory research samples. The structures of the non-metallised acid dyes used are given in Figures 4.2 – 4.6.

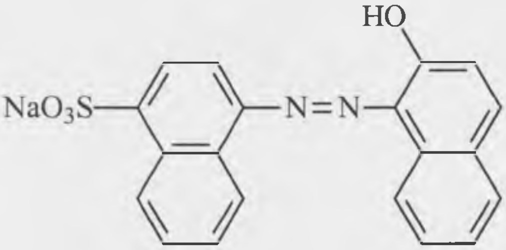


Figure 4.2 Structure of CI Acid Red 88

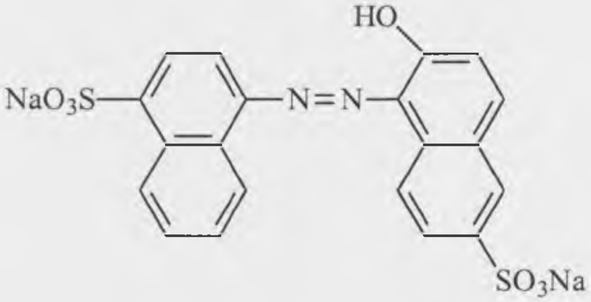


Figure 4.3 Structure of CI Acid Red 13

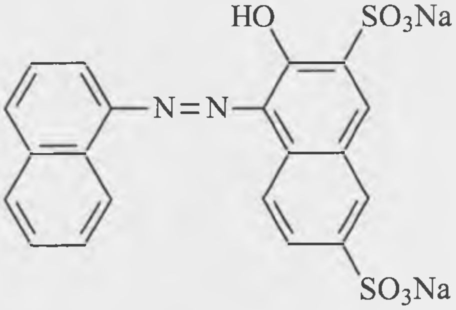


Figure 4.4 Structure of CI Acid Red 17

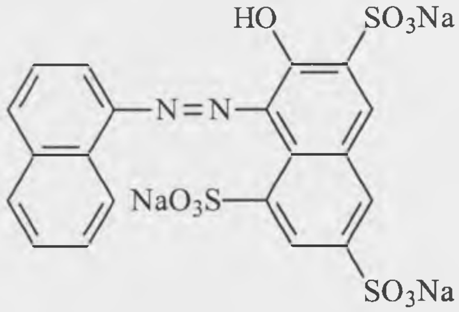


Figure 4.5 Structure of CI Acid Red 18

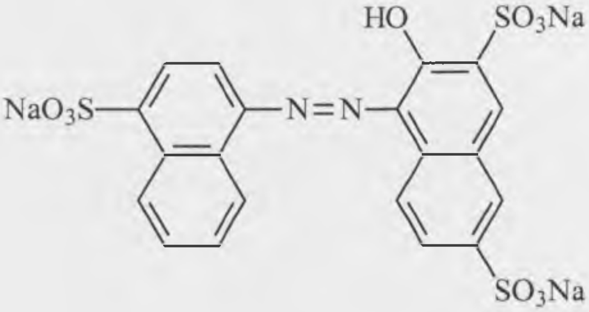


Figure 4.6 Structure of CI Acid Red 27

4.2.1.2 Dyeing profile

The dyeings were conducted at 1%, 2%, 4% and 6% o.m.f. at 100ºC for 60 minutes. The dyeing profile, for the given set of non-metallised acid dyes used to dye modified cotton is given in Figure 4.7.

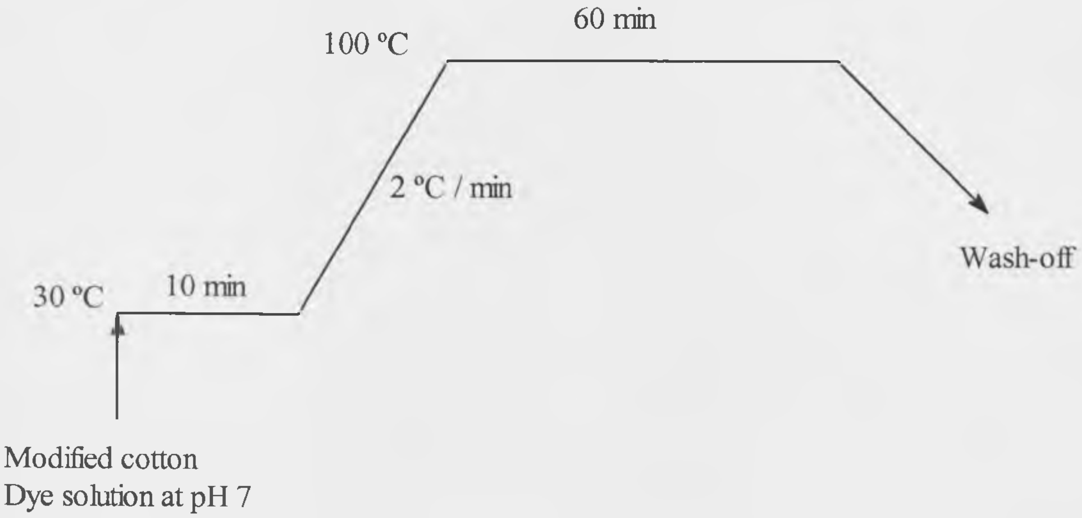


Figure 4.7 Profile for dyeing modified cotton with non-metallised acid dyes

4.2.1.3 Washing-off

The dyed fabric was washed-off at 100°C for 15 minutes using Sandozin NIE (2 g/l) [non-ionic polyethoxylated fatty alcohol surfactant] solution. Liquor to goods ratio was 25:1. Sandozin NIE was supplied by Clariant (UK).

4.2.2 Results and discussion

4.2.2.1 Exhaustion values for the dyeings from non-metallised acid dyes

Table 4.1 gives the exhaustion values for the dyeings from CI Acid Red 88, CI Acid Red 13, CI Acid Red 17, CI Acid Red 18 and CI Acid Red 27 on Servon XRK modified cotton.

Dyes used	Exhaustion values			
	1% o.m.f.	2% o.m.f.	4% o.m.f.	6% o.m.f.
CI Acid Red 88	98.4	96.2	90.1	85.6
CI Acid Red 13	99.2	93.5	67.2	51.6
CI Acid Red 17	100	95.6	70.8	55.9
CI Acid Red 18	100	99.1	70.2	56.4
CI Acid Red 27	100	96.2	66.8	53.2

Table 4.1 Exhaustion values for the dyeings from the given set of non-metallised acid dyes at 1%, 2%, 4% and 6% o.m.f.

The exhaustion values for the dyeings from mono-sulphonated acid dye CI Acid Red 88 on Servon XRK modified cotton with pale shades (1% and 2% o.m.f.) are higher than the exhaustion values for the dyeings at deep shades (4% and 6% o.m.f.) as given in Table 4.1. The exhaustion values for the dyeings from di-sulphonated acid dye CI Acid Red 17 are comparatively higher than the dyeings from CI Acid Red 13. The exhaustion values for the dyeings from CI Acid Red 17 and CI Acid Red 13 at 1% and 2% o.m.f. are higher than the exhaustion values for the dyeings at 4% and 6% o.m.f. In case of trisulphonated acid dyes, the exhaustion values for the dyeings from CI Acid Red 18 are higher than the exhaustion values for the dyeings from CI Acid Red 27. The dyeings from CI Acid Red 18 and CI Acid Red 27 at pale shades (1% and 2% o.m.f.) are higher than the deep shades (4% and 6% o.m.f.) as given in Table 4.1.

As the amount of the dye applied on the Servon XRK modified cotton increases, the exhaustion of the dye decreases because with deep shades such as 4% and 6% o.m.f. the distance between the positively charged amine of the fabric and the negatively charged sulphonate groups of the dye molecules increases and also the negatively charged sulphonate groups repel to coming dye molecules.

4.2.2.2 Colour yield values for the dyeings with pale and heavy shades

The modified cotton was dyed at pH 7 to give 1%, 2%, 4% and 6% dye on mass of fibre (o.m.f.). After soaping-off, fk values were calculated using the reflectance spectrophotometer. Pale shades were defined as those having fk40 (+/-5) and heavy shades were defined as those having fk100 (+/-5). Table 4.2 gives the fk values for the pale and heavy shades for the dyeings from the given set of dyes.

Dyes used	Pale shades (approximately fk 40)	Heavy shades (approximately fk 100)
CI Acid Red 88	39	97
CI Acid Red 13	39	105
CI Acid Red 17	40	105
CI Acid Red 18	42	103
CI Acid Red 27	42	98

Table 4.2 Colour yield values for pale and heavy shades for the dyeings with non-metallised acid dyes

4.2.2.3 Wash-fastness for the dyeings from given set of dyes

All the dyed fabrics were tested to the wash-fastness tests ISO2 and ISO3 [2].

Wash-fastness test ISO2 for the pale dyeings having fk value of 40

Table 4.3 gives the staining and shade change results for the pale dyeings for the ISO2 wash-fastness test.

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	shade change
CI Acid Red 88	3	2/3	2	5	5	3	4
CI Acid Red 13	5	3/4	4/5	5	5	4/5	4
CI Acid Red 17	4/5	3	4	5	5	4/5	4/5
CI Acid Red 18	5	5	5	5	5	4/5	3
CI Acid Red 27	5	4/5	5	5	5	4/5	3/4

Table 4.3 Staining and the shade change results for the pale dyeings having fk value of 40

The dyeings from the monosulphonated CI Acid Red 88 give the staining ratings on acetate, cotton, nylon and wool adjacent fabrics. The staining found on nylon and wool adjacent fabrics were significant with ratings of 2 and 3 respectively. The staining on acetate and cotton adjacent fabrics is rated as 3 and 2/3 respectively. The dyeings from CI

Acid Red 88 give a shade change result rated as 4 after the ISO2 wash-fastness test as given in Table 4.3.

The dyeings from disulphonated CI Acid Red 13 give staining on cotton, nylon and wool adjacent fabrics but there is no staining on acetate, polyester and acrylic adjacent fabrics. These dyeings stain on cotton (3/4) while the staining on nylon and wool adjacents is very slight rated as 4/5. The shade change result for the dyeings from CI Acid Red 13 is rated as 4 as given in Table 4.3. The dyeings from the disulphonated CI Acid Red 17 give staining on acetate, cotton, nylon and wool adjacent fabrics. The staining rating for the dyeings from CI Acid Red 13 is 1/2 point better than the dyeings from CI Acid Red 17 on acetate, cotton and nylon adjacent fabrics. Staining on wool adjacent fabric is similar for the dyeings from both the disulphonated dyes (CI Acid Red 13 and CI Acid Red 17). The shade change result for the dyeings from CI Acid Red 17 is rated as 4/5 (Table 4.3) which is 1/2 point better than the dyeings from CI Acid Red 13.

The dyeings from CI Acid Red 18 on modified cotton give slight staining on wool adjacent fabric (4/5) after the ISO2 wash-fastness test. The shade change result for the dyeings from CI Acid Red 18 is rated as 3. The dyeings from CI Acid Red 27 give similar staining results like the dyeings from CI Acid Red 18 but these dyeings also stain on cotton adjacent fabric slightly with rating of 4/5. The shade change result for the dyeings from CI Acid Red 27 was rated as 3/4 (Table 4.3) which is 1/2 point better than the dyeings from CI Acid Red 18.

Wash-fastness test ISO2 for the deep dyeings having fk value of 100

Table 4.4 gives the staining and the shade change results for the deep dyeings having fk value of 100 after the ISO2 wash-fastness test.

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	shade change
CI Acid Red 88	3	2/3	1/2	5	5	2/3	3/4
CI Acid Red 13	5	2/3	4	5	5	3/4	3/4
CI Acid Red 17	4	2/3	3	5	5	3/4	4
CI Acid Red 18	5	5	5	5	5	4/5	2
CI Acid Red 27	5	4/5	5	5	5	4/5	3

Table 4.4 Staining and the shade change results for the deep dyeings having fk value of 100

After the wash-fastness test ISO2, the dyeings from CI Acid Red 88 on modified cotton give significant staining on nylon adjacent (1/2). The staining on acetate adjacent is rated as 3 and the staining on cotton and wool adjacent fabrics rated as 2/3. These dyeings did not stain on polyester and acrylic adjacent fabrics. The shade change result for the dyeings from CI Acid Red 88 is rated as 3/4 as given in Table 4.4.

The dyeings from CI Acid Red 13 after the wash-fastness test ISO2 stain the cotton adjacent giving a rating of 2/3. The staining on nylon and wool adjacent fabrics is rated as 4 and 3/4 respectively. There is no staining on acetate, polyester and acrylic adjacent fabrics.

The shade change result for the dyeings from CI Acid Red 13 is rated as 3/4 (Table 4.4). The dyeings from CI Acid Red 17 with the same number of sulphonated groups as CI Acid Red 13 on its dye molecule give 1 point better staining results on acetate and nylon adjacent fabrics rated as 4 and 3 respectively. The shade change result for the dyeings from CI Acid Red 17 after the ISO2 wash-fastness test rated as 4 (Table 4.4) which is 1/2 point better than the shade change result for the dyeings from CI Acid Red 13.

The dyeings from CI Acid Red 18 on modified cotton give slight staining only on wool adjacent fabric (4/5). The dyeings do not stain on the other adjacent fabrics. The shade change result for the dyeings from CI Acid Red 18 is rated as 2. The dyeings from CI Acid Red 27 give the same staining results like the dyeings from CI Acid Red 18 but these dyeings also stain on cotton adjacent fabric (4/5). The shade change result for the dyeings from CI Acid Red 27 is rated as 3 (Table 4.4) which is 1 point better than the shade change result for the dyeings from CI Acid Red 18.

Wash-fastness test ISO3 for the pale dyeings having fk value of 40

Table 4.5 gives the staining and the shade change results for the pale dyeings having fk value of 40 after the ISO3 wash-fastness test.

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	shade change
CI Acid Red 88	2/3	2/3	2	5	5	2/3	3/4
CI Acid Red 13	5	3/4	4/5	5	5	4/5	3/4
CI Acid Red 17	4/5	3	4	5	5	3/4	4
CI Acid Red 18	5	5	5	5	5	4/5	2/3
CI Acid Red 27	5	4/5	5	5	5	4/5	3

Table 4.5 Staining and the shade change results for the pale dyeings having fk value of 40

After the ISO3 wash-fastness test, the dyeings from CI Acid Red 88 stain on acetate and cotton adjacent fabrics (2/3). The dyeings from CI Acid Red 88 significantly stain on nylon adjacent (2) and wool adjacent (2/3). There is no staining on polyester and acrylic adjacent fabrics. The shade change result for the dyeings from CI Acid Red 88 is rated as 3/4 as given in Table 4.5.

The dyeings from CI Acid Red 13 slightly stain on nylon and wool adjacent fabrics (4/5). The staining on cotton is rated as 3/4. The dyeings do not stain on acetate, polyester and acrylic adjacent fabrics. The shade change result for the dyeings from CI Acid Red 13 is rated as 3/4 (Table 4.5). The dyeings from CI Acid Red 17 stain on acetate, cotton, nylon and wool adjacent fabrics. There is no staining on polyester and acrylic adjacent fabrics. The shade change for the dyeings with CI Acid Red 17 is rated as 3/4. The dyeings from CI

Acid Red 13 give better staining results than the dyeings from CI Acid Red 17. The dyeings from CI Acid Red 13 give 1/2 point better staining results than the dyeings from CI Acid Red 17 on acetate, cotton and nylon adjacent fabrics and 1 point better staining results on the wool adjacent fabric. The shade change result for the dyeings from CI Acid Red 17 is rated as 4 (Table 4.5) which is 1/2 point better than the dyeings from CI Acid Red 13.

The dyeings from CI Acid Red 18 slightly stain on wool adjacent fabric only which is rated as 4/5 and the shade change result for the dyeings from CI Acid Red 18 is rated as 2/3 (Table 4.5). The dyeings from CI Acid Red 27 give similar staining results to the dyeings from CI Acid Red 18 but they also slightly stain on cotton adjacent fabric (4/5). The shade change result for the dyeings from CI Acid Red 27 is rated as 3 as given in Table 4.5 which is 1/2 point better than the shade change result for the dyeings from CI Acid Red 18.

Wash-fastness test ISO3 for the deep dyeings having fk value of 100

Table 4.6 gives the staining and the shade change results for the dyeings having fk value of 100 after the ISO3 wash-fastness test.

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	shade change
CI Acid Red 88	2/3	2/3	1/2	4/5	5	2	3
CI Acid Red 13	5	2/3	4	5	5	3/4	4
CI Acid Red 17	4	2/3	3	5	5	3	3/4
CI Acid Red 18	5	5	5	5	5	4/5	2
CI Acid Red 27	5	4/5	5	5	5	4/5	2/3

Table 4.6 Staining and the shade change results for the deep dyeings having fk value of 100

After the ISO3 wash-fastness test, the dyeings from CI Acid Red 88 stain on acetate and cotton adjacent fabrics (2/3). The dyeings significantly stain on nylon adjacent fabric (1/2). The staining on wool adjacent fabric is also significant which is rated as 2. The dyeings from CI Acid Red 88 slightly stain on polyester adjacent fabric with rating of 4/5. The dyeings do not stain on acrylic adjacent fabric. The shade change result for the dyeings from CI Acid Red 88 is rated as 3 as given in Table 4.6.

After the ISO3 wash-fastness test, the dyeings from CI Acid Red 13 do not stain on acetate, polyester and acrylic adjacent fabrics. Staining on cotton fabric is rated as 2/3 and staining on nylon and wool adjacent fabrics is rated as 4 and 3/4 respectively. The shade change result for the dyeings from CI Acid Red 13 is rated as 3 as given in Table 4.6. The staining results for the dyeings from CI Acid Red 13 are better than the dyeings from CI Acid Red

17. The dyeings from CI Acid Red 17 stain on cotton adjacent fabric (2/3) which is similar for the dyeings from CI Acid Red 13. The dyeings from CI Acid Red 13 give 1 point better staining results than the dyeings from CI Acid Red 17 on acetate and nylon adjacent fabrics. The dyeings from CI Acid Red 17 stain on acetate and nylon adjacent fabrics which is rated as 4 and 3 respectively. The staining on wool adjacent is rated as 3 which is 1/2 point lower than the staining of the dyeings with CI Acid Red 13. Shade change result for the dyeings with CI Acid Red 17 is rated as 3/4 which is 1/2 point lower than the dyeings with CI Acid Red 13.

The dyeings from CI Acid Red 18 stain slightly on wool adjacent (4/5). The shade change result for the dyeings from CI Acid Red 18 is rated as 2. The dyeings from CI Acid Red 27 stain slightly on cotton and wool adjacent fabrics (4/5). The shade change result for the dyeings from CI Acid Red 27 is rated as 2/3 as given in Table 4.6 which is 1/2 point better than the shade change result for the dyeings from CI Acid Red 18.

4.2.2.4 Light-fastness

Light-fastness results for the pale dyeings having fk value of 40

Table 4.7 gives the light-fastness results for the dyeings from the given set of dyes (CI Acid Red 88, CI Acid Red 13, CI Acid Red 17, CI Acid Red 18 and CI Acid Red 27) having fk value of 40.

Dyes used	Grey scale rating
CI Acid Red 88	2/3
CI Acid Red 13	1/2
CI Acid Red 17	2/3
CI Acid Red 18	4/5
CI Acid Red 27	3/4

Table 4.7 Light-fastness results for the pale dyeings having fk value of 40

The light-fastness for the dyeings from CI Acid Red 88 is rated as 2/3. The dyeings from CI Acid Red 13 give light-fastness result which is rated as 1/2. The dyeings from CI Acid Red 17 give 1 point better light-fastness results than the dyeings from CI Acid Red 13 as given in Table 4.7. It shows that the position of sulphonic acid groups on CI Acid Red 17 dye molecule is suitable for the improved light-fastness than the position of sulphonic acid groups on CI Acid Red 13 dye molecule.

The dyeings from CI Acid Red 18 give the light-fastness result rated as 4/5 which is 1 point better than the light-fastness result for the dyeings from CI Acid Red 27 rated as 3/4. It shows that the position of sulphonic acid groups on CI Acid Red 18 dye molecule is suitable for better light-fastness than the position of sulphonic acid groups on CI Acid Red

27. It can be concluded that the dyeings from trisulphonated acid dye CI Acid Red 18 having fk value of 40 (pale dyeings) give better light-fastness results than mono-sulphonated and disulphonated acid dyes as give in Table 4.7.

Light-fastness results for the deep dyeings having fk value of 100

Table 4.8 gives the light-fastness results for the deep dyeings having fk value of 100.

Dyes used	Grey scale rating
CI Acid Red 88	2
CI Acid Red 13	2
CI Acid Red 17	3
CI Acid Red 18	4
CI Acid Red 27	3/4

Table 4.8 Light-fastness results for the deep dyeings having fk value of 100

The light-fastness result for the dyeings from CI Acid Red 88 is rated as 2. Modified fabric dyed with CI Acid Red 17 changes its shade with a rating of 3 which is 1 point better than the dyeings from CI Acid Red 13 rated as 2 (Table 4.8). It shows that the position of sulphonate groups on CI Acid Red 17 dye molecule is suitable for light-fastness for deep dyeings (fk100) than the position of sulphonate groups on CI Acid Red 13 dye molecule.

The light-fastness result for the dyeings from CI Acid Red 18 is rated as 4 and the light-fastness result for the dyeings from CI Acid Red 27 is rated as 3/4. The dyeings from CI Acid Red 18 give 1/2 point better light-fastness result than the dyeings from CI Acid Red 27. It can be concluded that the dyeings from trisulphonated acid dyes give better light-fastness than the dyeings from disulphonated and trisulphonated acid dyes on Servon XRK modified cotton with deep dyeings.

4.2.2.5 Multi-wash tests for the dyeings from non-metallised acid dyes

The dyeings from CI Acid Red 13, CI Acid Red 17, CI Acid Red 18 and CI Acid Red 27 were washed-off for seven washes to analyse the washing-off for non-metallised acid dyes applied on Servon XRK modified cotton. The wash-off was conducted with a solution of Sandozin NIE (2 g/l) at 98°C. First wash was conducted for 15 minutes and then each subsequent wash was conducted for 10 minutes. The optical density of each wash-off solution was measured using a uv/vis spectrophotometer. The resulting graphs are shown in Figures 4.8 – 4.11 respectively.

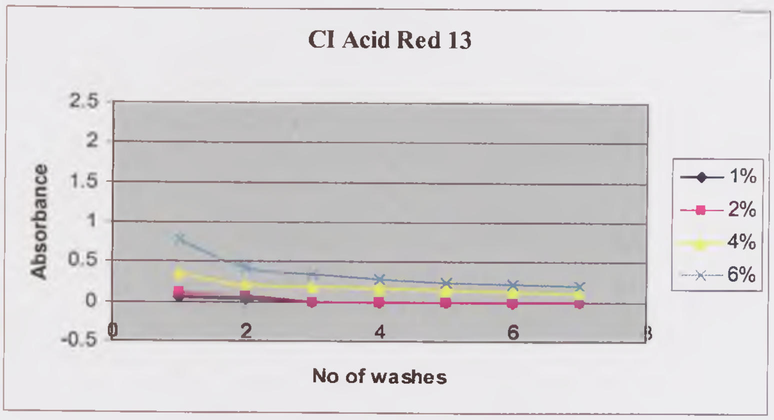


Figure 4.8 Wash-off graph for the dyeings with CI Acid Red 13

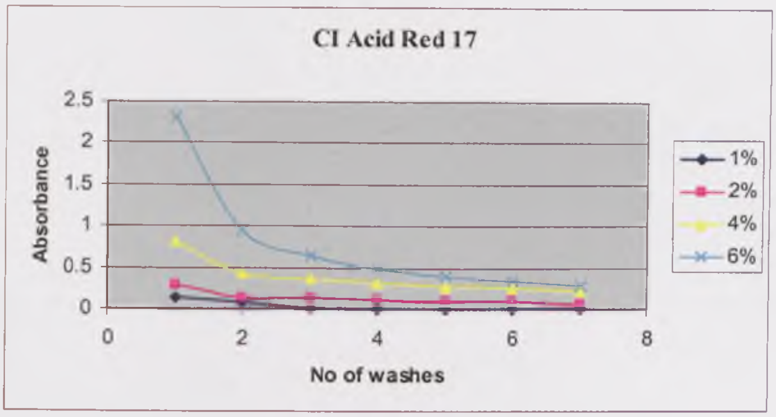


Figure 4.9 Wash-off graph for the dyeings with CI Acid Red 17

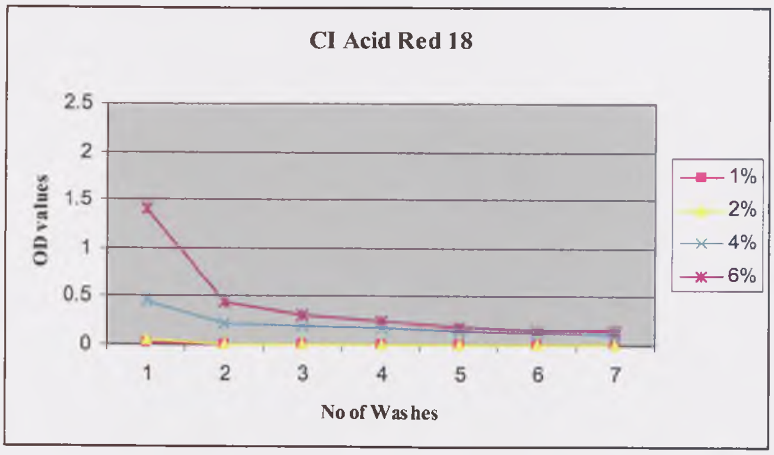


Figure 4.10 Wash-off graph for the dyeings with CI Acid Red 18

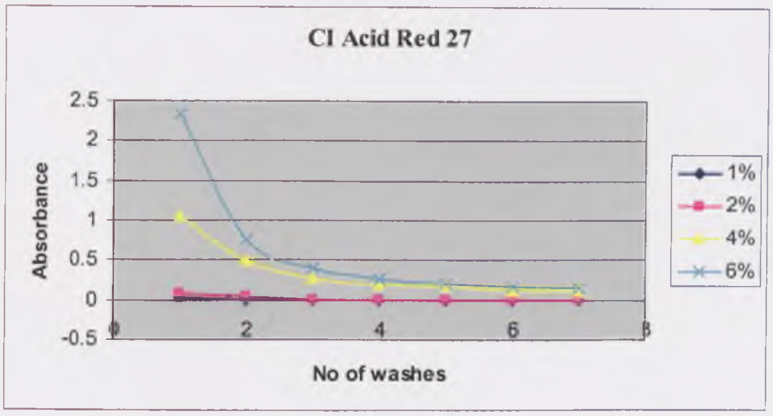


Figure 4.11 Wash-off graph for the dyeings with CI Acid Red 27

The dyeings from CI Acid Red 13 give better wash-off results than the dyeings from CI Acid Red 17 as CI Acid Red 13 and CI Acid Red 17 have similar molecular structures but with the difference of the position of the sulphonate acid groups on their dye molecules. The dyeings from CI Acid Red 13 at 2% o.m.f. do not loose any colour after the second wash but the dyeings from CI Acid Red 17 at 2% o.m.f. continuously loose their colour in the wash-off solution.

The dyeings from trisulphonated acid dyes CI Acid Red 18 and CI Acid Red 27 on modified cotton fibre give good wash-off results with 1% and 2% o.m.f. because after the second wash there is no increase in colour loss. The dyeings with heavy shades such as 4% and 6% o.m.f. the dye continuously washes-off even after the seventh wash but there is a reduction of colour in each wash.

Lewis [3] studied the different forces and their behaviour between dye and fibre. The negatively charged dye molecules which are closer to the positively charged cationic sites have stronger forces of electrostatic attraction but as the distance of the negatively charged sulphonate groups on the dye molecules increases from the positively charged centre of the cations, the electrostatic attraction decreases. So the dye molecules which are at a far distance from positively charged cationic sites of modified fibre come-off from the dyed fabric and stay in the wash-off solution but where the positively charged sulphonated dye molecules are very close to the positively charged centre of the modified fibre the dye molecules are retained on the fibre and do not wash-off.

4.2.2.6 Microscopic images of yarn/ fibre cross-sections

Figures 4.12 - 4.16 show the microscopic yarn/fibre cross-sectional images for the dyeings from CI Acid Red 88, CI Acid Red 13, CI Acid Red 17, CI Acid Red 18 and CI Acid Red 27 [4].

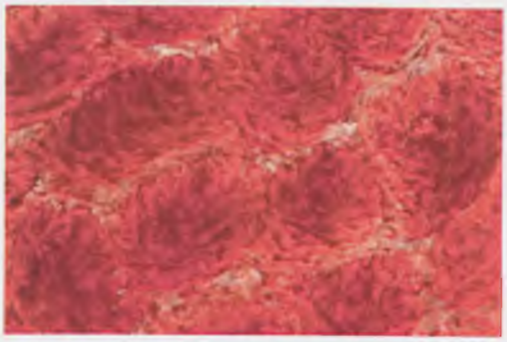


Figure 4.12 Microscopic images of yarn/fibre cross-sections for the dyeings from CI Acid Red 88

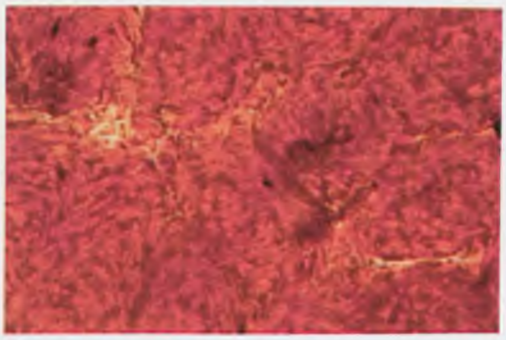


Figure 4.13 Microscopic images of yarn/fibre cross-sections for the dyeings from CI Acid Red 13

Figure 4.14 Microscopic images of yarn/fibre cross-sections for the dyeings from CI Acid Red 17

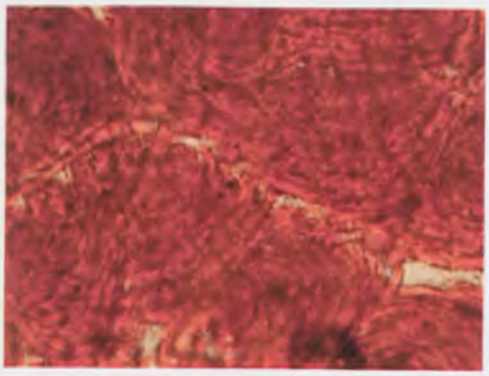


Figure 4.15 Microscopic images of yarn/fibre cross-sections for the dyeings from CI Acid Red 18

Figure 4.16 Microscopic images of yarn/fibre cross-sections for the dyeings from CI Acid Red 27

The dyeings from monosulphonated CI Acid Red 88 give no ring dyeing when applied to the Servon XRK modified cotton which shows that the dye has well penetrated throughout the fibre. The dyeings from disulphonated acid dyes CI Acid Red 13 and CI Acid Red 17 with two sulphonic acid groups on their dye molecules attached with different positions do not give ring-dyeing as shown in Figures 4.13 and 4.14. The dyeings from trisulphonated acid dyes CI Acid Red 18 and CI Acid Red 27 show similar results (Figures 4.15 and 4.16) as dyeings from monosulphonated and disulphonated acid dyes with no ring dyeing.

The microscopic images of the fibre/yarn cross-sections for the dyeings from CI Acid Red 88, CI Acid Red 13, CI Acid Red 17, CI Acid Red 18 and CI Acid Red 27 show that all the dyes are well penetrated inside the modified fibres.

4.3 Pre-metallised acid dyes

4.3.1 Experimental

4.3.1.1 Materials

Fabric samples

Servon XRK (6.5% o.m.f.) modified cotton and wool fabrics were used to conduct dyeings with CI Acid Blue 193 and CI Acid Violet 92.

Dyes

Two commercially available pre-metallised acid dyes CI Acid Blue 193 and CI Acid Violet 92 were used to conduct dyeings with Servon XRK modified cotton which were kindly supplied by DyStar as laboratory research samples. The structures of CI Acid Blue 193 and CI Acid Violet 92 are given in Figures 4.17 and 4.18.

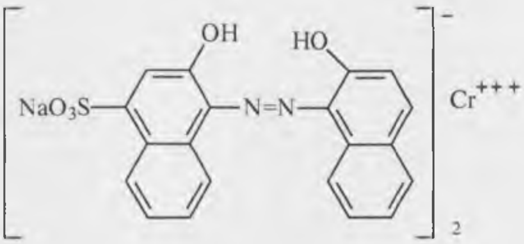


Figure 4.17 Structure of CI Acid Blue 193

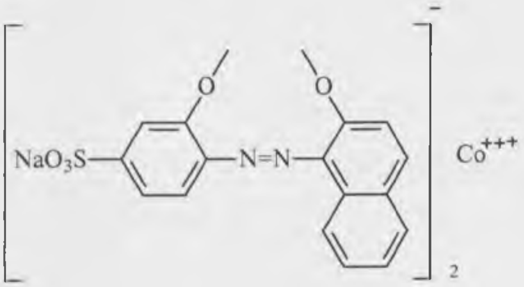


Figure 4.18 Structure of CI Acid Violet 92

4.3.1.2 Dyeing profiles

Dyeing profile for Servon XRK modified cotton

Servon XRK modified cotton was used to conduct dyeings with CI Acid Blue 193 and CI Acid Violet 92 at 1%, 2%, 4% and 6% o.m.f. at pH 7 and at 100 °C for 60 minutes. Figure 4.19 shows the dyeing profile for pre-metallised acid dyes (CI Acid Blue 193 and CI Acid Violet 92) to dye modified cotton.

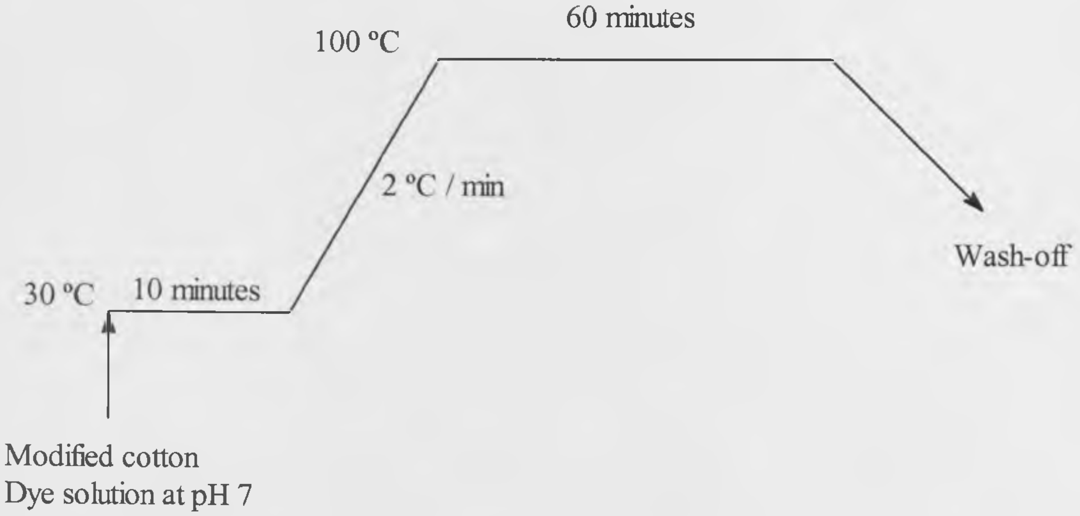


Figure 4.19 Profile for dyeing Servon XRK modified cotton with CI Acid Blue 193 and CI Acid Violet 92

Dyeing profile for wool

Wool fabric samples were dyed with CI Acid Blue 193 and CI Acid Violet 92 at 1%, 2%, 4% and 6% o.m.f. at pH 5.5 and at 100 °C for 60 minutes to compare the results with Servon XRK modified cotton. Figure 4.20 shows the dyeing profile for the given set of pre-metallised acid dyes (CI Acid Blue 193 and CI Acid Violet 92) to dye wool fabric samples.

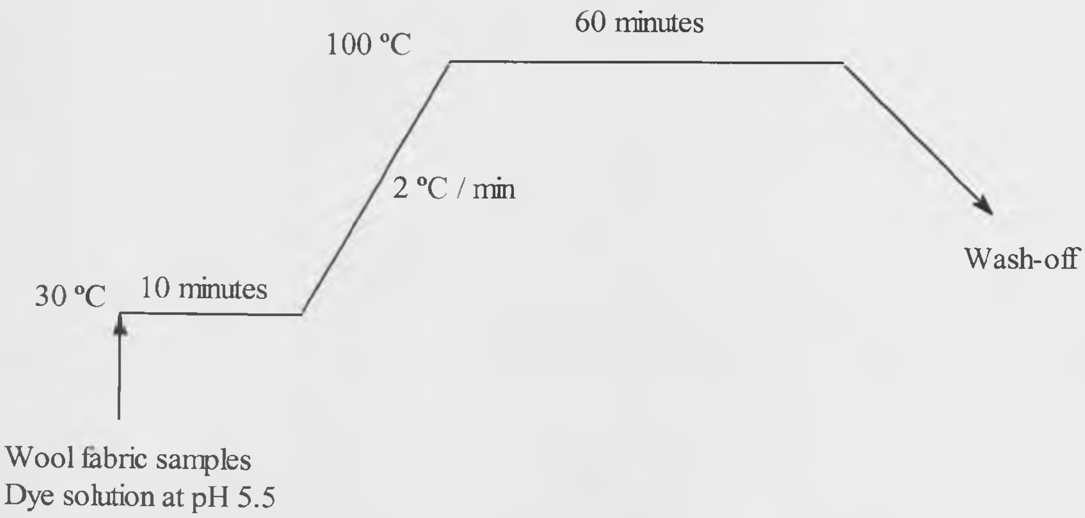


Figure 4.20 Profile for dyeing wool fabric with CI Acid Blue 193 and CI Acid Violet 92

4.3.1.3 Washing-off

The dyed samples were washed-off at 100°C for 15 minutes using Sandozin NIE (2 g/l) [a non-ionic polyethoxylated fatty alcohol surfactant] solution. Liquor to goods ratio was 25:1. Sandozin NIE was supplied by Clariant (UK).

4.3.2 Results and discussion

4.3.2.1 Exhaustion values for the dyeings from Pre-metallised acid dyes

Table 4.9 gives the exhaustion values for the dyeings from CI Acid Blue 193 and CI Acid Violet 92 on Servon XRK modified cotton.

Dyes used	Exhaustion values			
	1% o.m.f.	2% o.m.f.	4% o.m.f.	6% o.m.f.
CI Acid Blue 193	100	99.2	96.2	94.3
CI Acid Violet 92	100	100	99.5	97.1

Table 4.9 Exhaustion values for the dyeings from CI Acid Blue 193 and CI Acid Violet 92 on Servon XRK modified cotton at 1%, 2%, 4% and 6% o.m.f.

The exhaustion values for the dyeings from CI Acid Violet 92 are higher than the exhaustion values for the dyeings from CI Acid Blue 193. But the fixation values for the dyeings of CI Acid Blue 193 are higher than the fixation values for the dyeings of CI Acid Blue 193 because after washing-off CI Acid Violet 92 comes-off being smaller molecular size as compared to the molecular size of CI Acid Blue 193 molecules.

4.3.2.2 Colour yield values for the dyeings from pre-metallised acid dyes on Servon XRK modified cotton fabric and wool fabrics

Table 4.10 gives the colour yield values for the dyeings from CI Acid Blue 193 and CI Acid Violet 92 at 1%, 2%, 4% and 6% o.m.f. on Servon XRK modified cotton and wool fabrics.

Dyes used	Colour yield (fk) values							
	1% o.m.f.		2% o.m.f.		4% o.m.f.		6% o.m.f.	
	XRK	Wool	XRK	Wool	XRK	Wool	XRK	Wool
CI Acid Blue 193	98.7	152.9	173.8	302.3	264.55	479.7	335.8	540.9
CI Acid Violet 92	103.2	170.8	176.2	312.9	282.6	502.5	338.5	575.3

Table 4.10 Colour yield values for the dyeings from CI Acid Blue 193 and CI Acid Violet 92 on Servon XRK modified cotton and wool fabrics

Colour yield values for the dyeings from CI Acid Blue 193 and CI Acid Violet 92 on Servon XRK modified cotton are less than the colour yield values for the dyeings on wool fabric. The dyeings from CI Acid Violet 92 give higher colour yield values than the dyeings from CI Acid Blue 193 for each percentage of shade depth (1%, 2%, 4% and 6% o.m.f.) because CI Acid Violet 92 lacking one phenyl group on its dye molecule gives better exhaustion because it can penetrate easily into the fibre being a smaller molecule than CI Acid Blue 193. The dyeings from CI Acid Violet 92 also show higher colour yield values on wool fabric than the dyeings of CI Acid Blue 193 as shown in Table 4.10.

4.3.2.3 Wash-fastness

All the dyeings from CI Acid Blue 193 and CI Acid Violet 92 on Servon XRK modified cotton and wool were subjected to the wash-fastness tests ISO2 and ISO3 [2].

Wash-fastness test ISO2 for the dyeings of CI Acid Blue 193

Table 4.11 gives the staining and shade change results for the dyeings of CI Acid Blue 193 on Servon XRK modified cotton and wool after the ISO2 wash-fastness test.

Fabric	% omf	acetate	cotton	nylon	poly-ester	acrylic	wool	Shade change
Servon XRK	1 %	4/5	5	4	5	5	4/5	4/5
	2 %	4/5	5	3/4	5	5	4/5	4
	4 %	4	5	2/3	5	5	4	3/4
	6 %	4	5	2	5	5	4	3
Wool	1 %	4/5	5	4/5	5	5	4/5	4/5
	2 %	4	5	4	5	5	4	4/5
	4 %	4	5	3/4	5	5	4	4/5
	6 %	4	5	3	5	5	3/4	4/5

Table 4.11 Staining and the shade change results for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton and wool after the ISO2 wash-fastness test

The dyeings from CI Acid Blue 193 at 1% o.m.f. on Servon XRK modified cotton after the ISO2 wash-fastness test stain slightly on acetate and wool adjacent fabrics which is rated as 4/5. The staining on nylon adjacent is rated as 4. The dyeings did not stain on cotton, polyester and acrylic adjacents. The shade change result for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton at 1% o.m.f. is rated as 4/5 as given in Table 4.11.

The dyeings from CI Acid Blue 193 on wool fabric after the ISO2 wash-fastness test at 1% o.m.f. stain on acetate, nylon and wool adjacents (4/5). There is no staining on cotton, polyester and acrylic adjacents. The shade change result for the dyeings from CI Acid Blue 193 on wool fabric at 1% o.m.f. is rated as 4/5 which is similar to the shade change for the dyeings on Servon XRK modified cotton. The staining on nylon adjacent is 1/2 point higher on Servon XRK modified cotton than that of wool.

The dyeings from CI Acid Blue 193 at 2% o.m.f. on Servon XRK modified cotton stain slightly on acetate and wool adjacent fabrics which is rated as 4/5. The staining on nylon adjacent is rated is as 3/4. The shade change for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton at 2% o.m.f. is rated as 4 as given in Table 4.11. The dyeings from CI Acid Blue 193 at 2% o.m.f. on wool fabric stain on acetate, nylon and wool adjacents rated as 4. There is no staining on cotton, polyester and acrylic adjacent fabrics. There is 1/2 point lower staining on acetate, nylon and wool adjacents for the dyeings on Servon XRK modified cotton than for the dyeings on wool. The shade change result is rated as 4/5 which is 1/2 point higher than the shade change for the dyeings on Servon XRK modified cotton.

The dyeings from CI Acid Blue 193 at 4% o.m.f. on Servon XRK modified cotton after the ISO2 wash-fastness test stain on acetate, nylon and wool adjacents. The staining on acetate and wool adjacents is rated as 4 while staining on nylon adjacent is 2/3. The shade change result for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton at 4% o.m.f. is rated as 3/4 as given in Table 4.11. The dyeings from CI Acid Blue 193 on wool fabric stain on acetate, nylon and wool adjacents. The staining on acetate and wool adjacents is rated as 4 which is similar for the dyeings on Servon XRK modified cotton. The staining on nylon adjacent is rated as 3/4 which is 1 point higher than the staining on nylon adjacent for the dyeings on Servon XRK modified cotton. The shade change result is rated as 4/5 for the dyeings on wool which is 1 point better than the shade change for the dyeings on Servon XRK modified cotton.

The dyeings from CI Acid Blue 193 at 6% o.m.f. on Servon XRK modified cotton after the ISO2 wash-fastness test stain on acetate and wool adjacents. Staining on nylon is significant which is rated as 2. The shade change result for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton at 6% o.m.f. is rated as 3 as given in Table 4.11. The dyeings from CI Acid Blue 193 on wool fabric at 6% o.m.f. after the ISO2 wash-fastness test stain on acetate adjacent with rating of 4. The staining on nylon and wool adjacents is 3 and 3/4 respectively. The shade change result for the dyeings on wool fabric is rated as 4/5 which is significantly higher than the shade change for the dyeings on Servon XRK modified cotton.

Wash-fastness test ISO3 for the dyeings from CI Acid Blue 193

Table 4.12 gives the staining and the shade change results for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton and wool fabric after the ISO3 wash-fastness test.

Fabric	% omf	acetate	cotton	nylon	poly-ester	acrylic	wool	Shade change
Servon XRK	1 %	4/5	5	3	5	5	4	4
	2 %	4/5	5	2/3	5	4/5	3/4	3/4
	4 %	4	5	2	5	4/5	2/3	3
	6 %	4	4/5	1/2	5	4	2	2/3
Wool	1 %	4	4/5	2/3	4/5	4/5	4	4
	2 %	3/4	4	2	4	4	3/4	4
	4 %	3	4	2	4	3/4	2	4
	6 %	3	4	1/2	4	3/4	1/2	4

Table 4.12 Staining and the shade change results for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton and wool fabric after the ISO3 wash-fastness test

The dyeings from CI Acid Blue 193 at 1% o.m.f. on Servon XRK modified cotton after the ISO3 wash-fastness test stain on acetate, nylon and wool adjacents. The staining on acetate adjacent is rated as 4/5. The staining on nylon and wool adjacents is rated as 3 and 4 respectively. The shade change result for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton at 1% o.m.f. is rated as 4 as given in Table 4.12. The dyeings from CI Acid Blue 193 on wool fabric at 1% o.m.f. stain slightly on cotton, polyester and acrylic adjacents with rating of 4/5. The staining on acetate and wool adjacents is rated as 4. The staining on nylon adjacent is rated as 2/3. The dyeings from CI Acid Blue 193 on wool shows 1/2 point lower staining on Servon XRK modified cotton on acetate, cotton, nylon, polyester and acrylic adjacents. The shade change result for the dyeings from CI Acid Blue 193 on wool fabric at 1% o.m.f. is rated as 4 which is similar to the shade change for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton.

The dyeings from CI Acid Blue 193 at 2% o.m.f. on Servon XRK modified cotton stain slightly on acetate and acrylic adjacents with rating of 4/5. The staining on nylon and wool adjacent fabrics is rated as 2/3 and 3/4 respectively. The shade change result for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton at 2% o.m.f. is rated as 3/4 as given in Table 4.12. The dyeings from CI Acid Blue 193 on wool fabric stain on acetate and wool adjacents with rating of 3/4. The staining on cotton, polyester and acrylic adjacents is rated as 4. There is a significant staining on nylon which is rated as 2. The shade change result for the dyeings from CI Acid Blue 193 on wool fabric at 2% o.m.f. is rated as 4 which is 1/2 point better than the shade change for the dyeings on Servon XRK modified cotton.

The dyeings from CI Acid Blue 193 at 4% o.m.f. on Servon XRK modified cotton after the ISO3 wash-fastness test stain on acetate, nylon, acrylic and wool adjacent fabrics. There is no staining on cotton and polyester adjacents. The staining on acrylic adjacent is rated as 4/5. The staining on acetate and wool adjacents is rated as 4 and 2/3 respectively. There is significant staining on nylon adjacent which is rated as 2. The shade change result for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton at 4% o.m.f. is rated as 3 (Table 4.12). The dyeings from CI Acid Blue 193 on wool fabric stain significantly on nylon which is rated as 2. The staining on acetate adjacent is rated as 3. The staining on cotton and polyester adjacents is rated as 4. The staining on acrylic adjacent is rated as 3/4. The shade change result is rated as 4 which is 1 point better than the shade change for the dyeings on Servon XRK modified cotton.

The dyeings from CI Acid Blue 193 at 6% o.m.f. on Servon XRK modified cotton after the ISO3 wash-fastness test stain slightly on the cotton adjacent with rating of 4/5. The staining on acetate and acrylic adjacents is rated as 4. There is a significant staining on nylon and wool adjacents with rating of 1/2 and 2 respectively. There is no staining on polyester adjacent. The shade change result for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton at 6% o.m.f. is rated as 2/3 as given in Table 4.12. The dyeings from CI Acid Blue 193 at 6% o.m.f. on wool fabric after the ISO3 wash-fastness test stain significantly on the adjacent fabrics. The staining on nylon and wool adjacents is rated as 1/2. There is staining on acetate and acrylic adjacents rated as 3 and 3/4 respectively. The staining on cotton and polyester adjacents is rated as 4. The shade change result is rated as 4 for the dyeings on wool fabric which is 1/2 point higher than the shade change on Servon XRK modified cotton.

Wash-fastness test ISO2 for the dyeings from CI Acid Violet 92

Table 4.13 gives the staining and the shade change results for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton and wool fabric after the ISO2 wash-fastness test.

Fabric	% omf	acetate	cotton	nylon	poly-ester	acrylic	wool	Shade change
Servon XRK	1 %	5	5	3	5	5	4/5	4
	2 %	4/5	5	2/3	5	4/5	4	3
	4 %	4	4/5	2	5	4/5	4	2/3
	6 %	4	4/5	1/2	4/5	4	3/4	2/3
Wool	1 %	4	4/5	3/4	4/5	4/5	4/5	4
	2 %	4	4/5	2/3	4/5	4/5	4	4
	4 %	3/4	4/5	2	4/5	4	4	4
	6 %	3	4/5	2	4/5	4	3/4	4

Table 4.13 Staining and the shade change results for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton and wool after the ISO2 wash-fastness test

The dyeings from CI Acid Violet 92 at 1% o.m.f. on Servon XRK modified cotton stain only on nylon and wool adjacent fabrics. The staining on nylon adjacent is rated as 3 while the staining on wool adjacent fabric is rated as 4/5. The shade change result for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton at 1% o.m.f. is rated as 4 as given in Table 4.13. The dyeings from CI Acid Violet 92 on wool fabric at 1% o.m.f. after the ISO2 wash-fastness test stain slightly on cotton, polyester, acrylic and wool adjacents. The staining on nylon is rated as 3/4 which is 1/2 point better than the staining on nylon for the dyeings on Servon XRK modified cotton. The shade change result for the dyeings from CI Acid Violet 92 on wool fabric at 1% o.m.f. is rated as 4 which is the same as the shade change for the dyeings on Servon XRK modified cotton.

The dyeings from CI Acid Violet 92 at 2% o.m.f. on Servon XRK modified cotton give slight staining on acetate and acrylic adjacents after the ISO2 wash-fastness test. There is no staining on cotton and polyester adjacent fabrics. The staining on nylon and acrylic adjacents is rated as 2/3 and 4 respectively. The shade change result for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton at 2% o.m.f. is rated as 3 as given in Table 4.13. The dyeings from CI Acid Violet 92 on wool fabric slightly stain on cotton, polyester and acrylic adjacents with a rating of 4/5. The staining on acetate and wool adjacents is rated as 4. There is a staining on nylon adjacent fabric which is rated as 2/3. The shade change result for the dyeings from CI Acid Violet 92 on wool fabric at 2% o.m.f. is rated as 4 which is 1 point higher than the shade change for the dyeings on Servon XRK modified cotton.

The dyeings from CI Acid Violet 92 at 4% o.m.f. on Servon XRK modified cotton give a slight staining with rating of 4/5 on cotton and acrylic adjacents. The staining on acetate and wool adjacents is rated as 4. There is no staining on polyester adjacent fabric. It has been found a significant staining on nylon adjacent which is rated as 2. The shade change result for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton at 4% o.m.f. is rated as 2/3 as given in Table 4.13. The dyeings from CI Acid Violet 92 on wool fabric at 4% o.m.f. after the ISO2 wash-fastness give a slight staining with rating of 4/5 on cotton and polyester adjacents. The staining on acrylic and wool adjacents is rated as 4. There is a staining with rating of 3/4 on acetate adjacent. The staining on nylon adjacent is significant which is rated as 2. The shade change result for the dyeings from CI Acid Violet 92 on wool fabric at 4% o.m.f. is rated as 4 which is significantly higher than the shade change for the dyeings on Servon XRK modified cotton.

The dyeings from CI Acid Violet 92 at 6% o.m.f. on Servon XRK modified cotton after the ISO2 wash-fastness test stain slightly on cotton and polyester adjacents. The staining on acetate and acrylic adjacents is rated as 4. There is a staining with rating of 3/4 on wool adjacent. It has been found a significant staining on nylon adjacent which is rated as 1/2. The shade change result for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton at 6% o.m.f. is rated as 2/3 (Table 4.13). The dyeings from CI Acid Violet 92 at 6% o.m.f. on wool fabric stain significantly on adjacent fabrics. There is a slight staining with rating of 4/5 on cotton and polyester adjacents. The staining on acetate adjacent is rated as 3. The staining on acrylic and wool adjacents is rated as 4 and 3/4 respectively. There is a significant staining with rating of 2 on nylon adjacent. The shade change result for the dyeings on wool fabric is rated as 4 which is significantly higher than the shade change for the dyeings on Servon XRK modified cotton.

Wash-fastness test ISO3 for the dyeings from CI Acid Violet 92

Table 4.14 gives the staining and the shade change results for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton and wool fabric after the ISO3 wash-fastness test.

Fabric	% omf	acetate	cotton	nylon	poly-ester	acrylic	wool	Shade change
Servon XRK	1 %	4/5	5	3	5	4/5	3/4	3
	2 %	4	5	2	5	4	3	2/3
	4 %	3/4	4/5	2	4/5	3	2/3	2
	6 %	3/4	4/5	1/2	4/5	2/3	2	2
Wool	1 %	4	4	2/3	4	3/4	3	4
	2 %	3	4	2	4	3	2/3	4
	4 %	2/3	3	1/2	3	2/3	2	3/4
	6 %	2/3	3	1/2	3	2/3	1/2	3

Table 4.14 Staining and the shade change results for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton and wool after the ISO3 wash-fastness test

The dyeings from CI Acid Violet 92 at 1% o.m.f. on Servon XRK modified cotton after the ISO3 wash-fastness stain on the adjacent fabrics. There is no staining on cotton and polyester adjacents. The staining on acetate and acrylic adjacents is rated as 4/5. There is staining on nylon and wool adjacent fabrics which is rated as 3 and 3/4 respectively. The shade change result for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton at 1% o.m.f. is rated as 3 as shown in Table 4.14. The dyeings from CI Acid Violet 92 on wool fabric at 1% o.m.f. after the ISO3 wash-fastness test stain on the adjacent fabrics. The staining on acetate, cotton and polyester adjacents is rated as 4. The staining on acrylic adjacent is rated as 3/4. There is a significant staining on nylon and wool adjacent fabrics with a rating of 2/3 and 3 respectively. The shade change result for the dyeings on wool fabric is rated as 4 which is 1 point higher than the shade change for the dyeings on Servon XRK modified cotton.

The dyeings from CI Acid Violet 92 at 2% o.m.f. on Servon XRK modified cotton give a staining with rating of 4 on acetate and acrylic adjacents. The staining on nylon and wool adjacents is significant which is rated as 2 and 3 respectively. The shade change result for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton at 2% o.m.f. is rated as 2/3 as given in Table 4.14. The dyeings from CI Acid Violet 92 on wool fabric at 2% o.m.f. stain on cotton and polyester adjacent fabrics with rating of 4. There is a staining on acetate and acrylic adjacents which is rated as 3. The staining on nylon and wool adjacents is rated as 2 and 2/3 respectively. The shade change for the dyeings on wool fabric is rated as 4 which is better than the shade change for the dyeings on Servon XRK modified cotton.

The dyeings from CI Acid Violet 92 at 4% o.m.f. on Servon XRK modified cotton after the ISO3 wash-fastness test stain slightly on cotton and polyester adjacent fabrics (4/5). The staining on acetate and acrylic adjacents is rated as 3/4 and 3 respectively. There is a significant staining with a rating of 2 and 2/3 on nylon and wool adjacents respectively. The shade change result for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton at 4% o.m.f. is rated as 2 as given in Table 4.14. The dyeings from CI Acid Violet 92 on wool fabric at 4% o.m.f. give significant staining on the adjacent fabrics. There is a staining with a rating of 3 on cotton and polyester adjacents. The staining on acetate and acrylic adjacents is rated as 2/3. There is a significant staining on nylon and wool adjacents with rating of 1/2 and 2 respectively. The shade change result for the dyeings on wool fabric is rated as 3/4 which is significantly higher than the shade change for the dyeings on Servon XRK modified cotton.

The dyeings from CI Acid Violet 92 at 6% o.m.f. slightly stain on cotton and polyester adjacent fabrics which is rated as 4/5 after the ISO3 wash-fastness test. The staining on acetate and acrylic adjacents is rated as 3/4 and 2/3 respectively. There is a significant staining with a rating of 1/2 and 2 on nylon and wool adjacent fabrics respectively. The shade change result for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton at 6% o.m.f. is rated as 2 (Table 4.14). The dyeings from CI Acid Violet 92 at 6% o.m.f. on wool fabric give staining on acetate and acrylic adjacents with rating of 2/3 while the staining on cotton and polyester adjacents is rated as 3. It has been found a significant staining with rating of 1/2 on nylon and wool adjacents. The shade change result for the dyeings on wool fabric is rated as 3 which is 1 point higher than the shade change for the dyeings on Servon XRK modified cotton.

4.3.2.4 Light-fastness

Table 4.15 gives the light-fastness results for the dyeings from CI Acid Blue 193 and CI Acid Violet 92 on Servon XRK modified cotton and wool at 1%, 2%, 4% and 6% o.m.f.

Dyes used	1 % o.m.f.		2 % o.m.f.		4 % o.m.f.		6 % o.m.f.	
	XRK	Wool	XRK	Wool	XRK	Wool	XRK	Wool
CI Acid Blue 193	5	5	5	5	5	5	5	5
CI Acid Violet 92	5	5	5	5	5	5	5	5

Table 4.15 Light-fastness results for the dyeings from CI Acid Blue 193 and CI Acid Violet 92 on Servon XRK modified cotton and wool fabric

Light-fastness results for the dyeings from CI Acid Blue 193 and CI Acid Violet 92 on Servon XRK modified cotton and wool fabric at 1%, 2%, 4% and 6% o.m.f. which is rated as 5 (Table 4.15).

4.3.2.5 Multi-wash tests for the dyeings from pre-metallised acid dyes on Servon XRK modified cotton

The dyeings from CI Acid Blue 193 and CI Acid Violet 92 at 1%, 2%, 4% and 6% o.m.f. were washed-off with a solution of Sandozin NIE 2 g/l at 98 °C for seven washes to analyse the washing-off for pre-metallised acid dyes on Servon XRK modified cotton fabric. First wash was conducted for 15 minutes and then subsequent washes were conducted for 10 minutes. The absorbance value of each wash-off solution was measured in UV/Vis spectrophotometer. The graphs of absorbance values against number of washes have been shown in Figures 4.21 and 4.22.

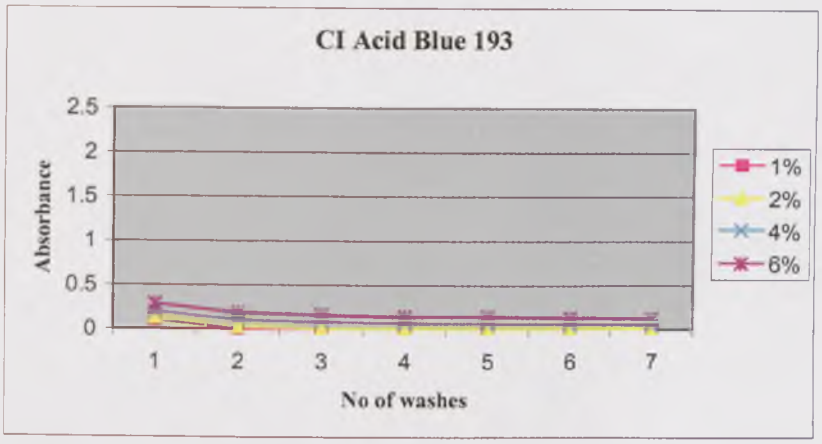


Figure 4.21 Wash-off graph for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton

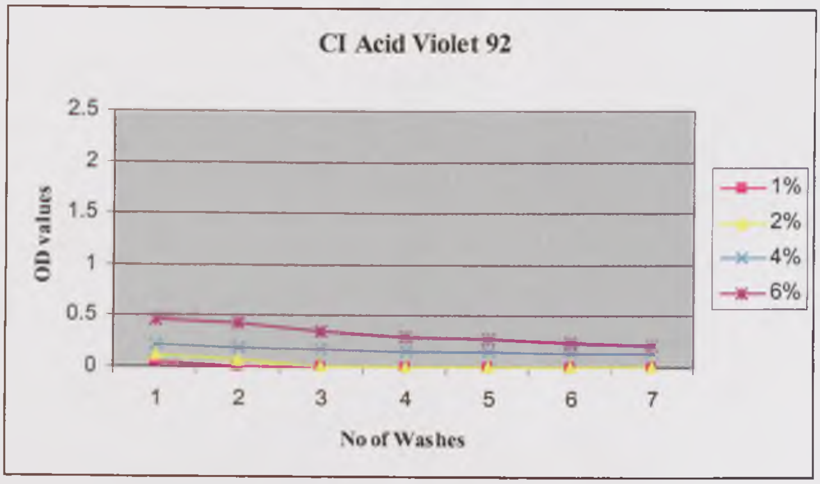


Figure 4.22 Wash-off graph for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton

Figures 4.21 and 4.22 show the multi-wash graphs for the dyeings from CI Acid Blue 193 and CI Acid Violet 92. The dyeings from CI Acid Blue 193 on Servon XRK modified cotton give better wash-off results than the dyeings from CI Acid Violet 92. The dyeings from CI Acid Violet 92 with deep shades loose more colour as compared to the dyeings from CI Acid Blue 193 during washing-off. The dyeings from CI Acid Violet 92 at 4% and 6% o.m.f. continuously loose colour in wash-off solution. The dyeings from CI Acid Blue 193 with deep shades (4% and 6% o.m.f.) continuously reduces its colour in each wash-off solution.

4.3.2.6 Microscopic images of yarn/fibre cross-section

Figures 4.23 and 4.24 show the microscopic images of the yarn/fibre cross-sections for the dyeings from CI Acid Blue 193 and CI Acid Violet 92 [4].

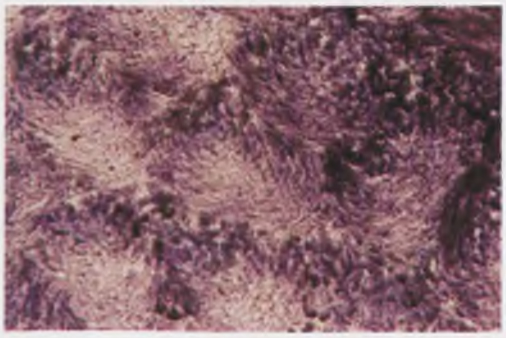


Figure 4.23 Microscopic images of yarn/fibre cross-sections for the dyeings from CI Acid Blue 193 on Servon XRK modified cotton

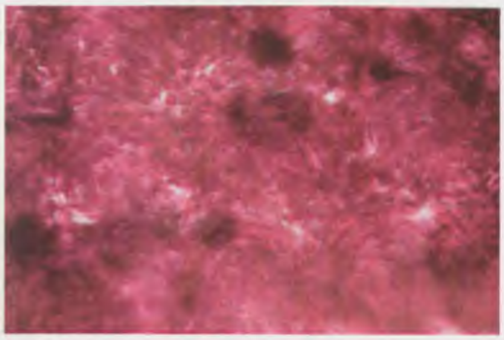


Figure 4.24 Microscopic images of yarn/fibre cross-sections for the dyeings from CI Acid Violet 92 on Servon XRK modified cotton

The dyeings from CI Acid Blue 193 give ring dyeing results as shown in Figure 4.24. The microscopic images of the yarn/fibre cross-sections for the dyeings from CI Acid Violet 92 (Figure 4.24) show that the dye has well penetrated inside the fibre being comparatively smaller in molecular than CI Acid Blue 193.

4.4 Conclusions

The dyeings from non-metallised acid dyes CI Acid Red 88, CI Acid Red 13, CI Acid Red 17, CI Acid Red 18 and CI Acid Red 27 have higher exhaustion values with their pale shades (1% and 2% o.m.f.) than the dyeings with their heavy shades (4% and 6% o.m.f.). It has been seen that non-metallised acid dyes with two sulphonic acid groups such as CI Acid Red 13 and CI Acid Red 17 give comparatively better wash-fastness results than the dye with one sulphonic acid group such as CI Acid Red 88 and the dyes with three sulphonic acid groups such as CI Red 18 and CI Acid Red 27. Mono-sulphonated acid dye CI Acid Red 88 after the ISO2 and ISO3 wash-fastness tests come-off from the dyed fabric and stains significantly on the adjacent fabrics where as tri-sulphonated acid dyes CI Acid

Red 18 and CI Acid Red 27 being highly soluble in water with a higher degree of sulphonic acid groups, come-off and intend to stain in the wash-off solution rather than staining on the adjacent fabric.

Tri-sulphonated acid dyes give better light-fastness results than monosulphonated and di-sulphonated acid dyes. The dyeings from all the non-metallised acid dyes applied on the Servon XRK modified cotton do not show any ring-dyeing.

After second wash the dyeings from di-sulphonated acid dye CI Acid Red 13 at 1% and 2% o.m.f. do not give any colour in was-off solution. But the dyeings from di-sulphonated CI Acid Red 17 at 1% and 2% o.m.f. continuously loose its colour in the wash-off solution but the amount of colour reduces in each wash. The dyeings at 4% and 6% o.m.f. continuously loose their colour even in seventh wash but with the reduction of colour in each wash test.

The dyeings from tri-sulphonated acid dyes CI Acid Red 18 and CI Acid Red 27 at 1% and 2% o.m.f. after second wash do not loose any colour in the wash-off solution but the dyeings at 4% and 6% o.m.f. loose their colour in each wash but the amount of gradually decreases. Modified cotton dyed with non-metallised acid dyes with heavy shades may not be recommended for soaping-off at higher temperatures for commercial uses.

The wash-fastness results for the dyeings from CI Acid Blue 193 and CI Acid Violet 92 on wool fabric at 1%, 2%, 4% and 6% o.m.f. are better than the dyeings on Servon XRK modified cotton. The wash-fastness results for the dyeings from CI Acid Blue 193 applied on Servon XRK modified cotton are better than the dyeings from CI Acid Blue 92.

The dyeings from CI Acid Blue 193 give better wash-off results than the dyeings from CI Acid Violet 92 during multi-wash tests. The dyeings from CI Acid Blue 193 and CI Acid Violet 92 at 1% and 2% o.m.f. after third wash do not loose any colour but at 4% and 6% o.m.f. the colour comes-off in each wash. The dyeings from CI Acid Violet 92 give more colour at 4% and 6% o.m.f. in each wash-off solution as compared to CI Acid Blue 193.

The light-fastness results for the dyeings from CI Acid Blue 193 and CI Acid Violet 92 on Servon XRK modified cotton at 1%, 2%, 4% and 6% o.m.f. are rated as 5. The dyeings from CI Acid Blue 193 give a little ring dyeing but the dyeings from CI Acid Violet 92 show better dye penetration.

4.5 References

1. C Hawkyard in, *Synthetic Fibre Dyeing*, C Hawkyard (ed.), Society of Dyers and Colourists, Bradford 2004.
2. *Methods for Colour Fastness of Textiles and Leather,* 5th edn., Society of Dyers and Colourists, Bradford 1990.
3. DM Lewis, *International Journal of Cosmetic Science,* **18** (1996) 123-135.
4. PH Greaves and BP Saville, *Microscopy of Textile Fibres,* Royal Microscopical Society, 1995.

Chapter 5

Application of Azoic Colourants to Unmodified and Modified Cotton (Modified with Servon XRK)

5.1 Introduction

The term ‘azoic’ is used to describe dyeings and prints produced by synthesising an insoluble azo compound inside the fibre by reacting together a coupling component and a diazonium salt. Naphthols are usually used for coupling components; azoic diazo components derived from primary amines or stabilized diazonium components are called respectively fast colour bases or fast colour salts [1]. Azoic colourants provide bright shades of moderate to good wet-fastness and good light-fastness on cellulosic fibres but being in a pigment form on the fibre, they suffer from rubbing problems.

Azo colours may be used as dyes or pigments, soluble or insoluble in water and contain one or more azo chromophores; the azo group is $—N{=}N—$; azo comes from the French word for nitrogen, azote [2].

The normal procedure for azoic dyeing includes four major stages [1] as shown in Figure 5.1.

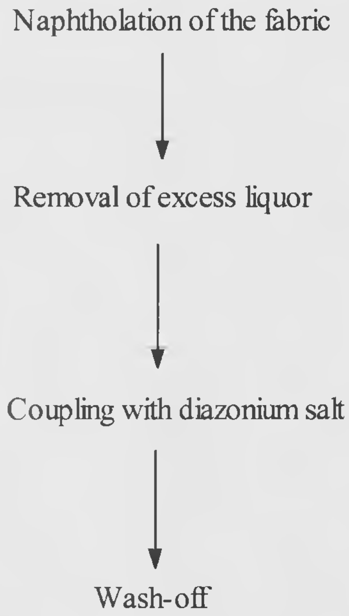


Figure 5.1 Dyeing procedure of cotton with azoic colourants

5.2 Experimental

5.2.1 Materials

5.2.1.1 Fabric

Two types of fabric were used in this research. Unmodified scoured and bleached cotton and cotton modified with Servon XRK (6.5% o.m.f.).

5.2.1.2 Coupling component

Naphthol AS (CI Azoic Coupling Component 2) was generously supplied by DyStar as a laboratory research sample. The structure of Naphthol AS is shown in Figure 5.2.

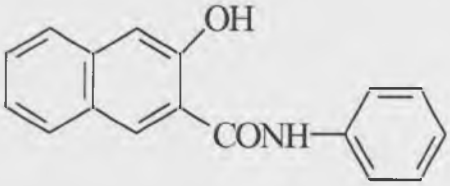


Figure 5.2 CI Azoic coupling component 2

5.2.1.3 Diazonium salt

The stabilised diazonium salt 'Fast Red Salt FRN' was used to synthesize the insoluble azo dye by reaction with the coupling component, 'Naphthol AS' inside the fibre.

5.2.1.4 Other reagents

Sandozin NIE (non-ionic surfactant) and Ufoxane 2 were obtained as samples from Clariant and DyStar. Sodium hydroxide was obtained from Aldrich, UK.

5.2.2 Application of Naphthol AS

Naphthol AS was applied to the unmodified and the modified cotton fabrics by the following methods:

5.2.2.1 Application of Naphthol AS by padding

Preparation of padding solution:

Naphthol AS	10 g
NaOH (32% w/v)	20 g

Ufoxane 2 (Dispersing agent)	2.5 g
H_2O (Distilled water)	467.5 g
Total volume of the solution	500 g

The solution of Naphthol AS (20 g/kg) was prepared: 467.5 g distilled water was taken in a glass beaker and heated up to 70 to 80 °C, then 10 g powdered Naphthol AS was stirred for a while and 2.5 g Ufoxane 2 (dispersing agent) was added. It was stirred for 5 minutes. Then 20 g NaOH solution was added and stirred for 30 minutes at 80 to 90 °C. After stirring the solution, it is ready to use. Figure 5.3 shows the conversion of insoluble form of Naphthol AS to soluble form.

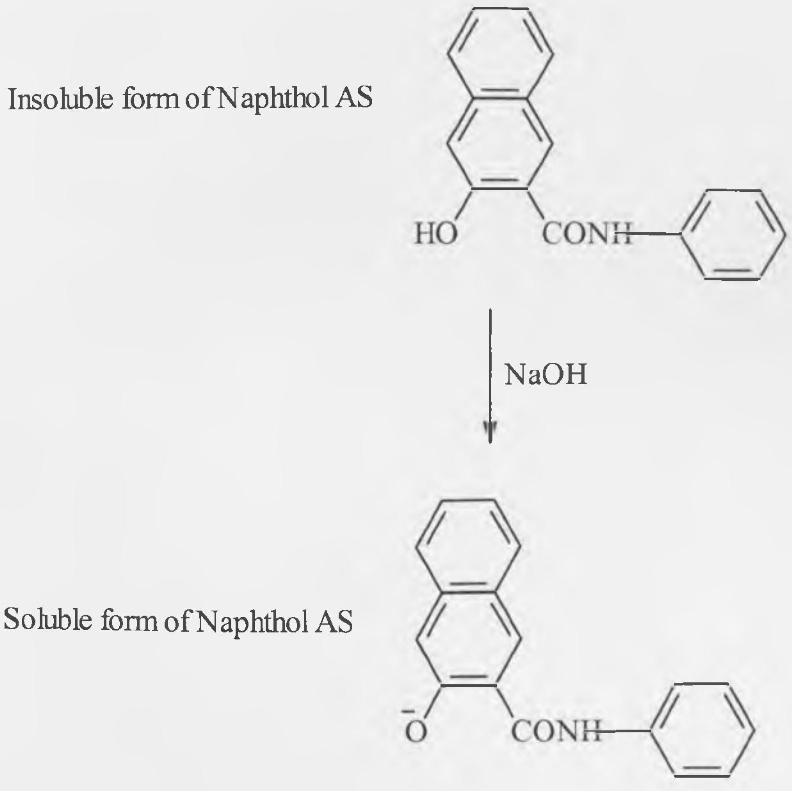


Figure 5.3 Soluble form of Naphthol AS

Padding

The Naphthol AS solution was applied to the unmodified and the modified cotton fabrics by pad-dry and pad-batch-dry methods.

- **Pad-dry method**

  The Naphthol AS (20 g/kg) was applied to the unmodified and the modified cotton fabrics using a pad mangle to give a wet pick up of 100%. After padding, the fabric was dried in a dryer and then the naphtholated fabric (2% o.m.f.) was coupled with a Fast Red Salt FRN (4g/l).

- **Pad-batch-dry method**

  After applying the Naphthol AS solution by padding at a wet pick up of 100%, the Naphtholated fabric was batched overnight (18 hours), dried in a dryer and then coupled with the Fast Red Salt FRN (4g/l).

5.2.2.2 Application of Naphthol AS by long liquor

A solution containing sufficient Naphthol AS to give 2 % o.m.f. was prepared as shown in 5.2.2.1. The solution was applied to the unmodified and the modified cotton fabrics by the long liquor method using the Labomat dyeing machine. The liquor to goods ratio was 10:1. The Naphthol solution was applied at 30°C and 60°C for 30 minutes to both the unmodified and the modified cotton fabrics and then coupled with the diazonium salt (Fast Red Salt

FRN). The profiles to apply Naphthol solution to the unmodified and the modified cotton fabrics are shown in Figures 5.4 and 5.5.

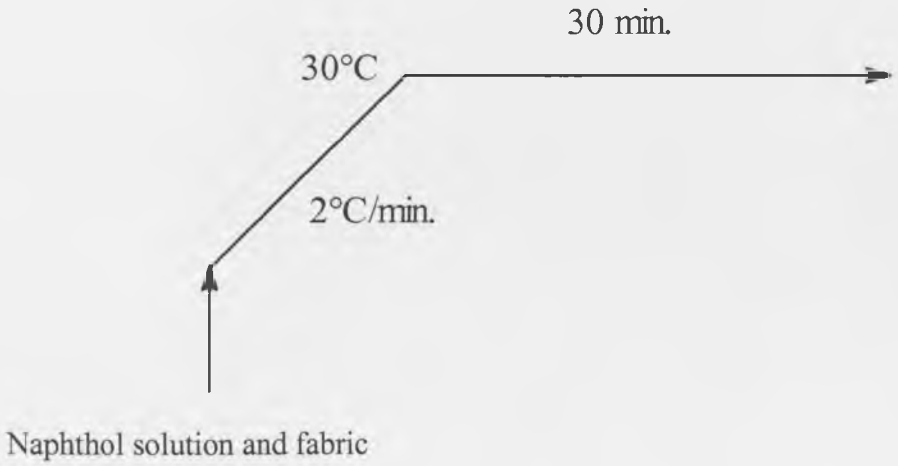


Figure 5.4 Application of Naphthol AS to the unmodified and the modified cotton at 30 °C

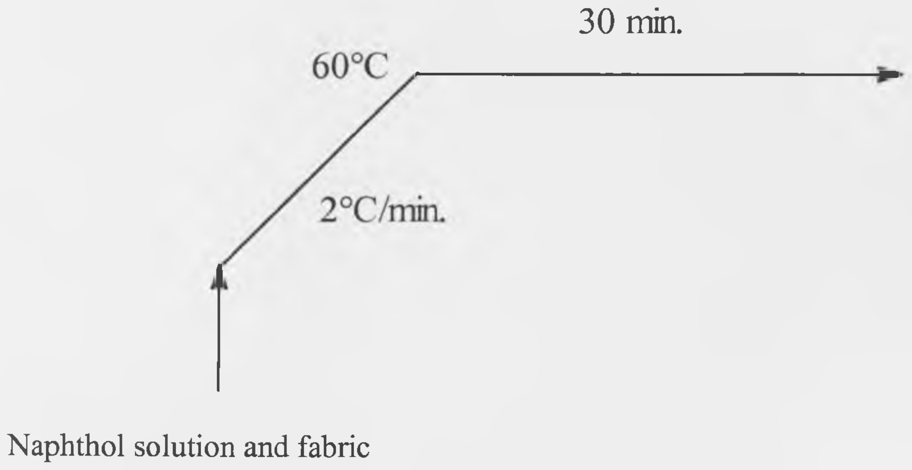


Figure 5.5 Application of Naphthol AS to the unmodified and the modified cotton fabrics at 60 °C

5.2.2.3 Co-application of Naphthol AS and Servon XRK

Preparation of pad liquor (Naphthol AS and Servon XRK)

Total volume of pad liquor (Solution of Servon XRK and Naphthol AS)	500 ml

Servon XRK solution

Servon XRK (65% w/w)	50 g
NaOH (50% w/v)	50 g
Sandozin NIE	5 g
Distilled water	195 g

50 g Servon XRK was diluted in 195 g distilled water; when equipment was ready for padding, 50 g NaOH was added drop-wise with stirring. Then 5 g of Sandozin NIE was added and the liquor stirred for a while.

Preparation of Naphthol AS solution

Naphthol AS	10 g
NaOH (32% w/v)	20 g
Ufoxane 2 (dispersing agent)	2.5 g
Distilled water	167.5 g

The Naphthol solution was prepared as mentioned in 5.2.2.1.

Padding

The solutions of Naphthol AS and Servon XRK were mixed and co-applied to the unmodified cotton fabric by the pad-dry and the pad-batch-dry method;

- **Pad-dry method**

  Naphthol AS/Servon XRK (both applied at 2% o.m.f.) were applied to the unmodified cotton at a wet pick up of 100%. After padding, the fabric was dried in a dryer and then coupled with the diazonium salt solution (Fast Red Salt FRN 4g/l).

- **Pad-batch-dry method**

  After applying Naphthol AS/Servon XRK solution by padding at a wet pick up of 100%, the Naphtholated fabric was batched overnight (18 hours), dried in a dryer and then coupled with the Fast Red Salt FRN (4 g/l).

5.2.3 Coupling (Development)

After the application of Naphthol AS/Servon XRK solution to the fabric, the Naphtholated fabric was coupled with a solution of the Fast Red Salt FRN (4 g/l). The liquor to goods ratio was 20:1 and the rinsing time was 30 minutes.

5.2.4 After-treatment

After coupling the samples were finished as follows;

- Rinsed in cold water.

- Rinsed in dilute hydrochloric acid (3 ml) at 40 °C.
- Again rinsed in cold water.
- Soaped-off for 30 minutes at 100 °C in a solution containing Sandozin NIE (3 g/l) and soda ash (2 g/l).
- Rinsed thoroughly in hot water and then in cold water.

5.3 Results and discussion

5.3.1 Application of Naphthol AS by padding

5.3.1.1 Colour yield

Table 5.1 gives the fk values for the dyeings evaluated by the application of Naphthol AS to the unmodified and the modified cotton fabrics by pad-dry and pad-batch-dry methods followed by coupling with the Fast Red Salt FRN.

Application methods of Naphthol AS	fk values	
	Unmodified cotton	Modified cotton
Pad-dry	187.97	203.25
Pad-batch-dry	195.91	223.50

Table 5.1 fk values for the dyeings on the unmodified and the modified cotton fabrics by pad-dry and pad-batch-dry methods

The colour yield values for the dyeings on the modified cotton are higher than for the dyeings on the unnmodified cotton in case of pad-dry method of Naphtholation which indicates that the modified cotton has better absorption of Naphthol AS solution during padding than the unmodified cotton. In the case of the pad-batch-dry method of Naphtholation, the dyeings on the modified cotton give higher colour yield values than the dyeings on the unmodified cotton fabric. The colour yield values for the dyeings evaluated by the application of Naphthol AS using the pad-batch-dry method are greater than the colour yield values evaluated by the application of Naphthol AS by the pad-dry method which shows that during batching Naphthol AS penetrates the fabric and this gives higher colour yield values on coupling with the Fast Red Salt FRN.

5.3.1.2 Wash-fastness

The wash-fastness tests ISO2 and ISO3 [3] have been conducted for the dyeings when Naphthol AS was applied to the unmodified and the modified cotton fabrics by pad-dry and pad-batch-dry methods followed by coupling with Fast Red salt FRN.

Wash-fastness test (ISO2)

Tables 5.2 and 5.3 give the staining and the shade change results for the dyeings on the unmodified and the modified cotton fabrics after the ISO2 wash-fastness test.

Methods of Naphtholation	acetate	cotton	nylon	polyester	acrylic	wool	shade change
Pad-dry	4/5	4	3	4/5	4/5	4	4
Pad-batch-dry	4/5	4/5	3	4/5	4/5	4/5	4

Table 5.2 Staining and the shade change results for the dyeings on the unmodified cotton fabric

Methods of Naphtholation	acetate	cotton	nylon	polyester	acrylic	wool	shade change
Pad-dry	4/5	4/5	3/4	4/5	4/5	4/5	4
Pad-batch-dry	4/5	4/5	3/4	4/5	4/5	4/5	4/5

Table 5.3 Staining and the shade change results for the dyeings on the modified cotton fabric

The dyeings evaluated by the application (pad-dry method) of Naphthol AS on the unmodified cotton fabric followed by coupling with the Fast Red Salt FRN, show significant staining on nylon adjacent rated as 3. The staining on cotton and wool adjacent fabrics is rated as 4. There is a slight staining on acetate, polyester and acrylic adjacents (4/5). The shade change result is rated as 4.

The dyeings on the modified cotton by pad-dry method of Naphtholation (Naphthol AS) followed by coupling with the Fast Red Salt FRN, stain the nylon adjacent (3/4) which is 1/2 point better than the staining on the unmodified cotton. There is slight staining on acetate, cotton, polyester, acrylic and wool adjacent fabrics rated as 4/5. The dyeings on the modified cotton give 1/2 point better staining results on cotton, nylon and wool adjacents than the dyeings on the unmodified cotton fabric. The shade change result is rated as 4 for the dyeings on the modified cotton fabric which is same as the shade change result for the dyeings the on unmodified cotton fabric.

In case of the pad-batch-dry method of Naphtholation, the dyeings on the unmodified cotton give significant staining on nylon adjacent which is rated as 3 but the staining on the other adjacent fabrics is rated as 4/5. The shade change result is rated as 4.

The dyeings from the application (pad-batch-dry method) of Naphthol AS on the modified cotton fabric followed by coupling with the Fast Red Salt FRN, show slight staining on each adjacent fabric which is rated as 4/5 but the staining on nylon adjacent is rated as 3/4 which is 1/2 point better than the staining result for the dyeings on the unmodified cotton. The shade change result for the dyeings on the modified cotton fabric is rated as 4/5 which is also 1/2 point better than the shade change result of the dyeings on the unmodified cotton.

Wash-fastness test (ISO3)

Tables 5.4 and 5.5 give the staining and the shade change results for the dyeings on the unmodified and the modified cotton fabrics after the ISO3 wash-fastness test.

Methods of Naphtholation	acetate	cotton	nylon	polyester	acrylic	wool	shade change
Pad-dry	4	4	2/3	4/5	4/5	4	3
Pad-batch-dry	4	4	2/3	4	4	4	¾

Table 5.4 Staining and the shade change results for the dyeings on the unmodified cotton fabric

Methods of Naphtholation	acetate	cotton	nylon	polyester	acrylic	wool	shade change
Pad-dry	4/5	4	3	4/5	4/5	4	4
Pad-batch-dry	4/5	4/5	3/4	4/5	4/5	4/5	4

Table 5.5 Staining and the shade change results for the dyeings on the modified cotton fabric

The dyeings on the unmodified cotton fabric evaluated by pad-dry method of Naphtholation followed by coupling with the Fast Red Salt FRN, significantly stain the nylon adjacent rated as 2/3. The staining on acetate, cotton and wool adjacents is rated as 4 but the staining on polyester and acrylic adjacents is slight (4/5). The shade change result for the dyeings is rated as 3.

The dyeings on the modified cotton fabric from pad-dry method of Naphtholation (Naphthol AS) followed by coupling (Fast Red Salt FRN), show staining on nylon adjacent (3) which is 1/2 point better than the staining on the nylon adjacent for the dyeings on the unmodified cotton fabric. The dyeings on the modified cotton fabric show 1/2 point better staining results on acetate adjacent than the dyeings on the unmodified cotton fabric which is rated as 4/5. The shade change result for the dyeings is rated as 4 which is 1 point better than the shade change result for the dyeings on the unmodified cotton fabric.

The dyeings on the unmodified cotton fabric from pad-batch-dry method of Naphtholation (Naphthol AS) followed by coupling with the Fast Red Salt FRN, stain acetate, cotton, polyester, acrylic and wool adjacent fabrics rated as 4. The staining on nylon adjacent is rated as 2/3 which is significant. The shade change result for the dyeings is rated as 3/4.

The dyeings on the modified cotton fabric evaluated by pad-batch-dry method of Naphtholation (Naphthol AS) give slight staining on acetate, cotton, polyester, acrylic and wool adjacent fabrics rated as 4/5 which is 1/2 point better than the dyeings on the unmodified cotton fabric. The staining on nylon adjacent is rated as 3/4 which is 1 point better than the dyeings on the unmodified cotton fabric. The shade change result for the dyeings on the modified cotton fabric is rated as 4 which is 1/2 point better than the shade change result for the dyeings on the unmodified cotton fabric.

5.3.1.3 Light-fastness

Table 5.6 shows the light-fastness results for the dyeings from the application of Naphthol AS to the unmodified and the modified cotton fabrics by pad-dry and pad-batch-dry methods followed by coupling with the Fast Red Salt FRN.

Methods of Naphtholation	Grey scale rating	
	Unmodified cotton	Modified cotton
Pad-dry	5	5
Pad-batch-dry	5	5

Table 5.6 Light-fastness results for the dyeings on the unmodified and the modified cotton fabrics

The light-fastness for the dyeings evaluated by pad-batch and pad-batch-dry methods of Naphtholation to the unmodified and the modified cotton fabrics followed by coupling with the Fast Red Salt FRN is rated as 5 as shown in Table 5.7.

5.3.1.4 Rub-fastness

Table 5.7 gives the rub-fastness results for the dyeings from the application of Naphthol AS to the unmodified and the modified cotton fabrics by pad-dry and pad-batch-dry methods and followed by coupling with the Fast Red Salt FRN.

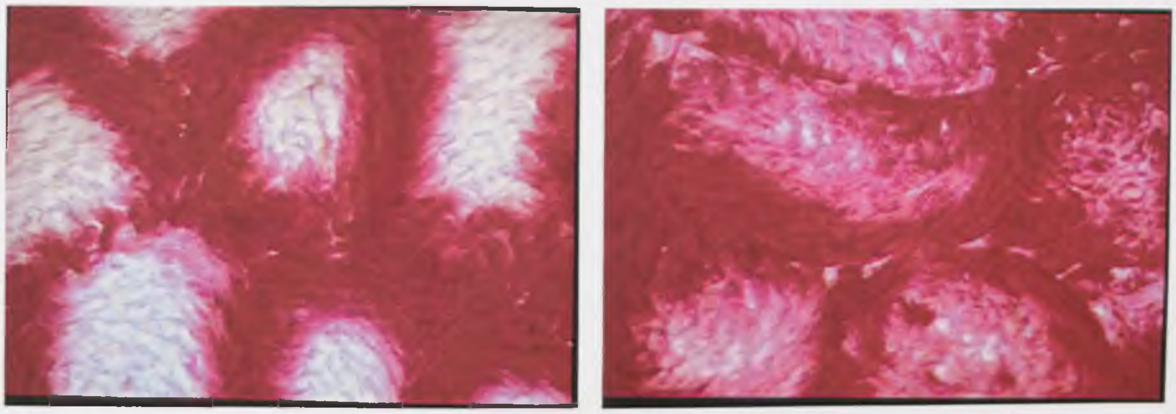
Methods of Naphtholation	Unmodified cotton		Modified cotton	
	Dry	Wet	Dry	Wet
Pad-dry	4/5	3	4/5	3
Pad-batch-dry	4/5	3	4/5	3

Table 5.7 Rub-fastness results for the dyeings on the unmodified and the modified cotton fabrics

Table 5.7 shows that the dry and the wet rub-fastness results for the dyeings on the unmodified and the modified cotton fabrics are the same rated as 4/5 and 3 respectively when Naphtholated by pad-batch and pad-batch-dry method. In both cases of Naphtholation (pad-batch and pad-batch-dry) the dyeings on the modified cotton fabric give higher colour yield values than the dyeings on the unmodified cotton but the rub-fastness results are same for both the dyeings (unmodified and modified cotton fabrics) which shows that the Naphthol has well penetrated to the modified cotton fibre and in a result the dyeings do not intend to come-off during rubbing test.

5.3.1.5 Microscopic images of yarn/fibre cross-sections

Figure 5.7 shows the microscopic images of the yarn/fibre cross-sections for the dyeings from Naphthol AS applied to the unmodified and the modified cotton fabrics by the pad-dry method followed by coupling with Fast Red Salt FRN [4].



Unmodified cotton Modified cotton

Figure 5.6 Microscopic images of yarn/fibre cross-sections on the unmodified and the modified cotton fabrics

The microscopic images of yarn/fibre cross-sections for the dyeings on the unmodified and the modified cotton fabrics show there is less ring dyeing for the modified cotton than on the unmodified cotton because the negatively charged Naphtholate anions are attracted by the positively charged quaternary amines to the modified cotton resulting in better penetration of Naphthol AS (Figure 5.7).

5.3.2 Application of Naphthol AS by long liquor method

5.3.2.1 Colour yield

Table 5.8 gives the colour yield values for the dyeings from Naphthol AS applied to the unmodified and the modified cottons at 30 °C and 60 °C by long liquor method followed by coupling with the Fast Red Salt FRN.

Exhaustion temperature	fk values	
	Unmodified cotton	Modified cotton
30°C	54.4	131.14
60°C	60.1	132.25

Table 5.8 Colour yield values for the dyeings obtained by the application of Naphthol AS to the unmodified and the modified cotton fabrics by a long liquor method followed by coupling with the Fast Red Salt FRN

The colour yield values for the dyeings on the modified cotton is significantly higher than the dyeings on the unmodified cotton as show in Table 5.8 when Naphthol AS was applied to the unmodified and the modified cotton fabrics at 30°C and 60°C. In case of the modified cotton, there is better absorption of Naphtholate anions than on the unmodified cotton giving higher colour yield values.

5.3.2.2 *Wash-fastness*

The wash-fastness tests ISO2 and ISO3 have been conducted to analyse the wet-fastness properties for the dyeings on the unmodified and the modified cotton fabrics with the application of Naphthol AS by long liquor method (exhaustion) followed by coupling with the Fast Red Salt FRN.

Wash-fastness test (ISO2)

Tables 5.9 and 5.10 give the staining and the shade change results after the ISO2 wash-fastness test for the dyeings when Naphthol AS was applied on the unmodified and the modified cotton fabrics at 30°C and 60°C by long liquor method followed by coupling with the Fast Red Salt FRN.

Exhaustion temperature	acetate	cotton	nylon	Polyester	acrylic	wool	shade change
30°C	4	4	3	4/5	4/5	4	3/4
60°C	4/5	4/5	3	4/5	4/5	4/5	3/4

Table 5.9 Staining and the shade change results for the dyeings with the application of Naphthol AS to the unmodified cotton by long liquor method followed by coupling with the Fast Red Salt FRN

Exhaustion temperature	acetate	cotton	nylon	Polyester	acrylic	wool	shade change
30°C	4/5	4/5	3/4	4/5	5	4/5	4
60°C	4/5	4/5	3/4	4/5	5	4/5	4

Table 5.10 Staining and shade change results following wash-testing the dyeings with the application of Naphthol AS to the modified cotton by long liquor method followed by coupling with the Fast Red Salt FRN

After the ISO2 wash-fastness test, the dyeings with the application of Naphthol AS at 30°C on the unmodified cotton followed by coupling with the Fast Red Salt FRN, stain acetate, cotton and wool adjacents rated as 4. There is slight staining on polyester and acrylic adjacent fabrics (4/5). The staining on nylon adjacent is significant which is rated as 3. The shade change result for the dyeings on the unmodified cotton fabric is rated as 3/4.

The dyeings evaluated by the application of Naphthol AS to the modified cotton by exhaustion method at 30°C followed by coupling with the Fast Red Salt FRN, stain slightly acetate, cotton, polyester and wool adjacents which is rated as 4/5. There is no staining on the acrylic adjacent which shows an enhancement in the staining results for the dyeings on the modified cotton fabric as compared to the staining results for the dyeings on the unmodified cotton fabric. The staining on nylon adjacent has been rated as 3/4 which is 1/2 point better than the staining results for the dyeings on the unmodified cotton. The shade change for the dyeings on the modified cotton is rated as 4 which is 1/2 point better than the shade change result for the dyeings on the unmodified cotton fabric.

The dyeings on the unmodified cotton when Naphtholated (Naphthol AS) at 60°C by the exhaustion method, stain slightly acetate, cotton, polyester, acrylic and wool adjacents rated as 4/5. The staining on nylon adjacent is significant which is rated as 3. The shade change result for the dyeings on the unmodified cotton fabric is rated as 3/4.

The dyeings on the modified cotton when Naphtholated at 60°C (exhaustion method) stain acetate, cotton, polyester and wool adjacents is rated as 4/5 which is similar to the staining results for the dyeings on the unmodified cotton fabric but there is no staining on acrylic adjacent which is 1/2 point better than the staining results for the dyeings on the unmodified cotton fabric. The staining on nylon adjacent is rated as 3/4. The shade change for the dyeings on modified cotton fabric is rated as 4 which shows 1/2 point higher shade change results for the dyeings on the unmodified cotton fabric when Naphtholated at 60°C (exhaustion method) followed by coupling with the Fast Red Salt FRN.

Wash-fastness test (ISO3)

Tables 5.11 and 5.12 give the staining and the shade change results after the ISO3 wash-fastness test for the dyeings when Naphthol AS was applied to the unmodified and the modified cotton fabrics at 30°C and 60°C by long liquor method followed by coupling with the Fast Red Salt FRN.

Exhaustion temperature	acetate	cotton	nylon	polyester	acrylic	wool	shade change
30°C	4	4	2/3	4	4/5	4	3
60°C	4/5	4	2/3	4	4/5	4	3

Table 5.11 Staining and the shade change results for the dyeings with the application of Naphthol AS to the unmodified cotton by long liquor method followed by coupling with the Fast Red Salt FRN

Exhaustion temperature	acetate	cotton	nylon	polyester	acrylic	wool	shade change
30°C	4/5	4	3	4/5	4/5	4/5	4
60°C	4/5	4/5	3	4/5	4/5	4/5	4

Table 5.12 Staining and the shade change results for the dyeings with the application of Naphthol AS to the modified cotton by long liquor method followed by coupling with the Fast Red Salt FRN

The dyeings from the application of Naphthol AS at 30°C to the unmodified cotton fabric by exhaustion method followed by coupling with the Fast Red Salt FRN after the ISO3 wash-fastness test, significantly stain on the nylon adjacent (2/3). The staining on acetate, cotton, polyester and wool adjacents is rated as 4. It has been found a slight staining on acrylic adjacent which is rated as 4/5. The shade change result for the wash-tested dyeings is rated as 3.

The dyeings on the modified cotton which have been evaluated by the application of Naphthol AS on modified cotton at 30°C by long liquor method followed by coupling with the Fast Red Salt FRN after the ISO3 wash-fastness test, stain slightly on acetate, polyester, acrylic, and wool adjacent fabrics (4/5) which shows 1/2 point better staining results on acetate, polyester and wool adjacent fabrics as compared to the staining results for the dyeings on the unmodified cotton fabric. The staining on the nylon adjacent is rated as 3 which is 1/2 point better than the staining result for the dyeings on the unmodified cotton fabric. The shade change for the dyeings is rated as 4 which is 1 point better than the shade change for the dyeings on the unmodified cotton.

The dyeings on the unmodified cotton from the application of Naphthol AS at 60°C (exhaustion method) followed by coupling with the Fast Red Salt FRN, stain slightly on acetate and acrylic adjacents (4/5). The staining on cotton, polyester and wool adjacents is rated as 4. It has been found that the staining on nylon adjacent is quite significant which is rated as 2/3. The shade change result for the dyeings is rated as 3.

The dyeings on the modified cotton evaluated by the application of Naphthol AS at 60°C (exhaustion method) followed by coupling with the Fast Red Salt FRN after the ISO3 wash-fastness test, show slight staining on acetate, cotton, polyester, acrylic and wool adjacent fabrics (4/5) which shows 1/2 point better staining results on cotton, polyester and wool adjacents than the dyeings on the unmodified cotton fabric. The shade change result for the dyeings on the modified cotton is rated as 4 which is 1 point better than the shade change result for the dyeings on the unmodified cotton fabric.

5.3.2.3 Light-fastness

Table 5.13 gives the light-fastness results for the dyeings from the application of Naphthol AS to the unmodified and the modified cotton fabrics (exhaustion method) at 30°C and 60°C followed by coupling with the Fast Red Salt FRN.

Exhaustion temperature	Grey scale rating	
	Unmodified cotton	Modified cotton
30°C	4	4/5
60°C	4	4/5

Table 5.13 Light-fastness results for the dyeings from the application of Naphthol AS to the unmodified and the modified cotton fabrics at 30°C and 60°C followed by coupling with the Fast Red Salt FRN

The light-fastness results for the dyeings from the application of Naphthol AS by the exhaustion method to the unmodified and the modified cotton fabrics at 30°C and 60°C followed by coupling with the Fast Red Salt FRN, are rated as 4 and 4/5 for the unmodified and the modified cotton fabrics respectively as shown in Table 5.13.

5.3.2.4 Rub-fastness

Table 5.14 gives the rub-fastness results for the dyeings from the application of Naphthol AS to the unmodified and the modified cotton fabrics (exhaustion method) at 30°C and60 °C followed by coupling with the Fast Red Salt FRN.

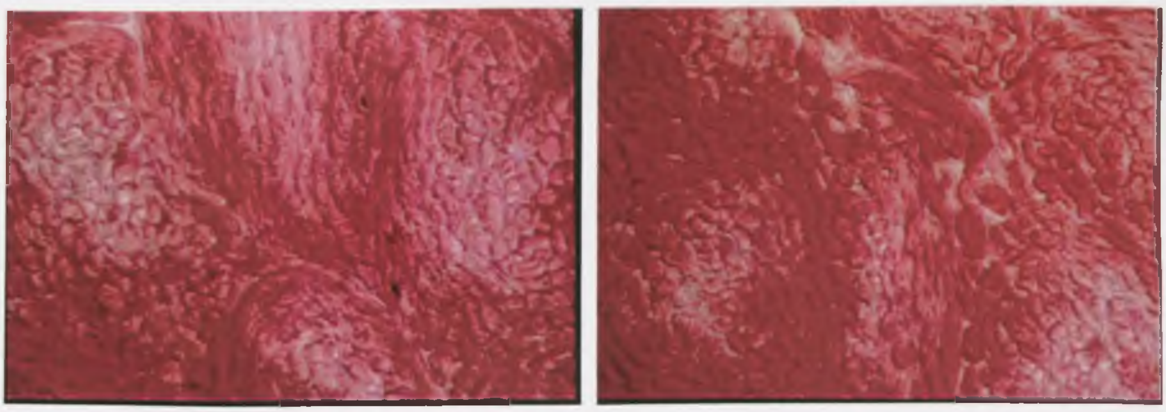
Exhaustion temperature	Grey Scale Rating			
	Unmodified cotton		Modified cotton	
	Dry	Wet	Dry	Wet
30°C	4/5	4	4/5	3/4
60°C	4/5	4	4/5	3/4

Table 5.14 Rub-fastness results for the dyeings from the application of Naphthol AS to the unmodified and the modified cotton fabrics at 30 °C and 60 °C followed by coupling with the Fast Red Salt FRN

The rub-fastness results for the dyeings on the unmodified and the modified cotton fabrics Naphtholated at 30°C and 60°C by exhaustion method are similar rated as 4/5 during dry rub test. The rub-fastness results for the dyeings on the unmodified cotton is rated as 4 and for the dyeings on the modified cotton rated as 3/4 after the wet rub test.

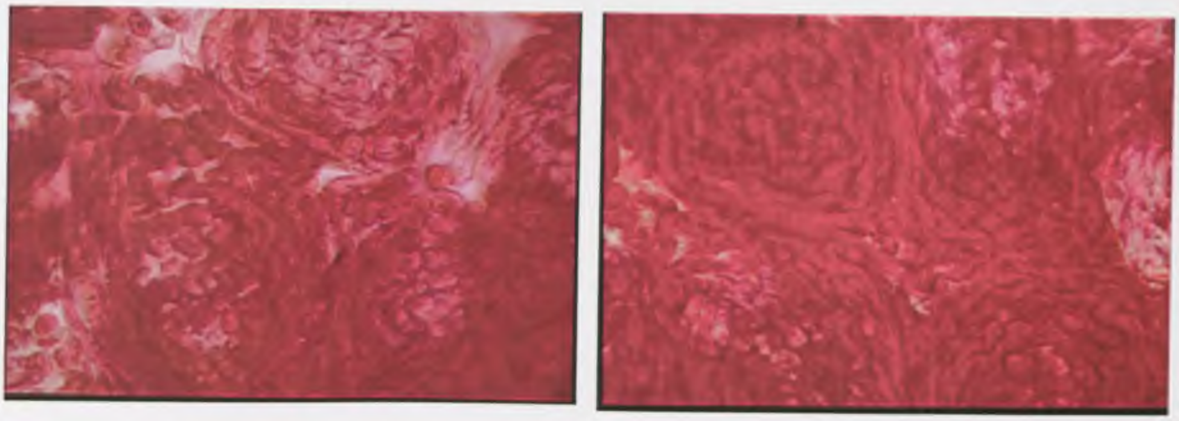
5.3.2.5 Microscopic images of the yarn/fibre cross-sections

Figures 5.8 and 5.9 show the microscopic images of the yarn/fibre cross-sections for the dyeings on the unmodified and the modified cotton fabrics when Naphtholated (Naphthol AS) by the exhaustion method at 30°C and 60°C followed by coupling with the Fast Red Salt FRN.



Unmodified cotton Modified cotton

Figure 5.7 Microscopic images of the yarn/fibre cross-sections for the dyeings on the unmodified and the modified cotton fabrics at 30°C



Unmodified cotton Modified cotton

Figure 5.8 Microscopic images of the yarn/fibre cross-sections for the dyeings on the unmodified and the modified cotton fabrics at 60°C

The dyeings evaluated by the application of Naphthol AS to the unmodified and the modified cotton fabrics by the exhaustion method at 30°C and 60°C followed by coupling with the Fast Red Salt FRN, show that the dyeings on the modified cotton fabric give better penetrated dyeings than the dyeings on the unmodified cotton fabric as shown in Figures 5.8 and 5.9. Naphtholate anions are well migrated into the modified cotton fibre resulting in the reduction in ring dyeing. The dyeings from the application of Naphthol AS to the modified cotton fabric at 60°C show better penetration than the dyeings from the application of Naphthol AS to the modified cotton fabric at 30°C followed by coupling with the Fast Red Salt FRN.

5.3.3 Application of Naphthol AS and Servon XRK to the unmodified cotton fabric (Co-application)

5.3.3.1 Colour yield

Table 5.15 gives the colour yield values for the dyeings from the co-application of Naphthol AS and Servon XRK to the unmodified cotton by pad-dry and pad-batch-dry methods followed by coupling with the Fast Red Salt FRN.

Methods of Naphtholation	fk values
Pad-dry	128.5
Pad-batch-dry	162.8

Table 5.15 Colour yield values for the dyeings obtained from the co-application of Naphthol AS and Servon XRK to the unmodified cotton fabric followed by coupling with the Fast Red Salt FRN

Table 5.15 gives the colour yield values for the dyeings when Naphthol AS and Servon XRK applied together (all in one method) to the unmodified cotton by pad-dry and pad-batch-dry method followed by coupling with the Fast Red Salt FRN. The colour yield values for the dyeings by pad-batch-dry method are higher than the colour yield values for the dyeings by pad-dry method because during batching Naphtholate anions have been seen well-absorbed thus giving higher colour yield values after coupling with the Fast Red Salt FRN as shown in Table 5.15.

5.3.3.2 Wash-fastness

The wash-fastness tests ISO2 and ISO3 have been conducted to analyse the wet-fastness properties for the dyeings from the co-application (all in one method) of Naphthol AS and Servon XRK by pad-dry and pad-batch-dry methods to the unmodified cotton fabric followed by coupling with the Fast Red Salt FRN.

Wash-fastness test (ISO2)

Table 5.16 gives the staining and the shade change results for the dyeings from the co-application of Naphthol AS and Servon XRK on the unmodified cotton fabric followed by coupling with the Fast Red Salt FRN after the ISO2 wash-fastness test.

Methods of Naphtholation	acetate	cotton	nylon	polyester	acrylic	wool	shade change
Pad-dry	4/5	4/5	4	4/5	4/5	4/5	3
Pad-batch-dry	4/5	4/5	4	4/5	4/5	4	3/4

Table 5.16 Staining and the shade change results for the dyeings from the co-application of Naphthol AS and Servon XRK to the unmodified cotton fabric followed by coupling with the Fast Red Salt FRN

The dyeings from the co-application of Naphthol AS and Servon XRK to the unmodified cotton fabric by pad-dry method followed by coupling with the Fast Red Salt FRN after the

ISO2 wash-fastness test, show slight staining (4/5) on all the adjacent fabrics except nylon adjacent which is rated as 4. The shade change result for the dyeings is rated as 3.

The dyeings from pad-batch-dry method of Naphthol AS co-applied with Servon XRK, stain on acetate, cotton, polyester and acrylic adjacent fabrics (4/5). The staining on nylon and wool adjacents is rated as 4. The rating of shade change result for the dyeings is rated as 3/4 which is 1/2 point better than the shade change result for the dyeings from pad-dry method of Naphthol AS co-applied with Servon XRK followed by coupling with the Fast Red Salt FRN after the ISO2 wash-fastness test.

Wash-fastness test (ISO3)

Table 5.17 gives the staining and the shade change results for the dyeings from the co-application of Naphthol AS and Servon XRK to the unmodified cotton fabric followed by coupling with the Fast Red Salt FRN after the ISO3 wash-fastness test.

Methods of Naphtholation	acetate	cotton	nylon	polyester	Acrylic	wool	shade change
Pad-dry	3/4	4	3	4	4/5	4	2/3
Pad-batch-dry	3/4	4	3/4	4	4/5	3/4	3

Table 5.17 Staining and the shade change results for the dyeings from the co-application of Naphthol AS and Servon XRK to the unmodified cotton fabric followed by coupling with the Fast Red Salt FRN

After the ISO3 wash-fastness test, the dyeings from the co-application of Naphthol AS and Servon XRK to the unmodified cotton fabric by the pad-dry method followed by coupling with the Fast Red Salt FRN, stain on cotton, polyester and wool adjacents which is rated as 4. The staining on acrylic adjacent is rated as 4/5. It has been found that staining on nylon adjacent is quite significant (3). The staining on acetate adjacent is rated as 3/4. The shade change result for the dyeings is rated as 2/3.

The ISO3 tested dyeings evaluated by the pad-batch-dry method of Naphthol AS co-applied with Servon XRK, stain on acetate, nylon and wool adjacents rated as 3/4. The staining on cotton and polyester adjacent fabrics is rated as 4. The dyeings show slight staining on acrylic adjacent which is rated as 4/5. The shade change result for the dyeings is rated as 3 which is 1/2 point better than the shade change result for the dyeings by pad-dry method after the ISO3 wash-fastness test.

5.3.3.3 Light-fastness

Table 5.18 gives the light-fastness results for the dyeings from the co-application of Naphthol AS and Servon XRK to the unmodified cotton by pad-dry and pad-batch-dry methods followed by coupling with the Fast Red Salt FRN.

Methods of Naphtholation	Grey Scale Rating
Pad-dry	4/5
Pad-batch-dry	4/5

Table 5.18 Light-fastness results for the dyeings from the co-application of Naphthol AS and Servon XRK to the unmodified cotton fabric

The light-fastness results for the dyeings by pad-dry and pad-batch-dry methods are similar which are rated as 4/5 as shown in Table 5.18.

5.3.3.4 Rub-fastness

Table 5.19 gives the rub-fastness results for the dyeings from the co-application of Naphthol AS and Servon XRK to the unmodified cotton fabric by pad-dry and pad-batch-dry methods followed by coupling with the Fast Red Salt FRN.

Methods of Naphtholation	Grey scale rating	
	Dry	Wet
Pad-dry	3/4	2
Pad-batch-dry	3/4	2

Table 5.19 Rub-fastness results for the dyeings from the co-application of Naphthol AS and Servon XRK to the unmodified cotton followed by coupling with the Fast Red Salt FRN

The rub-fastness results for the dyeings from the co-application of Naphthol AS and Servon XRK (all in one method) are same which are rated as 3/4 after dry rub test and 2 after wet rub test as shown in Table 5.19. The staining after wet rub test is quite significant for both methods of co-application (pad-dry and pad-batch-dry) of Naphthol AS and Servon XRK.

5.3.3.5 Microscopic images of yarn/fibre cross-sections

Figure 5.10 shows the microscopic images of the yarn/fibre cross-sections for the dyeings from the co-application of Naphthol AS and Servon XRK to the unmodified cotton fabric by pad-batch-dry method.

Figure 5.9 Microscopic images of the yarn/fibre cross-sections for the dyeings from the co-application of Naphthol AS and Servon XRK to the unmodified cotton by pad-batch-dry method

Microscopic images of the yarn/fibre cross-sections for the dyeings from the co-application of Naphthol AS and Servon XRK by pad-batch-dry method give a little ring dyeing as shown in Figure 5.10.

5.4 Conclusions

The overall dyeing results are better for the dyeings evaluated by the application of Naphthol AS to modified cotton fabric by pad-dry and pad-batch-dry method followed by coupling than the corresponding dyeings on the unmodified cotton fabric. The dyeings following application of Naphthol AS to the modified cotton fabric by a pad-batch-dry method give better colour yield, fastness and dye penetration results than the corresponding dyeings from the application of Naphthol AS to the unmodified cotton fabric by pad-dry method. Because during batching the Naphtholate anions become well penetrated throughout the fibre, the azoic colour developed by coupling gives good colour yield values, wash-fastness, rub fastness and ring dyeing results.

When Naphthol AS was applied by the exhaustion method to unmodified and modified cotton fabric followed by coupling with the Fast Red Salt FRN, the modified cotton fabric produced much higher colour yield values than the unmodified cotton fabric. The dyeings on modified cotton fabric gave better wash-fastness results than the dyeings on unmodified cotton fabric. The rub-fastness results for the dyeings on the modified cotton fabric gave similar results (4/5) as the dyeings on unmodified cotton fabric after dry rub test but after the wet rub test the rub-fastness results were 1/2 point lower for the dyeings on the modified cotton fabric as compared to the dyeings on the unmodified cotton fabric. The dyeings on the modified cotton fabric showed slightly better penetration than the dyeings on the unmodified cotton fabric.

The subsequent dyeings from fabrics treated by the co-application of Naphthol AS and Servon XRK (pad-dry and pad-batch-dry method) followed by coupling with the Fast Red Salt FRN, give better colour yield values with the pad-batch-dry application method than the pad-dry method. The wash-fastness (ISO2 and ISO3) results for the subsequent dyeings on fabrics treated by the pad-batch-dry method for co-application of Naphthol AS and Servon XRK are 1/2 point better than the dyeings with the pad-dry method. The light-fastness and the rub-fastness results are similar for the dyeings from the co-application of Naphthol AS and Servon XRK by pad-dry and pad-batch-dry method.

5.5 References

1. J Shore in, *Cellulosics Dyeing*, J Shore (ed.), Society of Dyers and Colourists, Bradford 1995.
2. J R Aspland in, *Textile Dyeing and Coloration*, J R Aspland (ed.), AATCC, 1997.
3. *Methods for Colour Fastness of Textiles and Leather,* 5th edn., Society of Dyers and Colourists, Bradford 1990.
4. PH Greaves and BP Saville, *Microscopy of Textile Fibres,* Royal Microscopical Society, 1995.

Chapter 6

Application of Reactive Dyes to Unmodified and Modified Cotton (Servon XRK) and Co-application with NNM Derivative

6.1 Introduction

Reactive dyes cover the major part of the textile dyeing industry. They offer bright shades with a full range colour. Reactive dyes became very popular after the first Reactive dye was introduced by ICI in 1956, the first dye for cellulosic fibres which would actually react with the fibre molecules to form a covalent dye-fibre bond [1]. Because of their covalent fixation with the fibre, the dyes exhibited good wet-fastness properties.

It has been found that some of the reactive dyes give dull shades when applied to the modified fabric [2, 3]. In this research, a set of reactive dyes (Sumifix Supra Blue BRF, Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarene Red K 4BL and Remazol Turquoise G) have been applied to the unmodified and the modified cotton by exhaustion and pad-batch methods to study their dyeing properties.

6.2 Experimental

6.2.1 Materials

6.2.1.1 Fabric

Two types of fabric were used in this research. The unmodified cotton (scoured, bleached and mercerised) and the cotton modified with Servon XRK.

6.2.1.2 Other reagents

All other chemicals used for this research were laboratory grade samples obtained from Aldrich.

6.2.1.3 Dyes

All dyes used in this research were kindly supplied by DyStar as laboratory research samples. Sumifix Supra Blue BRF, Sumifix Supra Red 3BF, Levafix Red E 2RN, Drimarine Red K 4BL and Remazol Turquoise G were used. The general chemical structures of Levafix E and Sumifix Supra dyes have been shown in the Figures 6.2 and 6.3. The structure of Drimarine Red K 4BL has been shown in Figure 6.4. The structures of the other dyes have not been disclosed by the dye manufacturers.

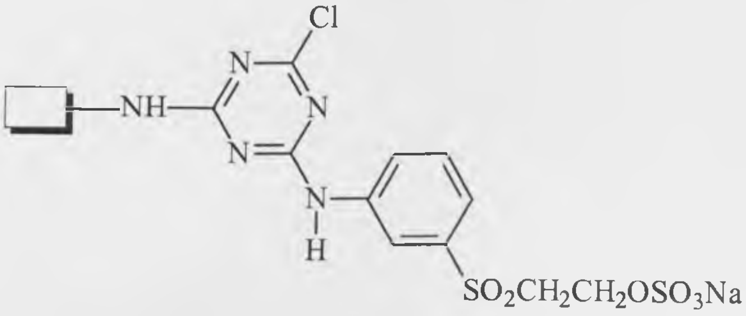


Figure 6.1 General chemical structure of Sumifix Supra dyes

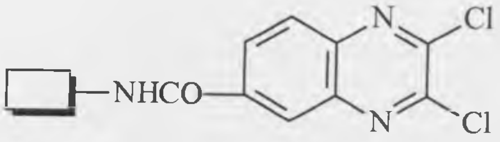


Figure 6.2 General chemical structure of Levafix E dyes

□ Denotes dye chromophore

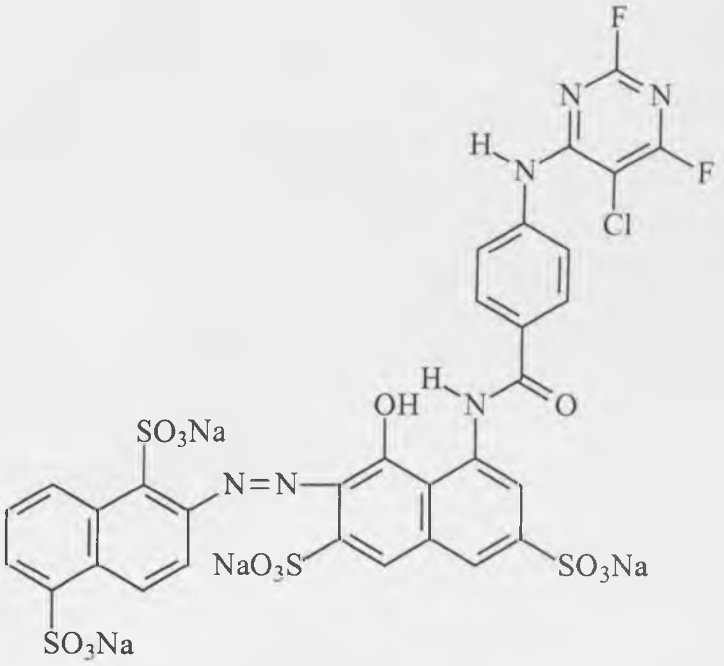


Figure 6.3 Structure of Drimarene Red K 4BL

6.2.2 Application of Reactive dyes by exhaustion method to the unmodified and the Servon XRK modified cotton fabrics

6.2.2.1 Dyeing method

Sumifix Supra Blue BRF and Sumifix Supra Red 3BF were applied to unmodified and the modified cotton fabrics at 2% o.m.f. For the dyeings on the unmodified cotton fabric, Glauber's salt 80 g/l and Sodium carbonate 20 g/l were used. For the dyeings to the modified cotton fabric there was no use of alkali or salt. The liquor to ratio used was 10:1.

6.2.2.2 Dyeing Profile

Figure 6.5 shows the dyeing profile for Sumifix Supra dyes;

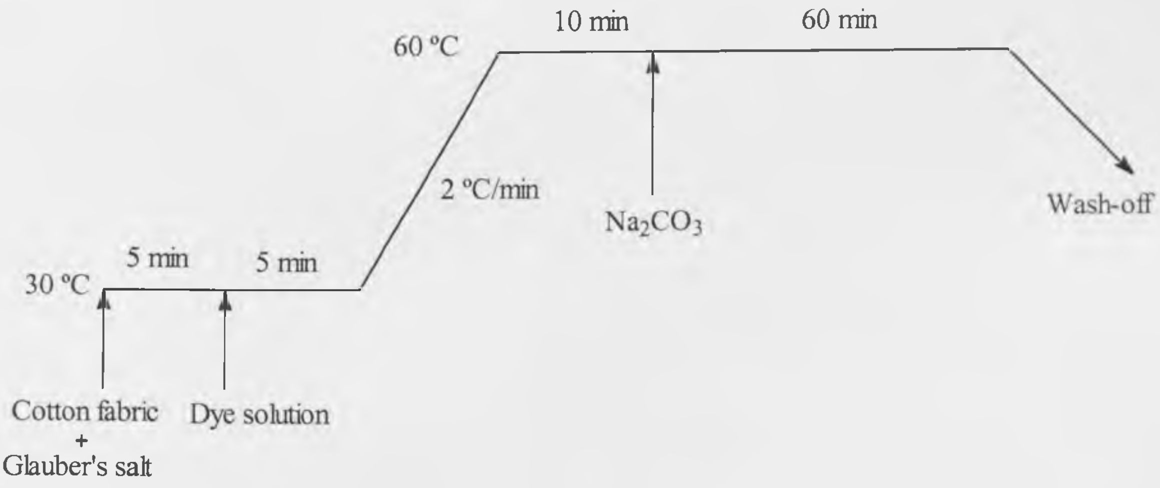


Figure 6.4 Profile for dyeing the unmodified and the Servon XRK modified cotton with Sumifix Supra dyes

6.2.3 Application of reactive dyes by pad-batch method

Four commercial reactive dyes named Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarine Red K 4BL and Remazol Turquoise G were applied to the unmodified cotton by pad-batch method with and without NMM.

6.2.3.1 Application method

Reactive dyes and NMM were co-applied to cotton by cold pad-batch method using 65% pick-up and batching for 24 hours by wrapping the padded piece of fabric on a roller sealing it with a cling film.

6.2.3.2 Preparation of padding solution

4.05g NMM made up to 10g by adding distilled water

2.01g NaOH (50% w/v) made up to 10g by adding distilled water

1.03 g dye made up to 10g by adding distilled water

3 drops of alcopol PET added to dye solution

All the ingredients were taken in grams. Total volume for padding solution was 30 gm. Each ingredient was weighed separately. When padder was ready all were mixed together and applied to the unmodified and the modified cotton fabrics. Sodium hydroxide was added to NNM and then this NNM solution was added to dye solution. Then 3 drops of alcopol PET was added to this dye solution.

6.2.3.3 Padding conditions

The pressure of pad mangles was set to 3.8 bar with a speed of 1.0 m/minutes to give a wet pick up of 65%. The padded fabric was batched for 24 hours at 25 °C.

6.2.3.4 Washing-off

A 4×10 cm piece of dyed fabric was cut and put in 100 ml cold water for 10-15 minutes meanwhile 100 ml distilled water was put on hot plate boiled at 100°C and 2 drops of Sandozin NIE. The dyed fabric was removed from the cold water and put into the boiling water and boiled for 10 minutes. The washed-off piece of fabric was taken out and air dried.

6.2.3.5 Control dyeings

Each dye should be pad-batch treated using recommended alkali (NMM and NaOH omitted). It is important that each control dyeing is the same depth of shade as those treated with NMM.

Alkali for control dyeings:

1. Levafix Red E-2RN (Na_2CO_3)
2. Sumifix Supra Red 3BF (TSP)
3. Drimarine Red K-4BL (Na_2CO_3)
4. Remazol Turquoise G (TSP)

6.3 Results and discussion

6.3.1 Application of Sumifix Supra dyes by exhaustion method

6.3.1.1 Exhaustion values for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF

Table 6.1 gives the exhaustion values for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF on the unmodified and the Servon XRK modified cotton fabrics.

Dyes used	% Exhaustion	
	Unmodified cotton	Modified cotton
Sumifix Supra Blue BRF	62	70
Sumifix Supra Red 3 BF	69	79

Table 6.1 Exhaustion values for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF

The dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3BF on the Servon XRK modified cotton fabric give better exhaustion values than the dyeings on the unmodified cotton fabric. The dyeings from Sumifix Supra Red 3BF on the unmodified and the Servon XRK modified cotton fabric give better exhaustion values than the dyeings from

Sumifix Supra Blue BRF on the unmodified and the modified cotton fabric as given in Table 6.1.

6.3.1.2 Colour yield values for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF

Table 6.2 gives the fk values for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF on the unmodified and the Servon XRK modified cotton fabrics.

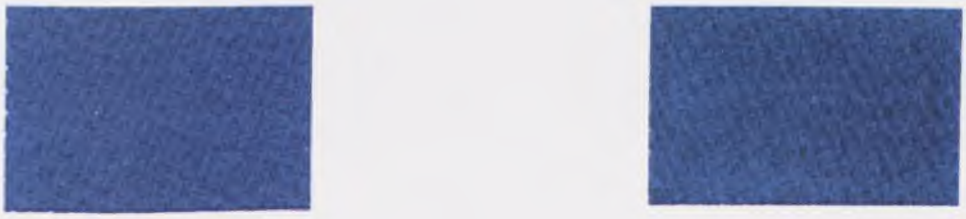
Dyes used	fk values	
	Unmodified cotton fabric	Modified cotton fabric
Sumifix Supra Blue BRF	78.7	91.8
Sumifix Supra Red 3 BF	117.8	137.4

Table 6.2 fk values for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF at 2 % o.m.f. on the unmodified and the modified cotton fabrics

The dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF on the Servon XRK modified cotton fabrics give higher colour yield values than the dyeings on the unmodified cotton fabrics. The dyeings from Sumifix Supra Red 3 BF give better colour yield values than the dyeings from Sumifix Supra Blue BRF on the modified cotton fabric as shown in Table 6.2.

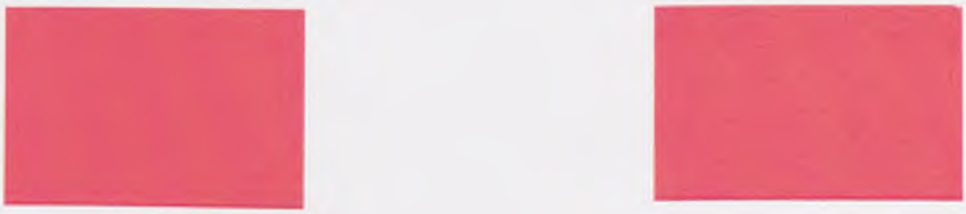
6.3.1.3 Investigation of shade dulling

Figures 6.5 and 6.6 show the fabric samples dyed with Sumifix Supra Blue BRF and Sumifix Supra Red 3FB. It has been found [2, 3] that Remazol dyes get dulling when applied to the pre-cationised cotton fabric.



Unmodified Modified

Figure 6.5 Unmodified and modified cotton fabrics dyed with Sumifix Supra Blue BRF



Unmodified Modified

Figure 6.6 Unmodified and modified cotton fabrics dyed with Sumifix Supra Red 3BF

The dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3BF do not give dull shades on the Servon XRK modified cotton fabrics as shown in Figures 6.5 and 6.6.

6.3.1.4 Wash-fastness

Wash-fastness test (ISO2)

Tables 6.3 and 6.4 give the staining and the shade change results for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF on the unmodified and the modified cotton fabrics after the ISO2 wash-fastness test [5].

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	Shade change
Sumifix Supra Blue BRF	4/5	2	4/5	5	5	4/5	3/4
Sumifix Supra Red 3 BF	5	4/5	5	5	5	5	4/5

Table 6.3 Staining and the shade change results for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF on the unmodified cotton fabric

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	shade change
Sumifix Supra Blue BRF	4/5	4/5	5	5	5	4/5	4
Sumifix Supra Red 3 BF	5	5	5	5	5	5	5

Table 6.4 Staining and the shade change results for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF on the modified cotton fabric

After the ISO2 wash-fastness test, the dyeings from Sumifix Supra Blue BRF on the unmodified cotton fabric slightly stain on acetate, nylon and wool adjacent fabrics (4/5). There is no staining on polyester and acrylic adjacent fabrics. The staining on cotton adjacent is quite significant which is rated as 2. The shade change for the dyeings from Sumifix Supra Blue BRF on the unmodified cotton fabric is rated as 3/4 as shown in Table 6.3.

The dyeings from Sumifix Supra Blue BRF on the modified cotton fabric after ISO2 wash-fastness test slightly stain on acetate, cotton and wool adjacent fabrics (4/5). It has not been found any staining on nylon, polyester and acrylic adjacents. The staining results for the dyeings from Sumifix Supra Blue BRF on the modified cotton fabric after ISO2 wash-fastness test are significantly better than the dyeings from Sumifix Supra Blue BRF on the unmodified cotton fabric. The shade change result for the dyeings from Sumifix Supra Blue BRF on the modified cotton fabric is rated as 4 (Table 6.4) which is 1/2 point better than the shade change for the dyeings from Sumifix Supra Blue BRF on the unmodified cotton fabric as shown in Table 6.3.

The dyeings from Sumifix Supra Red 3BF on the unmodified cotton fabric slightly stain on cotton adjacent fabric which is rated as 4/5. There is no staining on the other adjacent fabrics. The shade change result for the dyeings from Sumifix Supra Red 3BF on the unmodified cotton fabric is rated as 4/5 as shown in Table 6.3.

After the ISO2 wash-fastness test, the dyeings from Sumifix Supra Red 3BF on the modified cotton fabric absolutely do not stain on the multiple adjacent fabrics which is rated as 5. The shade change for the dyeings from Sumifix Supra Red 3BF on the modified cotton fabric is rated as 5 (Table 6.4) which is 1/2 point better than the shade change for the dyeings from Sumifix Supra Red 3BF on the unmodified cotton fabric as shown in Table 6.3.

Wash-fastness test (ISO3)

Tables 6.5 and 6.6 give the staining and the shade change results for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF on the unmodified and the modified cotton fabrics after the ISO3 wash-fastness test [5].

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	shade change
Sumifix Supra Blue BRF	4/5	1/2	4/5	5	5	4/5	3
Sumifix Supra Red 3 BF	5	4/5	5	5	5	4/5	4

Table 6.5 Staining and the shade change results for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF on the unmodified cotton fabric

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	shade change
Sumifix Supra Blue BRF	4/5	4	5	5	5	4/5	3/4
Sumifix Supra Red 3 BF	5	4/5	5	5	5	5	4/5

Table 6.6 Staining and the shade change results for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF on the modified cotton fabric

The dyeings from Sumifix Supra Blue BRF on the unmodified cotton fabric after the ISO3 wash-fastness test slightly stain on acetate, nylon and wool adjacent fabrics which is rated as 4/5. There is no staining on polyester and acrylic adjacent fabrics. The staining on cotton adjacent is quite significant which is rated as 1/2. The shade change for the dyeings from Sumifix Supra Blue BRF on the unmodified cotton fabric is rated as 3 as shown in Table 6.5.

After the ISO3 wash-fastness test, the dyeings from Sumifix Supra Blue BRF on the modified cotton fabric slightly stain on acetate and wool adjacent fabrics (4/5). The dyeings do not stain on nylon, polyester and acrylic adjacent fabrics rated as 5. The staining on cotton is rated as 4 which is significantly better than the staining on cotton adjacent for the dyeings on the unmodified cotton fabric. The shade change for the dyeings from Sumifix Supra Blue BRF on the modified cotton fabric is rated as 3/4 (Table 6.6) which is 1/2 point better than the shade change for the dyeings from Sumifix Supra Blue BRF on the unmodified cotton fabric.

After the ISO3 wash-fastness test, the dyeings from Sumifix Supra Red 3BF on the unmodified cotton fabric slightly stain on cotton and wool adjacent fabrics which is rated as 4/5. There is no staining on acetate, nylon, polyester and acrylic adjacent fabrics. The shade change for the dyeings from Sumifix Supra Red 3BF on the unmodified cotton fabric is rated as 4 as shown in Table 6.5.

After the ISO3 wash-fastness test, the dyeings from Sumifix Supra Red 3BF on the modified cotton fabric stain slightly on cotton adjacent fabric which is rated as 4. It has not been found staining on the other multiple adjacent fabrics. The dyeings on the modified cotton fabric give 1/2 point better staining results than the staining results for the dyeings on the unmodified cotton fabric. The shade change for the dyeings from Sumifix Supra Red 3BF is rated as 4/5 as show in Table 6.6 which is 1/2 point better than the shade change for the dyeings on the unmodified cotton fabric.

6.3.1.5 Light-fastness

Table 6.7 gives the light-fastness results for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3BF on the unmodified and the modified cotton fabrics.

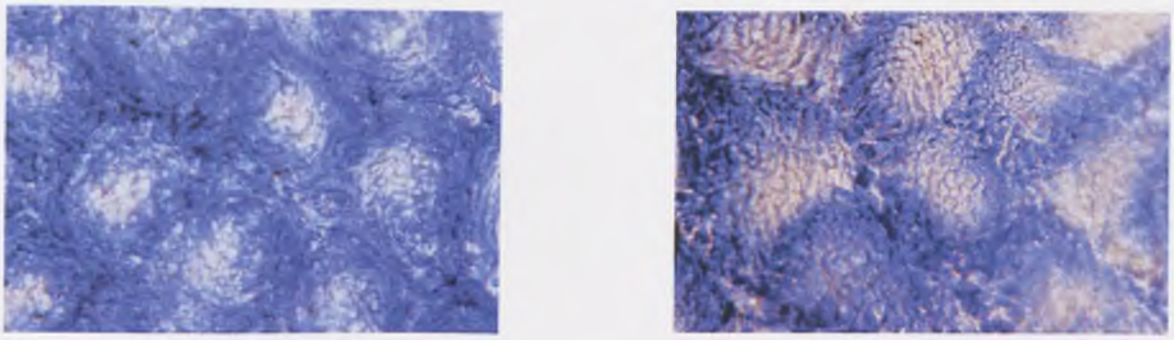
Dyes used	Grey scale rating	
	Unmodified cotton fabric	Modified cotton fabric
Sumifix Supra Blue BRF	4/5	4
Sumifix Supra Red 3BF	4/5	4/5

Table 6.7 Light-fastness results for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3 BF on the unmodified and the modified cotton fabrics

The light-fastness results for the dyeings from Sumifix Supra Blue BRF applied to the unmodified and the modified cotton fabrics by the exhaustion method are rated as 4/5 and 4 respectively as shown in Table 6.7. The light-fastness results for the dyeings from Sumifix Supra Red 3BF applied to the unmodified and the modified cotton fabrics is rated as 4/5.

6.3.1.6 Microscopic images of yarn/ fibre cross-sections

Figures 6.7 and 6.8 show the microscopic yarn/fibre cross-sectional images for the dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3BF on the unmodified and the Servon XRK modified cotton fabrics.



Unmodified cotton fabric **Modified cotton fabric**

Figure 6.7 Microscopic images of yarn/fibre cross-sections for the dyeings from Sumifix Supra Blue BRF on the unmodified and the modified cotton fabrics

Unmodified cotton fabric **Modified cotton fabric**

Figure 6.8 Microscopic images of yarn/fibre cross-sections for the dyeings from Sumifix Supra Red 3BF on the unmodified and the modified cotton fabrics

The dyeings from Sumifix Supra Blue BRF on both (unmodified and the modified) cotton fabrics give ring-dyeing (Figure 6.7) but the dyeings from Sumifix Supra Red 3BF on the unmodified and the modified cotton fabrics do not show any ring-dyeing as shown in Figure 6.8.

6.3.2 Application of reactive dyes by pad-batch method

6.3.2.1 Exhaustion values for the dyeings obtained without NMM and with NMM

Table 6.8 gives the exhaustion values for the dyeings from Levafix Red E 2RN, Sumifix Supra Red 3 BF, Drimarene Red K 4BL and Remazol Turquise G applied to the unmodified cotton fabric without NMM and with NMM.

Dyes used	% Exhaustion	
	Without NMM	With NMM
Levafix Red E 2RN	77	84
Sumifix Supra Red 3BF	71	82
Drimarene Red K 4BL	68	71
Remazol Turquise G	67	75

Table 6.8 Exhaustion values for the dyeings from Levafix Red E2RN, Sumifix Supra Red 3BF, Drimarene Red K 4BL and Remazol Turquise G

The dyeings from Levafix Red E 2RN, Sumifix Supra Red 3 BF, Drimarene Red K 4BL and Remazol Turquise G co-applied on the unmodified cotton fabric with NMM give better exhaustion values when applied without NMM. The dyeings from Levafix Red E 2RN give improved exhaustion values when co-applied with NMM than the exhaustion values for the dyeings from Sumifix Supra Red 3 BF, Drimarene Red K 4BL and Remazol Turquise G. The dyeings from Sumifix Supra Red 3 BF when co-applied with NMM give improved exhaustion values than the exhaustion values for the dyeings from Drimarene Red K 4 BL and Remazol Turquise G as give in Table 6.8.

6.3.2.2 Colour yield values for the dyeings obtained without NMM and with NMM

Table 6.9 gives the colour yield values for the dyeings from Levafix Red E2RN, Sumifix Supra Red 3BF, Drimarine Red K4BL and Remazol Turquise G applied to the unmodified cotton without and with NMM by cold pad-batch method.

Dyes used	fk values	
	Control	With NMM
Levafix Red E-2RN	125.9	151.7
Sumifix Supra Red 3BF	111.7	124.1
Drimarine Red K 4BL	84.9	93.8
Remazol Turquoise G	60.8	75.9

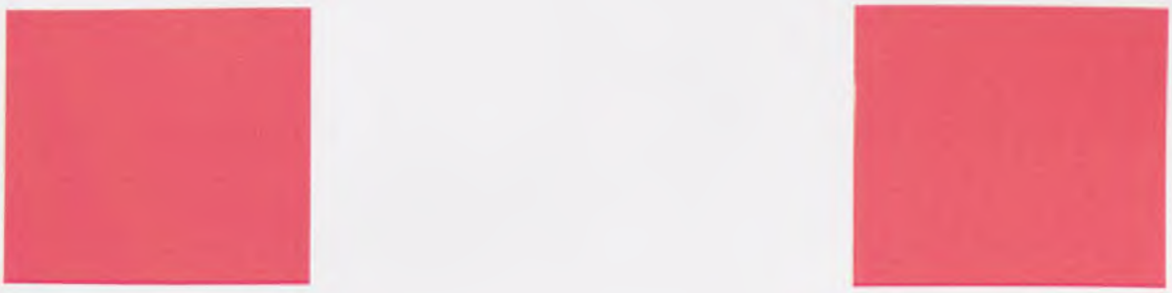
Table 6.9 Colour yield values for the dyeings from Levafix Red E2RN, Sumifix Supra Red 3BF, Drimarine Red K4BL and Remazol Turquise G applied to the unmodified cotton without and with NMM

The dyeings obtained by the co-application of NMM from Levafix Red E2RN, Sumifix Supra Red 3BF, Drimarine Red K4BL and Remazol Turquise G give higher colour yield values than the dyeings obtained without NMM as shown in Table 6.9. The dyeings from

Levafix Red E2RN have higher colour yield values than the dyeings from the other reactive dyes used. The dyeings from Sumifix Supra Red 3BF have higher colour yield values than the dyeings from Drimarene Red K 4BL and Remazol Turquoise G.

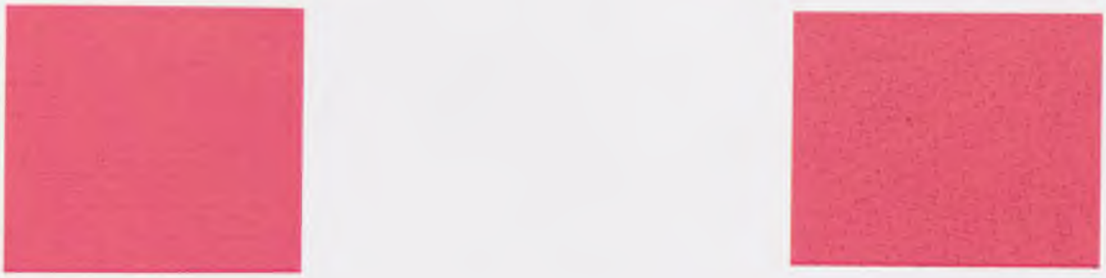
6.3.2.3 Investigation of shade dulling

Figures 6.9 - 6.12 show the fabric samples dyed with Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarene Red K 4BL and Remazol Turquoise G by pad batch method without NMM and with NMM.



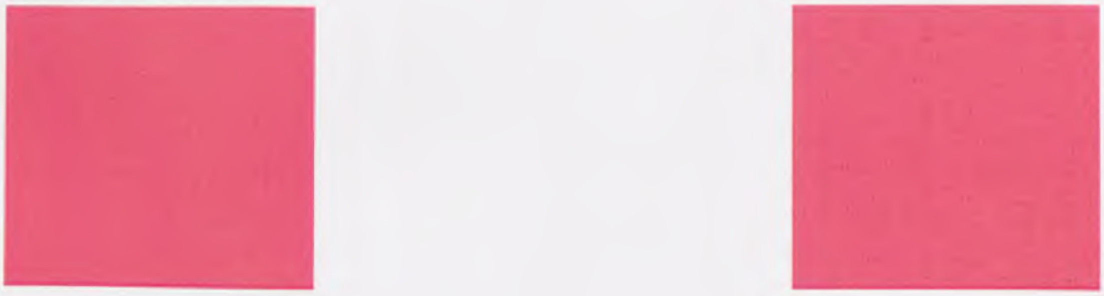
Without NMM **With NMM**

Figure 6.9 Fabric samples dyed with Levafix Red E 2RN by pad-batch method without and with NMM



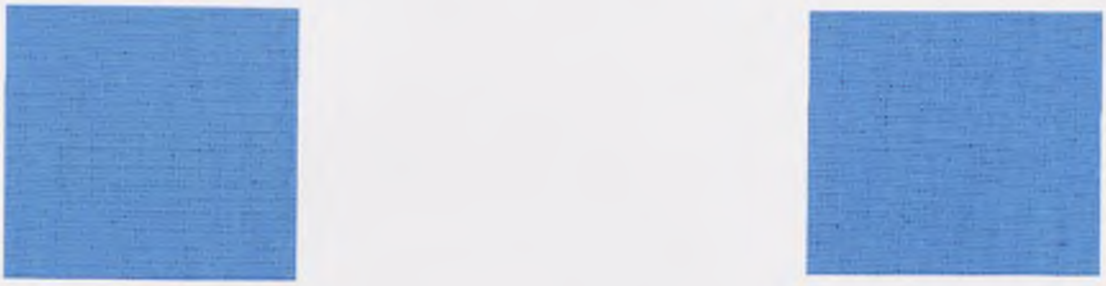
Without NMM **With NMM**

Figure 6.10 Fabric samples dyed with Sumifix Supra Red 3 BF by pad-batch method without and with NMM



Without NMM **With NMM**

Figure 6.11 Fabric samples dyed with Drimarene Red K 4BL by pad-batch method without and with NMM



Without NMM **With NMM**

Figure 6.12 Fabric samples dyed with Remazol Turquise G by pad-batch method without and with NMM

The dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF and Drimarene Red K 4BL applied to the unmodified cotton fabric with NMM by pad-batch method do not give any shade dulling but it has been found that the dyeings from Remazol Turquoise G applied with NMM to the unmodified cotton fabric give shade dulling.

6.3.2.4 Wash-fastness

Wash-fastness test (ISO2)

Tables 6.10 and 6.11 give the staining and the shade change results for the dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarine Red K 4BL and Remazol Turquoise G applied without and with NMM to the unmodified cotton fabric after the ISO2 wash-fastness test.

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	shade change
Levafix Red E 2RN	4/5	3/4	4/5	5	5	4/5	3/4
Sumifix Supra Red 3 BF	4/5	4/5	4/5	5	5	5	4/5
Drimarine Red K 4BL	4/5	4/5	4	5	5	4/5	4/5
Remazol Turquise G	4	3	4	4/5	4/5	4	3

Table 6.10 Staining and the shade change results for the dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarine Red K 4BL and Remazol Turquoise G applied to the unmodified cotton fabric without NMM

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	shade change
Levafix Red E 2RN	5	3/4	4/5	5	5	5	4
Sumifix Supra Red 3 BF	5	4/5	5	5	5	5	4/5
Drimarine Red K 4BL	4/5	4/5	3/4	4/5	5	5	4/5
Remazol Turquise G	4/5	3/4	4	5	4/5	4/5	3/4

Table 6.11 Staining and the shade change results for the dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarine Red K 4BL and Remazol Turquoise G co-applied with NMM to the unmodified cotton fabric

After the ISO2 wash-fastness test, the dyeings from Levafix Red E2RN applied to the unmodified cotton fabric without NMM by cold pad-batch method stain acetate, nylon and wool adjacent fabrics which is rated as 4. There is no staining on polyester and acrylic adjacent fabrics. The staining on cotton adjacent is rated as 3/4. The shade change for the dyeings from Levafix Red E2RN applied to the unmodified cotton by pad-batch method is rated as 3/4 as shown in Table 6.10.

The dyeings from Levafix Red E2RN applied to the unmodified cotton fabric with NMM by cold pad-batch method after ISO2 wash-fastness test do not stain on acetate, polyester, acrylic and wool adjacent fabrics. There is a slight staining on nylon adjacent (4/5). The staining on cotton adjacent is rated as 3/4. The shade change for the dyeings obtained by the co-application of Levafix Red E2RN with NMM is rated as 4 (Table 6.11) which is 1/2 point better than the shade change for the dyeings obtained from Levafix Red E2RN without NMM.

After the ISO2 wash-fastness, the dyeings from Sumifix Supra Red 3BF applied without NMM to the unmodified by cold pad-batch method, stain slightly on acetate, cotton and nylon adjacent fabrics rated as 5. The shade change for the dyeings from Sumifix Supra Red 3BF applied to the unmodified cotton fabric by cold pad-batch method is rated as 4/5 as shown in Table 6.10.

The dyeings obtained by the co-application of Sumifix Supra Red 3BF with NMM to the unmodified cotton fabric by pad-batch method, slightly stain on cotton adjacent only rated as 4/5. The dyeings do not stain on the other multiple (acetate, nylon, polyester, acrylic and wool) adjacent fabrics. The dyeings from Sumifix Supra Red 3BF co-applied with NMM give 1/2 point better staining results on acetate and nylon adjacents than the dyeings from Sumifix Supra Red 3BF applied without NMM to the unmodified cotton fabric. The shade change for the dyeings from Sumifix Supra Red 3BF co-applied with NMM is rated as 4/5 as shown in Table 6.11 which is similar to the shade change for the dyeings from Sumifix Supra Red 3BF applied without NMM to the unmodified cotton fabric.

The dyeings from Drimarene Red K4BL applied to the unmodified cotton fabric without NMM after the ISO2 wash-fastness test, stain slightly on acetate, cotton and wool adjacent fabrics which is rated as 4/5. There is no staining on polyester and acrylic adjacent fabrics (5). The staining on cotton adjacent is rated as 4. The shade change for the dyeings from Drimarine Red K4BL is rated as 4/5 after the ISO2 wash-fastness test as shown in Table 6.10.

The dyeings from Drimarene Red K4BL co-applied with NMM to the unmodified cotton fabric by cold pad-batch method after the ISO2 wash-fastness test, slightly stain acetate, cotton and polyester adjacent fabrics which is rated as 4/5. There is no staining on acrylic and wool adjacent fabrics (5). The staining on nylon is rated as 3/4 which is significant. The shade change for the dyeings from Drimarene Red K4BL co-applied with NMM to the unmodified cotton fabric by cold pad-batch method is rated as 4/5 (Table 6.11) which is similar to the shade change for the dyeings from Drimarene Red K4BL applied to the unmodified cotton fabric by pad-batch method.

After ISO2 wash-fastness test, the dyeings from Remazol Turquise G applied to the unmodified cotton fabric, slightly stain on polyester and acrylic adjacent fabrics (4/5). The staining on acetate, nylon and wool adjacent fabrics is rated as 4. There is a significant staining on cotton adjacent (3). The shade change for the dyeings from Remazol Turquise G applied to the unmodified cotton fabric is rated as 3 as shown in Table 6.10.

After the ISO2 wash-fastness test, the dyeings from Remazol Turquise G co-applied with NMM to the unmodified cotton fabric by the cold pad-batch method, stain slightly on acetate, acrylic and wool adjacent fabrics (4/5). There is no staining on polyester adjacent fabric (5). The staining on nylon adjacent is rated as 4. It has been found significant staining on cotton adjacent rated as 3/4 which is 1/2 point better than the staining on cotton adjacent for the dyeings from Remazol Turquise G applied to the unmodified cotton fabric with NMM by cold pad-batch method. The shade change for the dyeings from Remazol Turquise G applied to the unmodified cotton fabric with NMM by cold pad-batch method is rated as 3/4 (Table 6.11) which is 1/2 point better than the shade change for the dyeings from Remazol Turquise G applied to the unmodified cotton fabric with NMM by cold pad-batch method.

Wash-fastness test (ISO3)

Tables 6.12 and 6.13 give the staining and the shade change results for the dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarine Red K 4BL and Remazol Turquoise G applied without and with NMM to the unmodified cotton fabric after the ISO3 wash-fastness test.

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	shade change
Levafix Red E 2RN	4	3	4	4/5	4/5	4/5	3
Sumifix Supra Red 3 BF	4/5	3/4	3/4	4/5	4/5	4/5	4
Drimarine Red K 4BL	4	3/4	3/4	4/5	4/5	4	4
Remazol Turquise G	3	2/3	3	4/5	4	3/4	2/3

Table 6.12 Staining and the shade change results for the dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarine Red K 4BL and Remazol Turquoise G applied to the unmodified cotton fabric without NMM

Dyes used	acetate	cotton	nylon	polyester	acrylic	wool	shade change
Levafix Red E 2RN	4/5	3/4	4	4/5	4/5	4/5	3/4
Sumifix Supra Red 3 BF	4/5	4	4	4/5	4/5	4/5	4
Drimarine Red K 4BL	4	4	3/4	4/5	4/5	4/5	4/5
Remazol Turquise G	4	3	3	4/5	4/5	4	3

Table 6.13 Staining and the shade change results for the dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarine Red K 4BL and Remazol Turquoise G co-applied to the unmodified cotton fabric with NMM

After the ISO3 wash-fastness test, the dyeings from Levafix Red E2RN applied to the unmodified cotton fabric without NMM by cold pad-batch method, slightly stain on polyester, acrylic and wool adjacent fabrics which is rated as 4/5. The staining on acetate and nylon adjacents is rated as 4. There is a significant staining on nylon adjacent which is rated as 3. The shade change for the dyeings from Levafix Red E2RN to the unmodified cotton fabric without NMM by cold pad-batch method is rated as 3 as shown in Table 6.12.

The dyeings obtained from Levafix Red E2RN co-applied with NMM by cold pad-batch method to the unmodified cotton fabric, stain slightly on acetate, polyester, acrylic and wool adjacent fabrics. The staining on cotton and nylon adjacents is rated as 3/4 and 4 respectively. The shade change for the dyeings from Levafix Red E2RN co-applied with NMM by cold pad-batch method to the unmodified cotton fabric is rated as 3/4 (Table 6.13) which is 1/2 point better the shade change for the dyeings from Levafix Red E2RN applied to the unmodified cotton fabric without NMM by cold pad-batch method.

After the ISO3 wash-fastness test, the dyeings obtained by the application of Sumifix Supra Red 3BF without NMM to the unmodified cotton fabric by pad-batch method, stain slightly on acetate, polyester, acrylic and wool adjacent fabrics (4/5). The staining on cotton and nylon is rated as 3/4. The shade change for the dyeings from Sumifix Supra Red 3BF applied to the unmodified cotton fabric by cold pad-batch method is rated as 4 as shown in Table 6.12.

The dyeings obtained by the co-application of Sumifix Supra Red 3BF with NMM to the unmodified cotton fabric by the cold pad-batch method, slightly stain acetate, polyester, acrylic and wool adjacent fabrics which is rated as 4/5. The staining on cotton and nylon adjacents is rated as 4 which is 1/2 point better than the staining on cotton and nylon adjacents for the dyeings from Sumifix Supra Red 3BF applied to the unmodified cotton fabric without NMM. The shade change for the dyeings from Sumifix Supra Red 3BF co-applied with NMM to the unmodified cotton fabric is rated as 4 (Table 6.13) which is similar to the shade change for the dyeings from Sumifix Supra Red 3BF applied to the unmodified cotton fabric without NMM.

After the ISO3 wash-fastness test, the dyeings from Drimarene Red K4BL applied to the unmodified cotton fabric by cold pad-batch method without NMM, slightly stain on polyester and acrylic adjacents (4/5). The staining on acetate and wool adjacents is rated as 4. There is a staining on cotton and nylon adjacents rated as 3/4. The shade change for the dyeings from Drimarene Red K4BL applied to the unmodified cotton fabric without NMM is rated as 4 as shown in Table 6.12.

The dyeings obtained by the co-application of Drimarene Red K4BL with NMM to the unmodified cotton fabric by cold pad-batch method, stain slightly polyester, acrylic and wool adjacents which is rated as 4/5. The staining on acetate and nylon adjacents is rated as 4 and 3/4 respectively. The staining on cotton adjacent is rated as 4 which is 1/2 point better than the staining on cotton for the dyeings applied to the unmodified cotton fabric without NMM. The shade change for the dyeings obtained by the co-application of Drimarene Red

K4BL with NMM is rated as 4/5 (Table 6.13) which is 1/2 point better than the shade change for the dyeings from Drimarene Red K4BL applied to the unmodified cotton fabric without NMM.

After the ISO3 wash-fastness test, the dyeings from Remazol Turquise G applied to the unmodified cotton fabric without NMM by cold pad-batch method, slightly stain polyester (4/5). The staining on acetate and nylon adjacents is significant which is rated as 3. The staining on acrylic and wool adjacents is rated as 4 and 3/4 respectively. The shade change for the dyeings from Remazol Turquise G applied to the unmodified cotton fabric without NMM is rated as 2/3 as shown in Table 6.12.

The dyeings obtained by the co-application of Remazol Turquise G with NMM to the unmodified cotton fabric by cold pad-batch method, stain slightly on polyester and acrylic adjacents (4/5). The staining on acetate and wool adjacents is rated as 4. There is staining on cotton and nylon adjacents (3) which is quite significant but staining on cotton adjacent is 1/2 point better than the staining on cotton adjacent for the dyeings from Remazol Turquise G applied to the unmodified cotton fabric without NMM. The shade change for the dyeings from Remazol Turquise G co-applied with NMM to the unmodified cotton fabric by cold pad-batch method is rated as 3 (Table 6.13) which is 1/2 point better than the shade change for the dyeings from Remazol Turquise G applied to the unmodified cotton fabric without NMM by cold pad-batch method.

6.3.2.5 Light-fastness

Table 6.14 shows the light-fastness results for the dyeings from Levafix Red E2RN, Sumifix Supra Red 3BF, Drimarine Red K4BL and Remazol Turquise G on the unmodified and the modified cotton fabrics.

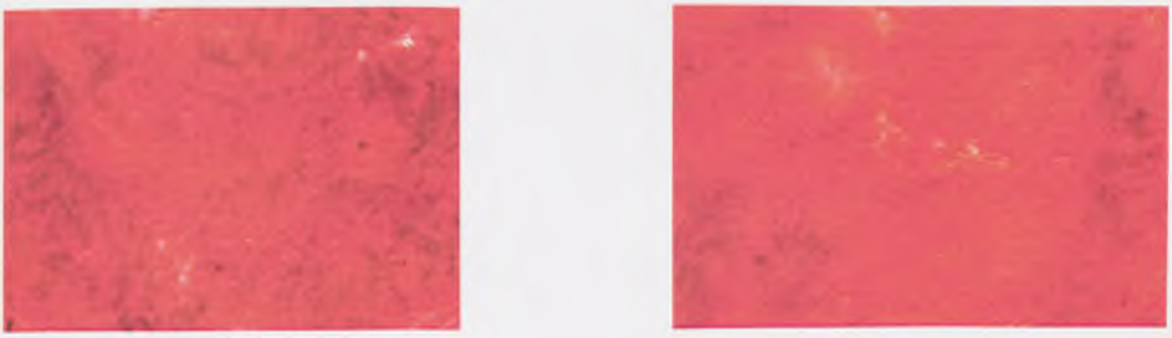
Dyes used	Grey Scale Rating	
	Control	With NMM
Levafix Red E 2RN	3/4	4
Sumifix Supra Red 3 BF	4/5	4/5
Drimarene Red K 4BL	4	4
Remazol Turquise G	4/5	4/5

Table 6.14 Light-fastness results for the dyeings from Levafix Red E2RN, Sumifix Supra Red 3BF, Drimarine Red K4BL and Remazol Turquise G on the unmodified and the modified cotton fabrics

The light-fastness results for the dyeings from Levafix Red E2RN on the unmodified cotton fabric without and with NMM are rated as 3/4 and respectively. The light-fastness results for the dyeings from Sumifix Supra Red 3BF and Remazol Turquise G on the unmodified cotton fabric without and with NMM are rated as 4/5 but the light-fastness results for the dyeings from Drimarene Red K4BL on the unmodified cotton fabric without and with NMM is rated as 4 as given in 6.14.

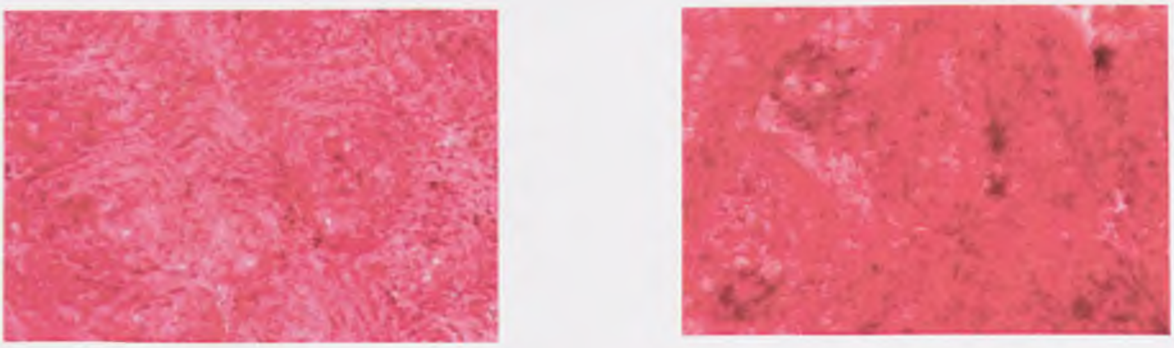
6.3.2.6 Microscopic images of yarn/fibre cross-sections

Figures 6.13 – 6.16 show the microscopic yarn/fibre cross-sectional images for the dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarene Red K 4BL and Remazol Turquoise G applied to the unmodified cotton fabric without and with NMM by cold pad-batch method.



Without NMM **With NMM**

Figure 6.13Microscopic images of yarn/fibre cross-sections for the dyeings from Levafix Red E 2RN applied to the unmodified cotton fabric without NMM and with NMM

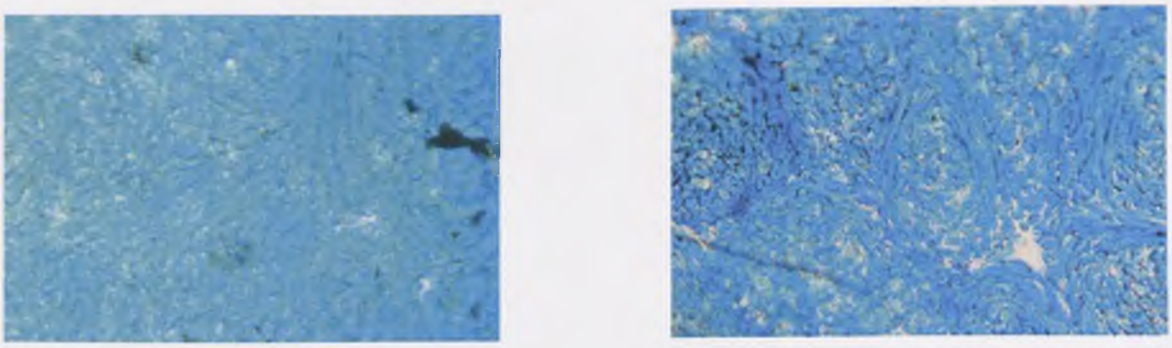


Without NMM **With NMM**

Figure 6.14 Microscopic images of yarn/fibre cross-sections for the dyeings from Sumifix Supra Red 3BF applied to the unmodified cotton fabric without NMM and with NMM

Without NMM **With NMM**

Figure 6.15 Microscopic images of yarn/fibre cross-sections for the dyeings from Drimarine Red K 4BL applied to the unmodified cotton fabric without NMM and with NMM



Without NMM **With NMM**

Figure 6.16 Microscopic images of yarn/fibre cross-sections for the dyeings from Remazol Turquise G applied to the unmodified cotton fabric without NMM and with NMM

Figures 6.13 – 6.16 show that the dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarene Red K 4BL and Remazol Turquoise G applied to the unmodifed cotton fabric without and with NMM do not show any ring dyeing. It shows that by batching the fabric overnight give better penetration throughout the fibre.

6.4 Conclusions

The dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3BF on the Servon XRK modified cotton fabric give better dyeing results than the dyeings on the unmodified cotton fabric. The dyeings from Sumifix Supra Red 3BF on the Servon XRK modified cotton fabric give better exhaustion and colour yield values than the dyeings on the unmodified coton fabric. The dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3BF on the Servon XRK modified cotton fabrics do not give any shade dulling.

The dyeings from Sumifix Supra Blue BRF and Sumifix Supra Red 3BF on the modified cotton fabric give improved wash-fastness results than the dyeings on the unmodified cotton fabric. The staining results on the cotton adjacent for the dyeings from Sumifix Supra Blue BRF on the modified cotton fabric are significantly better than the staining results on the cotton adjacent for the dyeings from Sumifix Supra Blue BRF on the unmodified cotton fabric. The dyeings from Sumifix Supra Blue BRF on the modified cotton fabric give more ring-dyeing results than the dyeings from Sumifix Supra Bulue BRF on the unmodified cotton fabric. The dyeings from Sumifix Supra Red 3BF on the unmodified and the modified cotton fabrics do not give any ring dyeing.

The dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarene Red K 4BL and Remazol Turquoise G obtained by the co-application with NMM on the unmodified cotton fabric give better exhaustion and colour yield values than the dyeings obtained without NMM. The dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF and Drimarene Red K 4BL applied to the unmodified cotton fabric with NMM do not give any shade dulling but the dyeings from Remazol Turquise G co-applied to the unmodified cotton fabric with NMM give slight shade dulling.

The wash-fastness (ISO2 and ISO3) results for the dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarene Red K 4BL and Remazol Turquoise G co-applied with NMM to the unmodified cotton fabric are better than the dyeings obtained without NMM. The dyeings from Sumifix Supra Red 3BF and Drimarene Red K 4BL obtained by the application without NMM and with NMM give improved wash-fastness results than the dyeings from Levafix Red E 2RN and Remazol Turquoise G obtained by the application without NMM and with NMM.

The dyeings from Sumifix Supra Red 3BF, Drimarene Red K 4BL and Remazol Turquoise G obtained by the co-application with NMM to the NMM modified cotton fabric give similar light-fastness results as the dyeings obtained without co-applying the NMM. The dyeings from Levafix Red E 2RN obtained by the co-application of NMM to the unmodified cotton fabric give 1/2 point better light-fastness results than the dyeings from Levafix Red E 2RN obtained without NMM. All the dyeings from Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarene Red K 4BL and Remazol Turquoise G obtained by the co-application of NMM and without applying NMM do not give any ring-dyeing.

6.5 References

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Chapter 7

Conclusions and Further Work

7.1 Conclusions

It has been noticed that Servon XRK gives an unpleasant odour. This was attributed to trimethylamine but NMM derivative does not have any smell. All the vat dyes (anthraquinone and indigoid) applied to modified cotton i.e. NMM derivative modified and Servon XRK modified gave overall better results than by them unmodified cotton. The colour yield values for both modified cotton fabrics are higher than unmodified cotton fabric. Colour yield values evaluated by applying them on Servon XRK modified cotton are higher than the cotton modified with NMM derivative.

Modified cotton fabrics dyed with anthraquinone vat dyes do not lose any colour after soaping off even with their deeper shades as on unmodified cotton fabric, it has been found that a significant amount of colour comes-off when both anthraquinone and indigoid dyes were applied on unmodified cotton. When CI Vat Blue 1 (indigo) was applied to both modified fabrics, at 2% shade depth there is no colour loss but at 4% shade depth, the wash-off liquors of both modified substrates (NMM derivative and Servon XRK) are cloudy which shows a presence of little wash-off dye molecules. The light-fastness results are excellent for all vat dyes (anthraquinone and indigoid) for all substrates with 2% and 4% shade depths are 5 according to blue wool scale rating of 4. The rub-fastness results for both indigoid and anthraquinone vat dyes have been improved on both modified substrates than on unmodified substrate. As the rub-fastness results evaluated are similar on unmodified and modified substrates but as the colour yield values have been increased on modified substrates than unmodified substrate. The ring dyeing results for CI Vat Violet 1 are same for all substrates CI Vat Red 13 has slightly better results on Servon XRK modified cotton than NMM derivative modified and unmodified cotton.

The non-metallised acid dyes with two sulphonated groups like CI Acid Red 13 and CI Acid Red 17 give better wash-fastness results than mono sulphonated like CI Acid Red 88 and tri sulphonated groups such as CI Acid Red 18 and CI Acid Red 27. Mono sulphonated dye, CI Acid red 88 comes-off from the dyed fabric and stains on adjacent fabric while tri sulphonated, CI Acid Red 18 and CI Acid Red 27 having higher degree of solubility come-off from dyed fabric and intend to stay in the solution. The light-fastness results for trisulphonated acid dyes are better than mono and disulphonated acid dyes. All the non-metallised acid dyes give no evidence of ring dyeing which shows the good penetration of the dyes throughout the Servon XRK modified cotton. Non-metallised acid dyes with mono, di and trisulphonated acid dyes applied on Servon XRK modified cotton may not be suggested to wash-off at higher temperatures. Servon XRK modified cotton fabric dyed with pre-metallised acid dye, CI Acid Violet 92 shows comparatively better results for ring dyeing than the Servon XRK modified cotton fabric dyed with CI Acid Blue 193 dyed fabric.

When applying Naphthol AS to the unmodified and the modified (Servon XRK) cotton fabric by the pad-dry and the pad-batch-dry method, followed by coupling with Fast Red Salt FRN, the modified cotton fabric gave overall better dyeing results than the unmodified cotton fabric. The dyeing results produced by the pad-batch-dry method are better than those from the pad-dry method. The Naphthol AS gives better penetration when it was applied to the unmodified and the modified cotton fabrics by the pad-batch-dry method than the pad-dry method. The colour yield values are greater on the modified cotton fabric than on the unmodified cotton fabric when applying the Naphthol by pad-batch-dry method. Following the wash-fastness tests (ISO2 and ISO3) the modified cotton fabrics show better results than unmodified cotton fabric. The ring-dyeing results for modified cotton fabric are better than unmodified cotton fabric because of the good penetration of the Naphthol AS molecules; the positive charge on the quaternary amine end groups of the modified cellulose attracts the negatively charged naphtholate anions and helps their distribution within the fibre. The modified cotton fabric has overall better dyeing properties than unmodified cotton fabric when the Naphthol AS solution was applied by exhaustion methods either at 30°C or 60°C to unmodified and modified cotton fabric. The ring-dyeing results are better for modified cotton fabric than unmodified cotton fabric, especially when naphtholating at 60°C. When Naphthol AS and Servon XRK were co-applied to cotton and then followed by coupling, the overall results were better than when the Naphthol was applied by the pad-batch-dry method.

The Sumifix Supra Red 3BF gives better colour yield values than Sumifix Supra Blue BRF on modified cotton than on unmodified cotton when the dyes were applied by the exhaustion method. Generally it has been found in this research that Sumifix Supra Blue BRF and Sumifix Red 3BF give better overall dyeing results on Servon XRK modified cotton than on unmodified cotton. Sumifix Supra Blue BRF gives slight more ring-dyeing on Servon XRK modified cotton than on unmodified cotton. Sumifix Supra Red 3BF does not give any evidence of ring dyeing on both unmodified and modified substrates. Levafix Red E 2RN, Sumifix Supra Red 3BF, Drimarene Red K4BL and Remazol Turquise G give overall improved results when co-applied to cotton by pad-batch method with NMM than without NMM. It has been noticed that Remazol Turquoise G shows a little shade dulling when applied to cotton with NMM. There is no evidence of ring-dyeing in both cases whether co-applied with NMM or without NMM.

7.2 Suggestions for further work

As the Servon XRK gives a “fishy” smell it should be replaced by other cationising agents like the NMM derivative which does not have any unpleasant odour. Acid, azoic and reactive dyes should be applied on the NMM modified cotton. The vat dyes could be applied to the modified cotton fabric at a high temperature, like 80 °C and 100 °C to get the dye penetrated inside the fiber, which can improve the rub-fastness of the dyeings by increasing the exhaustion and penetration of the molecules. When the dye is on the fiber surface in a pigment form, it is easily removed by rubbing. Other vat dyes should be applied on modified cotton to evaluate their dyeing properties.

Non-metallised acid dyes should be applied on the cotton modified with a cationising agent which has more than one positive charge in its molecular structure; this may enhance its wash-off and wash-fastness performance. Acid dyes are relatively cheaper than other classes of dyes. As reactive dyes are very popular in the textile dye market and give a full colour range so a significant number of reactive dyes should be applied to the modified substrates. Naphthol AS can be applied to cotton by some other methods such as by pad-steam-dry or pad-batch-steam method which will improve the exhaustion of Naphthol AS inside the fiber. After coupling the synthesized azoic dye is formed inside the fiber which will improve rub-fastness.