CHAPTER II

Literature Survey

2.1 Cellulosic fiber

Cellulose is the most abundant of all naturally occuring organic polymers. Of the many fibers of plant origin, cotton is without doubt that of greatest commercial importance, although flax, jute and hemp are also very significant. Cotton is the most versatile and the most widely used in textile industry, is composed of about 94% cellulose.(6) Cellulose is a macromolecule material which structurally comprises 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. On the molecular level, cellulose is composed of linear chains of glucose units. These chains form whisker-like crystals which are assembled in a superstructure.(7)

2.1.1 Molecular Structure

The chemical structural formula of cellulose can be written as in Figure 2.1(8). It is a linear polymer which is composed of glucose unit linking together by 1,4-β-(D)-glycosidic bond, i.e., a condensation polymer of β-(D)-glucopyranose with 1,4-glucosidic linkages. The repeating unit is the cellobiose which is two glucose units joined together at the terminal hydroxyl groups attached to carbon atoms position 1 and 4 with the loss to a molecule of water (Scheme 2.1)(9).

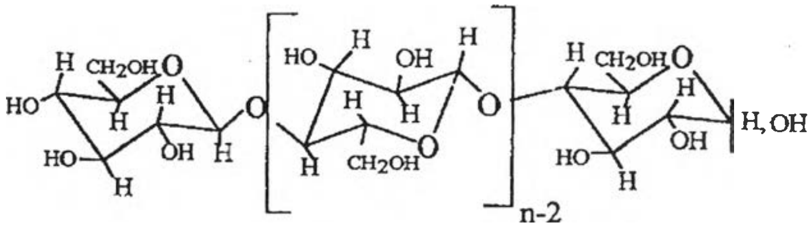
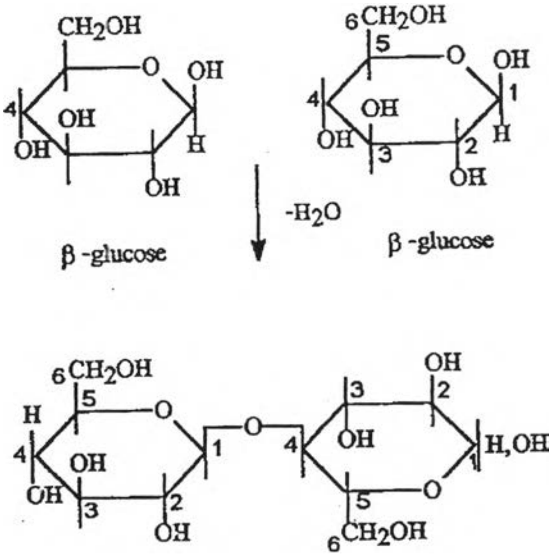
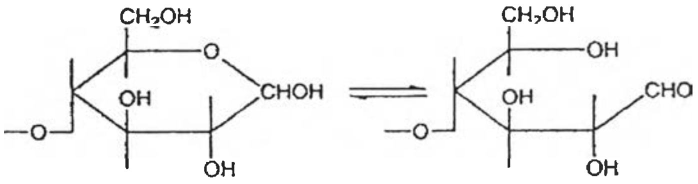


Figure 2.1 Structure of cellulose[8]



Scheme 2.1 Cellobiose unit[9]

The degree of polymerization (DP) of cellulose varies with source and is usually expressed as an average, since a wide distribution is found in most samples. In native cellulose, It may be as high as 14,000, but purification involving treatment with alkali usually reduces this to about 1,000 – 2,000, whereas with regenerated fibers it lies between 250 and 700(10). The intermediate unites possess one primary and two secondary alcohol groups each. The non-reducing end group possesses on extra secondary alcohol group at C_4, and the reducing end group is a cyclic hemiacetal. It exhibits the characteristics of both an alcohol and aldehyde under appropriate condition (Scheme 2.2)(10).



Scheme 2.2 Characteristics of alcohol and aldehyde of a cyclic hemiacetal of the reducing end group in cellulose chain.[10]

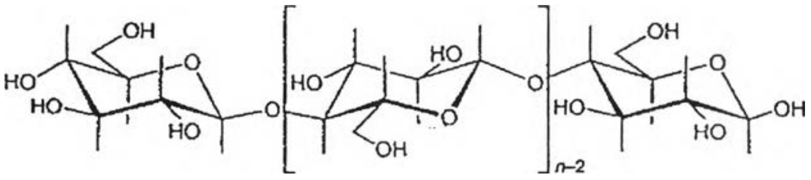


Figure 2.2 Cellulose fully extended conformational formula (flat ribbon).[10]

n = degree of polymerization (DP)

Since each glucose unit in the polymer chain contains 3 hydroxyl groups (two secondary and primary alcohol) at carbons in position 2,3 and 6. The large number of hydroxyl groups readily from hydrogen bonds with water and are therefore responsible for the hydrophilic nature of cellulosic fibers. The formation of the hydrogen bonds between adjacent cellulose chain has a particularly important effect. Cellulose will not dissolve in water, and in fact is insoluble in all but a few organic solvents. Moreover, the interaction between the polymer chains is so strong that cellulose does not melt on heating.

Cellulose contains no groups which will ionize readily in neutral solutions(8,9) but all polymers develop a negative charge on the fiber surface when immersed in water and the possibility of the formation of some few carboxylic groups (-COOH), during bleaching or other degradation processes. Since the pKa of these carboxylic groups is approximately 3.2, the cellulose fibers consequently carry a negative charge in aqueous conditions(11). As the dyebath pH rises above 7.0 the fiber becomes more negatively charged due to the ionization of the hydroxyl groups(4,11). Since the major classes of dye used for dyeing cellulosic fibers are applied as anion, exhaustion dyeing of such fiber is carried out in the presence of electrolyte with reduces dye-fiber repulsion and thereby promotes dye uptake.

2.1.2 Cotton Fiber

Cotton is usually a creamy off-white color although there are some diversities which are almost brown. Purified fiber is pure white, highly absorbent, tasteless and odorless, very smooth and soft, non-irritant and cool to touch. It is ideal therefore for all clothing uses because the properties just mentioned make it comfortable and it has no displeasing wearing properties. In addition to its purity, the cotton fiber is very chemically stable when purified. The absorbency of the pure fiber and its chemical stability give it a good affinity for dyes.

The mature staple fiber takes the form of flat, convoluted ribbon, varying in length, fineness, color, etc., according to source. Cross section of cotton looks like a bean-shaped. It is sometimes described as bilateral structure, which indicates that the density of packing of cellulose chains is not uniform across the fiber. Hence the accessibility of the chain segments to various reagents varies across the fiber. Three main zones (A, B and C in Figures 2.3)(10) have been identified by means of enzymic degradation. The rate of degradation increases from A to B to C, which is the order of decreasing density of packing. These characteristics make cotton easy to recognize under both optical and electron microscopes that are illustrated in Figures 2.4 and 2.5 (10), respectively and bilateral structure is in Figure 2.3(10).

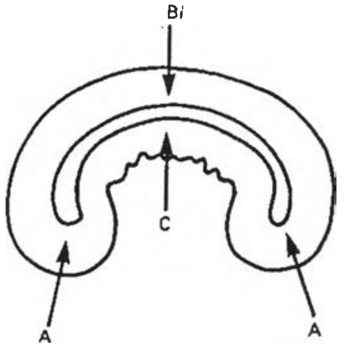


Figure 2.3 Bilateral structure of mature cotton (zones A, B and C differ in fibrillar packing density).[10]

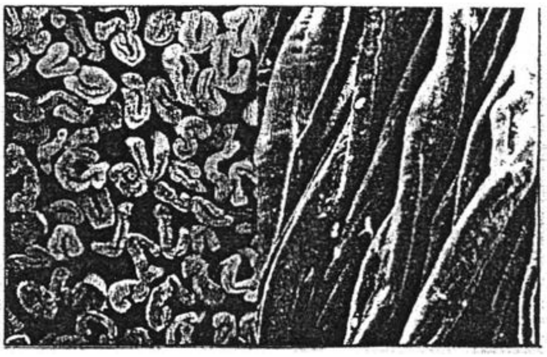


Figure 2.4 Scanning electron micrographs of raw cotton fibers.[10]

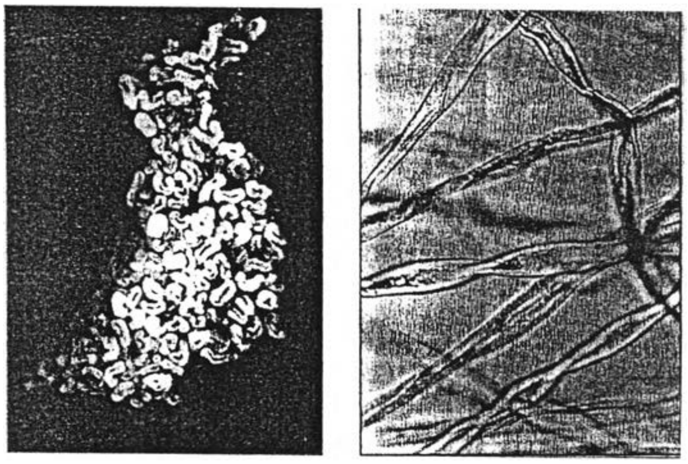


Figure 2.5 Optical micrographs of raw cotton fibers x 184.[10]

As well as 'normal' (i.e. mature) fibers, a typical batch of cotton may also contain some immature and dead fibers. A normal fiber may be defined as one that, after being swollen in aqueous sodium hydroxide, appears rod-like with no continuous lumen and no well–defined convolutions. The lumen is what remains of the central canal from which the layers of cellulose were laid down in the secondary wall while the fiber was growing: it contains some residual protein.

Cotton fibers have a fibrillar structure. Their morphology, illustrated schematically in Figure 2.6 , exhibits three main features: primary wall, secondary wall and lumen. The primarywall consists of a network of cellulose fibrils covered with an outer layer, or cuticle, of pectin, protein, mineral matter and wax. It accounts for only 5% of the weight of the fiber, it contains a greater proportion of the non-cellulosic constituents. The wax renders the fiber impermeable to water and aqueous solutions unless a wetting agent is present. 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.

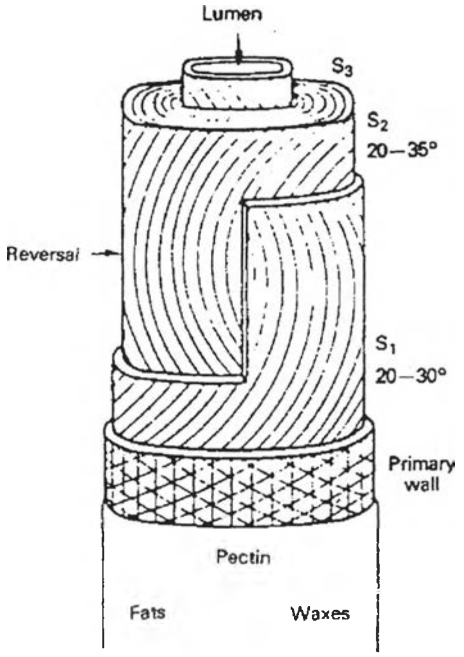


Figure 2.6 Idealised diagram of cotton morphology.[10]

The general state of knowledge of the chemical composition of a mature cotton fiber is presented in Table 2.1$^{(12)}$.

Table 2.1 Typical values for the composition of a mature dry cotton fiber[12]

	Composition of a fiber		
Constituent	Typical%	Low%	High%
Cellulose	94.0	88.0	96.0
Protein	1.3	1.1	1.9
Pectin substances	0.9	0.7	1.2
Wax	0.6	0.4	1.0
Mineral matters	1.2	0.7	1.6
Maleic, citric and other organic acids	0.8	0.5	1.0
Total sugars	0.3		

2.1.3 Degradation of cellulose

An industrially important feature of cellulosic fibers is chemical stability, enabling them to withstand degradation with its consequential loss of tensile strength under normal conditions of use. Even slight degradation during processing, however, may be accompanied by unacceptable loss of strength and other undesirable effects. The study of degradation, therefore, has important implications for satisfactory dyeing and finishing. Six different degradative agencies have been identified: acids, alkalis, oxidising agents, enzymes, heat and radiation$^{(10)}$. Under certain circumstances cellulose can also be degraded mechanically, but this is never a problem in industrial processing.

Ultimately the complete degradation of cellulose yields carbon dioxide and water. However, it is the early stages of partial degration that are important in the textile field. Only slight changes in composition may affect the physical properties of cellulose profoundly, sometimes even reducing it to powder. The water-insoluble products of the action of acids and oxidising agents are still frequently referred to by the traditional trivial names of 'hydrocellulose' and 'oxycellulose' respectively(10).

2.1.4 Cotton Properties

The properties of cotton are shown in Table 2.2(14)

Table 2.2 Properties of cotton[14]

Molecular Structure	Long chain of cellulose
Microscopic Features	
Length:	25 to 60 mm.
Width:	12 to 20 μm.
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^2.
Elongation:	4 to 13% elongation at break
Tenacity (g/den.):	3 to 5 (dry), 3.6 to 6 (wet)
Density (g/cm^3):	1.54 to 1.62
Moisture content:	8.50%
Resiliency:	Low
Toughness and stiffness:	High
Abrasion resistance:	Fair to good
Chemical Properties	
Sunlight and heat:	May be heated in the dry state to a temperature of 150°C 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
Acids and alkalis:	Highly resistant to alkalis. Strong mineral acids cause fiber damage readily and organic acids do a little damage.

Table 2-2 (continued)

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.
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
Transverse refraction:	1.534
Double refraction:	0.062
Electrical and Thermal Conductivity	Good heat conductor
Flamability Behaviour	Burns very readily and once ignited, a fabric will carry flame.

2.1.4.1 Appearance

Cotton is never truly white; all cotton samples have a soft creamy tint and various shades of brown due to it contains small quantities of fat and wax, pectin, proteins and natural colouring matter. The removal of these impurities is effected by appropriate methods of scouring, kier boiling and bleaching.

Cotton in its normal state is not lustrous. To obtain glazed and embossed effects by special chemical treatments or finishes, such as mercerization process or mechanical after treatment.(14)

2.1.4.2 Comfort

Cotton is very absorbent and it dries quickly, water vapor from the body is easily pass through the cloth for evaporation. This reason makes cotton an ideal fabric for the summertime, when an easy transpiration of body moisture makes a garment comfortable to wear.(14)

2.1.4.3 Maintenance

Though cotton is strong, it has very little elasticity and the fiber does not resist deformation so that cotton fabrics tend to crease easily. To overcome this problem, cotton may be treated with resins or other chemical finished. Unfinished cotton fabrics generally must be ironed after laundering. In addition to the hydrophilic nature of cotton results in water-borne stains by trapping the colorant in the fiber after water was evaporated.(14)

2.1.4.4 Chemical reactivity

The intermediate chain unit of cellulose contains three hydroxyl groups. It is generally accepted that the primary alcohol group at C_6 is usually much more reactive than the secondary groups at C_2 and C_3.(10) The overall relative reactivities of the three hydroxyl groups under heterogeneous conditions are determined by the combined effects of three factors: their inherent chemical reactivity, steric effects arising from the size of the entering group, and steric effects arising from the supramolecular structure of the cellulose. In most reactions the reactivity decreases in the order $C_6 \geq C_2 \geq C_3$. (10)

2.1.5 Impurities in Cellulosic Fibers

Most natural fibers are not pure cellulose but contain significant amounts of other materials. The analysis of various cotton and flax samples is summarised in Table 2.3. The pectins are polygalacturonic acids and their calcium, magnesium and iron salts, and the ash contains calcium, magnesium and potassium phosphates and carbonates. Not included in these figures is the vegetable debris produced by mechanical harvesting and ginning of the cotton. This includes cotton seed, leaf and clayx for cotton. The amount depends on the quality of the cotton fibers. Linters (short staple waste) used for medicinal cotton can contain up to 25% of this woody material.

Table 2.3 Impurities present in cellulosic fibers (% by weight)[10]

	Cotton			Flax	
	Average	American	Egyptian	Unretted	Retted
Cellulose	88.0-96.0	91.0	90.8	56.4	64.1
Hemicellulose				15.4	16.7
Pectins	0.7-1.2	0.53	0.68	2.5	1.8
Lignin				2.5	2.0
Proteins	1.1-1.9				
Wax	0.4-1.0	0.35	0.42	1.3	4.5
Ash	0.7-1.6	0.12	0.25		

To these natural impurities are added 10-15% of size, spin finish or knitting lubricant. The spin finishes and knitting lubricants contain surfactants and mineral oils applied alone or in admixture to decrease friction on machine parts. Sizes are film-forming materials used to coat the warp yarns of woven fabrics in order to minimise yarn breakage during fabric production. Starch, usually esterified or etherified, is the most common size but polyacrylates, cellulose ethers (e.g. carboxymethylcellulose), poly(vinyl alcohol) and poly(vinyl acetate) are also used. The source from which starch is obtained, e.g. corn or rice, can affect its ease of removal. Size plasticisers such as tallow or parafin wax are either added to the sizing liquor or applied, after the size has been dried onto the yarn, by kiss-roll coating.

Metallic ion contamiantion, particularly iron and copper, is of most concern during oxidative treatment as this can lead to chemical damage. This damage can manifest itself as very localised destruction of the fiber or reduced dye uptake. This form of contamination can result from the growing area where the plant absorbs the mineral matter through its roots or the wind simply blows the soil onto the fiber. It can also arise from washing off with contaminated water or heating with contaminated steam(10).

2.2 Bleaching

All natural fibers are coloured and the colouring matter confers a yellowish brown colour to the fibers. In the case of cotton, this is believed to be a condensation product of caffeic and quinic acids which is related to chlorogenic acid. The purpose of bleaching is to destroy this coloured material and to confer a pure white appearance to the fibers. Bleaching should also decolorise or remove any residual impurities left by scouring . The three chemicals used for bleaching are sodium hypochlorite, sodium chlorite and hydrogen peroxide. Bleaching is the linchpin of preparation and today really means bleaching with hydrogen peroxide(peroxide), since sodium hypochlorite (hypo) and sodium chlorite have both lost ground to peroxide.

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, batchwise or continuously).
3. A variety of activation routes is available.

It is well known that hydrogen peroxide can break down into water and oxygen (Scheme 2.3)(15).

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

Scheme 2.3[15]

For bleaching to occur this stability must be overcome by activation. Activators include alkalis, sulphuric acid, u.v. irradiation, hypochlorite, transition metals and O- and N-acyl compounds. The usual activator for textile bleaching is alkali, usually sodium hydroxide, and the peroxide molecule undergoes heterolytic fission to the perhydroxide ion, as shown in scheme 2.4(10).

$$H_2O_2 + OH^- \longrightarrow OOH^- + H_2O$$

Scheme 2.4[10]

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 colour 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(16,17) that peroxide bleaching takes place by such a mechanism (Scheme 2.5)(15).

Scheme 2.5[15]

Such free radicals might be produced by reaction of hydrogen peroxide with an electron donor, possibly derived from a metal cation or from a perhydroxyl anion. The reaction mechanism proposed in Scheme 2.6(15).

$$\begin{array}{llll}
 & \text{(a) } H_2O_2 & \longrightarrow & H^+ + HO_2^- \\
 & \text{(b) } H_2O_2 + M^{2+} & \longrightarrow & M^{3+} + HO^- + HO\bullet \\
\text{Or} & \text{(c) } H_2O_2 + HO_2^- & \longrightarrow & HO_2\bullet + HO\bullet + HO^- \\
 & \text{(d) } H_2O_2 + \bullet OH & \longrightarrow & HO_2\bullet + H_2O \\
 & \text{(e) } HO_2\bullet + M^{3+} & \longrightarrow & M^{2+} + O_2 + H^+
\end{array}$$

Scheme 2.6[15]

The free radicals are considered to induce decomposition through a chain mechanism. The decomposition within a given time interval is limited by the level of colour-bearing impurities or by inhibiting metal cations. The latter appear to protect the cellulose from chemical damage by minimising the production of molecular oxygen in the alkaline medium(15).

2.3 Choosing dyes of suitable substantivity

Coloration is a stepwise process that involves attraction of the dye from the liquid or print paste to the fiber surface, from where it diffuses into the fiber. Within the dye molecules move from one point of attachment to another. Unless they become chemically bonded to the fiber or converted to an insoluble pigment, this process continues for as long as the fibers remain in the dyebath. Both the speed with which the dye molecules move into the fiber and the ease with which they can move about (migrate) from site to site depend upon the strength of the attraction between dye and fiber. The substantivity of the dye is a measure of the strength of this attraction. Within any one class of dye are dyes with a range of substantivities, and this is of significance both in practical application and in the fastness to wet treatments of the end product.(18)

As a general rule of thumb, dyes with high substantivity have poor migration properties, since the strong interaction works against release of dye from the initial point of attachment. Such dyes are more difficult to distribute evenly-they are said to have poor levelling properties. But with high substantivity is associated the fastest exhaustion from the dyebath and the greatest resistance to washing off in clean water. Of course the converse is also true: dyes with lower substantivity exhaust more slowly, have better migration properties and are good levelling dyes.(18) The penalty in this case is poor wet fastness properties, since the weaker dye-fiber linkages allow easier reversal of the dyeing process.

Dyers are therefore obliged to strike a balance between these properties when fitting the choice of dyes to the intended use of the product. Dyeing methods are thus governed as much by application criteria for level dyeing as they are by the chemical nature of the dye and the fiber. Consequently the logical way to aid dye selection is by sorting dyes into groups according to their best method of application.

2.4 Reactive dyes for cellulose

During 1953 I D Rattee and W E Stephen discovered that dye molecules containing certain chemical groups (reactive groups) could react chemically with cellulose under alkaline conditions. Thus for the first time it became possible to make a dye react with the fiber and become part of it, rather than remaining as an independent chemical entity within the fiber.

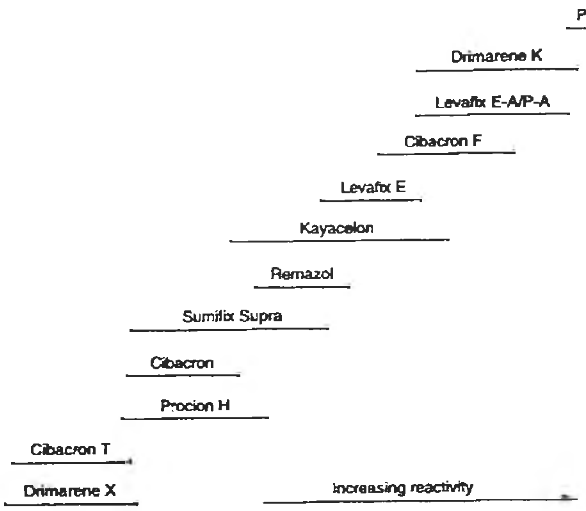


Figure 2.7 Relative reactivities of reactive dyes for cellulose fibers [18]

Rattee and Stephen's discovery was followed by the introduction of the Procion range of dyes by ICI, which illustrated the technical possibilities of producing bright shades of high fastness through a variety of application methods. Since then many similar dyes have become available. The current ranges of reactive dyes include many that have a broad spread in their level of reactivity and substantivity. Some examples are shown in Figure 2.7, in which their respective levels of reactivity are compared. Since their introduction of these dyes have played a dominant role in the dyeing of cellulosic fibers and, at the time of writing, their usage is still growing (Table 2.4).

Table 2.4 World consumption of dyes for cellulosic fibers by dye class[18]

Dye class	Consumption (tonne x 10^3/year)		
	1973	1979	1988
Direct	75	74	74
Vat	55	57	48
Sulphur	108	100	90
Azoic	29	29	26
Reactive	23	42	60
Total	290	301	300

Many reactive dyes possess a resistance to daylight previously only associated with vat dyes, and this is reflected in their use for top-quality curtains, furnishings and awnings. They also contribute to the colour quality of many domestic goods that require frequent washings, such as towellings, and are used extensively for shirtings, tapes, ribbons, dress goods and knitted sportswear; the last-named accounts for around 40% of the reactive dye market.

2.4.1 Selection of reactive dyes

Very many reactive dyes are now commercially available, with a variety of reactive groups. Their simplicity of application and broad spread of reactivity and substantivity makes them very versatile in application. But, as with other classes of dye, the quality of their dyeings depends upon careful dye selection. Appropriate levels of reactivity, substantivity and rate of diffusion are needed for the method of application best suited to the goods in hand. Indeed the dyeing of reactive dyes may be described quantitatively in these terms, but usually a simpler empirical representation is more appropriate on the shop floor.

The two essential stages in the application of reactive dyes are (a) diffusion of dye into the cellulose fiber, and (b) reaction between the dye and cellulose. The former is controlled by varying the dyeing time, the dyebath temperature and the salt concentration, and the latter is achieved by the selection of an appropriate alkalinity (pH).

2.4.2 Substantivity of reactive dyes

The low substantivity of the reactive dye molecules before fixation by alkali permits very easy levelling, but once they react with the fiber they cannot migrate further and they become resistant to normal domestic washing treatments. Inevitably, once alkali is added to the dyebath, reaction of the dye with cellulose begins. At the same time, however, the dye begins to react with water (hydrolysis), and the hydrolysed dye becomes a nuisance. It retains its substantivity but not its reactivity, and needs to be removed in the final washing-off. This situation is usually expressed in terms of the 'efficiency' of a dye or dyeing process, which is represented as a ratio of the amount of dye chemically combined ('fixed') to the amount of dye applied. This efficiency can never reach unity, because the presence of hydrolysed dye cannot be avoided even if the conditions could be adjusted to give 100% take-up (exhaustion) from the dyebath.

A wider range of substantivity levels is feasible for reactive dyes; these have been classified as shown in Table 2.5(10). Many reactive dyes of commercial interest have substantivity factors within the range 40-80%. It could be argued that values above about 80% are too high, since such dyes tend to strike rapidly, migrate with difficulty and wash-off slowly. The most successful dyes for exhaust methods often belong to the 60-80% category. Dyes with substantivity values less than 40% are more suitable for padding methods; in exhaust dyeing, especially at long liquor ratios, they give poor yields and reproducibility problems.

Table 2.5 Classification of reactive dyes by substantivity

Substantivity factor (%)	Category
> 80	Very high substantivity
60-80	High substantivity
40-60	Medium substantivity
< 40	Low substantivity

2.4.3 Dyeing temperature and reactivity

The decreased substantivity caused by raising the dyeing temperature aids both levelling before the addition and washing-off the unfixed dye at the end of the process. A great deal also depends upon the reactivity of the dye, however.

There are two groups of reactive dyes, differing in their level of reactivity. The first includes highly reactive dyes that can be applied efficiently at temperatures as low as room temperature; these are referred to as cold-dyeing reactive dyes. Dyes of the second group are approximately 1500 times less reactive and require temperatures of 80-100 °C for fixation; they are hot-dyeing reactive dyes(18).

The reactivity of a particular dye can be increased further by (a) increasing the alkalinity of the dyebath (i.e. increasing the pH value), and (b) raising the temperature. Higher temperature increases the reactivity of the dye, which itself carries a danger of unlevel dyeing; this in turn requires further control of reactivity through a reduction in the pH of the dyebath. Thus substantivity and reactivity are manipulated together to control the quality of dyeings.

2.4.4 Effect of salt concentration

In a neutral solution reactive dyes are anionic in character (like direct or acid dyes), but their substantivity is low. This lower level of substantivity that confers the excellent levelling properties on reactive dyes. Compensation is made for this in batchwise dyeing by using much higher salt concentrations than are used with other dyes for cellulosic fibers. The lowered substantivity persists until the reaction between dye and fiber is initiated by the addition of alkali to the dyebath. Once fixation has taken place, however, mistakes cannot be rectified(18).

2.4.5 Structure of Reactive Dyes

Reactive dyes are colored compounds which contain one or two groups capable of forming covalent bonds between a carbon or phosphorus atom of the dye ion or molecule and an oxygen, nitrogen or sulfur atom of a hydroxy, an amino or a mercapto group, respectively, of the substrate. Such covalent bonds are formed with the hydroxyl groups of cellulosic fibers, with the amino, hydroxyl and mercapto groups of protein fibers and with the amino groups of polyamides(19).

In general reactive dyes for cellulosic materials have certain characteristic structural features, represented diagrammatically in Figure 2.8(15)

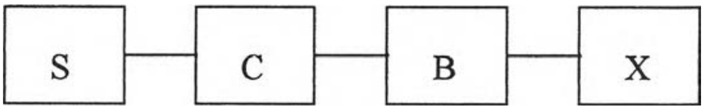


Figure 2.8 Characteristic structural features of a reactive dye[15]

S is the solubilising groups, usually sulphonic acid substituents attached to the chromophoric grouping.

C is the chromophoric grouping, contributing the colour and much of the substantivity for cellulose.

B is the bridging group that links the reactive system to the chromophore.

X is the reactive group, enabling the dye to react with the hydroxy groups in cellulose.

2.4.6 Advantage of reactive dyes

The production of reactive dyes of commercial interest numerous factors other than the chemistry of such reactions have to be taken into account. Some of the most important are the following(10)

(1) Economy - any reactive system selected as the basis of a range of dyes must enable them to be produced at acceptable cost.

(2) Availability – the system selected must be free from patent restrictions, health hazards or other limitations to exploitation.

(3) Facility – it must be possible to attach the reactive system to the dye chromophoric groupings readily in manufacture.

(4) Storage stability – the dye containing the reactive groups must be stable to storage under ambient conditions.

(5) Efficiency – the yield in manufacture of the reactive dye must be efficient and the dye fixation must be high under conventional conditions of application.

(6) Bond stability – the dye-fiber bond must be reasonable stable under severe conditions of washing and durable finishing.

2.4.7 Classification of Reactive dyes

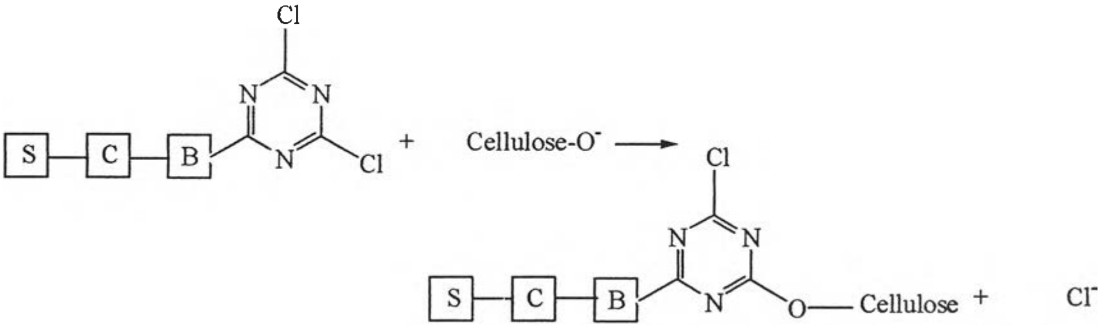
2.4.7.1 Dyes which react under acidic conditions

The structures of many of these dyes were based on the versatile intermediate 3-aminophenylphosphonic acid attached to typical monoazo chromogens in various ways. These dyes were usual in being applied to cellulosic fibers under mildly acidic conditions (pH 5-6)(20). A catalyst is required in order to fix a dye molecule to the fiber. Later, the phosphonic acid dyes were withdrawn from the market due to their disadvantages in terms of lack of versatile application and cause of fiber damage.

2.4.7.2 Dyes which react under alkali conditions.

The reactive systems which react under alkali conditions are mainly divided into two catagories:

- 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 (Scheme 2.7)(15). Amongst the principal reactive systems of this type are the halogeno-substituted triazine, pyrimidine, pyrazine, quinoxaline, thiazole and pyridazone groups.



Scheme 2.7 The nucleophilic substitution reaction[15]

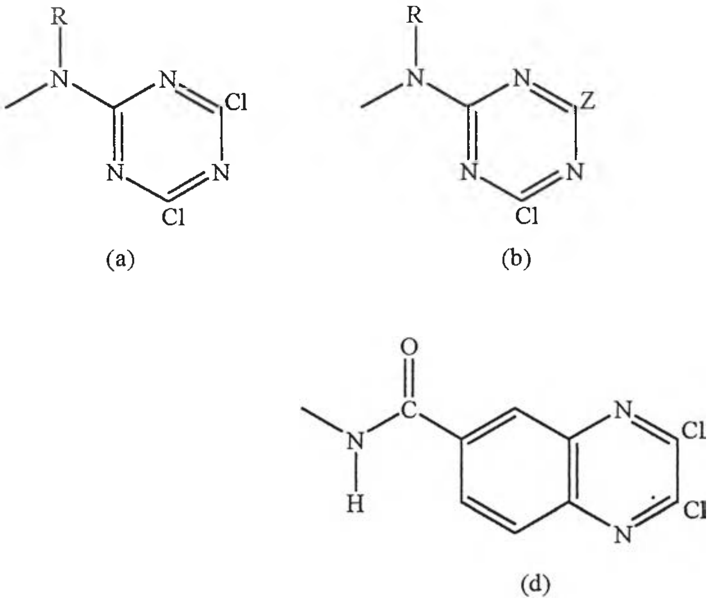


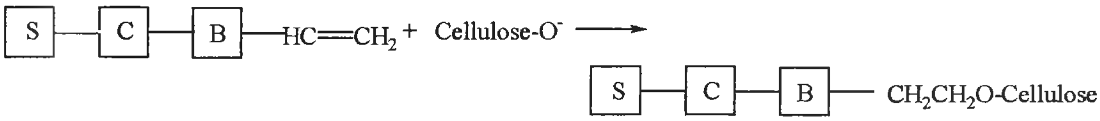
Figure 2.9 Important representatives of these reactive groups:[21]

(a), (b) di- or mono-chlorotriazines

(c) 2,4,5-trihalogenopyrimidine

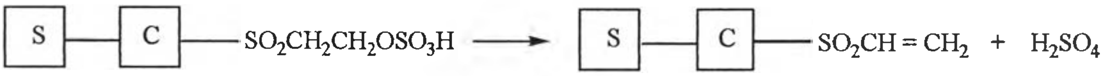
(d) 2,3-dichloroquinoxaline

- Those that react by the addition of a nucleophilic group to a carbon-carbon double bond of the reactive system (Scheme2.8)$^{(15)}$.



Scheme 2.8 The nucleophilic addition reaction[15]

In most instances the unsaturated reactive group is not present in the dye as supplied but is form 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 (Scheme2.9)$^{(15)}$.



Scheme 2.9[15]

The following are important representatives of this system(Figure 2.10)(19):

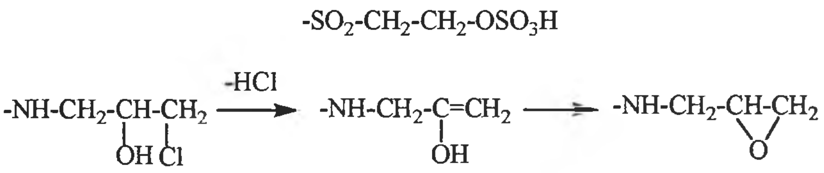


Figure 2.10[19]

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(19). 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(19) in Figure 2.11 and the rate of diffusion of the dye.

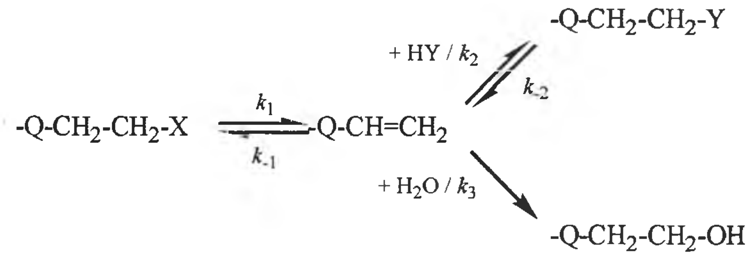


Figure 2.11 The specific base catalyzed addition of the nucleophilic functional group HY of the textile fiber[19]

2.4.8 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 ($Cell\text{-}O^-$) as the nucleophilic 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(22).

The efficiency of fixation is a function of(10):

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. More, high electrolyte concentrations in dye bath discharges may increases salinity or acidity in rivers and destroy delicate balance of waterways.

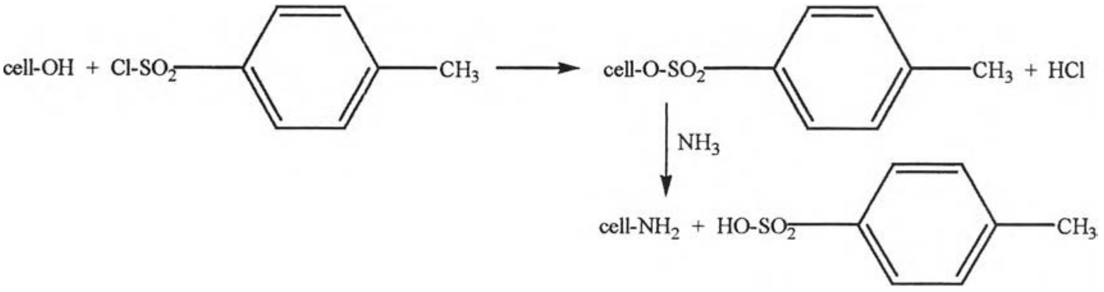
An increase of dyeing temperature lowers the substantivity ratio and accelerates the rate of hydrolysis of the dye; both of these effects reduce the fixation efficiency. An increase in electrolyte concentration always enhances substantivity without impairing reactivity providing the dye remains completely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

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. Furthermore, high risk of uneven dyeing as well as dye aggregation can be obtained.

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

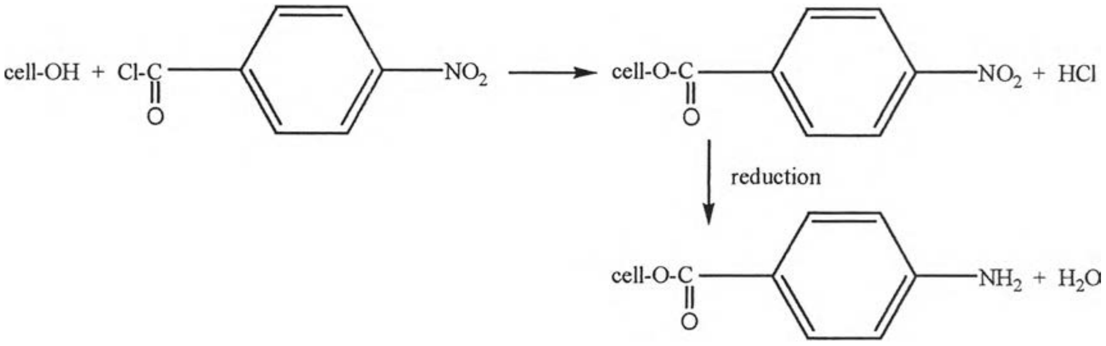
The main problem involving in reactive dyeing is a poor dye fixation on the fiber resulted in many efforts to develop natural and synthetic fibers with enhanced coloration properties. These developments often require chemical modification, applicable during the fiber production stage, prior to dyeing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

The attempts to modify cotton fibers to enhance their dyeability were previously proposed by Karrer and Wehrli 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 2.10(23) 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.



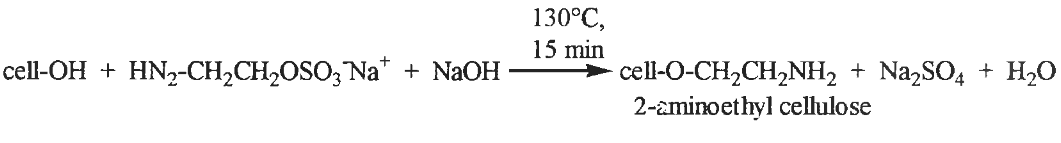
Scheme 2.10[23]

Another route to aminated cotton mentioned by Karrer and Wehrli is the reaction of cotton with p-nitrobenzoyl chloride followed by reduction of the group (Scheme 2.11)(23).



Scheme 2.11[23]

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 2.12)(24). 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 dyeability with most cotton dyes.

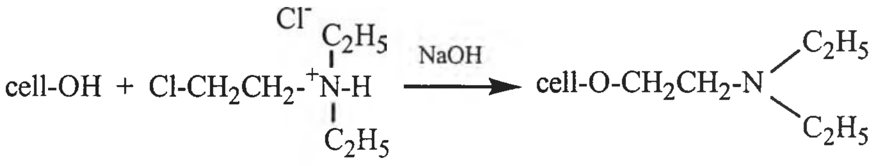


$$\text{cell-OH} + \text{HN}_2\text{-CH}_2\text{CH}_2\text{OSO}_3^-\text{Na}^+ + \text{NaOH} \xrightarrow{\substack{130^\circ\text{C,}\\ 15\ \text{min}}} \underset{\text{2-aminoethyl cellulose}}{\text{cell-O-CH}_2\text{CH}_2\text{NH}_2} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$

Scheme 2.12[24]

Herlinger et al. suggested a new two-stage dry fixation process for the production of aminoethylated cellulose with 2-aminoethylsulphuric acid(23). 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.

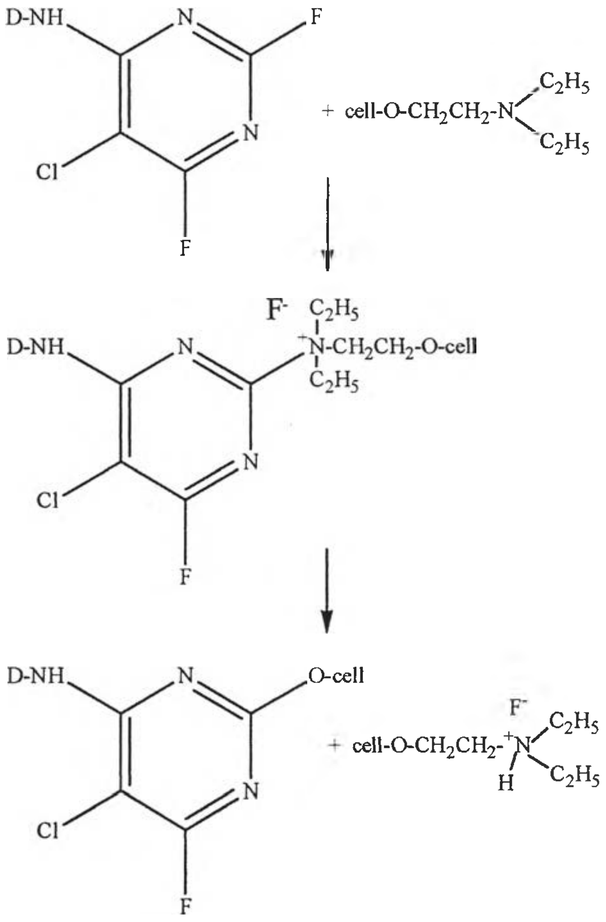
Soignet et al. found that the tertiary amino groups contained in diethylaminoethylcellulose (DEAE cellulose) acted as a 'built in' catalyst to increase the reactivity of epoxides and effectively quaternised the fiber(25). Tertiary amino groups have been incorporated into cellulose by reaction of cotton by reaction of cotton with β-chloroethyldiethylamine hydrochloride according to the Hartmann process, producing DEAE cellulose(26) (Scheme 2.13).



$$\text{cell-OH} + \text{Cl-CH}_2\text{CH}_2\text{-}{}^{+}\underset{\displaystyle C_2H_5}{\overset{\displaystyle Cl^- \; C_2H_5}{N}}\text{-H} \xrightarrow{\text{NaOH}} \text{cell-O-CH}_2\text{CH}_2\text{-N}(C_2H_5)_2$$

Scheme 2.13[26]

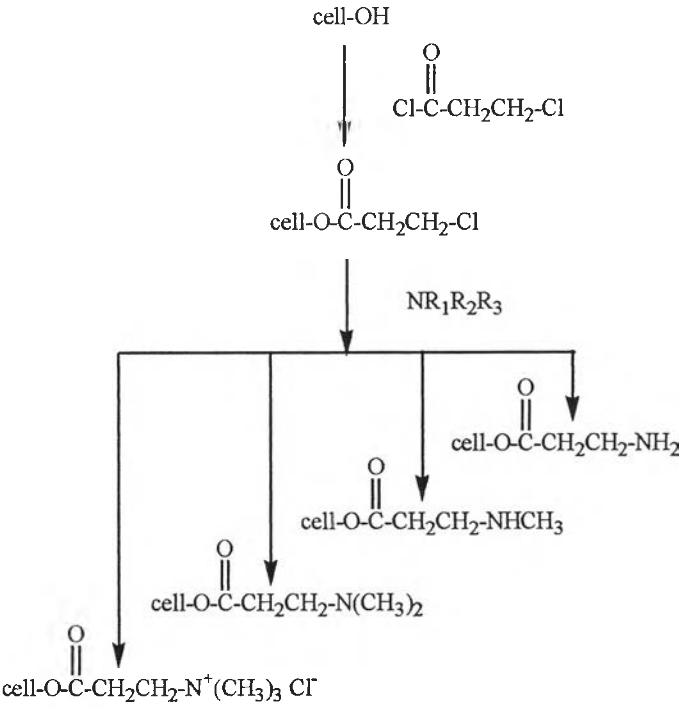
The DEAE cotton could be dyed, in the absence of salt, with direct, reactive,and acid dyes. Covalent fixation of a Drimarene K reactive dye occurred under neutral and slightly acidic dyebath conditions. EL-Alfy et al. explained this by proposing that the tertiaty amino groups of the DEAE cotton were behaving as a'built-in catalyst' (Scheme 2.14, where D is the dye chromophore)(26).



Scheme 2.14[26]

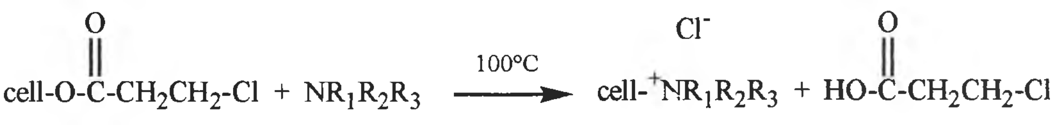
Tsuji and colleagues acetylated cotton and showed improved uptake of direct dye without adversely affecting fastness to laundering(27). Enhanced dyeability of the acetylated cotton was presumably due to changes in the cellulose's crystalline structure and hence dye accesibility within the fiber.

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(28). It was intially assumed that the reactions would take the course of Scheme 2.15, where R_1, R_2, R_3 = H or CH_3



Scheme 2.15[28]

Dyeing was carried out with reactive dyes under neutral to slightly acidic conditions in the absence of salt(23). The results show that the aminated cotton containing secondaty amino residues (treatment with methylamine) gave the highest color yields. But alkali washing showed the propionate stability to be poor. However, this problem was overcome as it was discovered that a more severe amination step (amine treatment at 100°C) did not produce modified cotton containing an ester linkage. Instead, bonds of the type Cell-$N^+R_1R_2R_3$ were obtained (Scheme 2.16), which gave reactive dyeings of excellent alkali stability.



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

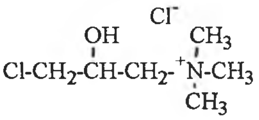
Scheme 2.16[23]

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 (29) (Figure 2.12).

Type 1 was the chlorohyddrin precursor to glycidyltrimethylammonium chloride

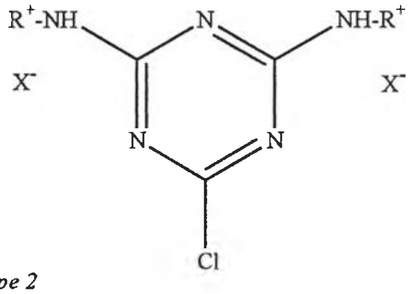
Type 2 compounds were monochloro-s-triazines containing bis-quaternary amines

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

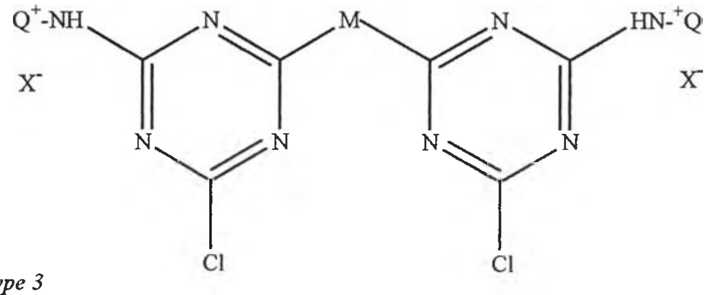


$$Cl\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}CH_2\text{-}{}^{+}\underset{CH_3}{\overset{CH_3}{N}}\text{-}CH_3 \quad Cl^-$$

Type 1



Type 2

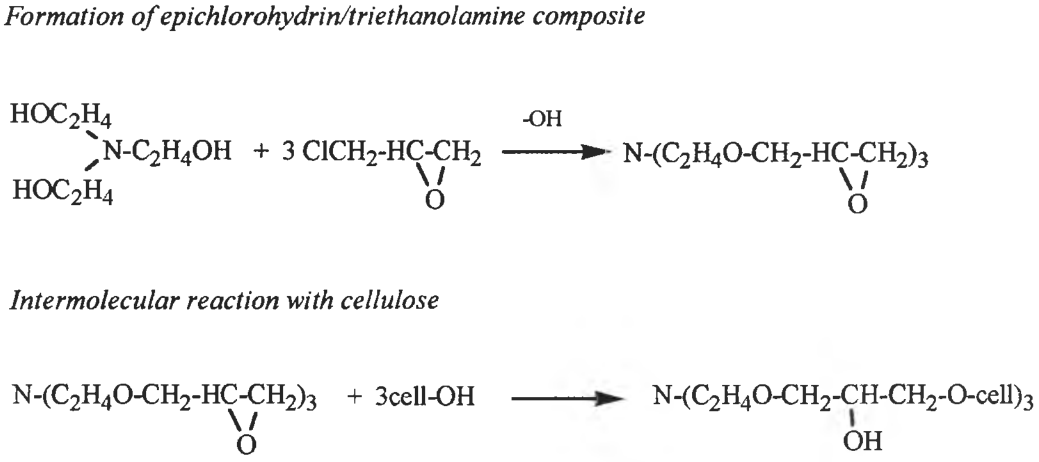


Type 3

Figure 2.12[29]

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(30). The treated cotton showed considerable crease recovery, suggesting the reaction to be intermolecular crosslinking (Scheme 2.17)(30). 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(30).



Formation of epichlorohydrin/triethanolamine composite

$$\begin{matrix}HOC_2H_4\\ \quad\searrow\\ \quad\nearrow\\ HOC_2H_4\end{matrix} N\text{-}C_2H_4OH + 3\,ClCH_2\text{-}\underset{\setminus/\atop O}{HC\text{-}CH_2} \xrightarrow{-OH} N\text{-}(C_2H_4O\text{-}CH_2\text{-}\underset{\setminus/\atop O}{HC\text{-}CH_2})_3$$

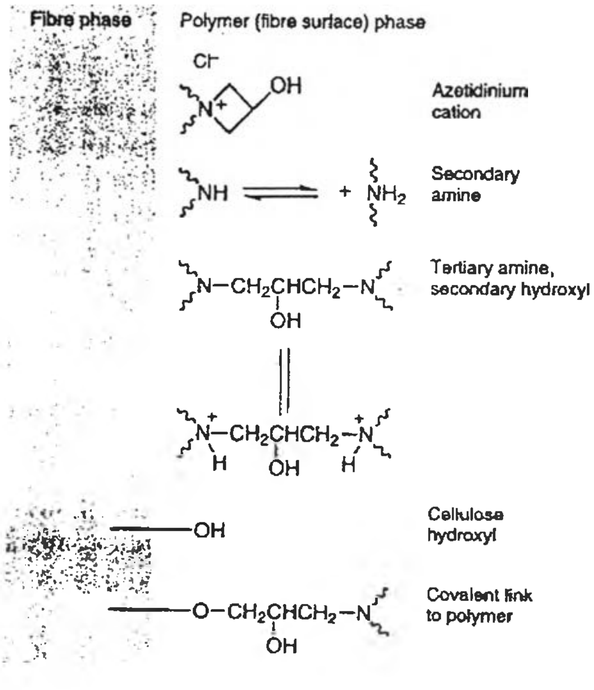
Intermolecular reaction with cellulose

$$N\text{-}(C_2H_4O\text{-}CH_2\text{-}\underset{\setminus/\atop O}{HC\text{-}CH_2})_3 + 3cell\text{-}OH \longrightarrow N\text{-}(C_2H_4O\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}O\text{-}cell)_3$$

Scheme 2.17[30]

The Sandene process was developed by Courtaulds and Clariant(23) 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(31). 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.

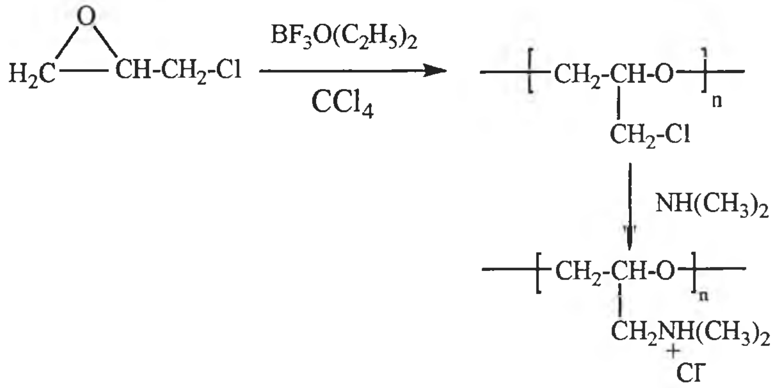
Hercosett 125 (Hercules) is a cationic, reactive polymer prepared by a condensation reaction of adipic acid and diethylenetriamine, followed by partial crosslinking of the polyamide with epichlorohydrin(23). Burkinshaw et al. applied Hercosett 125 to cotton by a pad-dry-cure(32). Scheme 2.18 represents the reactive and nucleophilic sites that mayexist on the surface of the polyamide-epichlorohydrin treated cellulose.



Scheme 2.18[32]

The pretreated polyamide-epichlorohydrin cotton could be dyed from neutral dyebaths, in the absence of salt, to give high exhaustion.

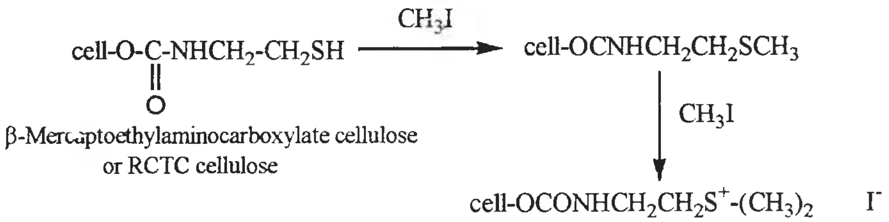
Wu and Chen applied polyepichlorohydrin-dimethylamine to cotton to improve its dyeability with direacts and reactives by polymerization of epichlorohydrin with a ring-opening mechanism in carbon tetrachloride with a boron trifluoride etherate catalyst to produce polyepichlorohydrin (PECH)(33-35). The amine derivative was achieved by adding dimethylamine to PECH at 95°C (Scheme 2.19).



Scheme 2.19[33]

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(36). The cotton was treated with bis-β-isocyanatoethyl-disulphide in dimethylformamide at 80°C followed by reductionwith 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 from the sulphonium salts (Scheme 2.20).



Scheme 2.20[36]

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(36).

Vigo and Blanchard immersed soda cellulose in an arylsulphonium salt solution(37). 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.

2.5 Concept of the Modification and Bleaching of Cotton Fabric in Single-bath Process

Firstly, scoured cotton fabric was treated with modifying agent that be synthesized in our laboratory. The consequent pretreatment was continued in the same bath with hydrogen peroxide and sodium hydroxide to finally obtain modified, bleached cotton fabric. Advantageously when compared to previous methods, the application of this modifying method is time and cost saving as a result of mininizing water and energy consumption as well as reducing waste volume. Therefore, it should be claimed that this process is environmentally friendly since salts which are considered as pollutant could be eliminated from cellulosic dyeing process and then recycling of discharged water is practicable. The modifying agent used in this experiment is a cationic reactive compound. The synthesis result will be followed as shown in reaction Figure 2.13.

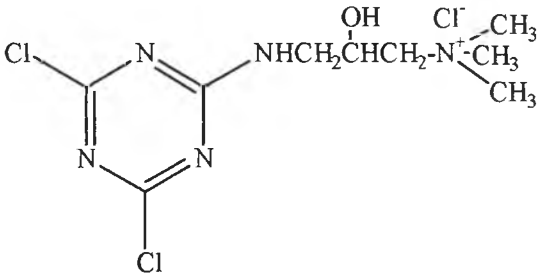
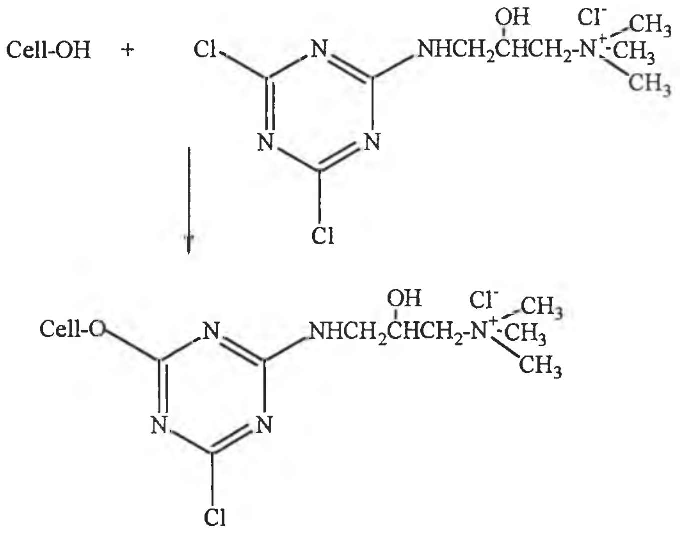


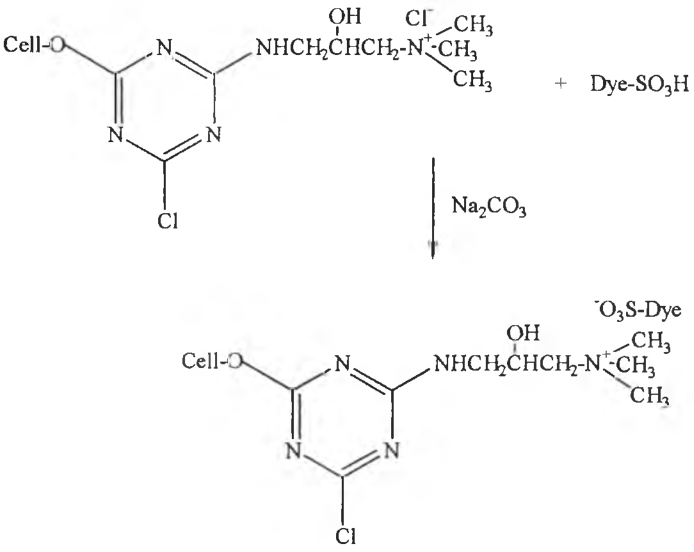
Figure 2.13

The modifying agent obtained will be applied to cellulosic fabrics during bleaching process. The reaction between cellulose hydroxyl group and the modifying agent could be written as shown in scheme 2.21.



Scheme 2.21

It is believe that this type of modifying agent could be readily self-absorbed into cotton fiber due to it contain the quaternary ammonium group which plays an important role in promoting dye adsorption that without the requirement of salts, as shown in Scheme 2.21.



Scheme 2.22

The fixation of this compound to cellulose usually can be achieved by either alkali assisted covalent bonding. In bleaching step, hydrogen peroxide was used to remove impurities consequently 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. 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 dyeing properties including color strength, the degree of dye fixation and color fastness to light will be evaluated and the compare to those obtained from the conventional dyeing of unmodified cotton fabric in the presence of salt.