

CHAPTER II

Literature Survey

2.1 Cellulose its structure and properties

Cellulose is the naturally occurring polymer which is great of importance as raw material for textile industry. Cotton is the purest form of cellulose found in nature. The cotton fiber is a single-cell structure taken from the cotton plant as a seed hair. Raw cotton has a creamy off-white color but after purification it is pure white, highly absorbent, tasteless and odorless, very smooth and cool to touch. In addition to its purity, the cotton fiber is chemically stable. The mature cotton fiber forms a flat ribbon-like structure with occasional convolutions along its length as it dries out. These characteristics make cotton easy to identify under both optical and electron microscopes as illustrated in Figure 2.1⁽¹⁾.

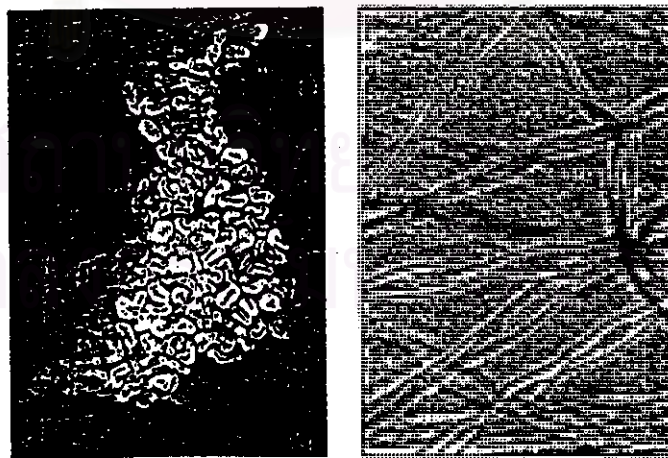


Figure 2.1 Scanning electron micrographs of raw cotton fibers.⁽¹⁾

Cotton fibers are also illustrated in cross-section in Figure 2.1 Their bean-shaped appearance is sometimes described as a 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 Figure 2.2⁽¹⁾) have been identified by means of enzymatic degradation, The rate of degradation increases from A to B to C, which is the order to decreasing density of packing. Between Zones A and C there appear to be limited areas(denoted by N) even more accessible then zone C.

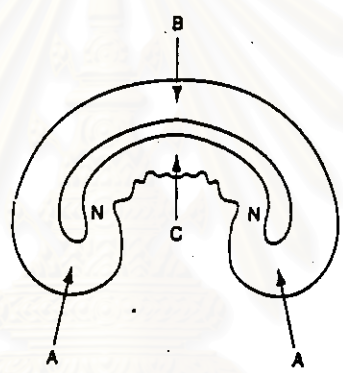


Figure 2.2 Bilateral structure of mature cotton (zones A, B, and N differ in fibrillar packing density).⁽¹⁾

2.2 Cotton morphology

Cotton fibers have a fibrillar structure. Their morphology exhibits three main features such as primary wall, secondary wall and lumen. The outermost layer of the fiber is the thin waxy cuticle, which protects the fiber from its environment. Before cotton can be used as a textile fiber this layer has to be removed by scouring. Beneath

this layer is the primary wall, which is composed of fine threads of cellulose laid down during growth and spiraling round the longitudinal fiber axis at an angle of about 70° ⁽²⁾. 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. The secondary wall consists of several layers and the spiral angle of the fibrils varies from one layer to the next, from about 20° to 35° ⁽²⁾. The lumen is the central air-filled channel, which provides nutrients while the plant is growing. As shown in Figure 2.3⁽²⁾, 2.4⁽¹⁾.

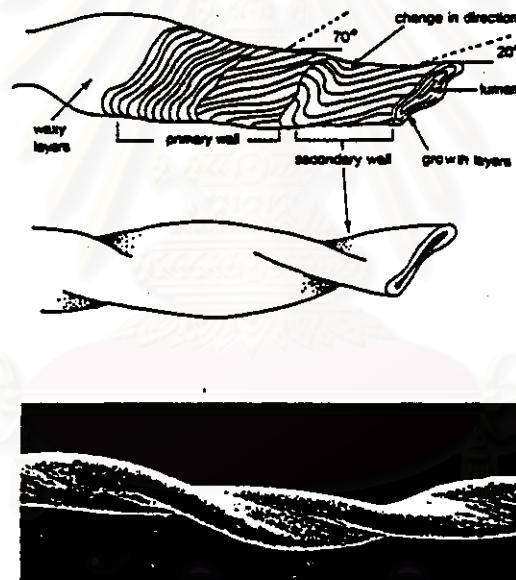


Figure 2.3 The structure of a cotton fiber, seen (above) diagrammatically and (below) in a photograph.⁽²⁾

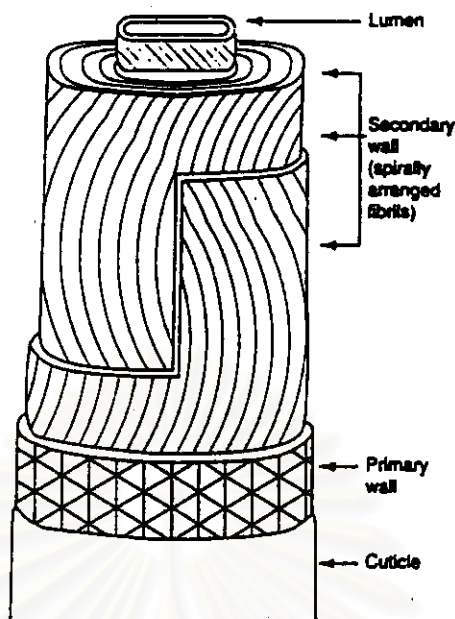


Figure 2.4 Structure of a cotton fiber.⁽¹⁾

2.3 Molecular structure of cellulosic fiber

The cellulose molecule is closely related to the simple sugar glucose. Glucose forms a ring structure comprising five carbon atoms and one oxygen atom. It may be described as a 1,4-(β -D-glucan, i.e., a condensation polymer of (β -D-glucopyranose with 1,4-glycosidic bonds.

The pyranose rings are in the 4C_1 conformation (Figure 2.5(a)⁽¹⁾). Although the Haworth Projections formula (Figure 2.5(b)⁽¹⁾) is easier to write quickly it obscures some important stereochemical aspects of the glucopyranose ring⁽¹⁾. Thus all the substituents, including the glycosidic bonds, are in the mean plane of the ring (equatorial) and not perpendicular to it (axial) as might be supposed from the Haworth formula. Only the C-H bonds are axial. The essential features of the polymer chain are the main sequence of the intermediate units (I), the non-reducing end group (II), the reducing end group (III) and glycosidic linkages.

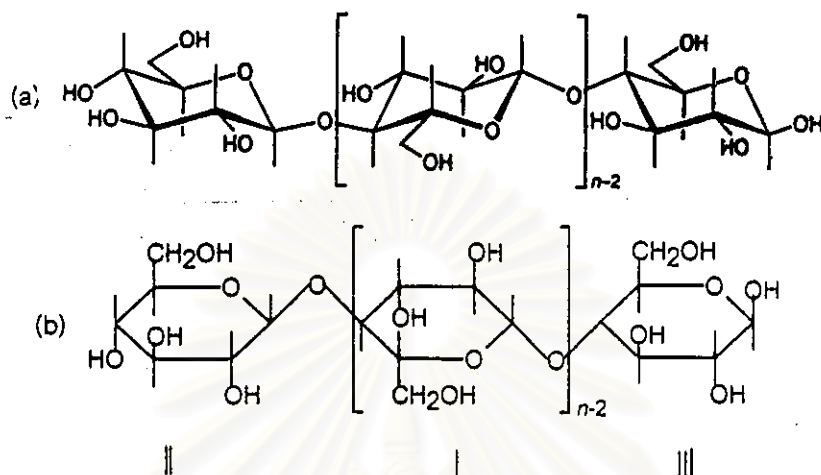
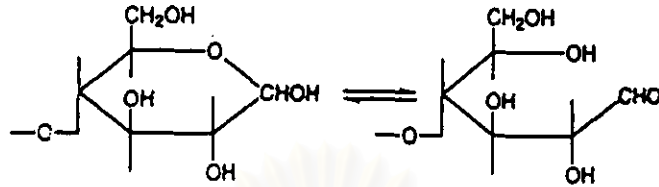


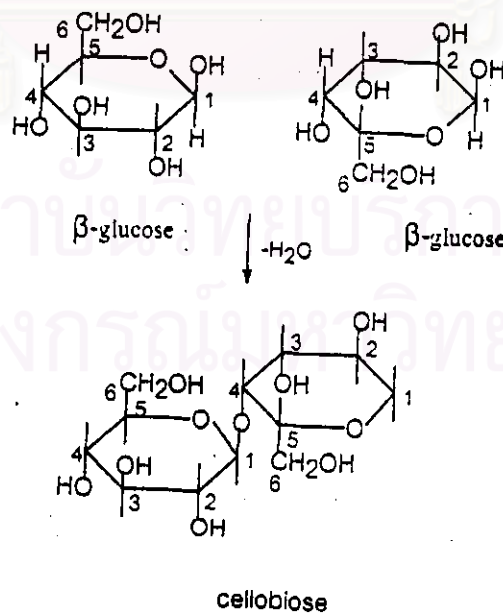
Figure 2.5 Cellulose: (a) Fully extended conformational formula; (b) the Haworth projection formula. n = degree of polymerisation (DP).⁽¹⁾

The intermediate units possess one primary and two secondary alcohol groups each. The non-reducing end group possess one extra secondary alcohol groups each. The non-reducing end group possess one extra secondary alcohol group at C_4 , and the reducing end group (so-called because it reduces Fehling's solution and ammoniacal silver nitrate) is a cyclic hemiacetal. It exhibits the characteristics of both an alcohol and an aldehyde under appropriate conditions (Scheme 2.1)⁽¹⁾.



Scheme 2.1 Scheme of the conversion between alcohol and aldehyde.⁽¹⁾

Glucose is the monomer unit of the cellulose polymer, whilst the repeat unit is cellobiose, a sugar formed by the joining of two glucose units at the terminal hydroxyl groups attached to carbon atom 1 and 4 with the loss of molecule of water (Scheme 2.2, in which the hydrogen and carbon atoms incorporated in the ring are omitted for clarity; notice the inversion of the second glucose unit in cellobiose).



Scheme 2.2 Scheme of the reaction of occurring cellobiose.⁽²⁾

Figure 2.6 represents the structure of the cellulose chain; the repeat unit is shown in brackets and marked with a subscript n , to indicate that there are many such units in the chain. For cellulose this number, often called the degree of polymerization, depends on the origin of the sample: for isolated cellulose n is of the order of 3000 (that is 6000 glucose unit)⁽²⁾ but for cellulose in fibers it may be twice this value, or even more.

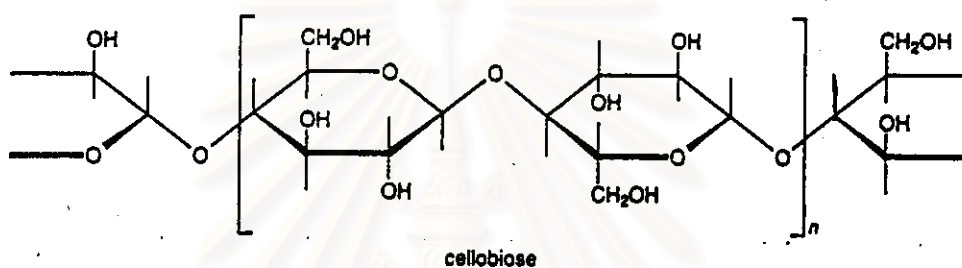


Figure 2.6 The structure of the cellulose chain.⁽²⁾

2.4 Fiber Morphology

Above the molecular level, cellulosic and other fibrous polymers all contain the long chain polymer molecules lying more or less parallel to the direction of the fiber axis.

In natural cellulose, the polymer molecules are held together quite firmly by the forces of hydrogen bonds. That crystallization will take place. These areas are called the crystalline regions. The manner in which the cellulose chains are arranged within the ordered regions of the cotton fiber are like the model as shown in Figure 2.7⁽³⁾.

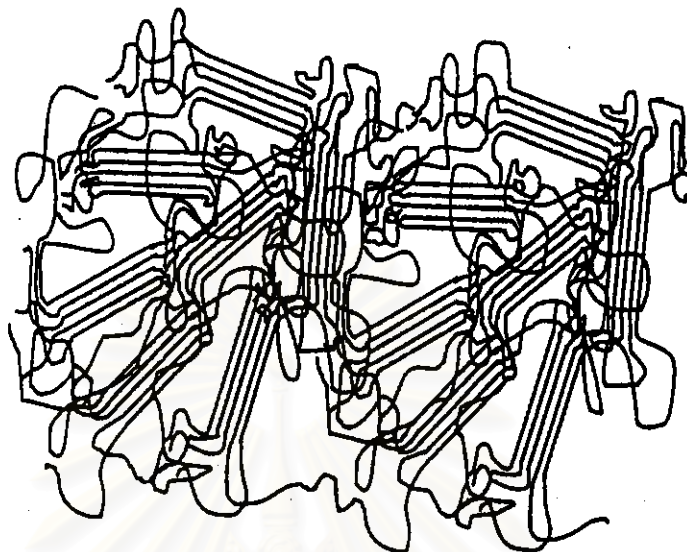


Figure 2.7 The model showing crystalline and amorphous zones in cotton fiber.⁽³⁾

In some place of polymer molecules, there will be little or no indication of order. The disordered regions are known as amorphous. Due to the irregular manner of the cellulose chains, there will be more space between chains in these areas and the forces holding neighboring chains together will be weaker than those existing in the crystalline regions. The penetration of chemicals, dyestuff and so the chemical reactions can occur only in the disordered regions.

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2.5 Fiber Properties

The properties of cotton are listed in Table 2.1

Table 2.1 Properties of cotton.⁽⁴⁾

Molecular Structure	Cellulose
Macroscopic Features	
Length :	0.3 to 0.5 cm. (depending on the source)
Cross-section :	Kidney-shaped.
Color :	Generally white, may be cream-colored.
Light reflection :	Low luster, dull appearance.
Physical Properties	
Tenacity (g/den.) :	3.0 to 5.0 (dry). 3.6 to 6.0 (wet).
Stretch and elasticity :	3 to 7 % elongation at break. At 2 % elongation recovery is 70%.
Resiliency :	Low.
Abrasion resistance :	Fair to good.
Dimensional stability :	Fabrics may shrink during laundering.
Moisture regain :	8.5 %
Specific gravity :	1.54
Chemical Properties	
Effects of bleaches :	Highly resistant to all bleaches.
Dyeability :	Good affinity for dyes. Dyeable with direct, vat, sulphur and reactive dyes.

Table 2.1 Properties of cotton.⁽⁴⁾ (continued)

Acids and alkalis :	Highly resistant to alkalis. Strong acids and hot dilute acids will cause disintegration.
Organic solvents :	Resistant to most organic solvents
Sunlight and heat :	Withstands high temperatures well. Prolonged exposure to light will cause. Yellowing due to oxidation.
Resistance to stains :	Poor resistance to water-born stains.
Biological Properties	
Effects of fungi and molds :	Highly susceptible to attack by mildew.
Effects of insects :	Starved cottons are attacked by silverfish.
Flammability Behavior	Burns rapidly. Smoldering red afterglow.
Electrical and Thermal Conductivity	Good heat conductor.

2.5.1 Appearance

Cotton is a dull fiber with low luster, It is often given special treatments or finishes, such as bleaching, mercerizing, etc., to improve its whiteness and light reflection.

2.5.2 Comfort

Its good absorbency makes cotton to be one of the most comfortable fibers.

It is suitable for hot weather and materials where absorbency is needed.

2.5.3 Maintenance

With its hydrophilic nature, cotton is susceptible to waterborne stains by trapping the colorant in the fiber after water was evaporated. In addition, as a result of its low elasticity and poor resiliency, cotton fabrics wrinkle easily and do not recover well from wrinkling, however, this problem can be overcome by special finishes. Unfinished cotton fabrics generally must be ironed after laundering.

2.6 Concept of Cellulose Cross-linking

Compared with other types of fabrics, the cellulosic fabrics tend to crease easily due to the structural characteristics of the cellulosic fibers. This is because cellulose polymer chains hold together by hydrogen bonding and Van der Waals forces which are not strong enough to maintain the dimension of the fiber when forces act on it after forces are removed, the displaced polymer chains are not able to return to the original position. This phenomenon results in the appearance of wrinkled fabric. This problem is quite significant when fabric is wet, such as during washing⁽⁵⁾.

In order to improve the crease resistant property of cellulose fabrics, it is necessary to introduce additional linkages between adjacent cellulose molecules in the amorphous regions; as graphically is illustrated in Figure 2.8⁽⁶⁾. With stable covalent crosslinks, the stress-induced slippage of polymer chains can be inhibited.

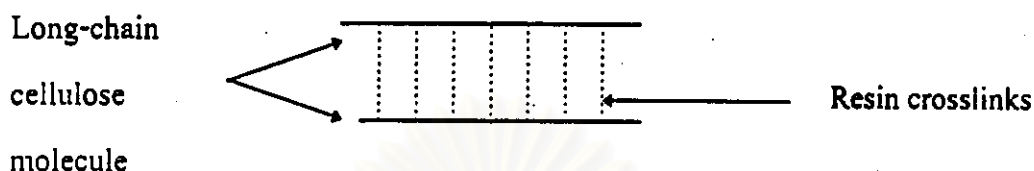


Figure 2.8 A reactant of resin with cellulose fiber.⁽⁶⁾

The additional linkages which act as bridges between adjacent cellulosic chains could be achieved through the crosslinking reaction of hydroxyalkyl group of anhydroglucose units with a crosslinking agent. The reaction occurs only with hydroxyl group in the amorphous or accessible regions of fiber. For the role of substrate in crosslinking reactions of cellulose, the considerations of fiber structure and morphology must be included.

The condition of the crosslinking reaction is governed by the presence of foreign substances, such as additives, dyes or colorants and contaminants, and by the amount of moisture present in the fiber during the reaction time.

Another important factor is the chemical structure of the cross-linking agent. The solubility and the concentrations required to achieve good performance of fabrics must be considered.

2.7 Crease Resistant Finishing Process

Crease Resistant Finishing Process is the method to apply the finishing agents onto the fabric to improve recovery from creasing. Due to the variety of fabrics, there are also various processes to apply the finishes. The difference between each process arise from the different temperature, curing time and moisture content of fabrics during treatment.⁽⁷⁾

2.7.1 Pad-Dry-Cure Process

This process, the fabric is immersed in the finishing solution containing crosslinking agent and catalyst. The fabric is squeezed in a pad roller to give 80-100% wet pick up. After padding, the padded fabric is then dried at 85-100 °C and cured at the temperature higher than 140 °C for one to five minutes.

In the drying and curing steps, the fabric is normally fixed on the stenter in order to control the dimension of fabric which is necessary to get smooth drying.

2.7.2 Moist Cure process

The finishing solution for this process contains the cross-linking agent and the strongly acid catalyst. The fabric will be passed through it and dried to a specific moisture content at about 6-12%. To prevent the change of moisture content the fabric is usually batched in polyethylene film for 12-24 hours at room temperature. During this period the cross-linking reaction will occur. Then treated fabrics are neutralized with sodium carbonate and washed.

This process is more suitable for cotton woven fabrics than weft-knitted fabrics. For long reaction time, the fabrics, however, are affected by degradation due to cellulose hydrolysis. Some cross-linking agents, such as urea formaldehyde, cannot be used in this process because the precipitation of pad bath solution due to the polymerization of cross-linking agent will occur as the strong acid catalyst is added.

2.7.3 Mild Cure Process

This is the single step process. The fabric is passed through the finishing solution containing cross-linking agent and strong acid catalyst. Without drying, the fabric is directly cured at about 120°C for a short period until the moisture content is reduced to 3-5% from the initial level. Finally, the fabric is neutralized with sodium carbonate solution.

2.7.4 Wet Cure Process

This process is similar to moist cure, but the pre-drying step before batching is neglected. The fabric is padded with the crosslinking agent and catalyst. After that, the fabric is then batched and rotated at room temperature (wrapped in polyethylene film to prevent loss of moisture) for 24 hours before being neutralized and dried.

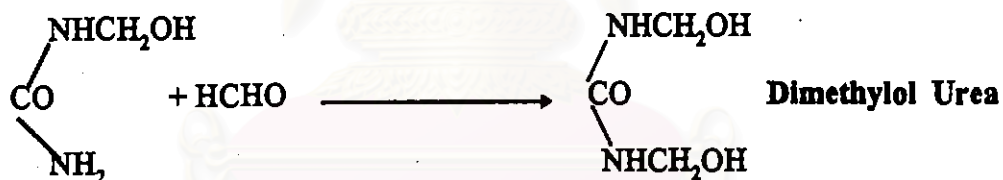
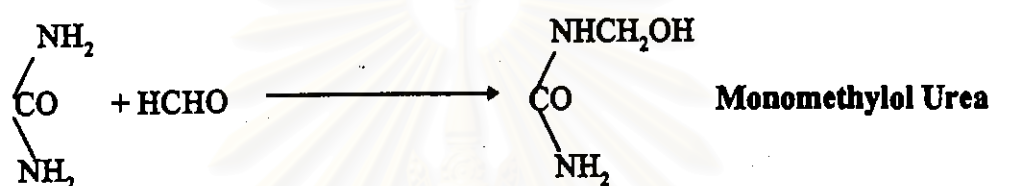
2.7.5 Wet Fix Process

The fabric is first padded with crosslinking agent in acidic condition and batched at room temperature for 12 to 24 hours. In the second step, the fabric is repadded again with catalyst, for example magnesium chloride. The fabric is then dried at 60°C for 4 minutes and cured at 160°C for 4 minutes.

2.8 Finishing agents

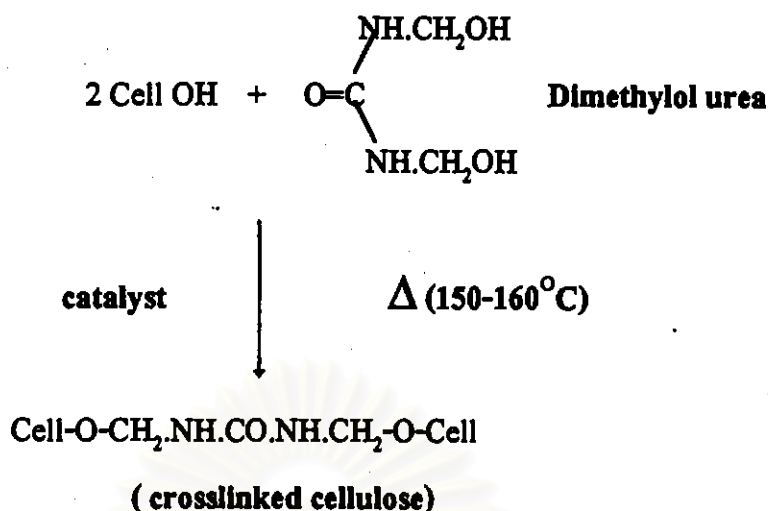
The most widely resin precursors used to impart the desired crease-resist properties to fabrics are based on urea-formaldehyde derivatives containing methylols as reactive groups.

The general formation for production of the resin was as follow⁽³⁾:



Scheme 2.3 The general formation for production of the resin.⁽³⁾

In the presence of an appropriate catalyst, these react with cellulosic materials forming stable and relatively strong crosslinks between the polymeric cellulose chains. In order to produce resin finished products, the fabric is impregnated with an aqueous solution of the resin containing a catalyst, dried and cured at high temperature. Scheme 2.4⁽⁸⁾ Finishing cellulose materials with urea formaldehyde resins.



Scheme 2.4 The finishing of cellulose materials with urea formaldehyde resins.⁽⁸⁾

A variety of commercial products was developed, each one containing formaldehyde, such as the following .

1. Urea-formaldehyde
2. Highly condensed urea-formaldehyde
3. Methylated urea-formaldehyde
4. Melamine-formaldehyde
5. Methylated melamine-formaldehyde
6. Ethylene urea-formaldehyde
7. Heterocyclic crosslinking agents based on malamine-formaldehyde
8. Glycol based reactants and derivatives thereof.

Examples of the chemical structures of these products are shown in Figure 2.9⁽³⁾.

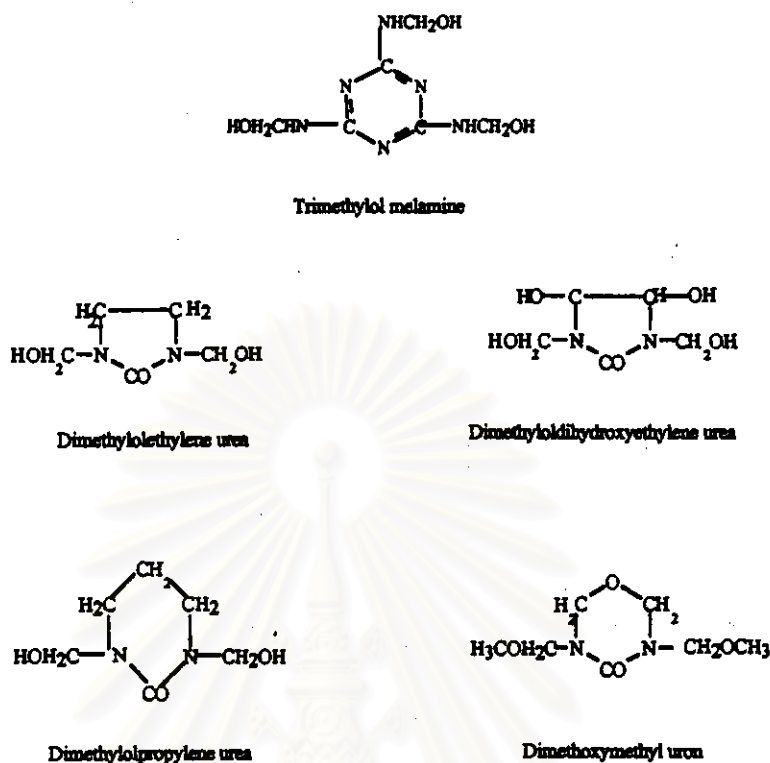


Figure 2.9 Examples of major resins used in the industry and their chemical structures.⁽³⁾

Each of these resins has its own particular part in the evolution of easy care finishes to produce present day standards.

The properties required by an easy care finished are:

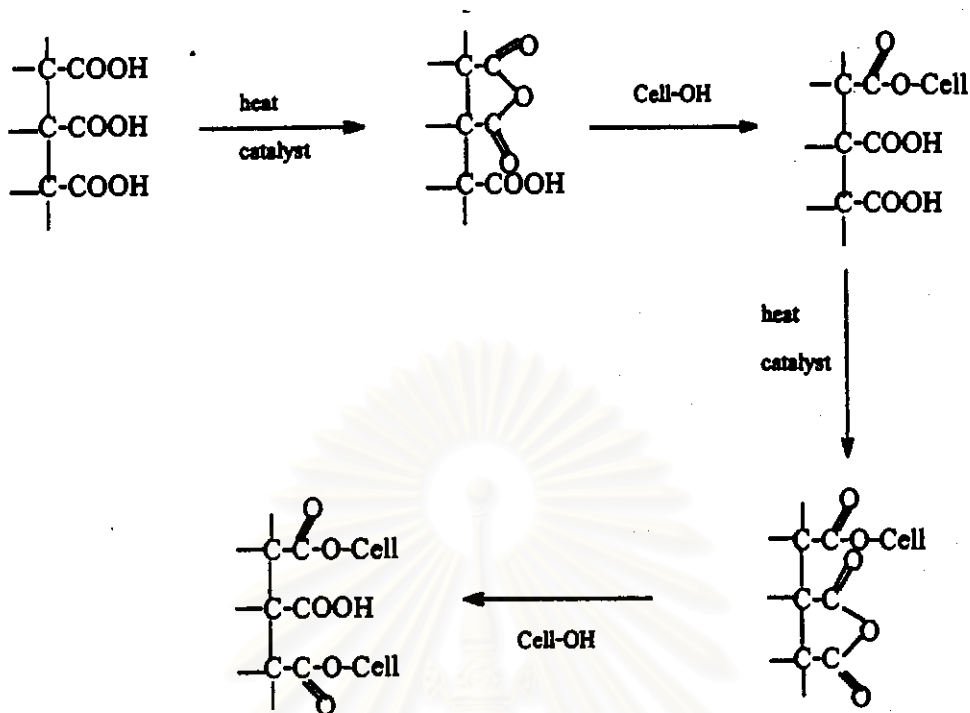
1. Dry and wet crease resistance
2. Good dimensional stability
3. Little loss in physical properties (i.e., tensile and abrasion)
4. Compatibility with other finishing agents (e.g., water-repellent, softeners, optical brightening agent)
5. Minimum effect on handle
6. Little effect on dye or print shade or the light-fastness of the dye
7. Little effect on rub fastness of dye or print
8. No effect on the Whiteness of the fabric

9. As low as possible formaldehyde release
10. Good environmental condition both in the application of the resin and the final making up of the fabric when finished
11. Ease of application and low cost add-on factor in both chemical and application cost.⁽³⁾

The crease resistance of cotton fabrics is improved by durable press finishes. However, the chemicals most commonly used for durable press treatments contain significant levels of formaldehyde (CH_2O) that can be released from the finished fabric into the surrounding environment of air, liquid and skin. The release of formaldehyde is a problem for human health and safety because formaldehyde is a suspected carcinogen.^(5,9,10-13)

An alternative approach that has been gaining increasing popularity is the use of a non-formaldehyde reactant to crosslink cellulose-containing fabrics. The newly developed polycarboxylic acid cellulose crosslinkers are being evaluated as a replacement for formaldehyde containing cellulose reactants. They react with cotton fibers at elevated temperatures to form ester type crosslinks with cellulose molecules (scheme 2.5⁽¹⁴⁾). The interesting carboxylic acid are shown in Figure 2.10.⁽¹⁴⁾

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Scheme 2.5 Formation of ester crosslinks in cotton. ⁽¹⁴⁾

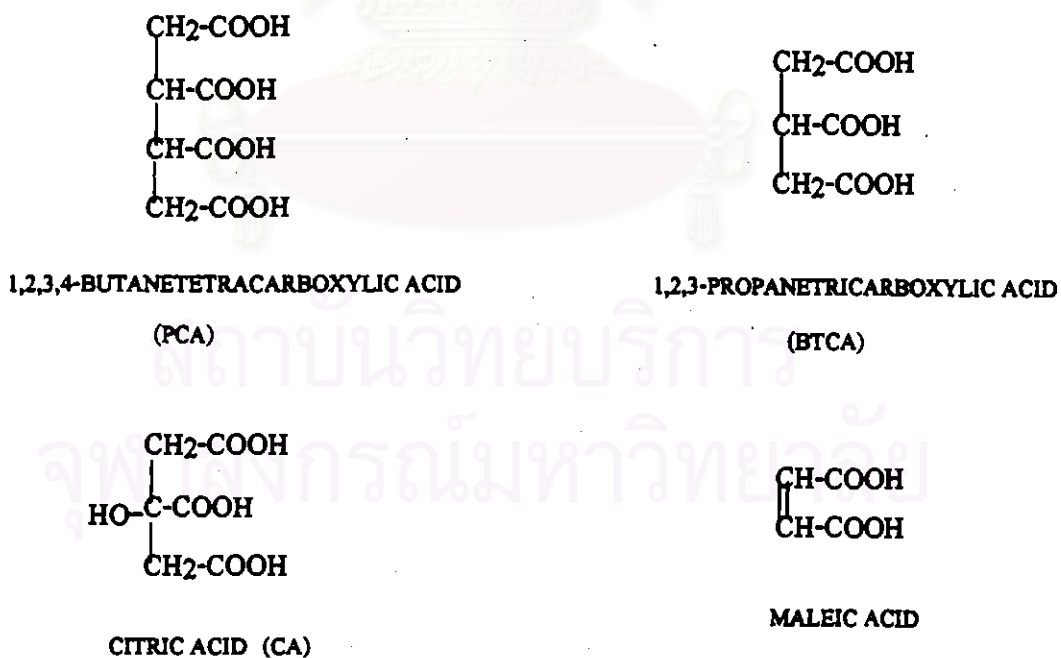


Figure 2.10 Acids effective in DP finishing: 1,2,3-propane-tricarboxylic acid; 1,2,3,4-butanetetracarboxylic acid; citric acid; and maleic acid. ⁽¹⁴⁾

A number of polycarboxylic acids have been shown to impart high levels of wrinkle resistance and smooth drying to cotton fabrics. The most effective of these agents is 1,2,3,4-butanetetra-carboxylic acid (BTCA).

2.8.1 1,2,3,4-Butanetetracarboxylic Acid (BTCA)

As a formaldehyde-free durable press finishing agent for cotton fabric, 1,2,3,4-butanetetracarboxylic acid was a highly reactive and effective crosslinking agent that meets many of the requirements for satisfactory performance, such as level of smooth drying properties, durability to laundering, fabric strength retention, low reagent volatility and absence of odor.⁽¹⁵⁾

In order to accelerate the cross-linking reaction and improve the fabric performance, the effect of catalysts in BTCA finishes have been studied. In the type of alkali metal salts of phosphorus-containing inorganic acids, Welch and Andrews⁽¹⁶⁾ as well as many researchers found that the highest levels of DP rating and wrinkle recovery angle along with the most satisfactory whiteness are obtained with the presence of sodium hypophosphite. Table 2.2 shows the effect of increasing the concentration of BTCA with sodium dihydrogenphosphate as catalyst. Very high DP rating were obtained at high BTCA concentrations while its effective results approached to the conventional DMDHEU-MgCl₂ treatment.⁽¹⁶⁾

By adjusting the curing times to import the same level of DP performance, the breaking and tearing strength of BTCA treated fabric tended to be little or no dependence on curing temperature in the range from 180-215 °C as shown in Table 2.3⁽¹⁶⁾.

Table 2.2 The effect of increasing the concentration of BTCA with sodium dihydrogenphosphate catalyst.⁽¹⁶⁾

BTCA Conc. ^a	DP Rating	WRA (w+f) Conditioned	Tearing	Breaking
			Strength Retention	Strength Retention
12%	4.8	286 ^o	43%	39%
10	4.8	275	45	40
8	4.3	260	47	39
6	4.3	264	50	42
4	3.9	245	50	40
2	2.7	230	63	54
DMDHEU/MgCl ₂ -Citric Acid ^b	4.0	261	42	31

^a BTCA/NaH₂PO₄ mole ratio: 1/1.5; wet pick up: 90-95% owf; predry at 85 °C for 5 minutes and cure at 180 °C for 90 seconds; no process rinse. All properties determined after one laundering cycle on 80x80 print cloth. ^b 5% DMDHEU-1.8% MgCl₂/citric acid mole ratio of 20/1. Cured at 160 °C/3 minutes.

Table 2.3 Fabric properties as a function of cure temperature and time.⁽¹⁶⁾

Cure Temp	Time ^a	DP Rating ^b	WRA (w+f)		Breaking Strength Retained	Tear Strength Retained	Stiffness Bending Moment ^c
			Cond	Wet			
180 °C	90 Sec	4.5	296	278	53%	54%	4.3
180	45	4.6	293	267	57	58	4.3
180	30	4.0	285	261	58	61	4.1
195	30	4.6	288	276	59	54	4.3
195	20	4.6	291	253	56	61	4.8
205	20	4.6	290	264	57	55	4.2
205	15	4.2	289	248	52	60	4.6
210	15	4.2	286	250	57	63	4.6
215	15	4.3	294	265	50	55	4.8
Untreated fabric		1.3	204	145	(100)	(100)	5.5

^a All-Cotton 80x80 print cloth treated to 119-125% wet pick up owf with 6.3% BTCA, catalyst and 1.0% polyethylene, then dried at 85 °C for 5 minutes, cured at 180 °C for 90 seconds, rinsed at 50 °C for 30 minutes and dried at 85 °C for 5 minutes. ^b After 5 laundering cycles. ^c Inch-pound, x 10⁴.

Shade change on dyed fabric finished with BTCA and phosphorus catalysts was illustrated by Brodmann.⁽¹⁷⁾ The shade change of various classes of dyed fabric finished with BTCA is similar to the shade of DMDHEU finished fabric except for sulfur dyed fabrics which was suggested to avoid those problem by using disodiumphosphite (Na_2HPO_3) as a catalyst.

Nonphosphorus catalysts for BTCA finishing of cotton were currently introduced by Choi, Welch, and Morris.⁽¹⁸⁾ Aromatic N-heterocyclic compounds, such as imidazoles and its derivatives, as well as mono or disodium salts of unsaturated carboxylic acids, such as fumaric, malelic, and itaconic, have been presented to be the considerable catalysts for the esterification reaction of BTCA.⁽¹⁹⁾

Although BTCA is found to be the most effective acid for the durable press finishing of cotton, but it is very expensive. To be considered for practical use, large amount of research projects have focused on modifying the BTCA system by using additives. Welch proposed the decrease of BTCA concentration by using alpha-hydroxy di or tricarboxylic acid, as a co-reactant additive.⁽¹⁵⁾ To modify the dyeability of cross-linked cotton fabric, Blanchard et al., have presented the effective additives such as triethanolamine and the amine hydrochloride derivative.⁽²⁰⁾

2.8.2 Catalysts

The catalysts is present to ensure that the crosslinking of reactant occurs with the fabric. It is the important factor for obtaining optimum effects in durable press finishing. They are commonly selected on the basis of effectiveness, safety, and economy. However, very little has been published in depth on how and why catalysts affect the balance of textile properties of treated fabric.

The crosslinking reactions of cellulose are known as acid-catalyzed reactions. This means the speed of the reaction at constant temperature is increased if the concentration of hydrogen ions in the system is increased by the addition of acidic substances. Many works have developed and reported various kinds of catalysts that being used to promote individual crosslinking system. The common types of catalysts for pad-dry-cure finishing process are as the following.

2.8.3 Acid Salts

Acid salts, especially alkali metal salts of phosphorus containing mineral acids show significantly greater activity as catalysts agents in the case of cross-linking with polycarboxylic acid. These kind of salts appear to play three roles. They serve as catalysts themselves, form partial salts of the polycarboxylic acid which are catalytic, and also act as efficient buffers. They can impart medium to high levels of durable press properties, while give marked decrease in acid-catalyzed tendering of the cotton fabric. Moreover, they minimize shade change during high temperature of curing. At present, sodium hypophosphite is known as the most effective catalyst, As shown in Table 2.4, but still has disadvantages of high cost, its tendency to cause shade changes in fabric dyed with most sulfur dyes, as well as some reactive dyes.⁽²¹⁾

Sodium dihydrogen phosphate is less expensive and with BTCA or PCA does not cause any shade changes problem.⁽¹⁷⁾ Sodium dihydrogen phosphate, a fairly active catalyst, has a tendency to produce a faint yellowing in cotton during treatment, however, the satisfactory whiteness can be obtained with the rinsing process.

Table 2.4 Catalysts of DP finishing with polycarboxylic acids (alkali metal phosphates, phosphites, and hypophosphites).⁽²¹⁾

Decreasing order of effectiveness:----->		
1	2	3
NaH_2PO_2	KH_2PO_2	$\text{Na}_2\text{HPO}_4, \text{K}_2\text{HPO}_4$
Na_2HPO_3	NaH_2PO_4	$\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$
	LiH_2PO_4	$\text{Na}_4\text{P}_2\text{O}_7$
		$\text{Na}_3\text{P}_3\text{O}_{10}$
		Na_3PO_4
		$\text{Na}_2\text{PO}_3\text{F}$

Various sodium salts of alpha-hydroxy acids, such as citric, malic, and tartaric acids have been investigated as alternative systems for BTCA finishing. Moreover, sodium salts of saturated carboxylic acids, such as formic, oxalic, malonic, succinic, glutaric and aspic acid were also studied. Choi and Welch⁽²²⁾ found that they were more effective than sodium carbonate, but less effective than sodium hypophosphite. In sodium salts of unsaturated system such as mono- and disodium salts of fumaric acid, maleic acid, and itaconic acid. Choi, Welch and Morris⁽²³⁾ demonstrated their use as alternative to phosphorus-containing catalysts for esterification and cross-linking of cellulose with BTCA.

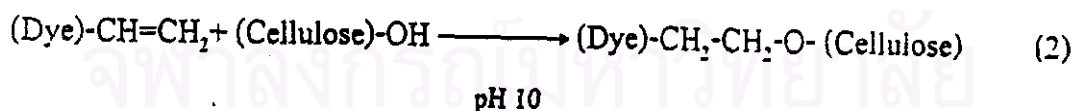
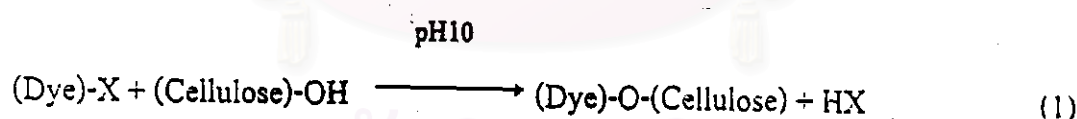
2.9 Dyeing of reactive dye

2.9.1 Dyeing of Cellulose with reactive dyes

Cellulose fibers can be dyed with various classes of dyes. Most interestingly, reactive dyes are widely employed for dyeing cellulose fibers because of their brilliance,

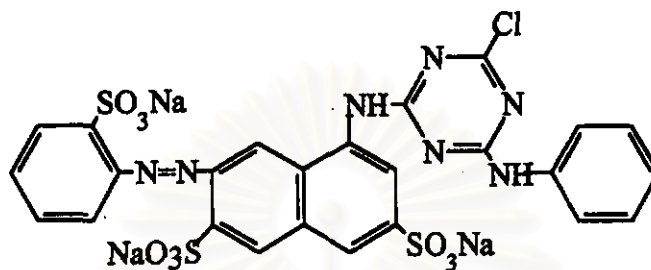
wide shade gamut and excellent fastness properties. Reactive dyes are colored compounds containing suitable groups which are capable of forming covalent bonds with the fiber, hence giving dyeings that are fast to washing. Theoretically, any group that is able to react with hydroxyl reactive sites in cellulose is a potential reactive group to be incorporated in a reactive dye. However, practically, incorporation of some types of some types of reactive groups is limited because of their level of reactivity, their stability to hydrolysis, stability of the dye-fiber bond and their ease of manufacture.

The most commercially practicable reactive dyes are dyes which function under alkaline dyeing conditions. These dyes can be called alkali-fixing reactive dyes which fall essentially into two classes. In the first class, the reaction takes place via nucleophilic substitution, in which the leaving group in the dye molecule is attached by activated hydroxyl groups of cellulose, as shown in equation 1. The second class of reactive dyes contains dyes which react by nucleophilic addition or the Michael reaction; an activated C=C bond adds directly as shown in equation 2, Scheme 2.6⁽¹⁾.



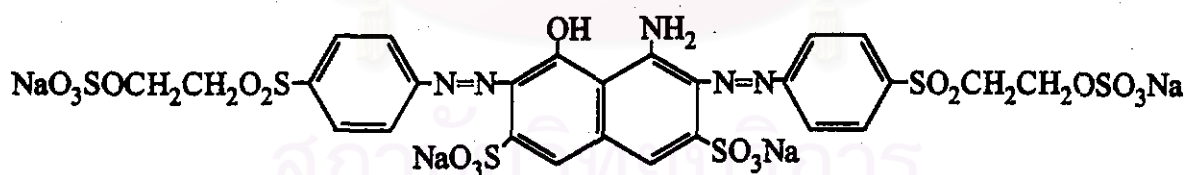
Scheme 2.6 Typical reactive dye reaction with cellulose.⁽¹⁾

Examples of reactive dyes which function under nucleophilic substitution (CI Reactive Red 3) and nucleophilic addition mechanism (CI Reactive Black 5) are given below, Figure 2.11 and Figure 2.12.⁽¹⁾



CI Reactive Red 3

Figure 2.11 The reactive dye operated under nucleophilic substitution.⁽¹⁾



CI Reactive Black 5

Figure 2.12 The reactive dye operated under nucleophilic addition.⁽¹⁾

To achieve good dye fixation, it is necessary that an alkali must be added to dyebath in order to activate cellulose hydroxyl group to able to react with the reactive dye. It is because of the requirement of the alkaline dyeing conditions that prevent the dyeing of conventional reactive dyes with the finishing process which usually requires the acidic catalyst in promoting the crosslinking reaction.

2.10 Concept of this research

In this research, the authors were interested in studying the simultaneous dyeing and finishing of cotton fabric in single step process. Combining those two processes is diffinitely attractive to the industry because of significant reduction in production costs. The fundamental idea of this project was to exploit a crosslinking agent which contains more than two functional groups. The first two groups were designed to undergo crosslinking reaction between adjacent cellulose polymer chains to impart wrinkle resistant properties to the fabric. In the mean time, by inclusion of hydroxyl group containing dye with the polyfunctional crosslinking agent, the hydroxyl group in the dye could also covalently react with the remaining functional groups of bonded crosslinking agent, thus binding the dye to the fiber. The functional crosslinking agent used in this study was butanetetracarboxylic acid (BTCA) which has the chemical structure as follows:

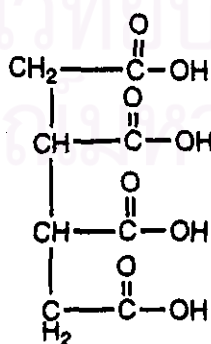
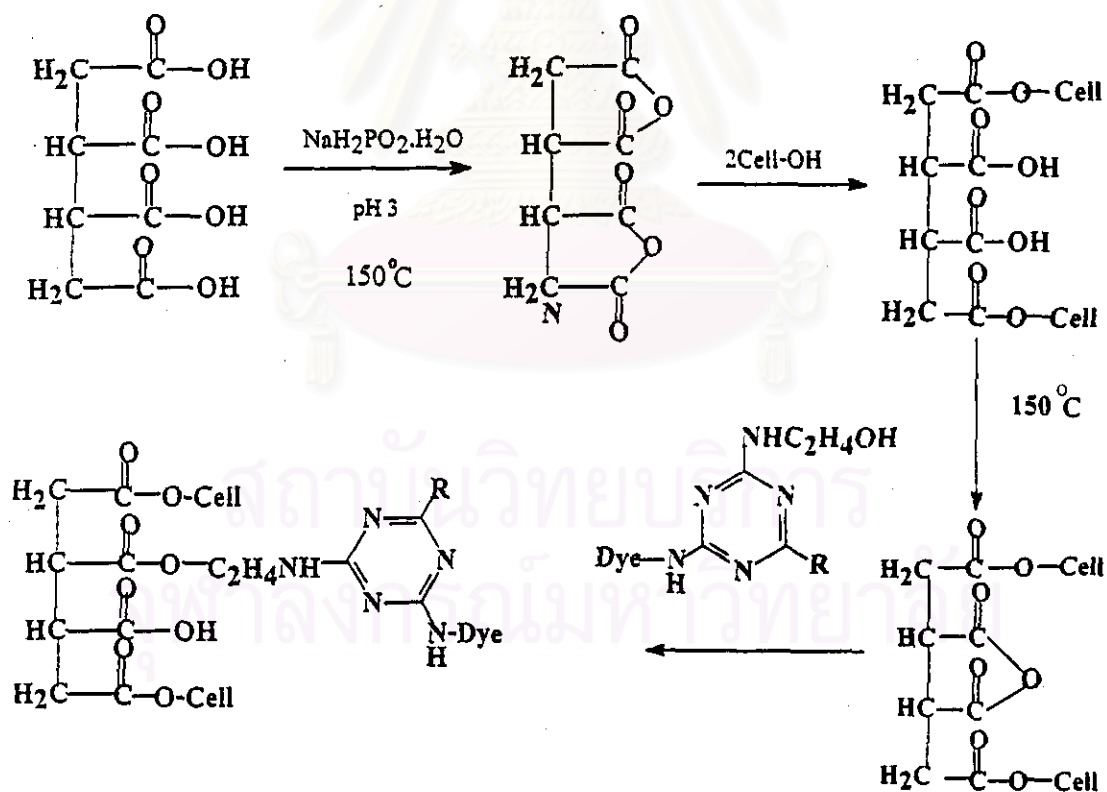


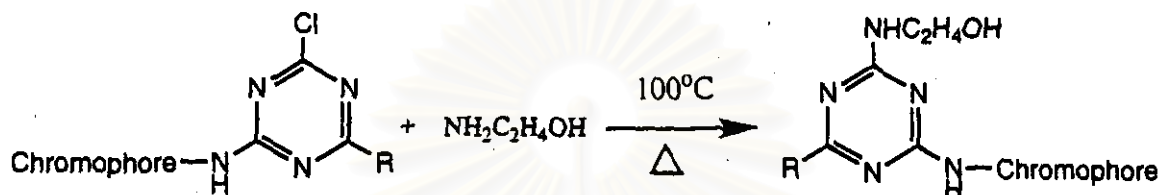
Figure 2.13 The chemical structure of BTCA. ⁽²⁴⁾

The selection of hydroxyl group containing dye is equally important. It was required that the reactivity of hydroxyl residue in the dye should be matched with those of hydroxyl group in the cellulose in order to achieve high dye fixation. There are a number of commercially available reactive dyes which have hydroxyl groups in dye molecule but all of them are attached to the aromatic ring, tending to possible poor reactivity. Hence, in this work, the modification of the dye was made by the reaction of commercial reactive dye with hydroxyethylamine (shown in Scheme 2.7). The result of the reaction yielded the dye which contained hydroxyalkyl residue. Like the cellulose hydroxyl groups, the hydroxyalkyl residue has the hydroxyl group which attached directly to aliphatic chain, therefore it reacted with crosslinking agent in similar fashion as did the cellulose hydroxyl group. The overall reaction scheme between the hydroxyalkyl dye, crosslinking agent and the cellulose hydroxyl group may be written as follows:



Scheme 2.7 The reaction scheme between the hydroxyalkyl dye, crosslinking agent and the cellulose hydroxyl group.

The idea of this project is to combine reactive dyeing and finishing of cotton fabric in single stage process. To achieve this, a crosslinking agent will act two important roles at the same time; one is to act as a crosslink between adjacent cellulose polymer chains and the other is to act as a bridge between dyes and the fiber. The reactive group of the dye should be able to react with a crosslinking agent under acidic conditions.



Scheme 2.8 The reaction scheme of monochlorotriazinyl dye and ethanolamine.

The modified dye obtained from Scheme 2.8 is so called hydroxyalkyl dye, from this study, it can be dyed cotton cellulose in the same condition as BTCA finishing agent react with cellulose under $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ catalyst (Scheme 2.7).

The application of hydroxyalkyl dye and the crosslinking agent is carried out by pad-dry-cure method. The effects of factors influencing the crosslinking reaction are extensively investigated. The easy-care properties as well as the physical properties of dyed fabrics are also studied.