Chapter II

Literature Survey

2.1 Basic information about cellulose

Cellulose, the major constituent of most land plants and other living systems, is often said to be the most abundant natural compound and the most plentiful polymer on earth. It can occur in a number of different forms; cotton, ramie, wood, wood bark, and mosses[3]. Although plant sources are the most familiar, cellulose is also present in bacteria, fungi, and algae[3]. In native cellulose, the molecules are aligned to form fibers, some regions of which have an ordered crystalline structure. The crystalline regions vary in size, are mechanically strong, and are resistant to chemical and enzymatic attack.

One of the key features of cellulose is that each of its monomers bears three hydroxyl groups. It is these hydroxyl groups and their hydrogen bonding ability that not only play a major role in directing crystalline packing but also in governing important physical properties of cellulose materials.

2.2 Cotton

The kind of vegetation that has the highest percentages of cellulose is cotton[4] (as indicated in Table 2-1). Cotton is the seed hair of plants of the genus Gossypium[5].

Table 2-1[4]

Plant Material	Percent Cellulose
Cotton	95-99
Ramie	80-90
Bamboo	40-50
Wood	40-50
Wood Bark	20-30
Mosses	25-30
Bacteria	20-30

Figure 2.1 and Figure 2.2 show the typical appearance of dry cotton fibers. The principal features are a ' kidney bean' cross-section, and the appearance of twists and kinks along the length (the so-called 'convolutions')[7].

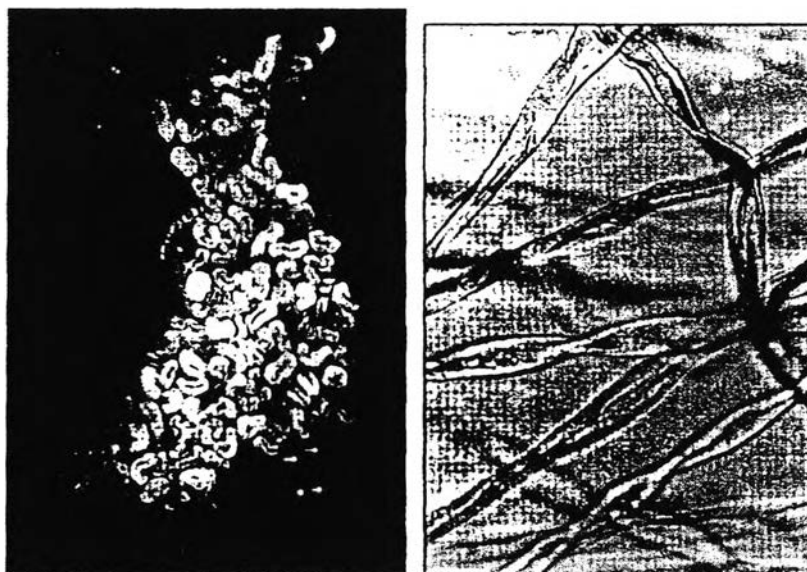Figure 2.1 Scanning electron micrographs of raw cotton fibers[6]

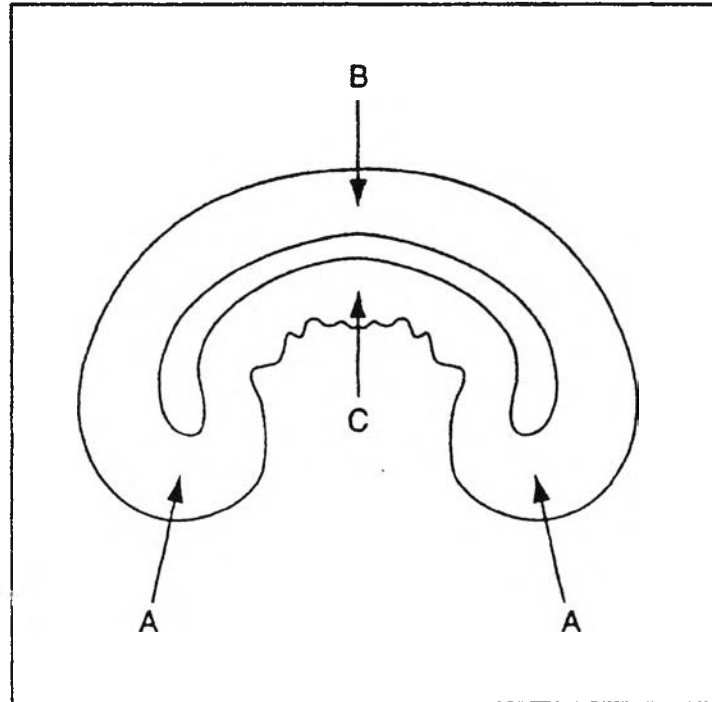Figure 2.2 Optical micrographs of raw cotton fibers x 184[6]

Figure 2.3 Bilateral structure of mature cotton (zones A, B, and C

differ in fibrillar packing density)[6]

The structures of cotton and other vegetable fibers were described in detail by Bailey et al. (1963)[7]. During the first few days of growth, cotton fibers emerge as hollow cylinders with a primary and secondary wall. As the fiber matures, fibrils are laid down on the inner wall until the lumen, the hole down the center, becomes quite small. Examination reveals that the fibrils are actually laid down in a helical form. The arrangement of the fibrils overall resemble to a twisted filament yarn with a hole down the center, but it is further revealed that the helix angle remains constant throughout the thickness of the fiber[6]. Also, bilateral structure of mature cotton indicates that the density of packing of cellulose chains is not uniform across the fiber. Three main zones (A, B, and C in Figure 2.3) have been identified by means of enzymatic degradation[6]. The rate of degradation increases from A to B to C, which is the order of decreasing density of packing.

2.3 Cotton fiber composition

Cotton is a complex composite material which structurally comprises into three hierarchical levels: (i) The molecular level of the single molecule; (ii) the supermolecular level concerning the packing and aggregation of the molecules in crystals called microfibrils; and (iii) the morphological level, i.e., the arrangement of microfibrils and interstitial voids in relation to the cell wall (Figure 2.4)[8].
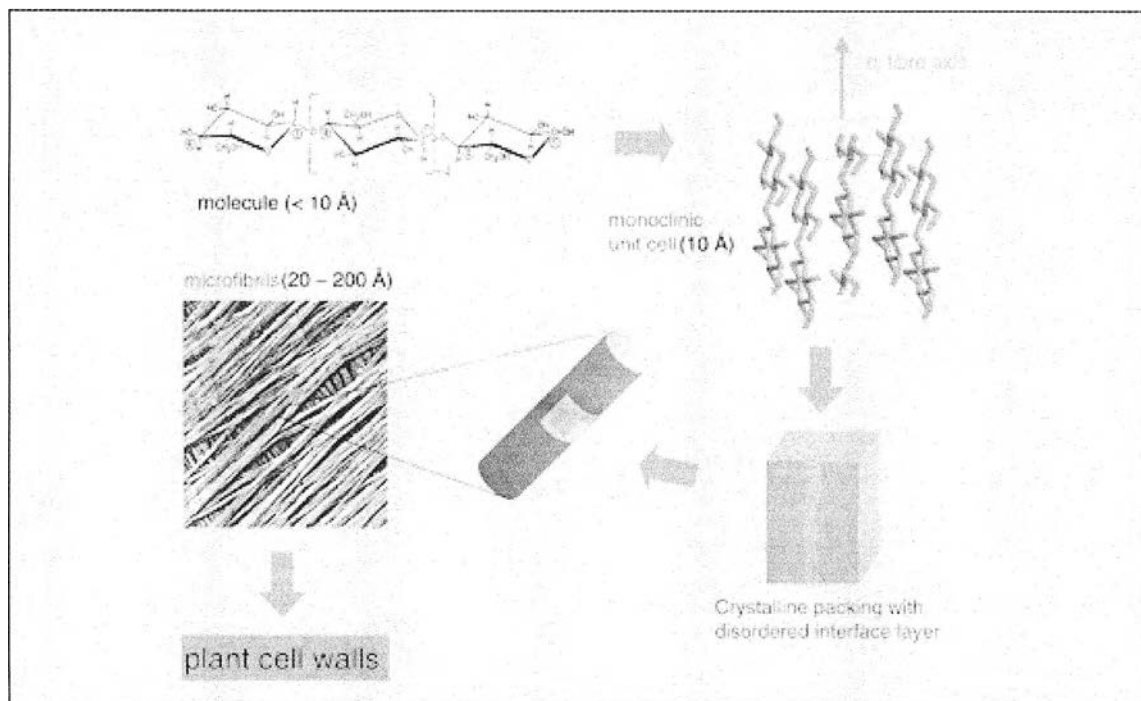

Figure 2.4 Hierarchical organization of cellulose. The polymer (top left) aggregates to cellulose nano-crystallites, which are interconnected by disordered interface layers (bottom right). These crystallites (20-200 A^0) are organized in bundles of single fibers (bottom left)[8].

2.3.1 Molecular Level

As indicated in Table 2-1, cotton fiber is composed of 95-99% cellulose. The main feature of the chemical structure of cellulose is a linear polymer of 1,4-linked-β-D-glucose with a degree of polymerization of more than 3000[3].
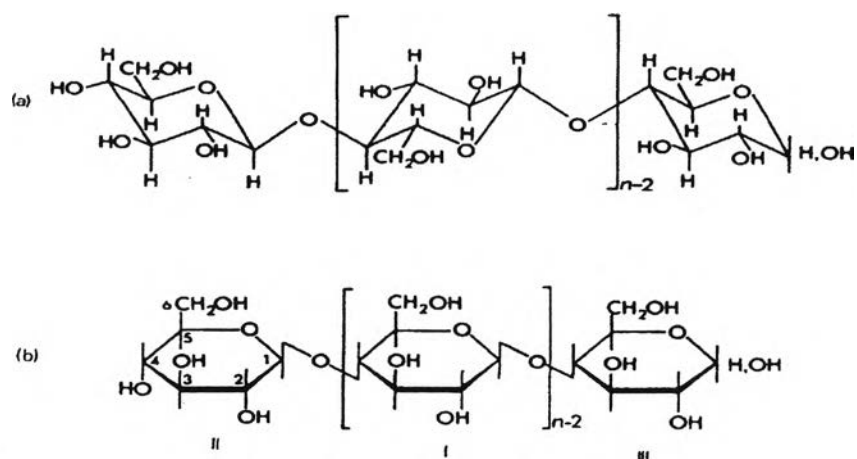
Figure 2.5 Representation of cellulose (n = degree of polymerization)[5]

Figure 2.5 (a) shows the pyranose rings in the $^4C_1$ conformation and Figure 2.5 (b) shows the Haworth projections formula[5] that easier to write but it may obscure some important aspects of the glucopyranose ring. The main sequence of intermediate units (I) which posses one primary and two secondary alcohol groups each, the non-reducing end group (II) that posses one extra secondary alcohol group at ^4C, the reducing end group (III) which is a cyclic hemiacetal, and glycosidic linkages are the essential features of the polymer chain. The reducing end group also exhibits the characteristics of both an alcohol and an aldehyde under appropriate conditions (Scheme 2.1).
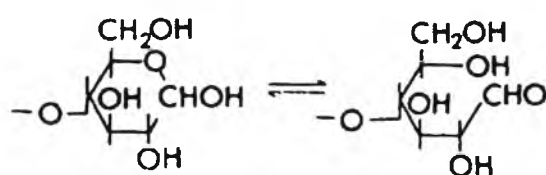
Scheme 2.1[5]

2.3.2 Supermolecular Level

Cellulose is a highly crystalline material, but it does not form discrete crystals like those of glucose from which it is derived. As already indicated, native cellulose fibers consists of crystalline fibrils varying in complexity and length. The chain molecules are fully extended to the form of flat ribbons having the minimum possible thickness in the direction perpendicular to the mean planes of the rings. The monoclinic unit cell of flat ribbons has dimensions of approximately a=0.82, b=0.79, c=1.034 nm (fiber axis) and $\gamma=97^0$[5]. A cross-

section of the cell in the ab plane, looking along the fiber axis, is shown in Figure 2.6[5]. The center and corner chains were parallel to one another in the ac plane (Figure 2.7) and the adjacent chains are held together in a system of hydrogen-bonded sheets in the ac planes as shown in Figure 2.8[5]. There is no hydrogen bonding between corner and center chains.
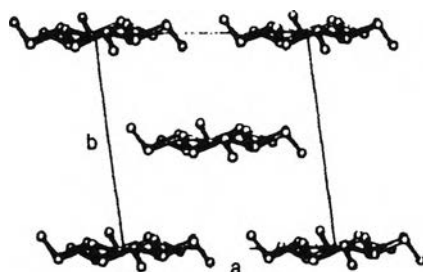

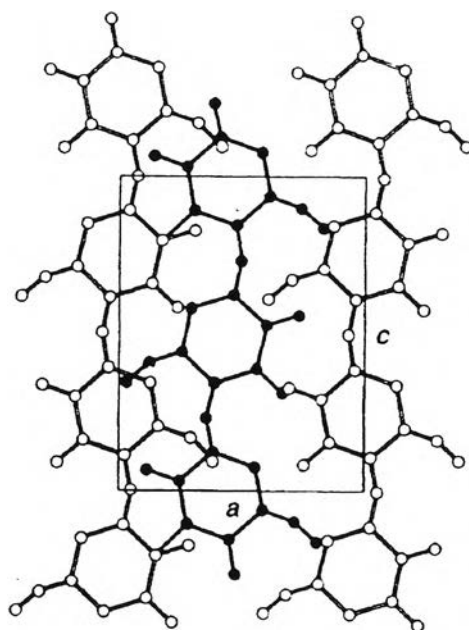Figure 2.6 Cross-section of unit cell in the ab plane (looking along the fiber axis) of cellulose

Figure 2.7 Unit cell in the ac plane[5]
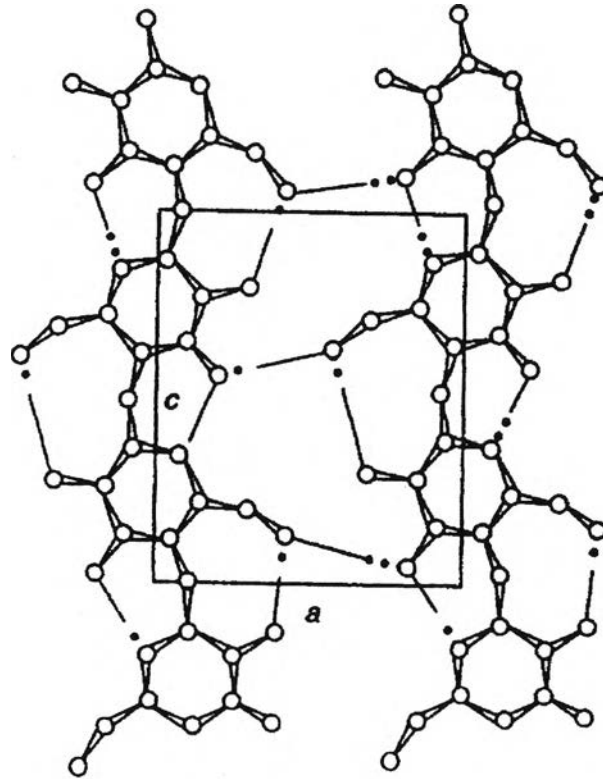
Figure 2.8 Hydrogen bonding in cellulose[5]

Also, the knowledge of the fine structure of cellulose is essential for a full understanding of dyeing processes since it is important to know precisely where a dye becomes attached to the fiber. It is generally accepted that reagents cannot penetrate the crystalline regions unless they can simultaneously disrupt them. In case of cellulose fiber, many applicable theories of its structure have been described by Hearle[6]. The fringed micelles, in which crystalline micelles are embedded in an amorphous matrix with individual chain molecules extending through several crystalline and amorphous regions, as in Figure 2.9 (a), held sway for a long time. This subsequently gave way to the concept of fringed fibrils, in which the fringed molecules that constitute the non-crystalline regions emerge from various points along crystalline fibrils, as in Figure 2.9 (b), rather than from the ends of brick-like micelles. These non-crystalline regions contribute more space between chains than those of crystalline regions and allow water, chemical molecules, or dyes to penetrate them.

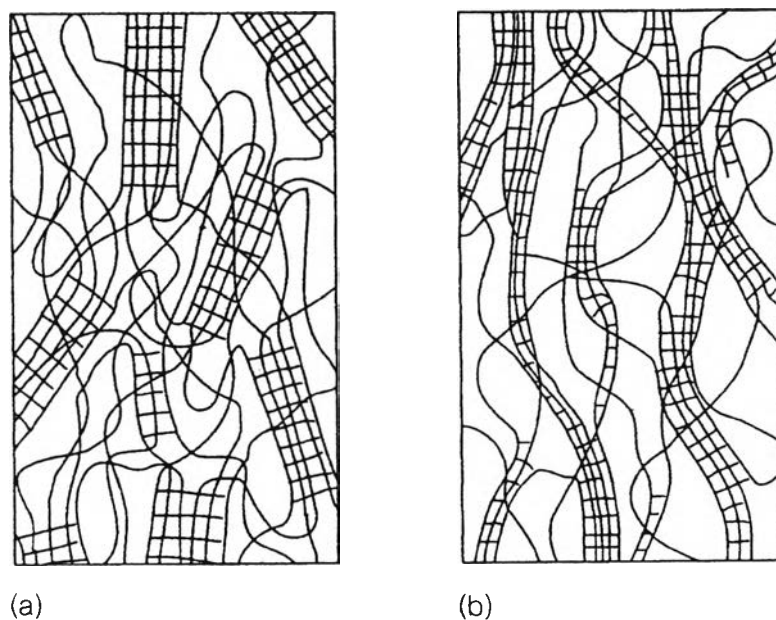(a)   (b)

Figure 2.9 Diagram of fine structure in cellulose: (a) fringed micelles, (b) fringed fibrils[6].

2.3.3 Morphological Level

As illustrated schematically in Figure 2.10, cotton fiber consists of primary wall, secondary wall, and lumen[6].
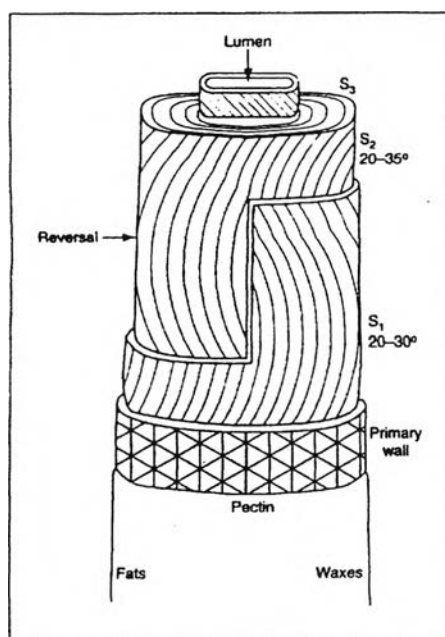

Figure 2.10 Idealized diagram of cotton morphology[6]

The primary wall composes of a network of cellulose fibrils covered with an outer layer, or cuticle, of pectin, protein, mineral matter, and wax[6]. The secondary wall constitutes the bulk of a mature fiber and consists almost entirely of fibrils of cellulose arranged spirally around the fiber axis, the direction of the spiral reversing (i.e. changing between S and Z twists) many times along a single fibril[6]. The secondary wall consists of several layers and the spiral angle of the fibrils varies from one layer to the next. Thus the cotton fiber consists of an assembly of fibrils in which the cellulose is accessible to most reagents only at fibrillar surfaces by way of a system of voids and channels. The lumen or cavity is the remainder of the central canal from which these layers are produced. It contains residual protein, mineral salts, and the natural coloring matter of the fiber[6]. It was laid down in the secondary wall while fiber became mature.

Table 2-2 gives comparative data for the typical cotton. The other substances are mostly water-soluble organic acids and sugars. The table illustrates the very high cellulose content of cotton, which surpasses all other natural sources in this respect.

Table 2-2 Composition of the typical cotton[5]

Constituent	Proportion of dry weight (%)	
	Whole fiber	Primary wall
Cellulose	94	54
Protein (%N x 6.25)	1.3	14
Pectin	1.2	9
Wax	0.6	8
Ash	1.2	3
Other substances	1.7	12

2.4 Properties of cotton fiber

The properties of cotton are shown in Table 2-3

Table 2-3

Molecular Structure	Long chain of cellulose
Microscopic Features	
Length:	25 to 60 mm[9].
Width:	12 to 20 μm[10].
Cross-section:	Bean-shaped
Color:	Usually a creamy off-white color
Light reflection:	Low luster, dull appearance
Physical Properties	
Tensile Strength:	96,700 pound/inch[11]
Elongation:	4 to 13%[11] elongation at break
Tenacity (g/den.):	3 to 5 (dry), 3.6 to 6 (wet)[11]
Density (g/cm^3):	1.54 to 1.62[11]
Moisture content:	8.5%[12]
Resiliency:	Low[13]
Toughness and stiffness:	High
Abrasion resistance:	Fair to good
Chemical Properties	
Sunlight and heat:	May be heated in the dry state to temperature of 150^0 C[14] without undergoing decomposition but can be damaged by excessive light
Organic solvents:	Resistant to most organic solvents
Effect of bleaches:	Can be bleached without fiber damage

Table 2-3 (continued)

Acids and alkalis:	Highly resistant to alkalis. Strong mineral acids cause fiber damage readily and organic acids do a little damage.
Resistant to stains:	Poor resistance to water-born stains
Dyeability:	Good affinity for various types of dyes. Dyeable with direct, vat, sulphur, and reactive dyes[15]
Biological Properties	
Effects of microorganisms:	Vulnerable to action by bacteria and mould.
Effects of insects:	Starched cottons are attacked by silverfish.
Optical Properties	
Axial refraction:	$1.596^{(11)}$
Transverse refraction:	$1.534^{(11)}$
Double refraction:	$0.062^{(11)}$
Electrical and thermal Conductivity	Good heat conductor
Flamability Behavior	Burns very readily and once ignited, a fabric will carry flame.

2.4.1 Strength

Tensile strength is a prime necessity in fibers if the resultant fabric is to withstand the strain of wear. Fibers differ in their resistance to tearing apart when subjected to tension. The ability of a fiber to resist wearing away by friction or rubbing, referred to as abrasion resistance, is another aspect of durability.

Cotton has good strength. When wet, its strength may increase temporarily by as much as 30%[16]. Cotton may be permanently strengthened by mercerization. It has good abrasion resistance.

2.4.2 Elasticity

Elasticity means that when the fiber is elongated or stretched, on release of tension, it will tend to return to its original length. Consequently, the less stress applied to stretch the fiber and the more nearly it returns to its original length, the more elastic it is. The greater the elastic quality, the more the fiber will resist tearing. Cotton has very little natural elasticity.

2.4.3 Resilience

Resilience means that the fiber can be compressed, on release of pressure, and will tend to return to its original shape.

Cotton lacks appreciable resilience. While special finishes reduce this disadvantage, the durability of the fabric is also reduced.

2.4.4 Drapability

Drapability is the ability of a fabric to hang and fall into graceful shape and folds. It depends upon the finish, construction, the kind of yarn used, and the fibers in the yarn.

Cotton does not has good draping compared with linen which is partially due to its shorter fibers[16].

2.4.5 Heat Conductivity

Heat conductivity is the ability of a fiber to conduct heat. The degree of heat conductivity helps determine whether fabrics are suitable for winter or for summer use.

Cotton fiber is a good conductor of heat[16]. Cotton fabrics are also suitable for summer clothing. The surfaces of the cloth have much to do with the degree of heat conductivity.

2.4.6 Absorbency

The quickness with which a fabric absorbs moisture and gives it up again in evaporation has an important bearing on health and comfort. A loosely constructed fabric or one with a napped surface, for example, is more absorptive than a smooth surfaced fabric. Cotton absorbs water rather well but does not dry very quickly.

2.4.7 <u>Cleanliness and Washability</u>

The fibers with smooth surfaces produce fabrics that are easy to launder. A napped surface of fibers makes it necessary to give the garment more care in washing.

The short cotton fiber produces a fabric with a relatively rougher surface than that of linen, silk, or rayon, and therefore soils easily. Nevertheless, cotton fabric is considered a hygienic material because it can be cleaned easily. Since cotton is stronger when wet[16], it withstands rough handling and hot water.

2.4.8 <u>Reaction to Bleaches</u>

Most white manmade fibers do not usually turn gray or yellow. Sometimes, however, the finish on the fabric may cause the discoloration and fabrics are bleached to get them whiter or to remove stains.

Cotton may be safely bleached by using normal care with the ordinary household bleaches containing sodium hypochlorite[16]. For more careful treatments, sodium perborate and hydrogen peroxide bleaches may be used[16].

2.4.9 <u>Shrinkage</u>

Shrinkage caused by water varies from considerable to none, depending upon the fiber.

Cotton shrinks considerably when wet. Shrink-resistant finishes are available to control this.

2.4.10 <u>Effect of Heat</u>

Heat affects different fibers in different ways and at different temperatures. Some fibers scorch and flame; others melt and flame or shrink. Some fibers are self-extinguishing; others are completely non-combustible.

Cotton is highly resistant to degradation by heat. It scorches at about 300^0 F (150^0 C) but does not burn until the temperature is 475^0 F (246^0 C)[16].

2.4.11 Effect of Light

Textiles are constantly exposed to the outdoors and light. Some need to be very resistant to degradation by sunlight. Cotton loses strength in sunlight and has a tendency to yellow.

2.4.12 Resistant to Insects

Certain kinds of insects may attack textile fibers that provide a source of food for them.

Cotton is not attacked by cloth moth or carpet beetle larvae[16]. Under extreme circumstances, it may be attacked by such insects as silverfish that are attracted to its cellulose content.

2.4.13 Reaction to Alkalis and Acids

Cotton is destroyed by concentrated inorganic acids such as hydrochloric, hydrofluoric, sulfuric, and nitric and is damaged when such acids are in dilute solutions. It is not injured by alkalis even in hot, strong solutions. Heavy-duty detergent may be used for washing cotton.

2.4.14 Affinity to Dyes

The readiness with which a fiber absorbs and retains dye affects the appearance and serviceability of a fabric. Affinity for dyes is usually determined by the porosity of a fiber.

Cotton has affinity for direct dyes, reactive dyes, certain azoic dyes, and sulfur and vat dyes in a reduced state. The fastness of direct dyes is improved by the aftertreatments that are sometimes given. Mercerized cotton absorbs and retains dyes better than cottons that are not so treated.

2.4.15 Resistance to Perspiration

Aside from the fact that perspiration may affect the color of fabrics and may stain some, it will cause deterioration of some textile fibers. To minimize this, frequent cleaning is advisable. Cotton, like add natural fibers, can be degraded by perspiration.

2.5 Structure of cotton in relation to dyeing

The dyeing properties of a cotton fiber are determined by its external and internal structure. The most obvious macrostructure feature to affect the dyeing of a fiber is its specific surface area, which is inversely related to its fineness. The finer the fiber, the greater is the rate of dyeing[6]. As already mentioned, any sample of cotton is likely to contain at least some exceptionally thin-walled fibers. These fibers lack a fully developed secondary wall and so the proportion of cellulose in the primary wall is greater than in normal fibers. The substantivity of many dyes for the primary wall is less than for the secondary, and so the dyed thin-walled fibers appear paler than the rest[6].

2.6 Bleaching of cotton with hydrogen peroxide

Cotton fibers are colored and the coloring matter confers a yellowish brown color to the fibers. This is believed to be a condensation product of caffeic and quinic acids[6]. The purpose of bleaching is to destroy this colored material and to confer a pure white appearance to the fibers.

Hydrogen peroxide has achieved its dominant position as a bleaching agent because of three factors:

1. It is environmentally innocuous (potentially it can decompose into oxygen and water)

2. It is versatile (it can be used hot or cold, in rapid or long-dwell processes, batch wise or continuously)

3. A variety of activation routes is available.

As mentioned above, hydrogen peroxide can break down into water and oxygen (Scheme 2.2)

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$$

Scheme 2.2[5]

Hydrogen peroxide as supplied by the manufacturers is extremely stable and has only slight bleaching effect on cellulose. For bleaching to occur this stability must be overcome by activation. The usual activator for textile bleaching is alkali, usually sodium

hydroxide, and the peroxide molecule undergoes heterolytic fission to the perhydroxide ion, as in Scheme 2.3[6]

$$H_2O_2 + OH^- \longrightarrow OOH^- + H_2O$$
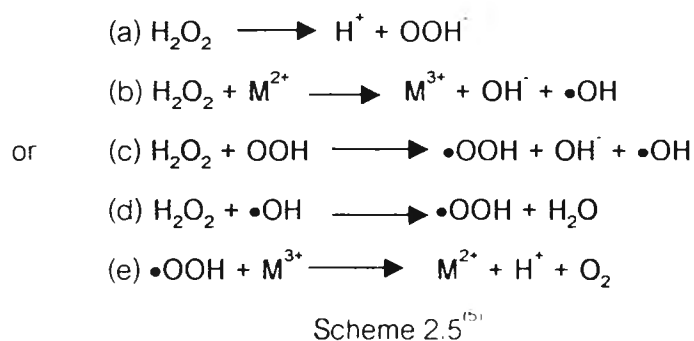
Scheme 2.3[6]
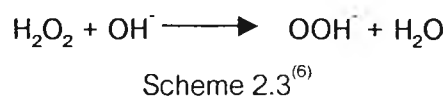
This nucleophile can react with organic compounds by a displacement reaction or by addition to a double bond.

It is probable that the pigments responsible for the natural color of cotton contain a chromophoric system of conjugated double bonds. These will be attacked by a free-radical system and it has been proposed by Cates and Taher[5, 6] that peroxide bleaching takes place by the mechanism indicated in Scheme2.4
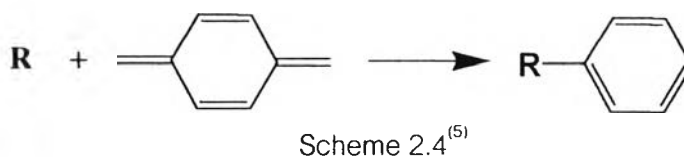
Scheme 2.4[5]

Such free radical might be produced by reaction of hydrogen peroxide with an electron donor, possibly derived from a metal cation or from a perhydroxide anion. The reaction mechanism proposed is shown in Scheme 2.5

(a) $H_2O_2 \longrightarrow H^+ + OOH^-$

(b) $H_2O_2 + M^{2+} \longrightarrow M^{3+} + OH^- + \bullet OH$

or   (c) $H_2O_2 + OOH^- \longrightarrow \bullet OOH + OH^- + \bullet OH$

(d) $H_2O_2 + \bullet OH \longrightarrow \bullet OOH + H_2O$

(e) $\bullet OOH + M^{3+} \longrightarrow M^{2+} + H^+ + O_2$

Scheme 2.5[5]

On the basis that the rate of bleaching with hydrogen peroxide increases with rise in pH, it was proposed that the bleaching action is due to the perhydroxyl anion formed by ionization [Scheme 2.5 (a)]

The free radicals are believed to initiate decomposition through a chain mechanism. The decomposition within a given time interval is limited by the concentration of colored

impurities or by inhibiting metal cations[5]. The latter appear to protect the cellulose from chemical damage by minimizing the formation of molecular oxygen in the alkaline medium.

2.7 Dyeing of cotton with reactive dyes
2.7.1 Structure of Reactive Dyes

The general chemistry of reactive dyes is azo dyes since approximately 80% of all reactive dyes are based on the azo chromogen[17].

Reactive dyes are colored compounds which contain one or two groups capable of forming covalent bonds between the reactive group of dyes and the substrates such as textile fibers[1]. Such covalent bonds are formed with the hydroxyl groups of cellulose fibers, with the amino, hydroxyl and mercapto groups of protein fibers and with the amino groups of polyamides[17].

In general reactive dyes for celullosic materials have certain characteristic structural features, represented diagrammatically in Figure 2.11

Figure 2.11 Characteristic structural features of a reactive dye[5]

Where S = Solubilising group
C = Colored molecule
B = Bridging group
X = Reactive group

2.7.2 Classification of reactive Dyes

The reactive dyes can be classified according to the reaction mechanisms of reactive groups, as follows:

2.7.2.1 Groups reacting by the nucleophilic substitution

The reactive system of this type is based on a heterocyclic ring containing carbon and nitrogen atoms. Below is an example of those that react by a nucleophilic substitution mechanism based on the presence of labile halogeno substituents in a heteroaromatic system, e.g., the chlorotriazinyl dyes[5] (Scheme 2.6).

Scheme 2.6[5]
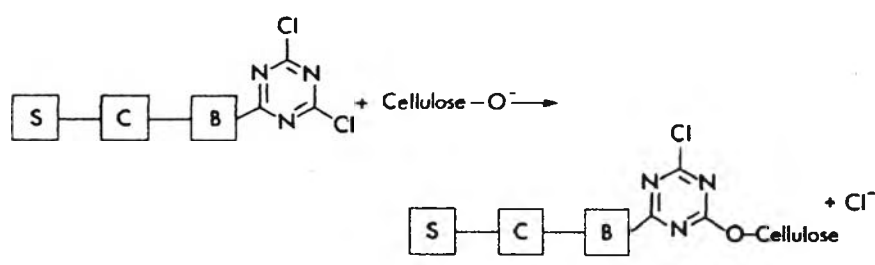
The characteristic feature of this mechanism is the attacking on the heterocyclic carbon of the reactive group by the most basic form of the nucleophilic group of the Cell-O⁻ groups of cellulose.

Amongst the principal reactive systems of this type are the halogeno-substituted triazine, pyrimidine, pyrazine, quinoxaline, thiazole, and pyridazone groups[5]. The following figures are important representatives of these reactive groups:

Figure 2.12 Dichlorotriazinyl reactive dye and monochlorotriazinyl reactive dye[18]

Di- and monochlorotriazinyl reactive dyes (Figure 2.12) were the first reactive dyes for cellulose fibers introduced commercially in 1956 and 1957[18], respectively.

The monofluorotriazinyl dyes (Figure 2.13) used in this research work were introduced by Ciba-Geigy in 1978[17]. Dyes with this reactive group were synthesized from cyanuric fluoride. It is very difficult to substitute two fluorine atoms in cyanuric fluoride by amines without significant hydrolysis[17]. Not until the mid-70s did research chemists of Ciba-

Geigy[17] find ways to minimize hydrolysis during the synthesis of monofluorotriazinyl dyes. For these dyes the greater electronegativity of fluorine results in a higher level of reactivity than that of the monochloro-s-triazinyl system.
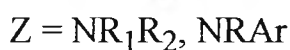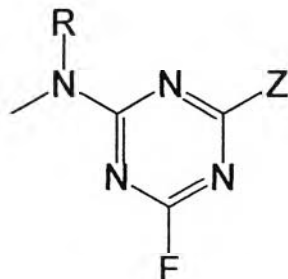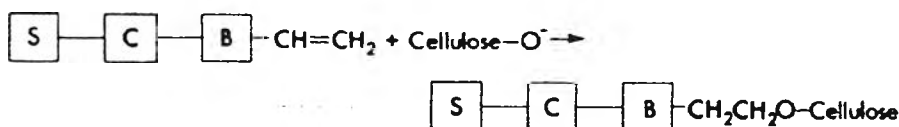

$$Z = NR_1R_2, NRAr$$

Figure 2.13 Monofluorotriazinyl dyes[18]

2.7.2.2 Groups reacting in accordance with a nucleophilic addition

The addition of a nucleophilic group to a carbon-carbon double bond of the reactive system is shown in Scheme 2.7
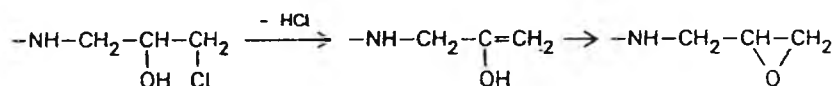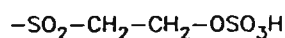

Scheme 2.7[5]

The double bond of the reactive group is in most cases not present in the reactive dye, but is formed later in the process of dyeing in the first, general base-catalyzed step of the reaction mechanism.

In most instances the unsaturated reactive group is not present in the dye as supplied but is formed from a precursor in the presence of alkali. The most important precursor for dyes of this type is the sulphuric acid ester of β-hydroxyethylsulphone, which forms a vinylsulphone in the dyebath by elimination of sulphuric acid[18] (Scheme 2.8)

Scheme 2.8[5]

The following are important representatives of this system[18]:

$$-SO_2-CH_2-CH_2-OSO_3H$$

$$-NH-CH_2-\underset{\underset{OH}{|}}{C}H-\underset{\underset{Cl}{|}}{C}H_2 \xrightarrow{- HCl} -NH-CH_2-\underset{\underset{OH}{|}}{C}=CH_2 \rightarrow -NH-CH_2-\underset{\diagdown\diagup}{\underset{O}{CH-CH_2}}$$

An important difference between the fixation reactions of substitution mechanism and addition mechanism is that the functional group of the textile fiber in substitution mechanism participates in the addition as well as the elimination reaction, whilst in addition mechanism the first elimination step is independent of the textile substrate[18].

Therefore, with the reactive systems of groups that react with addition mechanism, there is the possibility, at constant dyebath pH, of optimizing relative to each other the rate of formation of the vinylic intermediate[17] in Figure 2.14 and the rate of diffusion of the dye.
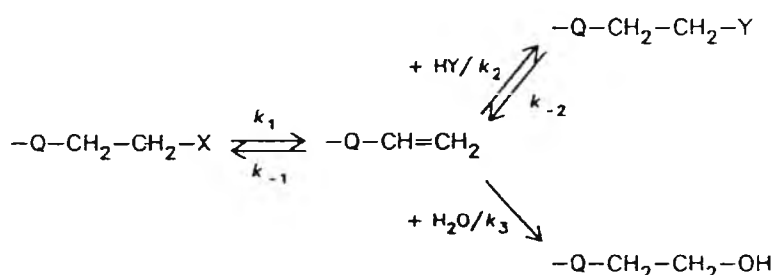
$$-Q-CH_2-CH_2-X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} -Q-CH=CH_2$$

+ HY/ k_2 ⇅ k_{-2} → $-Q-CH_2-CH_2-Y$

+ H_2O/k_3 ↘ → $-Q-CH_2-CH_2-OH$

Figure 2.14 The specific base catalyzed addition of the nucleophilic functional group HY of the textile fiber[17]

2.8 Problems of reactive dyeing

Even though reactive dyes offer unique advantages but certain problems such as poor exhaustion and dye lose due to hydrolysis remain the challenge to be solved. All conventional reactive dyes for cellulose rely on the reactivity of the cellulosate anion (Cell-O⁻) as the nucleophlic reagent and hence hydrolysis of the dye by reaction with hydroxide ions from water will always compete with the desired fixation reaction. Reaction between the dye and cellulose can occur only when the dye has been absorbed into the cellulose phase.

The efficiency of fixation is a function of:

1. The reactivity ratio, the ratio of rate constants for the fixation reaction and hydrolysis

2. The substantivity ratio, the relative concentrations of dye absorbed into the substrate and remaining in the dyebath

3. The diffusion coefficient of the dye in the substrate

4. The liquor ratio

5. The surface area of the substrate available for absorption of dye

Dyes of higher substantivity diffuse more slowly than less substantive dyes. Lowering the liquor ratio favor increases in the rate and efficiency of fixation. In order to attain the maximum rate and efficiency of fixation, more electrolytes is needed, but this increases the risk of aggregation and possible precipitation with dyes of limited solubility. Moreover, high electrolyte concentrations in dye bath discharges may increase salinity or acidity in rivers and destroy delicate balance of waterways.

An increase of dyeing temperature lowers the substantivity ratio and accelerates the rate of hydrolysis of the dye; both of these effects reduce the fixation efficiency. An increase in electrolyte concentration always enhances substantivity without impairing reactivity providing the dye remains completely dissolved.

Any reduction in the magnitude of liquor ratio must favor increases in efficiency and rate of dyeing. However, reducing the value of liquor ratio means that for a given depth of shade the dye concentration must be increased, putting a risk of uneven dyeing as well as dye aggregation.

2.9 Previous research works on chemical modification of cellulose fibers to improve dyeability

The main problem involving in reactive dyeing is a poor dye fixation on the fiber resulted in many efforts to develop natural and synthetic fibers with enhanced coloration properties. These developments often require chemical modification, applicable during the fiber production stage, prior to dyeing or, more desirably, during dyeing.

The attempts to modify cotton fibers to enhance their dyeability were previously proposed by Karrer and Wehrli[2] in 1926. They tosylated cotton and then reacted this modified cotton with various amines to produce fibers containing primary, secondary,
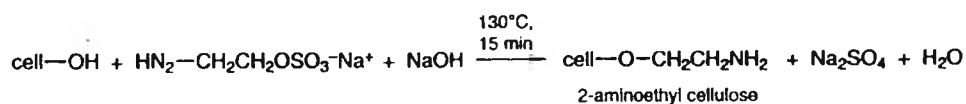
tertiary, and quaternary aliphatic amines. Scheme 2.9 shows the tosylation of cotton with p-toluenesulphonyl chloride, followed by nucleophilic displacement of p-toluenesulphonic acid with ammonia, to give cotton aminated with primary amino residues.
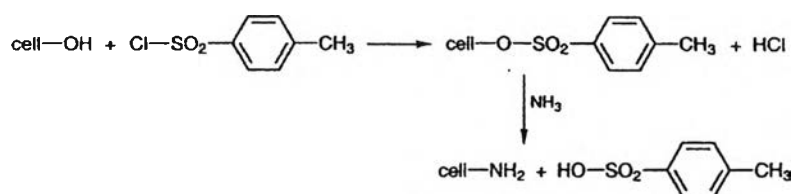
Scheme 2.9[2]

Another route to aminated cotton mentioned by Karrer and Wehrli is the reaction of cotton with p-nitrobenzoyl chloride followed by reduction of the nitro group (Scheme 2.10)[2].
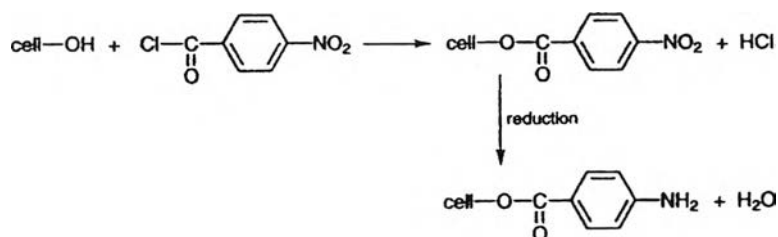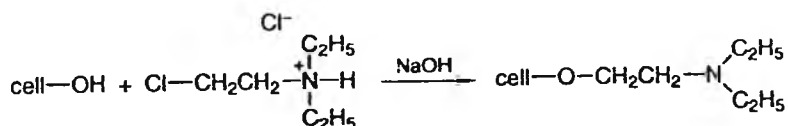

Scheme 2.10[2]

Hartmann described the preparation of 2-aminoethylcellulose by reacting 2-chloroethylamine and similar compounds with soda cellulose or cellulose treated with 18% sodium hydroxide (Scheme 2.11)[20]. Later, compounds related to 2- aminoethylsulphuric acid were introduced since it was found to be more efficient at producing a 2-aminoethylcellulose, relatively inexpensive, and not requiring organic solvents. Aminoalkylcelluloses were capable of enhancing dyeablility with most cotton dyes.

$$cell—OH + HN_2—CH_2CH_2OSO_3^-Na^+ + NaOH \xrightarrow[\text{15 min}]{\text{130°C,}} cell—O—CH_2CH_2NH_2 + Na_2SO_4 + H_2O$$

2-aminoethyl cellulose

Scheme 2.11[20]

Herlinger et al. suggested a new two-stage dry fixation process for the production of aminoehtylated cellulose with 2-aminoethylsulphuric acid[2]. If vinylsulphone dyes were added to the pad liquor, excellent color yields were obtained, and even hydrolysed vinylsulphone dyes were covalently bound to the fiber.

Soignet et al. found that the tertiary amino groups contained in diethylaminoethylcellulose (DEAE cellulose) acted as a 'built in' catalyst to increase the reactivity of epoxides and effectively quaternised the fiber[21]. Tertiary amino groups have been incorporated into cellulose by reaction of cotton with β-chloroethyldiethylamine hydrochloride according to the Hartmann process, producing DEAE cellulose[22] (Scheme 2.12).

cell—OH + Cl—CH$_2$CH$_2$—$\overset{C_2H_5}{\underset{C_2H_5}{\overset{+}{N}}}$—H $\xrightarrow{\text{NaOH}}$ cell—O—CH$_2$CH$_2$—N$\overset{C_2H_5}{\underset{C_2H_5}{}}$
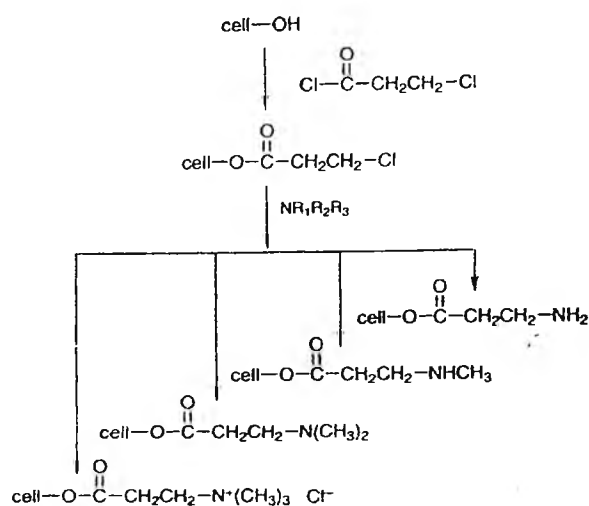
Cl⁻

Scheme 2.12[22]

The DEAE cotton could be dyed, in the absence of salt, with direct, reactive, and acid dyes. Covalent fixation of a Drimarene K reactive dye occurred under neutral and slightly acidic dyebath conditions. El-Alfy et al. explained this by proposing that the tertiary amino groups of the DEAE cotton were behaving as a 'built-in catalyst' (Scheme 2.13, where D is the dye chromophore)[22].
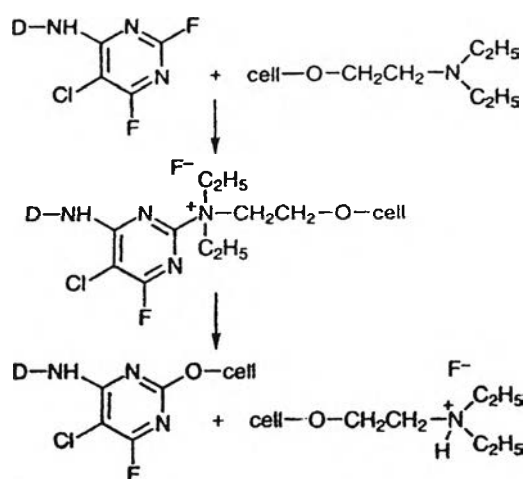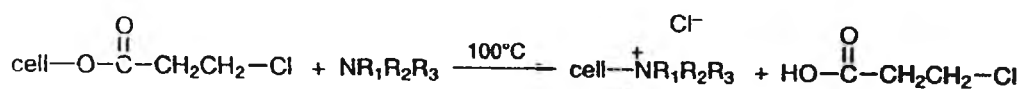
Scheme 2.13[22]

Tsuji and colleagues acetylated cotton and showed improved uptake of direct dye without adversely affecting fastness to laundering[23]. Enhanced dyeability of the acetylated cotton was presumably due to changes in the cellulose's crystalline structure and hence dye accessibility within the fiber.

Lewis and Lei esterified cotton with chloropropionyl chloride (CPC), and then aminated the modified cotton by nucleophilic substitution of the chloropropionate residue with various amines to produce cotton fabrics containing primary, secondary, tertiary, and quaternary amines[24]. It was initially assumed that the reactions would take the course of Scheme 2.14, where R_1, R_2, R_3 = H or CH_3

cell—OH

$$Cl-\underset{\underset{O}{\|}}{C}-CH_2CH_2-Cl$$

$$cell-O-\underset{\underset{O}{\|}}{C}-CH_2CH_2-Cl$$

$NR_1R_2R_3$

$$cell-O-\underset{\underset{O}{\|}}{C}-CH_2CH_2-NH_2$$

$$cell-O-\underset{\underset{O}{\|}}{C}-CH_2CH_2-NHCH_3$$

$$cell-O-\underset{\underset{O}{\|}}{C}-CH_2CH_2-N(CH_3)_2$$

$$cell-O-\underset{\underset{O}{\|}}{C}-CH_2CH_2-N^+(CH_3)_3 \quad Cl^-$$

Scheme 2.14[24]

Dyeing was carried out with reactive dyes under neutral to slightly acidic conditions in the absence of salt[2]. The results show that the aminated cotton containing secondary amino residues (treatment with methylamine) gave the highest color yields. But alkali washing showed the propionate ester stability to be poor. However, this problem was overcome as it was discovered that a more severe amination step (amine treatment at 100^0C) did not produce modified cotton containing an ester linkage. Instead, bonds of the type Cell-N$^+$R^{1}R^{2}R^3 were obtained (Scheme 2.15), which gave reactive dyeings of excellent alkali stability.

$$cell-O-\overset{O}{\overset{\|}{C}}-CH_2CH_2-Cl + NR_1R_2R_3 \xrightarrow{100^\circ C} cell-\overset{+}{N}R_1R_2R_3 \overset{Cl^-}{} + HO-\overset{O}{\overset{\|}{C}}-CH_2CH_2-Cl$$

Scheme 2.15[2]

Evans et al. carried out a comprehensive evaluation of three types of quaternary colorless compound, capable of covalently bonding to cellulose to impart cationic character which should enhance cotton's dyeability with reactive and simple acid dyes[25] (Figure 2.15).

Type 1 was the chlorohydrin precursor to glycidyltrimethylammonium chloride

Type 2 compounds were monochloro-s-triazines containing bis-quaternary amines

Type 3 compounds were bis-monochloro-s-triazines containing bis-quaternary amines.

$$Cl-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{+|}{N}}-CH_3 \quad Cl^-$$

Type 1

Type 2

Type 3
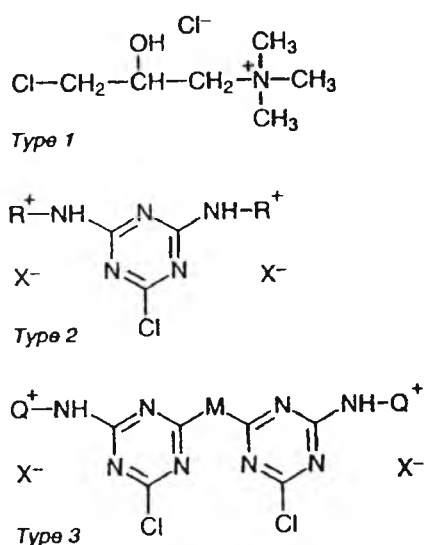
Figure 2.15[25]

Owing to the low substantivity of type 1 and type 2 compounds, their application to cotton demanded a semi or fully continuous process, and the compounds also showed poor penetration of the fiber due to migration of the agents to the surface during drying. Type 3 compounds are readily reactive and exhibit high substantivity towards cotton, but react preferentially at the surface of the fiber resulted in ring dyeing.
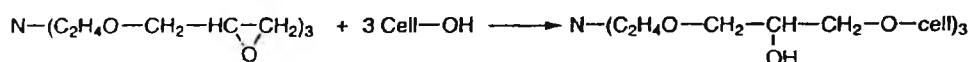
Waly et al. introduced tertiary amino groups by impregnating cotton fabric with a solution of epichlorohydrin and triethanolamine (3:1) in acetone and curing[26]. The treated

cotton showed considerable crease recovery, suggesting the reaction to be intermolecular crosslinking (Scheme 2.16). There was marked dye uptake on the treated cotton containing tertiary amino residues in the case of an acid dye and a dichloro-s-triazine (DCT) reactive dye. This was explained that the proximity of the protonated, cationic nitrogen to the secondary hydroxyl group might encourage ionization of the hydroxyl group, thus creating a nucleophile that promotes the fixation of DCT dyes under mild pH conditions[26].

*Formation of epichlorohydrin/triethanolamine composite*

$$N\underset{C_2H_4OH}{\overset{C_2H_4OH}{-C_2H_4OH}} + 3\ ClCH_2-HC-CH_2 \xrightarrow{-OH} N-(C_2H_4O-CH_2-HC-CH_2)_3$$
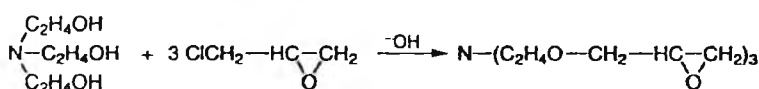
Intermolecular reaction with cellulose

$$N-(C_2H_4O-CH_2-HC-CH_2)_3 + 3\ Cell-OH \longrightarrow N-(C_2H_4O-CH_2-\underset{OH}{CH}-CH_2-O-cell)_3$$
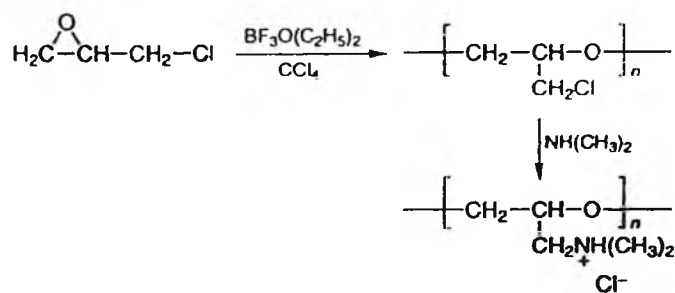
Scheme 2.16[26]

The Sandene process was developed by Courtaulds and Clariant[2] and involved the application of a cationic polymer, Sandene 8425, to cellulose fibers under alkaline conditions by an exhaust method to enhance the fiber's dyeability with anionic and reactive dyes[27]. The polymeric pretreated cotton provided a substrate that had high neutral substantivity for anionic dyes; reactive dyes could be covalently bound to the resin from neutral to slightly acidic dyebaths.

Hercosett 125 (Hercules) is a cationic, reactive polymer prepared by a condensation reaction of adipic acid and diethylenetriamine, followed by partial crosslinking of the polyamide with epichlorohydrin[2]. Burkinshaw et al. applied Hercosett 125 to cotton by a pad-dry-cure[28]. Scheme 2.17 represents the reactive and nucleophilic sites that may exist on the surface of the polyamide-epichlorohydrin treated cellulose.
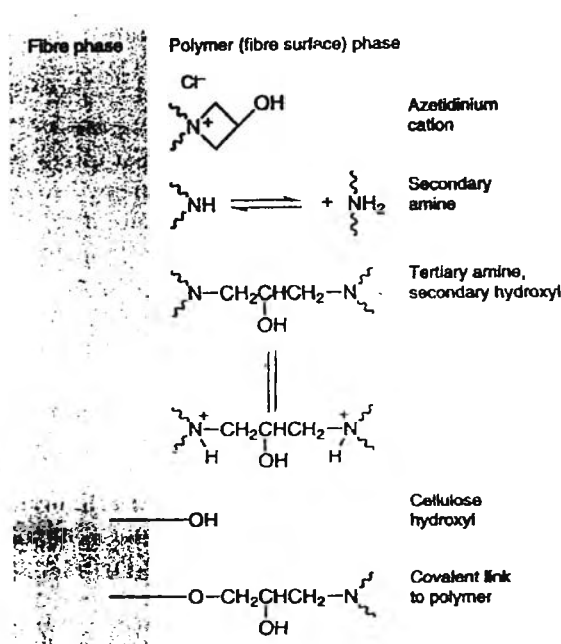
Scheme 2.17[28]

The pretreated polyamide-epichlorohydrin cotton could be dyed from neutral dyebaths, in the absence of salt, to give high exhaustion.
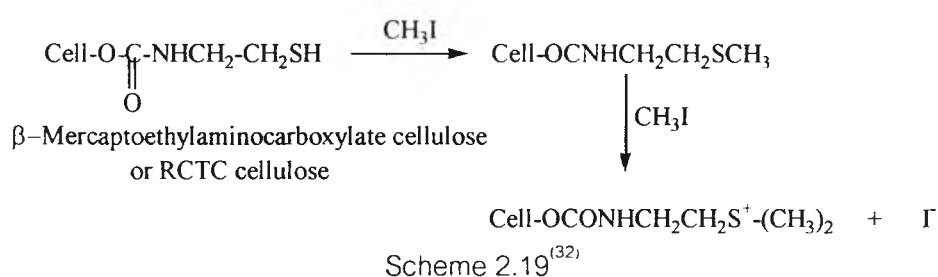
Wu and Chen applied polyepichlorohydrin-dimethylamine to cotton to improve its dyeability with directs and reactives by polymerization of epichlorohydrin with a ring-opening mechanism in carbon tetrachloride with a boron trifluoride etherate catalyst to produce polyepichlorohydrin (PECH)[29-31]. The amine derivative was achieved by adding dimethylamine to PECH at 95^0C (Scheme 2.18).

Scheme 2.18[29]

Higher total nitrogen content on the fiber resulted in dyeings of higher color yield. Polymers containing similar nitrogen content but different molecular mass when applied to

cotton showed the higher molecular mass species to give better color yields, presumably due to the higher substantivity of the higher molecular mass polymer.

Sakamoto et al. looked at the introduction of sulphonium derivatives into cotton[32]. The cotton was treated with bis-β-isocyanatoethyl-disulphide in dimethylformamide at 80^{0}C followed by reduction with tri-n-butylphosphine in methanol containing 10% water to give cellulose β-mercaptoethyl-aminocarboxylate (RDTC). The RDTC cellulose was then treated with methyl iodide to form the sulphonium salts (Scheme 2.19).

$$\underset{\substack{\text{O}}}{\text{Cell-O-C-NHCH}_2\text{-CH}_2\text{SH}} \xrightarrow{\text{CH}_3\text{I}} \text{Cell-OCNHCH}_2\text{CH}_2\text{SCH}_3$$

β–Mercaptoethylaminocarboxylate cellulose
or RCTC cellulose

$\downarrow \text{CH}_3\text{I}$

$$\text{Cell-OCONHCH}_2\text{CH}_2\text{S}^+\text{-(CH}_3)_2 \quad + \quad \text{I}^-$$

Scheme 2.19[32]

The sulphonium derivatives were dyed with Direct Sky Blue A and gave increased dye uptake due to ionic interaction; dye uptake increased with increasing sulphonium content[32].

Vigo and Blanchard immersed soda cellulose in an arylsulphonium salt solution[33]. Dyeing of the treated cellulose was carried out at pH 5.0 with direct, reactive, sulphur, and disperse dyes. Improved color strength was seen for all the aforementioned dye classes but dyebath exhaustion levels and fastness results were not reported.

It was true that all treatments described above were carried-out in separated process prior to dyeing. Additional process means longer production time and an increase in water and energy consumption. Hence, this might be one of reasons why the modification of cellulose fibers has not widely used in commercial process. It is believed that combining the dyeability modification with pretreatment process is interesting in terms of view points of practical textile chemist.

2.10 Concept of the modification and bleaching of cotton fabric in single-bath process

Firstly, scoured cotton fabric was treated with [3-(Methacryloylamino)propyl]trimethyl ammonium chloride (MAPTAC) in the presence of $K_2S_2O_8$ as redox initiator. The subsequent pretreatment was continued in the same bath with hydrogen peroxide and sodium hydroxide

to finally obtain modified, bleached cotton fabric. Advantageously when compare to previous methods, the application of this modifying method is time saving, cost saving in terms of minimizing water and energy consumption as well as reducing waste water volume. Moreover, it should be claimed that this process is environmentally friendly since there is no salt needed in dyeing process, leading to the possibility of an ease of water recycling. The reaction between cotton and modifying agent that occurs in the first stage can be written as follows:
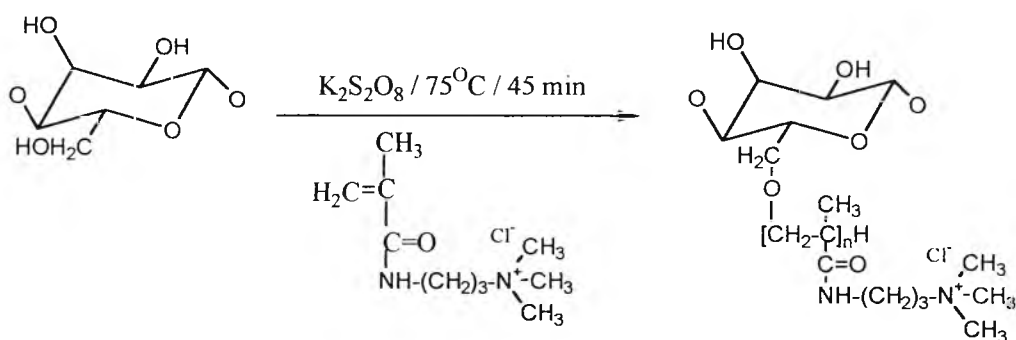

Scheme 2.20 Graft co-polymerization of MAPTAC onto cellulose

It is believe that this type of modifying agent can be readily self-absorbed into cotton fiber due to its cationic characteristic. Fixation can be achieved through graft copolymerization. In bleaching step, hydrogen peroxide was used to remove impurities in order to obtain standard whiteness and clean fabric suitable for subsequent dyeing process. Meanwhile, it is expected that unfixed modifying agent may be removed simultaneously under the bleaching condition. So that soaping process after bleaching is unnecessary. The bleaching performance of hydrogen peroxide is evaluated as whiteness index using Macbeth spectrophotometer. Characterization of modified fabric is also carried out using elemental analysis technique to determine nitrogen content.

The modified cotton fabric obtained from Scheme 2.20 contains free quaternary ammonium pendant group (N^+R_3) which is highly positive charge compared to hydroxyl groups of cellulose. Therefore, the absorption of commercial reactive dyes could be enhanced without the requirement of salts, as shown in Scheme 2.21. The exhausted dyes could be fixed onto cellulose by the addition of alkali. The dyeing properties including color strength, the degree of dye fixation and color fastness to light will be evaluated and then

compared to those obtained from the conventional dyeing of unmodified cotton fabric in the presence of salt.
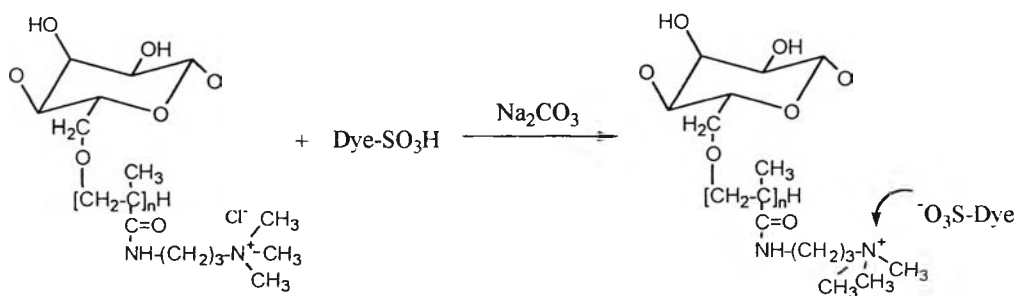
Scheme 2.21

In comparison to conventional dyeing, dyeing of modified cotton fabric in this system is expected to give an improvement in dye exhaustion. Advantageously, color discharge from dyeing industries could be reduced.