

## ABSTRACT

FU, SHA. High Efficiency Ultra-Deep Dyeings of Cotton via Mercerization and Cationization. (Under the direction of Dr. David Hinks and Dr. Peter Hauser).

Cotton has been a major textile fiber for centuries due to its unique comfort, good dyeability, ease of production, biodegradability, and relatively low cost. To satisfy consumers aesthetically, cotton products, like garments and household textiles, must have a large color gamut and satisfactory fastness. One of the most popular “colors” is black. However, obtaining deep shades, especially black, on cotton with good colorfastness properties in an environmentally responsible way is difficult since all kinds of blacks dyes have their own limitations, such as the environmental toxicity of sulfur dyes, poor wash fastness of direct dyes and large amount of dye and salt in the dye bath effluent of fiber-reactive dyes.

Instead of focusing on synthesis of new dyes and modification of cotton dyeing process, much research has focused on modification of cotton at the molecular level to obtain the desired dyeing performance and colorfastness properties with existing dyes. In all well-studied modifications of cotton, cationization has been shown to be effective in increasing the dye uptake of anionic dyes. Furthermore, it allows salt free dyeing with anionic dyes. In this work, cationization was used, in combination with mercerization, to develop a potentially environmentally responsible dyeing procedure for ultra-deep shades on cotton. In the cationization process, 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC) was applied on cotton fabrics using a cold pad-batch method.

Results show that both mercerization and cationization are effective in increasing the depth of shade on cotton fabrics. In addition, the colorfastness properties, except colorfastness to wet crocking, of mercerized-cationized cotton fabrics dyed without salt are much better than untreated cotton fabrics dyed using a conventional dyeing procedure.

Ultra-deep navy and black shades on mercerized-cationized cotton fabrics with near complete utilization of applied dyestuffs and good colorfastness properties were obtained with the same dyeing procedure but different concentrations of dyes. Unlike untreated cotton fabrics, the concentration of  $\text{Na}_2\text{CO}_3$  in the dyeing process of mercerized-cationized cotton fabrics was lowered from 20g/L to 5g/L without compromising dye fixation and colorfastness properties. In addition, with low concentrations of dyes and  $\text{Na}_2\text{CO}_3$  and no salt in the dye bath effluent, the dyeing procedure of mercerized-cationized cotton fabrics for ultra-deep shades is potentially a more environmentally benign method than conventional dyeing with fiber-reactive dyes.

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# High Efficiency Ultra-Deep Dyeings of Cotton via Mercerization and Cationization

by  
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A thesis submitted to the Graduate Faculty of  
North Carolina State University  
in partial fulfillment of the  
requirements for the degree of  
Master of Science

Textile Chemistry

Raleigh, North Carolina

2013

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## **DEDICATION**

This work is dedicated to my family for their care and encouragement.

## **BIOGRAPHY**

Sha Fu was born on June 22<sup>nd</sup>, 1991 in Zhangshu, Jiangxi Province of China. She is the only daughter of Qingzheng Fu and Yanwen Du. She graduated from Zhangshu High school in June, 2008, and got her bachelor degree from Donghua University, Shanghai in 2012. She attended the “3+X” program and entered North Carolina State University in August, 2011 to pursue her Master degree in Textile Chemistry.

## **ACKNOWLEDGMENTS**

First of all, I want to express my sincere thanks to Dr. David Hinks and Dr. Peter Hauser for their patience and guidance throughout my educational experience and research work. I really appreciate every mark on my thesis draft from Dr. Hinks and I will keep those pages forever. I'm also very thankful to Dr. Martin King for being my graduate committee member. Besides, I want to give my special thanks to Jeffrey Krauss for his help and how he tried to make me feel comfortable to do experiments in the pilot plant. As well, I need to thank Judy Elson for her kindness and help. I appreciate all the help from my teachers, classmates, staff in the college and other friends who have made my academic life so meaningful. Finally, I am indebted to my boyfriend, Nanshan, for his support, encouragement and all the sweet things he did. Research is not an easy thing, love either. But I will try my best for both of them.

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## **CHAPTER 1 INTRODUCTION**

### **1.1 Thesis Outline**

This thesis consists of seven chapters. Chapter 1 is a general introduction which outlines the major parts and research objectives of the research. Chapter 2 provides a literature review of the coloration of cotton fabrics and the pretreatments, mercerization and cationization, which would help to obtain deep black shades on cotton dyed with reactive dyes. Chapter 3 is the experimental section, describing the materials, equipment, cationization method, dyeing procedures and testing methods used in the research. Chapter 4 presents the results and discussion about how the pretreatments would improve the dyeing procedure and dyeing performance of cotton dyed with reactive dyes. The environmentally friendly dyeing procedure to obtain deep neutral black shades on mercerized-cationized cotton fabrics has also been discussed. Chapter 5 lists the conclusions and Chapter 6 gives a short discussion on recommended future work. Chapter 7 is a list of references cited throughout the thesis.

### **1.2 Research Objectives**

The objective of this research is to develop a new method to obtain an ultra-deep black shade on cotton fabrics using reactive dyes that have low environmental impact. Mercerization and cationization are to be used as pretreatments to improve the dyeing performance and colorfastness properties of cotton fabrics and eliminate the use of salt while dyeing with reactive dyes. Key variables will be assessed, including the concentrations of cationic reagent, dyes and alkali used in pretreatment and dyeing.

## CHAPTER 2 LITERATURE REVIEW

### 2.1 Composition of Cotton Fiber

As a major textile fiber, cotton has been dominant for centuries due to its unique combination of properties, including comfort, renewability, good dyeability and fastness properties, biodegradability and relatively low cost. Depending on the type of cotton and geographic region in which it is grown, the composition of cotton can vary significantly.

In a typical mature cotton fiber, more than 90% of the whole fiber is cellulose. As a natural fiber, cotton also contains small quantities of non-cellulosic materials like pectin, wax, mineral salts and some other impurities. The composition of typical cotton fiber is summarized in Table 1.<sup>1-3</sup>

**Table 1. Composition of Typical Cotton Fibers**

Constituent	Composition (% of dry weight)	
	Typical	Range
Cellulose	95.0	88.0-96.0
Protein	1.3	1.1-1.9
Pectic substances	0.9	0.7-1.2
Ash	1.2	0.7-1.6
Wax	0.6	0.4-1.0
Total Sugars	0.3	0.1-1.0

From outside to inside, the layered structure of cotton fiber can be broadly classified as cuticle, primary wall, winding layer, secondary wall and lumen as show in Figure 1.<sup>4</sup> Most of

the non-cellulosic materials are located on the cuticle or inside the lumen of the fiber whereas the first and second wall of cotton fiber comprises by highly crystalline, oriented cellulose.<sup>5</sup>

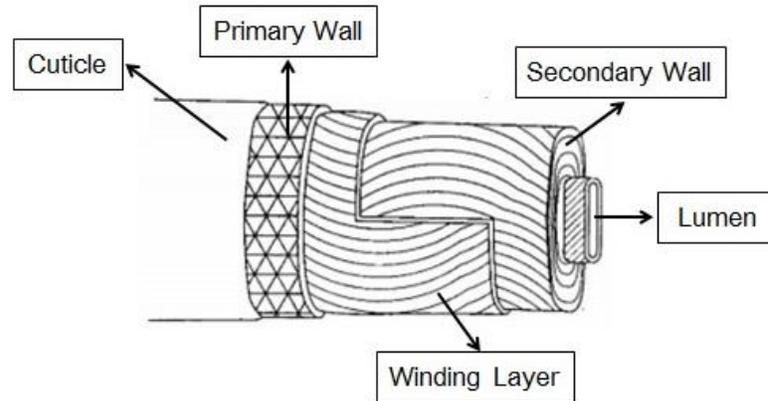


Figure 1. Structure of a Cotton Fiber

The cellulose is composed of 1, 4-β-D-glucose units as shown in Figure 2. Cellulose possesses both primary and secondary alcohol groups. Due to the structure of cellulose, cotton has good reactivity and affinity for a variety of chemicals and dyes.

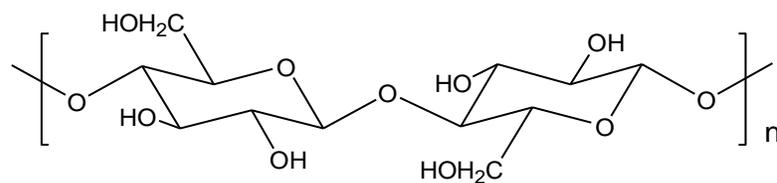


Figure 2. Chemical Structure of Cellulose

## 2.2 Coloration of Cotton

To produce commercially acceptable products that satisfy the consumers aesthetically, a large color gamut is required using dyes and dyeing processes that produce even dyeings of acceptable fastness. Since the first synthetic organic dye, mauveine, was discovered by William Henry Perkin in 1856, many chemical types and classes of dyes have been developed for cotton as well as for other fibers.<sup>6</sup> Unlike most fibers, cotton can be dyed with a variety of dye classes with a wide range of costs and application methods depending on the requirements for color and fastness properties. The relative cost for various dye classes are listed in Table 2.<sup>7</sup>

**Table 2. Relative Cost of Dyes for Cellulosic Fibers**

<b>Class</b>	<b>Relative cost*</b>
Vat leuco ester	1
Vat	2
Reactive	3
Copper-complex direct	4
Diazotisable direct	5
After-copperable direct	5
Azoic	6
Conventional direct	6
Sulfur	7

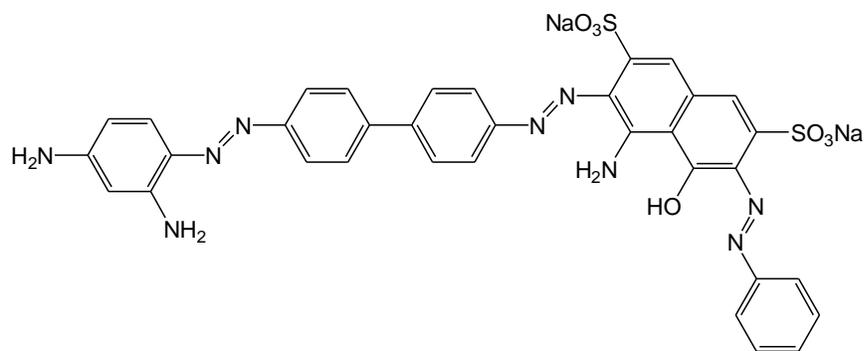
\* 1-most costly, 7-least costly

### **2.2.1 Classification of Dyes via the Color Index**

Dyes can be classified by chemical structure or application method but the chemical names of dyes can be very confusing due to their complicated structure. As a result, the Color Index (C.I.), which is a compendium of dyes, was edited by the Society of Dyers and Colourists in the UK and the American Association of Textile Chemists and Colorists in the USA to help name and identify individual dyes easily. In the Color Index system, a specific name (Color Index Generic Name) and a five digit number (Color Index Constitution Number) are assigned to each individual dye. The generic name is a code containing the application type, hue and an identifying number. For example, the C.I. generic name of indigo is C.I. Vat Blue 1 and its C.I. Constitution Number is 73000. From the name, it's clear that the application type of indigo is vat and the hue is blue. Based on the C.I. generic name, dyes are divided into classes by their application type, including acid, mordant, disperse, direct, reactive and so on. For the commonly used dye classes of cotton, the coloration mechanisms as well as their advantages and disadvantages are briefly introduced in the following sections.

### **2.2.2 Direct Dyes**

Direct dyes are one of the most popular types of colorant used for the dyeing and printing of cellulosic fibers.<sup>8</sup> They are so named because they have natural affinity for cellulose and can be applied without adding auxiliary chemicals.<sup>9</sup> Direct dyes have a relatively linear and coplanar structure with ionic groups and are attracted to cellulosic fibers through hydrogen bonds and Van der Waal's forces.<sup>7</sup> An example of one of the commonly used direct dye is C.I. Direct Black 38 (1).



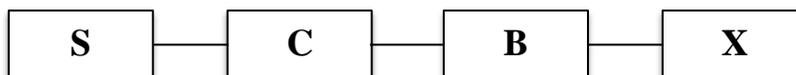
**1**

The advantages of direct dyes include low cost, easy of application and a wide range of available hues, while the major drawback is poor-to-moderate fastness, particularly to washing. After-treatments like applying dye-fixing agents improve the wet fastness but some of these processes would cause changes in shade, brightness and light fastness of the resultant dyed fabrics. But even suitably treated, the wet fastness properties of some direct dyes are still hard to meet current consumer demands for many apparel and furnishing end uses. Hence, the use of direct dyes has gradually decreased and been replaced to a great extent by higher performing dyes such as reactive dyes.<sup>10</sup>

### **2.2.3 Reactive Dyes**

Unlike all other classes of dyes, reactive dyes covalently bond with the fiber substrate and thus become an integral part of the substrate. The major benefit is the wet fastness of the dyed substrate is very good due to the stability of dye-fiber covalent bond unlike other systems that rely on the insolubility of the dyes in the fiber, or secondary forces between the

dyes and the substrate.<sup>11</sup> Generally the reactive dyes for cellulosic materials have the basic structure as shown in Figure 3.<sup>10</sup>



S is the solubilizing groups, confers water solubility to the dye

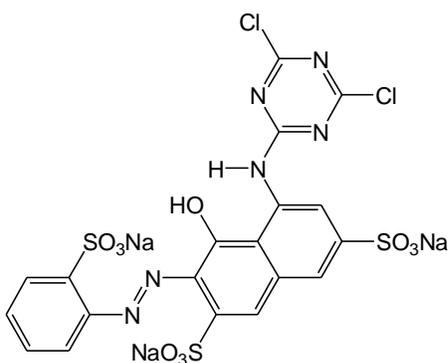
C is the Chromophore, which contributes color to the dye

B is the bridging group, which joins the reactive group to the chromophoric group

X is the reactive group, which enables the reaction between the dye and the substrate

Figure 3. General Structure of a Reactive Dye

An example of one of the historically important reactive dyes is C.I. Reactive Red 1 (**2**). In the structure, the sodium sulfonate is the solubilizing group, the diazo group is the chromophore, the secondary amino is the bridging group and the dichloro triazinyl moiety is the reactive group.



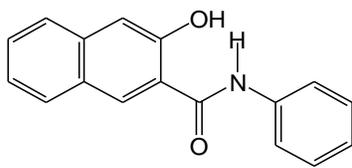
**2**

The first commercial reactive dye for cellulose was marketed in April 1956, just a century after the discovery of mauveine.<sup>12</sup> Due to previously unobtainable shades with excellent wet fastness properties, reactive dyes have been fully developed and are commercially widely used. Almost 45% of all textile dyes produced annually belongs to the reactive class due to the extensive use of these dyes for coloring cellulose and viscose materials.<sup>13</sup>

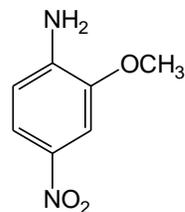
However, reactive dyes also have some drawbacks: fair light fastness, low chlorine resistance, relatively high cost and low reaction efficiency. Due to the competing hydrolysis reaction of the reactive dyes, dye fixation efficiency on cellulosic fibers is generally low. Cotton fabrics are predominantly dyed with reactive dyes in the presence of substantial amounts of electrolyte and alkali. Without expensive waste water treatment, the appreciable dye and salt concentrations in the dyeing effluent produce serious environmental problems. Ever since reactive dyes were commercialized, research has continued to improve the dyeing procedures and dyeing efficiencies of reactive dyes on cotton and other fabrics.

#### **2.2.4 Azoic Dyes**

Unlike all other kinds of dyes, azoic dyes are formed inside the textile material during the dyeing process by the reaction of naphthols (Azoic Coupling Components) and fast bases (Azoic Diazo Components). An example of the azoic coupling component is the C.I. Azoic Coupling Component 2 (**3**) and an example of the diazo component is the C.I. Azoic Diazo Component 5 (**4**).



**3**



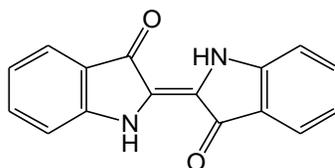
**4**

In the dyeing process with azoic dyes, the textile materials are first treated with naphthols which have affinity for the cellulosic materials. And the naphthols can be classified based on the affinity for cotton while the higher the affinity the better rubfastness the formed dye would have.<sup>9</sup> Then the base is converted into water-soluble diazo compound by the process called diazotization. Finally, the reaction between the diazotized form of the base and the treated material form the color inside the fabrics. This step is known as coupling or development.

Azoic dyes are especially strong in orange, red, scarlet and Bordeaux. The ranges of color also include dark blue and black, but there is no green or bright blue. Wash-fastness properties of azoic dyes are excellent and the cost of azoic dyes is relatively low. Even though the azoic dyes have advantages in some colors compared with other kinds of dyes, they have limitations of available hues which make the shade matching difficult. There are some other disadvantages of azonic dyes, for example, the application procedure is complicated and time-consuming.

### 2.2.5 Vat Dyes

Vat dyes are one of the most important dye-classes for cellulosic materials, since they provide excellent wash and light fastness properties.<sup>14</sup> They are used to dye cellulosic materials in relatively dull shades with good fastness, especially when fastness to chlorine is important. The most commonly used dye in the world is C.I. Vat Blue 1, indigo (**5**), due to the popularity of blue jeans. However, as an exception to the general rule of vat dyes having good colorfastness, indigo has poor colorfastness properties.



**5**

In fact, the good fastness properties of vat dyes are based on their chemical nature and method of application. Vat dyes are insoluble in water but the carbonyl groups enable the dyes to be converted into water-soluble leuco compounds under alkaline conditions. Therefore the application of vat dyes includes solubilisation by reduction, rapid penetration into the fiber and oxidization into insoluble pigment.<sup>9</sup> However, vat dyes are relatively costly and their application must be carefully controlled. Therefore this limits the commercial use of vat dyes.

### **2.2.6 Sulfur Dyes**

The use of sulfur dyes in dyeing involves the same principles as vat dyes, first convert the insoluble pigment into a leuco compound by reduction with sodium sulfide then oxidize the leuco compound inside the fiber. The chemistry of sulfur dyes is very complex since they are synthesized by heating simple amines or phenolic compounds in the presence of sulfur.<sup>9</sup> Sulfur dyes are economical and widely used for dyeing deep muted shades like black, navy, brown, olive and blue.<sup>14</sup> They have high washfastness, fair lightfastness and low bleachfastness.<sup>15</sup>

However, the large amounts of sodium sulfide used in the manufacture and application of sulfur dyes can cause serious environmental problems.<sup>16</sup> Therefore a lot of researches have been done to find suitable alternative reducing agents for sulfur dyes such as thiourea dioxide and glucose.<sup>17,18</sup>

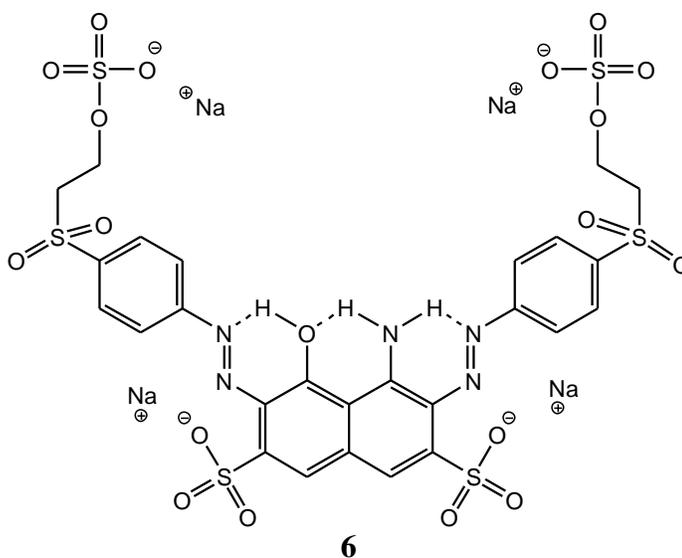
### **2.3 Dyeing of Cotton for Deep Black Shades**

Obtaining deep shades on cotton with good fastness properties is difficult, especially deep black shades. Sulfur blacks are still used to dye black and other heavy shades on cotton due to their low price and moderate light and wet fastness.<sup>19</sup> For example, C.I. Sulfur Black 1 is the bestselling individual dye for the coloration of textiles today.<sup>14</sup> However, during the dyeing process of sulfur dyes, the chemicals added to help dissolve the dyes, especially sodium sulfide, cause environmental problems. Based on the environmental concerns, the use

of sulfur dyes is limited and other dye classes are becoming more preferable. Moreover, none of the dye classes used for cotton can obtain ultra-deep blacks with good wash fastness.

Since direct dyes exhibit poor wash fastness properties, reactive dyes are the most common replacement of sulfur dyes, especially for dyeing deep black shades. Even though many commercial reactive black dyes have relatively good fastness properties and deep shades, they all have a common problem of high concentration of dye and salt in dye bath effluent. As reported, for most kinds of reactive black dyes, the fixation ratio is lower than 70% even with high concentration of salt added.<sup>19,20</sup> Hence, substantial amounts of dyes are released into the environment which also increases the cost of dyeing.

For example, C.I. Reactive Black 5 (**6**, e.g., Remazol Black B) is commonly used as the navy component in reactive black mixtures. However, its fixation ratio of it is relatively low.



C.I. Reactive Black 5 is an azo dye. The decoloration of effluent contains azo dyes is often a major concern in wastewater treatment since some azo dyes or their metabolites may be mutagenic.<sup>21</sup> A significant amount of research on the decolorization of dye bath effluent has been done, including biological treatment, membrane separation processes, adsorption, oxidation and reduction.<sup>22-25</sup> Many physical and chemical treatment processes are effective for the decolorization of dyeing effluent, but most of them are too expensive and difficult to apply.<sup>26</sup> So rather than trying to develop a good method to decolorize dye bath effluent, increasing dye fixation and developing a more environmentally responsible dyeing procedure would be a better solution since it can also help to obtain ultra-deep dyeings. To increase the dye uptake and fixation of the dyeing process with reactive dyes, pretreatments like combined mercerization and cationization would likely be effective.

#### **2.4 Pretreatments of Cotton to Improve Dyeing Properties**

Before dyeing, cotton fabrics go through several preparation steps to ensure good dyeability and uniform appearance. The common preparation steps before dyeing are listed in Table 3.<sup>7</sup>

**Table 3. Steps in the Preparation of Cotton before Dyeing**

<b>Process</b>	<b>Description</b>
Singeing	Burning off surface fibers to make the fabric smooth
Desizing	Removing the size from warp yarns in woven fabrics
Scouring	Chemical washing process to remove waxes, oils and other impurities
Bleaching	Oxidizing fibers to improve the whiteness of the fabric

The steps described above are the most common preparation steps before the dyeing of cotton, while to improve the dyeability of cotton fabrics and reduce the chemicals used in the dyeing process, pretreatments like mercerization and cationization may be employed.

### **2.4.1 Mercerization**

Mercerization was discovered by John Mercer in 1844 and patented in 1850. However, this process did not become popular until H. A. Lowe found that the luster of the fabric would be improved after the cold caustic soda acted on cotton under tension.<sup>27</sup> During the mercerization process, the fiber structure of cotton is greatly changed and results in changes of not only luster but also other properties like gain in strength, increased moisture absorption, dyeability and reactivity.

#### **2.4.1.1 Changes in Structure and Properties of Cellulose Due to Mercerization**

Unmercerized cotton fiber has a ribbon-like structure with spiral twists longitudinally, its cross-section is irregular and kidney shaped with a lumen inside. When cotton fiber is immersed in sodium hydroxide solution, the cellulose swells and the flat ribbon structure untwists and tends to become elliptical.<sup>28</sup> Figures 4 and 5 are optical micrographs of unmercerized and mercerized cotton fibers with 400 times magnification which show the changes in morphology of cotton after mercerization.



Figure 4. Optical Micrograph of Unmercerized Cotton Fibers

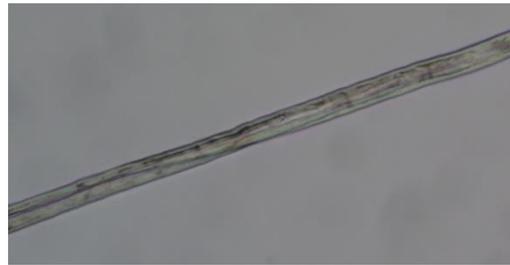


Figure 5. Optical Micrograph of Mercerized Cotton Fibers

The swelling breaks intermolecular hydrogen bonds and allows for reorganization of the cellulose chains. The reorganization includes changes in crystalline structure, reorientation and results in lower crystallinity and smaller crystal sizes of the cellulose fibers.<sup>29</sup> After removing the sodium hydroxide solution, the native cellulose I with parallel chains is converted into cellulose II with antiparallel chains, which is more stable.<sup>30</sup> As the fiber swells, it also shrinks in length.

Due to the structure changes, mercerized cotton fibers reflects light more evenly than the original kidney shaped structure and thereby improves the luster of the cotton fibers. The mercerization also increases the moisture regain and dye absorption of the cotton fabrics due

to the decreased crystallinity and crystal sizes in the fibers. Also, modifications in fiber structure cause changes in internal light scattering and increase the depth of shade even with the original dye absorption. So the increased depth of shade of mercerized cotton is caused by both the optical effects and increase of dye absorption.<sup>27</sup> There are also some improvements in mechanical properties of cotton fibers after mercerization, like improved strength and dimensional stability. These improvements are attributed to the change in orientation degree and the increased cohesion between cotton fibers.

#### 2.4.1.2 Mercerization Methods and Machines

For traditional mercerization, the concentration of caustic soda, applied tension, temperature and time all influence the degree of mercerization. For example, the luster of the fabric increases with the increase of the applied tension during mercerization.<sup>31</sup> In order to obtain good mercerization effects, mercerization is commonly conducted under following conditions, 15-18 °C and 31-35% caustic soda solution, dwelling period around 50 seconds, and under tension.<sup>27</sup> A number of different kinds of mercerization methodologies have been developed to produce different effects. For example, hot mercerization uses hot caustic soda at a temperature between 60-70 °C and this makes the cotton swell slower.<sup>22</sup> Other kinds of mercerization include liquid ammonia mercerization and foam mercerization.

Based on the form of cotton textiles, yarns, woven fabrics and knit fabrics, there are different kinds of machines for mercerization of cotton. Yarns are always mercerized in the form of hanks. The basic method of most hank mercerizing is stretching hanks on rollers while

impregnated in alkali and in the subsequent washing process.<sup>28</sup> Thus, almost all yarn mercerizing machines have similarities in design. A typical yarn mercerizing machine is the two sided yarn mercerizing machine made by Mather & Platt (Figure 6).<sup>27</sup>

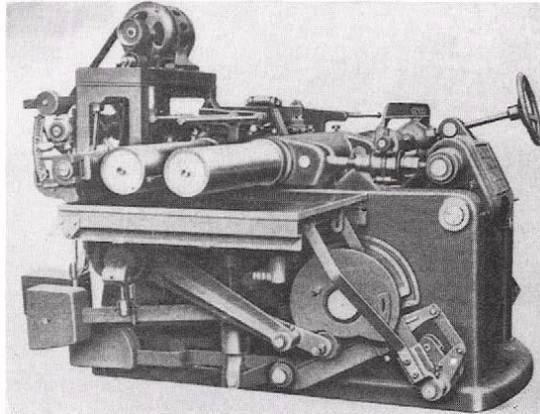


Figure 6. Yarn Mercerization Machine

For the mercerization of woven fabrics, machines can be broadly divided into two types, the chain type and the chainless type. Compared with chainless mercerizing machines, the chain mercerizing machine has an inherent disadvantage that the applied tension acts mainly on the edges of the fabric so the elongation at the edges is greater than in the middle of the fabric.<sup>32</sup> However, the traditional machines to mercerize woven fabrics cannot be used for mercerizing knit fabrics since knits are easily deformed. Thus, in knit goods mercerizing machines, tension controlling devices and other modifications like jets to balloon the tubular fabrics have been added. There are many machinery manufacturers offering equipment for tubular

knit fabrics mercerizing include Dornier, Jaeggli, Caber, etc. Figure 7 shows a typical Dornier continuous mercerizing range for tubular knit goods.<sup>27</sup>

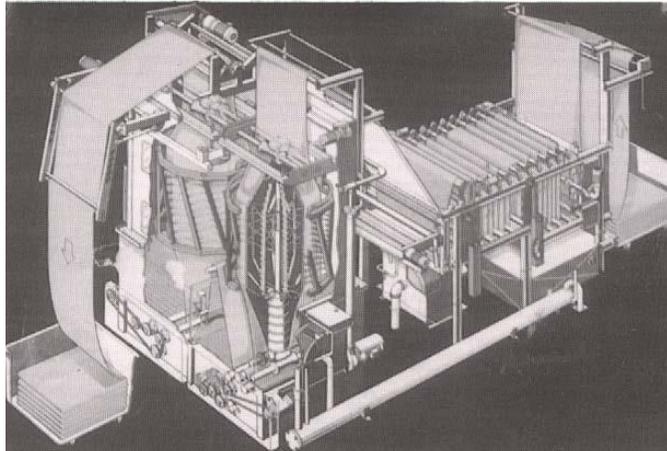


Figure 7. Knit goods mercerizer

#### 2.4.1.3. Evaluation of Mercerization Effects

Evaluation of mercerization effects is important for the quality control of textile products. The most commonly used method is determining the barium activity number<sup>33</sup> based on the standard method developed by the American Association of Textile Chemists and Colorists. However, the determination of barium number is a laborious procedure. Hence, other methods for the evaluation of mercerization degree have been developed, using near-infrared spectroscopy, for example.<sup>34</sup>

### 2.4.2 Cationization

While in contact with water, negative charges build up on the surface of cotton due to the partial ionization of hydroxyl groups, which produces electrostatic repulsion of negatively charged dyes like reactive dyes. Hence, high concentrations of electrolytes, such as sodium chloride and sodium sulfate, are used in the conventional dyeing procedure of cotton with reactive dyes to suppress the negative charge build-up and reduce the solubility of dyes, thereby increasing dye exhaustion.<sup>35</sup> But even with a high concentration of electrolytes, the dye uptake of reactive dyes is still relatively low. As a result, the dye bath wastewater typically contains high concentrations of both salt and unexhausted dye, which cause serious environmental problems. The wastewater pollution can be reduced by synthesis of better dyes, selection of chemicals, re-use of dye bath, process optimization and development of other sustainable technologies.<sup>36</sup> However, all these ideas require changes in existing method and equipment which involve significant research expenditures and capital investment.<sup>37</sup> Hence, in addition to optimizing the dyeing procedure, modifying the cotton fiber to have greater affinity to reactive dyes and improved reaction efficiency with reduced electrolyte usage is an attractive option to reduce environmental impact.

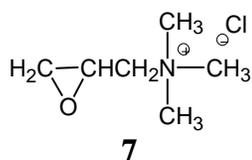
By far the most widely researched pretreatment to improve the affinity of reactive dyes to cotton is cationization of the fiber. Since reactive dyes carry anionic charges, they exhibit high affinity for cotton with cationic charges. For cationized cotton, the ionic attractions between cotton and reactive dyes may result in high dye uptake, reduced or no electrolyte use, less dye washing off and less water consumption.<sup>38-43</sup> Hence, the environmental problems

caused by salt and dye in the effluent can be potentially largely mitigated by cationization pretreatment of cotton yarns or fabrics.

#### 2.4.2.1 Cationic Reagents

Research has focused on the development of different kinds of cationic reagents for the cationization of cotton. Non-reactive cationic reagents are susceptible to desorption and may precipitate with anionic dyes, so cationization with non-reactive cationic reagents cannot be used as an effective pretreatment for cotton.<sup>44</sup> The reactive cationic reagents used for cationization of cotton can be divided into two groups, monomeric reagents and polymeric reagents.

In the monomeric reactive cationic reagents, a typical one is 2,3-epoxypropyl trimethylammonium chloride (**7**) formed by the reaction of its epichlorohydrin precursor, 3-chloro-2-hydroxypropyl trimethylammonium chloride with alkali, as shown in Figure 6. 3-chloro-2-hydroxypropyl trimethylammonium chloride is commercially available as 65% water solution from Dow Chemical Company under the trade name CR-2000.<sup>45</sup>



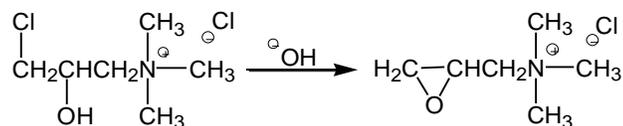
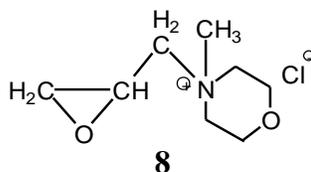
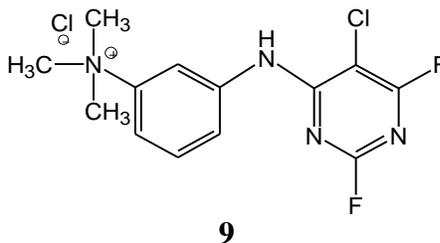


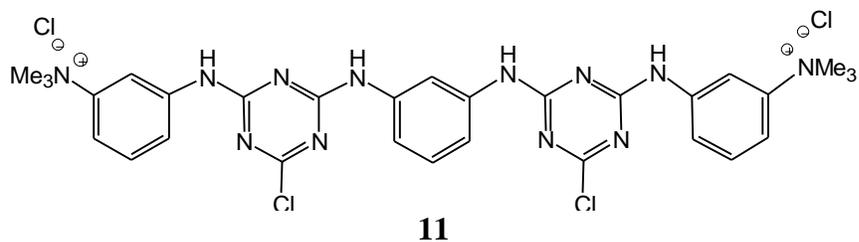
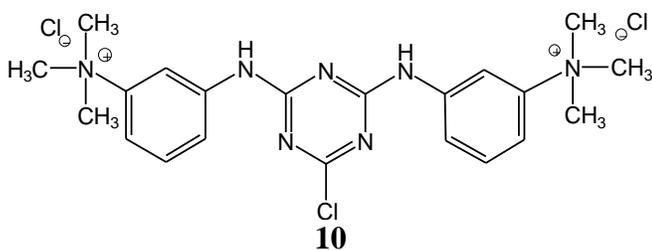
Figure 8. Reaction from 3-chloro-2-hydroxypropyl trimethylammonium Chloride to 2,3-epoxypropyl trimethylammonium Chloride

Bayer has marketed a similar product, glycidyl-N-methyl morpholinium chloride (**8**), under the trade name Levogen RS.<sup>46</sup>

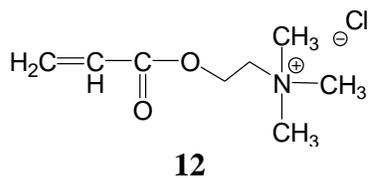


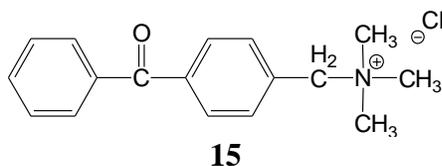
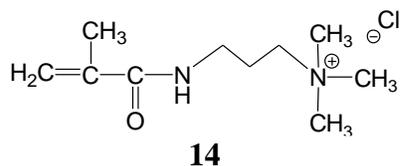
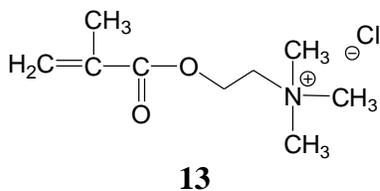
Another kind of cationic reagent used for the pretreatment of cellulose is in the structure of cationic groups attached to heterocyclic systems. Examples include mono-reactive mono-quaternary compounds (e.g., **9**), mono-reactive bis-quaternary compounds (e.g., **10**) and bis-reactive bis-quaternary compounds (e.g., **11**). These types of cationic agents exhibit better thermal stability compared with the epoxy types. And the bis-reactive bis-quaternary cationic reagent exhibit higher substantivity for cellulose compared with the mono-reactive ones.<sup>44</sup>





Other examples of monomeric cationic reagents which have been used for cationization to improve the dyeing performance of cotton include acryloyloxyethyl trimethylammonium chloride (**12**), methacryloyloxyethyl trimethylammonium chloride (**13**), Methacryloylaminopropyl trimethylammonium chloride (**14**) and 4-benzoylbenzyl trimethylammonium chloride (**15**).<sup>40</sup>





Research on the development and application of polymeric cationic reagents has also been investigated. For example, Lewis and Lei<sup>46</sup> studied the dyeing performance of cotton cationized with Hercosett 125 (Hercules Powder Corporation), a commercially available reactive polyamide-epichlorohydrin resin. Compared to monomeric cationic reagents, the disadvantage of polymeric reagents is the poor light fastness of subsequent reactive dyeing caused by ring dyeing.

#### 2.4.2.2 Cationization of Cellulose with CHPTAC

Perhaps the most common cationic reagent for pretreatment of cotton, 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC) has been well studied for its

cationization mechanism, application methods, effects in subsequent dyeing and some other properties.<sup>37,39,47-50</sup>

CHPTAC itself does not react with cellulose. It should first be converted into 2,3-epoxypropyl trimethylammonium chloride (EPTAC) according to the reaction scheme in Figure 6. Then EPTAC would react with alcohols under alkaline conditions to form ethers. So it can be attached to cellulose according to the reaction scheme in Figure 7.<sup>39,51</sup> With the electropositive quaternary ammonium attached to the cellulose chains, anionic dyes exhibit higher substantivity towards the fiber.

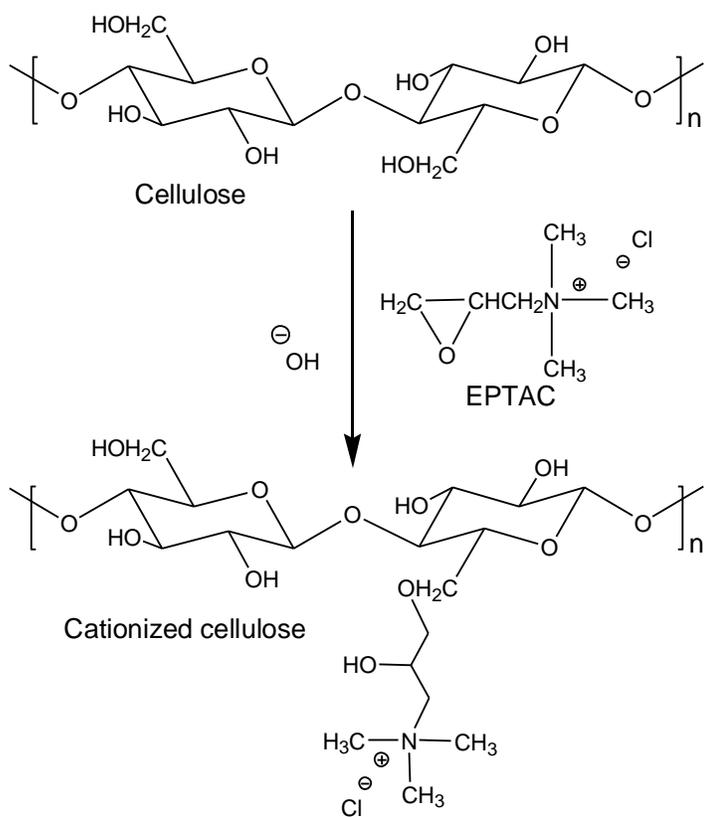


Figure 9. Reaction of EPTAC with Cellulose

A competing reaction under aqueous alkaline conditions is hydrolysis. Hence, EPTAC slowly hydrolyzes in aqueous alkaline solution to form 2,3, dihydroxypropyl trimethylammonium chloride, as shown in Figure 8.<sup>37,39</sup> The diol is not reactive, so the hydrolysis of EPTAC must be minimized.

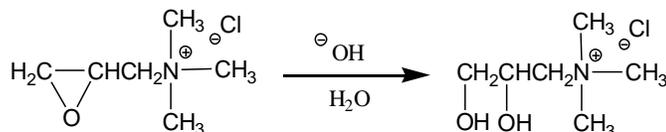


Figure 10. Hydrolysis of EPTAC

There are some other common reactions of EPTAC like reacting with carboxyl groups under alkaline conditions as show in Figure 9<sup>52,53</sup> and react with amines according to the reaction in Figure 10.<sup>54</sup>

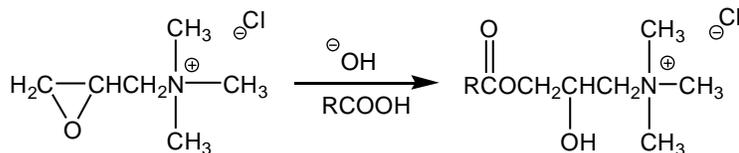


Figure 11. Reaction of EPTAC with Carboxyl under Alkaline Conditions

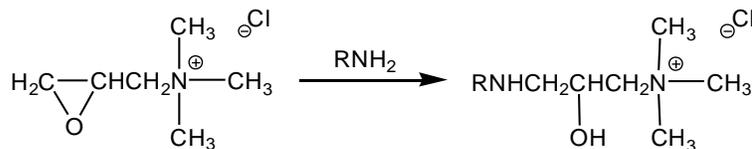


Figure 12. Reaction of EPTAC with Amine

#### 2.4.2.3 Application Techniques of CHPTAC

The cationization of cotton fabric with CHPTAC can be carried out by several methods, including cold pad-batch, pad-bake, pad-steam and exhaustion. The fixation of CHPTAC on cotton fabrics varies greatly with the selection of method, concentration of CHPTAC and alkali, time, temperature, and other variables. The cationization level on the treated cotton fabrics can be quantified by measuring the nitrogen content in the fabrics.

It has been reported that heat may cause the migration of reactants and would results in nonuniform cationization.<sup>54</sup> So compared with higher temperature application methods, cold pad-batch provides more uniform cationization of cotton.<sup>55</sup> Cold pad-batch is possibly the most efficient method to apply CHPTAC while exhaustion may be the least efficient.<sup>54</sup> Other research has shown that, compared with aqueous-based methods, the use of solvents like acetone produce higher cationization efficiency, since hydrolysis of CHPTAC is avoided. However, the use of organic solvents is not feasible for commercial production.<sup>48</sup>

## CHAPTER 3 EXPERIMENTAL

### 3.1 Materials

The fabrics and chemicals used are summarized in Table 4 including their names, brief descriptions and manufacturer.

**Table 4. Test materials and chemicals**

Name	Description	Manufacturer
Cotton Fabrics	Bleached Desized Cotton Print Cloth, style # 400, 102 g/m <sup>2</sup> , 45”	Testfabrics, Inc.
	Bleached Desized Mercerized Cotton Print Cloth, style # 400M, 107 g/m <sup>2</sup> , 44”	Testfabrics, Inc.
Cationic Reagent	3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC), 65% Solution	Dow Chemical
Base	Sodium Hydroxide, 50% aqueous solution	Fisher Chemicals
Acid	Citric Acid Anhydrous Crystalline, ≥ 99.5%, C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	Fisher Chemicals
Salts	Soda ash Anhydrous Powder, ≥ 99.5%, Na <sub>2</sub> CO <sub>3</sub>	Fisher Chemicals
	Sodium Sulfate Anhydrous Granular, ≥ 99%, Na <sub>2</sub> SO <sub>4</sub>	Fisher Chemicals
Dyes	Remazol Black B 133%	Dystar
	Remazol Yellow RR gran	Dystar

### 3.2 Equipment

A Werner Mathis HVF lab padding machine was used for the cationization of all fabrics. The rinse and neutralization of the cationized fabrics were performed by using a paddle washer. To dry the fabric samples, a Bock Centrifugal Extractor and Yamato Mechanical Convection

Oven DKN were used. Ahiba Texomat dyeing machine was used for all dyeings. Colorimetric assessments of dyed fabric samples were done by using Spectraflash SF 600X Datacolor Reflectance Spectrophotometer with iMatch software from X-Rite. An HP/Agilent 8453 UV-Vis Spectrophotometer was used to measure the concentration of dyes left in the dyeing bath. An Atlas LEF Launder-Ometer was used to test the colorfastness to laundering of dyed fabrics and an AATCC automated crockmeter made by Atlas was used to test the colorfastness to crocking. Also the colorfastness to light of dyed samples was measured by using an Atlas Ci 3000+ Weather-Ometer. Tensile properties of cotton yarns were measured by using MTS Q-Test/5 Universal Testing Machine. Pilling resistance of fabrics was measured by using Atlas Random Tumble Pilling Machine.

### **3.3 Cationization Pretreatment**

The cold pad batch method with following steps was used for cationization. In both cationization and dyeing procedures, city water was used as in commercial production.

- 1) A Mathis HVF lab padder was used to pad both unmercerized and mercerized cotton print cloth at 100% wet pick up (speed: 1.5 m/s, pressure: 1 bar) with varying concentrations of CHPTAC.
- 2) The padded samples were rolled onto hard paper tubes and wrapped in plastic to prevent contacting with air. Then the fabrics were batched at room temperature for 20 hours.
- 3) After removing the plastic wrap, the samples were washed to remove unfixed and hydrolyzed cationic reagent. Citric acid (~0.5 g/L) was added to neutralize the fabric pH.
- 4) The treated fabrics were then extracted and dried in a tumble dryer.

### 3.4 Dyeing Process

An Ahiba Texomat dyeing machine (Figure 11) was used for the dyeing of both uncationized and cationized cotton samples. A conventional dyeing procedure was used for uncationized cotton fabrics and the no salt dyeing procedure was used for the cationized cotton samples. A liquor ratio of 20:1 was used for all dyeings. Besides the dyes,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  were added in the dyeing procedure of uncationized cotton fabrics while only  $\text{Na}_2\text{CO}_3$  was added in the dyeing procedure of cationized cotton fabrics.



Figure 13. Ahiba Texomat Dyeing Machine

#### 3.4.1 Conventional dyeing procedure

- 1) Dissolve  $\text{Na}_2\text{SO}_4$  in water at room temperature.
- 2) Immerse the rolled fabric into the solution.
- 3) Heat to 30 °C.
- 4) Add dye in 5 minutes at 30 °C.

- 5) Hold at 30 °C for 5 minutes.
- 6) Add half of the Na<sub>2</sub>CO<sub>3</sub> in 5 minutes at 30 °C.
- 7) Hold at 30 °C for 5 minutes.
- 8) Heat to 60 °C at 1.0 °C/min.
- 9) Add the other half of Na<sub>2</sub>CO<sub>3</sub> in 5 minutes at 60 °C.
- 10) Hold at 60 °C for 25 minutes.
- 11) Cool to 40 °C then discard bath.
- 12) Wash and rinse manually for 10 minutes with room temperature water.
- 13) Neutralize with citric acid.
- 14) Wash and rinse manually for 10 minutes with room temperature water.
- 15) Extract fabric and dry.

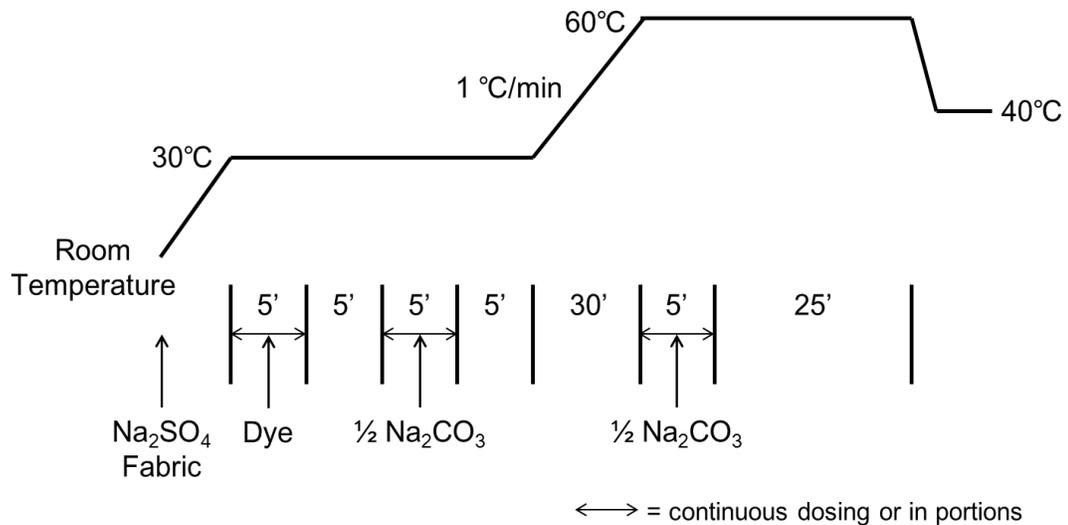


Figure 14. Conventional Dyeing Procedure

### 3.4.2 No Salt Dyeing Procedure

- 1) Dissolve dyes in water at room temperature.
- 2) Immerse the rolled fabric into the solution.
- 3) Heat to 30 °C.
- 4) Add  $\text{Na}_2\text{CO}_3$  in 5 minutes at 30 °C.
- 5) Hold at 30 °C for 5 minutes.
- 6) Heat to 60 °C at 1.0 °C/min.
- 7) Hold at 60 °C for 30 minutes.
- 8) Cool to 40 °C then discard bath.
- 9) Wash and rinse manually for 10 minutes with room temperature water.
- 10) Neutralize with citric acid.
- 11) Wash and rinse manually for 10 minutes with room temperature water.
- 12) Extract fabric and dry.

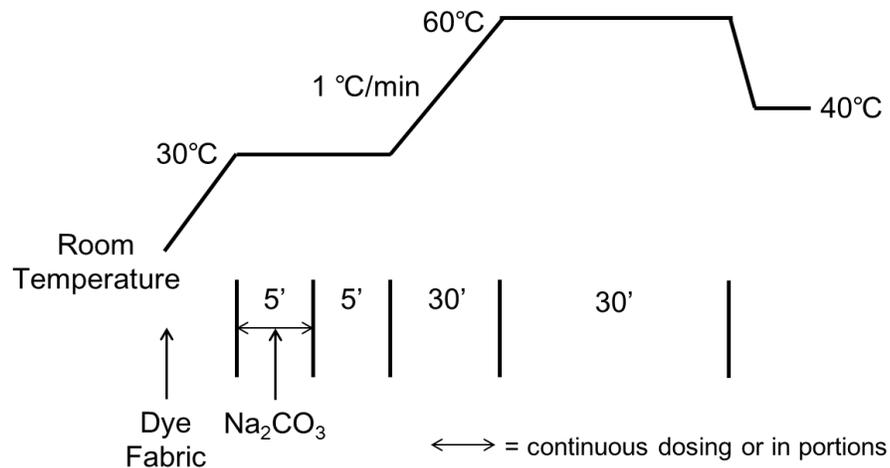


Figure 15. No Salt Dyeing Procedure

### **3.5 Nitrogen Content Analysis**

The percentage of nitrogen present in the cationized cotton fabric was used as an indicator of the amount of CHPTAC reacted with cellulose. The samples used for testing were cut from the cotton fabrics before dyeing procedure. The samples were tested by the Environmental and Agricultural Testing Service in the Department of Soil Science at North Carolina State University. The machine used for the measurement was the PE 400 CHN Elemental Analyzer. The method was based on the classical Pregal and Dumas methods. The samples were combusted in a pure oxygen environment.<sup>56</sup>

### **3.6 Color Measurement**

A calibrated Datacolor Spectraflash 600X Reflectance Spectrophotometer with iMatch software from X-Rite was used to measure the L\*, a\*, b\*, C\*, h° and the K/S values of the dyed fabrics following AATCC Evaluation Procedure 6.<sup>57</sup> The K/S value of the sample was calculated by adding the K/S values of each 10 nm from the wavelength of 360 nm to 750 nm.

The software was set to use illuminant D65 with the UV light included, and the CIE 10-degree supplemental standard observer. The sample being tested was folded two times. Each sample was measured ten times by rotating the sample and changing the measuring point randomly along the sample. The average value was recorded.

### **3.7 Evaluation of Dye Uptake**

An Agilent 8453 UV-VISqishi Spectrophotometer was used to measure the absorbance spectra of dye left in the bath after dyeing.

Solutions of dyes were prepared at the following concentrations, 5 mg/L, 15 mg/L, 25 mg/L and 50 mg/L. By measuring the absorbance of the solutions, a Beer's Law calibration plot of concentration vs. absorbance was produced at the wavelength of max absorption. Then by measuring the absorbance value of the solution after dyeing, the concentration of the solution was determined based on the relationship between concentrations and absorbance values. The dye uptake was calculated based on the concentration of dyes in solution before and after dyeing.

### **3.8 Colorfastness Tests**

#### **3.8.1 Colorfastness to Laundering**

Colorfastness to laundering of the dyed samples was measured using AATCC Test Method 61.<sup>58</sup> It is designed to evaluate colorfastness of textile products for home laundering. The machine used for the test was an Atlas LEF Launder-Ometer. Test specimens were cut into 50×150 mm and then sewn together with a sample of multi fiber test fabric. Test No. 2A was selected (See Table 5).<sup>58</sup> After running in canisters separately, the specimens were rinsed in beakers and then dried and both color change and staining of the specimens were evaluated.

**Table 5. Test Conditions for Washfastness**

Test No.	Temp	Total Liquor Volume (mL)	Percent Powder Detergent of Total Volume	Percent Liquid Detergent of Total Volume	Percent Available Chlorine of Total Volume	No. Steel Balls	No. of Rubber Balls	Time (Min)
	°C (±2)							
2A	49	150	0.15	0.23	None	50	0	45

For color change, visually assessed color changes were quantified based on AATCC Evaluation Procedure 1.<sup>59</sup> The visual evaluation was done under daylight simulation (D<sub>65</sub>) using a SpectraLight III viewing booth. The grade of color change was determined by comparing the color difference between the dyed fabrics before and after laundering with the standard AATCC Gray Scale for Color Change. Instrumental assessment of color change was quantified based on AATCC Evaluation Procedure 7.<sup>60</sup> Datacolor Spectraflash 600X Reflectance Spectrophotometer with iMatch software from X-Rite was used to measure the color difference of the dyed fabrics before and after laundering and a grade was given for the color change. For each sample, the average value of visually assessed color change and instrumentally measured color change was used as the final grade of color change.

For staining, Warp Stripe 13 Fiber Fabric (Testfabrics, Inc., PA, USA) with the style number of 43 was used as a multifiber test fabric for measuring the color transferred during standard laundering. Color transferred from the specimen to the multifiber test fabric was rated based on AATCC Evaluation Procedure 2.<sup>61</sup> A grade of staining was given for each kind of fiber based on the standard AATCC Gray Scale for Staining.

### 3.8.2 Colorfastness to Crocking

Colorfastness to crocking of the dyed samples was measured using AATCC Test Method 8.<sup>62</sup> Both dry and wet crocking test were measured using the AATCC automated crockmeter. In the experiment, the dyed sample was rubbed with a white woven fabric with the length of 50 mm. Each sample was rubbed by the finger in the crockmeter for 10 complete turns. Color transferred from the specimen to the white test square was rated using AATCC Evaluation Procedure 2. The grade of staining for each sample was determined by visual assessment using the standard AATCC Gray Scale for Staining.

### 3.8.3 Colorfastness to Light

Colorfastness to light of the dyed samples was measured using test option 3 in AATCC Test Method 16 (See Table 6).

**Table 6. Option 3 of Machine Exposure Conditions for Colorfastness to Light<sup>63</sup>**

Light Source	Black Panel Temperature	Chamber Air Temperature	Relative Humidity	Irradiance at 420 nm	Irradiance 300-400 nm
	°C	°C	%	W/m <sup>2</sup> /nm	W/m <sup>2</sup>
Xenon Continuous Light	63 ± 1	43 ± 2	30 ± 5	1.10 ± 0.03	48 ± 1

For each kind of dyed fabric, the color change after 20 and 40 continuous light-on operating hours were assessed separately. The visually assessed color change of the exposed area was

quantified using AATCC Evaluation Procedure 1. The color changes were also measured instrumentally using AATCC Evaluation Procedure 7. For each sample, the average value of visually assessed color change and instrumentally measured color change was used as the final grade of color change.

### **3.9 Mechanical Properties of Yarns**

The mechanical properties of yarns, including breaking load and elongation, were measured based on the ASTM Standard Test Method D2256-08.<sup>64</sup> The machine used for the test was MTS Q-Test/5 Universal Testing Machine. The gauge length was set as 250 mm and the rate of operation was 300 mm/min. Yarns were extracted from different positions of the cotton fabrics randomly. For each kind of yarn, ten specimens were measured and the average value of tensile strength was calculated after eliminating those values which deviated higher than 25% from the average value.

### **3.10 Pilling Resistance of Fabrics**

The pilling resistance of fabrics was measured using the ASTM Standard Test Method D3512-07.<sup>65</sup> Atlas Random Tumble Pilling was used for the test. After running three specimens of each kind of fabric for 30 minutes based on the standard, the appearance of the face of each specimen was rated by visual comparison with photographic standards. The scale used for rating is:

5–no pilling; 4–slight pilling; 3–moderate pilling; 2–severe pilling; 1–very severe pilling

## CHAPTER 4 RESULTS AND DISCUSSION

### 4.1 The Effects of Cationization and Mercerization

To discover the relationship between the concentration of CHPTAC and cationization effect, a series of experiments with different concentrations of CR2000 were designed. The NaOH: CHPTAC molar ratio for cationization was kept constant throughout the work based on previous work by Farrell which found the optimum NaOH: CHPTAC molar ratio to be 2:1.<sup>47</sup> In the experiment, both mercerized and unmercerized cotton fabrics were used. Summary data on the fabrics and cationization method are reported in Section 3.1 (page 26) and Section 3.3 (page 27). The concentrations of the cationization solutions are listed in Table 7.

**Table 7. Concentrations of Cationization Solutions**

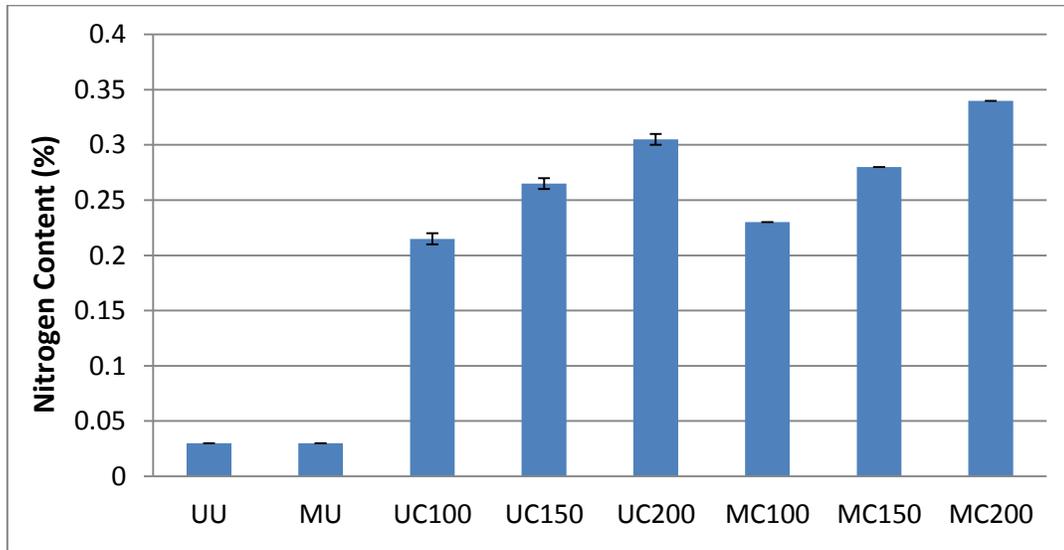
<b>Solution Number</b>	<b>Concentration of CR2000 (g/L)</b>	<b>Concentration of NaOH (g/L)</b>
1	100	60
2	150	90
3	200	120

#### 4.1.1 Nitrogen Content Analysis

After cationization treatment, the nitrogen contents of all the treated and untreated samples were measured in duplicate. The results are summarized in Table 8 and averaged data are shown in Figure 13.

**Table 8. Nitrogen Content of Cationized and Uncationized Cotton Fabrics**

Sample	Pretreatments	Concentration of CR2000 (g/L)	Specimen Number	Nitrogen Content (%)
UU	Unmercerized/Uncationized	-	1	0.03
			2	0.03
MU	Mercerized/Uncationized	-	1	0.03
			2	0.03
UC100	Unmercerized/Cationized	100	1	0.22
			2	0.21
UC150	Unmercerized/Cationized	150	1	0.26
			2	0.27
UC200	Unmercerized/Cationized	200	1	0.31
			2	0.30
MC100	Mercerized/Cationized	100	1	0.23
			2	0.23
MC150	Mercerized/Cationized	150	1	0.28
			2	0.28
MC200	Mercerized/Cationized	200	1	0.34
			2	0.34



**Figure 16. Nitrogen Concentent of Cationized and Uncationized Cotton Fabrics**

The results show that the nitrogen contents of the uncationized cotton fabrics, both unmercerized and mercerized, are close to zero. However, after cationization, the nitrogen content of the fabrics increased in proportion to the amount of CHPTAC applied. The data indicate that the cationization treatment produces derivatized cellulose consistent with the theoretical degree of cationization. For mercerized cotton fabrics, the increase in nitrogen content is slightly higher than corresponding unmercerized cotton fabrics cationized with the same method. This may be because, after mercerization, the reactivity of cotton was improved due to increased accessibility of primary and secondary hydroxyl groups.

#### **4.1.2 The Effects on Dyeing Performance**

To evaluate the dyeing properties of the cationized samples, the treated samples were dyed with 6% owf Remazol Black B (C.I. Reactive Black 5) following the dyeing method given in Section 3.4 (page 28). For uncationized cotton fabrics, the industrial suggested dyeing recipe of Remazol Black B was used, which includes 20 g/L  $\text{Na}_2\text{CO}_3$  and 80 g/L  $\text{Na}_2\text{SO}_4$ . For cationized cotton fabrics, just 20 g/L  $\text{Na}_2\text{CO}_3$  was added since the anionic dye has affinity to cationized cotton fabrics.

Reflectance spectra of dyed samples were measured using a Datacolor Spectraflash 600X Reflectance Spectrophotometer. Duplicate samples were dyed by the same method and the  $L^*$   $a^*$   $b^*$   $C^*$  and  $h^\circ$  values summarized in Table 9 are average values.

**Table 9. L\* a\* b\* C\* h ° Values of Dyed Samples**

<b>Sample</b>	<b>L*</b>	<b>a*</b>	<b>b*</b>	<b>C*</b>	<b>h °</b>
UU	19.71	-2.01	-10.83	11.02	259.5
MU	16.42	-0.19	-8.21	8.21	268.7
UC 100	16.70	-0.47	-9.05	9.06	267.0
UC 150	15.78	-0.01	-8.32	8.32	269.9
UC 200	15.28	0.25	-7.86	7.86	271.8
MC 100	14.33	1.09	-6.08	6.18	280.2
MC 150	13.82	1.26	-5.45	5.59	282.9
MC 200	13.75	1.42	-5.21	5.40	285.2

By comparing L\* values in Table 9, it's clear that both mercerization and cationization process decreased the lightness of the dyed fabrics, which means the depth of shade increased. Also, lightness decreased as a function of CR2000 consistent with the nitrogen content analysis.

The C\* and b\* values of the dyed samples indicate that none of the dyed samples was in neutral black since the C\* values are not close to zero and b\* are negative (blue). However, the results demonstrate that both mercerization and cationization increased the depth of shade since the pretreated samples have lower lightness and less chroma compared with those untreated ones. Also, C\* decreased as a function of CR2000 concentration. From the results, it's clear that the dyed color of MC 200 sample was the deepest and has the lowest chroma, although little difference was observed in the L\* a\* b\* and h ° values of MC150 and MC200.

Since the objective of this research is to develop ultra-deep black shades, the K/S values of the dyed samples were measured. The measurement method for the of K/S values was described in Section 3.6 (page 31). The K/S values of duplicate batches of dyed samples were measured and are presented in Table 10 and averaged data are shown in Figure 14. The differences between the K/S values of the duplicate samples are indicated by error bars.

**Table 10. K/S values of Two Batches of Dyed Samples**

Sample	K/S Values	
	Batch 1	Batch 2
UU	481.2	494.7
MU	642.2	651.2
UC 100	641.0	646.8
UC 150	706.4	711.3
UC 200	762.1	753.7
MC 100	828.8	818.2
MC 150	897.5	880.0
MC 200	913.9	889.1

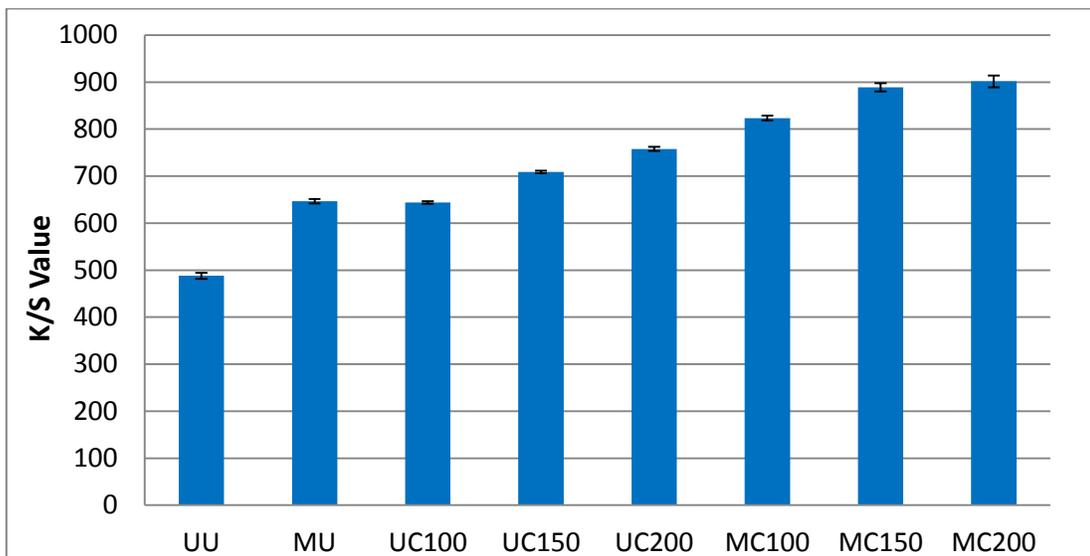


Figure 17. K/S Values of Dyed Samples

The results also show that both mercerization and cationization increase the K/S values of the samples as a function of the concentration of CR2000. However, the differences between MC150 and MC200 are small.

To better evaluate the effects of mercerization and cationization in dyeing properties, the dye uptake values of the two batches of samples were calculated by measuring the absorbance values at wavelength of maximum absorption ( $\lambda_{\max}$ ) of the dye bath solutions before and after dyeing. The uptake method is described in Section 3.7 (page 31). Table 11 and Figure 15 show the dye uptake values of all samples. The differences between dye uptake values of the duplicate samples are indicated by the error bars.

**Table 11. Dye Uptake of the Samples**

Sample	Dye Uptake (%)	
	Batch 1	Batch 2
UU	79.4	80.4
MU	84.3	83.7
UC 100	94.5	94.3
UC 150	97.5	97.3
UC 200	98.5	98.6
MC 100	97.8	98.3
MC 150	99.1	99.5
MC 200	99.3	99.6

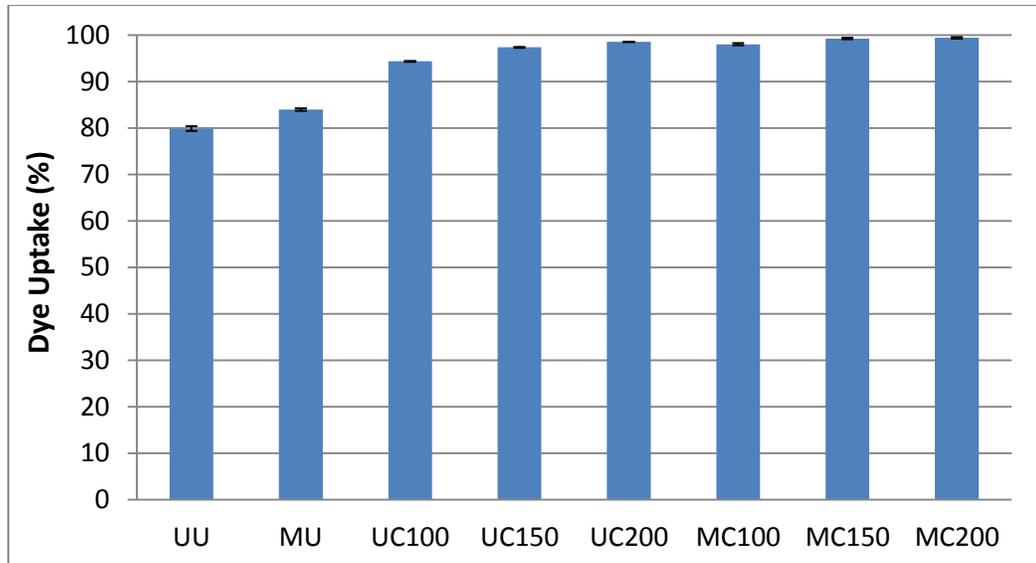


Figure 18. Dye Uptake of the Samples

The results show that both mercerization and cationization increase the dye uptake of the samples. The effect of cationization in increasing the dye uptake is much stronger than mercerization. However, the  $L^*$  and  $K/S$  values of MU and UC100 are similar, which indicates that mercerization and the cationization with 100 g/L CR2000 have similar effects in increasing the depth of shade. Nevertheless, the much higher dye exhaustion means that substantially less dye would be released as effluent. Dyeing with 6% owf Remazol Black B and higher than 95% dye exhaustion constitutes a substantial advance in reducing the environmental impact of dyeing black shades on cotton.

As can be speculated, the effect of cationization in increasing the depth of dyed sample is mostly achieved by attracting and fixing more dye molecules. Different from cationization, mercerization not only increases dye absorption, it also changes the shape of the fibers, thus

decreasing the light scattering on the surface and inside the fiber. So even with the same amount of dyes, the perceived color of mercerized samples is deeper. This can be also been proved by the fact that dye uptake values of unmercerized-cationized samples and mercerized-cationized samples are very close but the color of the dyed mercerized-cationized samples are much deeper. Since the effect of increasing color depth by mercerization is not just result from increasing the dye uptake, it is likely necessary to use both mercerization and cationization to obtain ultra-deep dyeings even though the dye uptake values of unmercerized-cationized samples are higher than 95%.

Based on previous results, both mercerization and cationization have been proved to be effective in increasing the depth of dyed color. But the principles of the two treatments in increasing the color depth are different. For mercerization, the effects result from both the increase of dye uptake and the change of fiber shape. For cationization, the increase of color depth is likely only achieved from the increase of dye uptake as a function of the cationization degree. However, the data show that there is a saturation point at high concentrations of cationization solution.

#### **4.1.3 The Effect of Mercerization and Cationization on Colorfastness**

Previous results show that both mercerization and cationization increase the color depth of dyed cotton fabric. The colorfastness of the samples is also a critical variable that determines whether those deep dyed samples are commercially viable. The colorfastness properties which need to be examined include wash fastness, rub fastness and light fastness.

#### 4.1.3.1 Colorfastness to Laundering

Colorfastness to laundering of the samples were measured following AATCC Test Method 61. The specific method used for testing the wash fastness was described in Section 3.8.1 (page 32). For each dyed sample, three samples were measured and the average values are summarized in Table 12. Table 12 just lists the staining on cotton strip since staining on other components in multi-fiber test fabric are similar as on cotton.

**Table 12. Colorfastness to Laundering**

<b>Sample</b>	<b>Color Change</b>	<b>Staining on Adjacent Cotton</b>
UU	4.5	$4 \pm 0.0$
MU	5	$4.3 \pm 0.2$
UC 100	5	$4.5 \pm 0.0$
UC 150	5	$4.5 \pm 0.0$
UC 200	5	$4.5 \pm 0.0$
MC 100	5	$4.5 \pm 0.0$
MC 150	5	$4.5 \pm 0.0$
MC 200	5	$4.7 \pm 0.2$

The results show that all the samples have good wash fastness and staining properties. However, cationization improved the laundering performance. Compared with unmercerized samples, the mercerized samples exhibited improved wash fastness. Hence, for the current method employed, mercerization and cationization have been proved to be effective in improving both dyeability, wash fastness, and staining of the dyed cotton samples.

#### 4.1.3.2 Colorfastness to Crocking

Both dry and wet crocking fastness properties of the dyed samples were tested using AATCC Test Method 8. The specific method used for testing the crockfastness is described in Section 3.8.2 (page 33). For each dyed sample, three samples were measured and the average values are summarized in Table 13.

**Table 13. Colorfastness to Crocking**

<b>Sample</b>	<b>Dry Crocking</b>	<b>Wet Crocking</b>
UU	$4.8 \pm 0.2$	$3.5 \pm 0.0$
MU	$5 \pm 0.0$	$3.5 \pm 0.0$
UC 100	$5 \pm 0.0$	$3.5 \pm 0.0$
UC 150	$5 \pm 0.0$	$3.5 \pm 0.0$
UC 200	$5 \pm 0.0$	$3.5 \pm 0.0$
MC 100	$5 \pm 0.0$	$3.2 \pm 0.2$
MC 150	$4.8 \pm 0.2$	$3.2 \pm 0.2$
MC 200	$4.8 \pm 0.2$	$3 \pm 0.0$

All the samples exhibited very good colorfastness to dry crocking. However, for the mercerized-cationized samples, the colorfastnesses to wet crocking of the treated samples were slightly lower than the untreated samples. It is important to note that the depth of dyeing and % exhaustion for the MC samples were higher than the untreated ones, so there was relatively higher amount of color transferred from the testing fabric during rubbing. Nevertheless, the rub fastness properties of all the samples are high for dry and acceptable for wet crocking.

#### 4.1.3.3 Colorfastness to Light

Colorfastness to light of the samples were tested by measuring the color change after 20 and 40 continuous light-on operating hours. The specific method for testing is described in Section 3.8.3 (page 34) and the results are summarized in Table 14 and Figure 16.

**Table 14. Colorfastness to Light**

Sample	Color Change	
	20h	40h
UU	4	3
MU	4	4
UC 100	3.5	3
UC 150	3.5	3
UC 200	3.5	2.5
MC 100	4	4
MC 150	4	3.5
MC 200	4	4

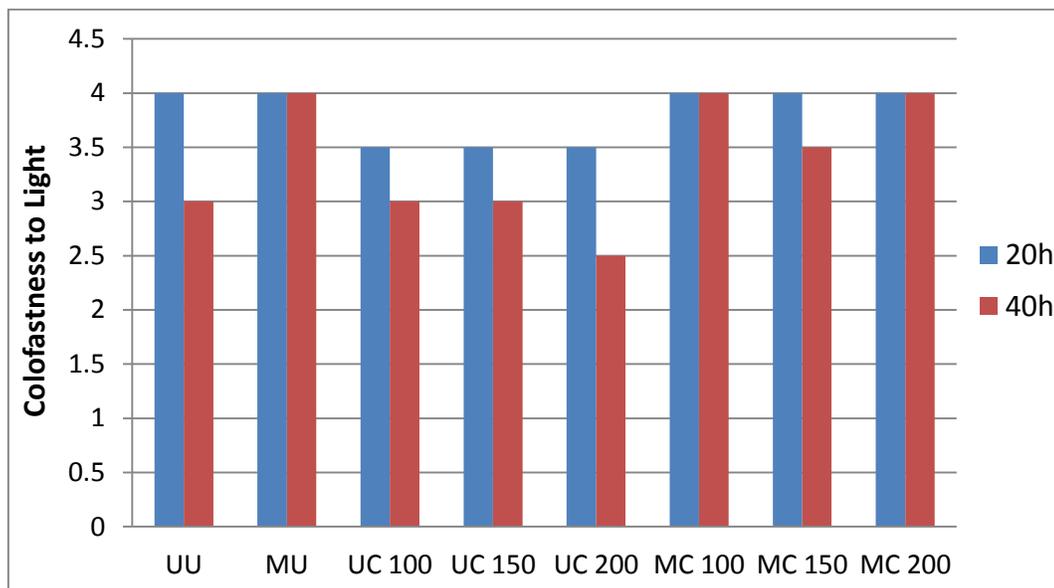


Figure 19. Colorfastness to Light

The data show that mercerization improves light fastness properties, whereas cationization is deleterious to photo stability. Cationic groups are probably removed for leading to reduced lightfastness, but this phenomenon appears to be mitigated by the mercerization process in the case of C.I. Reactive Black 5. Further work is warranted to elucidate the mechanism and to determine if this is generally applicable to fiber-reactive and other dye classes.

Previous results shown that cationization helps to improve colorfastness to laundering but has negative effect on colorfastness to wet crocking and light. Mercerization improves light fastness but it has a negative effect on the fastness to wet crocking, although the process does not appear to negatively affect colorfastness to laundering much. Moreover, the colorfastness to dry crocking is at the highest level in all of the samples.

In conclusion, except for colorfastness to wet crocking, all other colorfastness properties of the mercerized-cationized samples are good to excellent. Even for wet crock fastness, the mercerized-cationized samples are acceptable for most commercial applications, although further work is warranted to improve wet crocking.

#### **4.1.4 The Effects on Physical Properties**

In addition to dyeing performance and colorfastness, commercial viability is also dependent on physical properties of the treated samples. The physical properties measured in this work include peak load and elongation of the yarns and fabric pilling resistance.

#### 4.1.4.1 The Mechanical Properties of Yarns

Peak load and elongation at peak load of the both warp and filling yarns of all samples were measured using MTS Q-Test/5 Universal Testing Machine. The specific method and conditions used for the test are described in Section 3.9 (page 34). The average values of the test results are summarized in Table 15. Peak load and elongation at peak load of the samples are shown in Figure 17 and Figure 18 respectively.

**Table 15. Peak Load and Elongation of the Yarns**

Sample	Peak Load (gf)		Elongation at Peak Load (mm)	
	Warp	Filling	Warp	Filling
UU	262.9±17.6	171.2±13.5	13.8±1.1	32.5±4.2
UC 100	260.0±16.4	170.2±15.2	15.1±1.5	33.9±1.2
UC 150	265.8±19.8	173.4±18.5	14.3±1.4	32.7±3.8
UC 200	270.5±18.3	174.2±19.4	12.8±0.9	31.9±2.7
MU	312.2±13.1	186.4±12.5	12.0±0.9	33.3±7.4
MC 100	307.8±19.5	188.2±15.4	15.2±0.8	36.5±7.3
MC 150	315.6±25.8	182.9±13.1	12.6±1.3	34.4±7.9
MC 200	301.9±22.9	183.7±20.5	14.6±1.1	36.1±6.3

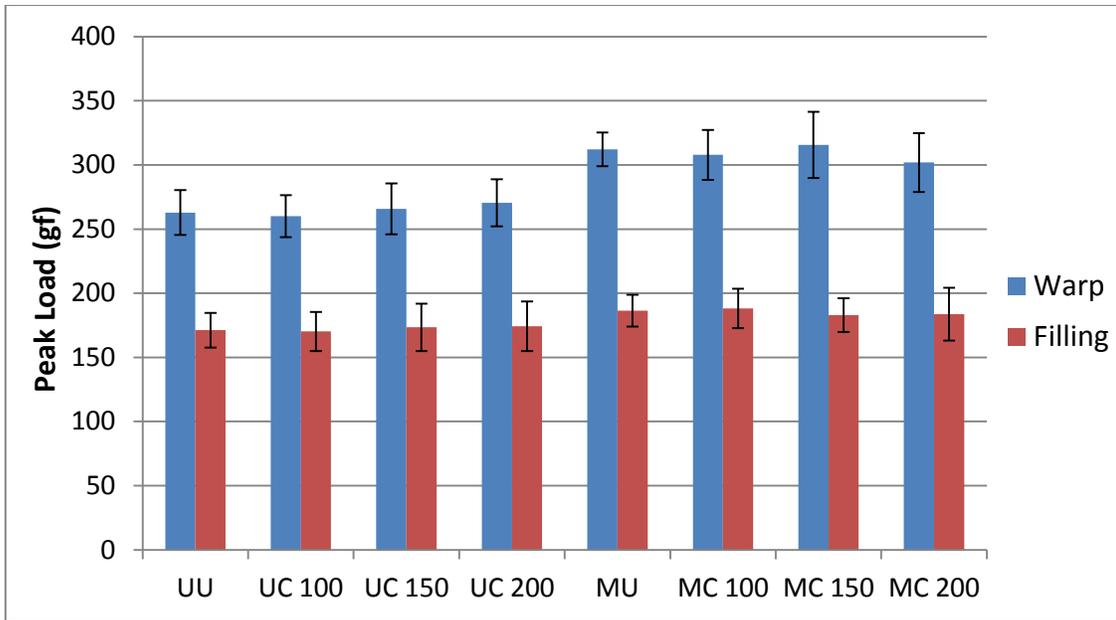


Figure 20. Peak Load of Yarns

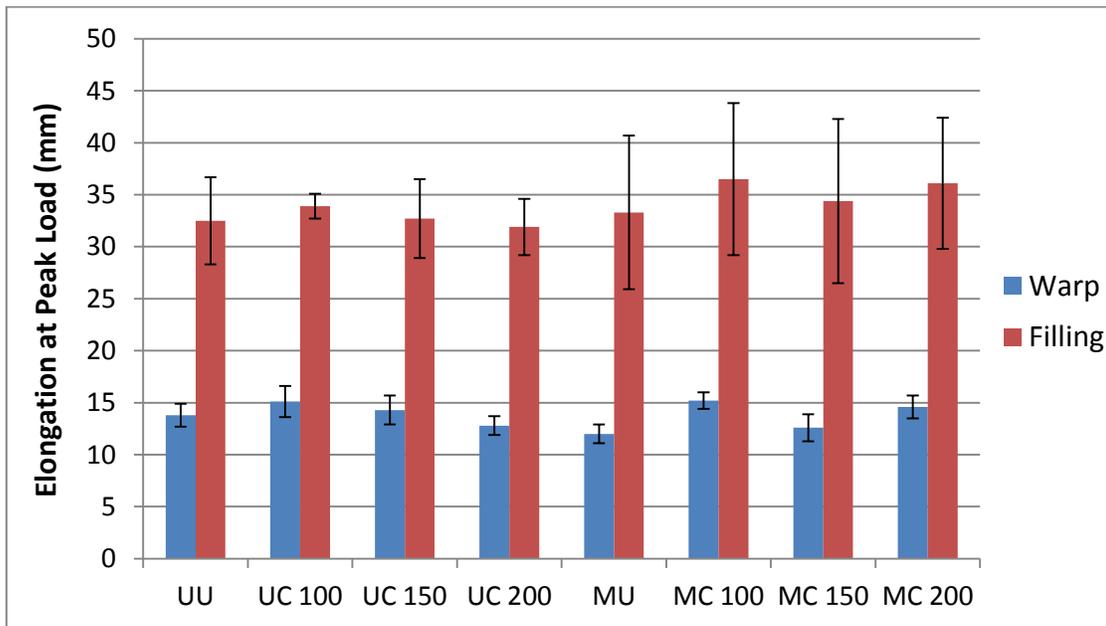


Figure 21. Elongation at Peak Load

From the peak load values of the yarns, it is clear that cationization did not influence the strength of the yarns significantly, but mercerization increased yarn strength, especially the warp yarns. Also, based on the elongation at peak load of the yarns, it is clear that neither cationization nor mercerization have a deleterious effect on elongation.

#### 4.1.4.2 Pilling Resistance of Fabrics

Pilling resistances of the samples were measured in duplicate by using a standard AATCC random tumble pilling method. The specific method is described in Section 3.10 (page 35).

The average results are summarized in Table 16.

**Table 16. Pilling Resistance of the Fabrics**

Sample	Pilling Resistance	
	1	2
UU	5	5
MU	5	5
UC 100	5	5
UC 150	5	5
UC 200	5	5
MC 100	5	5
MC 150	5	5
MC 200	5	5

The results show that all the samples exhibit excellent pilling resistance, indicating that cationization and mercerization treatment did not influence the pilling resistance of fabrics in the construction used for this work.

In conclusion, for the experiments conducted using C.I. Reactive Black 5 only:

- The lightness and K/S values of the samples show that both mercerization and cationization substantially increased the depth of shade.
- Cationization was especially effective in increasing the dye uptake.
- Dyeing performance of the fabrics was also improved as a function of CHPTAC concentration.
- Mercerized-cationized fabrics exhibited better colorfastness than untreated cotton fabrics, except for wet rub fastness.
- Cationization did not negatively affect the mechanical properties of the yarns and pilling resistance of the fabrics.
- Except for increasing the peak load of the yarns, mercerization did not influence other tested mechanical properties of the samples.

Even though the mercerized-cationized samples produced a very deep shade,  $a^*$   $b^*$   $C^*$   $h^\circ$  values and visual assessment of the samples show that the samples are all deep blue shades. As the goal of our project is to obtain black shades, further experiments were designed to obtain ultra-deep black shades on cotton.

## **4.2 Color Modification to Produce Ultra-Deep Black Shades**

### **4.2.1 Binary Dyeing Recipes**

Since the color of mercerized-cationized samples dyed with 6% owf Remazol Black B (C.I. Reactive Black 5) were in deep blue shades, different concentration of Remazol Yellow RR

were added to reduce the blueness of the dyed samples. The pretreated fabric selected was MC100, which was mercerized and cationized with 100 g/L CR2000. Different concentrations of Remazol Yellow RR were used, while all other variables in the dyeing recipe and dyeing method for MC 100 were constant. The L\* a\* b\* C\* h ° values of MC100 samples are summarized in Table 17 and Figure 19, which is an a\* b\* diagram and L\* scale showing the locations for each sample. In the figure, the coordinate axis on the left is for a\* b\* values and the one on the right is for L\* values.

**Table 17. L\* a\* b\* C\* h ° Values of MC100 Samples**

<b>Concentration of Yellow RR (owf)</b>	<b>L*</b>	<b>a*</b>	<b>b*</b>	<b>C*</b>	<b>h °</b>	<b>K/S Value</b>
0%	14.33	1.09	-6.08	6.18	280.2	823.5
0.5%	14.23	0.18	-3.75	3.75	272.8	853.2
1%	14.31	-0.19	-2.71	2.72	266.1	860.6
1.5%	14.16	-0.40	-1.54	1.59	255.6	877.8
2%	14.12	-0.48	-0.88	1.00	241.1	882.5
2.5%	14.34	-0.57	-0.32	0.65	209.4	876.7

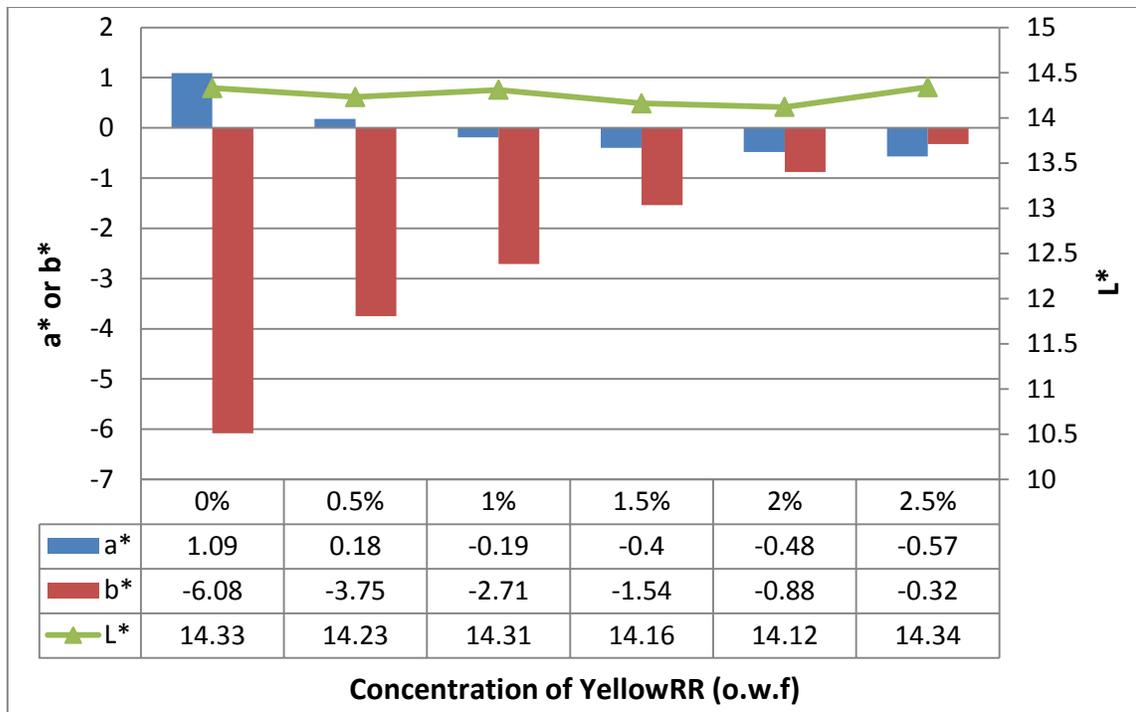


Figure 22.  $a^*$   $b^*$  and  $L^*$  values of MC100 Samples Dyed with 6% Remazol Black B and Different Concentrations of Yellow RR

From Figure 19, it's clear that by adding more Remazol Yellow RR, the  $a^*$  value decreased from 1.09 to -0.57 and the  $b^*$  value increased from -6.08 to -0.32.  $C^*$  values in Table 17 show that with the increase of concentration of Remazol Yellow RR, chroma decreased.  $C^*$  values of the samples dyed with 2% and 2.5% were close to zero and visual assessment of those samples indicated an excellent deep black hue. If the concentration of Remazol Yellow RR was increased to higher than 2.5%, the  $C^*$  value may increase further, since the  $a^*$  value would keep decreasing. Also, the K/S value increased as a function of concentration of Remazol Yellow RR, except for the 2.5% owf sample possibly because that the total concentration of the dyes for the sample is past saturation. Based on the results, both 2% and

2.5% o.w.f of Remazol Yellow RR were chosen to be applied to other mercerized-cationized samples to evaluate their dyeing performance and wash fastness properties.

#### 4.2.2 Dyeing Performance of MC Samples with Two-Dye Combination

Based on the results of MC100 samples, MC150 and MC200 samples were also dyed by adding 2% and 2.5% owf Remazol Yellow RR to the 6% Remazol Black B (C.I. Reactive Black 5) recipe. Since the total concentration of dyes could be beyond the saturation point, the mercerized-cationized samples were also dyed with 5% Remazol Black B plus 2% Remazol Yellow RR. The concentration of Na<sub>2</sub>CO<sub>3</sub> added and the dyeing procedure for cationized cotton fabrics were kept the same. L\* a\* b\* C\* h° values of all the samples were measured and are summarized in Table 18.

**Table 18. L\* a\* b\* C\* h° Values of MC Samples Dyed with Different Concentrations of Mixed Dyes**

Sample	Concentration of Dyes (owf)		L*	a*	b*	C*	h°
	Black B	Yellow RR					
MC100	5%	2%	14.75	-0.79	-0.96	1.24	230.6
	6%	2%	14.12	-0.48	-0.88	1.00	241.1
	6%	2.5%	14.34	-0.57	-0.32	0.65	209.4
MC150	5%	2%	14.42	-0.51	0.11	0.52	168.2
	6%	2%	14.09	-0.36	-0.15	0.40	202.8
	6%	2.5%	14.11	-0.36	0.06	0.37	170.7
MC200	5%	2%	14.27	-0.45	0.11	0.46	166.5
	6%	2%	14.04	-0.13	-0.10	0.23	205.9
	6%	2.5%	13.97	-0.13	0.12	0.18	139.0

The L\* and C\* values of the samples show that all dyed samples are in deep neutral black shade range, especially the MC150 and MC200 samples. Even though the samples dyed with 5% Black B plus 2% Yellow RR are slightly lighter than those samples dyed with 6% Black B plus 2% or 2.5% Yellow RR, the differences are small and the samples visually appear almost the same. To better compare the color depth of the dyed samples, K/S values of all the samples were measured and are summarized in Table 19 and Figure 20, which shows a bar chart of K/S values.

**Table 19. K/S values of MC Samples MC Samples Dyed with Different Concentrations of Mixed Dyes**

Sample	Concentration of Dyes (owf)		K/S Value
	Black B	Yellow RR	
MC100	5%	2%	812.1 ± 4.7
	6%	2%	882.5 ± 8.5
	6%	2.5%	876.7 ± 7.1
MC150	5%	2%	841.1 ± 5.4
	6%	2%	901.5 ± 3.9
	6%	2.5%	906.9 ± 6.7
MC200	5%	2%	854.5 ± 6.8
	6%	2%	915.4 ± 9.8
	6%	2.5%	947.3 ± 5.9

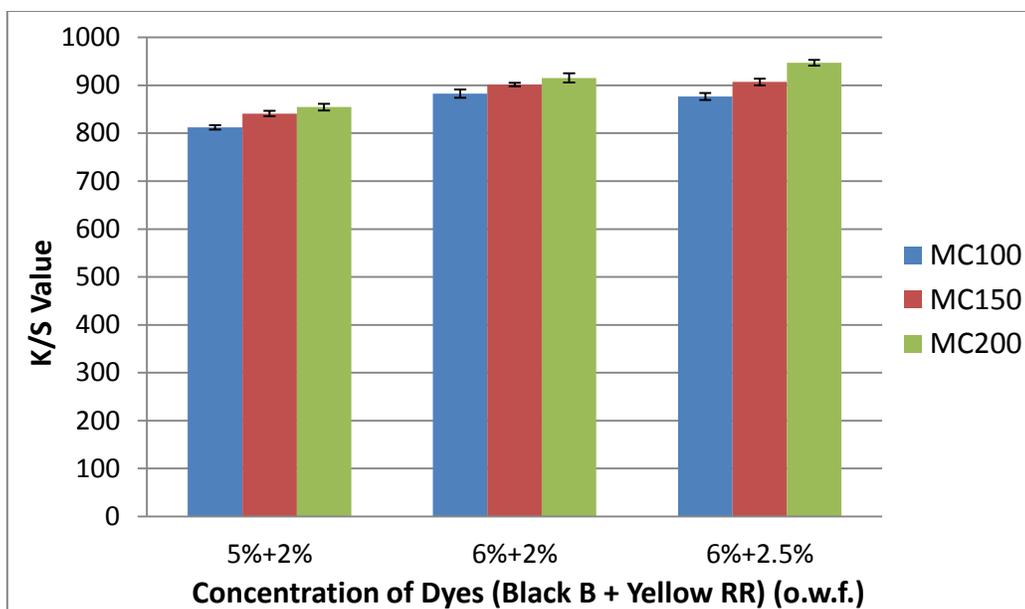


Figure 23. K/S Values of MC Samples MC Samples Dyed with Different Concentrations of Mixed Dyes

The K/S values also show that the shades of these samples are all very deep especially the MC200 samples dyed with 6% Black B plus 2.5% Yellow RR. Increasing the concentration of Remazol Black B from 5% to 6% increased the K/S values of all three kinds of samples, MC100, MC150 and MC200. At 6% owf for Black B, increasing the concentration of Yellow RR from 2% to 2.5%, the changes in K/S values of the three kinds of samples produced different effects.

For the MC100 sample, an increase in the amount of Yellow RR from 2 to 2.5% slightly decreased the K/S value. This is because the degree of cationization of MC100 is relatively low and it is possible that the MC100 fabrics were beyond the saturation point. In this scenario, the extra Yellow RR added competes with Remazol Black B for the limited reaction

sites on cotton fabric. However, for the MC150 and MC200 samples, increase in the concentration of Yellow RR from 2 to 2.5% increased the K/S values of dyed fabrics. The increase in K/S values of MC200 was more significant, since it has been shown to have higher cationization degree and could therefore absorb more dye.

To examine whether the concentration of dyes was beyond the saturation point, uptake of the samples were measured. Table 20 and Figure 21 show the dye uptake values of all the MC samples as a function of dye concentration.

**Table 20. Dye Uptake of MC Samples MC Samples Dyed with Different Concentrations of Mixed Dyes**

Sample	Concentration of Dyes (owf)		Dye Uptake (%)
	Black B	Yellow RR	
MC100	5%	2%	94.5
	6%	2%	94.4
	6%	2.5%	93.0
MC150	5%	2%	97.7
	6%	2%	97.6
	6%	2.5%	96.4
MC200	5%	2%	98.8
	6%	2%	98.4
	6%	2.5%	97.8

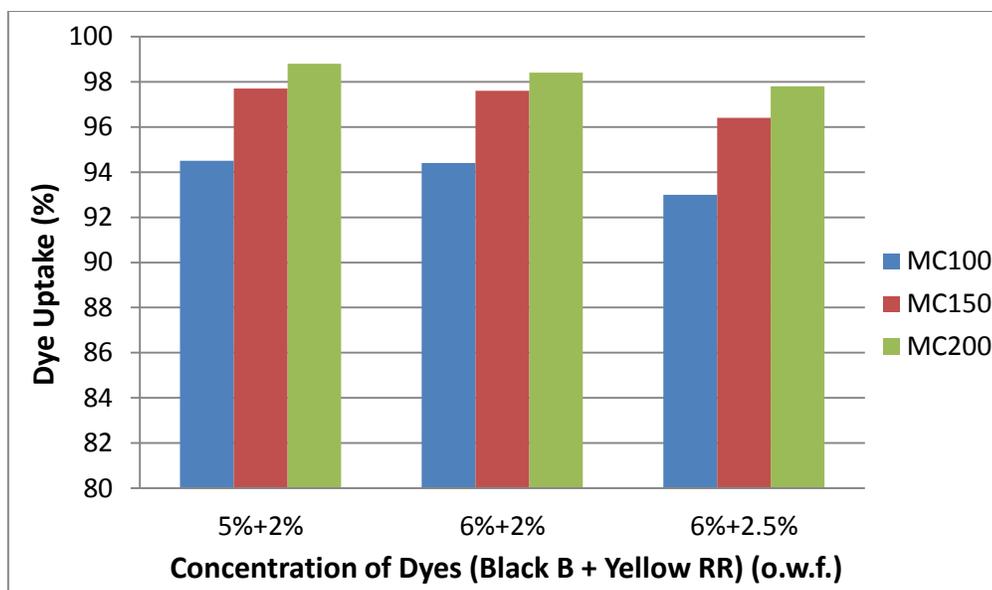


Figure 24. Dye Uptake of MC Samples MC Samples Dyed with Different Concentrations of Mixed Dyes

The trend of dye uptake values agrees with previous results that an increase in the concentration of CHPTAC increases the dye uptake. The figure also shows that increasing the concentration of Remazol Black B from 5% to 6% hardly decreased the dye uptake values. However, by further increasing the concentration of Yellow RR from 2% to 2.5%, the dye uptake values of all the samples decreased. Thus, to maintain relative high dye uptake values, MC150 or MC200 samples should be used. Also, the concentrations of dyes used should not be higher than 6% Black B plus 2% Yellow RR using the pretreatment and dyeing method described in this work.

In previous experiments, all mercerized-cationized samples dyed with modified dyeing recipe have deep neutral black shades especially those MC150 and MC200 samples.

Lowering the concentration of Black B from 6% to 5% is not effective in increasing the dye uptakes of the samples and decreased the depth of dyed color slightly (although visual differences were very small). Based on the depth of shade and dye uptake values of the samples, the MC150 and MC200 samples dyed with 6% Black B and 2% Yellow RR appear to exhibit best dyeing performances. Considering the cost of dyeing, the MC150 samples dyed with 6% Black plus 2% Yellow RR would likely be the best choice. However, if extremely deep black shades are required, the MC200 sample dyed with 6% Remazol Black B plus 2.5% Yellow RR could be used.

#### **4.2.3 Colorfastness of MC Samples**

Fastness properties including wash fastness, rub fastness and light fastness of the samples were measured using the same method as the previously reported experiments.

##### **4.2.3.1 Colorfastness to Laundering**

The colorfastness to laundering of each kind of samples were measured three times and the average values are summarized in Table 21. Table 21 just lists the staining on cotton strip since all stainings on other components in multi-fiber test fabric are similar as on cotton.

**Table 21. Colorfastness to Laundering of MC Samples Dyed with Different Concentrations of Mixed Dyes**

Sample	Concentration of Dyes (owf)		Color Change	Staining on Adjacent Cotton
	Black B	Yellow RR		
MC100	5%	2%	5 ± 0.0	4.7 ± 0.2
	6%	2%	5 ± 0.0	4.5 ± 0.0
	6%	2.5%	5 ± 0.0	4.5 ± 0.0
MC150	5%	2%	5 ± 0.0	4.5 ± 0.0
	6%	2%	5 ± 0.0	4.5 ± 0.0
	6%	2.5%	5 ± 0.0	4.5 ± 0.0
MC200	5%	2%	5 ± 0.0	4.7 ± 0.2
	6%	2%	5 ± 0.0	4.5 ± 0.0
	6%	2.5%	5 ± 0.0	4.5 ± 0.0

The results demonstrate that colorfastness to laundering of mercerized-cationized samples are as good as the samples dyed with 6% Remazol Black B only.

#### 4.2.3.2 Colorfastness to Crocking

Colorfastness to dry crocking and wet crocking of each of the dyed samples were measured three times and the average values are summarized in Table 22.

**Table 22. Colorfastness to Crocking of MC Samples Dyed with Different Concentrations of Mixed Dyes**

Sample	Concentration of Dyes (owf)		Dry Crocking	Wet Crocking
	Black B	Yellow RR		
MC100	5%	2%	5 ± 0.0	3.5 ± 0.0
	6%	2%	5 ± 0.0	3.3 ± 0.2
	6%	2.5%	4.7 ± 0.2	3.2 ± 0.2
MC150	5%	2%	5 ± 0.0	3.5 ± 0.0
	6%	2%	4.8 ± 0.2	3.5 ± 0.0
	6%	2.5%	4.7 ± 0.2	3.2 ± 0.2
MC200	5%	2%	5 ± 0.0	3.2 ± 0.2
	6%	2%	4.8 ± 0.2	3 ± 0.0
	6%	2.5%	4.8 ± 0.2	3 ± 0.0

The results show that both colorfastness to dry and wet crocking of the samples are similar to the equivalent sample dyed with 6% Remazol Black B only. Colorfastness to wet crocking of MC200 samples dyed with 6% Remazol Black B and different concentrations of Yellow RR are slightly worse than the other samples, possibly because these samples are in deeper shades with higher concentration of dye on the fiber, leading to higher dye transfer. These data agree with the previous results, reported in Section 4.1.3.2 (page 45)

#### 4.2.3.3 Colorfastness to Light

The light fastness of the samples was measured using the same method as described previously and the results are summarized in Table 23.

**Table 23. Colorfastness to Light of MC Samples Dyed with Different Concentrations of Mixed Dyes**

Sample	Concentration of Dyes (owf)		Color Change	
	Black B	Yellow RR	20 h	40 h
MC100	5%	2%	4	3.5
	6%	2%	4	3.5
	6%	2.5%	4	3.5
MC150	5%	2%	4	3.5
	6%	2%	4	3.5
	6%	2.5%	4	3.5
MC200	5%	2%	4	3.5
	6%	2%	4	3.5
	6%	2.5%	4	3.5

Results show that colorfastness to light of all the samples are the same regardless of concentration. By comparing with previous results, it has been proved that adding Yellow RR in dyeing did not influence the light fastness much compared to dyeings using Remazol Black B (C.I. Reactive Black 5) only. The light fastness of the samples is satisfactory for most commercial apparel applications.

Results from Section 4.2.2 showed that for mercerized-cationized cotton fabrics, especially MC150 and MC200, either adding 2% or 2.5% Remazol Yellow RR produced deep neutral black shades. Lowering the concentration of dyes to 5% Remazol Black B plus 2% Yellow RR decreased the depth of shade and was not very effective in increasing the dye uptake of the samples. Considering the colorimetric data, dye uptake and cost, the MC150 samples dyed with 6% Black B plus 2% Yellow RR appears to be the optimum method. The

colorfastness of the samples dyed with both Remazol black B and Yellow RR are as good as the samples dyed with Remazol Black B alone.

### **4.3 The Effects of Na<sub>2</sub>CO<sub>3</sub> on Dyeing with Remazol Black B**

As has been proved by previous results, deep black shade with very high dye uptake can be obtained by dyeing mercerized-cationized cotton fabrics without Na<sub>2</sub>SO<sub>4</sub>. This is a significant reduction in the environmental impact of the dyeing process. In previous experiments, the dyeing recipe of the mercerized-cationized samples includes 20 g/L Na<sub>2</sub>CO<sub>3</sub> which is commonly required for the fiber-reactive dyeing of untreated cotton. However, the amount of Na<sub>2</sub>CO<sub>3</sub> needed in dyeing mercerized-cationized cotton fabrics could be reduced. Based on this idea, MC150 and MC200 samples were dyed with 6% Remazol Black B and different concentrations of Na<sub>2</sub>CO<sub>3</sub>, from 0 to 20 g/L. The reason for choosing MC150 and MC200 is that the depths of shade were much better than the MC100 samples. Also, untreated samples were dyed with 6% Remazol Black B with different concentrations of Na<sub>2</sub>CO<sub>3</sub> as a control.

#### **4.3.1 The Effects of Na<sub>2</sub>CO<sub>3</sub> on Dyeing Performance**

The dyeing methods were the same as previous experiments. Average values of L\* a\* b\* C\* h ° of the samples dyed with different concentrations of Na<sub>2</sub>CO<sub>3</sub> are summarized in Table 24.

**Table 24. L\* a\* b\* C\* h ° Values of Samples Dyed with Different Concentrations of Na<sub>2</sub>CO<sub>3</sub>**

Sample	Concentration of Na <sub>2</sub> CO <sub>3</sub> (g/L)	L*	a*	b*	C*	h °
UU	0	67.29	-5.67	-11.24	12.58	243.24
	5	20.67	-2.48	-11.70	11.96	258.04
	10	20.15	-2.00	-11.24	11.42	259.90
	15	19.84	-1.79	-11.01	11.15	260.79
	20	19.72	-1.71	-10.99	11.13	261.16
MC150	0	14.34	0.98	-5.66	5.74	279.8
	5	13.64	1.01	-4.84	4.95	281.8
	10	13.65	1.08	-5.24	5.35	281.7
	15	13.74	1.32	-4.79	4.97	285.4
	20	13.80	1.14	-5.63	5.75	281.4
MC200	0	14.07	1.22	-4.14	4.31	286.5
	5	13.51	1.34	-4.22	4.42	287.6
	10	13.63	1.47	-5.10	5.31	286.0
	15	13.66	1.39	-4.31	4.53	287.9
	20	13.72	1.40	-4.86	5.06	286.1

Based on the data in Table 24, for the untreated control cotton samples, the lightness of the samples dyed without Na<sub>2</sub>CO<sub>3</sub> were much higher than those dyed with Na<sub>2</sub>CO<sub>3</sub>. As expected, increasing the concentration of Na<sub>2</sub>CO<sub>3</sub> decreased the lightness due to fixation increase in the dye exhausted onto the fiber.

For the mercerized-cationized cotton samples, the lightness of the samples dyed without Na<sub>2</sub>CO<sub>3</sub> were also lighter than those with Na<sub>2</sub>CO<sub>3</sub> added. The interesting point is that

lightness of both MC150 and MC200 samples increased while increasing the concentration of  $\text{Na}_2\text{CO}_3$  from 5 g/L to 20 g/L. This trend shows for mercerized-cationized cotton fabrics, only low concentration of  $\text{Na}_2\text{CO}_3$  are required to obtain deep dyeings possibly because the cationization contributes to significant fixation of the negatively charged dye, via electrostatic attraction. However, increasing the concentration of  $\text{Na}_2\text{CO}_3$  exhibited a negative effect in dyeing performance of mercerized-cationized samples.

The K/S values of the samples were measured and are summarized in Table 25 and Figure 22.

**Table 25. K/S Values of Samples Dyed with Different Concentrations of  $\text{Na}_2\text{CO}_3$**

Sample	Concentration of $\text{Na}_2\text{CO}_3$ (g/L)	K/S Value
UU	0	$15.9 \pm 0.7$
	5	$447.1 \pm 5.8$
	10	$464.7 \pm 6.2$
	15	$475.7 \pm 4.1$
	20	$484.6 \pm 7.5$
MC150	0	$798.6 \pm 8.2$
	5	$923.4 \pm 5.1$
	10	$916.9 \pm 3.7$
	15	$905.6 \pm 4.5$
	20	$893.1 \pm 4.6$
MC200	0	$830.0 \pm 3.9$
	5	$934.5 \pm 6.2$
	10	$919.0 \pm 5.5$
	15	$914.8 \pm 4.9$
	20	$907.7 \pm 7.0$

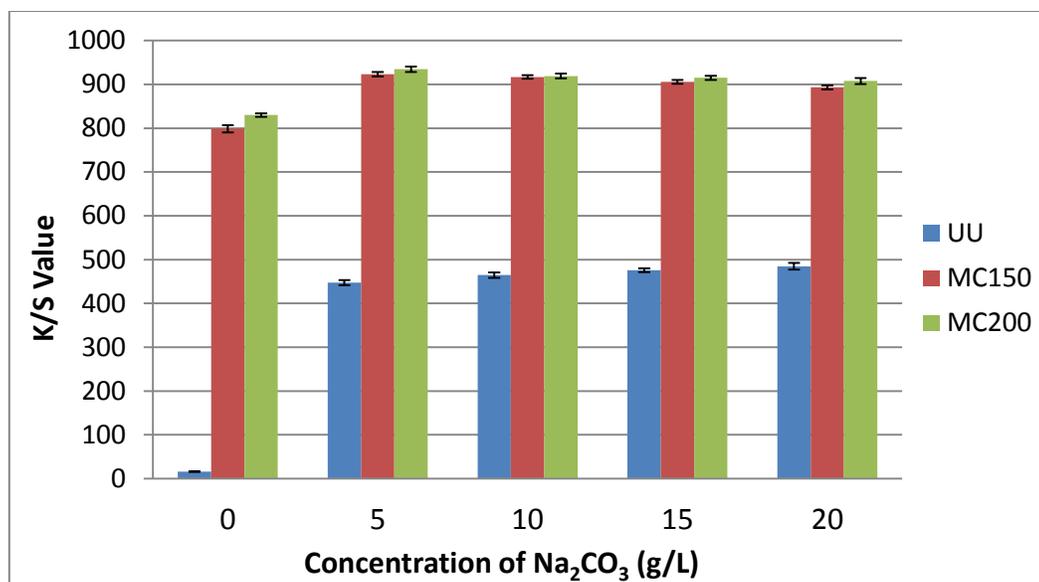


Figure 25. K/S Values of Samples Dyed with Different Concentrations of Na<sub>2</sub>CO<sub>3</sub>

For the untreated cotton samples, the K/S value of the sample dyed without Na<sub>2</sub>CO<sub>3</sub> is close to zero. K/S values of the dyed samples increased as a function of Na<sub>2</sub>CO<sub>3</sub> concentration, due to the requirement for alkali fixation in the PH range 10.5-12.0 to ensure adequate dyeing performances.

For the mercerized-cationized cotton samples, the K/S values of the samples dyed without Na<sub>2</sub>CO<sub>3</sub> were the lowest. Increasing the concentration of Na<sub>2</sub>CO<sub>3</sub> from 5 g/L to 20 g/L did not have significant influence on the K/S values of mercerized-cationized samples. Hence, 5 g/L Na<sub>2</sub>CO<sub>3</sub> appears to be the optimum concentration for dyeing mercerized-cationized cotton fabrics.

To further demonstrate the effects of Na<sub>2</sub>CO<sub>3</sub> on dyeing, the dye uptake of all the samples

were measured. The results, which show the same trend as for the K/S measurements, are presented in Table 26 and Figure 23.

**Table 26. Dye Uptake of Samples Dyed with Different Concentrations of Na<sub>2</sub>CO<sub>3</sub>**

<b>Sample</b>	<b>Concentration of Na<sub>2</sub>CO<sub>3</sub> (g/L)</b>	<b>Dye Uptake (%)</b>
UU	0	36.7
	5	78.1
	10	78.9
	15	79.4
	20	80.2
MC150	0	99.3
	5	99.7
	10	99.6
	15	99.5
	20	99.3
MC200	0	99.4
	5	99.8
	10	99.7
	15	99.6
	20	99.5

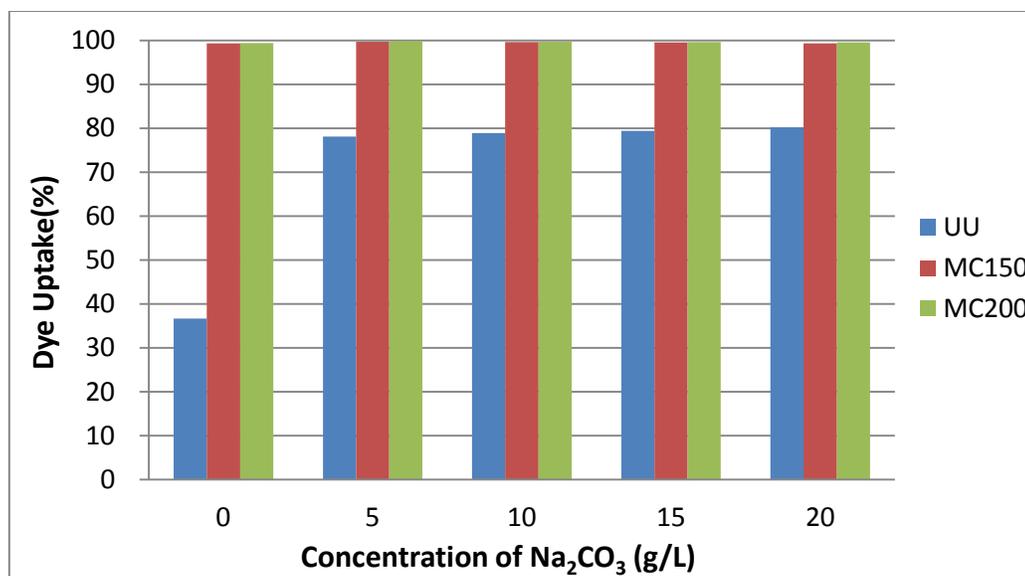


Figure 26. Dye Uptake of Samples Dyed with Different Concentrations of Na<sub>2</sub>CO<sub>3</sub>

The data show the same trends as for the K/S measurements. Based on previous results, it is clear that for both untreated and mercerized-cationized cotton fabrics, the dyeing performance of the samples dyed without Na<sub>2</sub>CO<sub>3</sub> are the worst. The depth of untreated samples increased as a function of Na<sub>2</sub>CO<sub>3</sub>. Thus, to obtain deep shades on untreated cotton fabrics, it is necessary to add 20 g/L Na<sub>2</sub>CO<sub>3</sub> while dyeing. However, for mercerized-cationized samples, 5 g/L appears to be the optimum concentration and further increasing the concentration of Na<sub>2</sub>CO<sub>3</sub> even slightly decreased the depth of shade. This finding, if viable commercially, would be an additional benefit in terms of reduced environmental impact of the dyeing process using mercerization and cationization as preparation procedure.

### 4.3.2 The Effects of Na<sub>2</sub>CO<sub>3</sub> on Colorfastness

The effects of Na<sub>2</sub>CO<sub>3</sub> on colorfastness properties were assessed by measuring colorfastness to laundering, crocking and light.

#### 4.3.2.1 Colorfastness to Laundering

Colorfastness to laundering of the samples dyed with different concentrations of Na<sub>2</sub>CO<sub>3</sub> was evaluated in triplicate. The average values are summarized in Table 27. Multi-fiber test fabric was used for testing but Table 27 just lists the staining on cotton strip.

**Table 27. Colorfastness to Laundering of Samples Dyed with Different Concentrations of Na<sub>2</sub>CO<sub>3</sub>**

<b>Sample</b>	<b>Concentration of Na<sub>2</sub>CO<sub>3</sub> (g/L)</b>	<b>Color Change</b>	<b>Staining on Adjacent Cotton</b>
UU	0	3.5 ± 0.0	4 ± 0.0
	5	4.5 ± 0.0	3.5 ± 0.0
	10	4.5 ± 0.0	4 ± 0.0
	15	4.5 ± 0.0	4 ± 0.0
	20	4.5 ± 0.0	4 ± 0.0
MC150	0	3.3 ± 0.2	3.2 ± 0.2
	5	5 ± 0.0	4.5 ± 0.0
	10	5 ± 0.0	4.5 ± 0.0
	15	5 ± 0.0	4.5 ± 0.0
	20	5 ± 0.0	4.5 ± 0.0
MC200	0	3.2 ± 0.2	3 ± 0.0
	5	5 ± 0.0	4.5 ± 0.0
	10	5 ± 0.0	4.5 ± 0.0
	15	5 ± 0.0	4.5 ± 0.0
	20	5 ± 0.0	4.5 ± 0.0

The results of color change show that both untreated and treated samples dyed without  $\text{Na}_2\text{CO}_3$  have poor colorfastness to laundering, as expected. The change of color significantly decreased as a function of  $\text{Na}_2\text{CO}_3$  being added. However, increase in concentration of  $\text{Na}_2\text{CO}_3$  from 5 g/L to 20 g/L produced identical results.

The staining results of mercerized-cationized samples also show that the samples dyed with 5 g/L  $\text{Na}_2\text{CO}_3$  exhibited low staining during laundering and further increase in the concentration of  $\text{Na}_2\text{CO}_3$  did not influence the depth of staining. However, the staining of untreated samples dyed with 5 g/L  $\text{Na}_2\text{CO}_3$  was worse than the sample dyed without  $\text{Na}_2\text{CO}_3$ , because the dye uptake on the untreated sample dyed without  $\text{Na}_2\text{CO}_3$  was very low and would not cause serious staining even though it has very poor colorfastness to laundering.

For untreated cotton fabrics, at least 10 g/L  $\text{Na}_2\text{CO}_3$  was required for adequate fastness. Even with high concentration of  $\text{Na}_2\text{CO}_3$ , colorfastness to laundering of untreated samples was poor-to-moderate. For the dyeing of mercerized-cationized cotton fabrics,  $\text{Na}_2\text{CO}_3$  was required to ensure good colorfastness to laundering. However, no more than 5 g/L  $\text{Na}_2\text{CO}_3$  was required since colorfastness to laundering of the samples was not further improved.

#### 4.3.2.2 Colorfastness to Crocking

Colorfastness to both dry and wet crocking of the samples was measured in triplicate using the same method as the previously reported experiments. The average values are summarized in Table 28.

**Table 28. Colorfastness to Crocking of Samples Dyed with Different Concentrations of Na<sub>2</sub>CO<sub>3</sub>**

Sample	Concentration of Na <sub>2</sub> CO <sub>3</sub> (g/L)	Dry Crocking	Wet Crocking
UU	0	5 ± 0.0	3.5 ± 0.0
	5	4.3 ± 0.2	3.5 ± 0.0
	10	4.5 ± 0.0	3.5 ± 0.0
	15	4.3 ± 0.2	3.5 ± 0.0
	20	4.5 ± 0.0	3.2 ± 0.2
MC150	0	4.3 ± 0.2	3.5 ± 0.0
	5	4.2 ± 0.2	3.5 ± 0.0
	10	4.2 ± 0.2	3.5 ± 0.0
	15	4.5 ± 0.0	3.5 ± 0.0
	20	4.5 ± 0.0	3.5 ± 0.0
MC200	0	4.5 ± 0.0	3.2 ± 0.2
	5	4.2 ± 0.2	3.5 ± 0.0
	10	4.5 ± 0.0	3.3 ± 0.2
	15	4.2 ± 0.2	3.5 ± 0.0
	20	4.5 ± 0.0	3.5 ± 0.0

For untreated samples, colorfastness to dry crocking of the sample dyed without Na<sub>2</sub>CO<sub>3</sub> was the best for the experiments conducted, probably because the color depth of the sample dyed without Na<sub>2</sub>CO<sub>3</sub> was much lighter than the other samples. Colorfastness to wet crocking of the untreated samples was in similar level while the one dyed with 20 g/L is slightly worse than others, probably because the shade of the sample dyed with 20 g/L Na<sub>2</sub>CO<sub>3</sub> was deeper than the others dyed with lower concentrations of Na<sub>2</sub>CO<sub>3</sub>.

For the mercerized-cationized samples, the colorfastness to dry crocking of all the samples were good-excellent. Also, colorfastness to wet crocking of all mercerized-cationized samples were similar. In conclusion, for mercerized-cationized cotton fabrics, the amount of  $\text{Na}_2\text{CO}_3$  added did not influence the colorfastness to both dry and wet crocking appreciably.

#### 4.3.2.3 Colorfastness to Light

Colorfastness to light was measured using the same method as the previously reported experiments and the results are summarized in Table 29.

**Table 29. Colorfastness to Light of Samples Dyed with Different Concentrations of  $\text{Na}_2\text{CO}_3$**

Sample	Concentration of $\text{Na}_2\text{CO}_3$ (g/L)	Color Change	
		20 h	40 h
UU	0	2.5	1.5
	5	4	3
	10	4	3.5
	15	4	3.5
	20	4	3.5
MC150	0	4	3
	5	4	3.5
	10	4	3.5
	15	4	3.5
	20	4	3.5
MC200	0	4	3
	5	4	3.5
	10	4	3.5
	15	4	3.5
	20	4	3.5

The results of the untreated samples show that color changes of the untreated samples dyed without  $\text{Na}_2\text{CO}_3$  are much more significant than others. Adding  $\text{Na}_2\text{CO}_3$  significantly improved the lightfastness for the untreated samples. Comparison between untreated samples dyed with different concentrations of  $\text{Na}_2\text{CO}_3$  show that increasing the concentration of  $\text{Na}_2\text{CO}_3$  from 5 g/L to 10 g/L improved the lightfastness for 40 hours exposure, but further increasing the concentration did not make any difference.

For the mercerized-cationized samples, color change of all samples after 20 hours exposure was good and was constant as a function of  $\text{Na}_2\text{CO}_3$  concentration. After 40 hours exposure, the color change of the samples dyed without  $\text{Na}_2\text{CO}_3$  were more significant than the samples dyed with  $\text{Na}_2\text{CO}_3$ . However, increasing the concentration of  $\text{Na}_2\text{CO}_3$  from 5 g/L to 20 g/L did not influence the lightfastness properties of mercerized-cationized samples.

In conclusion, as is well-known, untreated cotton fabrics cannot be dyed effectively without  $\text{Na}_2\text{CO}_3$ . The depth of dyed color and dye uptake value increases with the concentration of  $\text{Na}_2\text{CO}_3$ . If the amount of  $\text{Na}_2\text{CO}_3$  added is below 10g/L, colorfastness to laundering and light were poor. Thus, for the conventional dyeing of untreated cotton fabrics, adding 20 g/L  $\text{Na}_2\text{CO}_3$  is necessary for obtaining deep shades with relatively good colorfastness. For the dyeing of mercerized-cationized cotton fabrics, eliminating the use of  $\text{Na}_2\text{CO}_3$  has negative effects on colorfastness of the samples and may decrease the depth of dyed color. However, the concentration of  $\text{Na}_2\text{CO}_3$  needed for dyeing mercerized-cationized samples was found to be relatively low; the dyeing performance and colorfastness properties of the samples dyed

with 5 g/L  $\text{Na}_2\text{CO}_3$  were as good as those dyed with higher concentrations.

It should be noted that the data of the samples dyed with 20 g/L  $\text{Na}_2\text{CO}_3$  obtained in this section are different from those obtained in section 4.1. This is because the samples discussed here and those in previous section were cationized and dyed in different batches. Since both their dyeing performances and colorfastness properties are very close, good repeatability has been demonstrated.

#### **4.4 The Effects of $\text{Na}_2\text{CO}_3$ on Dyeing with Two-Dye Combination to Produce Ultra-Deep Neutral Black**

Previous results show that for dyeing of mercerized-cationized cotton fabrics, not only the use of salt can be eliminated but also the concentration of  $\text{Na}_2\text{CO}_3$  added can be reduced to 5g/L without negatively impacting the fastness properties. The results of both MC150 and MC200 show the trend that decreasing the concentration of  $\text{Na}_2\text{CO}_3$  from 20 g/L to 5 g/L did not influenced the color depth of the samples dyed with 6% Remazol Black B. This was be further examined by dyeing the treated samples with mixed dyes and different concentrations of  $\text{Na}_2\text{CO}_3$  to determine whether small amount of  $\text{Na}_2\text{CO}_3$  is enough for dyeing deep neutral black with good colorfastness.

Based on the results in section 4.2, this experiment used MC150 samples as substrate and 6% Remazol Black B plus 2% Yellow RR for dyeing and the experiments to investigate different concentrations of  $\text{Na}_2\text{CO}_3$ , from 0 to 20 g/L were repeated. All other factors were kept constant.

#### 4.4.1 The Effects of Na<sub>2</sub>CO<sub>3</sub> on Dyeing Performance

L\* a\* b\* C\* h ° values of MC150 samples dyed with different concentrations of Na<sub>2</sub>CO<sub>3</sub> are summarized in Table 30.

**Table 30. L\* a\* b\* C\* h ° Values of MC150 Samples Dyed with Different Concentrations of Na<sub>2</sub>CO<sub>3</sub>**

<b>Concentration of Na<sub>2</sub>CO<sub>3</sub> (g/L)</b>	<b>L*</b>	<b>a*</b>	<b>b*</b>	<b>C*</b>	<b>h °</b>
0	14.85	-0.78	-0.50	0.93	212.8
5	14.10	-0.40	-1.02	1.10	248.7
10	14.15	-0.21	-0.98	1.00	258.0
15	14.20	-0.33	-1.18	1.23	254.5
20	14.19	-0.17	-1.22	1.23	261.9

Similar to the dyeings on mercerized-cationized samples using 6% Remazol Black B, the lightness of the sample dyed without Na<sub>2</sub>CO<sub>3</sub> was higher than all others. The samples dyed with different concentrations of Na<sub>2</sub>CO<sub>3</sub> exhibit similar L\* values. The C\* values of all the samples were relatively low. Based on the lightness and C\* values of the samples, MC150 samples dyed with the two-component dye recipe and low concentration of Na<sub>2</sub>CO<sub>3</sub> obtained deep neutral black shades on fabrics. To better compare the color depth of dyed samples, the K/S values of the samples were measured and are summarized in Table 31 and Figure 24.

**Table 31. K/S Values of MC150 Samples Dyed with Different Concentrations of Na<sub>2</sub>CO<sub>3</sub>**

Sample	Concentration of Na <sub>2</sub> CO <sub>3</sub> (g/L)	K/S Value
MC150	0	822.4 ± 6.5
	5	903.5 ± 4.1
	10	891.7 ± 7.9
	15	894.0 ± 6.3
	20	892.5 ± 5.8

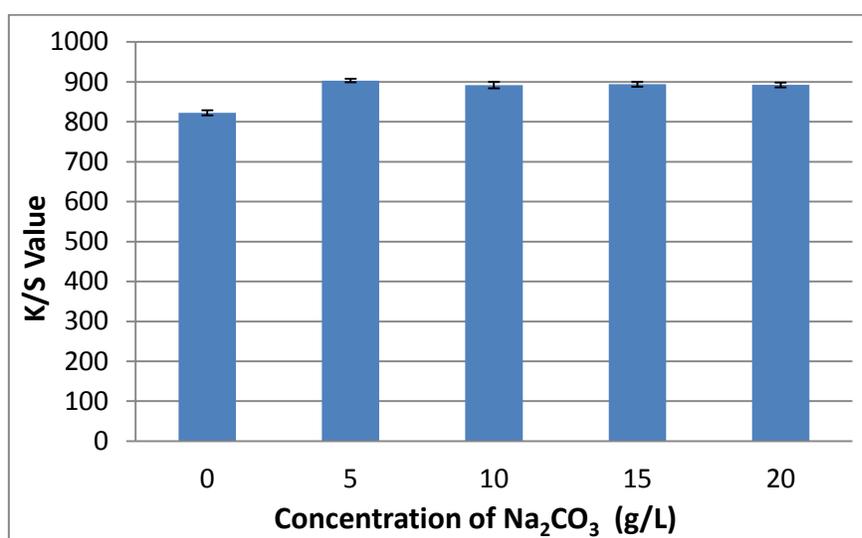


Figure 27. K/S Values of MC150 Samples Dyed with Different Concentrations of Na<sub>2</sub>CO<sub>3</sub>

The K/S values are consistent with the calculated L\* values. In the 5-20 g/L samples, no significant difference in K/S values was found. Reducing the concentration of Na<sub>2</sub>CO<sub>3</sub> from 20 g/L to 5 g/L did not reduce the color depth of MC150 samples dyed with the two-component dye recipe.

To further prove the effects of  $\text{Na}_2\text{CO}_3$  in dyeing performance when trying to obtain deep neutral black on mercerized-cationized cotton fabrics, dye uptake values of the samples were measured using the same method as the previously reported experiments and the results are summarized in Table 32 and Figure 25.

**Table 32. Dye Uptake of MC150 Samples Dyed with Different Concentrations of  $\text{Na}_2\text{CO}_3$**

Sample	Concentration of $\text{Na}_2\text{CO}_3$ (g/L)	Dye Uptake (%)
UU	0	97.8
	5	99.0
	10	98.5
	15	98.3
	20	97.6

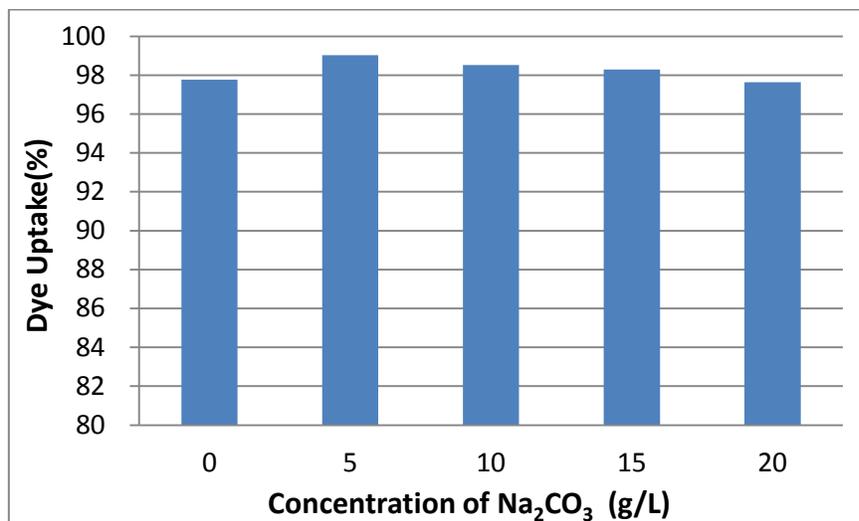


Figure 28. Dye Uptake of MC150 Samples Dyed with Different Concentrations of  $\text{Na}_2\text{CO}_3$

The results show very little change in dye uptake as a function of Na<sub>2</sub>CO<sub>3</sub> concentration, although the maximum uptake appears at 5 g/L, consistent with previous experiments using Remazol Black B only. Thus, based on the lightness, K/S and the dye uptake values, 5 g/L Na<sub>2</sub>CO<sub>3</sub> is the optimum concentration for obtaining deep neutral black shades on mercerized-cationized cotton fabrics using a binary combination of dyes.

#### 4.4.2 The Effects of Na<sub>2</sub>CO<sub>3</sub> on Colorfastness

The effects of Na<sub>2</sub>CO<sub>3</sub> on colorfastness of MC150 samples dyed with a binary dye mixture were assessed by measuring their colorfastness to laundering, crocking and light.

##### 4.4.2.1 Colorfastness to Laundering

The colorfastness to laundering of MC150 samples dyed with a binary mixture of dyes as a function of Na<sub>2</sub>CO<sub>3</sub> concentration was evaluated using the same method as previously described. Triplicate samples were measured and the average results are summarized in Table 33. Multi-fiber test fabric was used for testing but Table 33 just lists the staining on cotton.

**Table 33. Colorfastness to Laundering of MC150 Samples Dyed with Different Concentrations of Na<sub>2</sub>CO<sub>3</sub>**

Sample	Concentration of Na <sub>2</sub> CO <sub>3</sub> (g/L)	Color Change	Staining
MC150	0	3.5 ± 0.0	2.7 ± 0.2
	5	4.7 ± 0.2	4.5 ± 0.0
	10	4.7 ± 0.2	4.5 ± 0.0
	15	4.8 ± 0.2	4.5 ± 0.0
	20	4.8 ± 0.2	4.5 ± 0.0

Both the staining and color change ratings show that the sample dyed without Na<sub>2</sub>CO<sub>3</sub> has poor colorfastness to laundering. Other samples all have very good colorfastness. Decreasing the concentration of Na<sub>2</sub>CO<sub>3</sub> from 20 g/L to 5 g/L did not have a negative effect on the colorfastness to laundering.

#### 4.4.2.2 Colorfastness to Crocking

Colorfastness to crocking of MC150 samples dyed with a binary mixture of dyes as a function of Na<sub>2</sub>CO<sub>3</sub> concentration was evaluated using the same method as previously described. Triplicate samples were measured and the average results are summarized in Table 34.

**Table 34. Colorfastness to Crocking of MC150 Samples Dyed with Different Concentrations of Na<sub>2</sub>CO<sub>3</sub>**

<b>Sample</b>	<b>Concentration of Na<sub>2</sub>CO<sub>3</sub> (g/L)</b>	<b>Dry Crocking</b>	<b>Wet Crocking</b>
MC150	0	4.3 ± 0.2	3.5 ± 0.0
	5	4.2 ± 0.2	3.5 ± 0.0
	10	4.3 ± 0.2	3.5 ± 0.0
	15	4.3 ± 0.2	3.5 ± 0.0
	20	4.5 ± 0.0	3.5 ± 0.0

The results of dry and wet crocking show similar results regardless of Na<sub>2</sub>CO<sub>3</sub> concentration.

#### 4.4.2.3 Colorfastness to Light

Colorfastness to light of MC150 samples dyed with a binary mixture of dyes as a function of  $\text{Na}_2\text{CO}_3$  were measured using the same method as previously described and are summarized in Table 35.

**Table 35. Colorfastness to Light of MC150 Samples Dyed with Different Concentrations of  $\text{Na}_2\text{CO}_3$**

Sample	Concentration of $\text{Na}_2\text{CO}_3$ (g/L)	Color Change	
		20 h	40 h
MC150	0	3.5	3
	5	4	3.5
	10	4	3.5
	15	4	3.5
	20	4	3.5

Color changes of the samples after 20 and 40 hours light exposure show that the lightfastness of MC150 samples dyed without  $\text{Na}_2\text{CO}_3$  was worse than those dyed with  $\text{Na}_2\text{CO}_3$ . The change in concentration of  $\text{Na}_2\text{CO}_3$  from 5 g/L to 20 g/L did not influence colorfastness to light of the dyed samples.

In conclusion, for binary dyeings to produce ultra-deep neutral blacks on mercerized-cationized cotton fabrics, the use of  $\text{Na}_2\text{CO}_3$  cannot be eliminated based on the results of both color depth and colorfastness properties of the dyed samples. However, the concentration of  $\text{Na}_2\text{CO}_3$  added can be reduced from 20 g/L, which is required for conventional fiber-reactive dyeings, to 5 g/L since color depth and colorfastness properties of the sample dyed with this

level of  $\text{Na}_2\text{CO}_3$  are as good as those dyed with higher concentrations of  $\text{Na}_2\text{CO}_3$ . Moreover, the dye uptake of MC150 samples increased slightly at 5 g/L compared to 10-20 g/L  $\text{Na}_2\text{CO}_3$ . The results are consistent with those reported in section 4.3.

## CHAPTER 5 CONCLUSIONS

In this thesis, the development of high efficiency ultra-deep dyeing of cotton to produce black shade has been investigated using a mercerization-cationization method before dyeing with fiber-reactive dyes. Both mercerization and cationization have been proved to be effective in increasing the depth of shade of dyed cotton fabrics using Remazol Black B (C.I. Reactive Black 5) and Remazol Yellow RR. In addition, with the increase in concentration of the cationic compound, 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC), dyeing performance of cationized cotton fabrics was also improved with higher than 95% dye uptake being achieved. Another advantage of cationization is that the extensive use of salt for exhaustion of reactive dyes was avoided. Compared with untreated cotton fabrics dyed using a conventional dyeing procedure, mercerized-cationized cotton fabrics dyed without salt have better colorfastness properties, except colorfastness to wet crocking. Also, the mechanical properties of yarns and pilling resistance of the fabrics were shown to be similar before and after treatment.

Ultra-deep navy and black shades with good colorfastness on cotton fabrics were obtained with the same method but different concentrations of dyes. Even with high concentrations of binary dye mixtures, the dye uptake of mercerized-cationized cotton fabrics was very high. Thus, with respect to the low concentration of dyes and zero  $\text{Na}_2\text{SO}_4$  in dye bath effluent, dyeing of mercerized-cationized cotton fabrics for ultra-deep shades was shown to be more environmentally benign than conventional dyeing procedures using fiber-reactive dyes.

The effect of the concentration of  $\text{Na}_2\text{CO}_3$  in dyeing performance of both untreated cotton fabrics and mercerized-cationized cotton fabrics was evaluated. The results indicate that the use of  $\text{Na}_2\text{CO}_3$  while dyeing mercerized-cationized cotton fabrics is optimum at 5 g/L, which is much lower than is required in conventional fiber-reactive dyeing. Lowering the concentration of  $\text{Na}_2\text{CO}_3$  from 20 g/L to 5 g/L did not have any negative influence in dyeing performance or colorfastness properties on mercerized-cationized cotton fabrics using both Remazol Black B (C.I. Reactive Black 5) alone or in combination with Remazol Yellow RR to produce an ultra-deep neutral black shade.

While further work is required to elucidate the full scope and limitations of fiber-reactive dyeing of cotton pre-treated by mercerization-cationization, the data presented demonstrate the potential for obtaining high performance ultra-deep shades on cotton while at the same time reducing environmental impact by reducing the amounts of unfixed dye and electrolyte in dye bath effluent.

## CHAPTER 6 FUTURE WORK

The following areas are recommended for future work:

- (1) Previous experiments discussed the influence of cationization effect in dyeing performance and colorfastness properties. However, just one type of mercerized cotton fabric was used and there is no information about the influence of the mercerization effect on either cationization or dyeing with fiber-reactive dyes. Thus, samples of varying mercerization levels should be produced and used for assessing dyeing performance as a function of the level of mercerization.
- (2) The cationization and dyeing process for fabrics both with and without mercerization should be fully optimized by statistically-designed experiments. Once an optimized process has been devised, pilot trials should be run to validate both the cationization and dyeing process as a commercially viable process.
- (3) Current experiments focused on ultra-deep black shades. Other deep shades should be investigated, including maroon, turquoise, brown, olive and high chroma hues such as bright greens.
- (4) Dyeing performance and colorfastness properties of other classes of reactive dyes on mercerized-cationized cotton fabrics should also be investigated.

- (5) The mechanism of enhanced dye uptake and measured depth of shade should be elucidated as a function of level of mercerization and cationization.
- (6) The mechanism of photo fading of fiber reactive-dyed cotton as a function of cationization should be investigated.
- (7) Other dye classes such as sulfur and vat dyes should be investigated since the mercerization-cationization method has potential to improve the dyeing performance and environmental impact when using these dye classes.
- (8) A holistic investigation on the overall environmental impact of the combined mercerization, cationization, and dyeing method should be completed. Improving environmental impact of one segment of the textile wet processing does not necessarily confirm a reduction in environmental impact of the final product.

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