การประยุกต์เอนไซม์ในกระบวนการเตรียมด้ายและผ้าฝ้าย

นายธีระดล รุ่งเรืองกิจไกร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ภาควิชาวัสดุศาสตร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2542

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APPLICATIONS OF ENZYMES IN COTTON YARN AND FABRIC PREPARATION PROCESSES

Mr. Theeradol Rungraungkitkrai

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for the Degree of Master of Science in Applied Polymer Science and Textile Technology

Department of Materials Science

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By	Mr. Theeradol Rungraungkitkrai
Department	Materials Science
Thesis Advisor	Usa Sangwatanaroj, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

..... Dean of Faculty of Science

(Associate Professor Wanchai Phothiphichitr, Ph.D.)

THESIS COMMITTEE

..... Chairman

(Associate Professor Khemchai Hemachandra, Ph.D.)

..... Thesis Advisor

(Usa Sangwatanaroj, Ph.D.)

..... Member

(Associate Professor Paiparn Santisuk)

..... Member

(Assistant Professor Kawee Srikulkit, Ph.D.)

บทคัดย่อวิทยานิพนธ์

นายธีระดล รุ่งเรืองกิจไกร : การประยุกต์เอนไซม์ในกระบวนการเตรียมด้ายและผ้าฝ้าย. (APPLICATIONS OF ENZYMES IN COTTON YARN AND FABRIC PREPARATION PEROCESSES) อ. ที่ปรึกษา : ดร.อุษา แสงวัฒนาโรจน์ , 102 หน้า. ISBN 974-334-874-3.

ผ้าฝ้ายทอลายขัดและทอลายสอง ผ้าฝ้ายถักเจอร์ซี่และด้ายฝ้าย ได้ผ่านกระบวนการเตรียมด้วยเอนไซม์และกระบวนการเตรียมที่ใช้อยู่เดิม ตัวอย่างที่ผ่านการลอกแป้งด้วยเอนไซม์อะมัยเลสแสดงการลอกแป้งออกอย่างสมบูรณ์ ตัวอย่างที่ผ่านการกำจัดสิ่งสกปรกด้วยเอนไซม์เพคติเนสให้ความสามารถในการดูดซึมได้เป็นอย่างดี และมีการสูญเสียน้ำหนักต่ำกว่าตัวอย่างที่ผ่านการกำจัดสิ่งสกปรกด้วยกระบวนการที่ใช้อยู่เดิม การกำจัดสิ่งสกปรกทั้งสองวิธี ให้ความสามารถในการขจัดเพคตินได้ใกล้เคียงกัน โดยที่การกำจัดสิ่งสกปรกด้วยเอนไซม์ให้ประสิทธิภาพสูงกว่าเล็กน้อย ความแข็งแรงของผ้าทอลายขัดและด้ายเพิ่มขึ้นหลังจากการกำจัดสิ่งสกปรกด้วยเพคติเนส ในขณะที่ผ้าทอลายสองและผ้าถักเจอร์ซี่มีความแข็งแรงลดลง ผ้าถักเจอร์ซี่ที่ผ่านการกำจัดสิ่งสกปรกด้วยวิธีที่ใช้อยู่เดิม สูญเสียความแข็งแรงเป็น 2 เท่าของผ้าที่ผ่านการกำจัดสิ่งสกปรกด้วยเพคติเนส ตัวอย่างที่ผ่านการฟอกด้วยเอนไซม์กลูโคสออกซิเดส มีค่าดัชนีความขาวเพิ่มขึ้นเกือบ 20 โดยที่ความแข็งแรงลดลงประมาณ 3-13 เปอร์เซ็นต์

ภาควิชาวัสดุศาสตร์ ลายมือชื่อนิสิต.....

สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์ฯ ลายมือชื่ออาจารย์ที่ปรึกษา.....

ปีการศึกษา 2542

AN ABSTRACT

4072489223 : MAJOR APPLIED POLYMER SCIENCE AND TEXTILE TECHNOLOGY
KEY WORD: PREPARATION / TEXTILE / ENZYME / COTTON / PECTINASE / GLUCOSE OXIDASE

THEERADOL RUNGRUANGKITKRAI : APPLICATIONS OF ENZYMES IN COTTON YARN AND FABRIC PREPARATION PEROCESSES. THESIS ADVISOR : USA SANGWATANAROJ, Ph.D. 102 pp. ISBN 974-334-874-3.

Cotton plain and twill weave fabrics, cotton jersey knits and cotton yarn were treated under enzymatic and conventional preparation processes. Samples desized with amylase enzyme show complete sizes removal. Samples scoured with pectinase enzyme provide good absorbency and obtain lower weight loss than conventional scoured samples. Both scouring methods give almost comparable capability of pectin removal with a little higher efficiency in enzymatic scouring. Plain weave fabric and yarn increase in strength after pectinase scouring while twill weave fabric and jersey knits decrease. Scoured jersey knits lose strength twice higher from conventional scouring than from pectinase scouring. Samples bleached with glucose oxidase enzyme obtain whiteness index nearly 20 degree improvement with 3-13% strength loss.

ภาควิชาวัสดุศาสตร์ ลายมือชื่อนิสิต.....
สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์ฯ ลายมือชื่ออาจารย์ที่ปรึกษา.....
ปีการศึกษา 2542

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CONTENTS

Contents (Continued) Page

Contents (Continued) Page

Contents (Continued) Page

TABLES

Tables (Continued) Page

FIGURES

Figures (Continued) Page

DIAGRAMS

CHAPTER I

Introduction

The noncellulosic components in mature cotton fibers are usually found in the surface layers consisting of cuticle and primary cell wall. They contain lipids, waxes, pectins, organic acids, proteins/nitrogenous substances, noncellulosic polysaccharides, pigment matter, and other unidentified substances and they are approximately 10% of the total fiber weight. These surface layers protect the fiber against the environment during growing and lubricate them during yarn spinning. The layers also interfere with further aqueous chemical processing such as dyeing and finishing and need to be removed before such aqueous processing.

Boiling cotton yarn or fabric in sodium hydroxide solution is a conventional scouring process used by the textile industry to improve wettability of cotton and penetration of dyeing solution and finishing agent into cotton. This process involves large quantities of water and energy, and requires special handling of the sodium hydroxide effluent. Conventional bleaching process also involves high energy consumption and produces large amount of toxic wastes. Both processes consume high energy and generate considerable amounts of wastewater, presenting a major problem for the textile industry.

To solve these problems, enzymatic preparation process is one of many choices introducing to the textile wet process. Enzymes are being used in the textile industry mainly for three processes: desizing, stone washing and biopolishing. For many years, amylases have been used to desize fabrics of starch sizing. Cellulases have lately been

developed to replace or supplement some of chemical finishing processes intended for achieving aesthetic effects on cotton products.

The aim of this project was to reduce the amount of toxic effluent generated from the preparation processes, by introducing enzymes into the processes. Lipase, protease, and pectinase enzymes were used as scouring agents and xylanase, cellulase, and glucose oxidase were bleaching agents for the enzymatic scouring and bleaching, respectively. Cotton substrates prepared from conventional and enzymatic preparation processes were tested for properties for a comparison.

CHAPTER II

Literature Survey

2.1 Cotton fiber

Cotton is one of the most important and widely used fiber in the textile industry. It is a unicellular hair collected from the seed of cotton plant. The function of these hairs is to protect the young unripe seed and to assist in its dispersal when it is mature. Raw cotton has a creamy tint off-white color. It is smooth and soft, very absorbent and cool touching when impurities have been removed.

Mature cotton has a flat ribbon-like structure that resembles a bicycle inner-tube when air is removed, varying in width between 12 to 20 micrometer. It is highly convoluted and the number of convolutions varies between 4 to 6 per mm., reversing in direction about every millimeter along the fiber. These characteristics make cotton easy to recognize under both optical and electron microscopes as illustrated in Figure 2.1. Their cross section bean-shape is described as a bilateral structure shown in Figure 2.2.

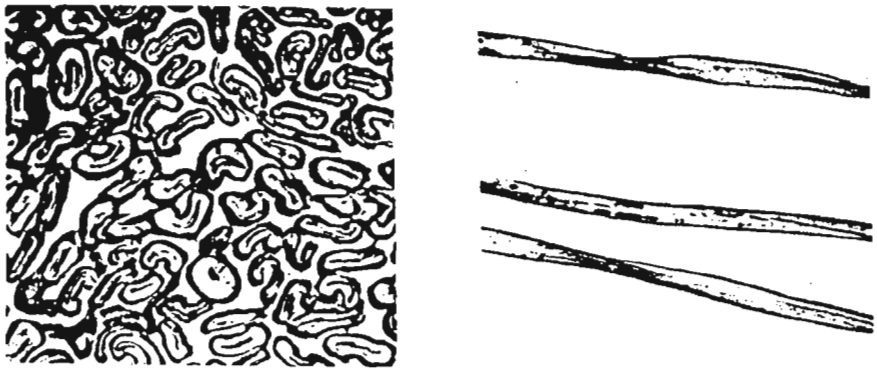


Figure 2.1 Scanning electron micrographs of cross section and longitudinal view of raw cotton fibers.[1]

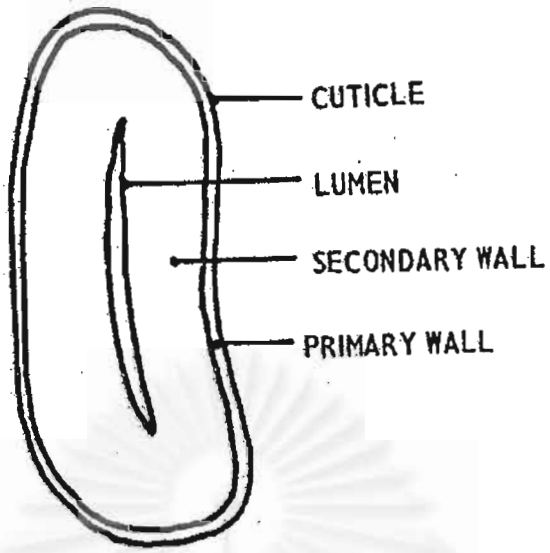


Figure 2.2 Bilateral structure of mature cotton [1]

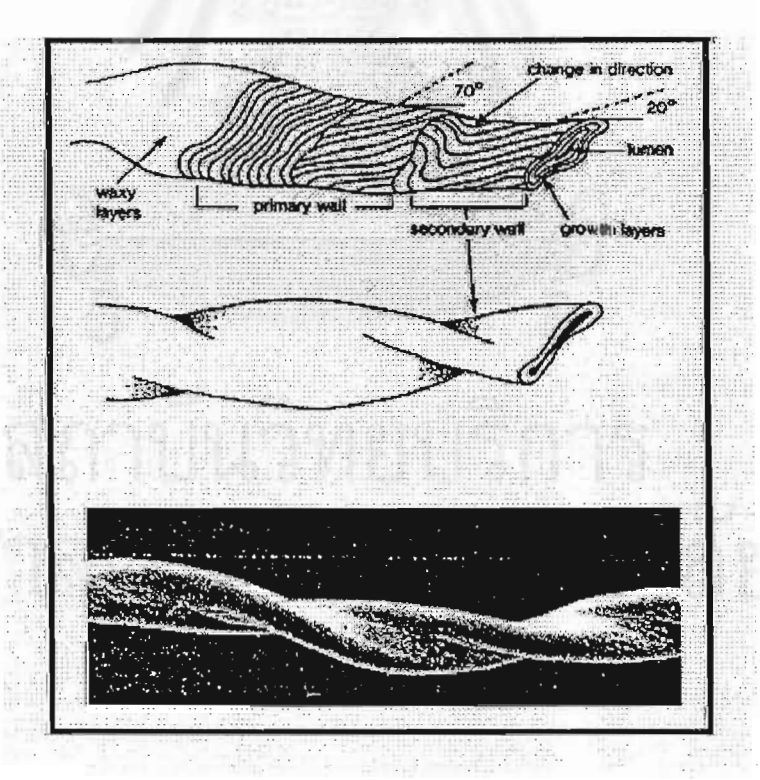


Figure 2.3 Fibrillar structure of cotton fiber [2]

2.1.1 Cotton Morphology

Cotton fiber has a fibrillar structure as illustrated in Figure 2.3. It consists of six parts.(see Figure 2.4)[3] **Cuticle** is the outer waxy layer containing pectins and proteinaceous materials. It serves as a smooth water-resistant coating to protect the rest of the fiber. **Primary wall** is the original thin cell wall. It is mainly cellulose, but also contains pectinaceous, proteinaceous, and waxy materials. **Winding layer** is the very first layer of the secondary thickening and differs somewhat in structure from either the primary wall or the remainder of the secondary wall. **Secondary wall** consists of concentric layers of cellulose which constitute the main portion of cotton fiber. **Lumen** is the central cavity or canal of the fiber and **lumen wall** appears to be more resistant to certain reagent than secondary wall layer. It is highly irregular in both size and shape and often contains solid dried matter, largely nitrogenous in composition.

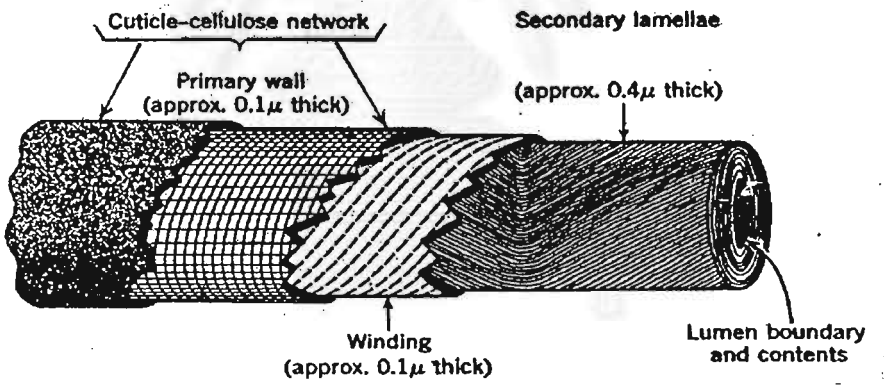


Figure 2.4 Schematic diagram of cotton fiber structure. [3]

2.1.2 Molecular Structure of Cotton Fiber

Raw state cotton fiber is composed of about 94% cellulose. Cellulose molecule is a polymer of glucose forming a ring structure. The chemical structure of cellulose may be conveniently described as a 1,4-β-D-glucan and a condensation polymer of β-D-glucopyranose with 1,4-glucosidic bonds as shown in Figure 2.5. The glucose unit in the polymer chain contains 3 hydroxyl groups (two secondary and one primary alcohol) at carbon positions 2, 3 and 6. The repeating unit is a cellobiose containing two glucose units joined together at the terminal hydroxyl groups in which attached to carbon positions 1 and 4 with the loss of a water molecule.

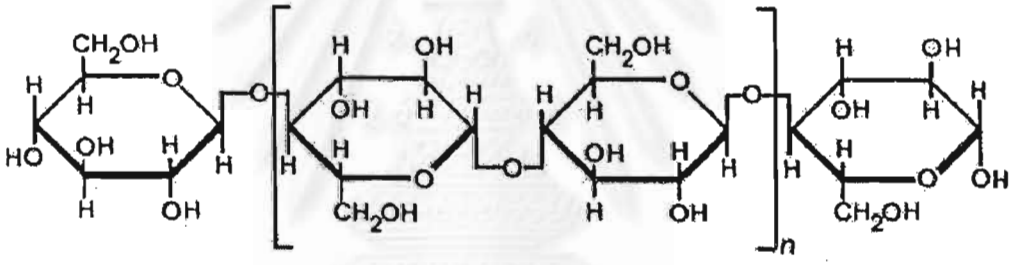


Figure 2.5 Chemical structure of cellulose.

2.1.3 Properties of Cotton Fiber

The properties of cotton fiber are listed in Table 2.1

Table 2.1 Properties of cotton fiber. [4]

Microscopic Features	
Length:	3 to 5 cm.(depending on the source)
Cross-section:	Kidney-shaped.
Color:	Usually a creamy off white color.
Light reflection:	Low luster, dull appearance.
Physical Properties	
Tenacity (g/den.):	3.0 to 5.0 (dry)
	3.6 to 6.0 (wet)
Elongation (%):	3 to 7% elongation at break.
	At 2% elongation, recovery is 70%.
Moisture content (%) at	
65% RH, 21°C:	8.5%
Resilience:	Low
Abrasion resistance:	Fair to good
Specific gravity:	1.54
Chemical Properties	
Bleaches:	Highly resistant to all bleaches.
Dyeability:	Good affinity for dyes. Dyeable with
	direct, vat, sulphur and reactive dyes.
Acids and alkalis:	Highly resistant to alkalis. Strong acids
	and hot dilute acids cause fiber damage.
Organic solvents:	Resistant to most organic solvents.

Table 2.1 (Continued)

Stain:	Poor resistance to water-born stains.
Sunlight and heat:	Good resistant to high temperatures. Prolonged exposure to light causes yellowing due to oxidation.
Biological Properties	
Fungi and molds:	Highly susceptible to attack by mildew.
Insects:	Starched cottons are attacked by silverfish.
Flammability Behavior	Burn rapidly. Smoldering red after glow.
Electrical and Thermal conductivity	Good heat conduction.

2.1.4 Constituents of Raw Cotton

The idealized constructions of raw cotton are illustrated in Figures 2.6 and 2.7. Raw cotton contains, in addition to cellulose, the usual constituents of vegetable cell. There are oils and waxes, pectoses and pectins, proteins and simpler related nitrogen compounds, organic acids, minerals and coloring matter. Cotton yarns or piece goods may contain, in addition, adventitious dirt, sizes, and machine oil. The chemical composition of a mature cotton fiber is presented in Table 2.2.

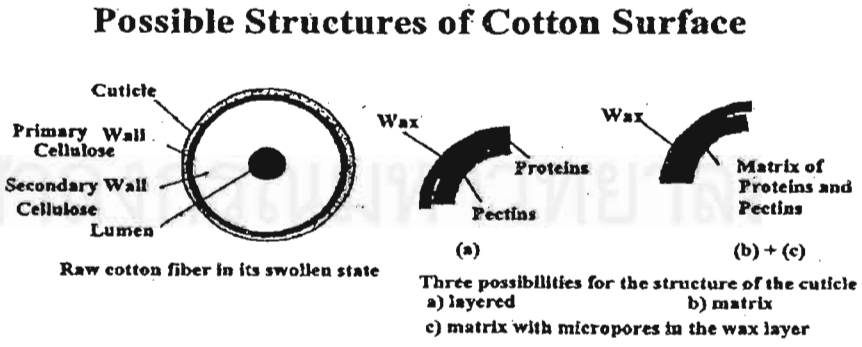


Figure 2.6 An idealized illustration of raw cotton structure in cross section and speculation on the cuticle structure.[5]

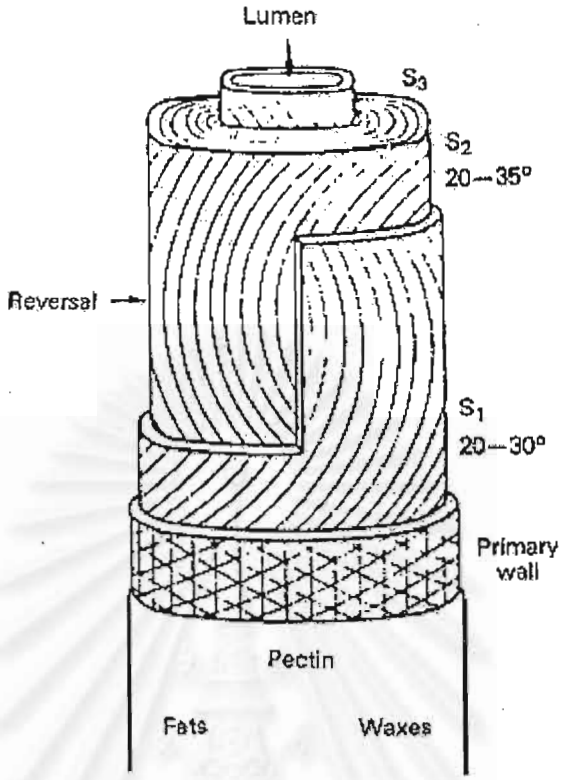


Figure 2.7 Idealized diagram of cotton morphology.[6]

Table 2.2 The composition of a mature dry cotton fiber.

Constituent	Composition of Cotton Fiber[7]			Composition of the Cuticle (%)[8]
	Typical (%)	Low (%)	High (%)	
- Cellulose	94.0	88.0	96.0	
- Protein	1.3	1.1	1.9	30.4
- Pectin	0.9	0.7	1.2	19.5
- Waxes and oils	0.6	0.4	1.0	17.4
- Minerals	1.2	0.7	1.6	6.5
- Maleic, citric and other organic acids	0.8	0.5	1.0	
- Total sugars	0.3			
- Cutin				8.7

2.1.4.1 Oils and Waxes

Cotton fibers contain approximately 0.5 per cent of oils and waxes. They are located mostly in cuticle. It is a mechanical coating outside the primary wall and some of its constituents are chemically combined with pectin, cellulose or protein in primary wall. Analyses of cotton[3] indicate that it contains all the even-numbered of carbon primary alcohols and the largest amount is n-triacontanol ($C_{30}H_{61}OH$). It also contains all the even-number of fatty acids from C_{24} to C_{34}. The one occurring in the largest amount is n-tetracosanoic acid ($C_{23}H_{47}COOH$). Small amounts of fatty acids such as palmitic, stearic, and oleic are found in waxes. The properties of cotton waxes from the extraction of Texas cotton with hot benzene is as follows[9]:

Melting point	68 to 71°C
Specific gravity	0.959
Saponification value	70.6
Acetyl value	73.1
Iodine value	24.5
Percentage of fatty acids	25.0
Percentage of unsaponifiable matter	69.0

2.1.4.2 Pectin

Pectin content in mature cotton fibers is about 0.6 to 1.2 % depending on the method of determination. It is difficult to extract pectin quantitatively from the fiber. The amount of pectins on fiber can be roughly indicated by an estimation of uronic acids[3].

Pectin is a high-molecular-weight carbohydrate with a chain structure similar to cellulose and consists of a chain of α-1,4-linked D-galacturonic acid units shown in Figure 2.8. Cellulose breaks down into glucose but pectin decomposes to give galactose, several pentoses, poly-galacturonic acid and methyl alcohol. Available

evidence[7] indicates that pectin may occur in cotton fiber in the form of insoluble calcium, magnesium, and iron salts of the poly-galacturonic acid. It is insoluble in water but soluble in alkali solutions.

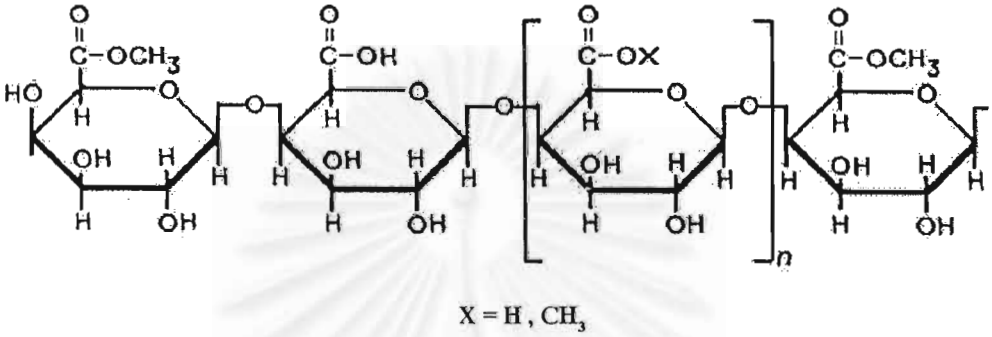


Figure 2.8 Molecular structure of pectin.

2.1.4.3 Minerals

Cotton may contain between 1 and 1.8 per cent of mineral matter. Its quantity and composition vary according to the nature of the soil on which the plant was cultivated. Silicon is always present and other elements such as iron, aluminium, calcium and magnesium are also found. When cotton is ashed, all the metallic organic salts appear as carbonates. Analysis of the ash shows the presence of the following: [10]

Potassium carbonate	44.8 %
Potassium chloride	9.9 %
Potassium sulphate	9.3 %
Calcium sulphate	9.0 %
Calcium carbonate	10.6 %
Magnesium sulphate	8.4 %
Ferric oxide	3.0 %
Aluminium oxide	5.0 %

The carbonates of potassium and calcium were not in that state originally, but are the products of the combustion of organic salts of those metals.

2.1.4.4 Nitrogen Compounds

Cotton contains approximately 1 % of nitrogen impurities. Unless removed, they can produce undesirable effects in the finished material. These compounds consist essentially of degraded products of the protoplasm, which cell contained when it was still living and growing. They are the composition of the outer primary wall. Their exact identity has not been established but it is reasonable to assume that they are protein and polypeptides left in lumen after cell dies.

2.1.4.5 Coloring Matter

When waxes and nitrogen impurities have been removed, cotton still has a yellowish or brown discoloration. This is caused by the natural coloring matter, which can only be removed effectively by oxidizing agent in bleaching step. It is present only traces and its composition has not been established with certainty. It may be related to the pigments of cotton flowers. The nature of the pigment responsible for coloring is not known.

2.1.4.6 Ash

Cotton taken directly from the gin shows approximately 2 to 3% ash content. Analysis of the ash shows that it consists mainly of magnesium, calcium, or potassium carbonates, phosphates, sulfates or chloride with the carbonates predominating.

2.2 Enzymes

The building blocks that produce enzymes are various amino acids as the following general form: NH_2-R-COOH. These simple molecules condense with the elimination of water to produce longer polypeptide chains [-NH-R-CONH-R-CO-]. As the polymeric chain length increases more and more, ionic and other interactions eventually cause the complex molecule. Enzymes, like other proteins, consist of long chains of amino acids held together by peptide bonds. They are present in all living cells, where they perform a vital function by controlling the metabolic processes, whereby nutrients are converted into energy and new cells. Moreover, enzymes take part in the breakdown of materials into simpler compounds. Enzymes are bio-catalyst, and by their mere presence, and without being consumed in the process, enzymes can speed up the chemical processes that would otherwise run very slowly. After the reaction is complete, enzyme is released and is ready to start another reaction. In principle, this could go on forever. But in practically, most catalysts have a limited stability. Over a period of time, they lose their activity and are not usable again. Generally, most enzymes are used only once and discarded after they have done their job.

Enzymes are very specific in comparison to inorganic catalysts such as acids, bases, metals and metal oxides. Enzyme can break down particular compounds. In some cases, their action is limited to specific bonds in the compounds with which they react. The molecule(s) that an enzyme acts on is known as its substrate(s), which is converted into a product or products. A part of large enzyme molecule will reversibly bind to the substrate(s) and then a specialised part(s) of the enzyme will catalyze the specific change of the substrate into a product. For each type of reaction in a cell there is a different enzyme. They are classified into six broad categories namely hydrolytic, oxidizing and reducing, synthesizing, transferring, lytic and isomerising.

Catalyst is a substance that enhances the rate of chemical reaction but is not permanently altered by reaction. Catalyst performs this feat because it decreases the activation energy required for a chemical reaction or provides an alternative reaction pathway that requires less energy[11]. Figure 2.9 shows a transition state occurring at the apex of both reaction pathways. During any chemical reaction, reactants with sufficient energy attain transition state configuration. For biochemical systems, this occurs when the substrate binds to the enzyme.

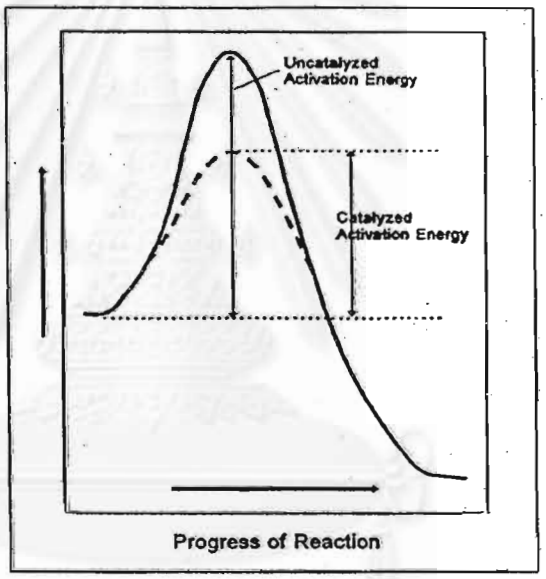


Figure 2.9 Activation energy for a given reaction in the presence and in the absence of catalyst.[11]

Enzymes work at atmospheric pressure and in mild conditions with respect to temperature and pH. Most enzymes function optimally at a temperature of 30°C-70°C and at pH near the neutral point (pH 7). Now-a-days, special enzymes have been developed to work at higher temperatures for specific applications. Enzyme processes are potentially energy saving and save investing in special equipment resistant to heat,

pressure or corrosion. Due to their efficiency, specific action, mild work conditions and high biodegradability, enzymes are very well suited for a wide range of industrial applications.

2.2.1 Mechanism of Enzymes Action

An enzyme has a quite specific three-dimensional shape. This shape and other factors, such as the location of active site on the enzyme, control the specificity of the molecule. An enzyme is absorbed onto a given substrate surface in "lock-and-key" fashion[12](Figure 2.10). At the surface of the substrate, the enzyme serves to accelerate the reaction of the substrate and the environment before converting into products. Since enzymes are catalysts, they themselves are not changed by the reaction that the substrate undergoes. After the reaction has taken place, the enzyme is released to be re-adsorbed onto another substrate surface. The process continues until the enzyme is poisoned by a chemical bogie or inactivated by extremes of temperature, pH, or by other negative conditions in the processing environment.

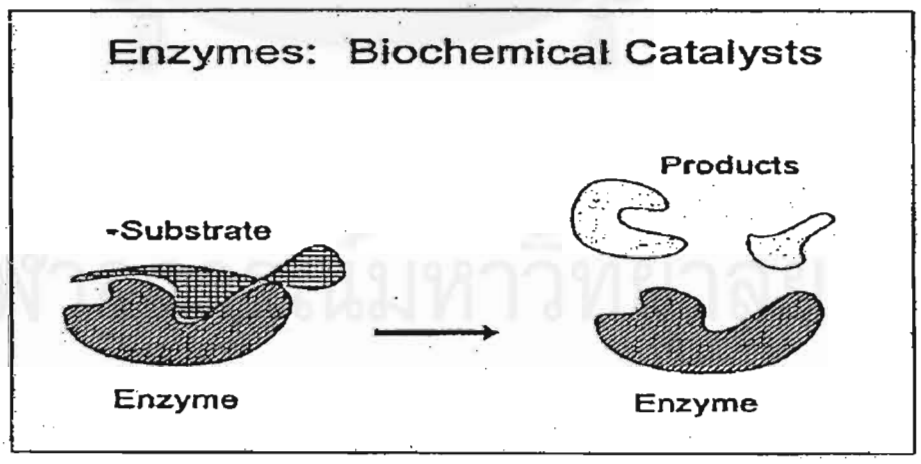


Figure 2.10 "Lock-and-key" mechanism for enzyme action. Enzyme is adsorbed at substrate surface, followed by releasing the reaction products and enzyme.[12]

2.2.2 Classification of Enzymes

An international classification has been established to define six major classes of enzyme function according to the type of chemical reaction it catalyzes.[13-15]

The following are the six major enzyme categories:

EC.1 ***Oxidoreductases*** catalyze oxidation-reduction reactions. Subclasses of this group include dehydrogenase, oxidases, oxygenases, reductases, peroxidase, and hydroxylases.

EC.2 ***Transferases*** catalyze transfers of groups such amino, carboxyl, carbonyl, methyl, acyl (RC=O), glycosyl, or phosphoryl. Common trivial names for the transferases often include the prefix "trans". Examples include transcarboxylases, transmethy-lases, and transaminases.

EC.3 ***Hydrolases*** catalyze cleavage of bonds between a carbon atom and some atom by addition of water. The hydrolases include the esterases, phosphatases, amylase, protease, lipase, cellulase, pectinase, and peptidases.

EC.4 ***Lyases*** catalyze breakage of carbon-carbon, carbon-sulfur, and certain carbon-nitrogen bonds. Decarboxylase, dehydratases, deaminases, and systhases are examples of lyases.

EC.5 ***Isomerases*** catalyze racemization of optical or geometric isomers and certain intramolecular oxidation-reduction reactions. Epimerases catalyze the inversion of asymmetric carbon atom. Mutases catalyze the intramolecular transfer of functional groups.

EC6. ***Ligases*** catalyze bond formation between two substrate molecules. The energy for these reactions is frequently derived from the hydrolysis of adenosine triphosphate. The names of many ligases include the term synthetase. Several other ligases are called carboxylases.

Each enzyme is individuated by four numbers: the first indicates the reaction catalyzed (class), the second is the function involved, the third gives more details on the reaction catalyzed indicating or the group acceptor or the substrate, the fourth is the serial number of the enzyme in its sub-subclass.

2.2.3 Amylase

The substrates of amylase are starches. Starch is composed of two components. One minor component calls amylose. It has a linear structure. The other major component names amylopectin. It contains a branched structure.

Amylases are enzymes that split starch into dextrins and water-soluble sugars by hydrolysis of the 1,4-glycosidic linkages. They are common in nature, occurring in saliva, pancreas and many plants such as cereals. In industry, amylases are produced from cultures of bacteria and fungi. There are α- and β amylases. α-amylases split the glycosidic linkage in the interior of the starch chain. And on the other hand, β amylases split moltose from the nonreducing end of the chains. In addition, some amyloglycosidases, liberate glucose residues stepwise from the end of the chain. (Figure 2.11)

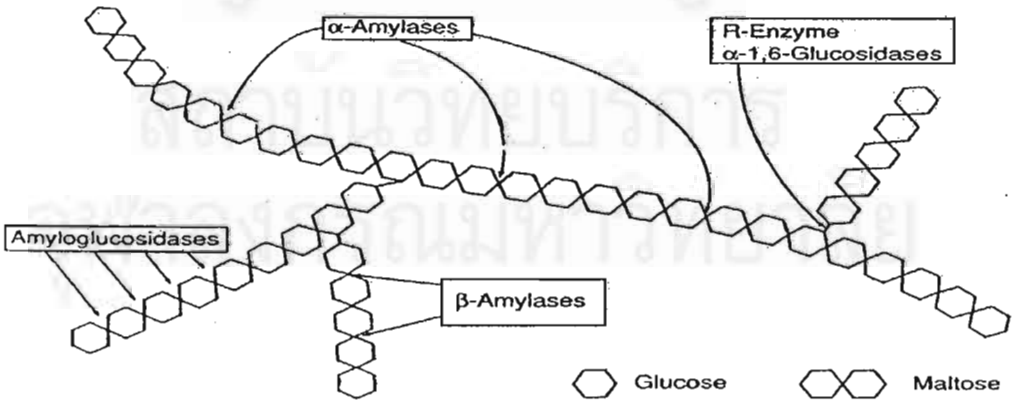


Figure 2.11 Starch hydrolysis by amylase.[16]

2.2.3.1 α-Amylase

The endoamylase or α-amylase (EC 3.2.1.1) catalyzes a superficially random hydrolysis of the starch component. The hydrolysis occurs at the α-1,4-glucosidic bonds in amylose, amylopectin and glycogen but α-1,6-glycosidic linkages in branched polymers are not attacked. Many α-amylases can be produced from malt, pancreas, *Aspergillus oryzae* and *Bacillus subtilis*. They differ in their temperature stability and optimum-activity pH. α-amylases are generally stable at pH 5.5-8.0 at 50-70°C. Some amylases can stand high temperature such as bacterial α-amylases. When they are use in the hydrolysis. $CaCl_2$ is added to function as the enzymatic stabilizer. Optimal pH of α-amylases normally occurs between 4.8-6.5[16] but differences enzymes show different shapes of pH activity curves and also the values of pH optima. Most purified α-amylases lose activity rapidly above 50°C but this inactivation may be retarded in the presence of calcium.

2.2.3.2 β-Amylase

β-amylases or exoamylases (EC 3.2.1.2) are found in cereals, malted cereals, sweet potatoes and other plants. β-amylases hydrolyze moltose residues at the α-1,4 linkage from the nonreducing end of the starch chain. β-amylases do not split the α-1,6 linkages. The reaction products from amylopectin are moltose and β-limit dextrin.

2.2.4 Lipase

Lipase is produced by numerous bacteria and fungi. The natural substrates of lipases are triglycerides of long-chain fatty acids. These triglycerides are insoluble in water and lipases are characterized by ability to rapidly catalyse. It catalyzes the hydrolysis of fats such as esters bonds of glycerol and fatty acid at the interface between the insoluble substrate and the aqueous phase in which the enzyme is soluble.

Lipase attacks the ester bonds in these fats, regenerates water soluble glycerol and water insoluble fatty acid and converts to water soluble salts by the addition of alkali.

Lipases cleave triglycerides into free fatty acids, produce intermediate 1,2- or 2,3-diglycerides, hydrolyse into 2-monoglycerides in step II and hydrolyze to free glycerol and fatty acid in step III. The hydrolysis reaction is show in Figure 2.12.

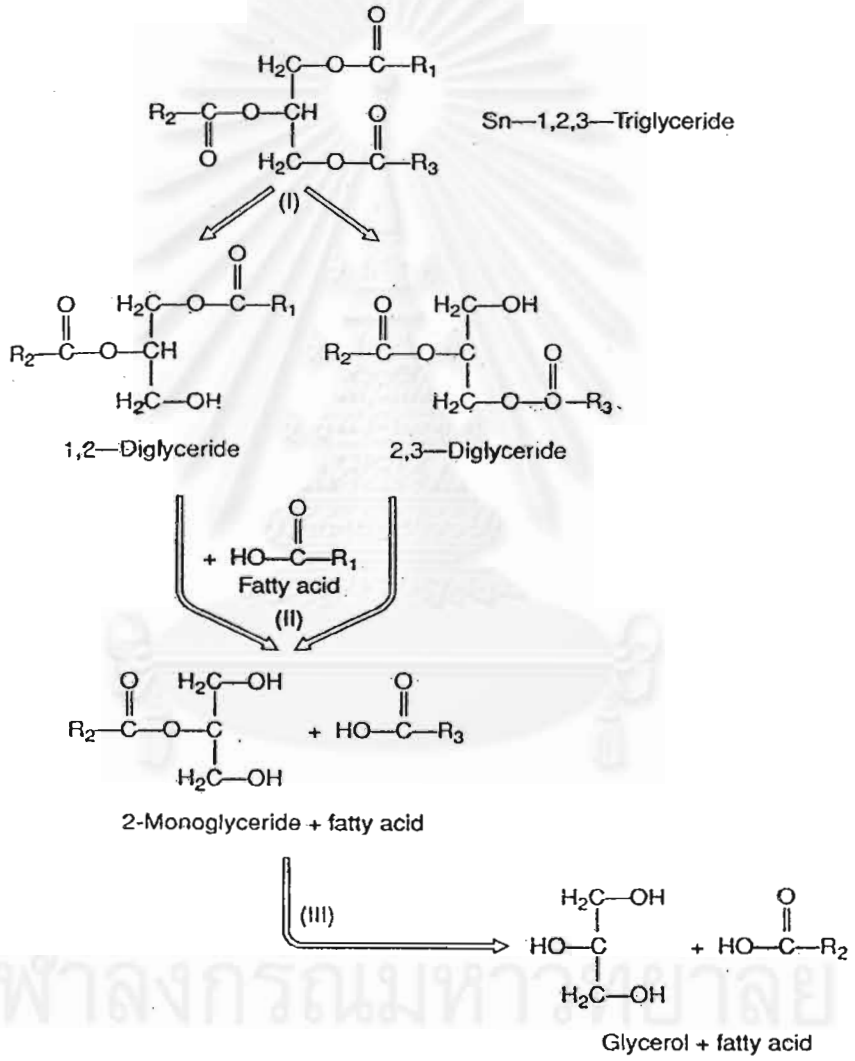


Figure 2.12. Reaction steps of lipase in triglyceride hydrolysis.[16]

Lipid hydrolysis depends on different parameters such as pH, temperature, water content and the phase boundary area. The optimum pH of most lipase lies between 7.5 and 9.0.[16]

2.2.5 Protease

Proteolytic enzyme seperates on this basis into proteinase (or proteases) and peptidase. They are obtained from plants and animal organs and microorganisms, with the majority obtained from bacteria. Peptidases catalyze the hydrolysis of esters and amide. And proteases catalyze the hydrolysis of amino acid chains in proteins. They hydrolyze large polypeptide substrates into smaller molecular entities. The peptide hydrolases of commercial interesting are proteases rather than peptidases.

2.2.6 Pectinase

Pectinases catalyze the hydrolysis of polygalacturonic acid backbone in pectins. The polygalacturonic acid is then converted into galacturonic acid monomers and removed from substrate. The typical individual components of pectinase are polygalacturonases, pectate lyases, pectin lyases and pectin esterases.

Polygalacturonases split the glycosidic linkages next to a free carboxyl group by hydrolysis (Fig.2.13). In consequence, highly methoxylated pectins are hardly attacked, whereas low methoxyl pectins are good, and pectate the best, substrate. The endo types split the pectic chain at random; small increase in reducing end groups will be accompanied by a strong reduction in viscosity of the substrate solution. The exo types split off mono- or dimers from the non-reducing end that means the viscosity of a substrate solution is reduced only very slowly.

Pectate lyases split glycosidic linkages like polygalacturonase. Pectate lyases split only linkages next to a free carboxyl group (Figure 2.13).

Pectin lyases split glycosidic linkages next to a methyl ester group by β-elimination. (Figure 2.13).

Pectin esterases can be obtained from higher plants, yeasts, bacteria and fungi. They split methanol off from the esterified carboxyl groups and transform pectin into low methoxyl pectin and pectate (Figure 2.13). The optimum pH for pectinesterase of fungi origin is generally lower than of bacteria. The fungi enzyme is completely active at pH 4-5 and temperature 40-50°C.

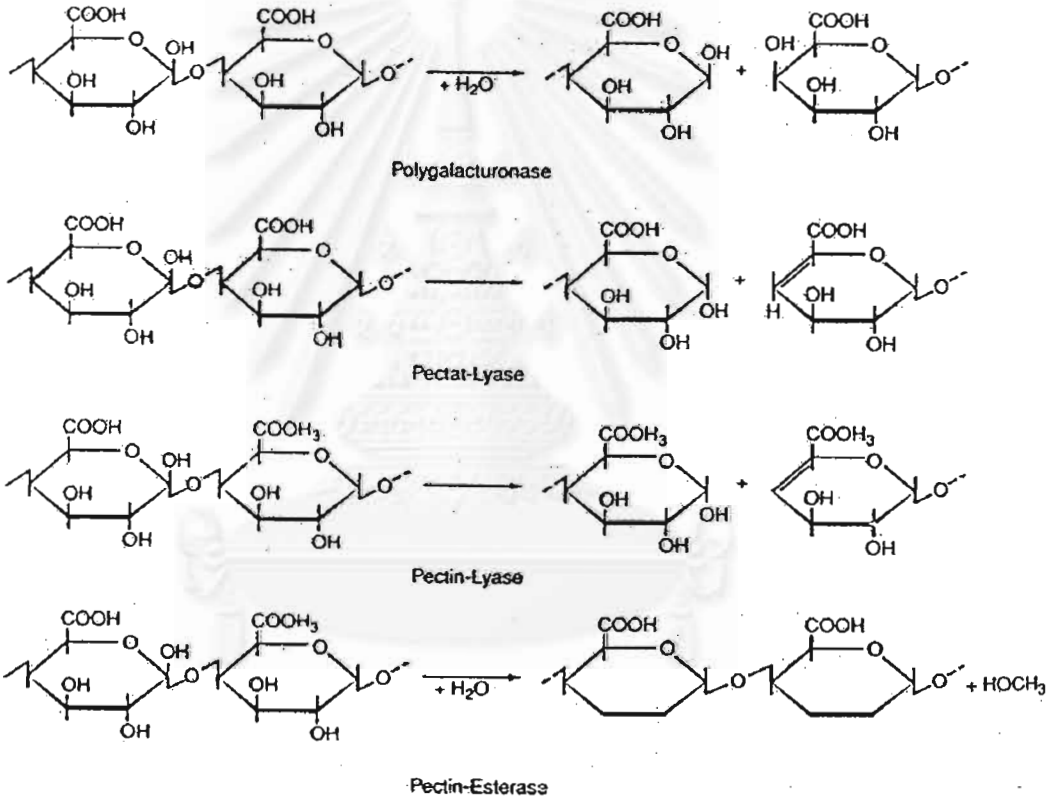


Figure 2.13 Ester hydrolysis and depolymerization of pectin.[16]

2.2.7 Cellulase

Cellulases are multi-component enzyme systems commonly produced by soil-dwelling fungi and bacteria. These fungi and bacteria produce cellulases to reduce cellulose to glucose to use as food. There are three types of cellulase components act in

degrading cellulose to glucose, endo-cellulase; exo-cellulase; and β-glucosidase. The current proposed mechanism of cellulase action is shown in Figure 2.14.

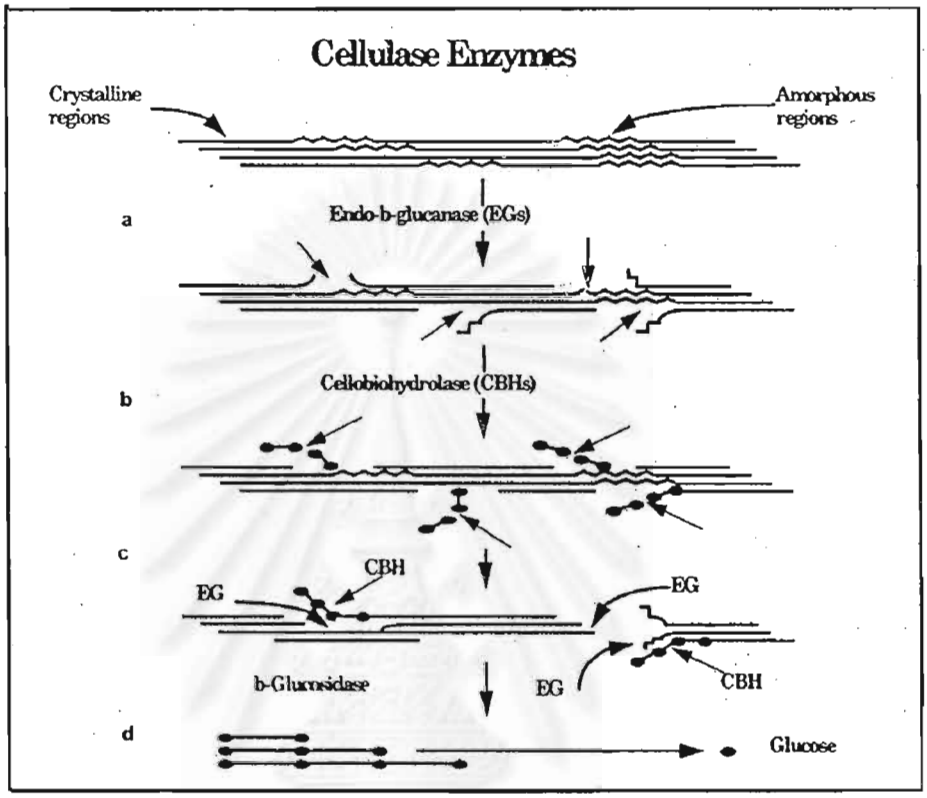


Figure 2.14. Schematic representation of synergistic action of cellulase on cellulose.[17]

Endoglucanases or endo-cellulases hydrolyze cellulose polymers randomly along the chains to form chain ends, preferentially attacking noncrystalline regions. Cellobiohydrolases or exo-cellulases attack the polymer chain ends and produces primarily cellobioses. Coupled with the binding domains associated with the enzyme, exo-cellulases may assist in degradation of cellulose by disrupting the crystalline cellulose structure which makes the region more susceptible to subsequent hydrolysis by endo-cellulases. β-glucosidases hydrolyze small chain oligomers, such as cellobioses, into glucoses.

Most commercial cellulases are derived from the fungal *Trichoderma* and *Penicillium* species. They may be produced both in powdered forms and as concentrated liquids 25% for active in brine for stability. The optimum activity of cellulase from fungi is at pH 4.5-5 and temperature 45°C.

2.2.8 Xylanase

Xylan is one of the most widely occurring polysaccharides. It is found in wood, rice straw and glasses. Xylans have chains of 1,4-linked β-D-xylopyranose residues. The (1,4)-β-D-xylans are the most abundant polysaccharides of the terrestrial plant hemicelluloses, and enzymes degrading this group are well documented. Xylanases are produced from *Aspergillus, Bacillus* and *Trichoderma* species. They are capable of hydrolyzing the (1,4)-β-D-xylopyranosyl linkages of arabinoxylans, arabino-glucuronoxylans, glucoronoxylans and unsubstitutes xylans to yield xyloses and xylobioses.

2.2.9 Glucose oxidase

Glucose oxidases are one type of glucose transforming enzymes. The enzyme is produced by various fungi including *Aspergillus niger, Penicillium notatum, Penicillium glaucum, Penicillium amagasakiense* and *Penicillium purpurogenum.* Glucose oxidases prepared from *Aspergillus niger* are the most readily available from the commercial manufacturers. The fungal process for the commercial production of D-glucono-δ-lactone and its free acid form, gluconic acid is catalyzed by glucose oxidase. Glucose oxidase catalyzing the conversion of glucose to δ-gluconolactane is highly specific for β-D-glucose (Figure 2.15).

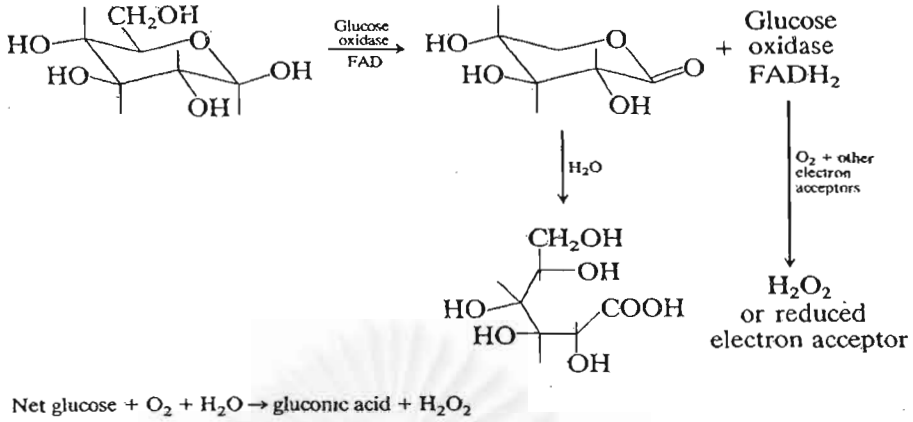


Figure 2.15 Reaction of conversion of glucose to δ-gluconolactone by glucose oxidase enzyme.[18]

The pH optima of glucose oxidase are broad, activity being constant between pH 4.5 and 7.0. The fall in activity at higher pH is due to instability of enzyme, whilst at lower pHs it is due to slowing of the rate of reaction. The optimum temperature of glucose oxidase is rarely mentioned. The rate of reaction is approximately constant between 30 and 60°C.

The most important application of glucose oxidase is the industrial-scale fermentation of gluconic acid. Gluconic acid and its salt are used for detergent, textile and food industries. Sodium gluconate is used as a metal sequestering agent for preventing the precipitation of lime and soap scum.

2.2.10 Catalase

Catalase is isolated from beef liver, *Aspergillus niger* and *Micrococcus lysodeikticus*. It catalyzes the decomposition of hydrogen peroxide. In one reaction, the enzyme decomposes two molecules of hydrogen peroxide into two water molecules and one oxygen molecule. One enzyme molecule is able to repeatedly decompose hydrogen peroxide one after another.

$$2H_2O_2 + \text{Catalase} \rightarrow 2H_2O + O_2$$

The catalase enzyme from *Micrococcus lysodeikticus* acts optimally at pH 7.0 at 30°C. It is stable at pH 7.0 for 15 min at 50-55°C.

2.3 Conventional Preparation Processes

Preparation processes of cotton are necessary for removing impurities from the fibers and for improving their aesthetic appearance and processability prior to dyeing, printing and/or mechanical and chemical finishings.

The need for good preparation has long been appreciated, but the developments taken place in dyeing processes, particularly continuous pad dyeing, have accentuated the importance of the correct preparation of cotton. Over long continuous runs, the fabric must be evenly treated to have excellent absorbency, low residual size and wax content, whiteness appropriate to the color to be dyed and minimal fiber degradation. This technical standard must be met against economic constraints relating to the cost of chemical, labor, power and water.

2.3.1 Conventional Desizing

During weaving, warp yarns are exposed to considerable mechanical strain. In order to prevent yarns from breaking, coating (sizing) with a gelatinous substance (size) is needed to reinforce them.

For cotton blends weaving, size material mostly contains native or modified starch and sometimes in combination with other polymers such as polyvinyl alcohol (PVA), polyacrylic acid (PAA) or carboxy methyl cellulose (CMC). Small amounts of fats or oils may be also added to the size, with the aim of lubricating the warp coat surface.

As a consequence of sizing, warp yarns in woven fabric are not able to absorb water, dyes or finishing agents to a sufficient degree. This means that first the size must be removed (desizing) before dyeing and finishing. Some sizes may be removed in a simple scouring process (water-soluble sizes). But in most cases, chemical breakdown of the size polymer in a separate desizing treatment is necessary in order to obtain the desired quality of the final fabric. In the conventional process of desizing, the breakdown of the size polymer is carried out using oxidizing agents such as ammonium persulfate or hydrogen peroxide at high pH and temperature. The treatment reduces the tensile strength of the fabric and results in poor removal of some PVA-containing sizes. They must therefore be removed before any subsequence wet processing of the fabric. The desize procedure depends on the type of size. It's therefore necessary to know what type of size is on the fabric before desizing.

Starch is the most difficult size to remove. It does not readily dissolve in water and must be broken down chemically into water-soluble compounds by either enzymes, oxidizing agents, or acids. Enzymes break down starch into water-soluble sugars and dextrins; oxidizing agents oxidize starch into compounds that are soluble in alkali solution; while acids hydrolyze starch into water-soluble compounds.

Starch is actually composed of two components, a straight chain polysaccharide of glucose (amylase) and a branched chain polysaccharide of glucose (amylopectin). Amylose, is relatively low in molecular weight, water soluble, and makes up 20-30% of starch. Amylopectin is relatively high in molecular weight, water insoluble, and makes up 70-80% of starch. It is therefore the amylopectin component that is difficult to remove in desizing.

2.3.2 Conventional Scouring

Scouring is almost invariably the first wet process (except desizing for only woven fabric) applied to textile material. The main purpose of scouring cotton fabrics

is to remove oils, fats, soluble impurities and any particulate or solid dirt adhering to the fiber. The process consists essentially of treatment with a detergent with or without the addition of alkali. Effective removal of impurities in cotton, particularly waxes, is achieved by boiling in 3-6 % sodium hydroxide solution or less frequently in dilute solutions of calcium hydroxide or sodium carbonate[19]. The proper choice of textile auxiliaries in the alkali bath is essential for good scouring. These include sequestering agents may be employed in areas where hard water is a problem. Where alkali is added to form oil soap, the presence of calcium or magnesium may lead to scum formation. Sequestrants act by forming soluble complexes with metal ions to prevent their reaction with other species. Surfactants such as anionic sodium lauryl sulfate are added into the bath as detergents, dispersing agents and emulsifying agents to remove unsaponifiable waxes. They must then be able to disperse the solid particles effectively and prevent their redeposition.

2.3.3 Conventional Bleaching

This process is generally applied to greige goods in order to remove natural colorants, water-borne stains and oil-borne soils. Bleaching is accomplished chemically with oxidizing or reducing agents. Chemical bleaching agents function by solubilizing colored substances, thus facilitating their removal from the fiber. They also function by reacting with these substances in such a manner as to alter or destroy their sites of unsaturation or conjugation. Most chemical bleaching agents are oxidative in nature.

Bleach formulations usually contain buffering and sequestering agents such as silicates, phosphates or oxalates. Some formulations call for metal salts, sodium hydroxide, ammonia or sodium nitrate. Other additives to the bleach bath are surfactants, antideposition agents and optical brighteners. Hydrogen peroxide is the most widely used bleaching agent for cellulosic fibers.

Hydrogen peroxide bleaching proceeds by dissociation into hydrogen ion (H^+) and perhydroxyl ions (HOO^-) once alkali is added because this reaction is favored by an alkali condition. At pH 11.5, the peroxide rapidly breaks down and molecular oxygen forms[20]. Cotton would become severely damaged under these conditions. Activators and stabilizers are added to the hydrogen peroxide bath to control the rate of bleaching. Sodium hydroxide and sodium carbonate are the alkalis for cellulosics bleaching. Sequestering agents are used to incapacitate heavy metal ions in the bleaching solution because these ions foster the decomposition of peroxide into radical species that attack and damage the fiber.

2.4 Enzymatic Preparation Processes

Csiszar, Szakacs, and Rusznak[21] studied cellulase enzyme to removal of seed-coat fragment in spinning blow room waste, by consecutive cellulase treatment and traditional pad-steam scouring. They assumed that the compact and resistant structure of lignocellulose in seed-coat fragment is loosened by the complex action of enzymes. When it is attacked by aqueous sodium hydroxide, the tiny fibers that attach the seed-coat fragments to the fabric are hydrolyzed by the enzyme, facilitating the removal of those impurities from the fabric surface. Approximately 80% of seed-coat fragments are dissolved.

Li and Hardin[5,8,22] proposed the action of pectinase and cellulase on structural changes in surfaces of cotton observed from staining tests and microscopy observations. The pectinase enzymes can destroy the cuticle structure by digesting the inner layer pectins in the cuticle and cellulases can destroy the cuticle structure by digesting the primary wall of cellulose immediately under the cuticle .

Buschle-Diller and El Mogahzy[23] presented the effect of cotton yarn scourings with pectinase and cellulase enzymes, with 1,1,1-trichloroethylene, and with caustic soda. They proposed that all three scouring methods increased yarn absorbency but caustic scouring gave yarn the highest degree of whiteness but left them with the most sensitive to oxidative damage during subsequent bleaching. Solvent extraction method increased yarn tenacity and damage at a minimum. Pectinase/cellulase scouring yielded very soft yarn with moderate yarn tensile strength and fiber deterioration.

Sawada et. al.[24] studied bioscouring of cotton using pectinase enzyme together with multiple mixed surfactants and D-limonene as a scouring agent. They found that the scouring abilities of a pectinase enzyme system may be greatly increased by the addition of mixed surfactant and D-limonene.

Hartzell and Hsieh[25] investigated four kinds of enzymes, i.e., pectinase, cellulase, protease and lipase, for their effectiveness in improving the water wetting and retention properties of cotton fabrics. Cellulase is the only enzyme to produce detectable improvements in water wettability of raw cotton. It is able to gain access to cellulose, and in due process, to remove hydrophobic noncellulosic components from the fabric surface. Pectinase, lipase and protease treatments alone do very little to improve water wetting when applied directly to raw cotton.

Sawada, Tokino and Ueda[26] studied once again on bioscouring of cotton with pectinase enzyme. They proposed a new method of scouring cotton in non-aqueous media using a reverse micellar system (RMS) in iso-octane and bis-2-ethylhexylsulphonate (Aerosol-OT,AOT) as a surfactant. They found that using the reverse micellar system rather than an aqueous bioscouring system reduces the concentration of enzyme and the treatment time required to achieve a full scouring effect.

Yachmenev, Blanchard and Lambert[27] used ultrasound energy in the reaction chamber during cellulase treatment of cotton fabric. They found that using ultrasonic energy could provide significant saving of processing time and cellulase enzyme concentration needed for the process, and obtain better uniformity of the treatment.

Ethers[28] used alkali pectinase in cotton preparation process. He proposed a new pectinase enzyme, which catalyzed pectin in alkali condition (pH 9.5) by pad-steam continuous process. Alkali pectinase scoured fabric gave better result of the wicking test and more uniform dyeing than the caustic scoured fabric at same depth.

Ishihara et. al.[29] studied biobleaching of cotton fabrics using glucose oxidase enzyme. They presented the effect of mixing desizing and bleaching using glucoamylase and glucose oxidase enzymes together in one bath. The results from those processes provided on bleached cotton substrate with high whiteness.

CHAPTER III

Experimental

3.1 Materials

Samples :

: Greige cotton woven fabric, plain, weigh 1.4996 g/100 cm^2

: Greige cotton w oven fabric, twill, weigh 3.8971 g/100 cm^2

: Greige cotton knitted fabric, single jersey, yarn count 50/1, weigh 1.1784 g/100 cm^2

: Greige cotton knitted fabric, single jersey, yarn count 24/2, weigh 2.7855 g/100 cm^2

: Greige cotton yarn, 50/1

Greige samples were tested for strength, extractable materials, size identification, water absorbency, and weight according to test procedures outlined in section 3.4.

Enzymes :

Table 3.1 Enzymes used in this project.

Enzyme	EC. Number	Source	Activity	Company
α-amylase (Termamyl 120 L)	EC.3.2.1.1	*Bacillus subtilis*	120,000 units/g	Novo Nordisk
Lipase	EC.3.1.1.3	*Pancreas*	15 units/g	Tokyo Chemical Industry
Protease	EC.3.4.23.6	*Aspergillus niger*	14,000 units/g	Tokyo Chemical Industry
Pectinase	EC.3.2.1.15	*Aspergillus niger*	1,700 units/g	Tokyo Chemical Industry
Cellulase	EC.3.2.1.4	*Aspergillus niger*	25,000 units/g	Tokyo Chemical Industry
Xylanase	EC.3.2.1.32	*Bacillus subtilis*	3.0 units/mg	Fluka
Glucose oxidase	EC.1.1.3.4	*Aspergillus niger*	18 units/mg	Tokyo Chemical Industry
Catalase (Reyonet S)	EC.1.11.1.6	*Micrococcus Lyzodeicticus*	50,000 units/ml	Negase Biochemical

Reagent Grade Chemicals :

Table 3.2 Chemicals used in this project.

Chemical	Company
Calcium chloride powder	APS Ajax Finechem
Sodium chloride powder	APS Ajax Finechem
Sodium silicate	N/A
Sodium hydroxide pellets 98%	EKA Chemicals
D-Glucose	APS Ajax Finechem
50% Hydrogen peroxide	N/A
Sodium acetate powder	APS Ajax Finechem
Glacial acetic acid	Fluka
Potassium hydrogen phosphate powder	APS Ajax Finechem
Disodium hydrogen phosphate powder	APS Ajax Finechem
Formic acid 99%	Carlo Erba
Womine TE (Wetting agent)	Tokai Seiyu

Dyes :

Table 3.3 Dyestuffs used in this project.

Dye	Company
Methylene blue	Nacali Tesque, Inc
Benzopurpurine 4B	Tokyo Chemical Industry

3.2 Equipment

1. pH meter, Denver Instrument, Model 215
2. Rotary dyeing machine & steel pots, Ahiba Polymat®
3. Magnetic stirrer, Framo® Geratetechnik, Model M 21/1
4. Macbeth reflectance spectrophotometer, COLOR-EYE® 7000
5. UV-Visible spectrophotometer, JENWAY, Model 6405
6. Temperature control bath, EYELA®, CA-101 Cool Ace
7. Oxygen tank (Aerator), Emagin Japan
8. Bursting strength tester, Osaka Koho Co.,Ltd, Model SD-223
9. Tensile strength tester, LR 5 K, LLOYD Instrument
10. Windy oven, EYELA®, Model WFO-600ND
11. Balance, Mettler Toledo, Model AB 204

3.3 Yarn and Fabric Preparation Processes

3.3.1 Desizing

Greige woven fabrics were treated in desizing solutions containing calcium chloride and sodium chloride as stabilizers, Womine TE as a wetting agent, and Termamyl 120L as an amylase enzyme in the Ahiba Polymat® laboratory dyeing machine (Figure 3.1) at a liquor ratio of 20:1 at pH 6.5 and commenced at room temperature. The temperature was raised to 100°C over 18 minutes (4°C/min.) and continued at this temperature for 45 minutes. The desizing formulation (see Table 3.4) and condition used in this experiment were based on the industrial guideline and on the theoretical data. Desized fabrics were then removed and rinsed in distilled water at 80° C for 20 minutes (liquor ratio at 20:1). The desizing procedure is as follows.

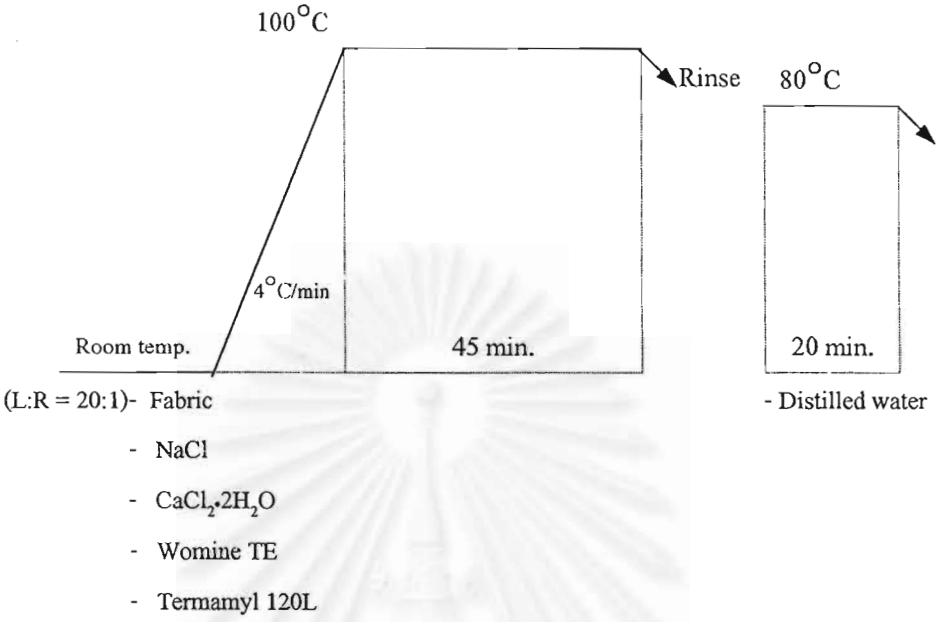


Diagram 3.1 The desizing procedure.

Table 3.4 The desizing formulations.

Chemical	Twill weave fabric	Plain weave fabric
Termamyl 120 L (g/l)	2.0	1.0
NaCl (g/l)	4.0	4.0
$CaCl_2 \cdot 2H_2O$ (g/l)	0.3	0.3
Womine TE (g/l)	1.0	1.0

After desizing, the fabrics were tested for the presence of residual sizes and pectin, weight loss, water absorbency, and strength according to test procedures outlined in section 3.4.

Figure 3.1 Rotary dyeing machine & steel pots, Ahiba Polymat®

3.3.2 Scouring

3.3.2.1 Conventional Scouring

Greige yarn, greige knitted fabrics, and desized woven fabrics were treated in scouring solutions containing Womine TE and sodium hydroxide in the Ahiba Polymat® laboratory dyeing machine at a liquor ratio of 20:1 and commenced at room temperature. The temperature was raised to 80°C over 12 minutes (4°C/min.) and continued at this temperature for 60 minutes. Scoured fabrics were then taken out and rinsed in distilled water at 80°C for 20 minutes (liquor ratio 20:1). The scouring formulation (see Table 3.5) and condition used in this experiment were based on the industrial guideline and on the theoretical data. The conventional scouring procedure is as follows.

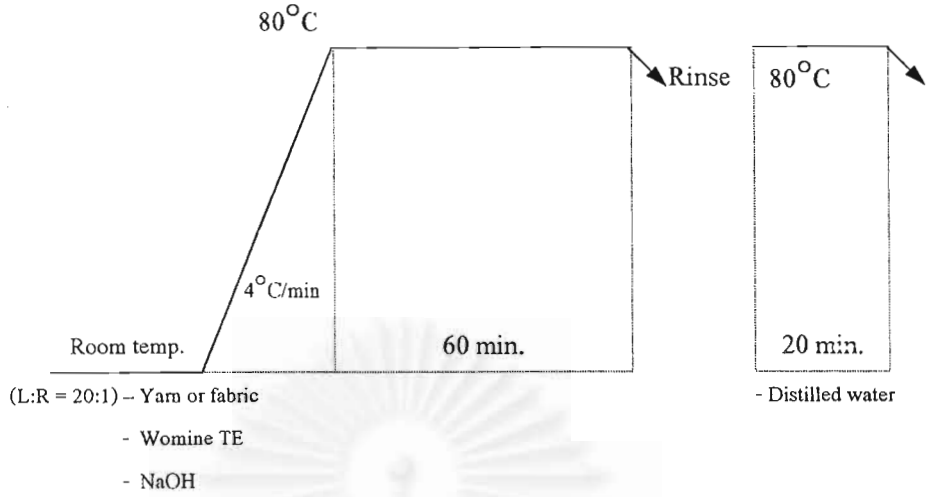


Diagram 3.2 The conventional scouring procedure.

Table 3.5 The conventional scouring formulations.

Cotton Substrate	**Sodium hydroxide (%owf.)**	**Womine TE (g/l)**
Twill weave fabric	4	3
Plain weave fabric	2	3
Knitted fabric (yarn count 50/1)	3	3
Knitted fabric (yarn count 24/2)	5	3
Yarn	3	3

3.3.2.2 Enzymatic Scouring

Three kinds of enzymes, pectinase; protease; and lipase were used as scouring agents for cotton substrates in this experiment.

Greige yarn, greige knitted fabrics, and desized woven fabrics were treated in solutions containing Womine TE and enzyme(s) at a liquor ratio of 50:1 at pH, temperatures and times indicated in Table 3.6. Scoured fabrics were then taken out and rinsed in hot water for 10 minutes. Many scouring trials were conducted first on greige

knitted fabric (yarn count 50/1) in order to find the best formulation and condition for enzymatic scouring, then conducted on other cotton substrates using the formulation and condition based on those obtained from enzymatic scouring of knitted fabric (yarn count 50/1). The enzymatic scouring procedure is as follows.

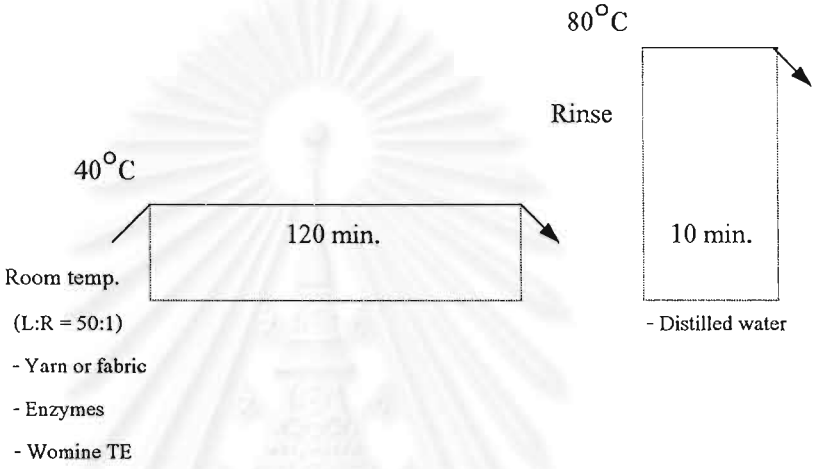


Diagram 3.3 The enzymatic scouring procedure.

Table 3.6 The enzymatic scouring formulations using various enzymes.

Cotton Substrate	Trial	Enzyme		Womine TE (g/l)	Condition		
		Type	g/l		Temp.(°C)	pH	Time(hr.)
Knitted fabric, yarn count 50/1	1	Lipase	2	-	40	8	0.5
	2	Lipase	2	-	40	8	1
	3	Lipase	2	-	40	8	2
	4	Lipase	2	-	40	8	6
	5	Lipase	2	-	50	8	2
	6	Lipase Protease	2 2	-	40	8	2
	7	Lipase Protease	2 2	-	40	7.5	2

Table 3.6 (Continued)

Cotton Substrate	Trial	Enzyme		Womine TE (g/l)	Condition		
		Type	g/l		Temp.(°C)	pH	Time(hr.)
Knitted fabric, yarn Count 50/1	8	Lipase Protease	2 2	-	40	7.5	2
		Pectinase	1	-	40	4	2
	9	Lipase Protease	2 2	-	40	7.5	2
		Pectinase	2	-	40	4	2
	10	Pectinase	1	-	40	4	2
	11	Pectinase	3	-	40	4	2
	12	Pectinase	5	-	40	4	2
	13	-	-	1	40	4	2
	14	Pectinase	1	1	40	4	2
	15	Pectinase	3	1	40	4	2
	16	Pectinase	5	1	40	4	2
Knitted fabric, yarn count 24/2	1	Pectinase	5	1	40	4	2
	2	Pectinase	7	1	40	4	2
Plain weave fabric	1	Pectinase	3	1	40	4	2
Twill weave fabric	1	Pectinase	5	1	40	4	2
Yarn	1	Pectinase	3	1	40	4	2

After scouring, samples were tested for the presence of residual pectin, weight loss, water absorbency, strength, and whiteness index according to test procedures outlined in section 3.4.

3.3.3 Bleaching

3.3.3.1 Conventional Bleaching

Conventional scoured substrates were treated in bleaching solutions containing hydrogen peroxide, sodium hydroxide, sodium silicate, and Womine TE in the Ahiba Polymat® laboratory dyeing machine at a liquor ratio of 20:1. Bleaching process was conducted at 95°C at pH 11.5 for 60 minutes. Bleached substrates were then taken out, rinsed in distilled water at 80°C for 20 minutes and neutralized in 1 g/l formic acid at room temperature for 10 minutes. The bleaching formulation (see Table 3.7) and condition used in this experiment were based on the industrial guideline and on theoretical data. The conventional bleaching procedure is as follows.

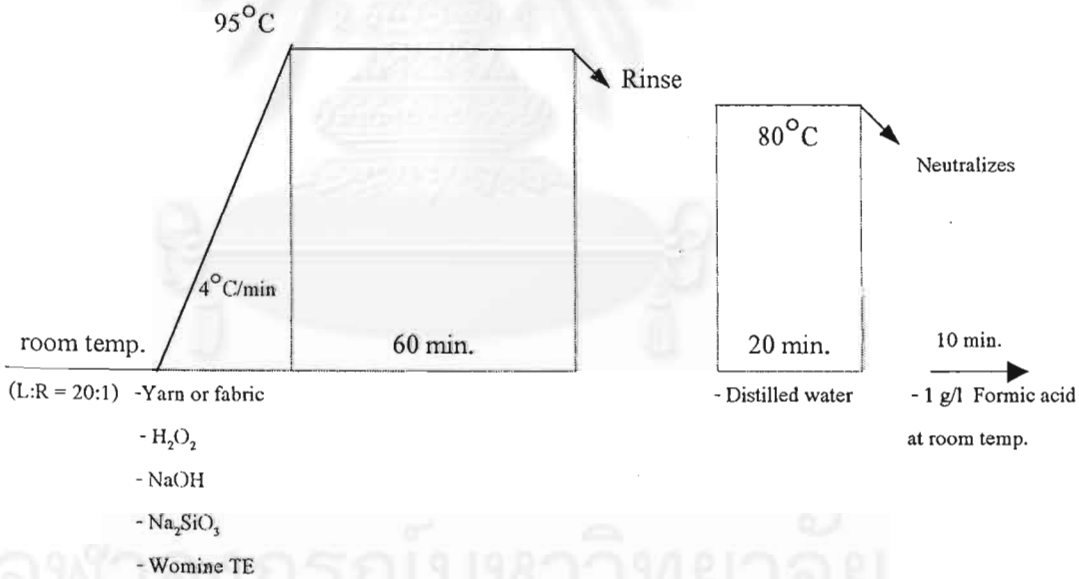


Diagram 3.4 The conventional bleaching procedure.

Table 3.7 The conventional bleaching formulations.

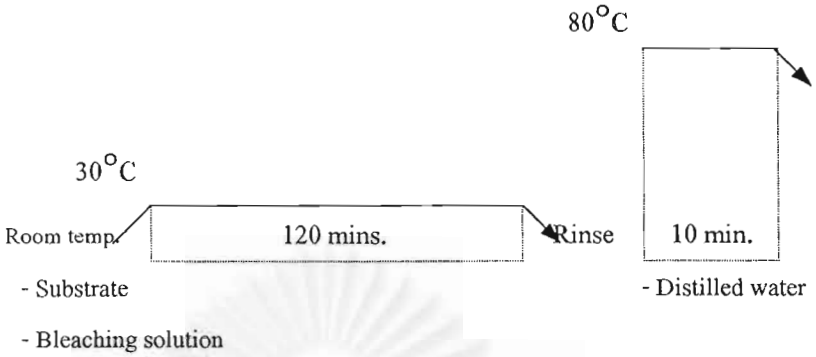
Cotton Substrate	H_2O_2(50%) (g/l)	NaOH (g/l)	Sodium silicate (g/l)	Womine TE (g/l)
Plain weave fabric	4	2	2	1
Twill weave fabric	7	3	2	1
Knitted fabric, yarn count 50/1	3	2	2	1
Knitted fabric, yarn count 24/2	4	2	2	1
Yarn	2	2	2	1

3.3.3.2 Pre-bleaching using Enzymes

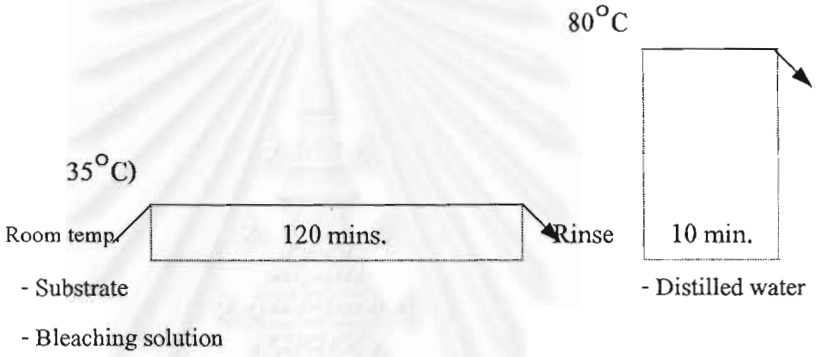
Three kinds of enzymes, xylanase; cellulase; and glucose oxidase were used as bleaching agents for cotton substrates in this experiment.

Enzymatic scoured substrates were treated in solutions containing enzyme(s) at liquor ratio, pH, temperatures and times indicated in Table 3.8. Many bleaching trials were conducted first on enzymatic scoured yarn (50/1) in order to find the best formulation and condition for enzymatic bleaching, then conducted on other scoured substrates using the formulation and condition based on those obtained from enzymatic bleaching of enzymatic scoured yarn (50/1). The enzymatic bleaching procedure is as follows.

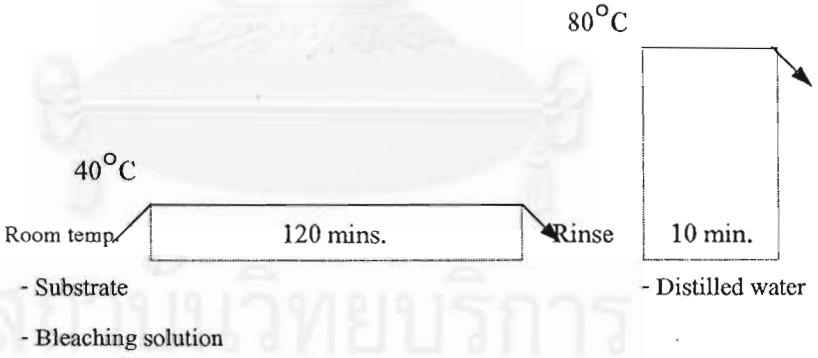
Process I



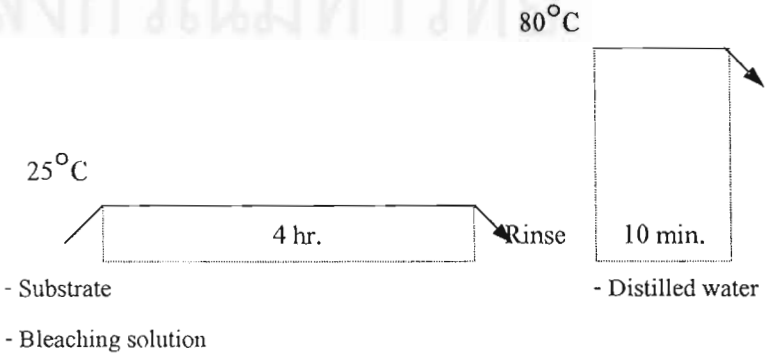
Process II



Process III



Process IV



Process V

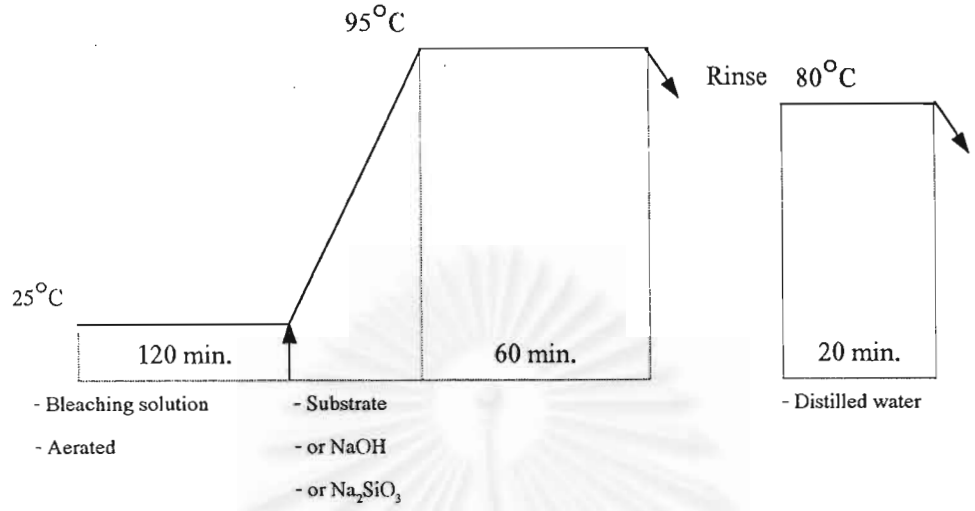


Diagram 3.5 The enzymatic bleaching procedure.

Table 3.8 The enzymatic bleaching formulations for cotton substrates using various enzymes.

Cotton Substrate	Trial No.	Enzyme		L:R	Condition			Process
		Type	g/l		Temp.(°C)	pH	Time(hr.)	
Yarn	1	Xylanase	4	10:1	30	4.5	2	I
	2	Xylanase	4	10:1	35	4.5	2	II
		Cellulase	4					
	3	Cellulase	8	50:1	40	4.5	2	III
	4	Cellulase	8	50:1	40	4.5	2	III
		Xylanase	4	10:1	40	4.5	2	III
Knitted-fabric Yarn count 50/1	1	Glucose oxidase + glucose	1 3.24	20:1	25	7	4	IV
	2	Glucose oxidase + glucose	1 10	20:1	25	7	4	IV
	3	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	4	IV

Table 3.8 (Continued)

Cotton Substrate	Trial No.	Enzyme Type	Enzyme g/l	L:R	Condition Temp.(°C)	Condition pH	Condition Time(hr.)	Process
Knitted-fabric Yarn count 50/1	4	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	V
		+ substrate			95		1	
	5	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	V
		+ substrate			95		2	
	6	Glucose oxidase + glucose + O_2	2 50	20:1	25	7	2	V
		+ substrate			95		1	
	7	Glucose oxidase + glucose + O_2	2 50	20:1	25	7	2	V
		+ substrate + NaOH	1		95		1	
	8	Glucose oxidase + glucose + O_2	2 50	20:1	25	7	2	V
		+ substrate + NaOH + Sod. Silicate	1 1		95		1	

Table 3.8 (Continued)

Cotton Substrate	Trial No.	Enzyme Type	Enzyme g/l	L:R	Condition Temp.(°C)	Condition pH	Condition Time(hr.)	Process
Knitted-fabric Yarn count 50/1	9	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	V
		+ substrate + NaOH	1		95		1	
Knitted-fabric Yarn count 24/2	1	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	V
		+ substrate + NaOH	1		95		1	
Plain weave fabric	1	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	V
		+ substrate + NaOH	1		95		1	
Twill weave fabric	1	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	V
		+ substrate + NaOH	1		95		1	
Yarn	1	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	V
		+ substrate + NaOH	1		95		1	

3.3.3.3 Peroxide Content in Enzymatic Bleach Liquors

Solutions containing 1 g/l of glucose oxidase enzyme and 50 g/l of D-glucose at pH 7 were aerated with oxygen at 25°C for 0, 1, 2, 3, 4 and 5 hours. Hydrogen peroxide content in each solution was measured by a method described in section 3.4.12.

Solutions of pH 7 containing 1 g/l of glucose oxidase and various concentrations of D-glucose (10 - 80 g/l) were aerated with oxygen at 25°C for 2 hours. Hydrogen peroxide content in each solution was measured by the same method as above.

3.3.3.4 Post-bleaching using Hydrogen Peroxide

Due to low whiteness index of enzymatic bleached substrates, they were further bleached in solutions containing hydrogen peroxide, sodium hydroxide, sodium silicate, and Womine TE in the Ahiba Polymat® laboratory dyeing machine at a liquor ratio of 20:1. Bleaching process was conducted at 95°C at pH 11.5 for 60 minutes. Bleached substrates were then taken out, rinsed in distilled water at 80°C for 20 minutes and neutralized in 1 g/l formic acid at room temperature for 10 minutes. To remove residual peroxide from bleached substrates, a bleach clean-up process using catalase enzyme was conducted on the substrates. Post-bleaching formulations for various substrates are shown in Table 3.9. The post-bleaching procedure is as follows.

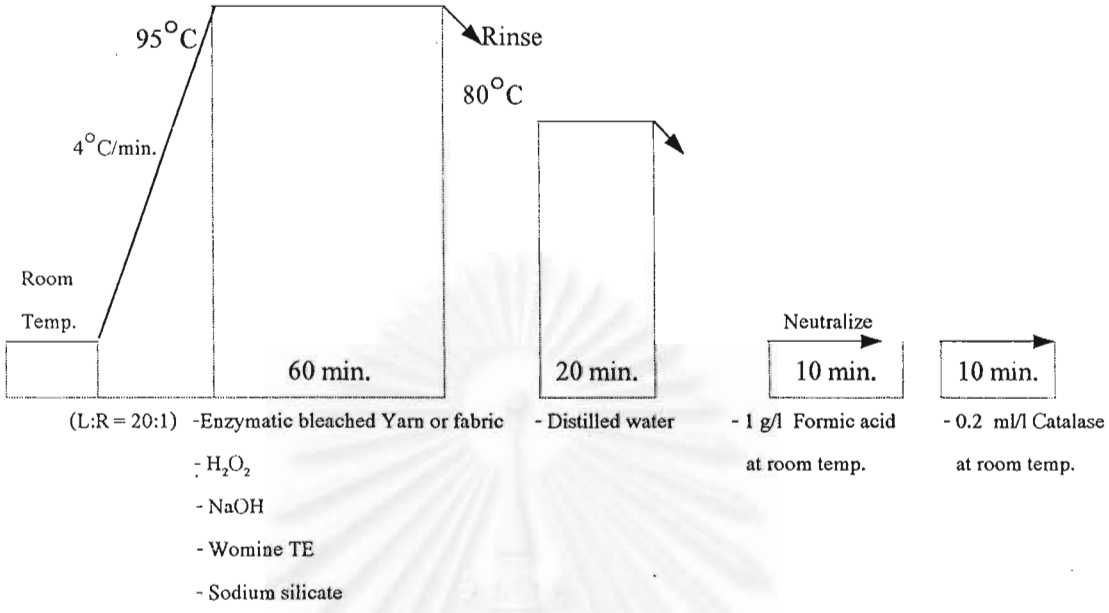


Diagram 3.6 The post-bleaching procedure.

Table 3.9 Post-bleaching formulations.

Cotton Substrate	H_2O_2(50%) (g/l)	NaOH (g/l)	Sodium silicate (g/l)	Womine TE (g/l)
Plain weave fabric	2	2	2	1
Twill weave fabric	5	3	2	1
Knitted fabric, yarn count 50/1	2	2	2	1
Knitted fabric, yarn count 24/2	2	2	2	1
Yarn	1	1	2	1

After bleaching, samples were tested for whiteness index, strength, residual peroxide, pH, and dyeing performance according to test procedures outlined in section 3.4.

General Standards for Well Prepared Cotton Yarn and Fabrics

Good prepared yarns and fabrics should contain the following properties

1. Sizes, waxes, motes etc., should be extracted uniformly and completely from prepared yarns and fabrics.

2. Prepared yarns and fabrics should be instantaneously and uniformly wet with water in order to provide uniform dyeing performance.

3. Prepared yarns and fabrics should contain a minimum whiteness index of 72.

4. After preparation, the strength of prepared yarn and fabric should not be less than 80-90% of their original strength.

5. Prepared yarns and fabrics should contain pH between 7-8.5.

6. Prepared yarns and fabrics should provide soft hand.

3.4 Test Procedures

3.4.1 Yarn and Fabric Strength

Yarn samples were tested for tensile strength using ASTM D 2256, Tensile Properties of Yarns by the Single-Strand Method.[30]

Woven fabrics were tested for tensile strength using ASTM D 5035, Tensile Properties of Woven Fabric: Reveled Strip Test-1R.[31]

Knitted fabrics were tested for bursting strength using the Standard for Method of Testing for Textiles, Volume 19, Diaphragm Bursting Strength and Busrting Distension Tester Method.[32]

3.4.2 Size Identification on Fabrics

The type of size on the greige woven fabrics was determined using spot tests introduced by Livengood.[33]

Figure 3.2 Tensile strength tester.

Figure 3.3 Bursting strength tester.

3.4.3 Presence of Starch on Fabrics

TEGEWA method is one of the commonest test methods for determining the presence of starch sizes on fabrics by dabbing the fabric with a solution of iodine/potassium iodide. A blue coloration indicates that starch size is still present on the fabric. In application of this test, it is important to know that even if only 1% of the original starch size is still present, i.e., if 99% have been removed, a blue coloration will still be visible. However, this slight amount of residual size will certainly no longer have any influence on the behaviour of the pretreated goods during dyeing or printing.

A remedy is offered by TEGEWA violet scale, which embraces nine shades denoted by ratings. A rating of 1 indicates poorest or no desizing; and of 9, practically completes desizing.

The test was conducted by immersing a specimen of fabric for 1 minute in a 0.005 mol/l iodine solution. Afterwards wash briefly in water, dab with filter paper, and compare immediately with the violet scale. The poorest rating is 1 and the best rating is 9.

3.4.4 Water Absorbency

Absorbency is one of several factors that determine the suitability of the fabric for dyeing. The absorbency test was conducted using AATCC Test Method 79, "Absorbency of Bleached Fabric[34]". A drop of water is allowed to fall onto the surface of the test specimen. The time required for the specula reflection of the water drop to disappear is measured and recorded as a wetting time. The shorter the time, the more absorbent is the textile. Three seconds or less is generally considered to represent adequate absorbency.

3.4.5 Fabric Weight

Fabric weight was determined by cutting the sample using a standard cutter and weighing the cut sample. The fabric weight was reported as mass in grams per unit area in 100 cm^2.

3.4.6 Extractable Materials in Yarn and Fabrics

The extractable materials in greige yarn and fabrics were determined using AATCC Test Method 97, "Extractable of Greige and/or Prepared Textiles".[35]

3.4.7 Yarn and Fabric Weight Loss

Yarn and fabric weight losses after each preparation process were determined using AATCC Test Method 20A.[36]

3.4.8 Presence of Pectin on Yarn and Fabrics

Yarn and fabric samples were tested for the presence of pectin by measuring the absorption of methylene blue onto the samples. This method is based on the interaction between the cationic dye of methylene blue and the carboxylate anion of the pectin on samples. The higher the dyes absorb onto the substrate, the higher the presence of pectin. A calibration curve indicating a relation dye solution concentrations and dye absorbance was constructed. Methylene blue solutions of various concentrations (0.0005, 0.001, 0.002, 0.003, 0.004,

Figure 3.4 UV-visible spectrophotometer.

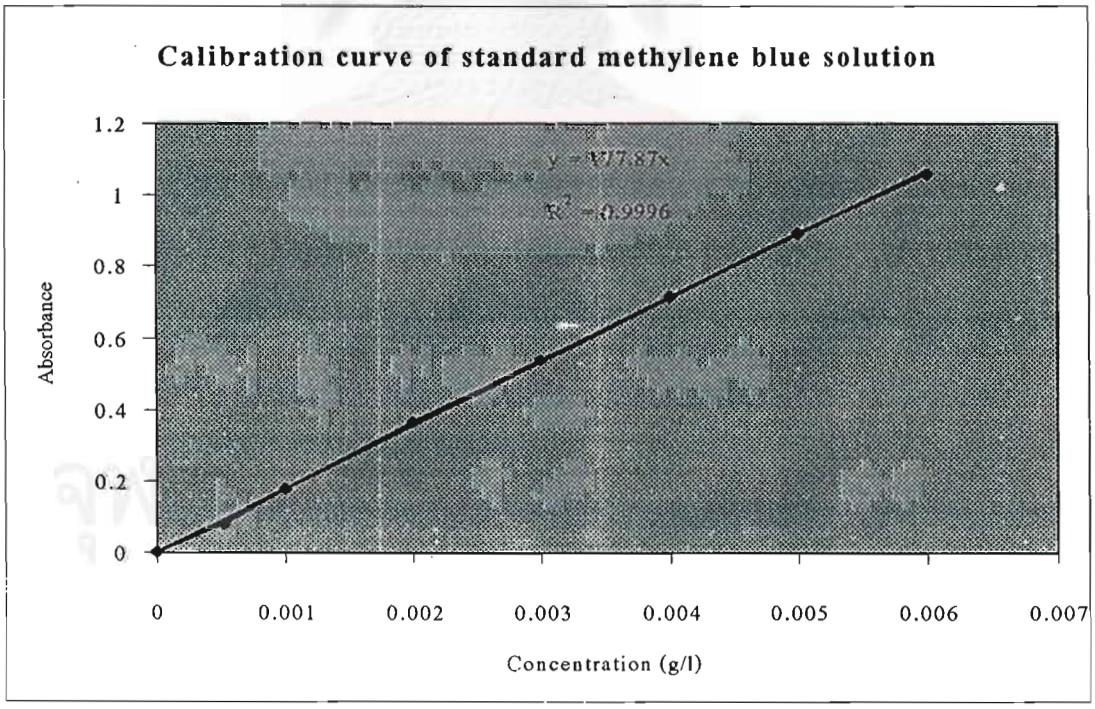


Figure 3.5 Concentration vs absorbance calibration curve of standard methylene blue solution.

Unscoured and scoured cotton substrates were treated in solutions containing 0.5 g/l methylene blue in the Ahiba Polymat® laboratory dyeing machine at a liquor ratio of 30:1. Treatment process was conducted at 70°C for 8 hours. The solution after dyeing was diluted 40 times with distilled water. Then it was measured for maximum absorption at wavelength 662 nm. using UV-visible spectrophotometer. Dye concentration of the solution after dyeing was determined using the calibration curve and was converted into dye concentration on cotton substrate.

3.4.9 Whiteness Index of Yarn and Fabrics

Whiteness index of yarn and fabric after bleaching process were determined with a Mac Beth color spectrophotometer (CIE Ganz). (see Figure 3.6)

3.4.10 Residual Peroxide on Bleached Yarn and Fabrics

Residual peroxide on bleached yarn and fabrics after bleaching process were determined using spot test introduced by Interax Chemicals Ltd.[37]

3.4.11 pH of Prepared Yarn and Fabrics

The pH of prepared yarn and fabrics after bleaching process were determined using AATCC Test Method 81, pH of the Water-Extract from Bleached Textiles.[38]

3.4.12 Peroxide Content Measurements.[37]

Hydrogen peroxide content in bleaching solution can be determined by titration against standard potassium permanganate.

The reaction involved is represented by the following equation:

$$5\ H_2O_2 + 2\ KMnO_4 + 3\ H_2SO_4 = 2\ MnSO_4 + K_2SO_4 + 5\ O_2 + 8\ H_2O$$

Usually 0.1 N $KMnO_4$ is used but special solutions can be made up e.g., AATCC Method 102 uses 0.588 N and in continental Europe 0.23 N is used. The major reason for these special solutions is that a simple relationship exists between the titre and the concentration of hydrogen peroxide in the bath.

To carry out the titration, measure 100 ml dilutes (10%) sulphuric acid into a 250 conical beaker. Pipette a suitable amount (V ml) of hydrogen peroxide bleached solution into a beaker containing a dilute acid and titrate immediately with potassium permanganate to the same faint pink color. Let the titre be *A* ml. of 0.1 N $KMnO_4$.

1 ml of 0.1 N $KMnO_4$ is equivalent to 0.0017g 100% H_2O_2, then *V* ml of bleach liquor sample will contain 0.0017 x *A* g 100% H_2O_2.

$$H_2O_2 \text{ content} = \frac{0.0017 \times A \times 1000}{V} \text{ g/l } H_2O_2 100\%$$

3.4.13 Dye Absorption Measurements

Bleached cotton substrates were dyed with direct dye, Benzopurpurine 4B 1% o.w.f. (of weight of fabric) in an Ahiba Polymat® laboratory dyeing machine at a liquor ratio of 30:1. The dyeing process was commenced at room temperature, raised to 95°C (5°C/minute) and maintained at this temperature for 45 minutes. The dyed fabrics were then removed from dye solution, rinsed thoroughly in running tap water, squeezed and dried. The dyeing process is illustrated in Diagram 3.7.

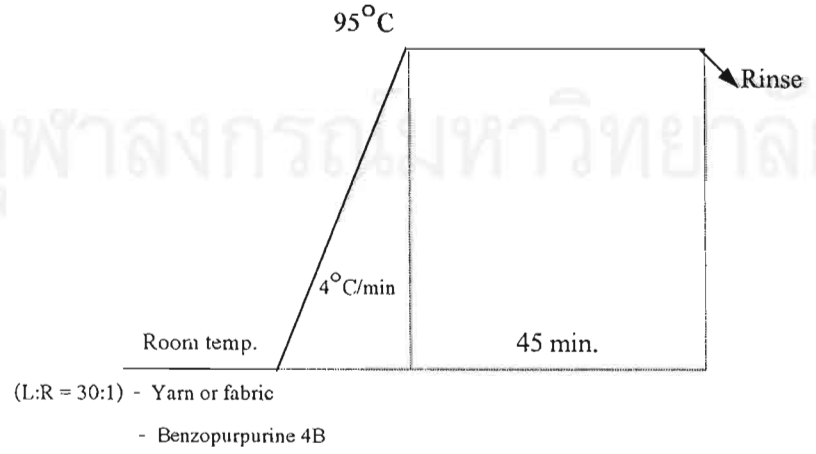


Diagram 3.7 The dyeing process.

After dyeing, samples were measures for color strength by using an Instrumental Color System, (I.C.S) Macbeth reflectance spectrophotometer (Figure 3.6) to measure the reflectance values of the samples at 520 nm. Increasing the concentration or strength of the dye on the fabric results in decreasing in fabric reflectance (R) at the wavelength of maximum absorption (λ_{max}). The sample with more dyestuff on gives higher color strength. The color strength of the dyed fabric can be expressed as K/S value calculated by the Kubelka Munk equation.

$$K/S = \frac{(1-R)^2}{2R}$$

where K is the absorption coefficient

S is the scattering coefficient

R is the reflectance of the fabric at the wavelength of maximum absorption (λ_{max})

Figure 3.6 I.C.S. Macbeth spectrophotometer (Color-eye 7000)

CHAPTER IV

Results and Discussion

4.1 Greige Yarn and Fabrics

Greige substrates were tested for various properties according to test procedures outlined in section 3.4 and their properties are shown in Table 4.1.

Table 4.1 Properties of greige yarn and fabrics.

	Plain weave Fabric	Twill weave fabric	Knitted fabric (50/1)	Knitted fabric (24/2)	Yarn (50/1)
Sizes	Starch	Starch/PVA	-	-	-
TEGEWA violet Scale (size presence)	1	1	-	-	-
MB(g) on substrate(kg) (presence of pectin)	See table 4.2	See table 4.2	12.08	11.80	12.59
Total Extractable Material (%)	9.029	9.129	2.959	2.391	3.352
Weight (g/100cm^2)	1.4996	3.8971	1.1784	2.7855	-
Breaking load (N)	368.9	815.7	-	-	1.63
Bursting strength (kg/cm^2)	-	-	6.04	13.98	-
Water absorbency	Did not absorb water				
Whiteness index	-4.843	-16.756	-0.725	-10.580	4.940
Yellowness	28.754	31.270	27.201	30.766	24.723

MB = Methylene blue

Breaking load [27] = Warp + Weft

4.2 Desizing

The desized fabrics were tested for various properties shown in Table 4.2.

Table 4.2 Properties of desized fabrics.

	Plain weave fabric	Twill weave fabric
TEGEWA violet scale (size presence)	8.5	8.5-9
MB (g.) on substrate (kg.) (presence of pectin)	11.96	13.21
% Weight loss	8.73	8.68
Water absorbency	Absorbed water after 1 minute	
Breaking load (N)	341.0	812.7
Whiteness index	8.92	-0.52
Yellowness	23.46	24.74

After desizing with the formulations from Table 3.4, the fabrics were almost completely free of sizes. Although around 8-9% of sizes and water soluble material were removed, the fabrics still did not absorb water well. Their fabric breaking loads decreased a little and whiteness index slightly increased from the greige fabrics.

4.3 Scouring

4.3.1 The Effects of Conventional and Enzymatic Scouring on Water Absorbency of Substrates.

The first priority required in substrates is they must be uniformly wet with water within 5 seconds at room temperature. For this work, a more rigorous standard of less than 3 seconds was used to signify an adequate absorbency.

Table 4.3 Water absorbency of scoured substrates using the conventional scouring formulations.

Cotton Substrate	Sodium hydroxide (% owf.)	Womine TE (g/l)	Water absorbency
Twill weave fabric	4	3	A
Plain weave fabric	2	3	A
Knitted fabric (yarn count 50/1)	3	3	A
Knitted fabric (yarn count 24/1)	5	3	A
Yarn	3	3	A

Water absorbency A = Absorbed immediately
B = Absorbed within 1-3 seconds
C = Absorbed within 1 minute
D = Stayed as water drop

After the conventional scouring process using the formulations in Table 4.3, all scoured substrates were instantaneously wet with water when they were tested for water absorbency.

Table 4.4 Water absorbency of scoured substrates using the enzymatic scouring formulations.

Cotton Substrate	Trial	Enzyme		Womine TE (g/l)	Condition			Water Absorb-ency*
		Type	g/l		Temp. (°C)	pH	Time (hr.)	
Knitted fabric, yarn count 50/1	1	Lipase	2	-	40	8	0.5	D
	2	Lipase	2	-	40	8	1	D
	3	Lipase	2	-	40	8	2	D
	4	Lipase	2	-	40	8	6	D
	5	Lipase	2	-	50	8	2	D
	6	Lipase Protease	2 2	-	40	8	2	D

Table 4.4 (Continued)

Cotton Substrate	Trial	Enzyme		Womine TE (g/l)	Condition			Water Absorb-ency*
		Type	g/l		Temp. (°C)	pH	Time (hr.)	
Knitted fabric, yarn count 50/1	7	Lipase Protease	2 2	-	40	7.5	2	D
	8	Lipase Protease	2 2	-	40	7.5	2	C
		Pectinase	1	-	40	4	2	
	9	Lipase Protease	2 2	-	40	7.5	2	C
		Pectinase	2	-	40	4	2	
	10	Pectinase	1	-	40	4	2	C
	11	Pectinase	3	-	40	4	2	C
	12	Pectinase	5	-	40	4	2	C
	13	-	-	1	40	4	2	D
	14	Pectinase	1	1	40	4	2	C
	15	Pectinase	3	1	40	4	2	C
	16	Pectinase	5	1	40	4	2	A
Knitted fabric, yarn count 24/2	1	Pectinase	5	1	40	4	2	C
	2	Pectinase	7	1	40	4	2	B
Plain weave fabric	1	Pectinase	3	1	40	4	2	A
Twill weave fabric	1	Pectinase	5	1	40	4	2	B
Yarn	1	Pectinase	3	1	40	4	2	A

* See Table 4.3 for descriptions of A, B, C and D

To increase water absorbency of cotton substrates, impurities on cotton fibers such as waxes, oils, pectins, proteins, etc. should be removed to some extent. Thin knitted fabric (yarn count 50/1) was first to be scoured using the enzymatic scouring formulations shown in Table 4.4. Using lipase alone or together with protease did not help improving the water absorbency of this fabric. Once pectinase was added as the

third enzyme into the system, some improvement of fabric absorbency occurred. Afterward, all substrates were scoured with only pectinase enzyme. The previous knitted fabrics were then scoured in solution of pectinase at elevates concentrations from 1, 3 to 5 g/l with and without the addition of 1 g/l wetting agent. Finally, the best scouring formulation for this fabric was found at 5 g/l pectinase with 1 g/l wetting agent at pH 4, temperature 40°C, and processing time 2 hours. Thick knitted fabric (yarn count 24/2) needed at least 7 g/l pectinase, thin woven fabric (plain weave) and yarn (yarn count 50/1) needed 3 g/l pectinase, and the thick woven fabric (twill weave) needed at least 5 g/l pectinase, in the presence of 1 g/l wetting agent at same pH, temperature and time as the thin knitted fabric (yarn count 50/1).

These lipase and protease enzymes might not be suitable for scouring process. Only a pectinase and a small amount of wetting agent are needed for scouring the substrates to the required water absorbency. An addition of a non-ionic wetting agent such as Womine TE helps reducing the surface tension of cotton substrate, assisting enzymes to penetrate into the micropores or cracks of fiber surface and helping enzymes orient themselves in favorable positions for catalytic functions. After the enzymatic catalytic functions are accomplished, enzymes may re-enter the solution to bind to new sites and continue their functions.

4.3.2 The Effect of Conventional and Enzymatic Scouring on Strength and Weight loss of Substrates.

Conventional scoured substrates (using the formulation in Table 4.3) and enzymatic scoured substrates (using the best formulations in Table 4.4) were tested for strength and weight loss for a comparison. Tables 4.5, 4.6 and 4.7 show data of % weight loss and % strength change of scoured woven fabrics, scoured knitted fabrics and scoured yarn respectively, using conventional and enzymatic scouring systems.

Figures 4.1, 4.3 and 4.5 show that enzymatic scouring process provided scoured substrates with lower % weight loss than conventional scouring process. They also show that woven fabrics loss the least weight compared to knitted fabrics and yarn and the reason for that could be woven fabrics had lost some impurities such as waxes, oils, pectins, etc. during previous desizing process and thus contained less impurities to be removed in scouring process. The loss of substrate weight after scouring may be due to the loss of waxes, oils, pectins, water soluble materials, etc.

In the case of conventional scoured substrates, the loss of substrate weight is probably due to the main removal of waxes, fats and water soluble materials during saponification and emulsification reactions rather than the removal of pectin. On the contrary, weight loss of enzymatic scoured substrates is possibly due to the main loss of pectin during hydrolysis reaction catalyzed by pectinase.

Figures 4.2 and 4.6 show that both conventional and enzymatic scouring processes increased the woven fabric and yarn strength 5-43 %, except for enzymatic scoured twill weave fabric. The degree of strength increase was higher in conventional scoured substrates than in enzymatic scoured substrates and scoured yarn obtained the maximum strength increase. Knitted fabrics from both processes lost strength after scouring and the degree of strength loss was twice higher in conventional scoured substrates than in enzymatic scoured substrates (see Figure 4.4). The strength shown in Table 4.5, 4.6 and 4.7 probably the true strength of substrate and impurities in the cuticle of fibers and the fabric structures can possibly change the substrate strength.

Table 4.5 % Weight loss and breaking load of scoured woven fabrics compare with greige and desized woven fabrics.

	Weight Loss (%)	Breaking Load (N)			
		Warp	Weft	Warp+Weft[27]	% Change*
Plain weave fabric					
Greige		213.6	155.3	368.9	
Desized		183.4	157.6	341.0	0.00 %
Scoured (conventional)	1.318 %	198.3	185.3	383.6	+ 12.49 %
Scoured (enzymatic)	0.721 %	192.6	181.7	374.3	+ 9.77 %
Twill weave fabric					
Greige		568.7	247.0	815.7	
Desized		511.1	301.6	812.7	0.00 %
Scoured (conventional)	1.607 %	540.9	314.2	855.1	+ 5.22 %
Scoured (enzymatic)	0.785 %	488.8	293.2	782.0	- 3.78 %

* Note * Compared with desized woven fabric.

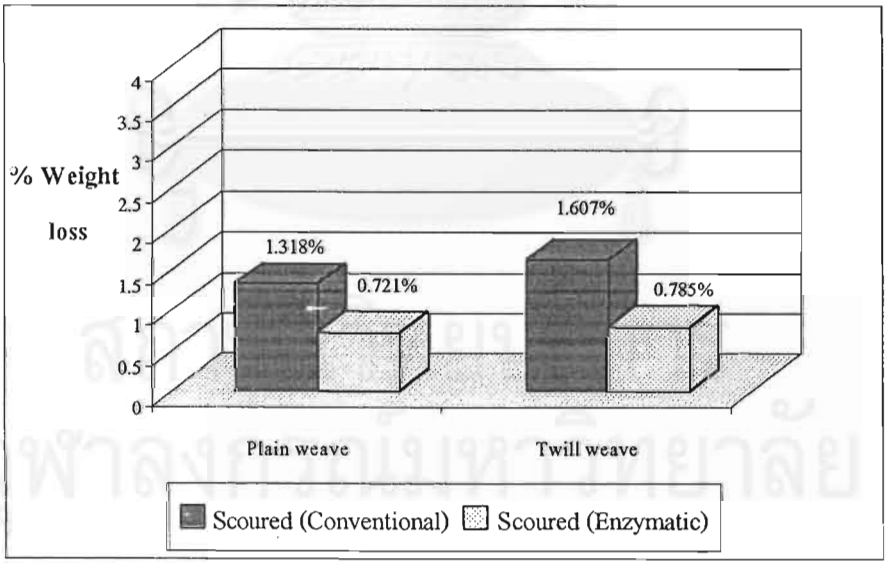


Figure 4.1 % Weight loss of scoured woven fabrics.

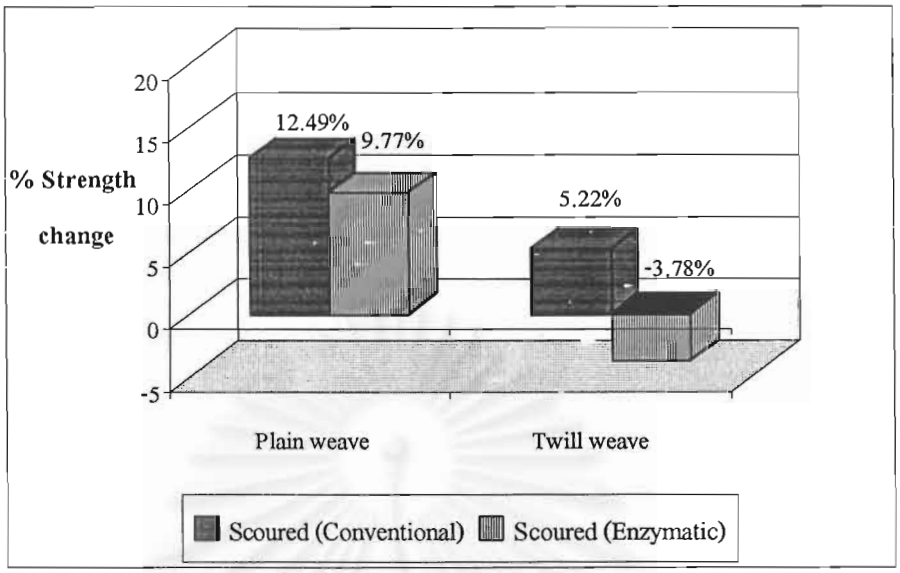


Figure 4.2 % Strength change of scoured woven fabrics.

Table 4.6 % Weight loss and bursting strength of scoured knitted fabrics compared with greige knitted fabrics.

	Weight Loss (%)	Bursting strength	
		kg/cm^2	% Change*
Knitted fabric (50/1)			
Greige		6.04	0.00 %
Scoured (conventional)	3.322 %	5.70	- 5.63 %
Scoured (enzymatic)	3.000 %	5.90	- 2.32 %
Knitted fabric (24/2)			
Greige		13.98	0.00 %
Scoured (conventional)	3.079 %	11.42	-18.31 %
Scoured (enzymatic)	2.700 %	12.76	- 8.73 %

* Note * Compared with greige knitted fabric.

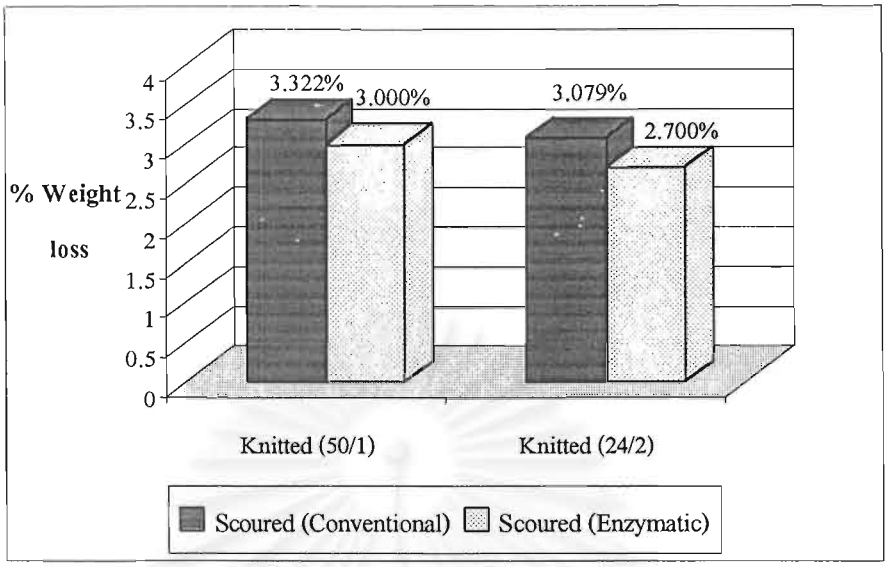


Figure 4.3 % Weight loss of scoured knitted fabrics.

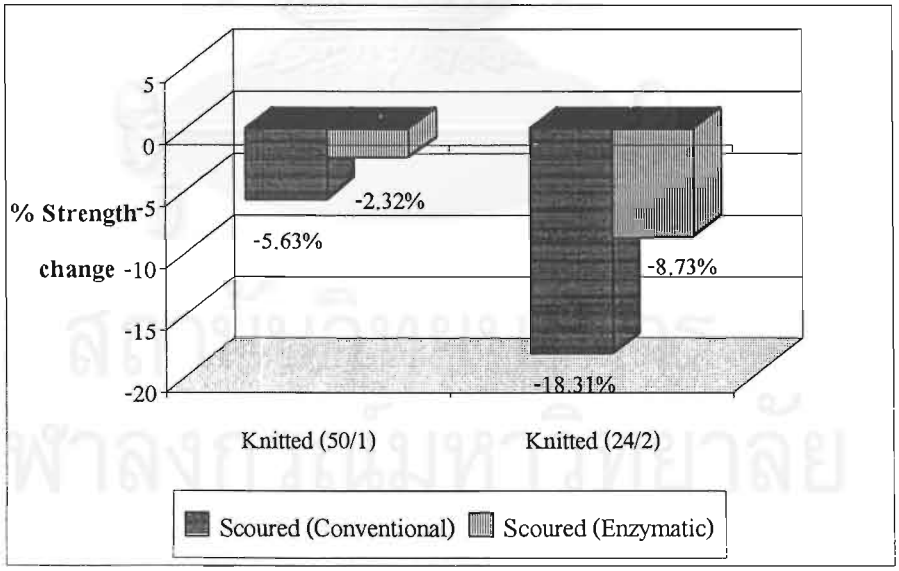


Figure 4.4 % Strength change of scoured knitted fabrics.

Table 4.7 % Weight loss and breaking load of scoured yarns compared with greige yarn.

	Weight Loss (%)	Breaking Load	
		(N)	% Change*
Yarn			
Greige		1.632	0.00 %
Scoured (conventional)	3.968 %	2.331	+ 42.83 %
Scoured (enzymatic)	3.178 %	2.203	+ 34.99%

* Note * Compared with greige yarn.

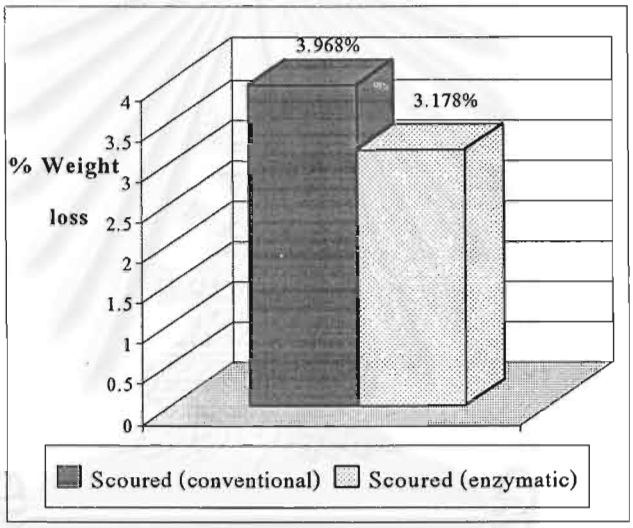


Figure 4.5 % Weight loss of scoured yarns.

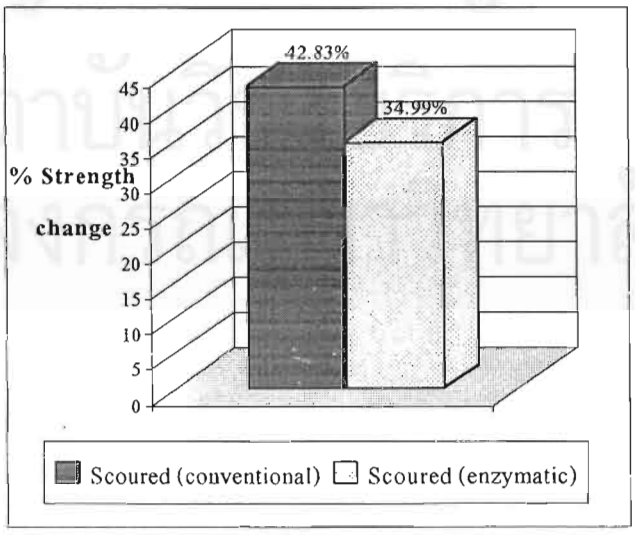


Figure 4.6 % Strength change of scoured yarns.

4.3.3 The Effects of Conventional and Enzymatic Scouring on the Removal of Pectins from Substrates and Whiteness Index of Substrates.

Table 4.8 shows the methylene blue content on scoured substrates and whiteness index / yellowness of scoured substrates compared with greige and desized substrates. The methylene blue content on substrates indicates the amount of pectins found in substrates. Figure 4.7 illustrates that scoured substrates contained less pectins than greige and desized substrates, and enzymatic scoured substrates contained lower level of pectins than conventional scoured substrates, except for scoured yarn. This result indicates that both scouring methods removed pectins from substrates to some extent but the enzymatic method provided slightly higher efficiency of pectin removal than the conventional scouring method.

Table 4.8 also shows that both scouring processes increased 18-24 degree whiteness index of substrates from greiges in the case of knitted fabrics and yarn and 2-5 degrees from desized substrates in the case of woven fabrics. Both scouring methods provided substrates with comparable whiteness index.

Overall results from scouring step reveal that enzymatic scouring process using pectinase enzyme and a small amount of wetting agent can be used to scour cotton substrates to their adequate absorbency with low % weight loss, low % strength loss and 2-24 degrees increase in whiteness index. This pectinase enzyme may be used in enzymatic scouring as comparable to sodium hydroxide in conventional scouring.

Table 4.8 Methylene blue content on scoured substrates, whiteness index and yellowness of scoured substrates compared with greige and desized substrates.

	MB (g/kg)	Whiteness Index	Yellowness
Plain weave fabric			
Greige		-4.843	28.754
Desized	11.96	8.921	23.455
Scoured (conventional)	11.70	10.947	22.773
Scoured (enzymatic)	11.21	10.783	22.942
Twill weave fabric			
Greige		-16.756	31.270
Desized	13.21	-0.525	24.745
Scoured (conventional)	11.46	4.486	24.134
Scoured (enzymatic)	10.98	3.404	24.701
Knitted fabric (50/1)			
Greige	12.08	- 0.725	27.201
Scoured (conventional)	10.70	23.612	19.822
Scoured (enzymatic)	10.61	23.242	20.422
Knitted fabric (24/2)			
Greige	11.80	- 10.580	30.766
Scoured (conventional)	10.78	7.884	25.259
Scoured (enzymatic)	10.12	7.269	25.509
Yarn			
Greige	12.59	14.940	24.723
Scoured (conventional)	10.96	38.364	16.535
Scoured (enzymatic)	10.96	38.174	16.681

MB = methylene blue (g.) per kg. of substrate

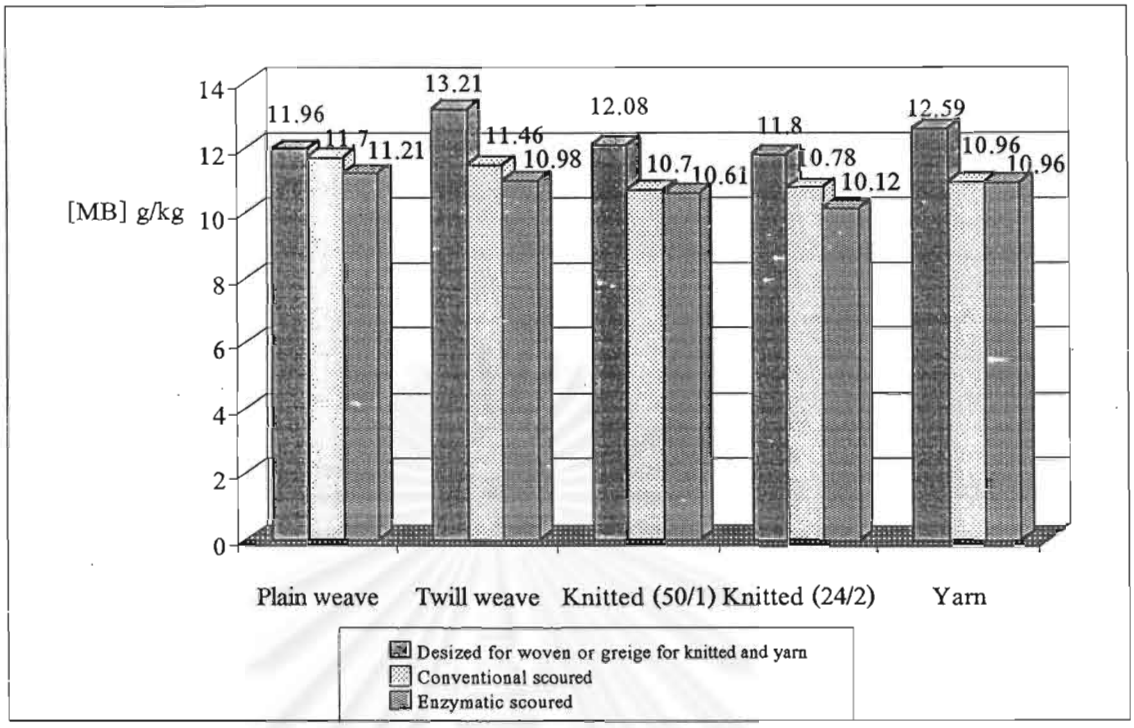


Figure 4.7 The presence of methylene blue on scoured substrates compared with greige and desized substrates.

4.4 Bleaching

4.4.1 The Effect of Conventional and Enzymatic Bleaching on Whiteness Index of Substrates

Scoured substrates with adequate absorbency were bleached using conventional and enzymatic bleaching methods. They were then tested for whiteness index, strength, pH, residual peroxide, and dye absorption and the results are as follows.

Table 4.9 shows the required conventional bleaching formulations for each substrate for obtaining whiteness index above or close to 72.

Table 4.9 Whiteness index of bleached substrates using conventional bleaching formulations.

Chemical / Cotton Substrate	H_2O_2(50%) (g/l)	NaOH (g/l)	Sodium silicate (g/l)	Womine TE (g/l)	Time (min)	WI CIE
Plain weave fabric	4	2	2	1	60	**72.683**
Twill weave fabric	7	3	2	1	60	**69.129**
Knitted fabric, yarn count 50/1	3	2	2	1	60	**76.333**
Knitted fabric, yarn count 24/1	4	2	2	1	60	**71.815**
Yarn	2	2	2	1	60	**81.100**

WI = Whiteness Index

Table 4.10 shows whiteness index of substrates bleached with enzymatic bleaching system. Yarn was the first to be bleached. Among four potential bleaching agents consisting of xylanase, cellulase, peroxidase and glucose oxidase, xylanase/cellulase system was firstly chosen and found that this system did not help increasing whiteness index of substrates.

Peroxidase enzyme was also not used for bleaching because it was brown in color and did stain this color on substrates during bleaching. Therefore the last choice was glucose oxidase enzyme. To conduct bleaching using glucose oxidase, bleach liquor must be prepared in order to produce the bleaching species "hydrogen peroxide". Peroxide content in bleach liquor was measured and the results are shown in section 4.4.2.

Knitted fabric (yarn count 50/1) was bleached in liquor containing glucose oxidase and glucose at various conditions (trials 1-9) and the maximum whiteness index obtained when bleaching substrate with the formulations of trials 7-9. That is

first to prepare the bleach liquor using glucose oxidase, glucose and oxygen at 25°C at pH 7 for 2 hours. Then adding sodium hydroxide and sodium silicate before adding substrate into the bleach bath and conducting bleaching at 95°C for 1 hour.

Table 4.10 Whiteness index of bleached substrates using enzymatic pre-bleaching formulations.

Cotton substrate	Trial No.	Enzyme		L:R	Condition			Process	Whiteness Index	
		Type	g/l		Temp. (°C)	pH	Time (hr.)		Before	After
Yarn	1	Xylanase	4	10:1	30	4.5	2	I	38.174	38.543
	2	Xylanase Cellulase	4 4	10:1	35	4.5	2	I	38.174	39.213
	3	Cellulase	8	50:1	40	4.5	2	I	38.174	39.427
	4	Cellulase	8	50:1	40	4.5	2	I	38.174	39.742
		Xylanase	4	10:1	40	4.5	2	I		
Knitted-fabric Yarn count 50/1	1	Glucose oxidase + glucose	1 3.24	20:1	25	7	4	I	23.242	24.027
	2	Glucose oxidase + glucose	1 10	20:1	25	7	4	I	23.242	24.279
	3	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	4	I	23.242	24.733
	4	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	II	23.242	32.803
		+ substrate			95		1			
	5	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	II	23.242	33.437
		+ substrate			95		2			
	6	Glucose oxidase + glucose + O_2	2 50	20:1	25	7	2	II	23.242	34.238
		+ substrate			95		1			

Table 4.10 (Continued)

Cotton substrate	Trial No.	Enzyme		L:R	Condition			Process	Whiteness Index	
		Type	g/l		Temp. (°C)	pH	Time (hr.)		Before	After
Knitted-fabric Yarn count 50/1	7	Glucose oxidase + glucose + O_2	2 50	20:1	25	7	2	II	23.242	41.237
		+ substrate + NaOH	 1		95		1			
	8	Glucose oxidase + glucose + O_2	2 50	20:1	25	7	2	II	23.242	41.694
		+ substrate + NaOH + Sod. silicate	 1 1		95		1			
	9	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	II	23.242	39.323
		+ substrate + NaOH	 1		95		1			
Knitted-fabric Yarn count 24/2	1	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	II	7.269	24.588
		+ substrate + NaOH	 1		95		1			
Plain weave	1	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	II	7.783	22.299
		+ substrate + NaOH	 1		95		1			
Twill weave	1	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	II	3.404	17.125
		+ substrate + NaOH	 1		95		1			

Table 4.10 (Continued)

Cotton substrate	Trial No.	Enzyme		L:R	Condition			Process	Whiteness Index	
		Type	g/l		Temp. (°C)	pH	Time (hr.)		Before	After
Yarn	1	Glucose oxidase + glucose + O_2	1 50	20:1	25	7	2	II	38.174	54.042
		+ substrate + NaOH	1		95		1			

Other substrates were then bleached using the formulations based on those obtained from knitted fabric (yarn count 50/1)

Table 4.10 indicates that enzymatic bleaching system using glucose oxidase as a catalyst can increase whiteness index of scoured substrate to nearly 20 degrees. It also shows that as soon as the bleaching species "hydrogen peroxide" occurred in the bleach liquor, sodium hydroxide was needed to be added in order to obtain an efficient bleaching system.

4.4.2 A Study for Peroxide Content in Enzymatic Bleach Liquors.

Section 3.3.3.3 describes a study of peroxide content measurement of the prepared bleach liquors at various times and various concentrations of D-glucose, and the results are shown in Tables 4.11 – 4.12 and Figures 4.8 - 4.9.

Table 4.11 Peroxide content in enzymatic bleach liquors containing 1 g/l glucose oxidase, 50 g/l D-glucose and oxygen at pH 7 at 25°C for 0 – 5 hours.

Time (hrs.)	Peroxide content (g/l)
0	0.000
1	0.850
2	1.076
3	1.130
4	1.162
5	1.162

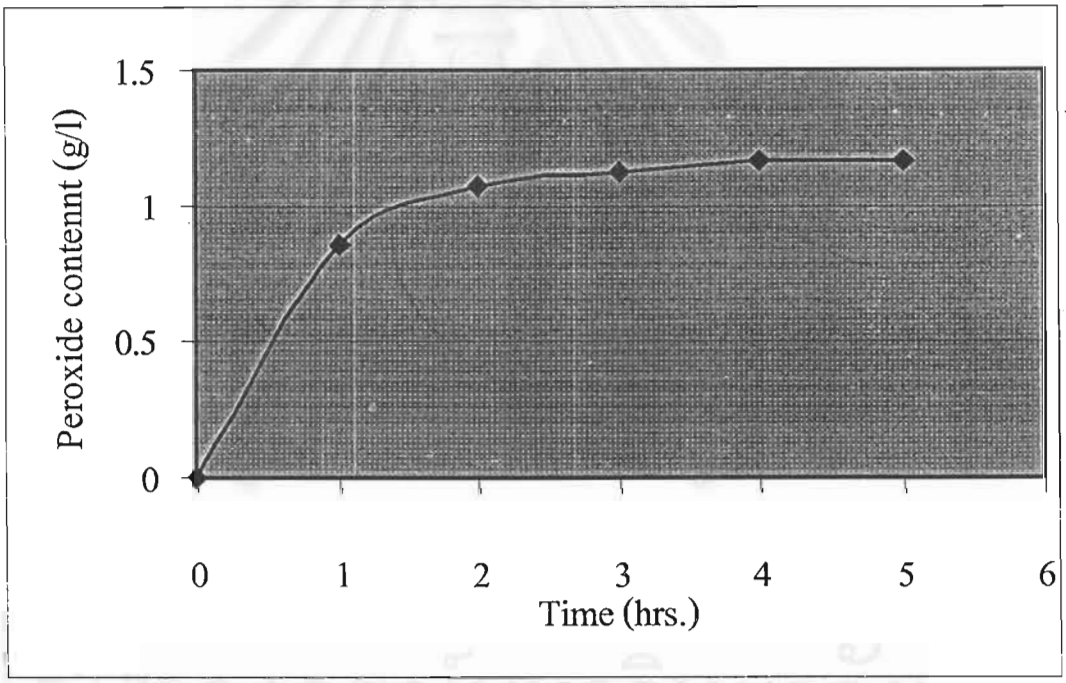


Figure 4.8 Peroxide content in enzymatic bleach liquors containing 1 g/l glucose oxidase, 50 g/l D-glucose and oxygen at pH 7 at 25°C for 0 – 5 hours.

Table 4.11 and Figure 4.8 show that when the bleach liquor was prepared using 1 g/l glucose oxidase, 50 g/l D-glucose and oxygen at pH 7 at 25°C for 0-5 hours, peroxide content in the liquor increased to the maximum level of a little over 1 g/l at 4

hours preparation then leveled off. For the reason of time saving, 2 hours period was chosen for the preparation of enzymatic bleach liquor.

Table 4.12 Peroxide content in enzymatic bleach liquors containing 1 g/l glucose oxidase, 0-80 g/l D-glucose and oxygen at pH 7 at 25°C for 2 hours.

D-glucose (g/l)	Peroxide content (g/l)
0	0.034
10	0.221
20	0.408
30	0.510
40	0.680
50	0.748
60	0.765
80	0.782

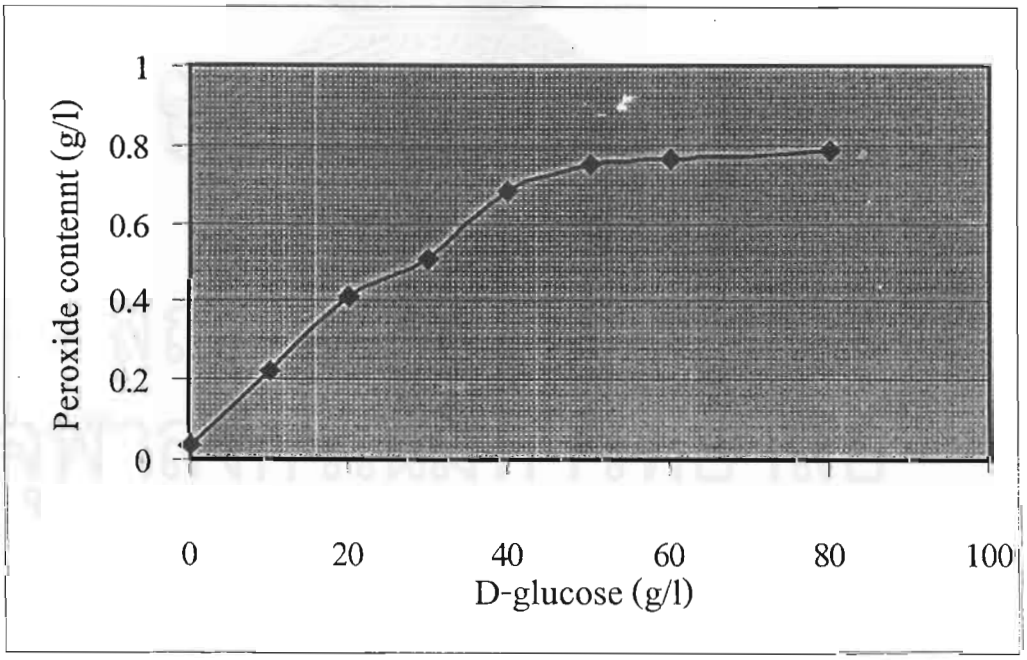


Figure 4.9 Peroxide content in enzymatic bleach liquors containing 1 g/l glucose oxidase, 0-80 g/l D-glucose and oxygen at pH 7 at 25°C for 2 hours.

Table 4.12 and Figure 4.9 show that when the bleach liquor was prepared using 1 g/l glucose oxidase, 0-80 g/l D-glucose and oxygen at pH 7 at 25°C for 2 hours, peroxide content in the liquor increased as the amount of D-glucose increased. For the reason of chemical saving, 50 g/l D-glucose was chosen for this bleach liquor preparation.

Therefore, the bleach liquor for the enzymatic bleaching step was prepared using 1 g/l glucose oxidase, 50 D-glucose, blowing oxygen into the system for 2 hours at pH 7 at 25°C.

4.4.3 Post-bleaching of Enzymatic Bleached Substrates Using Hydrogen Peroxide.

Because enzymatic bleached substrates obtained whiteness index lower than 72, they were rebleached in the post-bleaching step using hydrogen peroxide based on the conventional bleaching formulations. Whiteness index of rebleached substrates and the required bleaching formulations are shown in Table 4.13.

Table 4.13 Whiteness index of bleached substrates using conventional post-bleaching.

Chemical / Cotton Substrate	H_2O_2(50%) (g/l)	NaOH (g/l)	Sodium silicate (g/l)	Womine TE (g/l)	WI Before	WI After
Plain weave fabric	2	2	2	1	**22.299**	**71.753**
Twill weave fabric	5	3	2	1	**17.125**	**68.939**
Knitted fabric, yarn count 50/1	2	2	2	1	**39.323**	**74.531**
Knitted fabric, yarn count 24/1	2	2	2	1	**24.588**	**71.330**
Yarn	1	1	2	1	**54.042**	**78.600**

WI = Whiteness Index

4.4.4 The Effect of Conventional and Enzymatic Bleaching on Strength of Substrate.

Tables 4.14–4.16 and Figures 4.10 show % strength change of bleached substrates. Results indicate that conventional bleaching system provided substrates with lower strength loss compared with enzymatic bleaching system and the rebleaching step after pre-bleaching with enzyme significantly decreased the substrate strength. The reason for this could be that the enzymatic bleached substrates were bleached twice for the total time of 2 hours at 95°C. The other reason could be that during bleach liquor preparation, pH of liquor was decreased from original at pH 7 to 3.5 once gluconic acid took place in the liquor. These twice bleaching and the presence of gluconic acid in the bleach bath could damage the substrates resulting in lowering the strength of substrates.

Table 4.14 Breaking load of bleached woven fabrics compared with scoured woven fabrics.

	Breaking Load (N)			
	Warp	Weft	Warp+Weft[27]	% Change*
Plain weave fabric				
Scoured (conventional)	198.3	185.3	383.6	0.00 %
Scoured (enzymatic)	192.6	181.7	374.3	0.00 %
Bleached (conventional)	174.5	166.7	341.2	- 11.05 %
Bleached (enzymatic) Pre	176.7	160.5	337.2	- 9.91 %
Bleached (conventional) Post	161.6	147.8	309.4	- 17.34 %
Twill weave fabric				
Scoured (conventional)	540.9	314.2	855.1	0.00 %
Scoured (enzymatic)	500.6	293.2	793.8	0.00 %
Bleached (conventional)	519.3	310.4	829.7	- 2.97 %
Bleached (enzymatic) Pre	436.3	271.3	707.6	- 10.86 %
Bleached (Conventional) Post	401.1	234.2	635.3	- 19.97 %

* Note * Compared with scoured woven fabrics.

Table 4.15 Bursting strength of bleached knitted fabrics compared with scoured knitted fabrics.

	Knitted fabric (50/1)		Knitted fabric (24/2)	
	kg/cm^2	% Change*	kg/cm^2	% Change*
Scoured (conventional)	5.70	0.00 %	11.42	0.00 %
Scoured (enzymatic)	5.90	0.00 %	12.76	0.00 %
Bleached (conventional)	5.58	- 2.11 %	11.35	- 0.61 %
Bleached (enzymatic) Pre	5.54	- 6.10 %	11.08	- 13.17 %
Bleached (conventional) Post	4.72	- 20.00 %	8.40	- 37.17%

* Note * Compared with scoured knitted fabrics.

Table 4.16 Breaking load of bleached yarns compare with scoured yarns..

	Breaking Load	
	(N)	% Change*
Scoured (conventional)	2.331	0.00 %
Scoured (enzymatic)	2.203	0.00 %
Bleached (conventional)	2.183	- 6.35 %
Bleached (enzymatic) Pre	2.009	- 8.81 %
Bleached (conventional) Post	1.993	- 9.53 %

* Note * Compared with scoured yarns.

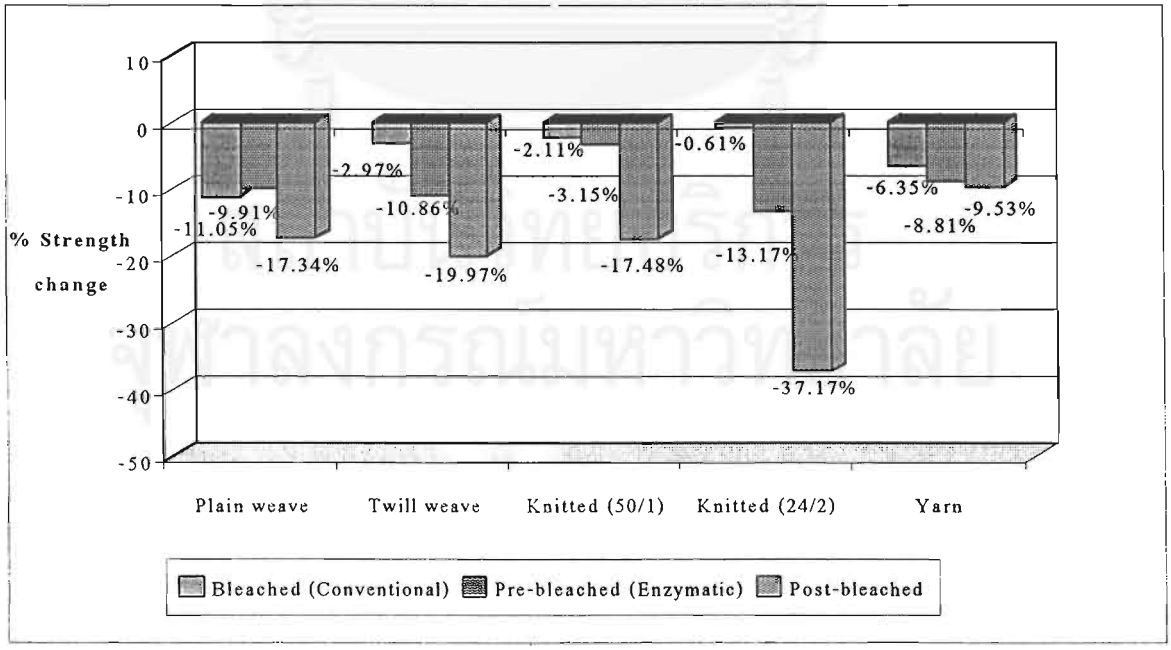


Figure 4.10 % strength change of bleached substrates.

Table 4.17 Whiteness index and yellowness of bleached substrates compared with scoured substrates.

	Whiteness Index	Yellowness
Plain weave fabric		
Scoured (conventional)	10.947	22.773
Scoured (enzymatic)	10.783	22.942
Bleached (conventional)	72.683	4.037
Bleached (enzymatic) Pre	22.299	19.956
Bleached (conventional) Post	71.753	4.062
Twill weave fabric		
Scoured (conventional)	4.106	24.134
Scoured (enzymatic)	3.404	24.701
Bleached (conventional)	69.129	4.487
Bleached (enzymatic) Pre	17.125	21.190
Bleached (conventional) Post	68.939	5.808
Knitted fabric (50/1)		
Scoured (conventional)	23.612	19.822
Scoured (enzymatic)	23.242	20.422
Bleached (conventional)	76.333	3.064
Bleached (enzymatic) Pre	39.329	15.138
Bleached (conventional) Post	74.531	3.274
Knitted (24/2)		
Scoured (conventional)	7.884	25.259
Scoured (enzymatic)	7.269	25.509
Bleached (conventional)	71.815	4.794
Bleached (enzymatic) Pre	24.588	15.138
Bleached (conventional) Post	71.330	4.822
Yarn		
Scoured (conventional)	38.364	16.535
Scoured (enzymatic)	38.174	16.681
Bleached (conventional)	81.100	3.067
Bleached (enzymatic) Pre	54.042	11.110
Bleached (conventional) Post	78.600	3.161

After bleaching processes, bleached cotton substrates were tested for pH and residual hydrogen peroxide and found that all bleached substrates contained pH in an acceptable range and contain no residual peroxide

4.4.5 The Effects of Conventional and Enzymatic Bleaching on Dye Absorption of Substrates.

Table 4.18 Color strength of bleached substrates

	K/S (Conventional)	K/S (Enzymatic)
Plain weave fabric	4.171	4.054
Twill weave fabric	4.346	3.476
Knitted fabric (50/1)	5.479	5.209
Knitted fabric (24/2)	4.782	4.448
Yarn	5.160	4.627

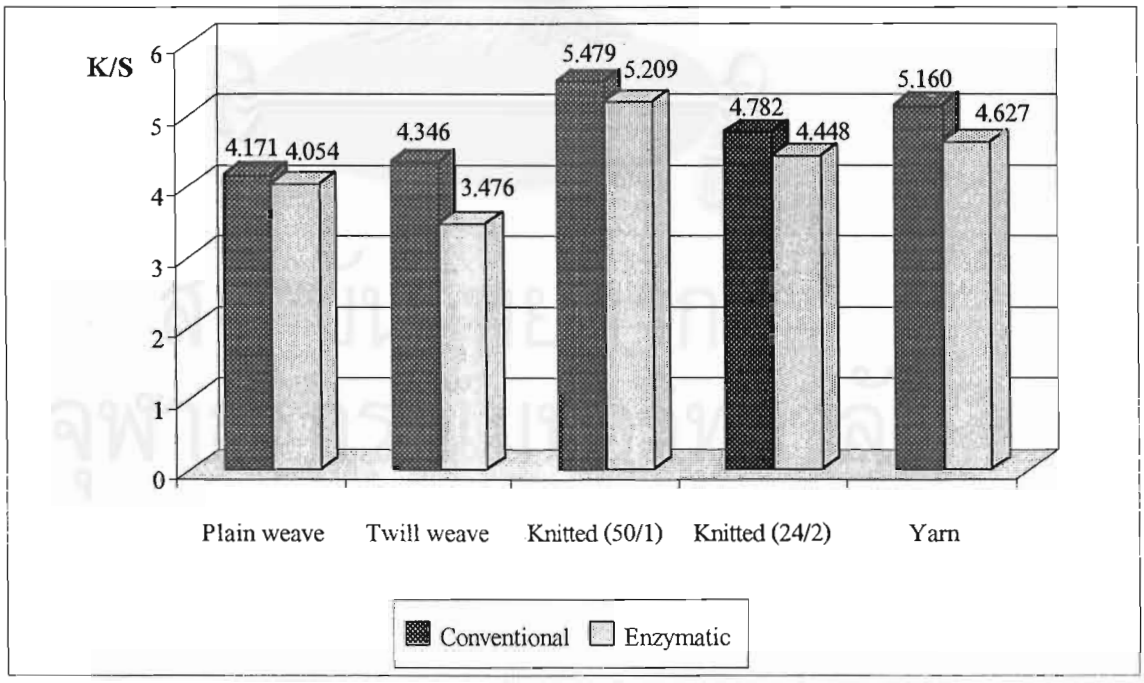


Figure 4.11 Color strength of bleached substrates.

Table 4.18 and Figure 4.11 indicate that the conventional bleaching system provided substrates with a little higher dye absorption ability than the enzymatic bleaching.

From over all bleaching results reveal that enzymatic bleaching process using glucose oxidase, glucose and oxygen might not be proper choice for bleaching cotton substrates at this stage due to high loss of strength and low degree of whiteness index of bleached substrates, but a careful control of pH bleach liquor could prevent high strength loss and increase whiteness index of bleached substrates to the required level.

CHAPTER V

Conclusions

From the results and discussion shown in Chapter IV, some conclusions can be drawn as follows.

Scouring process

1. Among three types of enzymes consisting of lipase, protease, and pectinase, pectinase is the most effective scouring catalyst.

2. A wetting agent is always needed for scouring cotton substrates using pectinase enzyme.

3. Enzymatic scouring process using pectinase enzyme and a small of wetting agent can be used to scour cotton substrates to their adequate absorbency with low % weight loss, low % strength loss and some 20 degree increase in whiteness index. This pectinase enzyme may be used in enzymatic scouring as comparable to sodium hydroxide in conventional scouring .

Bleaching process

1. Among four types of enzymes, xylanase, cellulase, peroxidase and glucose oxidase, glucose oxidase is the most effective bleaching catalyst.

2. The pre-bleaching using glucose oxidase provides bleached substrates with nearly 20 degrees increase in whiteness index but still much lower than whiteness index of substrates bleached by conventional bleaching.

3. The pre-bleaching with glucose oxidase enzyme can highly damage the cotton substrate.

4. Enzymatic bleaching process using glucose oxidase, glucose and oxygen might not be proper choice for bleaching cotton substrates at this stage due to high loss of strength and low degree of whiteness index of bleached substrates, but a careful control of pH bleach liquor could prevent high strength loss and increase whiteness index of bleached substrates to the required level.

CHAPTER VI

Recommendation

1. A study on controlling the pH bleach liquor for enzymatic bleaching using glucose oxidase should be conducted in order to search for the best enzymatic formulations.

2. An experiment on one step desizing-bleaching using amylase and glucose oxidase enzymes should be conducted in order to shorten the preparation step and to make uses of glucose wastes from desizing.

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Appendix

Appendix

Table A1 Breaking loads (N) in warp direction of greige, desized, scoured and bleached plain weave fabrics.

Trial No.	Greige	Desized	Scoured		Bleached	Enzymatic Bleached	
			Conventional	Enzymatic	Conventional	Pre	Post
1	219.7	169.1	204.7	180.3	191.0	181.4	168.6
2	200.3	186.2	198.9	204.0	176.8	175.3	162.9
3	220.9	178.1	191.5	200.1	170.8	178.4	154.4
4	213.9	196.3	192.3	186.4	160.3	170.6	165.8
5	213.2	187.1	204.2	192.3	173.7	177.7	156.3
Mean	**213.6**	**183.4**	**198.3**	**192.6**	**174.5**	**176.7**	**161.6**

Table A2 Elongation (%) in warp direction of greige, desized, scoured and bleached plain weave fabrics.

Trial No.	Greige	Desized	Scoured		Bleached	Enzymatic Bleached	
			Conventional	Enzymatic	Conventional	Pre	Post
1	14.08	18.65	22.23	18.13	20.45	21.64	22.33
2	13.69	19.702	22.51	22.51	20.80	20.93	23.79
3	14.33	19.29	20.07	20.24	20.60	21.33	21.64
4	17.01	20.29	21.89	19.68	19.61	20.62	23.24
5	13.77	19.05	21.44	21.17	21.08	21.04	23.36
Mean	**14.58**	**19.40**	**21.63**	**20.35**	**20.51**	**21.38**	**22.87**

Table A3 Breaking loads (N) in warp direction of greige, desized, scoured and bleached twill weave fabrics.

Trial No.	Greige	Desized	Scoured		Bleached	Enzymatic Bleached	
			Conventional	Enzymatic	Conventional	Pre	Post
1	565.0	506.6	546.8	497.5	540.3	461.8	402.8
2	577.5	514.6	518.3	525.1	513.1	427.2	388.0
3	581.4	496.2	522.5	495.7	517.4	436.2	407.0
4	562.6	529.0	553.4	483.9	542.5	420.1	406.6
5	557.1	509.3	563.4	-	-	-	-
Mean	**568.7**	**511.1**	**540.9**	**500.6**	**519.3**	**436.3**	**401.1**

Table A4 Elongation (%) in warp direction of greige, desized, scoured and bleached twill weave fabrics.

Trial No.	Greige	Desized	Scoured		Bleached	Enzymatic Bleached	
			Conventional	Enzymatic	Conventional	Pre	Post
1	17.05	25.64	29.17	26.43	29.57	27.37	28.91
2	18.00	26.56	29.17	28.73	30.34	28.73	30.84
3	16.45	25.95	29.32	26.51	28.97	27.20	27.92
4	16.44	26.03	29.17	27.20	28.31	27.08	29.08
5	16.47	26.25	28.97	27.35	-	-	-
Mean	**16.88**	**26.09**	**29.16**	**27.24**	**29.30**	**27.60**	**29.19**

Table A5 Breaking loads (N) in weft direction of greige, desized, scoured and bleached plain weave fabrics.

Trial No.	Greige	Desized	Scoured		Bleached	Enzymatic Bleached	
			Conventional	Enzymatic	Conventional	Pre	Post
1	162.7	150.7	198.6	169.5	174.9	165.9	157.9
2	156.5	166.9	195.5	191.2	153.0	155.7	147.1
3	146.6	158.6	156.6	176.0	157.7	151.9	143.9
4	146.6	154.6	176.8	190.5	185.5	168.8	141.6
5	164.3	157.2	199.2	181.3	165.3	160.2	148.3
Mean	**155.3**	**157.6**	**185.3**	**181.7**	**166.7**	**160.5**	**147.8**

Table A6 Elongation (%) in weft direction of greige, desized, scoured and bleached plain weave fabrics.

Trial No.	Greige	Desized	Scoured		Bleached	Enzymatic Bleached	
			Conventional	Enzymatic	Conventional	Pre	Post
1	11.31	11.59	14.59	14.33	13.64	14.41	14.59
2	12.05	13.73	14.01	14.39	13.64	14.23	14.31
3	11.37	12.71	12.56	14.05	14.21	14.65	15.08
4	10.03	13.73	14.24	14.44	14.89	14.07	13.57
5	10.63	13.22	14.16	13.44	13.81	14.15	14.45
Mean	**11.08**	**13.00**	**13.91**	**14.13**	**14.04**	**14.30**	**14.40**

Table A7 Breaking loads (N) in weft direction of greige, desized, scoured and bleached twill weave fabrics.

Trial No.	Greige	Desized	Scoured		Bleached	Enzymatic Bleached	
			Conventional	Enzymatic	Conventional	Pre	Post
1	260.9	274.1	345.2	314.0	317.4	268.7	236.4
2	242.8	302.8	312.0	272.1	305.1	277.6	227.1
3	250.8	304.9	281.4	273.2	304.0	280.6	228.1
4	229.0	312.3	335.5	281.0	317.9	259.1	245.4
5	251.4	314.0	297.1	325.8	-	-	-
Mean	**247.0**	**301.6**	**314.2**	**293.2**	**310.4**	**271.3**	**234.2**

Table A8 Elongation (%) in weft direction of greige, desized, scoured and bleached twill weave fabrics.

Trial No.	Greige	Desized	Scoured		Bleached	Enzymatic Bleached	
			Conventional	Enzymatic	Conventional	Pre	Post
1	8.72	10.28	11.83	11.83	11.06	11.88	11.95
2	9.37	10.15	11.33	10.85	11.20	11.91	11.80
3	9.35	10.92	11.21	11.59	11.37	11.39	12.32
4	8.95	11.00	12.05	11.89	12.13	12.08	12.14
5	9.59	10.59	10.95	11.97	-	-	-
Mean	**9.20**	**10.59**	**11.47**	**11.63**	**11.44**	**11.81**	**12.05**

Table A9 Breaking loads (N) of greige, scoured and bleached yarns.

Trial No.	Greige	Scoured		Bleached	Enzymatic Bleached	
		Conventional	Enzymatic	Conventional	Pre	Post
1	1.396	2.243	2.248	2.142	2.121	1.898
2	1.450	2.293	2.369	2.065	1.896	2.064
3	1.705	2.491	1.979	2.214	1.945	2.140
4	1.472	2.670	2.056	2.418	1.959	1.965
5	1.851	2.167	2.342	2.095	2.033	1.701
6	1.656	1.907	1.936	2.055	1.911	2.079
7	1.811	2.369	2.319	1.948	1.865	2.033
8	1.602	2.351	2.293	2.207	2.190	2.247
9	1.789	2.380	2.407	2.246	2.143	1.905
10	1.587	2.438	2.083	2.423	2.025	1.896
Mean	**1.632**	**2.331**	**2.203**	**2.183**	**2.009**	**1.993**

Table A10 Elongation (%) of greige, scoured and bleached yarns.

Trial No.	Greige	Scoured		Bleached	Enzymatic Bleached	
		Conventional	Enzymatic	Conventional	Pre	Post
1	5.864	7.576	7.584	7.224	8.18	7.884
2	5.160	8.104	6.836	7.172	8.104	8.012
3	4.872	7.364	3.788	6.532	7.364	7.056
4	5.272	8.468	7.676	6.960	8.468	6.608
5	5.364	6.080	7.288	7.464	6.080	6.890
6	5.532	6.464	6.564	6.804	6.464	8.324
7	4.444	7.364	6.968	7.468	7.64	8.292
8	5.420	7.304	7.656	7.092	7.576	9.112
9	4.964	7.268	8.072	7.428	7.268	7.636
10	5.264	7.572	7.88	7.496	7.572	7.488
Mean	5.216	7.356	7.031	7.164	7.472	7.730

Table A11 Bursting strength (Kg/cm^2) of greige, scoured and bleached knitted fabrics (yarn count 50/1).

	Greige	Scoured		Bleached	Enzymatic Bleached	
		Conventional	Enzyme	Conventional	Pre	Post
1	6.1	5.8	6.1	5.4	5.4	4.8
2	5.8	5.9	5.8	5.5	5.5	4.8
3	6.1	5.5	5.9	5.8	5.8	4.7
4	6.2	5.5	5.6	4.9	4.9	4.7
5	6.0	5.8	6.1	6.1	6.1	4.6
Mean	**6.04**	**5.70**	**5.90**	**5.54**	**5.54**	**4.72**

Table A12 Bursting strength (Kg/cm^2) of greige, scoured and bleached knitted fabrics (yarn count 24/2).

	Greige	Scoured		Bleached	Enzymatic Bleached	
		Conventional	Enzyme	Conventional	Pre	Post
1	14.1	11.7	12.8	11.2	10.9	8.5
2	14.3	11.3	12.3	11.4	10.9	8.4
3	13.8	11.3	13.0	11.5	11.2	8.3
4	13.8	11.6	13.1	11.3	10.8	8.4
5	13.9	11.2	12.6	-	11.6	-
Mean	**13.98**	**11.42**	**12.76**	**11.35**	**11.08**	**8.40**

Table A13 Weight of greige woven and knitted fabrics (g / 100 cm^2).

Trial No.	Plain weave	Twill weave	Knitted 50/1	Knitted 24/2
1	1.4952	3.9051	1.1772	2.7973
2	1.5020	3.9176	1.1802	2.7885
3	1.5015	3.8685	1.1778	2.7707
Mean	**1.4996**	**3.8971**	**1.1784**	**2.7855**

Table A14 Extractable materials in plain weave fabrics: hot water, enzymatic and solvent extractions.

	Trial 1		Trial 2		Trial 3		Mean
	g.	%	g.	%	g.	%	
Greige fabric	2.5341		2.4623		2.4396		
Hot Water ext. fabric	2.4452		2.3712		2.3498		
Enz. ext. fabric	2.3198		2.2424		2.2210		
Sol. ext. fabric	2.3103		2.2345		2.2119		
- Water soluble		3.508		3.370		3.681	**3.520%**
- Enzyme extractable		4.948		5.231		5.280	**5.153%**
- Sol. extractable		0.375		0.321		0.373	**0.356%**
Total ext. materials		**8.832**		**8.922**		**9.334**	**9.029%**

Table A15 Extractable materials in twill weave fabrics: hot water, enzymatic and solvent extractions.

	Trial 1		Trial 2		Trial 3		Mean
	g.	%	g.	%	g.	%	
Greige fabric	2.3506		2.3386		2.2668		
Hot Water ext. fabric	2.2519		2.2400		2.1700		
Enz. ext. fabric	2.1449		2.1383		2.0380		
Sol. ext. fabric	2.1369		2.1279		2.0563		
- Water soluble		4.199		4.216		4.270	**4.228 %**
- Enzyme extractable		4.552		4.349		4.500	**4.467%**
- Sol. extractable		0.340		0.445		0.516	**0.434%**
Total ext. materials		9.091		9.010		9.286	**9.129%**

Table A16 Extractable materials in knitted fabric (yarn count 50/1) : hot water, enzymatic and solvent extractions.

	Trial 1		Trial 2		Trial 3		Mean
	g.	%	g.	%	g.	%	
Greige fabric	2.5219		2.4830		2.4723		
Hot Water ext. fabric	2.4602		2.4216		2.4091		
Enz. ext. fabric	2.4607		2.4224		2.4082		
Sol. ext. fabric	2.4486		2.4103		2.3970		
- Water soluble		2.447		2.473		2.557	**2.492%**
- Enzyme extractable		-		-		-	-
- Sol. extractable		0.460		0.455		0.489	**0.468%**
Total ext. materials		**2.907**		**2.923**		**3.046**	**2.959%**

Table A17 Extractable materials in knitted fabric (yarn count 24/2) : hot water, enzymatic and solvent extractions.

	Trial 1		Trial 2		Trial 3		Mean
	g.	%	g.	%	g.	%	
Greige fabric	2.4831		2.4721		2.5061		
Hot Water ext. fabric	2.4321		2.4225		2.4550		
Enz. ext. fabric	2.4327		2.4258		2.4546		
Sol. ext. fabric	2.4232		2.4141		2.4456		
- Water soluble		2.054		2.006		2.039	**2.033%**
- Enzyme extractable		-		-		-	-
- Sol. extractable		0.358		0.340		0.375	**0.358%**
Total ext. materials		**2.412**		**2.346**		**2.414**	**2.391%**

Table A18 Extractable materials in yarns: hot water, enzymatic and solvent extractions.

	Trial 1		Trial 2		Trial 3		Mean
	g.	%	g.	%	g.	%	
Greige fabric	2.3665		2.3818		2.3884		
Hot Water ext. fabric	2.2989		2.3147		2.3185		
Enz. ext. fabric	2.2996		2.3151		2.3183		
Sol. ext. fabric	2.2881		2.3031		2.3063		
- Water soluble		2.857		2.817		2.927	**2.867%**
- Enzyme extractable		-		-		-	-
- Sol. extractable		0.456		0.487		0.511	**0.485%**
Total ext. materials		**3.313**		**3.304**		**3.438**	**3.352%**

Table A19 Weight loss (%) of desized and scoured plain weave fabrics.

	Conventional Process			Enzymatic Process		
	Trial 1	Trial 2	**Mean**	Trial 1	Trial 2	**Mean**
Greige (g)	5.0231	5.0111		5.0401	4.9389	
Desizing (g)	4.5812	4.5717		4.6125	4.5016	
Scoured (g)	4.5214	4.5109		4.5813	4.4671	
% Weight Loss after desizing	8.797 %	8.768 %	**8.783%**	8.484 %	8.854 %	**8.669%**
% Weight Loss after scouring	1.305 %	1.330 %	**1.318%**	0.676 %	0.766 %	**0.721%**

Table A20 Weight loss (%) of desized and scoured twill weave fabrics.

	Conventional Process			Enzymatic Process		
	Trial 1	Trial 2	**Mean**	Trial 1	Trial 2	**Mean**
Greige (g)	5.0194	4.9825		4.9404	4.8394	
Desizing (g)	4.5836	4.5544		4.5103	4.4162	
Scoured (g)	4.5073	4.4839		4.4704	4.3860	
% Weight Loss after desizing	8.683%	8.592%	**8.639%**	8.705%	8.740%	**8.723%**
% Weight Loss after scouring	1.665%	1.548%	**1.607%**	0.885%	0.684%	**0.785%**

Table A21 Weight loss (%) of scoured knitted fabrics (yarn count 50/1).

	Conventional Process			Enzymatic Process		
	Trial 1	Trial 2	**Mean**	Trial 1	Trial 2	**Mean**
Greige (g)	5.0643	5.0520		4.9867	4.9390	
Scoured (g)	4.8961	4.8841		4.8356	4.7923	
% Weight Loss after scouring	3.321%	3.323%	**3.322%**	3.030%	2.970%	**3.000%**

Table A22 Weight loss (%) of scoured knitted fabrics (yarn count 24/2).

	Conventional Process			Enzymatic Process		
	Trial 1	Trial 2	**Mean**	Trial 1	Trial 2	**Mean**
Greige (g)	4.9448	4.9417		4.9076	4.8943	
Scoured (g)	4.7934	4.7887		4.7769	4.7608	
% Weight Loss after scouring	3.062%	3.096%	**3.079%**	2.663%	2.728%	**2.700%**

Table A23 Weight loss (%) of scoured yarns.

	Conventional Process			Enzymatic Process		
	Trial 1	Trial 2	**Mean**	Trial 1	Trial 2	**Mean**
Greige (g)	4.5100	4.6980		4.6961	4.5294	
Scoured (g)	4.3290	4.5137		4.5504	4.3821	
% Weight Loss after scouring	4.013	3.923	**3.968%**	3.103	3.252	**3.178%**

Table A24 Adsorption of methylene blue (MB) on fabrics and yarn.

Substrate	Absorbance of sol. after dyeing (dilute 40 times)	MB (g/l) in sol. after dyeing (dilute 40 times)	MB (g/l) in sol. after dyeing	MB(g/l) on substrate	MB(g) on substrate (kg)
Plain weave					
Desized	0.450	0.00253	0.1012	0.3988	**11.96**
Scoured (Conventional)	0.534	0.00300	0.1200	0.3900	**11.70**
Scoured (Enzymatic)	0.562	0.00316	0.1264	0.3736	**11.21**
Twill weave					
Desized	0.265	0.00149	0.0596	0.4406	**13.21**
Scoured (Conventional)	0.524	0.00295	0.1180	0.3820	**11.46**
Scoured (Enzymatic)	0.596	0.00335	0.1340	0.3660	**10.98**
Knitted (yarn count 50/1)					
Greige	0.432	0.00243	0.0972	0.4028	**12.08**
Scoured (Conventional)	0.637	0.00358	0.1432	0.3568	**10.70**
Scoured (Enzymatic)	0.651	0.00366	0.1464	0.3536	**10.61**
Knitted (yarn count 24/2)					
Greige	0.475	0.00267	0.1068	0.3932	**11.80**
Scoured (Conventional)	0.626	0.00352	0.1408	0.3592	**10.78**
Scoured (Enzymatic)	0.724	0.00407	0.1628	0.3372	**10.12**

Table A24 (Continued)

Substrate	Absorbance of sol. after dyeing (dilute 40 times)	MB (g/l) in sol. after dyeing (dilute 40 times)	MB (g/l) in sol. after dyeing	MB(g/l) on substrate	MB(g) on substrate (kg)
Yarn					
Greige	0.358	0.00201	0.0804	0.4196	**12.59**
Scoured (Conventional)	0.600	0.00337	0.1348	0.3652	**10.96**
Scoured (Enzymatic)	0.599	0.00337	0.1348	0.3652	**10.96**

Sol. = Solution

Note : a. The solutions after dyeing were diluted 40 times and were measured for the maximum absorbances at wavelength 662 nm using a UV-Vis spectrophotometer.

b. The amount of methylene blue (g/l) in the solutions after dyeing (diluted 40 times) were directly drown from the calibration curve in Figure 3.5 at the maximum absorbance (see note a.).

c. Substrates with higher amount of methylene blue on indicate higher amount of pectin presence.

Table A25 Whiteness index of greige, desized, scoured and bleached plain weave fabrics.

Trial No.	Greige	Desized	Scoured		Bleached	Enzymatic Bleached	
			(Conventional)	(Enzymatic)	(Conventional)	Pre	Post
1	-4.972	9.451	11.019	10.700	72.510	21.997	71.389
2	-5.050	9.186	10.701	11.057	72.801	22.463	72.251
3	-4.791	9.619	10.399	11.422	72.648	22.107	71.981
4	-3.577	8.044	11.122	10.423	72.751	21.994	72.150
5	-5.825	8.305	11.494	10.313	72.705	22.934	70.993
Mean	**-4.843**	**8.921**	**10.947**	**10.783**	**72.683**	**22.299**	**71.753**

Table A26 Whiteness index of greige, desized, scoured and bleached twill weave fabrics.

Trial No.	Greige	Desized	Scoured		Bleached	Enzymatic Bleached	
			(Conventional)	(Enzymatic)	(Conventional)	Pre	Post
1	-17.017	-0.890	5.792	3.584	69.117	16.819	68.860
2	-16.869	-1.535	3.507	3.652	69.968	17.012	68.935
3	-16.503	-2.102	3.413	3.207	69.065	17.451	69.314
4	-16.647	0.947	3.385	3.016	68.775	17.355	69.211
5	-16.743	0.957	4.833	3.559	68.718	16.984	68.367
Mean	**-16.756**	**-0.525**	**4.186**	**3.404**	**69.129**	**17.125**	**68.939**

Table A27 Whiteness index of greige, scoured and bleached knitted fabrics (yarn count 50/1)

Trial No.	Greige	Scoured		Bleached	Enzymatic Bleached	
		(Conventional)	(Enzymatic)	(Conventional)	Pre	Post
1	0.295	24.476	22.513	76.634	40.619	74.545
2	-0.890	23.913	23.229	76.239	38.270	74.681
3	-1.107	24.515	23.556	76.439	38.636	74.604
4	-1.382	22.880	23.828	76.126	39.295	74.007
5	-0.540	22.274	23.086	76.227	39.824	74.819
Mean	**-0.725**	**23.612**	**23.242**	**76.333**	**39.329**	**74.531**

Table A28 Whiteness index of greige, scoured and bleached knitted fabrics (yarn count 24/2)

Trial No.	Greige	Scoured		Bleached	Enzymatic Bleached	
		(Conventional)	(Enzymatic)	(Conventional)	Pre	Post
1	-10.735	6.397	6.754	72.477	23.848	71.235
2	-10.879	7.226	7.233	71.497	25.919	71.868
3	-9.986	8.093	7.639	71.691	25.441	70.844
4	-10.766	7.934	7.586	71.500	23.254	71.315
5	-10.533	9.772	7.132	71.910	24.476	71.390
Mean	**-10.580**	**7.884**	**7.269**	**71.815**	**24.588**	**71.330**

Table A29 Whiteness index of greige, scoured and bleached yarns.

Trial No.	Greige	Scoured		Bleached	Enzymatic Bleached	
		(Conventional)	(Enzymatic)	(Conventional)	Pre	Post
1	15.812	39.104	37.784	81.379	53.328	78.328
2	15.939	38.257	38.08	80.778	54.780	77.854
3	14.199	37.651	38.974	80.860	54.415	78.411
4	14.216	39.14	37.659	81.698	53.93	79.015
5	14.532	37.666	38.374	80.773	53.759	79.392
Mean	**14.940**	**38.364**	**38.174**	**81.100**	**54.042**	**78.600**

Table A30 Yellowness of greige, desized, scoured and bleached plain weave fabrics.

Trial No.	Greige	Desized	Scoured		Bleached	Enzymatic Bleached	
			(Conventional)	(Enzymatic)	(Conventional)	Pre	Post
1	28.747	23.375	22.315	23.010	4.074	19.913	4.033
2	28.877	23.443	23.433	22.843	4.034	19.811	4.123
3	28.663	23.260	23.582	22.748	3.995	20.031	4.082
4	28.300	23.652	22.350	23.074	4.062	19.999	4.023
5	29.184	23.544	22.185	23.033	4.021	20.024	4.047
Mean	**28.754**	**23.455**	**22.773**	**22.942**	**4.037**	**19.956**	**4.062**

Table A31 Yellowness of greige, desized, scoured and bleached twill weave fabrics.

Trial No.	Greige	Desized	Scoured		Bleached	Enzymatic Bleached	
			(Conventional)	(Enzymatic)	(Conventional)	Pre	Post
1	31.244	24.917	23.683	24.522	5.600	21.396	5.903
2	31.251	25.000	24.535	24.329	5.155	20.949	5.886
3	31.337	24.949	24.440	25.011	5.891	21.154	5.874
4	31.301	24.224	24.181	25.107	5.412	21.205	5.781
5	31.217	24.634	23.829	24.534	5.379	21.248	5.597
Mean	**31.270**	**24.745**	**24.134**	**24.701**	**4.487**	**21.190**	**5.808**

Table A31 Yellowness of greige, scoured and bleached knitted fabrics

(yarn count 50/1)

Trial No.	Greige	Scoured		Bleached	Enzymatic Bleached	
		(Conventional)	(Enzymatic)	(Conventional)	Pre	Post
1	26.869	19.818	20.485	2.967	14.882	3.401
2	27.193	19.958	20.466	3.124	15.421	3.243
3	27.290	19.749	20.399	3.153	15.177	3.253
4	27.431	20.073	20.257	3.005	15.203	3.384
5	27.221	19.513	20.502	3.074	15.005	3.091
Mean	**27.201**	**19.822**	**20.422**	**3.064**	**15.138**	**3.274**

Table A32 Yellowness of greige, scoured and bleached knitted fabrics (yarn count 24/2)

Trial No.	Greige	Scoured		Bleached	Enzymatic Bleached	
		(Conventional)	(Enzymatic)	(Conventional)	Pre	Post
1	30.933	25.849	26.015	4.657	14.882	4.823
2	31.009	25.547	25.432	4.833	15.421	4.847
3	30.322	24.957	25.648	4.795	15.177	4.784
4	30.957	25.283	25.241	4.953	15.203	4.821
5	30.607	24.660	25.207	4.733	15.005	4.835
Mean	**30.766**	**25.259**	**25.509**	**4.794**	**15.138**	**4.822**

Table A33 Yellowness of greige, scoured and bleached yarns.

Trial No.	Greige	Scoured		Bleached	Enzymatic Bleached	
		(Conventional)	(Enzymatic)	(Conventional)	Pre	Post
1	25.027	16.360	16.540	2.627	11.043	3.093
2	24.884	16.859	17.123	3.395	11.327	3.154
3	24.515	16.733	16.778	3.099	11.117	3.242
4	24.508	16.003	16.869	3.082	11.054	3.004
5	24.683	16.721	16.095	3.131	11.015	3.310
Mean	**24.723**	**16.535**	**16.681**	**3.067**	**11.110**	**3.161**

BIOGRAPHY

Mr. Theeradol Rungraungkitkrai was born in Bangkok, Thailand, on June 18, 1974. He received a Bachelor of Engineering degree with a major in Textile Chemistry Engineering from Rajamangala Institute of Technology in 1997. He started as a graduate student in the Department of Materials Science with a major in Applied Polymer Science and Textile Technology, Faculty of Science, Chulalongkorn University in November 1997, and completed the program in April 2000.