

CHAPTER II

Literature Survey

2.1 Cotton fiber

Cotton is the most versatile and the most widely used textile fiber. It is usually a creamy off-white color although there are some varieties 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 objectionable 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 cotton fiber forms a flat ribbon. It is highly convoluted, the number of convolutions varies between four and six millimeter, reversing in direction every millimeter or so along the fiber. These characteristics make cotton easy to recognise under both optical and electron microscopes that are illustrated in Figures 2.1 and 2.2⁽²⁾, respectively. Their bean-shaped is described as a bilateral structure in Figure 2.3⁽²⁾.

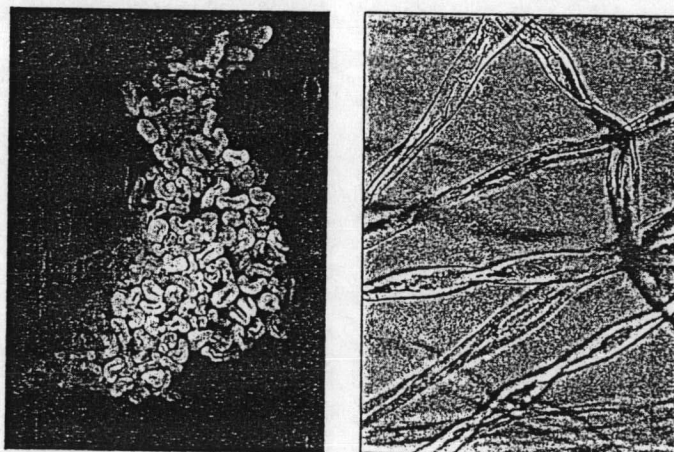


Figure 2.1_ Optical micrographs of raw cotton fibers.[2]

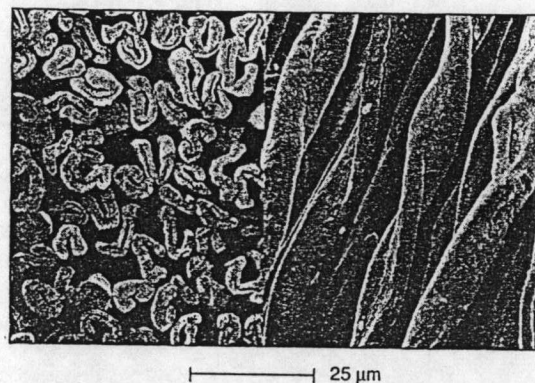


Figure 2.2 Scanning electron micrographs of raw cotton fibers.[2]

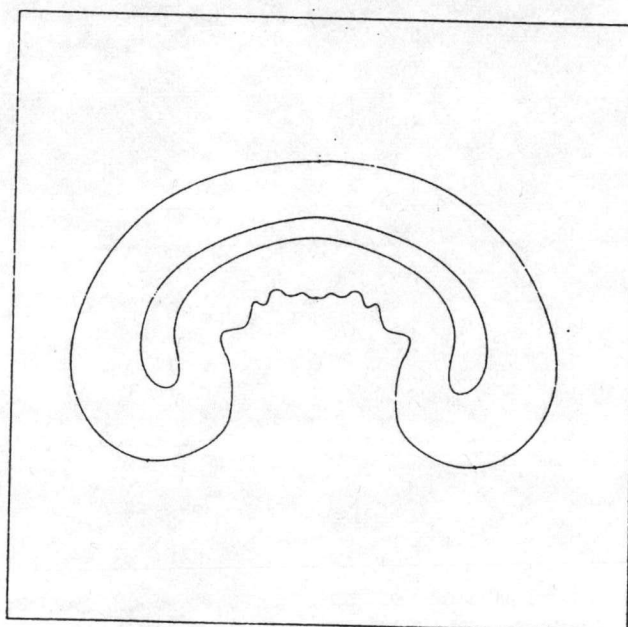


Figure 2.3 Bilateral structure of mature cotton.[2]

2.2 Fiber Composition

2.2.1 Macrostructure

The cotton fibers have a fibrillar structure. Their morphology, illustrated in Figure 2.4⁽²⁾, exhibits three main features : primary wall, secondary wall and lumen.

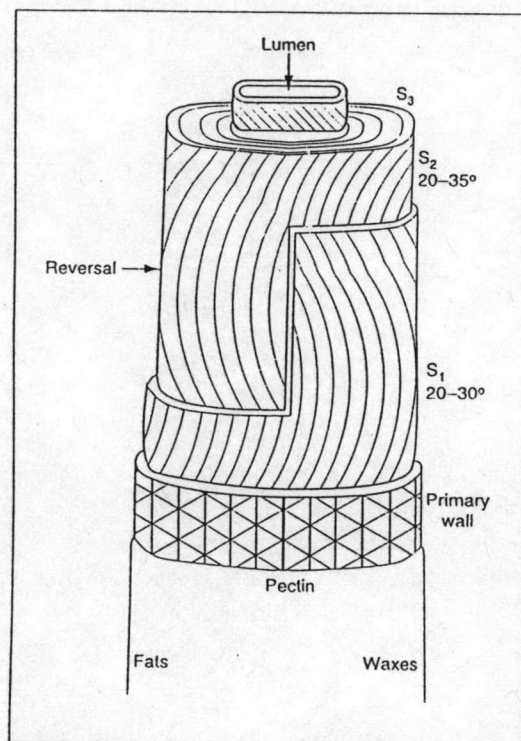


Figure 2.4_ Idealised diagram of cotton morphology.[2]

The primary wall 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 secondary wall constitutes the bulk of the mature fiber and consists almost entirely of fibrils of cellulose arranged spirally around the fiber axis but they are not packed as tightly as in the primary wall.

The lumen or cavity is the remainder of the central canal from which these layers are produced and contains residual protein, mineral salts and the natural coloring matter of the fiber. They were laid down in the secondary wall while the fiber was growing.

Table 2.1⁽¹⁾ gives comparative data for a typical cotton. The other substances are mostly water-soluble organic acids and sugars.

Table 2.1 Composition of cotton fibers.[1]

Constituent	Proportion of dry weight/%	
	Whole fibre	Primary wall
Cellulose	94.0	54.0
Protein (%N × 6.25)	1.3	14.0
Pectin	1.2	9.0
Wax	0.6	8.0
Ash	1.2	3.0
Other substances	1.7	12.0

2.2.2 Molecular Structure.

Cotton fiber in its raw state is composed of about 94% cellulose⁽¹⁰⁾ and a small amount of wax as indicated in Table 2.1. The chemical structure of cellulose may be most conveniently described as a 1,4- β -D-glucan, i.e., a condensation polymer of β -D-glucopyranose with 1,4-glucosidic linkages. Its molecule is composed of a large number of repeating units of anhydroglucose as shown in Figure 2.5⁽⁸⁾. The degree of polymerisation (DP) of cellulose may be as high as 3,000-5,000.⁽²⁾ The essential features of the polymer chain are the main sequence of the intermediate unit (I), the non-reducing end group (II), the reducing end group (III) and glucosidic linkages as shown in Figure 2.6⁽²⁾. The intermediate unit possesses one primary and two secondary alcohol groups each. The non-reducing end group possesses one extra secondary alcohol group at C₄, and the reducing end group is a cyclic hemiacetal that exhibits the characteristics of alcohol and aldehyde under appropriate conditions (scheme 2.1)⁽²⁾

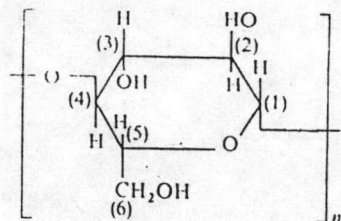


Figure 2.5 Anhydroglucose repeating units.[8]

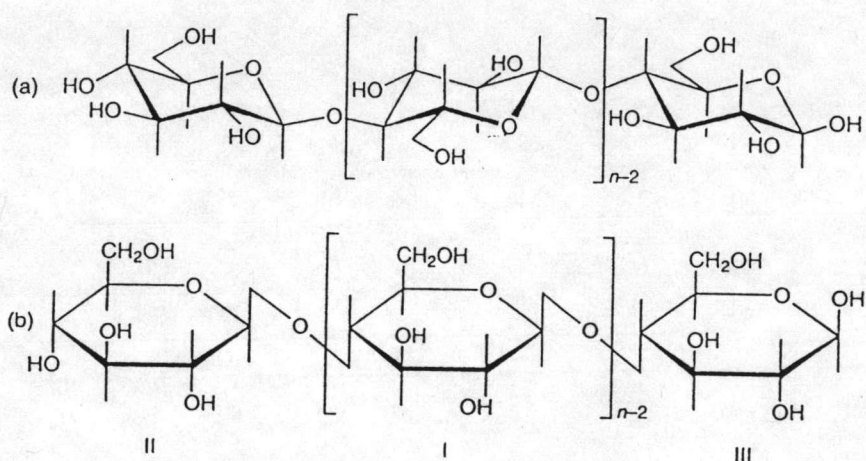
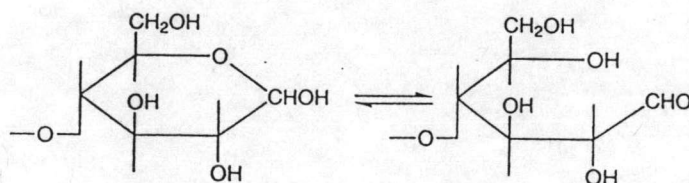


Figure 2.6 Cellulose (a) fully extended conformational formula (flat ribbon).

(b) the Haworth projection formula.[2]

n = degree of polymerisation (DP)



Scheme 2.1 Characteristics of alcohol and aldehyde of a cyclic hemiacetal of the reducing end group in cellulose chain.[2]

2.2.3 Supramolecular Structure.

Naturally, the polymeric cellulose chains of cotton are fully extended to form of flat ribbons. The flat ribbons just described pack together into a monoclinic unit cell of dimensions approximately $a = 0.82$, $b = 0.79$, $c = 1.034$ nm (fiber axis) and $\gamma = 97^\circ$ ⁽²⁾. A cross-section of the cell in the ab plane, looking along the fiber axis, is shown in Figure 2.7(a)⁽²⁾. The center and corner chains were parallel to one another in the ac plane (Figure 2.7(b)⁽²⁾). Adjacent chains are held together by extensive hydrogen bonding between hydroxyl groups as shown in Figure 2.8⁽²⁾. These areas are called crystalline regions (approximately 85-95%)⁽²⁾, these regions are not enough space between neighboring cellulose. Consequently, the crystalline regions are not penetrated by such molecules.

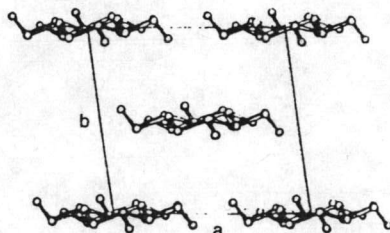


Figure 2.7 (a) Cross-section of unit cell projection in the ab plane.[2]

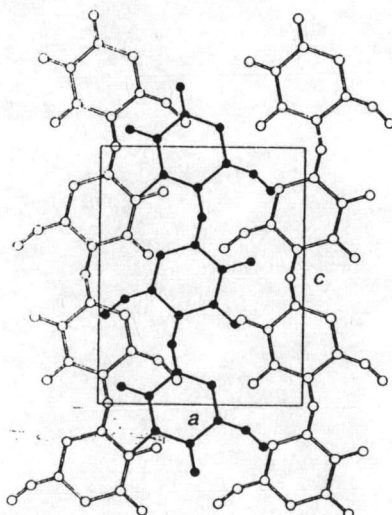


Figure 2.7(b) Unit cell projection in the ac plane.[2]

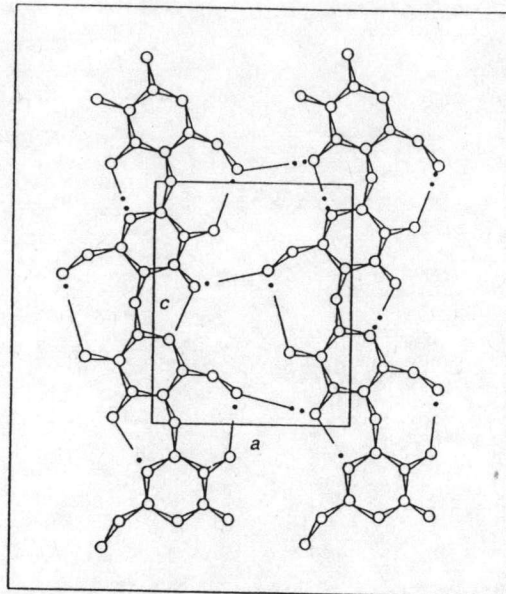


Figure 2.8 Hydrogen bonding in cellulose.[2]

In the case of cotton fiber the idea of fringed micelles, in which crystalline micelles are embedded in an amorphous matrix with individual chain molecules extending through several crystalline and amorphous regions, as shown in Figure 2.9⁽²⁾. The less ordered areas in amorphous regions, there will be more space between chains and the forces holding neighboring chains together will be weaker than those existing in the crystalline regions. Hence, this area can readily allow water, chemical molecules or dyestuffs to penetrate them.

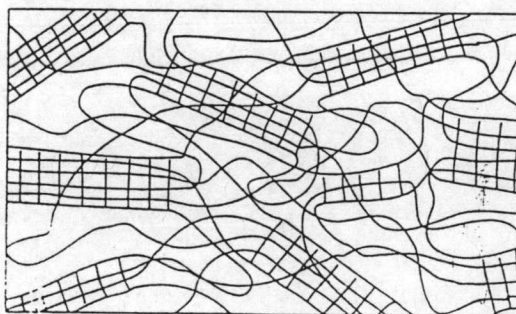


Figure 2.9 Fine structure in cellulose: fringed micelles.[2]

2.3 Cotton Properties

The properties of cotton are shown in Table 2.2

Table 2.2 Properties of cotton

Molecular Structure	Long chain of cellulose
Microscopic Features	
Length:	25 to 60 mm. ⁽¹⁴⁾
Width:	12 to 20 μm . ⁽¹¹⁾
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 . ⁽¹³⁾
Elongation:	4 to 13% ⁽¹³⁾ elongation at break
Tenacity (g/den.):	3 to 5 (dry), 3.6 to 6 (wet) ⁽¹³⁾
Density (g/cm ³):	1.54 to 1.62 ⁽¹³⁾
Moisture content:	8.5% ⁽¹⁵⁾
Resiliency:	Low ⁽⁹⁾
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 ⁽¹²⁾ without undergoing decomposition but can be damaged by excessive light

Table 2.2 (continued)

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.
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. ⁽⁶⁾
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 ⁽¹³⁾
Transverse refraction :	1.534 ⁽¹³⁾
Double refraction:	0.062 ⁽¹³⁾
Electrical and thermal Conductivity	Good heat conductor
Flamability Behaviour	Burns very readily and once ignited, a fabric will carry flame.

2.3.1 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 mercerisation process or mechanical after treatment.

2.3.2 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.

2.3.3 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.

2.3.4 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 .⁽¹⁷⁾ 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 $C_6 \geq C_2 \geq C_3$.⁽¹⁷⁾

Cellulose can be esterized with most inorganic and organic acids to give many of the products, but the most important has been the acetates and nitrates via acetylation and nitration, respectively and to obtain sodium cellulose xanthate for the manufacturing of regenerated fibers.

Furthermore, cellulose ethers may be prepared via etherification such as methyl cellulose, carboxymethyl cellulose and hydroxyethyl cellulose.

2.4 Dyeing of cotton fiber with reactive dyes

All of the dyes currently employed for dyeing cotton cellulose, reactive dyes show the greatest growth potential. High consumption of reactive dyes due to some of their value dominance such as brilliant colors, good wetfastness property and wide shade gamut. Generally, reactive dyes for cellulosic fibers have certain characteristic structure features, represented in Figure 2.10⁽¹⁾.



S = Solubilising group

C = Chromophore

B = Bridging group

X = Reactive group with actively leaving group

Figure 2.10 Characteristic structures of reactive dyes.[1]

These dyes can be classified into two types :

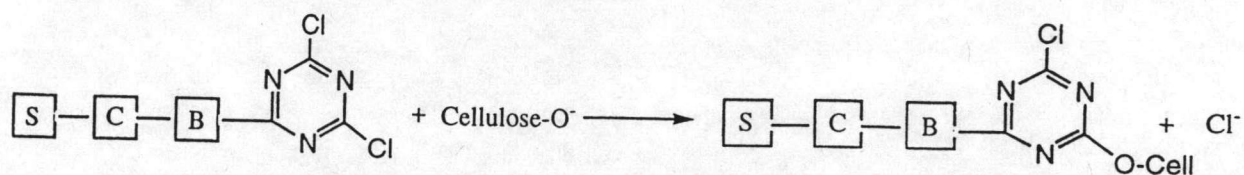
2.4.1 Dyes which react under acidic conditions.

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).⁽⁷⁾ 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 inversatile application and cause of fiber damage.

2.4.2 Dyes which react under alkali conditions.

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

- Those reacted by a nucleophilic substitution.



Scheme 2.2 The nucleophilic substitution reaction between dichlorotriazinyl dye and ionised cellulose.[1]

- Those reacted by a nucleophilic addition.



Scheme 2.3 The reaction between vinylsulphone dye and ionised cellulose.[1]

2.5 Reactive systems of dyes reacted by nucleophilic substitution

The reactive system of this type is based on a heterocyclic ring containing carbon and nitrogen atoms. The most widely used reactive groups based on a heterocyclic ring are as follows :

2.5.1 Reactive groups based upon triazines

2.5.1.1 Dichloro-s-triazinyl dye

In comparison with the diazines, the dichloro-s-triazinyl systems have the inductive effects of the "extra" nitrogens lead to an even greater susceptibility to nucleophilic attack. Leaving groups (chlorine atoms) at the C_2 , C_4 or C_6 positions⁽¹⁸⁾ of triazine ring can be displaced by nucleophiles, with the negative charge of the intermediate delocalised over all nitrogen atoms. The dichlorotriazinyl systems are shown in Figure 2.11.⁽²⁰⁾

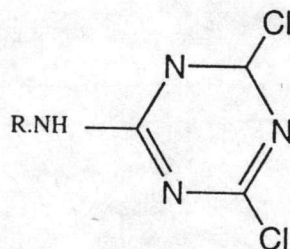
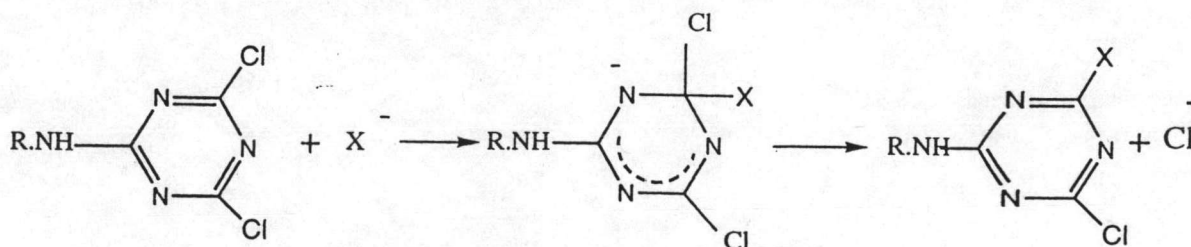


Figure 2.11 Dichloro-s-triazinyl systems.[20]

So that nucleophilic attack can take place in the manner indicated in Figure 2.12⁽⁴⁾, in which X^- represents a nucleophile such as OH^- or, ionised cellulose ($Cell-O^-$). The electronic influences present in the system make it more susceptible to nucleophilic attack.



Scheme 2.4 Nucleophilic attack in the dichloro-s-triazinyl systems.⁽⁴⁾

The dichloro-s-triazinyl dyes are highly reactive and can be applied to cellulosic fibers at temperatures in the range of 30-40°C.⁽³⁾

2.5.1.2 Monochloro-s-triazinyl dye

Replacement of one of the halogen atom (chlorine atom) by other substituents gives monochloro-s-triazinyl dyes and affects the reactivity of the remaining halogen atoms to a lesser extent due to the effect of electrochemical character of the substituent, the positional relationship in the ring between the halogen atom and the substituent, and the type of bonding between them. The examples of these types are Cibacron and Zeneca H dye ranges, which have lower degree of reactivity than the dichlorotriazinyl dyes or Zeneca M dyes.

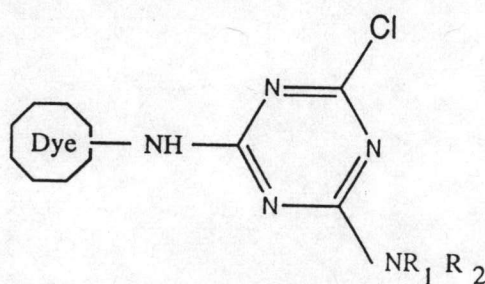


Figure 2.12 Structure of Zeneca H dye range.[19]

The substituents most commonly encountered are amino and substituted amino (Figure 2.12).⁽¹⁹⁾ Other groups that have been examined are methyl, phenyl, hydroxyl, mercapto and certain other groups containing divalent sulphur.

2.5.1.3 Monofluoro-s-triazinyl dyes

A monofluoro-s-triazinyl system is obtained when a fluorine atom is used as a leaving group instead of a chlorine atom. This system is found in the Cibacron F dyes (Figure 2.13).⁽²⁰⁾

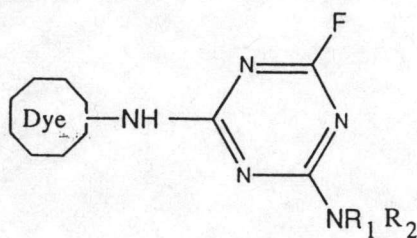


Figure 2.13 Structure of Cibacron F dye.[20]

For these compounds the greater electronegativity of fluorine results in a higher level of reactivity than that of the monochloro-*s*-triazinyl system. Cibacron Red F-B which will be used in this study is also one type of monofluoro-*s*-triazinyl system.

2.5.2 Reactive groups based upon diazines

The diazine ring system contain four carbon and two nitrogen atoms, so that three isomeric structures, (I), (II) and (III) in Figure 2.14⁽⁸⁾, are possible. These are described as 1,2-diazine, 1,3-diazine and 1,4-diazine, respectively, although the trivial names pyridazine, pyrimidine and pyrazine are more generally used.

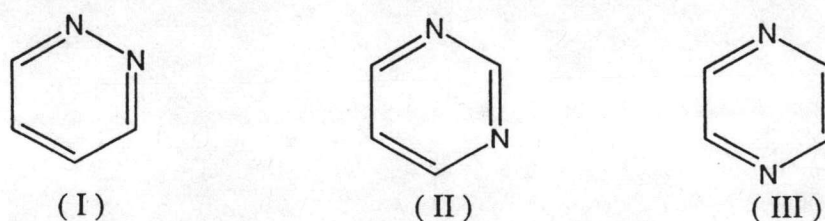
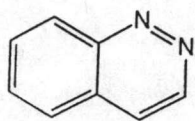


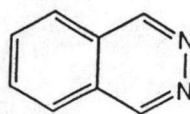
Figure 2.14 Examples of diazine ring system.[8]

Two isomeric benzopyridazines are derived from (I), according to whether the aromatic ring is fused to the 3,4- or the 4,5- positions of the pyridazine ring; the former (IV) is named cinnoline and the latter (V) phthalazine. Pyrimidine and pyrazine

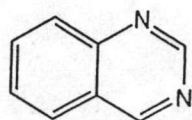
each give rise to only one benzo derivative, quinaxoline (VI) and quinoxaline (VII), respectively.



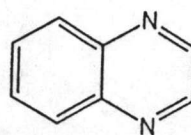
(IV)



(V)



(VI)



(VII)

Of the diazinyl systems theoretically available, pyrimidine has proved to be the most important commercially. Others have been used including pyridazine, quinoxaline and phthalazine.

2.5.2.1 Pyrimidines.

Pyrimidine is the most closely related to s-triazine in structure, one of the hetero nitrogen atoms being replaced by a =CH- group, the earliest reactive dyes of this type were dichloro-pyrimidinyl compounds, but in 1960, several reactive dyes containing the trichloro-pyrimidinyl group were also produced on the market.

Ackermann and Dussy⁽²⁶⁾ investigated the reactivity of di- and trichloro-pyrimidinyl dyes in relation to cellulose. They obtained the values for the rate constant shown in Table 2.3⁽⁸⁾ for the three dyes indicated. It will be noticed that the chloropyrimidinyl dyes are less reactive than the monochlorotriazinyl dyes in both alcoholysis and hydrolysis reaction.

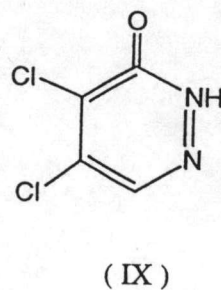
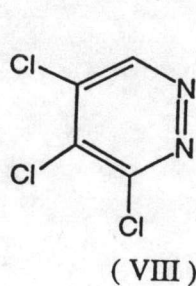
Table 2.3 Rate constant of alcoholysis and hydrolysis reactions of monochlorotriazinyl, di- and trichloro pyrimidinyl dyes.[8]

X	$K_{(OC_2H_5)}^{(Cu)} \cdot 10^5 (s^{-1})$	$K_{(OH)}^{(Cu)} \cdot 10^5 (s^{-1})$	$\frac{K(OC_2H_5)}{K(OH)}$
	20	2.0	10
	1.4	0.24	5.8
	0.83	0.13	6.4

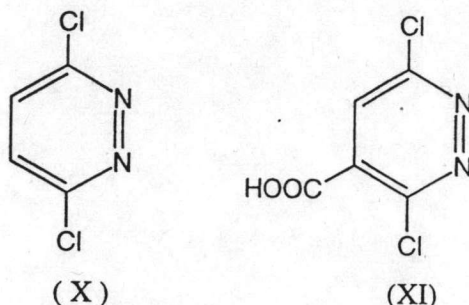
2.5.2.2 Pyridazines

Pyridazines are strongly resistant to attack by electrophilic reagents and has no "aromatic" position analogous to that of pyrimidine, 3,4,5-trichloro-pyridazine (VIII) was used in synthesising reactive dyes proved unfruitful, mainly because the stepwise replacement of chlorine did not proceed smoothly. Two alternative ways of using chlorinated pyridazines have results in the development of technologically useful reactive dyes.

In the first method the chlorinated pyridazines is used in the form of a 4,5-dichloro-6-pyridazone⁽⁸⁾ (IX)

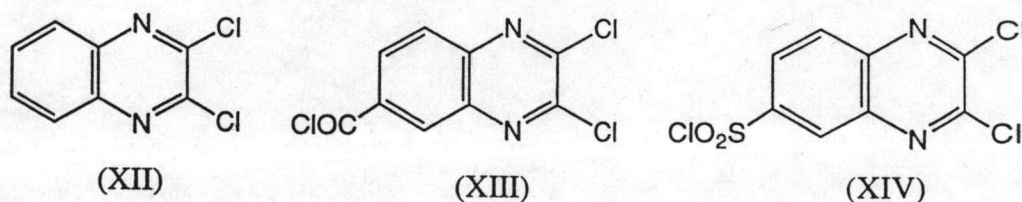


In the second method of using chlorinated pyridazines a carboxylic group is introduced into the 3,6-dichloropyridazine⁽⁸⁾ (X) molecule in order to activate the chlorine and to provide a way of attaching the heterocycle to the chromophore⁽⁸⁾ (XI).



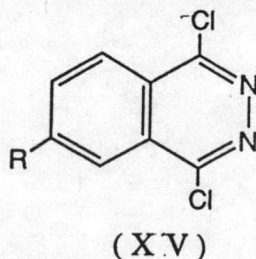
2.5.2.3 Quinoxalines

Only one dichloroquinoxaline having both chlorine atoms in the hetero ring is possible such as 2,3-dichloroquinoxaline⁽¹⁶⁾ (XII). However, it is possible to introduce chlorocarbonyl or chlorosulphonyl groups into the carboxylic ring of 2,3-dichloroquinoxaline that give 2,3-dichloro-6-carbonylchloride⁽¹⁶⁾ (XIII) and 2,3-dichloro-6-sulphonylchloride⁽¹⁶⁾ (XIV), respectively.



2.5.2.4 Phthalazines

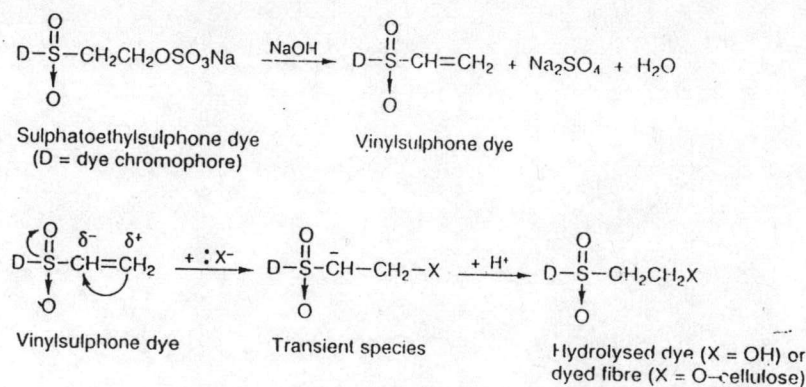
The only possible dichlorophthalazine having both chlorine atoms in the hetero ring is the 1,4-dichlorophthalazine derivative (XV).



This compound is less reactive than 2,3-dichloroquinoxaline.

2.6 Reactive system of dyes reacted by nucleophilic addition

The only type of reactive dyes which react by a nucleophilic addition is vinylsulphone. These dyes contain a β -sulphatoethylsulphone precursor when reacted with alkalis, eliminates sulphuric acid producing a vinylsulphone group which the carbon-carbon double bond in this group is polarised by the powerfully electron-attracting sulphone group. The polarisation results in occurring the positive charge to the terminal carbon atom so that nucleophilic addition of ionised cellulose (Cell-O^-) occurs. Finally, the addition of proton completes the dye-fiber reaction (scheme 2.4)⁽²⁾.



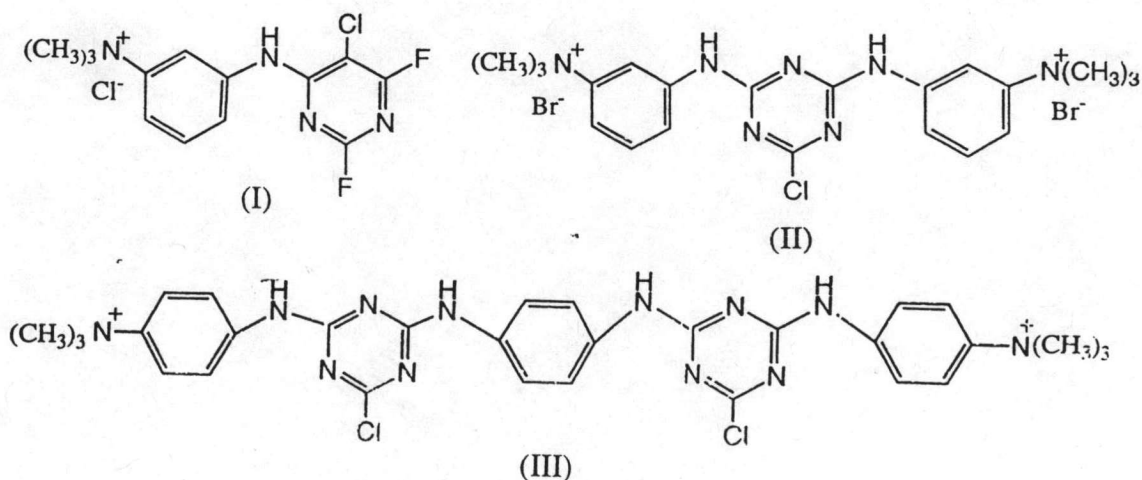
Scheme 2.5 Nucleophilic addition mechanism of vinylsulphone dye.[2]

These dyes are intermediate in reactivity between the mono- and dichloro-s-triazinyl dyes.

2.7 Previous research works on chemical modification of cotton fabrics.

It is known that cotton fabric when dyed with any reactive dyes possesses several advantages in terms of brilliant color, a wide range of shade gamut and very high wetfastness properties. However, the main problem arising from reactive dyeing is that competing hydrolysis reaction of reactive dyes causes a poor dye fixation on the fiber. Hydrolysed dyes discharging from dyehouse are hazardous to environment. Concerning on environmental impact, law regulators have enacted tougher laws to mandate dye users to minimize color in dyehouse effluent. To meet such requirement, the dyeing industry has to adopt more efficient dyeing process as well as choosing dyes which can give high dye fixation. In other targeting of research, in a bid to obtain high dye fixation, the chemical modification by incorporating the reactive groups into cotton fiber has attracted much attention. Several papers have been reported as follows:

The attempts to modify the dyeability of cotton fibers for anionic dyes was previously developed in the laboratories of Research Department of ICI plc. by G.E. Evans et al.⁽²⁷⁾ By pretreating cotton fibers with reactive colorless compounds containing one or more quarternary nitrogen atoms that is a means of introducing fixed cationic sites which have a marked effect on the uptake of anionic dyes. For example, mono-reactive mono-quarternary (I) and mono-reactive bis-quarternary (II) compounds which react more readily with cellulose and show better thermal stability than the epoxypropyl types but both classes share the disadvantage of relatively low substantivity for cellulose.



In the case of bis-reactive bis-quarternary (III) agents offer more use for achieving high substantivity, but the dyeing of modified cotton with these agents resulting in marked difference in hue and brightness when compared with conventional dyeing.

El-Alfy et al.⁽²⁸⁾ suggested the method to improve cotton dyeability via introducing diethyl aminoethyl group into the molecular structure of cotton. Diethylaminoethyle (DEAE)-cotton can be prepared by reacting cotton with β -chloroethyldiethylamine hydrochloride in the presence of NaOH. The DEAE-cotton can be easily dyed with acid dyes, and its affinity for direct dyes increases. The dyeing properties of modified cotton were investigated and compared with those of untreated cotton and cotton treated with an alkali under conditions similar to that used in chemical modification but in the absence of etherifying agent. Dyestuffs used included direct, acid and reactive dyes. The dyeing was carried out according to the exhaustion method as well as the pad-dry fixation method. The clearly results show that the color strength of DEAE-cotton is significantly higher than the alkaline-treated and untreated cotton, respectively.

Hebeish and El Alfy⁽²⁹⁾ studied untreated, alkali-treated and DEAE-cottons that were first treated with hydrochloric, sulfuric or phosphoric acids at different concentrations. The acid-treated samples were reacted with dimethylol dihydroxy ethylene urea (DMDHEU) in presence of magnesium chloride hexahydrate as an external catalyst. The crosslinked cottons so obtained were dyed with a direct dye. Color strength of the samples were found to depend upon kind and concentration of the acid and nature of the substrate.

To determine specific dyeing characteristics of cotton fabric, Blanchard and reinhardt⁽³⁰⁾ investigated the dyeability of cotton fabric that was treated with 4,5-

dihydroxy-1,3-dimethyl-2-imidazolidinone (DHDMI), and dyed with low, medium, and high molecular weight direct dyes, as well as reactive dyes. DHDMI treated cotton fabric had good affinity for low molecular weight direct dye, but dyeability was poor with higher molecular weight direct dyes indicating that the molecular size of the dyes was too large to penetrate the crosslinked structure. The crosslinked fabric had some affinity for reactive dyes, but the results were not as good as those obtained on untreated cotton. A notable improvement in the dyeability of DHDMI treated fabric was achieved when mercerised material was used.

Burkinshaw, Lei and Lewis⁽³¹⁾ proposed the method to improve dye fixation efficiency by pretreating cotton with reactive polyamide-epichlorohydrin resin. A commercial polyamide-epichlorohydrin polymer solution, Hercosett 125, was used to modify cotton in order to produce a modified cellulose that can be dyed with reactive dyes in the absence of salt and under neutral pH conditions and giving high fixation efficiency and good dyeing quality. Pretreatment is carried out by padding with a solution containing Hercosett 125 and Sandozin NIE without adjustment of pH. This treated cotton may be dyed at pH 7 in the absence of electrolyte. However, the limitation of application method to only by padding method makes this technique unpopular.

Waly, Rafai and El-Rafie⁽³²⁾ has presented the novel method for preparing cotton fabric with improved dyeability by amination of cotton fabric via introduction of tertiary amino groups in the molecular structure of cotton cellulose. The technique adopted involved padding the fabric with sodium hydroxide solution followed by impregnation in a nonaqueous solution consisting of a mixture of epichlorohydrin/triethanolamine (3:1 mol) in acetone. Dyeing was carried out according to the pad-dry-thermofixation method using either a reactive dye or an acid dye, aminated cotton displayed greater dyeability with respect to acid dye. When dyed

with reactive dye, the aminized cotton acquires much greater color strength than the unmodified cotton and displays outstanding retention of this color strength after several washings. This is because the tertiary amino groups in the aminised cotton seem to contribute to dye association with the cotton cellulose through facilitating dye diffusion and helping to establish ionic bonds between the dye and the modified cotton cellulose.

Burkinshaw et al.⁽³³⁾ studied once again about the modification of cotton to improve its dyeability. They proposed a new method of pretreating cotton with an aqueous solution containing polyamide-epichlorohydrin(PAE) resin and thiourea mixture that markedly improves the reactive dyeability of this fiber, when compared with the earlier results achieved on PAE-modified cotton alone. The addition of thiourea to the PAE pad liquor is believed to form isothiuronium salts in the fiber surface which would not initially decrease the total number of cationic sites in the resin and might subsequently increase the concentration of strongly nucleophilic centers in this substrate due to the decomposition of isothiuronium salt to thiol residues during the dyeing process. Dyeing can be carried out under neutral pH conditions in the absence of salt to give good color yields and good dye fixation. The wash fastness and mechanical properties of treated cotton are excellent but the light fastness of dyeings was lowered by this pretreatment.

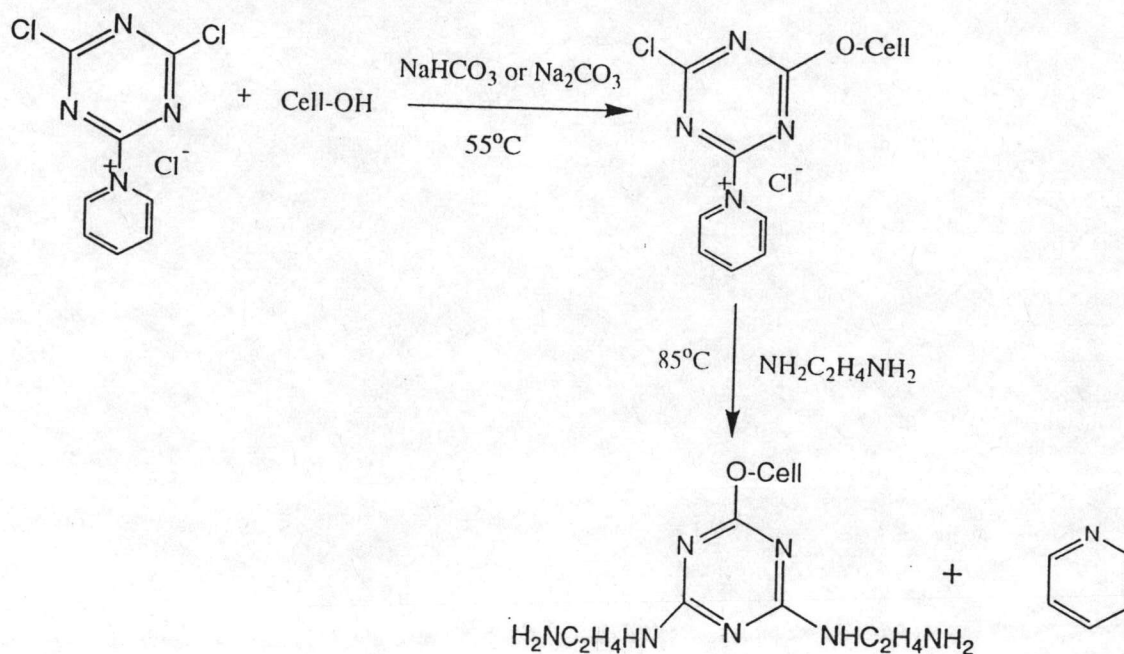
The effect of pretreating cotton with a polyamide-epichlorohydrin resin and ethylenediamine was described by Lei and Lewis.⁽³⁴⁾ In this study increased amounts of amino groups have been introduced into the substrate with the hope of achieving efficient dyeing with dyes of low reactivity. The treated substrate has enhanced substantivity for reactive dyes, which may be applied under weakly acidic conditions without the necessity to add electrolyte. Dyed samples exhibit good brightness and very high wash fastness, but in many cases the light fastness is impaired.

The modification of cotton to provide cationic sites is an important method for improving the substantivity of cotton for anionic dyes. Lewis et al. reported that a promising result could be achieved by modifying cotton with DMAC (1,1-dimethyl-3-hydroxyazetidinium chloride). The modified cotton may be dyed with reactive dyes under neutral pH conditions in the absence of salt, yielding high fixation efficiency and good dyeing quality. Studied by Guo and Chen⁽³⁶⁾ have found that the dyeability of the DMAC-treatment does not seem appreciably influenced by drying and baking, and therefore the present process, (i.e., a cold process) can effect a greater savings in energy consumption than the original DMAC process. Again, the drawback of this type of cotton modification involved the incorporation of cationic residue into the fiber which can cause the catalytic photofading of colored textiles.

Huang and Yen⁽³⁷⁾ examined how the dyeing properties of cotton fabrics may be influenced when the fabrics are pregrafted by a MAA/MAM monomer mixture. Experimental results indicate that dyed fabrics, which are pregrafted, have a better color strength and exhaustion than unpregrafted ones. With increment of the monomer and neutral salt concentrations, the color strength and exhaustion of the fabrics are enhanced. Furthermore, the dyed fabrics' color strength and exhaustion are optimum when the fabrics are pregrafted by MAA/MAM at a 4/6 mixing ratio. Some reports used to hold that N-methylol acrylamide (MAM) facilitates enhancing the crease resistant of cotton fabric and when pregrafted by a MAA/MAM mixed monomer is preferable to those pregrafted by one monomer.

2.8 Concepts of chemical modifying of cotton fabrics

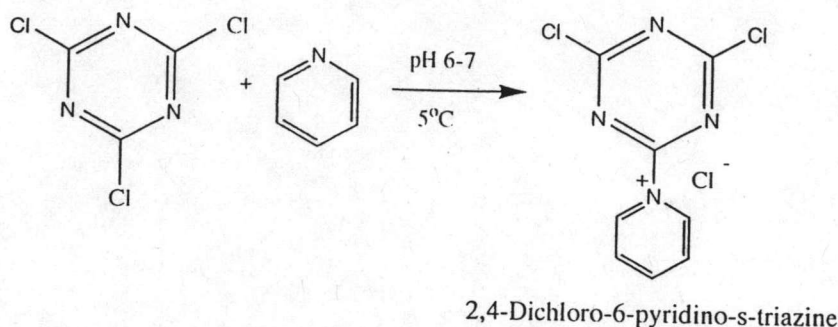
In this project, the idea on how to modify cotton cellulose involves two step reactions. Firstly, cotton fabric is chemically treated with 2,4-dichloro-6-pyridino-s-triazine derivative, (DCPT) under alkaline conditions. Then further treatment of the DCPT cotton cellulose with suitable amines such as ethylenediamine or tris-(2-aminoethyl) amine is carried out in order to obtain reactive fiber. Advantagously when compared to previous methods, the application of this modifying agent is simply achieved using dyeing machine as widely used in dyehouse. The overall reactions can be written as follows:



Scheme 2.6 The reaction scheme between 2,4-dichloro-6-pyridino-s-triazine, cellulose and ethylenediamine to produce aminised cellulose.

In this study, also, the synthesis of the modifying agent, 2,4-dichloro-6-pyridino-s-triazine derivative can be easily prepared by the reaction of cyanuric

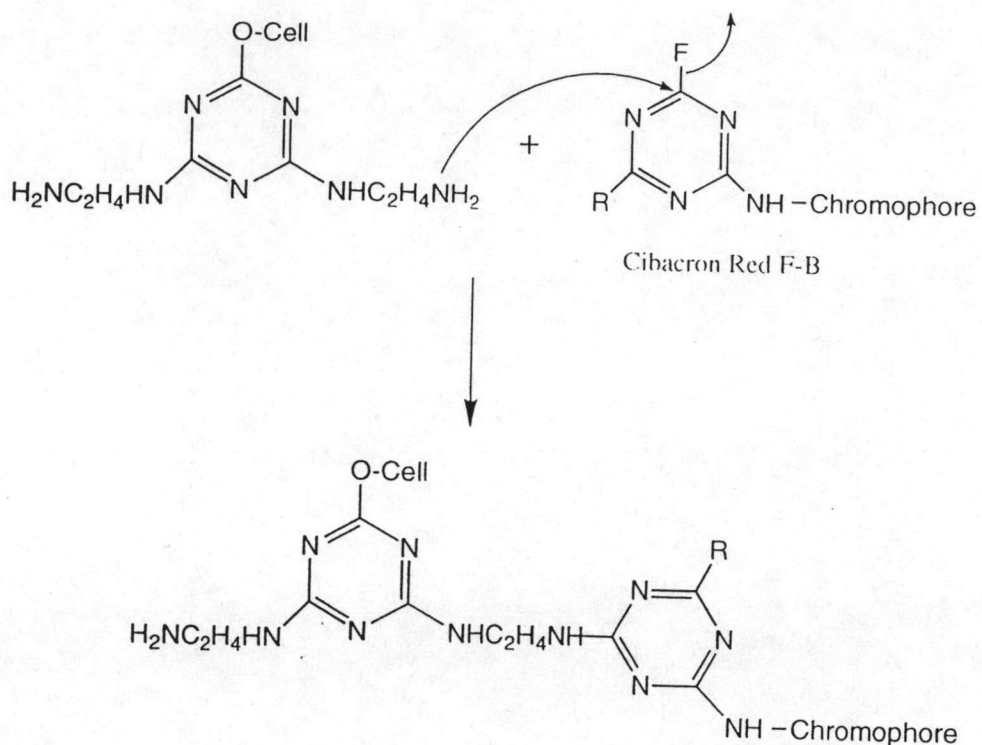
chloride with pyridine at temperature of 5°C. The reaction scheme may be written as follows:



Scheme 2.7 The reaction between cyanuric chloride and pyridine.

This type of modifying agent can be readily absorbed into cotton fiber due to its cationic characteristic, hence eliminating the addition of electrolyte during cotton modification.

The modified cotton fabric obtained from scheme 2.6 is so called reactive fiber since the free amino residue on the fiber is highly reactive when compared to hydroxyl group of cellulose; and so does its nucleophilicity. Therefore, the reaction between reactive cellulose and commercial reactive dye, for example in this case Cibacron Red F-B, can be achieved in neutral dyeing condition as illustrated in Scheme 2.8.



Scheme 2.8 The reaction of commercial reactive dye with reactive cotton cellulose in the neutral dye bath.

By comparison with conventional dyeing, this dyeing system is expected to give an improved dye fixation and minimized dye hydrolysis. More attractively, discharge of dye waste from dye house can also be reduced.