CHAPTER II

Literature Survey

Cotton Fiber

Cotton is the most important natural cellulosic fiber and the most widely used textile fiber. The purified cotton fiber is pure white, tasteless and odourless, highly absorbent, very smooth and soft, non-irritant and cool to touch. That is the ideal properties for clothing it possesses over other fibers.

1. Fiber Composition

1.1 Macrostructure

The cotton fiber appears as a ribbonlike structure that is twisted at irregular intervals along its length. Its color ranges from yellowish to pure white.
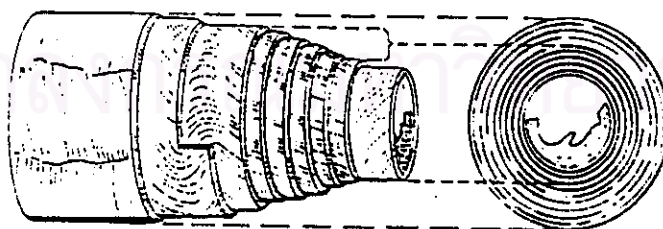
Figure 2.1   Schematic of cross-sectional cotton fiber showing primary wall, secondary wall and lumen (Tortora, 1978).

Seen in microscopic cross section (Figure 2.1) the fiber displays a central hollow core known as the lumen which provides nutrients while the plant is growing. The fiber is found to consist of an outer shell, or cuticle, surrounding the primary wall which, in turn, covers the secondary wall. The cuticle imparts abrasion resistant to cotton whereas the primary wall is made up of fibrils (short fibers). The fibrils support the cuticle, and with it, stiffen and strengthen the fiber. The secondary wall is also composed of fibrils but they are not packed as tightly as in the primary wall. Not only flexibility that is provided from this layer, but a small amount of slippage between the layers of the primary and secondary walls also provides elasticity.

1.2 Microstructure

The cotton fiber is composed of about 95% cellulose which is a high molecular weight polymer. The polymeric cellulose chain of cotton is constructed with as many as 6,000 -7,000 repeating 1,4 -β- anhydroglucose units connected to each other by oxygen atom in the same plane as the glucose rings. This structure allows the long molecules to pack together in parallel rows within the fibrils.
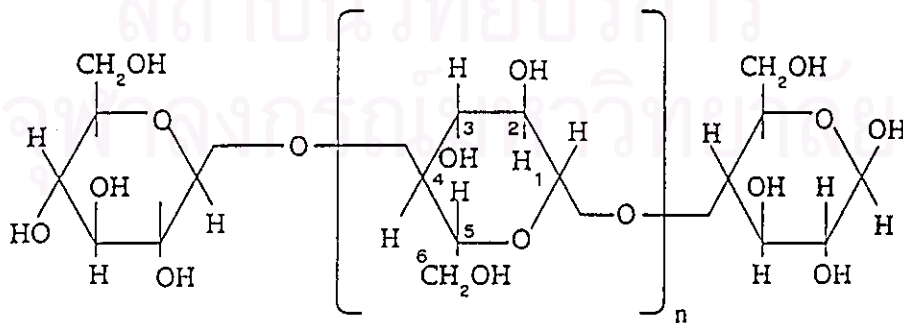
Figure 2.2 Structure of cellulose molecule.

The hydroxyl hydrogens in cellulose molecules are hydrogen bonded which will arrange several adjacent cellulose chains in parallel to one another with close alignment. These areas are called crystalline regions (approximately 85-95%). There is not enough space between neighboring cellulose molecules to accommodate water molecules, resin molecules, and the like. Consequently, the crystalline regions are not penetrated by such molecules. 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 2.3.
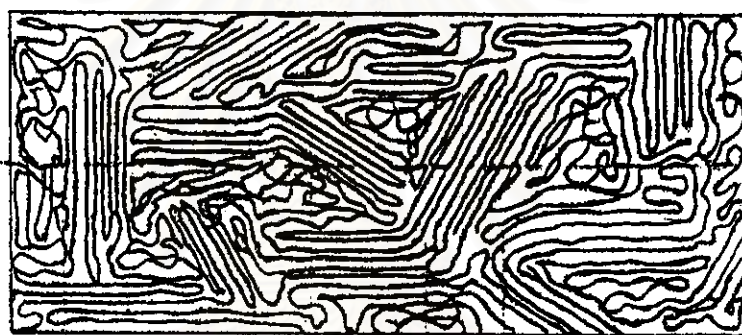
Figure 2.3 The model showing crystalline and amorphous zones in cotton fiber.

Between the crystalline regions, unordered areas are formed. These are called amorphous regions. 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. Hence there is enough space between the cellulose chains into which can readily allow chemical molecules, dyestuff and the like to penetrate.

2. Fiber Properties

The properties of cotton are listed in Table 2.1.

Table 2.1 Properties of cotton (Smith and Block, 1982).

Molecular Structure	Cellulose.
Macroscopic Features	
Length:	0.3 to 5.5 cm.
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.
Acids and alkalies:	Highly resistant to alkalies. 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.
Dyeability:	Good affinity for dyes. Dyed with direct, vat, and basic dyed.
Biological Properties	
Effects of fungi and molds:	Highly susceptible to attack by mildew.
Effects of insects:	Starched cottons are attacked by silverfish.
Flammability Behavior	Burns rapidly. Smoldering red afterglow.
Electrical and Thermal Conductivity	Good heat conductor.

2.1 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.

2.2 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.

2.3 Maintenance

With its hydrophilic nature, cotton is susceptible to water-borne 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.

Concept of Cellulose Cross-linking

The crease of cellulosic fabrics depends on the structural characteristics of the cellulosic fibers. The amorphous regions are significant for the physical and chemical properties. Certain configurations of the fiber are stabillized by hydrogen bonds and Van der Waals forces. Because of the reduced forces binding neighboring cellulose chains together, forces arising during creasing can cause the displacement of the cellulose chains and the binding forces will be insufficient to pull the cellulose molecules back to their original positions after the creasing forces have been removed (Tesoro, 1985). 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. With stable covalent crosslinks, the stress-induced slippage of polymer chains can be inhibited.

Figure 2.4 Resins cross-links between long-chain cellulose molecules.

The essential considerations are the availability and reactivity of hydroxyl groups at C-2, C-3 and C-6 positions of the anhydroglucose units along the molecular chains. The reaction occurs only with hydroxyl groups in the amorphous or accessible regions of the fiber. For the role of substrate in cross-linking 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.

Previous Research in Crease Resistant Finishing of Cotton Fabrics

Treatment of cellulosics with reactive compounds to modify performance properties has been invented for centuries. Cross-linking processes is probably the most important development in textile finishing of this century. Its origin was from the search for method of making cellulosic fabrics resistant to creasing. It has been closely associated with new concepts expressed by terms such as durable press, minimum-iron, non-iron, smooth drying, easy-care and wash-and-wear.

The crease-resist process was firstly developed in the laboratories of Tootal Broadhurst Lee Co. Ltd., of Manchester, England in 1929. The process was begun by padding the fabric with a solution of a water-soluble urea-formaldehyde precondensate and an acid catalyst, then drying and finally curing by heating the fabric to 130°C (Whewell, 1984). The treated fabrics, especially from regenerated celluose were found to have significantly improved its dry crease resistance. It was originally attributed to the penetration of polymer inside the fiber molecules. Subsequently research, however, stressed the importance of cross-linking that occurs. As a result, many cross-linking and polymer based finishes were widely developed.

In 1975, Forg and Payet proposed the method to improve the durable press properties of cellulose fabrics by subjecting to steam in a rising temperature, exposed to formaldehyde and sulphur-dioxide vapors and steam at a higher temperature, allowing the temperature to fall, the air from the outside was circulated to remove steam and free chemicals, the circulating dry heated air in a closed system to raise the temperature of the treated fabrics to around 250°F. At the last

step, cool air and water spray are employed to return the fabrics to room temperature.

Franklin *et al.* (1977) described durable press methods for cellulosic textiles by using methylol reagents and half amides or half salts of dicarboxylic acids. The fabrics were impregnated with an aqueous solution containing a methylol crosslinking agent and either a half amide of 1,2- or 1,3-dicarboxylic acid or a half ammonium, sodium, or potassium salt of a 1,2- or 1,3-dicarboxylic acid. High levels of crosslinking as indicated by high resilience could be achieved after curing.

Bertoniere *et al.* (1977) suggested the durable press process via polymeric N-methylol reagents. To reduce losses in strength and improve abrasion resistance of the fabrics, the process should include (1) application of a solution containing a methylolated urea modified polyethylenimine alone or in combination with other cross-linking agents and a cross-linking catalyst, (2) drying the impregnated fabrics, and (3) curing at elevated temperatures.

To minimize releasing of formaldehyde during drying and uncontrolability excessive degradation of cotton, Jones *et al.* (1982) described attempts to develop techniques that suffer less from these deficiencies. The experiments were focused on developing a version of the gaseous formaldehyde/sulfur dioxide process for continuous processing of fabric. The formaldehyde should be applied with constant and at low moisture content. It would be effective when formaldehyde was applied at a low wet pick-up, as an aqueous solution than as a gas. They suggested that either aqueous or gaseous sulfur dioxide produced high levels of reaction, reproducibly and satisfactory for natural blend fabrics, unfortunately, too severe for 100% cotton. By using metal salt catalysis, although the process at lower levels of

reaction can be controlled, but the strength losses on 100% cotton fabrics are greater than with conventional resin finishing.

Hunsucker *et al.* (1982) have describes a method for reducing released formaldehyde without detracting from or adding to the other properties of finished fabric by substituted alkyl nitro alcohol, ReForm™, textile reactant modifier for 35% of dimethyloldihydroxyethyleneurea (DMDHEU) by active weight. Residual formaldehyde was lowered by 59% when zinc nitrate was used as a catalyst in both the buffered and the nonbuffered systems. They purposed that the nitro alcolol textile reactant modified is suitable for both cotton and blends of polyester/cotton.

Frick and Harper (1982) has presented the work of the Southern Regional Research Center about formaldehyde-free finishes investigations. They described that, in commercial usage, the dihydroxyimidazolidinones (dihydroxyethyleneureas) are the most attractive, but they still have disadvantages on lack economy and effectiveness. It seemed that the best prospects for success remain in aldehyde-amide reaction products. Bis(dihydroxyimidazolidinone) have given slightly improved fabric performances than the mono(dihydroxyimidazolidinones), but it is rather expensive. Adducts of glyoxal and amides other than ureas have had less reactivity than the dihydroxyimidazolidinones. The products which approach to the reactivity of the dihydroxyimidazolidinones are 1-substituted-2,6-dihydroxypiperidines or their ethers, produced by glutaraldehyde and amides reaction.

Studied by Welch and Danna (1982), glyoxal was found to impart a high degree of wrinkle resistance and smooth drying to all cotton print cloth. Aluminum salts, especially aluminum sulfate, were mentioned as effective catalysts. All of

discoloration almost eliminated while increased the durable-press appearance ratings by the addition of ethylene glycol or glycerol to the treating solutions. Different from formaldehyde, glyoxal monomer, dimers, and trimers have structures favorable for chelation by polyvalent metal ions, and such complexes may play a part in the crosslinking reactions. At normal concentrations of glyoxal, the durable-press treatments produced a serious strength losses in the fabric, but it resulted in large improvement of strength retention when using higher concentrations.

Various types of non-formaldehyde cross-linking agents for cotton fabrics, such as glyoxal, polyacetal, bis-hydroxyethyl sulfone, propylene glycol diglycidylether, and glyoxal adducts of urea and its derivatives were studied by Yamamoto (1982). It was found that glyoxal and polyacetal treated fabrics imparted excellent light fastness and good resistant to chlorine bleach, but had a great loss of tensile strength, poor whiteness, and low wet crease recovery angle (WCRA). For finishing with the glyoxal-amide adduct dihydroxyethyleneurea (DHEU), tensile strength, light fastness as well as dry and wet crease recovery angle (DCRA and WCRA) were improved, but had great deterioration of whiteness and no resistance to chlorine bleach. With excellent whiteness, good resistance to chlorine damage, great retention of tensile strength together with the improvement of DCRA and WCRA, dihydroxydimethylethyleneurea (DHDMEU) and dihydroxydiethylethylene-urea (DHDEEU) seem to be the best agents among those types of non-formaldehyde cross-linkers for practical purposes.

Free-formaldehyde finishing agent for fabrics containing cellulose was prepared from equimolar amounts of methyl carbamate and glutaraldehyde by Frick and Harper (1982). Although the reaction product was unstable in dilute aqueous solution, but it could be applied to fabric from concentrated aqueous solution or

could be methylated for application in dilute solution form. The desirable properties such as wrinkle resistance and durable press could be achieved with no release of formaldehyde from the treated fabrics.

By pad-dry-cure techniques, Welch (1988) have studied a formadehyde-free durable press finishing of cotton fabrics by using polycarboxylic acid, 1,2,3,4-butanetetracarboxylic acid (BTCA) and all-cis-1,2,3,4-cyclopentanetetracarboxylic acid, as crosslinking agents. Weak bases, especially mono-sodiumphosphate, have proven to be active catalyst. Satisfactory performance such as, level of reactivity, DP rating, durability to laundering, fabric strength retention as well as low reagent volatility and absence of odor can be achieved when BTCA was used. Moreover, the amount of tetracarboxylic acid required could be decreased by two-thirds by having citric or tartaric acid present as a co-reactant additives.

In 1989 Welch and Andrews discussed developments in nonformaldehyde finishing of cotton with number of polycarboxylic acids in the presence of alkali metal salt of phosphorus-containing inorganic acids. A higher concentration of 1,2,3-propanetricarboxylic acid was needed than was the case for BTCA. When all-cis-1,2,3,4-cyclopentanetetracarboxylic acid was used as the finishing agent, the DP ratings were greatly decreased after laundering. Citric acid is a particularly interesting agent because of its low cost, safe for use and ready availability. However, it produces yellowing when heated with cotton fabric at 180°C.

Formaldehyde in Textiles

Formaldehyde has promoted much discussion over the last few decades. Its presence in consumer products is regarded as extremely critical to health by consumer protection agencies.

The UK Health and Safety Commission's Advisory Committee on Toxic Substances classifies formaldehyde as a severe respiratory irritant. Its vapour causes coughs and temporary short of breath. It is also classified as a severe eye irritant that it will dissolve readily in eye fluids leading to inflammation. At the atmospheric concentration of 4.0 ppm most people's eyes will be affected and respiratory irritation may be observed. Repeated contact of the skin with formaldehyde can cause irritation at the concentrations as low as 2% by weight (Hewson, 1994).

To date, although there is no evidence that formaldehyde has caused cancer in humans, the stricter control of direct skin contact with formaldehyde as well as atmospheric concentration limit are needed to go on. In addition, the tests method must be developed to investigate the fabrics that will cause irritation to human health.

Table 2.2 Limitation of free formaldehyde content allowed on clothing textiles.

Clothing Textiles	Free formaldehyde content (ppm)
Outerwear	300
Worker's protective clothing	300
Shirts	75
Blouses	75
Sport fabrics	75
Nightwear	75
Underwear	75
Textiles for babies and infants	20

Source: BASF.

Previous works have shown that the release of formaldehyde from resin-finished fabrics into the atmosphere during the processes is caused by several factors as the following:

- The choice of resin/catalyst system.

- Inadequate curing of the products during resin treatments.

- No washing-off or operating cleaning procedures after curing.

- Large quantities of products are stored in confined spaces.

- The efficiency of local ventilation.

- The products are stored in the conditions that enhance the rate of formaldehyde release from textiles, such as high temperatures and humidities.

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 curing (Pratuangtip Panbumrung, 1991).

1. Pad-Dry-Cure Process

This process, the fabric is padded with 80-100% wet pick-up in the finishing solution containing crosslinking agent and catalyst. After padding, the fabric is then dry at 85-100°C and cured at the temperature higher than 140°C.

In the drying and curing steps, the fabric is normally fixed on the stenter in order to control the dimensions (necessary for smooth drying).

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 more degraded due to the 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 soon as the strong acid catalyst is added.

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 $120^{\circ}C$ for a short period until the moisture content is reduced to 3-5% from the initial level (after padding). Finally, the fabric is neutralized with sodium carbonate solution.

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 cross-linking 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.

5. Wet Fix Process

Wet fix is the two-step process. In the initial step, the reaction will occur at room temperature and the second step is then applied after the resin deposition.

The fabric is padded with cross-linking agent in acidic condition and batched at room temperature for 12-24 hours. In the second step, the fabric is reactivated with catalyst, for example magnesium chloride. The fabric is then dried at 60°C for 4 min and cured at 160°C for 4 min.

Crease Resistant Finishing Agents for Cotton Fabrics

1. Cross-Linking Agents

A fiber cross-linking agent is a chemical compound that can form cross-links with fibers like cellulose to improve the aesthetics and crease recovery of fabrics and to improve fabric appearance after washing, laundering or during wear.

1.1 Resin Finishes

Resin finishing is essentially based on drying into the textile material an aqueous solution of a resin precondensate and then heating the fabric to promote conversion within the fibers of the water-soluble precondensate into a fully formed resin which can resist removal in subsequent laundering. It is also possible for these resin particles to combine chemically with adjacent cellulose molecules and so cross-linking which give the fibers a more rigid structure will be taken place.

The normal agents used for cross-linking cellulose are the polymethylol compounds of organic amides, produced by reacting together formaldehyde and the organic amide (Mark, Wooding and Atlas 1971).

1.1.1 Urea-Formaldehyde

The first polymethylol amide used to produce crease resistance was formed by condensing formaldehyde with urea in a ratio of 1.6 molecules of formaldehyde to 1 molecule of urea. The resulted precondensate solution was a mixture of mono-methylolurea (1) and dimethylolurea (2).

$$H_2NCONH_2 \; + \; CH_2O \; \rightarrow \; H_2NCONHCH_2OH$$
$$(1)$$
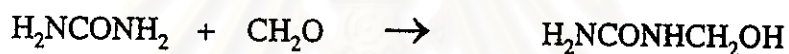
$$(1) \; + \; CH_2O \; \rightarrow \; HOCH_2NHCONHCH_2OH$$
$$(2)$$

Figure 2.5 Urea-formaldehyde reaction.

Although good wash-and-wear performance can be obtained by the use of such precondensates, It has been observed that when finished cotton or rayon fabrics are subsequently bleached with hypochlorite, a considerable amount of active chlorine will be absorbed by this resin and causes severe tendering of the fabric.

1.1.2 Melamine-Formaldehyde

In order to overcome the chlorine-retention problem the United States resin manufacturers introduced methylolmelamines to the textile industry.
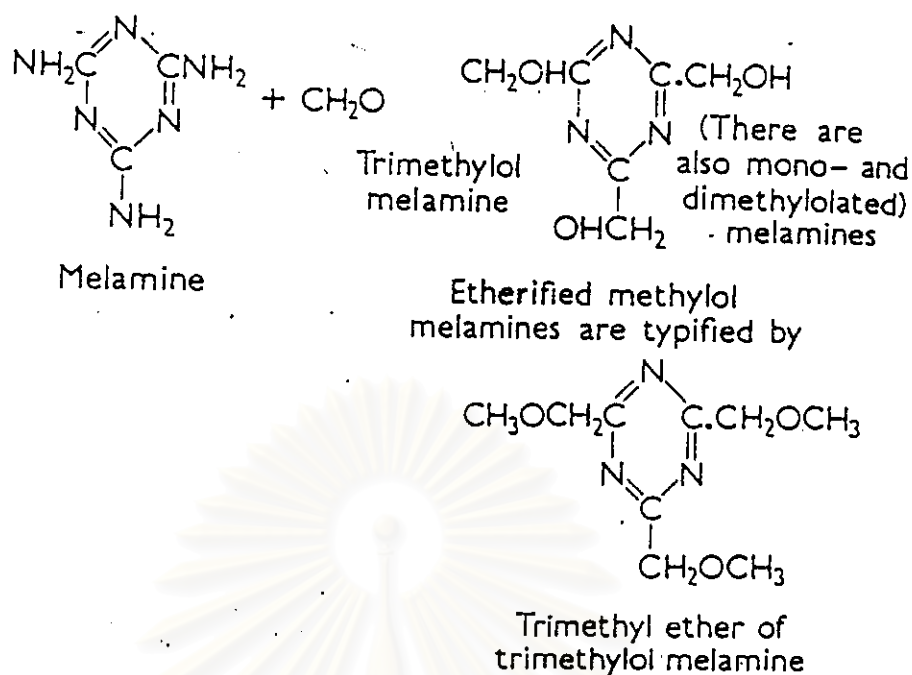
Figure 2.6 Melamine-formaldehyde resin preparation.

Unfortunately, white fabrics finished with melamine-formaldehyde resins, though resistant to tendering by chlorine, become yellow during bleaching. Although the yellow coloration can be removed by giving the fabric an antichlor treatment, this added complication to the laundering treatment did not find ready acceptance. Moreover, it is found that resins such as those obtained from urea and melamine are fairly easily decomposed into their components by treatment with a hot aqueous solution of a strong acid such as hydrochloric acid (Hall, 1966).

1.1.3 Tetramethylacetylenediurea

The earliest attempt to produce a cross-linking reactant that did not contain free NH-groups and would not therefore absorb chlorine was probably the production of tetramethylolacetylenediurea. This is produced by the reaction of urea, glyoxal, and formaldehyde to form first acetylenediurea (1) and then tetramethylolacetylenediurea (2).
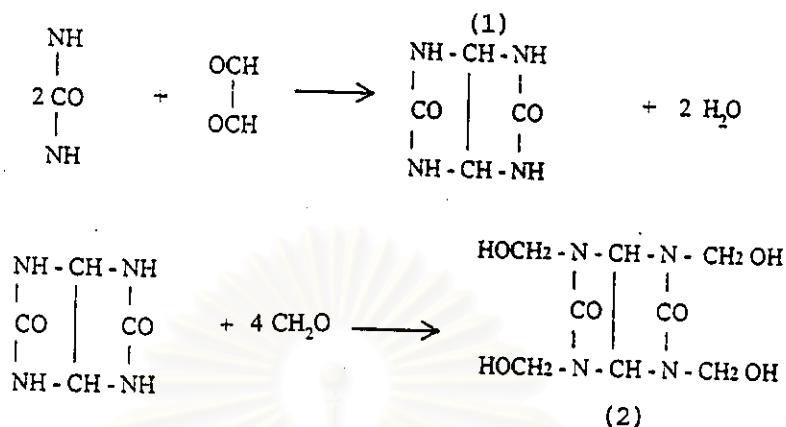
Figure 2.7 Synthetic reaction of tetramethylolacetylenediurea.

However, like most glyoxal-urea product, it tenders to produce a yellow coloration when applied to fabric. Although this is sometimes acceptable in the case of dyed or printed fabrics, it was not considered acceptable for white wash-and-wear shirtings.

1.1.4 Dimethylolethyleneurea (DMEU)

Dimethylol cylic ethyleneurea is prepared by heating together urea and ethylenediamine and subsequently treating the ethyleneurea reaction product with formaldehyde to give the dimethylol derivative.

Cyclic ethylene urea   Dimethylol ethylene urea
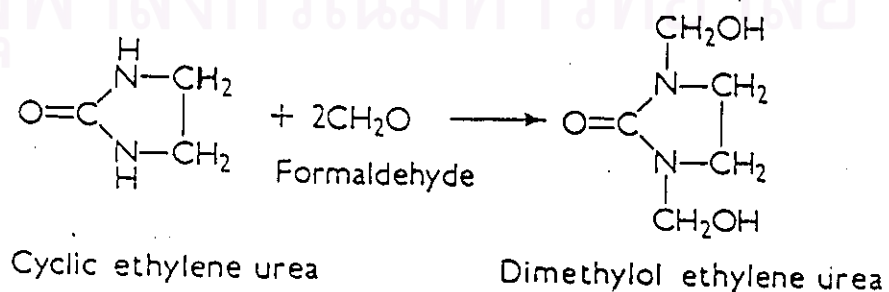
Figure 2.8 Preparation of dimethylolethyleneurea.

Since this compound has only two methylol groups and no free NH-groups, it cannot form a thermosetting resin and would not absorb chlorine. Furthermore, it can react with cellulose only to cross-link two neighboring cellulose chains. It is extremely effective in producing excellent crease resistance and wash-and-wear properties. However, it has some serious disadvantages that it causes a marked deterioration in the lightfastness of many direct and reactive dyestuffs and from its low hydrolysis stability, free formaldehyde can be released from DMEU-treated fabrics. Over the years the use of DMEU has decreased.

1.1.5 Urons

Urons are produced by the reaction in methanol solution of formaldehyde and urea in 4:1 ratio. The resulting solution of tetramethylolurea is then refluxed under controlled pH to cause cyclization and etherification of the methylol groups.
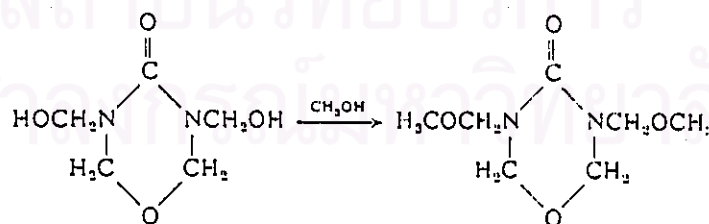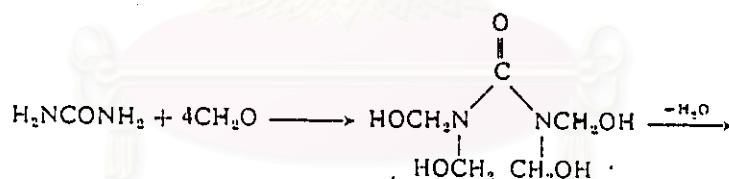

Figure 2.9 Preparation of urons.

As with DMEU, it is not possible to ensure 100% cross-linking during the curing operation, and subsequent multiple laundering as well as hypochlorite bleaching process. However, the decay in resistance to chlorine damage is slower than those obtained from DMEU finish.

1.1.6 Triazones

Triazones are produced by making tetramethylolurea in aqueous solution and closing the ring by reaction with a primary amine.
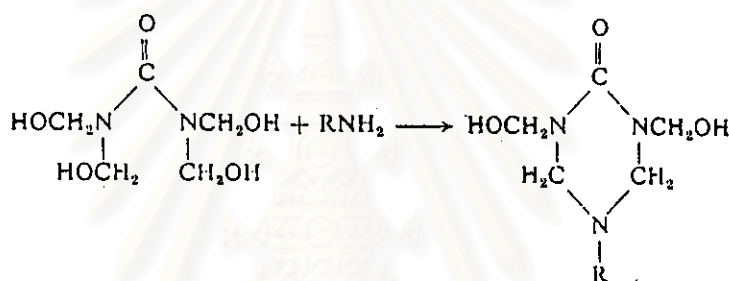

Figure 2.10 Triazones preparation.

Triazones are extremely effective cellulose reactants, have excellent chlorine resistance when catalyzed with metal salts, and can produce excellent smooth-drying effects on cotton fabrics even after machine washing and spin drying. Unfortunately, triazones posses the disadvantages that if fabrics are not given a hot alkaline wash after curing, 'fish' odors are often produced during storage or in subsequent wear.

1.1.7 Dimethyloldihydroxyethyleneurea (DMDHEU)

Since the early 1960's, dimethyloldihydroxyethyeneurea has achieved widespread use. It was first produced from glyoxal, urea and formaldehyde.
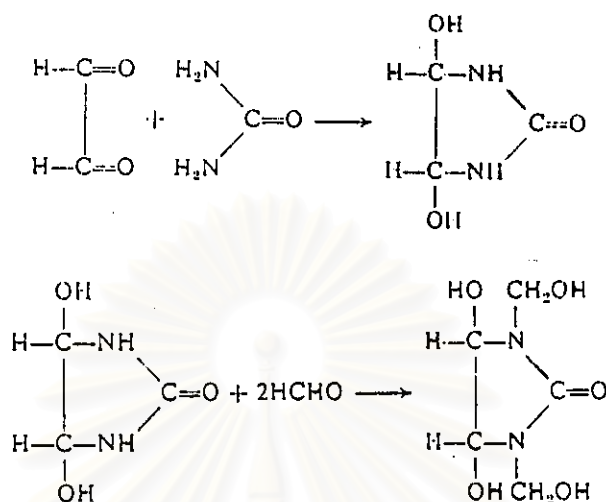
Figure 2.11 Synthetic reaction of DMDHEU.

Although DMDHEU is widely used in the production of durable press garments, its use results in fabrics that are not only chlorine retentive but also prone to some degree of yellowing. This is a disadvantage common to all reactants derived from glyoxal, and though the degree of yellowing is not a major problem in the finishing of colored goods, it is sufficient to cause dissatisfaction with white fabrics. Moreover, it can produce a formaldehyde release because of the unreacted N-methylol group.

Even though DMDHEU releases less free formaldehyde than DMEU, it is still a problem like the other formaldehyde-based reactants.

1.1.8 Methylol Carbamates

The compounds are based on esters produced by the reaction of methanol or ethanol with urea. It posses only one NH_2-group that only two

molecules of formaldehyde can be added per ester molecule to produce the dimethylol carbamate.

$$C_2H_5OCONH_2 + 2CH_2O \longrightarrow C_2H_5OCON \begin{array}{l} CH_2OH \\ \\ CH_2OH \end{array}$$
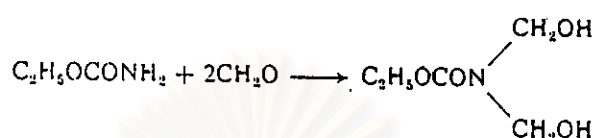
Figure 2.12 Preparation of dimethylol carbamate.

Dimethylol methyl carbamate is reported to be a carcinogen and because of this has not been widely used in textile finishing. However, dimethylol ethyl carbamate is reported to be free of this danger and is gaining increasing use in wash-and-wear finishing. Although the methylol carbamates have good resistance to chlorine, to hydrolysis and cause less yellowing, they still have problem of formaldehyde release.

1.2 Low Formaldehyde Finishes

According to the chemical reactions of N-hydroxymethyl compounds, free formaldehyde release on the finished goods is unavoidable. Figure 2.13 shows that not only the occurrence of cross-linking reaction with cellulose (a), but also self-condensation (b), the cleavage (c) and the hydrolysis (d) of the finishing agent.
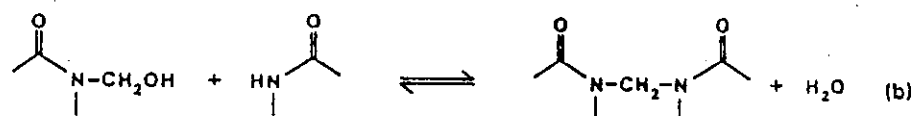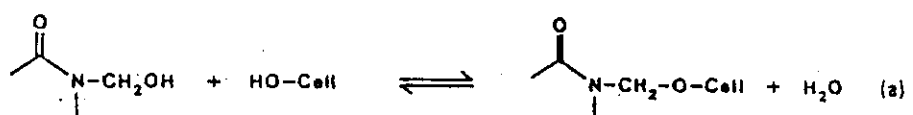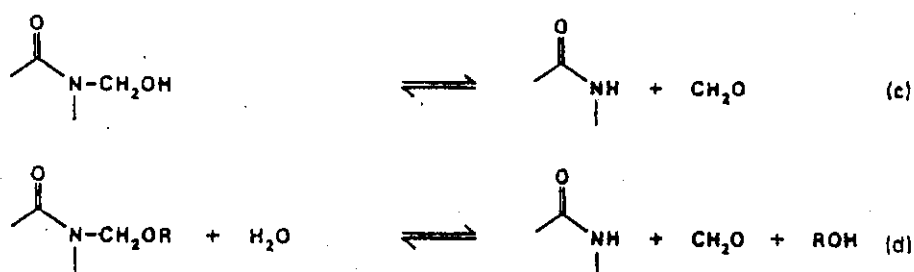
Figure 2.13 Reactions of N-hydroxymethyl compounds (Petersen, 1985).

The more stable compounds, N-alkoxyethyl derivatives, have been developed by etherify the N-hydroxy-methyl groups with alcohols, especially with water-soluble alcohols such as methanol. Such compounds are stable at normal or slightly elevated temperatures to alkaline and neutral media but can be hydrolysed under acidic conditions. Free-formaldehyde released from N-alkoxy methyl compounds finishes is less than those from unetherified hydroxy methyl compounds.

To improve the stability to hydrolysis under acidic condition and lower the formaldehyde value, more stable compounds such as dimethoxymethyl-4-methoxy-5,5-dimethylpropyleneurea and dimethoxymethyl compounds of methoxyethyl-carbamate have been invented (Figure 2.14).
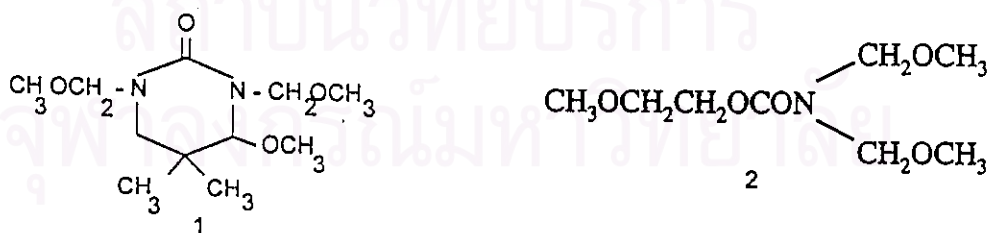

Figure 2.14 Structure of dimethoxymethyl-4-methoxy-5,5-dimethylpropyeneurea (1) and dimethoxymethyl compounds of methoxyethyl carbamate (2).

From investigations toward formaldehyde-free finishes, the adducts of urea and glyoxal have been reported to be the most attractive. The primary compound that seems to be the best alternative to formaldehyde adducts and has been available commercially is 4,5-dihydroxy-2-imidazolidinone derivatives (R= H, CH_3) (Figure 2.15). However, the analog which R= CH_3 (4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone or DHDMI) is still lack of effectiveness and expensive because it needs to be pure enough to avoid discoloration of fabric. The analog without the 1,3-methyl substituents is less expensive, however it causes severe discoloration problem (Frick and Harper, 1982).

The well-known and commercially important compound that has been presented since 1954 is dimethyloldihydroxyethyeneurea or DMDHEU (R= CH_2OH) which attains good properties, especially high DP value, low shrinkage and high crease recovery angle. Base on the DMDHEU structure, lower formaldehyde release can be success by etherify the hydroxyl groups with methanol to give dimethoxymethyl dimethoxyethyleneurea or DMDMEU, however, the DP rating is poorer than DMDHEU. When the hydroxyl groups of DMDHEU were etherified with diethylene glycol (Figure 2.16), very low formaldehyde and good DP performance can be achieved but it still has limitation with high cost.
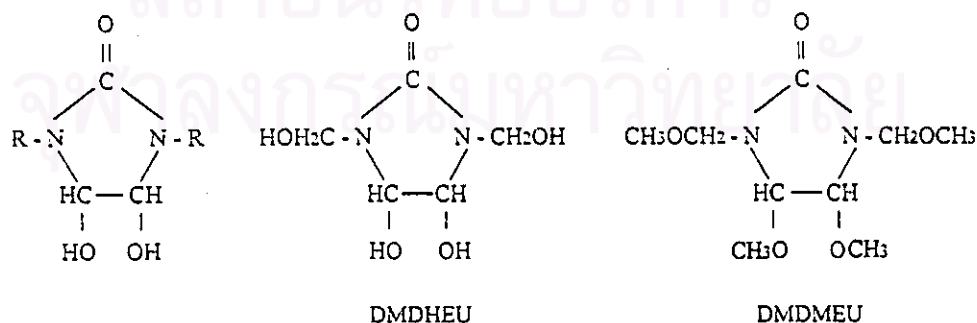

Figure 2.15 4,5-Dihydroxy-2-imidazolidinone derivatives.
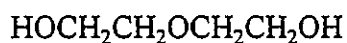
$$HOCH_2CH_2OCH_2CH_2OH$$

Figure 2.16 Diethylene glycol

Polyfunctional carbamates is another class of low formaldehyde crosslinking agents developed for easy care finishes of polyester/cotton fabrics. These products have higher molecular weight than the hydroxymethyl compounds of cyclicureas and are suitable for the swelling and cross-linking cellulose under high-temperature curing conditions. Moreover, good absorbency, the significant factor to be considered for fabrics that are to be printed, can be obtained with this finish (Table 2.3).

Table 2.3 Comparison of the finishing properties of dihydroxymethyl-4,5-dihydroxyethyleneurea and polyfunctional carbamate (Petersen, 1985).

Properties	DMDHEU	Polyfunctional Carbamate
DP Rating	3.8 - 4.0	3.8 - 4.0
Shrinkage	(1.0-1.5 x 0.3-0.8)%	(1.0-1.5 x 0.3-0.8)%
Softener in the Padbath	Requires softener	Does not require softener
Suface Hand	Full, somewhat harsher hand without the aid of a softener	Smooth, vibrant hand
Pigment Printing on Finished Fabrics	Marginal acceptance of color value and fastness properties	Maintains bright color value, excellent definition of prints and good fastmess properties
Absorbency (drop method)	3 min	5 - 10 sec
Chlorine Scorch Resistance	Marginal acceptance	Excellent
Fabric Whiteness and Shade Retention	Good	Good
Accelerator Abrasion Loss	10 - 15 %	4 - 7 %
Resistance to Soil Redeposition	Poor	Excellent

1.3 Non-Formaldehyde Finishes

As a result of human health risk in continued exposure to formaldehyde vapor, the desirability of finding cross-linking agents to be used in place of formaldehyde or N-methylol agents that ralease formaldehyde has increased.

For practical use in easy care finishing of cotton fabrics, a cellulose cross-linking agent must meet a number of significant requirements (Welch, 1988).

- The agent and its catalyst must be non-yellowing to cotton at all temperatures upto $210^{\circ}C$.

- The agent must be of low toxicity, odorless, nonvolatile and non-irritating to skin at the concentrations present in treated, unwashed fabric.

- The agent must be water soluble, but after finishing, it must withstand a large number of laundering during normal usage over a period of several years.

- The agent should not increase the fabric stiffness.

- The agent nust be simple to manufacture from inexpensive and abundant starting materials.

Various types of reagents such as higher aldehydes, diepoxides, polyhalides, or activated divinyl compounds were used as cross-linkers by forming two or more ether linkages between each molecule of the cellulose and reagent. However, the high cost, toxicity, and yellowing problems indicated that they were not suitable for practical use.

Recently, formaldehyde-free durable press (DP) finishes for cotton fabric have been developed by utilize polycarboxylic acids as the cross-linking agent. These acids react with cellulose hydroxyl groups to form ester linkages connecting adjacent cellulose chain in a 3-dimensional network inside the cotton

fibers. The recently improved catalysts for polycarboxylic acid finishing, alkali metal salts of phosphorus containing inorganic acids, have produced non-formaldehyde cottons with performance comparable to that from the conventional formaldehyde containing agents. As seen in Figure 2.17, such catalysis involves a mechanism of anhydride intermediate formation which requires at least three carboxyl groups present in each acid molecule.
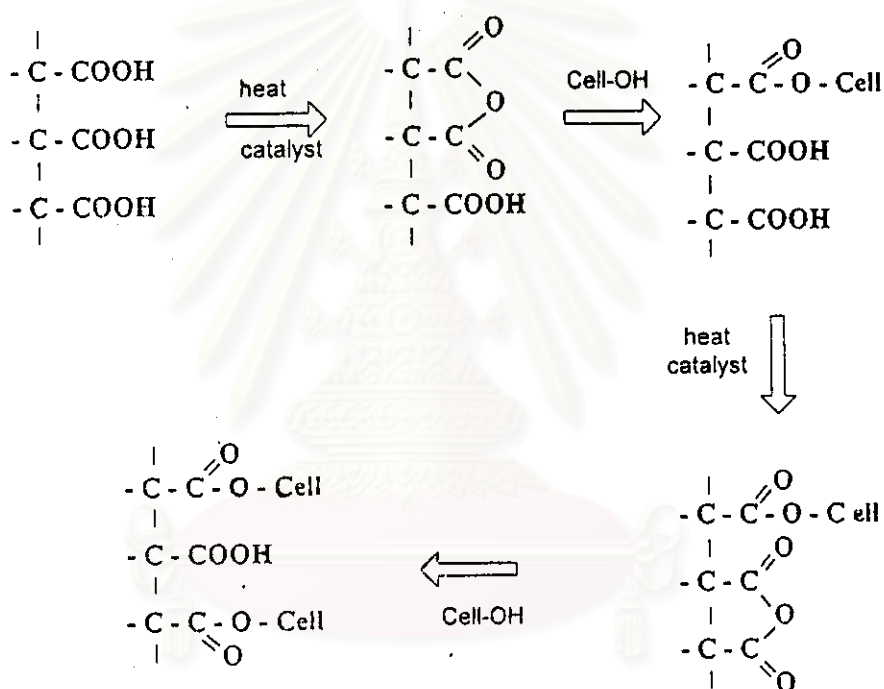
Figure 2.17 Formation of ester cross-links in cotton (Welch, 1994).

A number of polycarboxylic acids have been shown to impart high levels of wrinkle resistance and smooth drying to cotton fabrics, such as 1,2,3,4-butanetetracarboxylic acid (BTCA), citric acid (CA), 1,2,3-propanetricarboxylic acid (Tricarballylic acid) and propenetricarboxylic acid (aconitic acid), etc. However, the to date most interesting acids that found to be suitable for DP finishing are BTCA and citric acid.

1.3.1. 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 found to be the most effective cross-linking 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 (Welch, 1988).

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, many researchers as well as Welch and Andrews (1989) 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 2.4 shows the effect of increasing the concentration of BTCA with sodium dihydrogenphosphate catalysis. Very high DP ratings were obtained at high BTCA concentrations while its effective results approached to the conventional DMDHEU-MgCl$_2$ treatment.

By adjusting the curing times to impart 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 2.5.
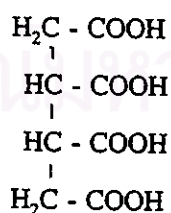
$$
\begin{array}{c}
H_2C - COOH \\
| \\
HC - COOH \\
| \\
HC - COOH \\
| \\
H_2C - COOH
\end{array}
$$

Figure 2.18 Structure of BTCA.

Table 2.4 BTCA treatments with NaH_2PO_4 catalysis without a fabric softener[a] (Welch and Andrews, 1989).

BTCA Conc	DP Rating	WRA (w+f) Conditioned	Tearing Strength Retention	Breaking Strength Retention
12%	4.8	286*	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/MgCl₂-Citric Acid[b]	4.0	261	42	31

[a]BTCA/NaH_2PO_4 mole ratio: 1/1.5; wet pickup: 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% $MgCl_2.6H_2O$ with $MgCl_2$/ citric acid mole ratio of 20/1. Cured at 160C/ 3 minutes.

Table 2.5 Fabric properties as a function of cure temperature and time[a] (Welch and Andrews, 1989).

Cure Temp	Time	DP Rating[b]	WRA (w+f) Cond	Wet	Breaking Strength Retained	Tear Strength Retained	Stiffness Bending Moment[c]
180C	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 pickup owf with 6.3% BTCA, catalyst and 1.0% polyethylene, then dried at 85C for 5 minutes, cured at 180C for 90 seconds, rinsed at 50C for 30 minutes and dried at 85C for 5 minutes. [b]After 5 laundering cycles. [c]Inch-pound, x 10^4.

Shade change on dyed fabric finished with BTCA and phosphorus catalysts was illustrated by Brodmann (1990). 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 (1994). Aromatic N-heterocyclic compounds, such as imidazoles and its derivatives, as well as mono-or disodium salts of unsaturated carboxylic acids, such as fumaric, maleic, and itaconic, have been presented to be the considerable catalysts for the esterification reaction of BTCA.

Although BTCA is found to be the most effective acid for the durable press finishing of cotton, but it is very expensive and its safety in the environment is assumed. To be considered for practical use, large amount of research projects have focused on modifying the BTCA system by using additives. Welch proposed the decrement of BTCA concentration by using alpha-hydroxy di- or tricarboxylic acid, as a co-reactant additive (Welch, 1988). 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 (Blanchard, Reinhardt and Andrews, 1991).

1.3.2. Citric Acid (CA)

Not only the fact that citric acid have been approved its safety for food use, its low cost and ready availability have also encouraged itself to be an interesting agent. Unlike succinic acid which has only two carboxyl groups and can not undergo the cross-linking reaction with cellulose, citric acid, an alpha-hydroxy acid, has three adjacent carboxyl groups available to esterify cotton at high

temperature by forming cyclic anhydride as cellulose reactive intermediates (Andrews, Welch, and Trask-Morrell, 1989).
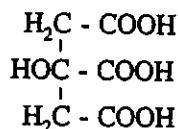
$$H_2C - COOH$$
$$HOC - COOH$$
$$H_2C - COOH$$

Figure 2.19 Structure of citric acid.

Similar to BTCA finishing, use of alkali metal salts of phosphorus-containing inorganic acids has produced satisfactory properties of fabric in treatment with citric acid. Their effects on cotton fabric compared with the finishes from formaldehyde based, DMDHEU and the nitrogenous nonformaldehyde agent, DHDMI were reported by Andrews, Blanchard, and Reinhardt (1993) in Table 2.6. Although the CA/sodium hypophosphite system, which is considered to be the most suitable catalysts, does not impart appearance properties as good as those from DMDHEU finishes, its efficiency is better than the DHDMI system.

Table 2.6 Fabric properties from treatments with 7% citric acid and sodium salts of inorganic phosphorus-containing acids[a] (Andrews, Blanchard and Reinhardt, 1993).

Catalyst	CIE Whiteness Index[b]	Add-On	Durable Press Rating	Conditioned Wrinkle Recovery Angle, w+f	Breaking Strength (warp)
4.5% Na$_2$HPO$_4$	71	7.6%	3.0	238	37 lb.
4.4% NaH$_2$PO$_4$.H$_2$O	41	3.3	3.5	249	25
4.1% NaH$_2$P$_2$O$_7$	21	7.3	3.5	259	29
6.5% NaH$_2$PO$_2$.H$_2$O	56	5.6	3.5	268	31
DMDHEU control[c]	67	4.0	4.0	261	24
DHDMI control[c]	48	-	3.0	249	25
Untreated	87	-	1.0	177	56

[a]The citric acid-finished fabrics were cured at 180C for 90 seconds. [b]CIE Whiteness index was measured on unwashed fabics. [c]DMDHEU and DHDMI were used in 5% solids pad bath concentrations with 1.8% 20/1 MgCl$_2$.6H$_2$O/CA catalyst.

Andrews (1990) has studied the effect of citric acid to catalyst ratio and the concentration of acid for the citric acid/sodium hypophosphite system on fabric properties as shown in Table 2.7 and Table 2.8 subsequently.

Table 2.7 Fabric properties from treatments with 7% citric acid and sodium hypophosphite over a range of citric acid / sodium hypophosphite ratios[a] (Andrews, 1990).

CA / $Na_2H_2PO_2.H_2O$ Ratio	CIE Whiteness Index[b]	Durable Press Rating	Conditioned Wrinkle Recovery Angle, w+f	Breaking Strength (warp)
1 : 1	41	3.3	249	19 lb.
1 : 1.5	56	3.5	268	31
1 : 1.75	61	3.5	264	31
1 : 2	64	3.5	261	28

Fabric were cured at 180C for 90 seconds. Whiteness index was measured on unwashed fabric.

Table 2.8 Influence of agent concentration on properties of fabrics finished with citric acid and sodium hypophosphite in agent to catalyst ratios of 1 : 1.75 and 1 : 2[a] (Andrews, 1990).

Citric Acid Concentration	Add-On	CIE Whiteness Index U[b]	W[b]	Durable Press Rating	Conditioned Wrinkle Recovery Angle, w+f	Breaking Strength (warp)
Citric acid / $NaH_2PO_2.H_2O$ = 1 : 1.75						
5%	4.1%	67	73	3.5	256	34 lb.
7	6.0	61	70	3.5	264	31
9	7.4	50	65	3.5	260	30
12	9.5	30	53	3.5	262	29
Citric acid / $NaH_2PO_2. H_2O$ = 1 : 2						
5	3.9	71	75	3.5	255	34
7	5.8	63	71	3.5	261	26
9	7.6	55	68	3.5	264	28
12	9.7	30	56	3.5	257	29
Untreated	-	83	-	1.0	194	56

Fabric were cured at 180C for 90 seconds. [b]U = Unwashed fabric; W = Fabric laundered once.

The preferable properties appeared to be at a ratio of 1 : 1.5. Whiteness and strength properties tended to decrease as citric acid concentration was increased. However, the discoloration problem was caused by mostly from the unreacted finish residues, not in the fabric, so the aftertreatment procedure such as washing can recover the whiteness thereof.

Andrews has also investigated the influence of curing temperature on fabric properties (Table 2.9) and concluded that when higher temperature-shorter time curing was used, the whiteness indices were generally lower but the higher DP ratings can be obtained.

Table 2.9 Effect of high temperature curing on fabric properties from treatments with 7% citric acid (Andrews, 1990).

Curing Temp*	CIE Whiteness Index		Durable Press Rating		Conditioned Wrinkle Recovery Angle.		Breaking Strength (warp)	
	60	90	60	90	60	90	60	90
				6.5% $NaH_2PO_2.H_2O$				
170C	74	69	3.5	3.5	247*	253*	32 lb.	30 lb.
180	66	64	4.0	4.0	247	252	32	34
190	59	-	4.0	-	262	-	27	-
200	51	- .	4.3	-	270	-	27	-
				4.2% $NaH_2PO_2.H_2O$				
170	69	61	2.8	3.3	195	219	32	30
180	58	38	3.5	3.8	222	239	29	27
190	60	35	4.5	4.5	261	267	31	27
200	44	-	5.0	-	267	-	27	-

*Cure times were either 60 or 90 seconds.

The information of the cellulose fabric finished with citric acid can be determined in both qualitative and quantitative by the use of infrared spectroscopy as presented by Morris, Andrews, and Catalano (1994) in Figure 2.20. The presence of acid/ester carbonyl peak at 1730 cm^{-1} is the characteristic of esterified cotton. The lower concentrations (2-8%CA) show an increase in the size

of carbonyl peak as increasing the citric acid concentration. In quantitative analysis, the peak at 1730 cm^{-1} and the CH$_2$ bending peak at 1373 cm^{-1} will be helpful for plotting calibration curve by using peak ratio method which has been applied from BTCA system.
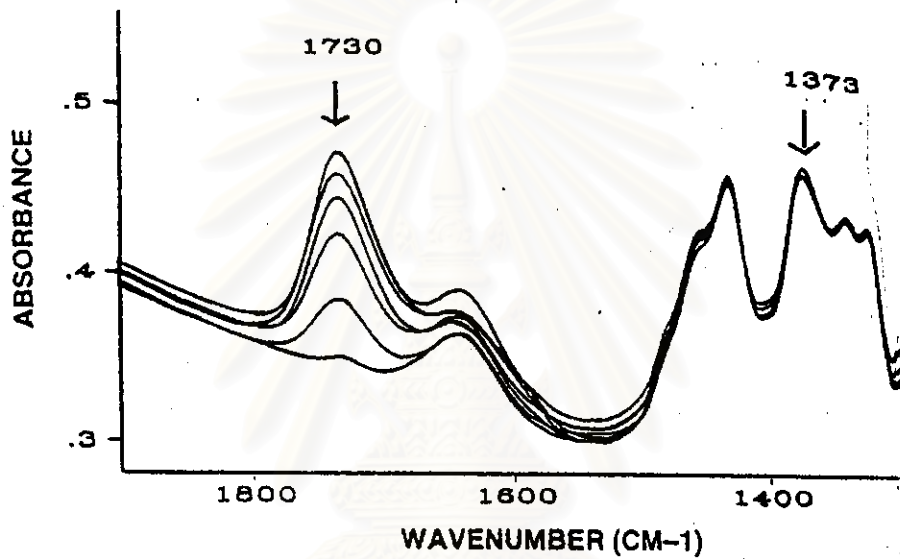

Figure 2.20 Infrared spectra of carbonyl region of untreated cotton fabric and of cotton fabric treated with six different levels of citric acid. (Morris, Andrews and Catalano, 1994)

Since yellowing problem is troublesome for the practical use of citric acid, researchers have recently proposed modified system by using additives, for instance hydroxylalkyl amine or quartemary hydroxylalkyl ammonium salt (Andrews, 1990).

2. Catalysts

The catalyst 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 cross-linking 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 is 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 cross-linking system. The common types of catalysts for pad-dry-cure finishing process are as the following:

2.1 Ammonium Salts

Although ammonium salt catalysts were developed for use with urea-formaldehyde precondensate, but they are effective enough for the majority of methylol cross-linking agents. Ammonium phosphate, ammonium dihydrogen phosphate, ammonium chloride and ammonium sulfate are the kinds of salts that have been widely used. To use these catalysts, however, can result the finished fabrics possessing unpleasant fishlike odors or developing such odors in subsequent storage or wear. The odor occurrence is due to the formation of trimethylamine resulted by curing at too high temperature and too long time. To solve this problem, the finished fabric may be subjected into a wash with hot soda-ash solution, but this treatment is only suitable for fabrics that are to be manufactured into wash-and-wear garments without pressed creases.

2.2 Amine Salts

Instead of the ammonium salts it is possible to use organic amine salts such as ethanolamines, triethanolamine hydrochloride and the hydrochloride of 2-amino-2-ethyl-1-propanol which can improve stability of the precondensate bath and are much less tendency to odor formation. Although they do not entirely eliminate odor formation, but they have been widely used in the production of fabric for wash-and-wear products that do not contain pressed creases.

2.3 Organic Acids

The organic acids, for example tartaric acid, citric acid, maleic acid, etc., are found to be the effective catalyst for this purpose. Tartaric acid was invented in the early works to be used in place of boric acid in the methylolurea finish. With the necessary to cure the fabric at the very high temperature and the fairly high dissociation constant of tartaric acid caused the limitation in practical use.

2.4 Metal Salts

With the concept of the required catalyst properties that the catalyst should has little or no substantial acidity at normal temperatures but subsequently develops substantial acidity at elevated temperatures during curing, metal salts are among the catalyst possessing such characteristic. Shih and Rowland (1982) has compared the effects of three commonly used catalysts in the treatment of cotton with DMEU. They found that the retention of strength and abrasion resistance decreased in the order: zinc nitrate > magnesium chloride > aluminum chlorohydroxide. With zinc nitrate catalysis, the lowest molecular degradation of cellulose can be achieved.

2.5 Alkaline Catalysts

Besides acid catalyst, alkaline catalysts, such as sodium hydroxide, sodium carbonate, lithium carbonate etc., can also produce the treated fabric with crease resistant improvement. Andrews, Welch and Trask-Morrell (1989) mentioned that pH alone is not important in the esterification. Although the BTCA-sodiumhydroxide and BTCA-sodium carbonate pad baths have the same pH, the fabric finished with the two systems have obviously different performance levels. Even though they give rather great advantages, such as dimensional stability, more retention of strength and higher elasticity than the acid-catalysis cross-linking, the whiteness of fabrics finished with alkaline catalyst remains poor (Welch and Andrews, 1989).

2.6 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 2.10, 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 (Welch and Peters, 1993).

Sodium dihydrogen phosphate is less expensive and with BTCA or PTCA does not cause any shade changes problem (Brodmann, 1990). Sodium dihydrogen phosphate , a fairly active catalyst, has a tendency to produce a

faint yellowing in cotton during heat curing, however, the satisfactory whiteness can be obtained with the rinsing process.

Table 2.10 Catalysts of DP finishing with polycarboxylic acids (alkali metal phosphates, phosphites, and hypophosphites) (Welch, 1994).

Decreasing order of effectiveness: ---------->		
1	2	3
NaH_2PO_2	KH_2PO_2	Na_2HPO_4, K_2HPO_4
Na_2HPO_3	NaH_2PO_4	$Na_2H_2P_2O_7$
	LiH_2PO_4	$Na_4P_2O_7$
		$Na_5P_3O_{10}$
		Na_3PO_4
		Na_2PO_3F

Various sodium salts of alpha-hydroxy acids , such as citric, malic, and tartaric acids have been investigated as alternative systems (Welch and Peters, 1993) for BTCA finishing. Moreover, sodium salts of saturated carboxylic acids, such as formic, oxalic, malonic, succinic, glutaric ,and adipic acid were also studied. Choi and Welch (1994) 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 (1994) demonstrated their use as alternative to phosphorus-containing catalysts for esterification and cross-linking of cellulose with BTCA.

2.7 Mixed Catalysts

Mixed catalysts have been used in cross-linking of cotton fabrics for many years in order to modify appearance properties and minimize formaldehyde release. They allow a reduction in the catalyst concentration, curing temperature, and/or curing time. The mixed catalysts systems containing combination of a metal salt and organic acid, such as magnesium chloride with citric acid or tartaric acid, zinc nitrate with glycolic acid etc., were found to be highly reactive catalysts. Catalysts systems containing aluminium chlorohydroxide and phosphoric acid were effective in pad-dry-cure process with several types of finishing agents, such as hydroxymethyl compounds of ureas, cyclic ureas, and carbamates (Petersen, 1985).