ABSTRACT

FU, SHA. Studies on Dyeing Cationized Cotton. (Under the direction of Dr. Peter Hauser and Dr. David Hinks).

Even with the extensive research and rapid development of synthetic fibers, cotton is still the dominant raw material due to its unique combination of properties, especially the natural comfort. Based on its cellulosic structure, cotton has good reactivity or affinity for a variety of dyes. With advantages in wet fastness properties and a wide range of hue, reactive dyes are one of the most commonly used dyes for cotton coloration. However, the conventional reactive dyeing process is plagued with a high degree of salt utilization and colored effluent due to unexhausted, unfixed, and hydrolyzed dyestuffs. This is caused by the same anionic charges of both reactive dyes and cotton in water, resulting in poor affinity of most reactive dyes for cotton.

With the need for cleaner, cost-effective, and colorfast textile products, innovative technologies and improved processes have been developed for cotton coloration. As an important root to obtaining the desired dyeing performance with existing dyes, chemical modification of cotton fiber to impart cationic charges have been widely researched in recent years. By introducing cationic groups into cotton fibers, the affinity of anionic dyes for cotton was significantly improved, which allows the dyeing of cotton fabrics without salt and up to 100% reactive dye utilization. With less chemical, water, and energy consumption, the dyeing of cationized cotton is a potentially environmentally responsible process. The most commonly used cationic agent is 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC) due to its relatively good reaction efficiency and low cost.

Cationization can also be used with other treatment methods to further improve the dyeing performance and other properties of cotton fabrics. In this research, cationization with
CHPTAC was used in combination with mercerization to obtain ultra-deep reactive dyeing on cotton. The effects of mercerization and cationization degrees on dyeing performance and colorfastness properties were evaluated. Further, the influence of liquor ratio and dyestuff in producing ultra-deep black dyeing on mercerized cationized cotton was also investigated and compared with conventional reactive dyeing. Results showed that the ultra-deep black shade on mercerized cationized cotton was not obtainable using uncationized cotton, even with very low liquor ratio and drastically increased dye amount.

With high concentrations of dyes applied, levelness of dyeing is not a critical issue for ultra-deep reactive dyeing on cationized cotton. However, when shades with light to medium depth are required, reactive dyeing of cationized cotton may suffer from the problem of poor levelness due to ionic attractions between anionic dyes and cationic cotton fibers. Thus, the influence of temperature, dye structure, addition of soda ash, and leveling agents on dyeing kinetics and levelness were evaluated for cationized cotton. Suggestions on dyeing procedures and chemical recipes were made for different dye structures. With controlled dyeing process and effective leveling agents, dye strike rate and dyeing levelness of cationized cotton were effectively controlled.

Finally, a comparative life-cycle analysis of cationization dyeing versus conventional reactive dyeing of cotton was conducted to evaluate the environmental impacts of applying cationization. Among the six environmental impact categories assessed, the conventional reactive dyeing system has higher environmental impacts in half of the categories, including global warming, acidification, and ecotoxicity potential. For the cationization dyeing system, the use of CHPTAC for cationization caused high impacts in eutrophication and human health. Due to the limitations in database and assessment methodologies, there is no firm
conclusion on which dyeing system is more environmentally beneficial. Feasible cleaner production proposals were suggested for both dyeing systems.
Studies on Dyeing Cationized Cotton

by
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DEDICATION

This work is dedicated to my grandparents.
BIOGRAPHY

Sha Fu was born on June 22nd, 1991 in Zhangshu, Jiangxi Province of China. She is the only daughter of Qingzheng Fu and Yanwen Du. She got her bachelor degree from Donghua University, Shanghai in 2012. By attending the “3+X” program, Sha entered North Carolina State University and got her Master degree in Textile Chemistry in 2013. After that, she continued her study and research in the Fiber and Polymer Science Doctoral program at North Carolina State University.
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CHAPTER 1 INTRODUCTION

1.1 Background

As one of the most important textile materials, cotton has been dominant for centuries due to its comfort, relatively low cost, good dyeability and colorfastness properties. To produce commercially acceptable cotton products that satisfy consumers aesthetically, a great variety of dyes were applied on cotton, including reactive dyes, direct dyes, sulfur dyes, vat dyes, and azoic dyes. With excellent wet fastness properties and a wide range of hue, reactive dyes are one of the most commonly used dyes for the coloration of cotton.

However, the affinity of reactive dyes for cotton is poor since both cotton fibers and reactive dyes carry negative electrical charges in water and there is electric repulsion between them. In conventional reactive dyeing, high concentrations of electrolytes are required to enable the adsorption of the dyes. Even with substantial amounts of salt added, the fixation rate of most reactive dyes on cotton is still relatively low, especially when deep shades such as black are attempted. Thus, there are high concentrations of dyes and electrolytes remaining in the wastewater of dyeing and they may cause serious environmental problems.

To eliminate the use of salt and increase dyeing efficiency, cationization of cotton with numerous chemicals has been widely researched in recent years. One of the most commonly used monomeric cationizing agents is 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC). It is first converted into 2,3-epoxypropyl trimethylammonium chloride (EPTAC) by the reaction with alkali and then reacts with the hydroxyl groups on cotton under alkaline conditions. Cationization with CHPTAC can also been used in combination
with other treatment methods, such as mercerization, to obtain high efficiency ultra-deep dyeing on cotton. However, there is no systematic study on evaluating the influence of mercerization and cationization degrees on obtaining deep dyeing on cotton with reactive dyes.

In another aspect, cationized cotton used for pale dyeing suffers from the problem of poor levelness. This is because, in exhaust dyeing, the levelness of dyeing is directly related to the dye strike rate. With cationic sites attached to cellulose chains, ionic attractions exist between anionic dyes and cationic cotton fibers and the dye is adsorbed on fiber surface rapidly by ion exchange. To control the degree of levelness, which is an important quality criterion of dyeing, the dye strike rate need be controlled to an appropriate value. The dye strike rate might be influenced by several factors, including cationization degree, dye structure, temperature, addition of soda ash, leveling agents and so on.

With reduced water, energy, and chemical consumption, the dyeing process of cationized cotton is more environmentally benign compared with conventional reactive dyeing process, especially for ultra-deep shades. Since the cationization stage also requires a large amount of chemicals and rinsing water, life-cycle assessment of the innovative cationization dyeing process is required to systematically compare its environmental impacts with conventional reactive dyeing.
1.2 Research Objectives

The main objectives of this research are:

1. Systematic evaluation of ultra-deep dyeing on mercerized cationized cotton and comparing it to conventional reactive dyeing from the color depth, dyeing efficiency, colorfastness and some other aspects.

2. Obtain level light to medium dyeings on cationized cotton with a variety of commercially significant reactive dyes and evaluate the influence of temperature, dye structure, soda ash, and leveling agents on dye strike rate of cationized cotton.

3. Evaluate the environmental impacts of using cationization dyeing process.

1.3 Research Outline

This dissertation consists of seven chapters. In Chapter 1, the research background and objectives are described. In Chapter 2, literatures including basic theories and previous researches are reviewed to set the foundation for this research. The study mainly focused on three aspects: deep dyeing on mercerized cationized cotton (CHAPTER 3), real-time dyebath monitoring of cationized cotton for levelness control (CHAPTER 4), and life-cycle assessment of cationization and dyeing of cotton (CHAPTER 5). In Chapter 3, different aspects pertaining to deep dyeing on mercerized cationized cotton are discussed, including the influence of mercerization and cationization degrees, liquor ratio, and dyestuff amount on dyeing performance and colorfastness properties of cotton. In Chapter 4, real-time dyebath monitoring is used to evaluate the dye strike rate of commercially significant reactive dyes on cationized cotton. Various factors including temperature, dye structure, addition of soda ash and leveling agents are controlled to reduce dye strike rate and improve dyeing levelness. In
Chapter 5, a life-cycle assessment of deep dyed cationized cotton has been conducted and compared to conventionally dyed cotton fabrics to investigate the environmental impacts of applying cationization. Finally the general conclusions were made in Chapter 6 and potential future work was suggested in Chapter 7.
CHAPTER 2 LITERATURE REVIEW

2.1 Coloration of Cotton

2.1.1 Introduction

With extensive research and rapid development, the use of synthetic fibers has accelerated in recent years. However, in the textile industry, cotton is still the dominant raw material due to its unique combination of properties, including comfortable soft hand, good dyeability and color retention, easy to handle, breathability, good absorbency, and relatively low cost. By referring to the annual global production and consumption of cotton in Figure 1\(^1\), it can be verified that in the 21\(^{st}\) century, we are even producing and using more cotton than before. It accounts for around 40\% of the worldwide textile fiber consumption\(^2\).

![Annual Global Cotton Production and Consumption](image)

**Figure 1** Annual global production and consumption of cotton from 1984 to 2015

Among the wide range of cotton textile products in the market, a large color gamut with
relatively good fastness properties were provided to satisfy consumers aesthetically. In fact, with 88% to 96% of cellulose content\(^2,3\) content, cotton has good reactivity or affinity for a variety of dyes, including reactive dyes, direct dyes, sulfur dyes, vat dyes, and azoic dyes.

2.1.2 Basic Chemistry of Cotton Coloration

As the major component of cotton, cellulose is a linear carbohydrate polymer of 1,4-β-D-glucose units covalently linked by valence bonds between the C4 and the C1 carbon atom on adjacent glucose molecules\(^4\). As Figure 2 shows, each glucose unit in cellulose possesses three hydroxyl groups, two secondary and one primary\(^5\). Cellulose is resistant to alkali and bleaching agents but can be easily damaged by concentrated acids and strong oxidizers, which can cause breakdown of the polymer chain\(^4\).

![Figure 2 Molecular structure of cellulose (n = degree of polymerization)](image)

With hydroxyl groups as the only functional groups, there are three types of color retention mechanisms for cellulose. Fiber reactive dyes, the only kind of dye which can form covalent bonds with the hydroxyl groups on cellulose, usually have good wash fastness. Direct dyes rely upon both van der Waals forces and hydrogen bonds between cellulose and long planar dye molecules. In the case of sulfur, vat, and azoic dyes, water soluble precursors are applied to the fiber and then, the water-insoluble dye molecules are generated inside the fiber and trapped within the fiber pores\(^6\).
With different application methods and mechanisms, dye classes for cotton can be selected based on the requirements for shade, colorfastness properties and cost. The relative cost of various dye classes for cotton are listed in Table 1. To better understand the coloration of cotton, it is important to highlight the specific coloration mechanisms of the commonly used dye classes as well as their drawbacks and advantages.

<table>
<thead>
<tr>
<th>Class</th>
<th>Relative cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vat</td>
<td>$$$$$</td>
</tr>
<tr>
<td>Reactive</td>
<td>$$</td>
</tr>
<tr>
<td>Azoic</td>
<td>$</td>
</tr>
<tr>
<td>Direct</td>
<td>$</td>
</tr>
<tr>
<td>Sulfur</td>
<td>$</td>
</tr>
</tbody>
</table>

2.1.3 Fiber Reactive Dyes

The first commercial reactive dye for cellulose was marketed in April 1956, just a century after the discovery of mauveine. Due to the wide range of shades with excellent wet fastness properties, reactive dyes have been well developed and are commercially widely used. Almost 45% of all textile dyes produced annually belong to the reactive class due to the extensive use of these dyes for coloring cellulose and viscose materials.

As previously mentioned, unlike all other classes of dyes, reactive dyes covalently bond with the fiber substrate and thus become an integral part of the substrate. As shown in Figure 3, a typical structure of reactive dye contains a chromogen (C), solubilizing groups (S), a bridging group (B), and a reactive group (R) with leaving groups (L). The chromogen is a
conjugated system containing one or more chromophores which provides the color to the dye. The reactive group is capable of reacting with the hydroxyl groups on cellulose by addition or substitution reactions. In between the two functional groups, a bridge group connects but also insulates the chromogen from the reactive group to prevent the color generated by the chromogen from changing\textsuperscript{11}.

As one of the first invented reactive dyes, Reactive Orange 1 in Figure 3 has the dichlorotriazine (DCT) as its reactive group. There are also many other reactive groups with a wide range of reactivities. Reactive groups can be based on, but not limited to, triazine, vinyl sulfone, quinoxaline, and pyrimidine\textsuperscript{12}. Some of the typical reactive groups in fiber reactive dyes are presented in Figure 4. The reactivity and correlated application temperature of the reactive groups are listed in Table 2.
Figure 4 Typical reactive groups in commercial fiber reactive dyes\textsuperscript{13}
Table 2 Reactivity and application temperature of typical reactive groups in commercial fiber reactive dyes

<table>
<thead>
<tr>
<th>Reactive group</th>
<th>Commercial name</th>
<th>Reactivity</th>
<th>Exhaust dyeing temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCT</td>
<td>Procion MX (BASF)</td>
<td>High</td>
<td>25-40</td>
</tr>
<tr>
<td>MCT</td>
<td>Procion H (BASF)</td>
<td>Low</td>
<td>80-85</td>
</tr>
<tr>
<td></td>
<td>Basilen (BASF)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MFT</td>
<td>Novacron F (Huntsman)</td>
<td>Moderate</td>
<td>40-60</td>
</tr>
<tr>
<td>TCP</td>
<td>Drimarene X (Clariant)</td>
<td>Low</td>
<td>80-95</td>
</tr>
<tr>
<td>DFCP</td>
<td>Drimarene K (Clariant)</td>
<td>Moderate to high</td>
<td>30-50</td>
</tr>
<tr>
<td></td>
<td>Levafix E-A (DyStar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VS</td>
<td>Remazol (DyStar)</td>
<td>Moderate</td>
<td>40-60</td>
</tr>
<tr>
<td>DCQ</td>
<td>Levafix E (DyStar)</td>
<td>Low</td>
<td>50-70</td>
</tr>
<tr>
<td>NT</td>
<td>Kayacelon React (Nippon Kayaku)</td>
<td>Moderate to high</td>
<td>100-130 (React under neutral conditions)</td>
</tr>
</tbody>
</table>

All the typical reactive groups mentioned above can be divided into two main types. First, for the halogenic heterocyclic derivatives (such as DCT), the reaction mechanism with cellulose is a nucleophilic substitution (Figure 5) of a labile chlorine, fluorine, or nicotinyl leaving group activated by an adjacent nitrogen atom in the heterocyclic ring. On the other hand, the vinyl sulfone group reacts with cellulose by nucleophilic addition to the carbon-carbon double bond activated by the adjacent electron-attracting sulfone group. As shown in Figure 6, the vinyl sulfone is not present in the dye molecule initially and should be generated in the dyebath by elimination of sulfate ion from a sulfatoethyl sulfone group under basic conditions.
However, for both reaction mechanisms, alkaline conditions are required to enable the reaction and there are competing hydrolysis reactions of the dye (Figure 5 and Figure 6). Thus, many reactive dyes applied with exhaustion methods, especially with high liquor ratio, have relatively low fixation rates. To obtain a higher fixation rate, many of the newer reactive dyes have more than one reactive group. Those bifunctional reactive dyes can have two identical or different reactive groups in the dye molecule. As an example, C.I. Reactive Black
5 (I), the first commercial reactive dye with two identical reactive groups, has increased probability of reaction with the fiber than the dyes with only one vinyl sulfone group.

The large amount of unfixed and hydrolyzed reactive dyes in wastewater may cause serious environmental problems since they are water-soluble and cannot be easily removed by conventional treatment systems\textsuperscript{14–16}. Also, the affinity for cotton of most commercially available reactive dyes is poor since both reactive dyes and cotton carry anionic charges in water. High concentrations of electrolytes are required to help exhaust the reactive dyes. For dark shades with conventional reactive dyeing, the concentrations of electrolytes added can be as high as 100 g/L\textsuperscript{17}. Most of the electrolytes remain in the effluent after dyeing and they may also cause an environmental problem if dyehouse effluent is discharged without treatment.

The substantial level of unfixed and hydrolyzed dyes is also a major reason for the heavy water consumption for rinsing. Even though reactive dyes are known for their excellent wet
fastness properties, multiple soaping and rinsing are commonly needed to remove unfixed dyes and ensure acceptable wash fastness of dyed cotton fabrics. The rinsing cycles required for removing hydrolyzed reactive dyes greatly extended the entire dyeing process.

2.1.4 Direct Dyes

Direct dyes are named so because they have inherent substantivity for cotton and other cellulosic fibers and can be applied without adding mordants. Direct dyes usually have long, coplanar molecular structure and are attracted to cellulosic fibers through hydrogen bonds and Van der Wall’s forces. Sulfonated mono-, bis-, and poly-azo dyes constitute the predominant group of direct dyes. C.I. Direct Blue 130 (2) is an example of typical bis-azo direct dyes. By introducing more azo groups, the conjugated double-bond system extends and the wavelength of light absorption often becomes longer.

Most of the direct dyes are relatively inexpensive and can be applied with simple dyeing procedure. Based on their substantivity and dyeing behavior, the Society of Dyers and Colourists (SDC) classified direct dyes into three types: Class A, self-leveling direct dyes which migrates wells; Class B, salt controllable direct dyes with relatively poor leveling
characteristics; Class C, salt and temperature controllable direct dyes which exhibit poor migration and are highly sensitive to both salt and temperature\textsuperscript{13}.

The advantages of direct dyes include low cost, easy of application and a full range of hues. However, due to the relative weak retention mechanism, direct dyes have 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\textsuperscript{10}.

2.1.5 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). The naphthols are phenols, which are insoluble in water but soluble in alkaline solution. They are substantive to cotton, particularly in presence of salt. The naphthols can be classified based on the substantivity for cotton. In general, the higher the substantivity the better rubfastness the formed dye would have, since less azo pigment forms on the fiber surface\textsuperscript{4,13}.

In the dyeing process with azoic dyes, the textile materials are first treated with naphthol solution. Then the base is converted into water-soluble diazo compound by the process called
diazotization. Finally, the diazotized form of the base react with the naphthol on treated material to form the color inside the fabrics. This step is known as coupling. After coupling, soaping and rinsing are applied to remove superficial pigment. With Naphthol AS as the coupling component and Orange GC as the diazo component, Figure 7 presents an example of the basic reactions involved in the application of azoic dyes.

Azoic dyes are especially strong in orange, red, scarlet and bordeaux shades. The ranges of color also include dark blue and black, but there is no green or bright blue\textsuperscript{13}. 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.

2.1.6 Vat Dyes

From the use of natural indigo in ancient times, vat dyes have been one of the most important and oldest types of dyes. Vat dyes are used to dye cellulosic materials in relatively dull shades and can provide the best overall fastness properties. However, due to the high cost and complex application method, vat dyes are only used for high-quality products.

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 reduced to water-soluble leuco compounds under alkaline conditions. The reduced leuco compounds have substantivity for cotton and often possess a different color from the original vat pigment. The application of vat dyes includes solubilization by reduction (vatting process), rapid penetration into the fiber and oxidization back into insoluble pigment.

Based on the chemical structure, vat dyes are mainly indigoid or anthraquinoid. The most commonly used vat dye is indigo, C.I. Vat Blue 1, 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. The popularity of indigo is from the attractive worn look and its styling possibilities. As an example of vat dyeing chemistry, Figure 8 shows the reduction and oxidation reaction of indigo during dyeing. During application, the insoluble
dye is converted into a soluble yellow-green form with sodium hydroxide and sodium hydrosulfite, which is the most commonly used reduction bath. After immersion into the dyebath, the yarns are exposed to air for oxidation back to insoluble blue form. The repeated immersion followed by air oxidation leads to ring dyed yarns with faded stylish look\textsuperscript{18}.

![Reduction of Indigo](image1)

\textbf{Reduction of Indigo}

![Oxidation in Air](image2)

\textbf{Oxidation in Air}

\textbf{Figure 8 Basic reactions involved in indigo dyeing}

\section*{2.1.7 Sulfur Dyes}

Among all dye classes used for cotton, sulfur dyes have the dullest range of colors. Sulfur dyes are economical and widely used for dyeing deep muted shades like black, navy, brown, olive and blue\textsuperscript{19}. They have good wash fastness, fair light fastness and low bleach fastness. Currently, sulfur dyes are still irreplaceable for producing deep dull shades, such as black, with satisfactory fastness properties and low cost\textsuperscript{13}.

The chemistry of sulfur dyes is very complex since they are synthesized by heating simple amines or phenolic compounds in the presence of sulfur. In their final form after
application, sulfur dyes are water-insoluble macromolecular compounds characterized by di- and polysulfide bonds \((-S_n-)\) between aromatic residues\(^{12}\).

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. Due to the high efficiency and low cost, sodium sulfide (Na\(_2\)S) and sodium hydrogen sulfide (NaHS) are the most commonly used reducing agents. However, with either sulfur based reduction agent, the sulfide ion in the waste dye baths can liberate poisonous hydrogen sulfide if acidified. In consideration of environment, the sulfur based reducing agents should be excluded. Therefore, a lot of researches have been done to find alternative reducing agents for sulfur dyes such thiourea dioxide\(^{20}\) and glucose\(^{21-23}\).

2.1.8 Developments in Cotton Coloration

With a great variety of dyes available, there are still limitations for cotton coloration. As an example, obtaining ultra-deep shades on cotton with good colorfastness in an environmentally responsible way is difficult. Sulfur blacks, as the most commonly used black dyes for cotton, have advantages on low cost and high washfastness over other dyes. However, they are not environmentally friendly due to the large amounts of sodium sulfide used in manufacture and application. Other classes of black dyes used for cotton also have their own limitations, such as the poor washfastness of direct dyes and large amounts of dye and salts in the dye bath effluent of reactive dyes when applied in conventional dyeing processes\(^{24}\).
With the need for cleaner, cost-effective, and colorfast textile products\textsuperscript{25}, innovative technologies and improved processes have been developed for cotton coloration. The innovations mainly focused on three aspects: 1) Development of new dyes and auxiliaries; 2) Developments in dyeing machinery and processes; 3) Chemical modifications of cotton fiber prior to dyeing.

2.1.8.1 Developments in Dye Structure

With the unique dye structure and application mechanism, much attention from both industry and research has been focused on the development of reactive dyes. To increase the fixation efficiency and reduce chemical waste, reactive dyes with two or more reactive groups have been developed and commercialized. The bifunctional reactive dyes, including homobifunctional dyes (containing two identical reactive groups, e.g. the Procion H-E dyes) and heterobifunctional dyes (containing two different reactive groups, e.g. the Everzol dyes), were already widely used in industry\textsuperscript{26}. There are also successful commercial trifunctional reactive dyes such as the Avitera SE dyes form Huntsman which are claimed to save energy and time and reduce water consumption\textsuperscript{27}. Researchers also came up with some polyfunctional reactive dyes with more than three reactive groups, but none of them have been commercially applied yet\textsuperscript{28-30}. A typical example is the reddish-grey to black chromium complex (3) patented by Hoechst. The drawbacks with more reactive groups include higher cost and lower color strength. The extra reactive groups “dilute” the color value of a dye by increasing the molecular weight of the dye but do not enhance chromogenic strength\textsuperscript{31}. 
Besides the increase in reactive groups, other innovations on reactive dyes include high strength economic chromophores, high lightfastness chromophores\textsuperscript{26}, neutral-fixing\textsuperscript{32,33} or acid-fixing reactive dyes\textsuperscript{34}, and cationic reactive dyes\textsuperscript{35-37}.

2.1.8.2 Developments in Dyeing Machinery and Processes

To reduce the chemical, water, and energy consumption in exhaust dyeing, a wide number of low liquor-to-fiber ratio dyeing machines have been developed\textsuperscript{38-40} such as the Luft-roto Plus dyeing machine from Thies with the minimum liquor ratio as 4:1\textsuperscript{41,42}. While for pad dyeing, new padders and low capacity padding troughs were designed to reduce liquor waste and eliminate tailing\textsuperscript{39,40}. Also, the Econtrol dyeing process developed jointly by BASF and Monforts eliminates the use of urea and salt for continuous dyeing of cellulosic fibers\textsuperscript{43}. While for washing-off, new approaches such as the “enzymatic after soaping” process for exhaust dyeing were announced for water and energy savings.

In consideration of environment, electrochemical reducing methods, both indirect and direct,
were investigated as a replacement of the non-regenerative-reducing agents currently used for the application of vat and sulfur dyes\textsuperscript{44,45}. Compared with indirect electrochemical reduction with mediators, direct electrochemical reduction is more attractive in view of economic and ecological aspects\textsuperscript{46–48}.

Other emerging technologies on cellulosic dyeing include the use of ultrasonic energy, microwave heating, and supercritical carbon dioxide (scCO\(_2\)). The studies on ultrasonic-assisted cotton coloration shown that the use of ultrasound can result in better color yield and savings in energy, water, time, and chemicals\textsuperscript{49–53}. Compared with the conventional heating method, microwave is a volumetric heating which can shorten the heating time for coloration at the same time of improving color yield and dye fixation efficiency\textsuperscript{54,55}. In another aspect, cotton can be dyed with disperse reactive dyes in scCO\(_2\), which eliminates the use of water\textsuperscript{56}. Also, cotton modified to be less hydrophilic can be dyed with disperse dyes in scCO\(_2\)\textsuperscript{57,58}.

2.1.8.3 Modification of Cotton Fiber Prior to Dyeing

Synthesis of new dyes and modification of cotton dyeing processes, while valid for obtaining qualified black cotton dyeings, are likely to involve significant capital investment and development costs\textsuperscript{59}. Thus, much attention has focused on modification of cotton fiber as another route to obtaining the desired dyeing performance and fastness properties with existing dyes and processes. Cationization of cotton is one of the most widely researched modifications in recent years since both direct and reactive dyes carry anionic charges and they exhibit high affinity for positively charged cotton\textsuperscript{24}. Numerous chemicals and methods have been used to introduce cationic groups into cotton fiber.
2.2 Cationization of Cotton

2.2.1 Reasons for Cationization

As previously mentioned, cellulose is the major component of cotton. While in contact with water, negative charges build up on the surface of cotton due to the partial ionization of hydroxyl groups on cellulose. Thus, cotton fibers have electrostatic repulsion to reactive and direct dyes, which are sulfonated and negatively charged. Anionic dyes have to overcome a significant adverse charge barrier before they are adsorbed on cotton fibers. 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. Even with electrolytes added, the fixation rate of reactive dyes is still relatively low, especially when high concentrations of dyes are applied. As a result, the dye bath wastewater typically contains high concentrations of both salt and unexhausted dye, which causes serious environmental problems.

By introduction of cationic groups into cotton fibers, the affinity of reactive dyes for cotton can be significantly improved. The ionic attractions between cationized cotton and reactive dyes can result in increased dye uptake, reduced or no electrolyte use, less dye washing off and less water and energy consumption. The environmental problems caused by dye and salt in effluent can be potentially mitigated by cationization pretreatment of cotton.

2.2.2 Cationic Reagents

Researchers have investigated different kinds of cationic reagents for the cationization of cotton. Based on the molecular weight, the cationic reagents can be divided into two groups,
monomeric reagents and polymeric reagents.

2.2.2.1 Monomeric Cationic Reagents

Introduction of amine groups into the cellulose structure has long been recommended for cationization of cotton. A typical form of the cationic reagent is the quaternary ammonium compound with a reactive group which can form covalent bond with cellulose. The 2,3-epoxypropyl trimethylammonium chloride (EPTAC, 4) and its epichlorohydrin precursor, 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC, 5) are very commonly used cationization reagents for cotton to improving dyeability\textsuperscript{59,61–63}. The epoxy group can react with cellulose under alkaline conditions.

Other aminated epoxy derivatives have also been synthesized and applied on cellulose for cationization. For example, N-Oxiranylmethyl-N-methylmorpholinium chloride (6) was reported to have higher reactivity with cellulose than EPTAC\textsuperscript{64}. Figure 9 shows the structure of the cationic reagents with different alkyl groups attached to ammonium. It was reported
that, the cationization efficiency and amount of dye adsorbed decreased as the length of the hydrocarbon chain attached to the ammonium group increased\textsuperscript{65}. As shown in Figure 10, there are other cationic reagents with substituted counter ions and hydrocarbon chains\textsuperscript{66}.

\[ R_1 = R_2 = R_3 = C_2H_5: \text{Triethylamine} \]
\[ C_3H_7: \text{Tripropylamine} \]
\[ C_5H_{11}: \text{Tripentylamine} \]

\[ R_1 = R_2 = CH_3, R_3 = (CH_2)_nCH_3: \text{Dimethyltetradecylamine} \]

Figure 9 Aminated epoxy based cationic reagents

\[ X = OSO_3CH_3, OSO_3C_2H_5, SO_3C_6H_4CH_3 \]

Figure 10 Alkyl di-allyl ammonium salts

To increase cationization efficiency, aminated epoxy derivatives with multiple functional groups were synthesized and applied on cotton. A bi-functional cationic agent (7) was
reported to have higher cationization efficiency than EPTAC while applied using exhaustion method\textsuperscript{67}. Cotton modified with 2,4,6-tri-[(2-hydroxy-3-trimethyl-ammonium) propyl]-1,3,5-triazine chloride (Tri-HTAC) (8) showed improved printing performance with reactive dyes compared with untreated cotton\textsuperscript{68}. However, reaction efficiency of Tri-HTAC was not compared with the mono-reactive agent EPTAC.

Cotton treated with chlorotriazine type quaternary ammonium compounds was also found to have increased exhaustion with anionic dyes\textsuperscript{69,70}. This kind of cationic agent exhibit better thermal stability compared with the epoxy based agents. Figure 11 and Figure 12 show typical structures of mono-chlorotriazine type cationic reagent with either mono\textsuperscript{71,72} or bis-quaternary ammonium. Since mono-chlorotriazine type cationic reagent was reported to have relatively low substantivity for cellulose, bis-chlotriazine bis-quaternary agents (e.g. 9) were employed for cationization of cotton\textsuperscript{73}. With promoted dye exhaustion and fixation, dyed cotton fabric pre-treated with bis-reactive bis cationic quaternary agent may suffer a decrease
in light fastness\textsuperscript{74}.

\[
\begin{align*}
R &= H, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{H}_9, \text{C}_6\text{H}_{13}, \text{C}_{10}\text{H}_{21}, \text{C}_6\text{H}_{11}, \text{C}_6\text{H}_5\text{CH}_2, (\text{C}_6\text{H}_5)_2\text{CH}, \text{C}_{10}\text{H}_7\text{CH}_2 \\
X &= \text{Cl}, \text{Br}, \text{I} \text{ or other simple anion}
\end{align*}
\]

Figure 11 Mono-chlorotriazine mono-quaternary cationic reagents

\[
\begin{align*}
R &= -\text{H}_2\text{H}_2\text{N}(\text{CH}_3)_3 \\
X &= -\text{H}_2\text{H}_2\text{N}(\text{CH}_3)_3 \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_3
\end{align*}
\]

Figure 12 Mono-chlorotriazine bis-quaternary cationic reagents
With the acrylamide as the reactive group, 1-acrylamido-2-hydroxy-3-trimethylammonium propane chloride (AAHTAPC) can react with cellulose under alkaline conditions (Figure 13). Cotton pad-baked with the agent can be dyed with reactive dyes without salt or alkali. Some other acrylic-based cationic agents can be fixed on cotton by grafting polymerization.

![Figure 13 Reaction between AAHTAPC and cellulose under alkaline conditions](image)

By using crosslinking agents, the non-reactive cationic agent choline chloride (10) can also be used for producing cationized cotton with good reactive dye uptake under acidic conditions in absence of salt. Various crosslinking agents trimethylolmelamine (TMM), trimethylolacetylene diureine (3ACD), dimethyloldihydroxyethylene urea (DMDHEU), and dimethylpropylcarbamate (DMPC), which are normally associated with durable-press finishing processes, were used to bind choline chloride to cotton fabric by a pad-dry-cure method.
Besides cationization by introducing quaternary ammonium, introduction of amine groups (ammonization) can also improve the dyeability of cotton with anionic dyes under acid to neutral conditions. As show in Figure 14, 1,1-dimethyl-3-hydroxy azetidinium chloride (DMAC) forms covalent bond with cotton while in presence of alkali. Treated cotton showed excellent substantivity for reactive dyes under neutral condition in the absence of electrolyte.

![Figure 14 Reaction between DMAC and cellulose under alkaline conditions](image)

2.2.2.2 Polymeric Cationic Reagents

Polymeric cationic reagents, which are mainly polymeric amines or amides, have been applied for cationization of cotton due to their good affinity for cellulose. Polyamide-epichlorohydrin resin (Hercosett 125; Hercules Powder Corp.), is a reactive cationic polymer prepared by the initial condensation of adipic acid with diethylenetriamine followed by
reaction and partial cross-linking with epichlorohydrin\textsuperscript{81,82}. The main reactive group in the polymer is 3-hydroxy azetidinium chloride which can react with nucleophiles\textsuperscript{83}. Figure 15 presents the reactive and nucleophilic sites that may exist on the surface of the polyamide-epichlorohydrin treated cotton substrate\textsuperscript{82}. Under neutral conditions in absence of salt, the treated cotton showed good dyeability with highly reactive dichloro-s-triazine (DCT) and difluorochloropyrimidine (FCP) type reactive dyes. However, the system did not work well for low reactivity dyes including monochloro-s-triazine (MCT) and dichloroquinoxaline (DCQ) reactive dyes\textsuperscript{79}. In another aspect, introduction of thiourea\textsuperscript{84} or ethylenediamine\textsuperscript{85} into the application process of polyamide-epichlorohydrin has beneficial effects on the results obtained.
Polyepichlorohydrin dimethylamine (PECH-amine) was also applied on cotton for cationization\(^{86-88}\). It was prepared by initial polymerization of epichlorohydrin with boron trifluoride etherate as catalyst, followed by amination with dimethylamine (Figure 16)\(^{86}\). With good affinity, the PECH-amine can be applied to cotton by exhaustion method. Treated cotton was reported to have improved dyeability for direct\(^{86}\), reactive\(^{88}\), and acid dyes\(^{89}\).
Sandene 8425, developed by Courtaulds and Clariant (formally Sandoz), is a polyamino cationic resin with high substantivity to cotton under alkaline conditions\textsuperscript{60,79}. It can be applied on cotton by an exhaustion method. The treated cotton not only attracts anionic dyes, but also offers new dyeable groups for fixation that complement the cellulose hydroxyl groups\textsuperscript{19}. The major disadvantages of the pretreatment include a reduction in lightfastness of some azo chromophores and a dulling in shade\textsuperscript{60,90}. Since most synthetic chemicals used for cationization of cotton are not safe environmentally, chitosan, the natural biopolymer, has been used as a substitute for improving cotton dyeability. Chitosan is a long-chain unbranched polymer derived from chitin by deacetylation with hot alkali. It has very similar structure to cellulose except that the hydroxyl group in the C\textsubscript{2} position of the glucose ring has been replaced by an amino group. Figure 17 shows the structure of cellulose, chitin and fully deacetylated chitosan. In slightly acidic conditions, the amino group in chitosan can accept a proton and creates positive charge to attract anionic dyes. Rippon improved the dyeability of immature cotton for direct dyes by pretreatment
with chitosan. However, decreased wash and rub fastness were observed on treated cotton dyeing. Bandyopadhaby et al. applied chitosan on cotton using a pad-dry method. With chitosan-treated cotton, the amount of salt required can be reduced to 50% to produce a comparable shade to that of untreated fabric.

![Figure 17 Structure of cellulose, chitin, and chitosan](image)

To improve cationization efficiency, Lim and Hudson treated cotton with a fiber-reactive chitosan derivative, O-acrylamidomethyl-N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (NMA-HTCC). The compound was applied to cotton under alkaline conditions using a cold pad-batch method and was able to form a covalent bond with cellulose (Figure 18). Treated cotton dyed with direct and reactive dyes without salt showed higher color yield than conventional dyeing on untreated cotton.
There are many other cationic polymers which were successfully applied for cotton cationization. Cai et al. modified cotton with a commercial cationic acrylic copolymer, Polymer PL, using a pad-dry method. Treated cotton was reported to have increased dyeability with reactive dyes and comparable lightfastness. Ma et al. investigated the pretreatment with poly(vinylamine chloride) (11) for salt-free dyeing of cotton with reactive dyes. Higher dye fixation, excellent wash fastness, and good rub fastness was obtained on treated cotton. Zhang et al. improved cotton dyeability with reactive dyes using cationic starch, which was treated with EPTAC. El-Shishtaway and Nassar improved printability of cotton with pigment and anionic dyes by applying Solfix E, which is a polyaminochlorohydrin quaternary ammonium polymer with epoxide functionality.
Besides linear polymers, some innovative hyperbranched polymers with amino groups were also applied on cotton for improving dyeability. Burkinshaw et al. applied a commercial dendrimer product using an exhaustion method. The structure shown in Figure 19 is only one of the isomers present in the product\textsuperscript{97}. Zhang et al. synthesized a water-soluble amine-terminated hyperbranched polymer from methyl acrylate and diethylene triamine by melt polycondensation and applied on cotton using a pad-dry-cure method\textsuperscript{98}. In both of the researches, treated cotton showed improved dyeability with reactive dyes. However, the treatment efficiency and applicability should be further investigated and compared with regular cationic agents.

![Dentrimers structure](image)

Figure 19 Dentrimer used for cotton modification
All agents used for cationization, both monomeric and polymeric, have their limitations. Monomeric cationic agents, such as EPTAC, often suffer from relatively low substantivity, poor thermal stability, and unpleasant odor. While for polymeric cationic agents, ring dyeing, poor lightfastness, and change of hue are the major issues. Thus, for optimum cationization efficiency and dyeing performance, the cationic agent and its application method should be carefully selected.

2.2.3 Cationization with CHPTAC

2.2.3.1 CHPTAC and EPTAC

As previously mentioned, 2,3-epoxypropyl trimethylammonium chloride (EPTAC) and its epichlorohydrin precursor, 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC) are perhaps the most commonly used cationic reagent used for cotton. They are also widely applied for cationization of starch. Since EPTAC is unstable and mutagenic, it is often generated in situ from CHPTAC before application. Figure 20 shows the reaction mechanism between CHPTAC and alkali to form EPTAC.

![Reaction mechanism between CHPTAC and alkali to form EPTAC](image)

As shown in Figure 21, CHPTAC can be produced from the reaction of epichlorohydrin and trimethylamine hydrochloride. Due to the solubility of CHPTAC in water, it is typically
found as an aqueous solution of 50-70%. CR-2000 from Dow Chemical is a typical commercial product of CHPTAC with 65% activity. The product is clear and odorless and is completely miscible with water. To make CHPTAC resistant against hydrolysis, the commercial product is slightly acidic, typically with a pH form 4 to 6.\(^9\)

![Figure 21 Synthesis of CHPTAC](image)

CHPTAC is currently classified as Category 3 carcinogen. It is slightly toxic to freshwater organisms and has low levels of oral and dermal toxicity for humans.\(^99-101\). It is not a skin or eye irritant. Since it has a vapor pressure lower than \(10^{-3}\) Pa, inhalation risks are not expected.\(^102\) However, CHPTAC can convert to EPTAC, which is a genotoxic carcinogen. With pH of 7.8 and temperature of 12°C, the half-life of CHPTAC to EPTAC conversion is 21 days.\(^102\) Thus, in most application conditions, the concern of CHPTAC is about its conversion to EPTAC. EPTAC is a Category 2 Carcinogen and irritating to skin, eye and membranes.\(^102,103\) Even though EPTAC has higher stability than CHPTAC, it can still degrade to diol under alkali conditions (Figure 22). Its half-life is highly dependent on pH and temperature of the surroundings. Under strong acid conditions, EPTAC may be converted back to CHPTAC. However, this reverse reaction is slow and requires heat (higher than 60°C).\(^102\)
2.2.3.2 Reaction Mechanism with Cellulose

After the formation of EPTAC, it is reacted with cellulose under alkaline conditions to form stable ether bonds. As the reaction mechanism presented in Figure 23, the cationization reaction starts from the formation of an alkoxide from a hydroxyl group of the cellulose in alkali solution. Then the alkoxide attacks the epoxy group and opens it to form an ether linkage. However, under aqueous alkaline conditions, hydrolysis of EPTAC can also form unreactive diol (Figure 22). This competing reaction should be avoided to ensure efficient cationization of cotton.
2.2.3.3 Application Techniques

Since the first attempt made by Rupin\textsuperscript{61,62}, cationization of cotton using CHPTAC and EPTAC has been widely studied by researchers over decades. Common textile application techniques including exhaustion, cold pad-batch, pad-bake, and pad-steam were all investigated and compared for cationization efficiency. 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.

Exhaustion method is easy to be applied in the textile industry, however, it is the least...
efficient with typically around 10% fixation\textsuperscript{61,63}. Cold pad-batch and pad-dry-steam method are more efficient, with fixations around 50\%\textsuperscript{24,63}. If pad treated samples were not dried before steaming, the cationization efficiency can only be around 25\%. Compared with other methods, pad-bake method is more efficient and preferable for continuous processing in industry. However, temperature as high as 120–150 °C will cause migration of reactants during the reaction, which results in non-uniform cationization and dyeing. Hashem et al. showed, 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\textsuperscript{63}.

Thus, in consideration of both efficiency and uniformity, cold pad-batch could possibly be the most appropriate method to apply. With this method, the fabrics should be batched at room temperature for 12-24 h to ensure good reaction efficiency. Around 1:1 molar ratio of NaOH and CHPTAC should be mixed to form reactive EPTAC and certain amount of extra NaOH should be added to provide the alkali conditions for reaction with cellulose. With all application methods, cationized cotton after reaction should be fully washed and neutralized with citric acid to remove both the chemical residues and stinky fishy smell, which was caused by free amines released from the EPTAC under alkali conditions.

2.2.3.4 Dyeing of Cationized Cotton

By introducing the positively charged quaternary ammonium group, dyeing of cationized cotton with reactive and direct dyes can be performed without addition of salt. Also, cationized cotton fabrics have improved affinity for acid dyes. Researchers have also
evaluated the printing performance of cationized cotton with different kinds of inks.

Compared with conventional reactive dyeing, cationized cotton dyed without electrolytes have higher color yields and almost complete dye exhaustion. By applying reactive dyes with different reactive groups, it was shown that the reactive groups have minor influence on dyeing cationic cotton\textsuperscript{104,105}. However, the influence of the overall dye molecule structure is quite important and some dyes may behave significantly different from others with the same reactive group\textsuperscript{105}. Cannon and Hauser\textsuperscript{106} also demonstrated that, when applied on cationized cotton in high concentrations, some dyes have lower $L^*$ but leveled off $C^*$. Compared with untreated cotton, the non-linear color buildup behaviors were observed on cationized cotton at lower concentrations. Thus, even though Farrell et al.\textsuperscript{107} demonstrated the possibility of recipe prediction for cationized cotton to shade match cotton conventionally dyed with reactive dyes, extra caution is needed during application, especially for dye mixtures. Printing of cationized cotton with reactive inks also showed increase in color yield and reduction in time, energy, and chemical consumption\textsuperscript{108,109}.

Similar to dyeing with reactive dyes, direct dyes can be applied on cationized cotton without addition of salt and still provide high color yield and clear final dyebath. Cationized cotton can be dyed with reduced time than conventional dyeing which requires less energy. There was no significant decrease in colorfastness properties of cationized cotton fabrics dyed with reactive and direct dyes\textsuperscript{59,110}, which indicates that no ring dyeing was occurred. In general, the colorfastness to laundering of cationized cotton dyed with direct and reactive dyes are even better than uncationized cotton.
Dyeing cationized cotton with acid dyes produces dyed fabrics with significant darker shade and better fastness properties than acid dyeings on untreated cotton. However, the fastness properties were still inferior to acid-dyed nylon\textsuperscript{59,110}. While for printing with cationized cotton, dye selection is of crucial importance. Hauser and Kanik\textsuperscript{111} obtained successful printings on cationized cotton using disulfonated acid dyes and monosulfonated 1:2 metal complex dyes but not with monosulfonated acid dyes with low molecular weights.

2.2.3.5 Environmental Impact of Using Cationized Cotton

Due to the poor affinity and limited reaction efficiency of reactive dyes, there are high concentrations of dye and electrolyte remain in the wastewater when reactive dyes are applied on cotton in conventional dyeing processes, which causes serious environmental problems. Also, substantial level of unfixed and hydrolyzed dyes on fiber requires heavy water consumption for multiple soaping and rinsing. These environmental concerns about conventional reactive dyeing promote the use of cationized cotton.

As proved by previous research, the reactive dyeing procedures of cationized cotton are shorter, consume less water and chemicals, and require less energy than the corresponding procedures for untreated cotton\textsuperscript{59,112}. Also, dyebath effluent of cationized cotton has much lower chemical oxygen demand (COD), biological oxygen demand (BOD), and total dissolved solids (TDS) than untreated cotton dyed with conventional method\textsuperscript{113}. With respect to all these factors, the dyeing process of cationized cotton with reactive dyes is much more environmentally benign than conventional reactive dyeing. However, to comprehensively evaluate the environmental impact of using cationized cotton, the environmental impact of
the cationization stage should also be included. With some of the safety and toxicity data of CHPTAC and EPTAC available\textsuperscript{100–102}, a full life-cycle assessment of cationized cotton can be done and compared to conventional cotton.

2.3 Mercerization of Cotton

Besides cationization, mercerization is another chemical treatment method which can significantly increase color yield of cotton dyeings. With longer history than cationization of cotton, mercerization was discovered by John Mercer in 1844 and patented in 1850. He found treating cotton cloth with cold 20\% aqueous NaOH solution caused considerable fiber swelling, shank the overall fabric size, and increased the fabric strength and dyeability. It became popular since H. A. Lowe found that the luster of cotton fabric would be improved after the cold caustic soda acted on cotton under tension\textsuperscript{114}. Mercerization permanently changes the fiber morphology and crystallinity and increases luster, strength, moisture absorption, dyeability and reactivity.

2.3.1 Changes in Structure of Cotton on Mercerization

2.3.1.1 Crystal Structure

Cotton undergoes chemical, physic-chemical and structural modifications on treatment with caustic soda solution of mercerizing strength\textsuperscript{114}. As a polymer, cellulose can have different forms of crystalline structure, including Cellulose I, II, III, and IV. Upon mercerization, the unit cell of cellulose changes from Cellulose I, which is the crystal structure in native cotton, to Cellulose II\textsuperscript{115}. Cellulose I exists in a parallel chain conformation while Cellulose II exists in an antiparallel chain conformation\textsuperscript{116}. Figure 24 shows a model of cellulose crystal unit
which contains five full cellobiose units\textsuperscript{117,118}. The dimensions of Cellulose I and II are presented in Table 3\textsuperscript{119,120}. Mercerization without tension allows complete conversion of Cellulose I to Cellulose II to take place. However, for mercerization with tension, mixtures of the two forms exist\textsuperscript{121,122}.

![Figure 24 The crystal unit of cellulose](image)

Table 3 Dimensions of unit cell of Cellulose I and Cellulose II

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>Cellulose I</th>
<th>Cellulose II</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>8.35</td>
<td>8.14</td>
</tr>
<tr>
<td>b (Å) (fiber axis)</td>
<td>10.30</td>
<td>10.30</td>
</tr>
<tr>
<td>c (Å)</td>
<td>7.90</td>
<td>9.14</td>
</tr>
<tr>
<td>B (degrees)</td>
<td>84</td>
<td>62</td>
</tr>
</tbody>
</table>

Figure 25\textsuperscript{125} illustrates how the conversion from Cellulose I to Cellulose II occurs with a simplistic representation of cellulose structure (top view of crystal unit cell). Starting with
Cellulose I, the cellulose swells immediately after in contact with concentrated sodium hydroxide aqueous solution. The swelling breaks intermolecular hydrogen bonds and allows for reorganization of the cellulose chains. As presented in the Figure 25(B), at this point, the structure is entitled as alkali cellulose with distended and distorted lattice. The small circles in between cellulose represents for NaOH molecules. When cotton was transferred to water and well washed, water replaces the NaOH and the cellulose hydrate is formed. As shown in Figure 25(C), the smalls circles represents for water molecules. The structure is still distended, but slightly less than the alkali cellulose. Besides distention, the angle of the unit cell also changed significantly. Finally, complete drying of the cellulose hydrate freezes the transformation of Cellulose I to Cellulose II. The changes in crystalline structure and orientation result in lower crystallinity and smaller crystal sizes of the cotton fibers.

![Figure 25 Conversion of cellulose crystal unit during mercerization](image)

2.3.1.2 Fiber Morphology

Compared with the change in crystal structure, the morphology changes of cotton fibers on mercerization are easier to be observed. Unmercerized cotton fiber has a ribbon-like structure with spiral twists longitudinally. Its surface is rough and non-uniform. As shown in Figure
the cross-section is irregular and kidney shaped with a lumen inside. All these factors result in less luster\textsuperscript{114}. When a cotton fiber is immersed in a sodium hydroxide solution of mercerization strength, the cellulose begins to swell immediately and the cross-section turns into elliptical in a few seconds (Stage 4). On further swelling (Stage 5), the section rounds off with larger size and collapsed lumen. After washing with water, the cotton fiber shrinks (Stage 6). After drying, a further and final shrinkage occurs (Stage 7). Swelling is more significant while there is no tension applied for mercerization. However, with no tension, fiber surfaces after mercerization still show residual creases and wrinkles which will influence the luster of the fabric.

Longitudinally, as the fiber swells, it also shrinks in length. The flat ribbon structure untwists and turns into cylindrical form. Figure 27 and Figure 28 are optical micrographs of native and mercerized cotton fibers with 400 times magnification. The figures clearly show the changes in morphology of cotton after mercerization.
2.3.2 Changes in Properties of Cotton on Mercerization

2.3.2.1 Luster

Due to the structure changes, mercerized cotton fibers with uniform cylindrical cross-section reflect light more evenly than the original kidney shaped structure and therefore improves the luster of the cotton fibers. The silky luster is one of the most valuable properties of mercerized cotton. The luster depends on the quality of raw material while long-staple fiber obtains a greater luster than short-staple. Also, twisted double yarns are more lustrous than non-twisted loose yarn after mercerization\(^4\). As previously mentioned, cotton mercerized without tension has wrinkled surface and no increase in luster can be observed.
2.3.2.2 Mechanical Properties

Mercerization, both slack and with tension, increases the tensile strength of cotton fibers\textsuperscript{121}. Cotton mercerized under tension has reduced elongation with significantly increased Young’s modulus while slack mercerized cotton has increased extensibility accompanied with increased strength. The increase in strength of mercerized cotton is mainly attributed to improved cohesion between cotton fibers and increased orientation of the crystallites. Mercerization also eliminates the weak points along the fiber, including internal strains (spiral reversals)\textsuperscript{125,126}, low cross-sectional areas, and high distortion spots\textsuperscript{4}. Other important factors for fiber strength may be the reduction in crystallinity of the fiber, the decreases in lengths of crystallites and fiber deconvolution\textsuperscript{114,127}. Mercerized woven cotton fabrics also have improved dimensional stability\textsuperscript{128} and crease recovery performance.

2.3.2.3 Moisture Regain

Mercerized cotton has higher moisture regain and is more easily to wet out than unmercerized cotton fabrics. Swelling in caustic soda significantly reduces the degree of crystallinity and breaks the hydrogen bonds in cotton fiber. The broken of intermolecular hydrogen bonds can increase the number of available hydroxyl groups by 25%. Since moisture is mostly absorbed by suitable groups in the amorphous region of cotton fiber, the increase in both amorphous content and available hydroxyl groups ensure significant increase in moisture regain. Slack mercerized cotton has even lower crystallinity and higher moisture regain than cotton mercerized under tension. In general, native cotton has moisture content of about 7%, while mercerized cotton with and without tension has moisture content of about 9% and 11% respectively\textsuperscript{114}. 
2.3.2.4 Dyeability and Reactivity

Besides moisture regain, the reduced crystallinity and increased number of reactive groups also increased the chemical reactivity and dye absorption of mercerized cotton fabrics. Mercerized cotton shows increased depth of shade as well as faster dyeing rate. The deeper color depth can be attributed to both the increased dye uptake and the optical effects of modified cotton structure. The more uniform swollen fibers absorb more and scatter less light. Thus, the changes in internal light scattering by mercerization can increase the perceived depth of shade on cotton even with the original dye absorption and significantly save the cost of dyes. The decrease in crystallinity increases moisture regain, dye absorption, and chemical reactivity but at the same time accelerates the hydrolysis of cellulose under acidic conditions and damage by oxidizing agents\textsuperscript{13}.

2.3.3 Control Variables and Machinery for Mercerization

2.3.3.1 Control Variables

To obtain the desired mercerization effect, the concentration of caustic soda, applied tension, temperature, and time for mercerization should be carefully selected. First, as discussed previously, the application of tension is the critical factor for the increased luster of mercerized cotton. To secure an increase in luster, cotton fabrics must be stretched lengthwise and widthwise during both the alkali treatment and washing process. It is necessary not to release tension before caustic concentration is lowered to about 60 g/L\textsuperscript{4}. Also, luster increases with the increase of applied tension during mercerization\textsuperscript{114,129}. However, in consideration of other aspects, mercerization without tension might be beneficial. Without tension applied, cotton has higher degree of swelling during caustic treatment, which enables
complete structure transformation from Cellulose I to Cellulose II and higher decrease in crystallinity. With these structural changes, slack mercerized cotton has higher moisture regain, reactivity, and dye absorption.

Temperature can also influence the mercerization effect. Generally, swelling of cellulose increases with a decrease in temperature, as the formation of alkali-cellulose compounds is an exothermic process. At 0°C the swelling of cellulose in alkali (8% to 9% by weight) can be as high as 800%\textsuperscript{114}. However, The rapid and extensive swelling also has disadvantages. The fiber becomes more compact in swelling condition, which may diminish the further penetration of caustic soda into the fiber. Also, at low temperature, the viscosity of caustic solution is relatively high which restricts the further penetration. With slower alkali penetration, mercerization of the fiber core can be lower than on its surface. Thus, in spite of lower swelling value, luster increases with increase in temperature of mercerization.

The extent of swelling also greatly depends on the concentration of alkali. With a NaOH concentration of 8 to 9% by weight, the fiber has maximum swelling. Further increase in NaOH concentration first decreases (minimum at around 13% alkali) then slightly increases the swelling\textsuperscript{130}. Traditionally, mercerization is conducted under tension using a cold solution (15-18 °C) of around 25% by weight of sodium hydroxide and the average dwell time is 55 seconds.
2.3.3.2 Mercerization Machinery

Mercerization can be carried out on grey cotton fibers or after scouring/bleaching. If mercerized in the grey state, the residual sodium hydroxide is not necessary to be removed since it is useful for the scouring process. Mercerization with scoured and bleached cotton is preferred since the penetration of alkali is faster and a more uniform and satisfactory effect can be obtained\textsuperscript{114,131}. 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. Almost all yarn mercerizing machines have similarity in design\textsuperscript{118}.

For mercerization of woven fabrics, machines can be broadly divided into two types, chain and chainless. In a typical clip chain mercerization (Figure 29), after impregnation in caustic soda, cotton fabrics passing through timing drums and get into an open tenter frame. In the tenter frame, the fabrics are held between two continuous chains with clips which hold the fabrics to a certain width. While for the wrap direction, then tension is applied by running the rollers of the second nip at a faster rate than the first one\textsuperscript{115,131}. The chain mercerization method has one inherent disadvantage that a greater elongation takes place at the edges than in the middle of the fabric. This is because the force for applying tension acts mainly on the outer edges and the line of force diminishes towards the middle. Thus, the chainless or roller mercerizing machines were developed as an alternative. In this kind of mercerizing machine (Figure 30), the fabric after padding with mercerizing liquor is passed through a set of
expander rollers rather than the tenter frame to stretch the material widthwise. The expander rollers are specially curved and dimensioned to make the fabric evenly expanded over than whole width\textsuperscript{114,132}.

Since knit goods are easily deformed and extended, the traditional machines for mercerizing woven fabrics are inadequate for knit fabrics. Thus, to suit knit goods, the chainless mercerizing machines are modified by either installing tension controlling device or processing between conveyer belts\textsuperscript{133}. Also, air is introduced into the fabric by means of jets to balloon the fabric tube and eliminate edge creases of the flattened tube. Figure 31 shows a typical Dornier continuous mercerizing range for tubular knit goods\textsuperscript{114}. 

![Chain mercerization machinery](image1)

**Figure 29 Chain mercerization machinery**

![Chainless mercerization machinery](image2)

**Figure 30 Chainless mercerization machinery (Courtesy of Swastik)**
2.3.4 Evaluation of Mercerization Effects

Evaluation of mercerization effects is important to ensure that the process has been applied properly. The most commonly used method for determining the mercerization degree is the Barium Activity Number (BAN) based on the standard Test Method 89\textsuperscript{134} developed by the American Association of Textile Chemists and Colorists. AATCC Test Method 89, "Mercerization in Cotton", is a quantitative method for determining the completeness of the reaction between the cotton and the mercerization bath. The method is based on the fact that mercerized cotton fabrics can absorb a higher amount of barium hydroxide compared to unmercerized cotton. This is because with decreased crystallinity and broken intermolecular hydrogen bonds by swelling, mercerized cotton has more accessible hydroxyl groups for barium hydroxide to react with. The BAN is calculated by dividing the amount of barium absorbed by the mercerized fabric by the unmercerized fabric then multiplied by 100. Thus, a higher BAN indicates a higher degree of mercerization. According to AATCC Test Method 89, a BAN in the range of 100-105 indicates no mercerization while a BAN above 150 indicates substantially complete reaction between the cotton and the mercerizing bath.
Intermediate numbers indicate either incomplete reaction or use of a weak mercerizing bath\textsuperscript{134}.

However, the determination of barium number using the AATCC standard method is a lengthy and laborious process. Hence, other methods such as near-infrared spectroscopy (NIRS) have been developed for the evaluation of mercerization degree. Previous research indicates that, with proper machine set up and calibration, the mercerization index obtained using near-infrared spectroscopy agreed well with the BAN measured using AATCC standard method. Compared with BAN measurement, the NIRS method for mercerization is quick, timesaving, and non-destructive\textsuperscript{135}.

2.3.5 Mercerized Cationized Cotton

As previously mentioned, both mercerization and cationization can help significantly increase color yield of cotton dyeing. The change in color yield of cotton dyeing by cationization is mostly from the increase in affinity for anionic dyes and subsequent higher dye uptake, while the improved color yield of mercerized cotton can be attributed to both the slightly increased dye uptake and the optical effects of modified cotton structure. Due to the changes in internal light scattering, mercerization can increase the perceived color depth on cotton even with the original dye absorption. Thus, with different mechanisms, mercerization can be applied in combination with cationization to further increase color yield of cotton dyeing.
Tarbuk et al.\textsuperscript{136,137} evaluated the chemical and morphological properties of cotton cationized after and during the mercerization process. The mercerized-cationized cotton retained all the beneficial properties of mercerized cotton with a change of surface charge which can further improve the dyeing performance with anionic dyes. Also, Fu et al. showed how deep black shades were obtained on mercerized cationized cotton utilizing higher than 95% of applied CI Reactive Black 5 (Remazol Black B) with no salt, and reduced alkali amount\textsuperscript{24}. Further experiments on evaluating the mercerization degree on cationization and dyeing performance of cotton should be performed.

2.4 Kinetics of Cotton Dyeing with Reactive Dyes

2.4.1 Basic Dyeing Theory

Coloration with dyes is based on physico-chemical equilibrium processes, namely diffusion and sorption of dye molecules or ions\textsuperscript{12}. For dyeing of cotton with reactive dyes, these processes are followed by chemical reactions inside and on the surface of the substrate. To obtain a uniform dyeing with satisfactory fastness properties, the control of the dyeing process and strike rate are of critical importance since reactive dyeing of cotton is irreversible. Two important and fundamentally different branches of dye theory should be understood, which are dyeing kinetics (transport and reaction phenomena, rates) and thermodynamics (dyeing equilibria, isotherms)\textsuperscript{12}. Basic dyeing theory and models related to conventional reactive dyeing of cotton are described below.
2.4.1.1 Dyeing System in Equilibrium

Chemical thermodynamics analyses the interrelation of energy with chemical reactions and applies to a system in its equilibrium state. It concerns about the final state rather than the speed with which the state is reached\cite{4}. For a semi-quantitative evaluation of a dyeing process, the investigation of the equilibrium dye distribution between the dye bath and the substrate is very important\cite{12}. An adsorption isotherm correlates the concentration of a substrate adsorbed on a solid surface ($D_f$) to its concentration in the surrounding fluid ($D_s$) when the system is at equilibrium\cite{13}. Adsorption isotherms can be linked to a certain sorption mechanism. There are three major types of dyeing adsorption isotherms, which are Nernst, Langmuir\cite{138} and Freundlich\cite{139} (Figure 32)\cite{19,140}.

Figure 32 Adsorption isotherms of dye-fiber systems
The linear Nernst isotherm indicates that the fiber behaves as a solvent for the dye. Disperse dyes on many synthetic fibers such as polyester follow this type of isotherm. The Freundlich isotherm appears similar to the Nernst isotherm except the addition of the exponent, N, which is an empirical constant between zero and one. It is based on the fact that in most dye-fiber systems the partition coefficient decreases with increasing surface coverage. The Langmuir isotherm assumes that the adsorption of dye takes place on specific sites in the fiber, of which the number is limited. The sorption speed is proportional to the number of unoccupied sites as well as the concentration of the molecules in contact with the solid phase. This isotherm is often applied to acid dyeing of nylon and wool. Both Freundlich and Langmuir isotherms have been used to describe the adsorption of direct dyes on cellulose. Even though there is no specific dye site in cellulose for direct dyes, Langmuir isotherm still shows a higher correlation for direct dye adsorptions than Freundlich isotherm.

However, for cotton dyeing with reactive dyes, the situation is more complex since the exhaust phase (described by an isotherm) is followed by a reactive phase (not reversible and cannot be described by any isotherm). Without the addition of alkali, the chemical reaction between cellulose and dye can hardly happen. Thus, the adsorption of reactive dye on cotton with no alkali is similar to direct dyes and either Freundlich or Langmuir isotherm can be applied. With alkali added, the dye reacts with both the hydroxyl groups on cellulose for fixation and the hydroxide in water for hydrolysis. The chemical reaction does not proceed in the reverse direction. While the word thermodynamics is usually applied only to reversible equilibrium systems, the fiber reactive dyeing process was generally considered to be a non-equilibrium situation in which the reaction stops when the dye is either fixed or hydrolyzed.
Thus, for cotton dyeing with reactive dyes, the dyeing kinetics is of greater practical importance than adsorption equilibrium.

2.4.1.2 Kinetics of Dyeing

During the dyeing process, dye is transferred from the dyebath to the fiber. The fiber reactive dyeing process includes four typical stages, including:

1. Convectional diffusion of the dye to the fiber surface, occurring in the dyebath;
2. Adsorption of the dye at the fiber surface;
3. Diffusion of the dye into the fiber (sorption);
4. Irreversible chemical reaction with the fiber.

For conventional reactive dyeing, the first three stages are generally referred as the exhaustion process while the last stage is referred as the dye fixation process. In the exhaustion process, no matter the adsorption equilibrium has been reached or not, the dyes exhausted are still free to migrate since the adsorption is reversible. Once the dye hydrolyzes or reacts with cellulose, no reverse reaction can happen. As the hydrolyzed dye cannot react with the fibers, the extent to which hydrolysis occurs during dyeing directly governs the practical usefulness of a reactive dyeing. For the chemical reaction to occur inside the textile substrate, a flow of reagents from or to the interfaces as well as into the interior of the substrate is necessary. Therefore, kinetics of fixation as well as hydrolysis of reactive dyes are partly determined by the diffusion behavior of the dye in the substrate\textsuperscript{143}. For the most efficient and level reactive dyeing, good exhaustion of the dye onto the substrate must be assured before either hydrolysis or fixation takes place.
Over the past decades a great deal of research effort has been devoted to understanding the physico-chemical mechanism of the dyeing of cotton with reactive dyes\textsuperscript{144–149}. Different dyeing kinetic models have been derived based on different simplifying assumptions and diffusion models\textsuperscript{150–152}. However, due to the complexity of the heterogeneous dye-water-cellulose system, the use of physico-chemical models has been almost exclusively restricted to research laboratories\textsuperscript{153}. To help understand the kinetics of reactive dyeing generally, some well-established fundamental equations rather than the derivation of specific physico-chemical models will be discussed here.

First, for dye adsorption on fiber surface, the attraction can either from physical or chemical forces between the dye and the fiber. Since the adsorption process is much faster than following diffusion process, it can be regarded as an instantaneous process and dyes may accumulate on the surface\textsuperscript{4}. The amount of dye adsorbed is a function of its affinity ($\Delta \mu$), which is a function of temperature (T):

$$-\Delta \mu^0 = RT \ln K + zF\psi$$

\textbf{Equation 1}

where R is the Gas constant, K is the partition coefficient of the dye, z is the ionic charge of the dye, F is Faraday constant, and $\psi$ is the electrical potential existing between fiber surface and surrounding solution\textsuperscript{153}.

Compared with the other two steps in exhaustion (transportation from bath to fiber and adsorption), diffusion of the dye into the fiber is the slowest process, and therefore rate-determining for the exhaustion of dye. Two types of models are most commonly used to
describe the diffusion of a dye into a fiber: the Pore-Volume and the Free-Volume model. Dye diffusion into cellulose is normally described with the Pore-Volume model\textsuperscript{154–156}. The Pore-Volume model assumes that the fiber possesses capillary channels through which the dye in the solution travels, which means that diffusion takes place only in water-filled pores and that the adsorption occurs on the inner surfaces of these pores\textsuperscript{4}.

Modelling of diffusion through the fiber is usually based on Fick’s second law of diffusion. While the fiber is regarded as a cylinder, the radial diffusion into a one-dimensional cylinder can be written as:

\[
\frac{\partial [D]_i}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (r D \frac{\partial [D]_i}{\partial r})
\]

Equation 2

where \([D]_i\) is the dye concentration in fiber interior, \(r\) is the fiber radius, while \(D\) is the diffusion coefficient of the dye in the fiber.

Since the Pore-Volume model is used and the hydroxide concentration in bulk solution and pore solution may be different, two equations are required for dye hydrolysis in the two different systems:

\[
\frac{\partial [D]_{s,hyd}}{\partial t} = k_h [OH^-]_s [D]_s
\]

Equation 3

\[
\frac{\partial [D]_{i,hyd}}{\partial t} = k_h [OH^-]_i [D]_i
\]

Equation 4
in which \([D]_{s,\text{hyd}}\) and \([D]_{i,\text{hyd}}\) are the hydrolyzed dye concentration in bulk solution and pore solution respectively, \([OH^-]_s\) and \([OH^-]_i\) are the concentration of hydroxide ion in bulk solution and pore solution, \([D]_s\) is the dye concentration in bulk solution and \(k_h\) is the hydrolysis constant. In the other phase for fixation, the diffusion of the dye into cellulose needs be taken into consideration. Similar to the hydrolysis reaction, the fixation of dye is based on a second-order equation:

\[
\frac{\partial [D]_{f,\text{fix}}}{\partial t} = k_f [CellO^-]_f [D]_i
\]

Equation 5

where \([D]_{f,\text{fix}}\) is the concentration of fixed dye, \([CellO^-]_f\) is the concentration of ionized hydroxyl groups in cellulose and \(k_f\) is the fixation reaction constant.

The reactive dyeing efficiency is defined as the rate ratio of the fixation and hydrolysis. The efficiency is influenced by a lot of factors including temperature, pH, electrolyte concentration, fiber structure, and dye structure\(^{144}\). For example, the increase in electrolyte concentration decreases the electrostatic repulsion forces between fiber and dye, increases the dye adsorption and thus improves dyeing efficiency. While for the dye structure, the reactive group of the dye determines the \(k_h\) and \(k_f\) and the overall structure of the dye molecule regulates the affinity for the fiber as well as the extent of aggregation\(^{143}\). To assure level dyeing with good fixation efficiency, all dyeing conditions must be carefully chosen and controlled.
2.4.2 Dyeing of Cationized Cotton

Taking cotton cationized using CHPTAC as an example, the dyeing kinetics of cationized cotton with reactive dyes are different from conventional reactive dyeing. Acharya et al.\textsuperscript{157} evaluated the reactive dye exhaustion kinetics of cotton cationized with CHPTAC using the HueMetrix Monitor system. The result showed that the well cationized cotton has a significantly increased exhaustion rate. This is because with the ammonium group attached to cellulose chains, strong ionic attractions exist between the anionic reactive dyes and cationic cotton fiber and the dye is adsorbed on fiber surface by ion exchange.

As previously mentioned, the kinetics of conventional reactive dyeing includes four typical stages: dye diffusion in bath, adsorption, diffusion into the fiber, and chemical reaction. Except for dye diffusion in the bath, all other kinetic stages of reactive dyeing are influenced by cationization. First, with the cationic group attached, the adsorption of anionic reactive dyes happens rapidly without the help of salt. Different from the reversible dye adsorption in conventional reactive dyeing, reactive dyes adsorbed on cationized cotton by ionic exchange mechanism are hard to migrate. With the significantly improved affinity for reactive dyes and increased dye concentration on the fiber surface, cationized cotton has an increased concentration gradient for diffusion of the dye into the fiber. The increase in concentration gradient is expected to accelerate the dye diffusion. However, with ionic attraction between the fiber and the dye, the diffusion coefficient might be reduced which results in slower diffusion rate. Also, if the concentration of cationic sites on the fiber surface is higher than the inner part of fiber, the diffusion of the dye will be further influenced. While for the reaction process, with less dye in solution and more adsorbed on fiber surface, the hydrolysis
of reactive dyes can be prevented in some degree. Even with reduced dye hydrolysis, only a portion of the total dye exhausted forms covalent bonds with cotton fiber while the remaining portion is held by ionic bonds.

In conventional reactive dyeing, the dye adsorption and diffusion process are reversible and the exhausted dyes are still free to migrate. Thus, as long as the reactive dyes were adequately exhausted before fixation, the reaction rate and levelness of dyeing can easily be controlled by dosing of alkali. However, for cationized cotton, once the dye was ionically bonded to the cationic site, very little migration can happen. Thus, the dyeing should be very level from the start, especially for pale dyeings.

2.4.2.1 Control Factors for Dye Strike Rate

To obtain level dyeing on cationized cotton with reactive dyes, the kinetics of exhaustion is even more important than the fixation process. The exhaustion rate can be influenced by several factors, including cationization degree, dye structure, temperature, addition of alkali, leveling agents and so on.

First, the cationization degree represents the number of cationic sites attached to cotton fiber and it is related to the concentration of cationic reagents applied. It should be determined by the concentration of dye to be applied on the cotton. The cationization degree should be high enough to exhaust all applied dyes without salt. However, if cotton was over-cationized for a pale dyeing, the dye will exhaust too fast and the levelness of dyeing will be a problem. Also,
the pale dyed cationized fabric is easy to be stained while contacting with other dyed fabrics or free dyes during laundering since there are free cationic sites on the fiber.

For conventional reactive dyeing, the reactive group essentially determines the kinetics of the reaction and also the dyeing rate. However, for dye exhaustion on cationized cotton, overall structure of the dye molecule may be more important since it regulates the affinity for the fiber as well as the extent of aggregation. With the same ion exchange mechanism for adsorption, exhaustion kinetics of dyeing cationized cotton with reactive dyes is similar to dyeing nylon with acid dyes under acidic conditions. The influence of dye sulfonation degree on dye substantivity, rate of dyeing, and migration are relatively complicated but one thing for sure is that the saturation value of the dye decreases with increasing degree of sulfonation.

Temperature and leveling agents are the two common ways to control the dye strike rate during the dyeing process. The temperature influences the rate of dyeing mostly by changing the diffusion coefficient. Even though the kinetics of dye transfer to the fiber surface and adsorption will also be influenced by temperature, both of these processes are too rapid to be controlled at practical range of dyeing temperatures. At low dyeing temperatures, the rapid dye adsorption on fiber surface and slow diffusion in fiber may cause ring dyeing. Different from the control of temperature, leveling agents control the rate of dye adsorption process and reduce dye concentration gradient effective for diffusion. The retarder does not affect the diffusion coefficient. The effects of temperature and leveling agents are especially different in pale dyeings. Since the small amount of dye present in the dyebath can be fully
accommodated on the fiber surface, unlevelness caused by rapid adsorption cannot be controlled by temperature\textsuperscript{19}.

2.4.2.2 Leveling Agents

To effectively control the dye strike rate of cationized cotton, addition of leveling agents is necessary. Similar to dyeing nylon or acrylic fibers, leveling agents for dyeing cationized cotton can be either fiber substantive or dye substantive\textsuperscript{13}. Anionic leveling agents are substantive towards positively charged cationized cotton while cationic leveling agents can form complexes with anionic dyes.

The mechanism (Figure 33) by which anionic leveling agents work is that, as they are substantive towards the fiber, they initially block or compete with the anionic dye for the cationic ammonium ion sites within and on the surface of the substrate\textsuperscript{158,159}. This decreases the initial rate of dye adsorption and promotes level dyeing. However, the blocking effect is temporary and eventually the more substantive dye molecules will displace the anionic surfactant by ion exchange\textsuperscript{13}. The anionic leveling agents can be used to pretreat the fabric before dyeing or added to the dyebath directly. When acting in this manner, these leveling agents are often called blocking agents. Too much anionic leveling agents can cause excessive blocking and lowers final dyebath exhaustion. The anionic leveling agents can be either monomeric or polymeric. Leveling agents with small molecular size, such as sulfates or sulfonates, have good penetration into the fiber but relatively low affinity\textsuperscript{13,19}. 
The retarding mechanism of cationic leveling agents is quite different (Figure 33). Cationic agents form complexes with anionic dyes in the dyebath and prevent the adsorption of the dye. With the increase of temperature, the dye-cationic agent complex become less stable and will finally dissociate, thereby gradually releasing the dye anions for adsorption on to the fiber. In order to prevent precipitation in the bath or on fabric surface, a non-ionic portion in the leveling agent is needed to solubilize the anionic dye-cationic agent complex. A cationic polyethoxylated amine (e.g. 12) mixed with a non-ionic product is a typical kind of cationic leveling agents. Some leveling agents are amphoteric (e.g. 13), with both anionic and cationic groups present. Clearly, leveling agents need be carefully selected to ensure good leveling effect and uninfluenced final exhaustion rate.
2.4.3 Dyebath Monitoring

Quantification of dye concentrations in solution by spectroscopic measurements, both on-line and off-line, are useful to help understand and optimize the dyeing process\textsuperscript{160}. The importance and usefulness of dyebath analysis is because in exhaust dyeing the levelness of dyeing is directly related to the dye exhaustion rate. Thus, the degree of levelness, which is an important quality criterion of dyeing, can be controlled by adjusting the dye uptake rate to an appropriate value\textsuperscript{4}. Also, dyebath analysis can be used for evaluating dye compatibility, which is another important aspect of process optimization\textsuperscript{161,162}. The available methods for dyebath measurement can be generally categorized upon the following dichotomies\textsuperscript{4}:

- On-line (dynamic, real-time) monitoring versus off-line (static) measurement
- Direct dyebath monitoring versus dyebath sampling techniques
- Closed-loop control versus open-loop control
- Laboratory scale versus bulk scale
- Reflectance versus transmission measurement
- Continuous dyeing versus batch (exhaust) dyeing.
Except for highly concentrated pad liquors used in continuous dyeing\textsuperscript{163}, transmission spectrophotometry is the choice for dyebath monitoring systems. Of all measurement methods based on transition spectrophotometry, the Beer-Lambert law is used to convert the absorbance value to the dye concentration. However, many dyestuffs in solution deviate substantially from the Beer-Lambert law, which cause inaccuracy in measurement of dye concentration.

2.4.3.1 Beer-Lambert Law and Deviations

In the ideal case, the response of light passing through a dye solution is governed by the Beer-Lamber law, which states that monochromatic light passing through a non-scattering medium is diminished in intensity in proportion to the distance it travels through the medium, the concentration of the absorbing species, and a characteristic value called the extinction coefficient or molar absorptivity\textsuperscript{164}:

\[
\lg \frac{1}{T} = A = abc
\]

Equation 6

where \( T \) is transmittance, \( A \) is absorbance, \( a \) is molar absorptivity (or extinction coefficient) of the absorbing species, \( b \) is the path length through the medium, and \( c \) is the concentration of the absorbing species\textsuperscript{165}.

Beer-Lambert law can also be applied to a sample containing several components. If there are no interactions between the components, the individual absorbance, \( A_i \), is additive:
\[ A_{\text{mix}} = \sum_{i=1}^{n} A_i = \sum_{i=1}^{n} a_i b c_i \]

Equation 7

which means the combined absorbance spectrum of the components is equal to the sum of the absorbance spectra of individual species.

While applied for dyeing, the Beer-Lambert law suggests a linear relationship between the absorbance and dye concentration. However, in many cases, deviations from the ideal behavior occur. Deviations from linearity are mainly divided into three types: optical, instrumental, and chemical\textsuperscript{166}. First, absorptivity of the solution depends on its refractive index, which varies with the concentration of the solution. Only for sufficiently low concentrations, is the refractive index a constant and the calibration curve is linear. Instrumental deviations originate from polychromaticity, slit width, bandwidth, stray radiation, and additivity of the instrument\textsuperscript{167}. Chemical deviations include variation in pH, association or dissociation, solvent-solute interaction, and photochemical reactions\textsuperscript{166}. Dye molecules tend to be planar, which make them easy to stack upon each other\textsuperscript{160}. The tendency of dyes to form aggregates in the solution is the main cause of deviation from the Beer-Lambert law\textsuperscript{168}. Dye species present in aggregates generally give lower absorbance than the same amount of dye present as single molecules, which will cause a negative deviation from linearity in Beer-Lambert law, as shown in Figure 34.
The absorption spectra of many dyes in aqueous solution are also influenced by temperature, pH, and electrolyte concentration. As the temperature increased, the dye aggregates break down and increase the absorbance. The presence of electrolyte promotes aggregation. Similarly, changes in pH will affect the degree of aggregation and cause further deviations from the Beer-Lambert law.

2.4.3.2 Real-Time Monitoring of Dyebath Exhaustion

Difficulties in accurately determining the dye concentration in solution arise because of deviations from the Beer-Lambert law. Basically, two types of approach have been developed to overcome these difficulties. First, the direct dyebath monitoring (DDM) system directly measures the concentration in the dyebath by predicting the effects of temperature, pH, and dye concentration on the extinction coefficient of the dye. All these effects were taken into account in the conversion from absorbance to concentration values. For example, empirical equations have been derived to describe the temperature-dependency of the absorbance of a basic dye during acrylic dyeing. In the DDM system, the dyebath normally...
circulated through a transmission cell with fixed path length, which limits the concentration range that can be measured. Also, the influence of dyebath pH and salt are difficult to predict.

Due to the limitations of DDM systems, there developed another method to help avoid the deviations from the Beer-Lambert law, which is to bring the dyebath sample to standard conditions that allow an accurate and precise analysis before the absorbance measurement. This typically includes control of temperature, pH, and dye concentration. Flow injection analysis (FIA), which using a carrier stream for dilution, buffering, and dissolution (in the case of vat and disperse dyes), is designed based on the concept of standardizing measurement conditions. Also, a cooling device is used to control the temperature of the dyebath before it is mixed with the carrier stream. The FIA is able to make measurements over a larger dynamic concentration range due to precise control of the sample dilution.

With the more complicated device, each measurement by FIA takes about 1 to 2 minutes, which is much longer than the DDM but normally sufficient for control purposes under typical industry conditions. In the case of monitoring reactive dyes, FIA can be coupled with high performance liquid chromatography (HPLC) to distinguish hydrolyzed reactive dyes from active reactive dyes in dyebath.

Conceived by Ruzicka and Marshall, sequential injection analysis (SIA) is based on similar principle of FIA but with different injection and propulsion components. The primary difference between FIA and SIA is that SIA uses a selection valve instead of an injection valve to deliver accurately measured volumes of carrier, sample and reagent. SIA does not
require a continuous carrier flow like FIA. The carrier was only pumped during the measuring cycle, which can results in less chemical consumption and waste\textsuperscript{179}.

For predicting mixtures of dyes which may interact with each other, there are relative high errors when using the ideal spectral additivity of Beer-Lambert law. Thus, although the dye mixture is diluted and brought to standard conditions, methods such as multiple linear regression (MLR)\textsuperscript{180}, partial least square (PLS), and neutral networks\textsuperscript{181} have to be used to deal with deviations from the Beer-Lambert law.

2.4.3.3 HueMetrix Dye-It-Right\textsuperscript{TM} Monitoring System

HueMetrix Dye-It-Right Monitor is one of the extraordinary real-time dyebath monitoring systems that became commercially available in recent years. The monitoring system of it is based on sequential injection analysis (SIA). As show in Figure 35, the monitor is connected to a dyeing machine by small circulation loop and at the other end it is connected to a computer for data analysis and display\textsuperscript{182}. The detailed components of the monitor are presented in Figure 36.
Before monitoring dye concentrations, the instrument has to be calibrated for each dye. During the dyeing process, the instrument takes a micro sample (0.1 mL) of dyebath via the circulation loop in about every 90 seconds. The sample is conditioned, physically using
cooling and bubble removing device and chemically by mixing with carrier fluid, to ensure optimum spectral analysis. The carrier fluid should be selected based on the type of dye being used. After conditioning and dilution, the absorbance of each micro sample is measured using the integrated UV-Vis spectrophotometer and the concentration is determined in real-time by the HueMetrix software based on the calibration curve of the dye. Additional information such as the temperature, pH, and conductivity of the dyebath can be measured by optional sensors before dilution\textsuperscript{182}.
CHAPTER 3 DEEP DYEING ON MERCERIZED CATIONIZED COTTON

3.1 Influence of Mercerization and Cationization Degrees on Obtaining Ultra-Deep Dyeing on Cotton with Reactive Dyes

Abstract: Bleached cotton fabrics were mercerized with 18% to 27% (w/v) NaOH and cationized with 50 g/L to 200 g/L 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC). The differently treated cotton fabrics were used to investigate the effects of different degrees of mercerization and cationization on dyeing performance and colorfastness properties of cotton fabrics dyed with reactive dyes. Considering both dyeing performance and cost effectiveness, the optimum treatment conditions were 21% NaOH for mercerization and 125 g/L CHPTAC for cationization. Both color yield and dye uptake leveled out with further increases in chemical concentration. Compared with untreated cotton dyed with a conventional dyeing procedure, well mercerized cationized cotton fabrics dyed without electrolytes have improved colorfastness to laundering, higher color durability, slightly reduced colorfastness to dry crocking and comparable performance on other colorfastness properties.

Keywords: Cotton, Mercerization, Cationization, Dyeing, Reactive dye, Colorfastness

3.1.1 Introduction

With excellent wet fastness properties and a wide range of hue, reactive dyes are one of the most commonly used dyes for the coloration of cotton and both cotton fibers and reactive dyes carry negative electrical charges in water. Due to the electric repulsion between the
negatively charged sites, the affinity for cotton of reactive dyes is poor to moderate at best. Thus, in conventional reactive dyeing, high concentrations of electrolytes are required to enable the adsorption of dyes. Even with substantial amounts of salt added, the fixation rate of most reactive dyes on cotton is still relatively low, especially when deep shades such as black are attempted.

To introduce electrostatic attraction and increase the interactions between fiber and reactive dyes, cationization of cotton with numerous chemicals, both polymeric and monomeric, has been widely researched in recent years. One of the most commonly used monomeric cationizing agents is 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC). CHPTAC is first converted into 2,3-epoxypropyl trimethylammonium chloride (EPTAC) by the reaction with alkali and then reacts with the hydroxyl groups on cotton under alkaline conditions. Its application methods and effects in subsequent dyeing performance have been well studied.

In order to further improve the dyeability of cotton, other chemical treatments, such as mercerization have been used in combination with cationization. Mercerization permanently changes cotton microstructure, morphology and cellulose chain conformation which results in changes in internal light scattering, reactivity and dyeability. Tarbuk et al. investigated the interface phenomena, chemical and morphological changes and of cotton cellulose cationized with EPTAC during and after the mercerization process. Even though an ultra-deep shade had been obtained on mercerized cationized cotton with low concentrations of dyes and Na$_2$CO$_3$ and no electrolyte left in the dye bath effluent, the mercerization
degree of commercially obtained mercerized cotton was hard to control. Thus, the present article is an investigation of how the degree of mercerization influences the cationization efficiency and dyeing performance of cotton fabrics. With cotton fabrics mercerized with varying concentrations of NaOH and cationized with different concentrations of CHPTAC, the optimum treatment conditions for obtaining deep dyeing on cotton with reactive dyes were determined.

3.1.2 Experimental

3.1.2.1 Materials

Bleached woven cotton fabrics (style # 400, 102 g/m², 45”) were obtained from Testfabrics, Inc., USA. The commercial reactive dye, Remazol Black B 133 (C. I. Reactive Black 5) was supplied by DyStar, Germany. The cationic reagent used was CR2000, 65% solution of 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC), obtained from Dow Chemical Co., USA. Other chemicals used in this study were commercially available laboratory grade sodium hydroxide (50% w/w), citric acid, acetic acid (97%), sodium carbonate, and sodium sulfate.

3.1.2.2 Mercerization

Mercerization of cotton fabrics was performed manually using a setup of a non-adjustable pan and frame. A piece of fabric was fixed to the pins of the steel frame and submerged into the concentrated NaOH solution for 60 seconds. Then the frame with the fabric still attached was transferred to a sink and rinsed with hot water to remove the majority of the alkali. After detaching from the frame, the fabric was rinsed and neutralized in a laboratory washing
machine and dried in an oven. As an indicator of the mercerization degree, the barium number of the mercerized cotton fabrics was determined by Cotton Incorporated (Cotton Incorporated, 6399 Weston Pkwy, Cary, NC 27513) using both an NIRS method and AATCC Test Method 89. The instrument used in the NIRS method was a FOSS XDS with Optiprobe: Vision software version 3.5.0.0.

3.1.2.3 Application of Cationic Reagent
A solution consisting of specified concentrations of 65% CHPTAC solution and 50% NaOH was pad applied onto cotton woven fabrics at 100% wet pick up using a Mathis laboratory pad (speed: 1.5 m/s, pressure: 1 bar). The CHPTAC and NaOH solutions were mixed just prior to application to minimize hydrolysis of the cationic reagent. After padding, the fabrics were rolled onto plastic wrapped hard paper tubes and then wrapped in plastic to minimize air contact. The fabrics were batched at room temperature for 20 h. After removing the plastic, the samples were rinsed to remove alkali and unfixed cationic reagent and then neutralized with citric acid (~0.5 g/L). Finally, the treated fabrics were extracted and dried in a tumble dryer.

3.1.2.4 Nitrogen Content Analysis
The percentage of nitrogen present in the cotton fabric was used as an indicator of the amount of CHPTAC that had reacted with cellulose. The analysis was conducted using a PE 400 CHE Elemental Analyzer using the classical Pregal and Dumas methods. After been cut into 2 mm squares, the cotton samples were combusted in a pure oxygen environment before elemental analysis.
3.1.2.5 Dyeing

All dyeings in the study were carried out using an Ahiba Spectradye Plus lab dyeing machine at a liquor ratio of 20:1 with 8% dye on weight of fabric. The same dyeing procedure (Figure 37) was used for both uncationized and cationized cotton fabrics. No salt was added for dyeing cationized cotton fabrics while 80 g/L Na\textsubscript{2}SO\textsubscript{4} was added at the beginning of dyeing uncationized cotton. To build up the alkali condition gradually, 20 g/L Na\textsubscript{2}CO\textsubscript{3} was added in two separate stages. After dyeing, both uncationized and cationized cotton fabrics were rinsed thoroughly, then neutralized with citric acid and rinsed again.

![Figure 37](image)

Figure 37 Dyeing procedure for both uncationized and cationized cotton fabrics

3.1.2.6 Color Measurement

A calibrated Datacolor Spectraflash 600X reflectance spectrophotometer with iControl software was used to calculate L*, a*, b*, C*, h° and K/S values of dyed fabrics. The software settings were illuminant D65, UV light included, and CIE 10-degree supplemental standard observer. K/S value was calculated by summation of the K/S values at 10 nm intervals from the wavelength of 400 nm to 700 nm. While testing, the sample was folded
twice. Each sample was measured five times by changing the measuring point randomly to calculate the average value.

3.1.2.7 Evaluation of Dye Uptake

After dyeing, the absorbance of the exhausted dye solutions was measured using an Agilent Cary 300 UV-Vis Spectrophotometer. First, a calibration plot of concentration vs. absorbance was produced at the wavelength of max absorption ($\lambda_{\text{max}}$) by measuring the absorbance of dye solutions at different concentrations. Then the residual dye solution was diluted if necessary and the absorbance measured at $\lambda_{\text{max}}$. The concentration of the solution was calculated based on the calibration plot. The percentage of dye uptake was calculated from $100 \times (1 - A_0/A)$ where $A_0$ and $A$ are the absorbance of the dye solution before and after dyeing, respectively.

3.1.2.8 Colorfastness Tests

Colorfastness to laundering was measured using AATCC Test Method 61\textsuperscript{188} using an Atlas LEF Launder-Ometer. A multi-fiber test fabric was attached to each sample to evaluate the staining and the test conditions were set according to test No. 2A. Colorfastness to crocking was measured according to AATCC Test Method 8\textsuperscript{189}. Both dry and wet crocking tests were measured using an AATCC automated crockmeter. Colorfastness to light of the dyed samples was measured using test option 3 in AATCC Test Method 16\textsuperscript{190}. The color change after 20 continuous light-on operating hours of each dyed sample was measured using an Atlas Ci 3000+ Weather-Ometer. Colorfastness to repeated home laundering was measured using AATCC Standardization of Home Laundry Test Conditions\textsuperscript{191}. Standard washing and tumble
drying machines were used. For all colorfastness tests, the evaluation of shade change and staining were made according to AATCC Evaluation Procedure 1 and AATCC Evaluation Procedure 2 using grey scale ratings from 1 to 5 where 5 implies no shade change.

3.1.3 Results and Discussion

3.1.3.1 The Effect of NaOH Concentration on Mercerization Degree

To obtain cotton fabrics with varying degrees of mercerization, bleached cotton fabrics were manually treated with 18% to 27% (w/v) NaOH. The concentration of NaOH solutions applied, the corresponding barium number of the treated fabrics, the pH and residue alkali of mercerized cotton fabrics after rinsing are all summarized in Table 4. The barium number of the fabrics increased with the concentration of NaOH applied. Since a barium number in the range of 100 to 105 indicates no mercerization of the fabric and a barium number around 150 indicates substantially complete reaction between the cotton and the mercerizing bath, the four mercerized samples with barium numbers from 115 to 145 were representative for evaluating the effect of mercerization degrees on cationization and dyeing performance of cotton fabrics. Also, since the amount of residue alkali in mercerized cotton fabrics was relatively low, it had no influence on a subsequent cationization process.
### Table 4 Barium number, pH and residue alkali of cotton fabrics mercerized with varying concentrations of NaOH

<table>
<thead>
<tr>
<th>Sample</th>
<th>NaOH conc.</th>
<th>Barium number</th>
<th>Residue alkali</th>
<th>Fabric pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmercerized</td>
<td>-</td>
<td>100.8±0.3</td>
<td>0.02%</td>
<td>7.14</td>
</tr>
<tr>
<td>Mercerized</td>
<td>18%</td>
<td>115.0±0.6</td>
<td>0.04%</td>
<td>7.74</td>
</tr>
<tr>
<td></td>
<td>21%</td>
<td>130.9±1.0</td>
<td>0.05%</td>
<td>7.78</td>
</tr>
<tr>
<td></td>
<td>24%</td>
<td>138.1±2.3</td>
<td>0.05%</td>
<td>7.81</td>
</tr>
<tr>
<td></td>
<td>27%</td>
<td>145.3±0.5</td>
<td>0.05%</td>
<td>7.86</td>
</tr>
</tbody>
</table>

### 3.1.3.2 Cotton Fabrics with Varying degrees of Mercerization and Cationization

Both unmercerized and mercerized cotton fabrics were cationized with varying concentrations of cationic reactant solutions. The concentrations of CHPTAC and NaOH applied are presented in Table 5. Thus, 25 samples with varying levels of either mercerization or cationization were obtained and measured for nitrogen content. As shown in Figure 38, the nitrogen content of the fabrics increased in proportion to the amount of CHPTAC applied. For cotton fabrics cationized with 50 g/L CHPTAC, the difference in nitrogen content between unmercerized and mercerized cotton fabrics was not significant since the cationization degree was limited by the low concentration (50 g/L) of the cationic agent. However, with higher concentration of CHPTAC applied, the cationization efficiency was highly influenced by the reactivity of the cotton fabrics and caused the significant difference in nitrogen content between unmercerized and mercerized cotton fabrics. The results demonstrate that compared with unmercerized cotton, well mercerized cotton fabrics have significantly improved reactivity with the cationic agent.
Table 5 Concentration of cationization solutions

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>CR2000 (g/L)</th>
<th>NaOH (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>85</td>
</tr>
</tbody>
</table>

3.1.3.3 The Effect of Mercerization and Cationization on Dyeing Performance

To evaluate the dyeing properties of the mercerized cationized cotton fabrics, the samples were dyed with 8% on weight of fabric (owf) Remazol Black B (C.I. Reactive Black 5). After dyeing, colorimetric values ($L^*$, $a^*$, $b^*$, $C^*$ and $h^\circ$) of all samples were measured (Table 6).
In addition, K/S values were calculated for each sample (Figure 39).

Table 6 Colorimetric values of all samples dyed with 8% owf Remazol Black B

<table>
<thead>
<tr>
<th>Sample</th>
<th>CHPTAC (g/L)</th>
<th>Colorimetric Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L*</td>
<td>a*</td>
</tr>
<tr>
<td>Unmercerized</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>16.75</td>
<td>-0.22</td>
</tr>
<tr>
<td>50</td>
<td>17.57</td>
<td>-0.45</td>
</tr>
<tr>
<td>100</td>
<td>16.15</td>
<td>0.07</td>
</tr>
<tr>
<td>150</td>
<td>15.62</td>
<td>0.50</td>
</tr>
<tr>
<td>200</td>
<td>15.21</td>
<td>0.59</td>
</tr>
<tr>
<td>18%*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>14.03</td>
<td>1.17</td>
</tr>
<tr>
<td>50</td>
<td>13.94</td>
<td>1.13</td>
</tr>
<tr>
<td>100</td>
<td>13.30</td>
<td>1.44</td>
</tr>
<tr>
<td>150</td>
<td>13.03</td>
<td>1.72</td>
</tr>
<tr>
<td>200</td>
<td>12.76</td>
<td>1.83</td>
</tr>
<tr>
<td>21%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>12.91</td>
<td>1.33</td>
</tr>
<tr>
<td>50</td>
<td>12.69</td>
<td>1.26</td>
</tr>
<tr>
<td>100</td>
<td>12.18</td>
<td>1.37</td>
</tr>
<tr>
<td>150</td>
<td>12.05</td>
<td>1.57</td>
</tr>
<tr>
<td>200</td>
<td>12.04</td>
<td>1.66</td>
</tr>
<tr>
<td>24%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>12.83</td>
<td>1.37</td>
</tr>
<tr>
<td>50</td>
<td>12.67</td>
<td>1.22</td>
</tr>
<tr>
<td>100</td>
<td>12.19</td>
<td>1.35</td>
</tr>
<tr>
<td>150</td>
<td>12.07</td>
<td>1.53</td>
</tr>
<tr>
<td>200</td>
<td>12.02</td>
<td>1.58</td>
</tr>
<tr>
<td>27%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>12.74</td>
<td>1.33</td>
</tr>
<tr>
<td>50</td>
<td>12.71</td>
<td>1.21</td>
</tr>
<tr>
<td>100</td>
<td>12.20</td>
<td>1.28</td>
</tr>
<tr>
<td>150</td>
<td>12.02</td>
<td>1.52</td>
</tr>
<tr>
<td>200</td>
<td>12.05</td>
<td>1.61</td>
</tr>
</tbody>
</table>

*18%, 21%, 24% and 27%: Mercerized cotton fabrics, the number corresponds to the concentration of NaOH applied for mercerization*
The results of L* and K/S values show that applying mercerization increased the depth of shade of dyed samples relative to the control. Also, the depth of shade increased while increasing the NaOH concentration for mercerization from 18% to 21% (barium number increases from 115 to 131). In consideration of color yield, 21% of NaOH was the optimum concentration for mercerization since the depth of shade leveled out with further increases in NaOH concentration. The data also show that the depth of dyeing is highly related to the concentration of CHPTAC applied for cationization. Cotton fabrics cationized with 50 g/L CHPTAC have similar or even lower depth of shade compared with uncationized cotton. With higher concentrations of CHPTAC applied (100-200 g/L), the depth of dyed cotton increased significantly. However, for highly mercerized cotton fabrics (21%-27% NaOH applied), the difference in L* and K/S between samples cationized with 150 g/L and 200 g/L CHPTAC was negligible. Thus, in consideration of color yield, the optimum treatment conditions were 21% of NaOH for mercerization and 150 g/L CHPTAC for cationization.

Figure 39 Effect of mercerization and cationization on color yield
To better evaluate the effect of mercerization cationization degrees in dyeing performance of cotton fabrics, the dye uptake was measured. As shown in Figure 40, applying mercerization increased the dye uptake of both uncationized and cationized cotton fabrics. The degree of mercerization also has an effect on dye uptake but the influence was relatively small compared with cationization. For highly cationized cotton fabrics (150 g/L and 200 g/L CHPTAC applied), the difference in dye uptake between samples mercerized with varying NaOH concentrations was negligible. The effect of cationization in dye uptake agrees with the lightness and K/S data.

![Figure 40 Effect of mercerization and cationization on dye uptake](image)

Except for samples cationized with 50 g/L CHPTAC, cationized cotton fabrics have substantially improved dye uptake compared with uncationized cotton. Also, the dye uptake increased with an increase in the concentration of CHPTAC applied. Mercerized cotton fabrics cationized with 150 g/L CHPTAC have higher than 95% of dye uptake and further
increasing the concentration of CHPTAC has little effect on improving dye uptake.

3.1.3.4 The Effect of Mercerization and Cationization on Colorfastness Properties

To evaluate the effect of mercerization and cationization on colorfastness properties, colorfastness to laundering, crocking and light of all dyed cotton fabrics were measured and compared.

Colorfastness to laundering was characterized by staining (Table 7) and color change. The results of staining show that the highly mercerized cationized cotton samples have improved staining performance compared with the control. In another aspect, the color change to laundering of all samples was higher than 4.5 which indicate excellent wash fastness. Thus, applying relatively high degrees of mercerization and cationization improved the colorfastness to laundering of deep dyed cotton fabrics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CHPTAC for cationization (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Unmercerized</td>
<td>4</td>
</tr>
<tr>
<td>18%</td>
<td>4.5</td>
</tr>
<tr>
<td>21%</td>
<td>4.5</td>
</tr>
<tr>
<td>24%</td>
<td>4.5</td>
</tr>
<tr>
<td>27%</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Table 8 presents the colorfastness to dry crocking of all the samples. Compared with untreated cotton, colorfastness to dry crocking of mercerized cationized samples was slightly
reduced. This may because the shades of mercerized cationized cotton fabrics were much deeper than the untreated sample and have higher amounts of dye transferred during rubbing. The colorfastness to wet crocking of all samples ranged from 2.5 to 3 and the difference between samples was not significant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CHPTAC for cationization (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Unmercerized</td>
<td>5</td>
</tr>
<tr>
<td>18%</td>
<td>5</td>
</tr>
<tr>
<td>21%</td>
<td>5</td>
</tr>
<tr>
<td>24%</td>
<td>5</td>
</tr>
<tr>
<td>27%</td>
<td>5</td>
</tr>
</tbody>
</table>

Color change after 20 h continuous xenon light exposure of all dyed samples were measured and listed in Table 9. Data in the first column of the table indicate that mercerized samples have improved colorfastness to light. By comparing the lightfastness between uncationized and cationized samples, it was seen that cationization slightly reduced the colorfastness to light of dyed samples. However, with both treatments applied, the highly mercerized cationized samples have excellent colorfastness to light.
Table 9 Effect of mercerization and cationization on colorfastness to light

<table>
<thead>
<tr>
<th>Sample</th>
<th>CHPTAC for cationization (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Unmercerized</td>
<td>4</td>
</tr>
<tr>
<td>18%</td>
<td>4.5</td>
</tr>
<tr>
<td>21%</td>
<td>4.5</td>
</tr>
<tr>
<td>24%</td>
<td>4.5</td>
</tr>
<tr>
<td>27%</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The results in the previous section indicate that mercerization with 21% NaOH and cationization with 150 g/L CHPTAC were the optimum treatment conditions in consideration of color yield and dye uptake. Compared with untreated cotton, cotton fabric treated with the optimum condition has improved colorfastness to laundering, slightly reduced colorfastness to dry crocking and comparable performance on other colorfastness properties.

3.1.3.5 Modification on CHPTAC Concentration for Cationization

To further examine the optimum treatment conditions for obtaining deep dyeing on cotton, the dyeing performance of cotton fabrics cationized with 125 g/L CHPTAC and 62.5 g/L NaOH was evaluated. Other treatment and dyeing conditions were kept the same as previous experiments. Table 10 lists the colorimetric data of cotton fabrics cationized with 125 g/L CHPTAC and dyed with 8% Remazol Black B. In the table, the L* values of cotton mercerized with 21% NaOH was comparable with the samples mercerized with higher concentrations. It agrees with the results in the previous section and proves again that 21% was the optimum NaOH concentration for mercerization.
Table 10 Colorimetric Values of Samples Cationized with 125 g/L CHPTAC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Colorimetric data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L*</td>
</tr>
<tr>
<td>Unmercerized</td>
<td>15.64</td>
</tr>
<tr>
<td>18%</td>
<td>13.04</td>
</tr>
<tr>
<td>21%</td>
<td>12.06</td>
</tr>
<tr>
<td>24%</td>
<td>12.03</td>
</tr>
<tr>
<td>27%</td>
<td>12.05</td>
</tr>
</tbody>
</table>

In Figure 41 and Figure 42, K/S and dye uptake of the samples cationized with 125 g/L CHPTAC are compared with cotton fabrics cationized with 100 and 150 g/L CHPTAC. As shown in the figures, K/S value and dye uptake of the samples cationized with 125 g/L CHPTAC were close to the samples cationized with 150 g/L CHPTAC. Based on the colorimetric data and dye uptake, reducing the concentration of CHPTAC from 150 g/L to 125 g/L has no significant influence on the dyeing performance of mercerized cationized cotton. Thus, if both cost and dyeing performance were considered, 125 g/L was the optimum CHPTAC concentration for obtaining deep dyeing on cotton with 8% Remazol Black B.
Figure 41 K/S value of samples treated with modified CHPTAC concentration

Figure 42 Dye uptake of samples treated with modified CHPTAC concentration
3.1.3.6 The Effect of Mercerization Cationization Treatment on Colorfastness to Repeated Home Laundering

To evaluate the effect of the optimized mercerization cationization treatment on colorfastness to repeated home laundering, cotton treated with optimized conditions (mercerization with 21% NaOH; cationization with 125 g/L CHPTAC) were dyed with 8% Remazol Black B and exposed to repeated home laundering up to 30 cycles. As a comparison, colorfastness to repeated home laundering of dyed untreated cotton was also measured. Table 11 and Table 12 list the changes in colorimetric data of untreated and mercerized cationized samples after 5, 10, 15, 20, 25, and 30 laundering cycles respectively. By comparing the results in the two tables, it is clear that the color change of untreated cotton after repeated home laundering was more significant than mercerized cationized cotton. Thus, applying the optimized mercerization cationization treatment on cotton before dyeing also enhances the color durability of dyed cotton fabrics to repeated home laundering.

<table>
<thead>
<tr>
<th>Wash cycles</th>
<th>Change in colorimetric data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DL*</td>
<td>Da*</td>
</tr>
<tr>
<td>5</td>
<td>0.23 L</td>
<td>-0.50 G</td>
</tr>
<tr>
<td>10</td>
<td>0.30 L</td>
<td>-0.46 G</td>
</tr>
<tr>
<td>15</td>
<td>0.55 L</td>
<td>-0.58 G</td>
</tr>
<tr>
<td>20</td>
<td>0.57 L</td>
<td>-0.45 G</td>
</tr>
<tr>
<td>25</td>
<td>0.60 L</td>
<td>-0.51 G</td>
</tr>
<tr>
<td>30</td>
<td>0.61 L</td>
<td>-0.56 G</td>
</tr>
</tbody>
</table>
Table 12 Color change of dyed mercerized cationized cotton after repeated home laundering

<table>
<thead>
<tr>
<th>Wash cycles</th>
<th>Change in colorimetric data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DL*</td>
</tr>
<tr>
<td>5</td>
<td>0.04 L</td>
</tr>
<tr>
<td>10</td>
<td>0.11 L</td>
</tr>
<tr>
<td>15</td>
<td>0.13 L</td>
</tr>
<tr>
<td>20</td>
<td>0.25 L</td>
</tr>
<tr>
<td>25</td>
<td>0.15 L</td>
</tr>
<tr>
<td>30</td>
<td>0.21 L</td>
</tr>
</tbody>
</table>

3.1.4 Conclusions

In this research, the effect of mercerization and cationization degrees on dyeing performance and colorfastness properties of cotton fabrics were evaluated. To obtain ultra-deep dyeing on cotton with 8% Remazol Black B, the optimum NaOH concentration for mercerization was 21% (barium number around 130) since further increases in mercerization degree has little influence on color yield. With the increase in concentration of cationic agent (CHPTAC), color yield and dye uptake of cationized cotton fabrics were increased, with the extensive use of salt for exhaustion of reactive dyes being avoided. However, the difference in dyeing performance between mercerized cotton cationized with 125 g/L, 150 g/L and 200 g/L CHPTAC was not significant. Thus, in consideration of both cost and dyeing performance, the optimum treatment conditions were 21% NaOH for mercerization and 125 g/L CHPTAC for cationization.

Compared with untreated cotton, the well mercerized cationized cotton samples have improved colorfastness to laundering, slightly reduced colorfastness to dry crocking and
comparable performance on other colorfastness properties. Also, cotton fabric mercerized with 21% NaOH and cationized with 125 g/L CHPTAC has improved colorfastness to repeated home laundering which indicates an improved durability of color.
3.2 Influence of Liquor Ratio and Dyestuff Amount in Producing Ultra-Deep Black Dyeing on Mercerized Cationized Cotton

Abstract: Cationized cotton allows the dyeing of cotton fabrics without salt and up to 100% anionic dye utilization. The employment of cationized cotton in the dyeing of high depths of shades with reactive dyes holds marked potential for sustainable improvements by less dye consumption, decreased water usage, and zero salt utilization; all while obtaining shade depths darker than possible with conventional reactive dyeings. This work builds upon previous work in obtaining ultra-deep dyeings of cotton utilizing cationized and mercerized cotton by investigating the effects of liquor ratio in dyeing and amount of dye applied. Surprisingly, for mercerized only cotton fabric, it was found that nearly equivalent depths of shade, as indicated by L*, were obtained independent of the liquor ratio and the amount of CI Reactive Black 5 applied from 7%-10% (owf). However, the strengths of the dyeings indicated by K/S sum show slight increases with increasing amounts of dye but not when lowering the liquor ratio. Similarly, for mercerized cationized cotton, the liquor ratio had a negligible effect on the depth of shade obtained, but increasing the amount of CI Reactive Black 5 resulted in an increase in shade depth and color strength. Very deep shades with high color strength were obtained with mercerized cationized cotton that were not obtainable with uncationized cotton, even with very low liquor ratio and drastically increasing the amount of CI Reactive Black 5.

Keywords: Cotton, Mercerization, Cationization, Reactive dye, Ultra-deep dyeing
3.2.1 Introduction

The coloration of textile fabrics has become increasingly scrutinized due to more informed and conscientious consumers, as well as the influence of Non-Governmental Organizations (NGO)\textsuperscript{194,195}. The desire to improve the sustainability of the coloration of textiles has seen many commercially available and applied advances in the last few decades. As illustrative examples, in terms of processing or process parameters, some examples of technological advances include smarter rinsing, low liquor ratio dyeing machines, and super critical carbon dioxide dyeing\textsuperscript{196–201}. On the other hand, mostly for the coloration of cotton, high efficiency dyestuffs, low salt dyes, and cationic cotton have been introduced with varying successes\textsuperscript{202–204}. With an emphasis on the reactive dyeing of cotton, notoriously, this process is plagued with a high degree of salt utilization and colored effluent due to unexhausted, unreacted, and/or hydrolyzed dyestuffs. The best demonstrative example of this are deep black dyeing of cotton fabrics that typically utilize 6% (owg) or more of dye and 100 g/L or more of salt.

To eliminate the use of salt and reduce the dyestuff waste in effluent, cationization of cotton with various cationic agents has been widely researched in recent years. Cotton cationized with 3-chloro-2-hydroxypropyltrimethylammonium chloride possesses a covalently bound positive charge that allows the ionic attraction of negatively charge dyestuffs commonly used in the coloration of cotton\textsuperscript{59,61,63}. The ionic attraction negates the necessity of copious amounts of salt as required in conventional reactive dyeing of cotton. The ionic attraction can fully exhaust and ionically and/or covalently bond applied dyestuffs, greatly increasing the efficiency of dye utilization. Other modifications, such as mercerization, can be used in combination with cationization to further improve the dyeability of cotton. Tarbuk et al.
evaluated the chemical and morphological properties of cotton cationized after and during the
mercerization process. The mercerized cationized cotton retained all the beneficial properties
of mercerized cotton with a change of surface charge which can further improve the dyeing
performance with anionic dyes\textsuperscript{136,137}. Our previous research showed how deep black shades
were obtained on mercerized cationized cotton utilizing 95\%\+ of CI Reactive Black 5
(Remazol Black B) with zero salt, and reduced alkali\textsuperscript{24}.

In another aspect, according to Equation 8\textsuperscript{10}, the efficiency of fixation ($E$) of fiber reactive
dyeing of cellulose in water can be described as

$$E = \frac{\text{Rate of fixation}}{\text{Rate of hydrolysis}} = \frac{S[D]_F (Dk'_F)^{1/2}}{L[D]_S k'_H}$$

Equation 8

Where

$S$ defines the surface area of the substrate

$[D]_F$ is the equilibrium concentration of dye at the surface of the fiber

$D$ is the diffusion coefficient of the dye in the material

$k'_F$ is the reaction constant for reaction of dye with substrate

$L$ is the liquor ratio

$[D]_S$ is the concentration of dye in the aqueous phase

$k'_H$ is the reaction constant of hydrolysis

With reference to Equation 8, it is clear that the lower the liquor ratio of a fiber reactive
dyeing of cotton, the higher the expected efficiency of fixation. The objective of this work is
to establish the effects of liquor ratio and amount of dyestuff applied in obtaining deep black dyeings of mercerized cotton and mercerized-cationized cotton.

3.2.2 Experimental

3.2.2.1 Materials

Commercially mercerized twill cotton fabric (253 g/m²) with a barium number 130 was provided by Cotton Incorporated, USA. Even though only a barium number of 150 or above represent for substantially complete reaction between the cotton and the mercerizing bath, the fabric was selected since previous work indicated that mercerized cotton with barium number 130 has the optimum dyeing performance and further increase in mercerization degree has little influence on color yield. The commercial reactive dye, Novacron Super Black R (shaded Reactive Black 5) was supplied by Huntsman, USA. The cationic reagent used was CR2000, 65% solution of 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC), obtained from Dow Chemical Co., USA. The chemicals used for the permanent press treatment were obtained from Cotton Incorporated. All other chemicals, including sodium hydroxide (50% solution), citric acid, sodium carbonate, and sodium sulfate were supplied by Fisher Scientific, USA.

3.2.2.2 Application of Cationic Reagent

A solution consisting of 150 g/L CHPTAC (65%) and 70 g/L NaOH (50%) was pad applied on mercerized twill cotton fabric at around 85% wet pick up (pressure: 1 bar). The NaOH and CHPTAC solutions were mixed just prior to application to minimize hydrolysis of the cationic reagent. The padded samples were wrapped in plastic to minimize air contact before
batching at room temperature for 24 hours. After removing the plastic, the samples were rinsed with water to remove unfixed and hydrolyzed cationic reagent and then neutralized with citric acid (~0.5 g/L). Finally, the treated fabrics were air dried at room temperature.

3.2.2.3 Dyeing

Dyeing of both uncationized and cationized cotton samples were carried out using an Ahiba Spectradye Plus lab dyeing machine. Before any chemical was added, samples were all wetted to 100% wet pick up. The same dyeing procedure (Figure 43) was used for both uncationized and cationized cotton fabrics. No Na$_2$SO$_4$ was added for dyeing cationized cotton fabrics while 110 g/L Na$_2$SO$_4$ was added at the beginning of dyeing uncationized cotton. For some reactive dyes, cationized cotton can be dyed in neutral conditions. However, Reactive Black 5 is a vinyl sulfone dye which requires alkali for dyeing to activate the reactive group of the dye to ensure adequate colorfastness properties. Thus, both cationized and uncationized cotton fabrics were dyed with alkali added but the applied alkali amount was determined based on the liquor ratio, dye concentration and treatment. To build up the alkali condition gradually, Na$_2$CO$_3$ and NaOH were added in two separate stages. After dyeing, all samples were rinsed, neutralized with citric acid and finally air dried at room temperature.
3.2.2.4 Color Measurement

A calibrated Datacolor Spectraflash 600X reflectance spectrophotometer with iControl software was used to calculate L*, a*, b*, C*, h° and K/S values of dyed fabrics. The software settings were illuminant D65, calibrated UV light included, and CIE 10-degree supplemental standard observer. K/S value was calculated by summation of the K/S values at 10 nm intervals from the wavelength of 400 nm to 700 nm. While testing, the sample was folded two times. Each sample was measured five times by changing the measuring point randomly to calculate the average value.

3.2.2.5 Evaluation of Dye Uptake

After dyeing, exhausted dye solutions were measured using an Agilent Cary 300 UV-Vis Spectrophotometer. First, a calibration plot of concentration vs. absorbance was produced at the wavelength of max absorption (λ_max) by measuring the absorbance of dye solutions with certain concentrations. Then the residual dye solution was diluted if necessary and measured at λ_max for absorbance. The concentration of the solution was calculated based on the

---

Figure 43 Dyeing procedure for both uncationized and cationized cotton fabrics
calibration plot. The percentage of dye uptake was calculated from \(100 \times (1 - A_0/A)\) where \(A_0\) and \(A\) are the absorbance of the dye solution before and after dyeing, respectively.

3.2.2.6 Colorfastness Tests

Colorfastness to laundering was measured using AATCC Test Method 61 using an Atlas LEF Launder-Ometer. A multi-fiber test fabric was attached to each sample to evaluate the staining and the test conditions were set according to the Test No. 2A. Colorfastness to crocking was measured according to AATCC Test Method 8. Both dry and wet crocking test were measured using the AATCC automated crockmeter. Colorfastness to light of the dyed samples was measured using test option 3 in AATCC Test Method 16. The color change after 20 and 40 continuous light-on operating hours of each dyed sample was measured using an Atlas Ci 3000+ Weather-Ometer. For all colorfastness tests, the evaluation of shade change and staining were made according to AATCC Evaluation Procedure 1 and AATCC Evaluation Procedure 2 using grey scale ratings from 1 to 5 where 5 implies no shade change.

Since the selected mercerized twill cotton fabrics are commercially used for making pants, the dyed fabrics were made into pant legs and applied with permanent press treatment. As the treatment conditions listed in Table 13, a pad-dry-cured method was used for the permanent press treatment. Also, Table 14 lists the chemicals used for the treatment. The treated pant legs were used to evaluate the colorfastness to repeated home laundering using AATCC Standardization of Home Laundry Test Conditions. Standard washing and tumble drying machines were used.
Table 13 Permanent press treatment conditions applied on dyed twill cotton fabrics

<table>
<thead>
<tr>
<th>Process</th>
<th>Conditions</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pad</td>
<td>Pressure: 40 PSI</td>
<td>-</td>
</tr>
<tr>
<td>Dry</td>
<td>110°C</td>
<td>1 min</td>
</tr>
<tr>
<td>Cure</td>
<td>177°C</td>
<td>1.5 min</td>
</tr>
</tbody>
</table>

Table 14 Chemicals used for the permanent press treatment

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domowet 500</td>
<td>2</td>
</tr>
<tr>
<td>Permafresh 113 (DMDHEU)</td>
<td>80</td>
</tr>
<tr>
<td>Marsil GSS</td>
<td>30</td>
</tr>
<tr>
<td>Turpex ACN New</td>
<td>20</td>
</tr>
<tr>
<td>Catalyst KR</td>
<td>25</td>
</tr>
<tr>
<td>Acetic acid (56%)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

3.2.3 Results and Discussion

3.2.3.1 Dyeing of Mercerized and Mercerized Cationized Cotton

Before dyeing, the barium activity number of the mercerized-cationized cotton was measured as 140 according to AATCC Test Method 89. It is higher than the mercerized cotton (BAN 130) due to the increase of available hydroxyl groups by cationization rather than the change of mercerization degree of the fabric.

As listed in Table 15, mercerized cotton samples were dyed with 7% to 10% on weight of fabric (owf) of Novacron Super Black R with very low (2:1) and high (15:1) liquor ratio. With changing liquor ratio and dye concentration, the concentration of alkali for each dyeing was modified to maintain a pH around 11.5 for mercerized cotton samples. Also, mercerized cationized cotton samples were dyed with 6% and 7% of Novacron Super Black R with 2:1
and 15:1 liquor ratio. For dyeing mercerized cationized cotton, the amount of alkali required for fixation is lower than conventional dyeing\textsuperscript{24,205}. Thus, the reduced amount of alkali was used for dyeing mercerized cationized cotton.

### Table 15 Dye and chemical concentrations for dyeing differently treated cotton

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dye conc.</th>
<th>Liquor ratio</th>
<th>(\text{Na}_2\text{SO}_4) g/L</th>
<th>(\text{Na}_2\text{CO}_3) g/L</th>
<th>50% NaOH g/L</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercerized</td>
<td>7%</td>
<td>2:1</td>
<td>110</td>
<td>11.5</td>
<td>6.9</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td></td>
<td>4</td>
<td>2.4</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>8%</td>
<td>2:1</td>
<td></td>
<td>12.8</td>
<td>7.7</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td></td>
<td>4</td>
<td>2.4</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>9%</td>
<td>2:1</td>
<td></td>
<td>14</td>
<td>8.4</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td></td>
<td>4</td>
<td>2.4</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>10%</td>
<td>2:1</td>
<td></td>
<td>15</td>
<td>9</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td></td>
<td>4</td>
<td>2.4</td>
<td>11.6</td>
</tr>
<tr>
<td>Mercerized Cationized</td>
<td>6%</td>
<td>2:1</td>
<td>0</td>
<td>7.2</td>
<td>4.3</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td></td>
<td>3</td>
<td>1.8</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>7%</td>
<td>2:1</td>
<td></td>
<td>8</td>
<td>4.8</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td></td>
<td>3</td>
<td>1.8</td>
<td>11.6</td>
</tr>
</tbody>
</table>

#### 3.2.3.2 Colorimetric Values and Color Strength

After dyeing, colorimetric values (\(L^*\), \(a^*\), \(b^*\), \(C^*\) and \(h^\circ\)) and K/S value of all dyed mercerized and mercerized-cationized cotton samples were measured (Table 16). To better compare the data, K/S value and \(L^*\) for each sample are presented in Figure 44 (the coordinate axis on the left is for K/S and the axis on the right is for \(L^*\)). In the figure, M and MC represent for mercerized and mercerized cationized cotton respectively, followed by the amount of dye applied.
Table 16 Colorimetric data and K/S of differently treated cotton dyed with varying dye concentration and liquor ratio

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dye conc.</th>
<th>Liquor ratio</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>hº</th>
<th>K/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercerized</td>
<td>7%</td>
<td>2:1</td>
<td>13.72</td>
<td>1.11</td>
<td>-0.35</td>
<td>1.16</td>
<td>342.3</td>
<td>940.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td>13.75</td>
<td>1.10</td>
<td>0.16</td>
<td>1.11</td>
<td>8.39</td>
<td>937.5</td>
</tr>
<tr>
<td></td>
<td>8%</td>
<td>2:1</td>
<td>13.66</td>
<td>1.27</td>
<td>0.38</td>
<td>1.32</td>
<td>16.61</td>
<td>954.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td>13.71</td>
<td>1.19</td>
<td>0.27</td>
<td>1.22</td>
<td>12.77</td>
<td>953.5</td>
</tr>
<tr>
<td></td>
<td>9%</td>
<td>2:1</td>
<td>13.66</td>
<td>1.31</td>
<td>0.36</td>
<td>1.36</td>
<td>15.45</td>
<td>967.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td>13.71</td>
<td>1.06</td>
<td>0.19</td>
<td>1.07</td>
<td>10.21</td>
<td>967.8</td>
</tr>
<tr>
<td></td>
<td>10%</td>
<td>2:1</td>
<td>13.64</td>
<td>1.34</td>
<td>0.48</td>
<td>1.42</td>
<td>19.76</td>
<td>985.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td>13.71</td>
<td>1.01</td>
<td>0.23</td>
<td>1.04</td>
<td>12.89</td>
<td>977.8</td>
</tr>
<tr>
<td>Mercerized Cationized</td>
<td>6%</td>
<td>2:1</td>
<td>13.68</td>
<td>0.74</td>
<td>0.24</td>
<td>0.78</td>
<td>18.09</td>
<td>995.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td>13.49</td>
<td>0.71</td>
<td>0.08</td>
<td>0.71</td>
<td>6.73</td>
<td>1001.2</td>
</tr>
<tr>
<td></td>
<td>7%</td>
<td>2:1</td>
<td>13.05</td>
<td>0.67</td>
<td>0.16</td>
<td>0.68</td>
<td>13.14</td>
<td>1073.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td>13.04</td>
<td>0.81</td>
<td>0.16</td>
<td>0.83</td>
<td>10.90</td>
<td>1072.4</td>
</tr>
</tbody>
</table>

Figure 44 Effect of liquor ratio and dye concentration on shade depth and color strength of mercerized and mercerized cationized cotton

The results of L* and K/S show that, for all mercerized and mercerized-cationized cotton
dyed with shaded CI Reactive Black 5 (Novacron Super Black R), increasing the liquor ratio from 2:1 to 15:1 has no significant influence on the obtained shade depth and color strength. Even though a lower liquor ratio is expected to result in a higher efficiency of fixation as illustrated by Equation 8, it is not a critical factor here since very high concentrations of dye were applied and the difference in unfixed dye is not significant enough to obtain an appreciable difference.

To evaluate whether there are significant difference in both L* and K/S between the samples dyed with varying dye concentrations, student’s t-tests with significance value (α) set as 0.05 have been done using JMP software. As show in Figure 45, there is no significant difference in L* among mercerized cotton samples dyed with different dye concentrations. Thus, for mercerized cotton, the obtained shade depth (L*) was not influenced by the amount of dye applied. In another aspect, the t-tests of K/S value (Figure 46) show that increasing the dye concentration from 7% to 10% significantly increased the color strength (K/S value). As indicated by the K/S value, a slight extra amount of dye can be fixed on the fabric with dye concentration increased from 7% to 10%. However, the limited amount of extra dye fixed can hardly help to obtain a deeper black shade (lower L*) on mercerized cotton.
In comparison, mercerized-cationized cotton dyed with 6% dye has a similar shade depth but higher color strength than all mercerized samples dyed with 7%-10% (owf) of CI Reactive Black 5. Increasing the dye from 6% to 7% (owf) significantly increased both the depth and color strength of dyed mercerized-cationized cotton. Thus, with CI Reactive Black 5 (Novacron Super Black R) applied, mercerized-cationized cotton has significant advantage in producing ultra-deep shade compared to mercerized cotton.

Also, as noted by the a*, b*, and chroma, mercerized-cationized cotton produced not only a
deeper, but also a truer black shade, in terms of closer proximity to the origin coordinate in the CIE color space. This is assumed and attributed to cationic cotton being able to more readily exhaust and fix the shading components as compared to the conventional dyeing.

3.2.3.3 Dye Uptake

Dye uptake of all samples were measured and presented in Figure 47. The dye uptake percentages show that, for mercerized cotton dyed with conventional method, lower liquor ratio allows a higher degree of dye exhaustion. Since there is no corresponding increase in shade depth and strength, most of the dye exhausted by low liquor ratio was unfixed and must be removed by rinsing. With the increase of dye concentration from 7% to 10%, dye uptake of mercerized cotton decreased, especially for samples dyed with 15:1 liquor ratio. However, due to the ionic attraction, all mercerized-cationized samples have higher than 99% of dye uptake and the effects of liquor ratio and dye concentration are not significant.

![Figure 47 Effect of liquor ratio and dye concentration on dye uptake of mercerized and mercerized cationized cotton](image-url)
3.2.3.4 Colorfastness Properties

To evaluate the effect of cationization treatment, dye concentration, and liquor ratio on colorfastness properties, all dyed samples were tested for colorfastness to laundering, crocking, and light. As can be seen from Table 17, all samples have little color change after laundering while mercerized cationized samples have lighter staining on adjacent cotton. This indicates a slightly improved colorfastness to laundering by cationization. All samples have excellent colorfastness to dry crocking and identical colorfastness to wet crocking. The relatively poor colorfastness to wet crocking may because of the very deep shade of all samples, which resulted in high amount of dye transferred during rubbing. Also, the samples showed little color change after even 40 continuous light-on operating hours, which indicates excellent colorfastness to light of all samples. Thus, in consideration of staining performance, applying cationization slightly improved the colorfastness to laundering. Changing dye concentration and liquor ratio has no influence on colorfastness properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dye Conc.</th>
<th>Liquor Ratio</th>
<th>Wash fastness</th>
<th>Rub fastness</th>
<th>Light fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Color Change</td>
<td>Staining</td>
<td>Dry</td>
</tr>
<tr>
<td>Mercerized</td>
<td>7%</td>
<td>2:1</td>
<td>5</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td>5</td>
<td>3.5-4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>8%</td>
<td>2:1</td>
<td>5</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td>5</td>
<td>3.5-4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>9%</td>
<td>2:1</td>
<td>5</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td>5</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>10%</td>
<td>2:1</td>
<td>5</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td>5</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Mercerized Cationized</td>
<td>6%</td>
<td>2:1</td>
<td>5</td>
<td>4.5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td>5</td>
<td>4.5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>7%</td>
<td>2:1</td>
<td>5</td>
<td>4.5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15:1</td>
<td>5</td>
<td>4.5</td>
<td>5</td>
</tr>
</tbody>
</table>
To evaluate the effect of cationization on colorfastness to repeated home laundering, mercerized cationized cotton dyed with 6% Remazol Black B (2:1 LR) and mercerized cotton dyed with 7% Remazol Black B (2:1 LR) were exposed to up to 30 cycles of repeated home laundering. Figure 48 and Figure 49 present the changes in colorimetric data of the dyed samples after 5, 10, 15, 20, 25, and 30 laundering cycles.

Figure 48 Changes in L* and K/S of dyed fabrics after repeated home laundering
As presented in Figure 48, after the first 5 cycles of home laundering, the color depth of both mercerized and mercerized cationized samples increased slightly. With the increase of laundering cycles, the depth and color strength of both dyed samples gradually decreased. However, with up to 30 cycles of repeated home laundering, the changes in L* and K/S of both dyed mercerized and mercerized cationized samples are relatively small. This indicates that both samples have good performance in retaining the color depth and the influence of cationization treatment is not significant. In another aspect, Figure 49 compares a* and b* values of the two fabrics after the treatment and different home laundering cycles. Compared with the mercerized cotton dyed with 7% of dyes, the mercerized cationized cotton dyed with 6% of dyes has smaller changes in a* and b* values after both the permanent press treatment and the laundering. Thus, mercerized cationized cotton has better performance in maintaining the hue of the dyed fabrics.

Figure 49 Changes in a* and b* of dyed fabrics after repeated home laundering
3.2.4 Conclusions

For conventional ultra-deep dyeing with shaded Reactive Black 5 (Novacron super black R), the shade depth is not influenced by liquor ratio or dye concentration. However, the color strength of mercerized cotton slightly increased as the increase of dye amount from 7% to 10% (owf). Although higher dye uptake values were observed for samples dyed with lower liquor ratio, there is no corresponding increase in either shade depth or color strength. This indicates a large amount of unfixed dye for all conventional dyeings that must be removed and discharged into the effluent.

In comparison, mercerized-cationized cotton dyed with 6% dye has a similar shade depth but higher color strength than all mercerized samples. Increasing dye amount from 6% to 7% (owf) further increased both the depth and color strength of dyed mercerized cationized cotton. Due to the ionic attraction, all mercerized cationized samples have higher than 99% of dye uptake while liquor ratio has no influence on the dyeing performance. Compared with conventionally dyed mercerized cotton, mercerized cationized cotton has slightly improved colorfastness to laundering and color retention performance while the performances on other colorfastness properties of both fabrics are comparable. Liquor ratio and dye concentration have no significant influence on any colorfastness property. In conclusion, mercerized cationized cotton has significant advantages in producing ultra-deep black dyeing than mercerized cotton.
CHAPTER 4 REAL-TIME DYEBATH MONITORING OF CATIONIZED COTTON
FOR LEVELNESS CONTROL


Abstract: Chemical cationization of cotton has been a subject of increased interest due to the ability of cationized cotton to attract negatively charged dyes, which eliminates the use of electrolytes during dyeing and increases color yield. However, electrostatic attractions between cationized cotton and anionic dyes also result in significantly increased dye strike rate, which may cause levelness problems, especially when light to medium shades are required. In this study, cotton fabric cationized using 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC) was used to investigate the method for obtaining appropriate dye strike rate and level reactive dyeing on cationized cotton. To effectively control the dyeing kinetics of reactive dyes on cationized cotton, real-time exhaustion of six commercially significant reactive dyes was monitored. The influence of temperature, dye structure, and addition of soda ash on dyeing kinetics and levelness of cationized cotton were evaluated.

Keywords: Cotton, Cationization, Reactive dye, Dyeing kinetics, Real-time monitoring, Levelness
4.1.1 Introduction

With advantages in hydrophilicity, breathability, biodegradability, and relatively low cost, cotton is one of the predominant raw materials in the textile industry. The major component of cotton is cellulose, which is a linear carbohydrate polymer consisting of β-D-glucose units covalently linked by 1,4-glycosidic bonds. The hydroxyl groups present on glucose units enable dye fixation and other chemical reactions on cotton. As the only kind of dye which can form covalent bonds with the hydroxyl groups on cellulose, fiber reactive dyes are commercially widely used due to the wide range of brilliant shades with excellent wet fastness properties. However, the affinity for cotton of most commercially available reactive dyes is poor since both reactive dyes and cotton carry anionic charges in water. Even with high concentrations of electrolytes, such as sodium sulfonate and sodium chloride, added to suppress the repulsive forces between negative charges of the dye and the fiber, the exhaustion rate of most reactive dyes is still relatively low, with around 40% of the dye in effluent. Therefore, conventional reactive dyeing is not an environmentally benign process due to the discharge of a highly colored and saline dyebath.

The use of cationic reagents, such as 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC), to produce cationized cotton has been a subject of increased interest due to the ability of positively charged sites on cotton to attract negatively charged dyes. With electrostatic attractions between cationized cotton and anionic dyes, increased dye exhaustion and color yield can be obtained without adding electrolytes during dyeing. Besides higher dying efficiency and improved wet fastness properties, other advantages of cationization include shorter dyeing and afterwashing cycle, which results in saving in water.
and energy\textsuperscript{112}.

In the previous chapter, ultra-deep shades with increased dye uptake and color yield were obtained on mercerized cationized cotton. For ultra-deep shades on cationized cotton, levelness of dyeing is not a critical issue. However, if shades with light to medium depth are required on cotton with relatively high cationization level, dyeing of cationized cotton may suffer from the problem of poor levelness. This is because, in exhaust dyeing, the levelness of dyeing is highly related to the dye strike rate. With ionic attractions exist between anionic dyes and cationic cotton fibers, dye molecules are adsorbed on fiber surface rapidly by ion exchange. Previously, Acharya et al. evaluated the effect of the cationization level on the exhaustion kinetics of reactive dyes on cationized cotton fabrics\textsuperscript{157}. However, there are very limited studies available on the influence of other factors, such as dye structure, temperature, addition of soda ash and leveling agents on exhaustion kinetics of reactive dyes on cationized cotton.

In this study, cotton fabric was cationized with CHPTAC. To effectively control the dyeing kinetics of reactive dyes and obtain level dyeing on the cationized cotton, real-time exhaustion of six commercially significant reactive dyes was monitored. The influence of temperature, dye structure, and soda ash on dyeing kinetic and levelness of cationized cotton were evaluated.
4.1.2 Experimental

4.1.2.1 Materials

Cationized cotton yarns were provided by ColorZen, USA. For the cationization of the yarns, the reagent used was 3-chloro-2-hydroxy propyltrimethylammonium chloride (CHPTAC). Six commercial reactive dyes (Table 18) were obtained from Everlight Chemical Inc., Taiwan. The dye structures are presented in Figure 50 (Everzol dyes) and Figure 51 (Evercion dyes). The chemicals used for scouring the cotton fabrics include Marsperse 6000 (polyacrylate, textile dispersant) and Marlube CMN (polyacrylamide, non-ionic textile dispersant) from Marlin Co., USA and Sultafon D (non-ionic scouring agent) from Bozzetto Group, Italy. Other chemicals used, including anhydrous sodium acetate, glacial acetic acid, sodium carbonate, urea, and Triton X-100 were supplied by Fisher Scientific, USA and Sigma-Aldrich, USA.

Table 18 Commercial dyes used for monitoring

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>CI generic name</th>
<th>Reaction temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everzol Red 3BS</td>
<td>CI Reactive Red 239</td>
<td></td>
</tr>
<tr>
<td>Everzol Yellow 3RS</td>
<td>CI Reactive Yellow 176</td>
<td>60°C</td>
</tr>
<tr>
<td>Everzol Blue BRF</td>
<td>CI Reactive Blue 221</td>
<td></td>
</tr>
<tr>
<td>Evercion Red H-E7B</td>
<td>CI Reactive Red 141</td>
<td></td>
</tr>
<tr>
<td>Evercion Yellow H-E4R</td>
<td>CI Reactive Yellow 84</td>
<td>80°C</td>
</tr>
<tr>
<td>Evercion Blue H-ERD</td>
<td>CI Reactive Blue 160</td>
<td></td>
</tr>
</tbody>
</table>
Figure 50 Molecular structures of Everzol dyes
Figure 51 Molecular structures of Evercion dyes
4.1.2.2 Preparation of Cationized Cotton Fabrics

The 20/1 cationized cotton yarns provided by ColorZen were knitted into jersey fabric with the density of 107 g/m² by Cotton Inc., USA. After knitting, mild scour with soda ash was applied on the cotton fabrics. The liquor ratio for scouring was controlled as 10:1 to 15:1. The chemicals added for scouring included 2 g/L Marsperse 6000, 1 g/L Sultafon D, 1 g/L Marlube CMN, and 2 g/L soda ash. The cotton fabrics were scoured at 82°C for 20 minutes before warm rinsing. Finally, 0.5 g/L 56% acetic acid was added for neutralizing. The final pH of the fabrics after rinsing was controlled as 6-7. The prepared cationized cotton was used directly for dye exhaustion rate monitoring.

4.1.2.3 Nitrogen Content Analysis

The percentage of nitrogen present in the cotton fabric was measured in duplicate and used as an indicator of the level of cationization. The analysis was conducted using a PE 400 CHE Elemental Analyzer using the classical Pregal and Dumas methods. After being cut into 2 mm squares, the cotton samples were combusted in a pure oxygen environment before elemental analysis¹⁸⁷.

4.1.2.4 Sample Dyeing

Cationized cotton samples were dyed using an Ahiba Spectradye Plus lab dyeing machine at a liquor ratio of 15:1. The dyeing procedure is presented in Figure 52 (no salt, 15 g/L Na₂CO₃). After dyeing, cationized cotton fabrics were rinsed thoroughly, then neutralized with citric acid and rinsed again. Finally, the samples were air dried at room temperature.
4.1.2.5 Dyebath Monitoring Using the Hue-Metrix Monitor System

To measure dye concentration and monitor the dye exhaustion rates on cationized cotton, a HueMetrix Dye-It-Right system was used. Before the dyeing process can be monitored, calibration should be made for each individual dye. In the calibration process, dye solutions with different concentrations: 0.05, 0.1, 0.2, 0.5, 1 and 2 g/L (cover the range of concentrations expected to occur during the dyeing process) were prepared and each concentration was injected into the machine for five times. The absorbance value at the wavelength corresponding to the maximum absorbance ($\lambda_{\text{max}}$) of a specific dye was determined using the integrated UV-Vis spectrophotometer. A validated calibration plot of concentration vs. absorbance was generated for each dye.

To enable real-time dyebath monitoring, the Mathis JFL dyeing machine interfaces with the HueMetrix Monitor through a circulation loop to facilitate the flow of dyebath between the dyeing machine and instrument continuously during the dyeing (Figure 53). During the dyeing process, the HueMetrix automatically collects a microsample (0.1 ml) equivalent to a fraction of a drop from the dyebath every 90 s. The absorbance at $\lambda_{\text{max}}$ of the sample was
measured using the integrated UV–Vis spectrophotometer and the dye concentration in bath was calculated based on the calibration curve pre-determined for the dye. The percentage of dye exhaustion at certain time was calculated from $100 \times \left(1 - \frac{C_0}{C_t}\right)$ where $C_0$ and $C_t$ are the concentrations of the dye in the dyebath at the beginning of dyeing and at time $t$, respectively.

For all dyeing, after monitoring at selected conditions for certain time, the dyeing temperature was increased to the reaction temperature of the dye and soda ash was added if necessary to enable the fixation of dyes. After dyeing, all samples were rinsed thoroughly with both warm and cold water to remove unfixed dyes.

Since reactive dyes were selected for monitoring, carrier fluid B was used for both calibration and monitoring. Fluid B was composed of 8.2 g/L anhydrous sodium acetate, 6 g/L glacial acetic acid, 0.05 g/L Triton X-100, and deionized water. It conditions the sample to ensure consistent sample analysis. The details of operating the HueMetrix system were described in the HueMetrix Technical Manual.$^{209}$

![HueMetrix Monitor System](Figure 53 Hue-Metrix Monitor System)
4.1.2.6 Color Measurement and Determination of Levelness

Reflectance spectra of all dyed samples were measured using an X-Rite® Datacolor Spectraflash 600X spectrophotometer equipped with iControl software from X-Rite. L*, a*, b*, C*, h° and K/S values of the dyed samples were calculated using the following instrument settings (illuminant D65, 10° supplemental standard observer, specular included, UV included). While testing, the sample was folded two times. Each sample was measured ten times by changing the measuring point randomly to calculate the average value.

To evaluate levelness of dyed fabrics, first, ten measurements of ΔEcmc were taken in one place on the fabric to obtain a standard deviation of the instrument σinstrument. Next, ten measurements of ΔEcmc were taken along and across the sample at random to determine the standard deviation of the sample σsample. The overall standard deviation for ΔEcmc represented as σ was calculated by210:

\[
\sigma = \left( \sigma_{\text{sample}}^2 - \sigma_{\text{instrument}}^2 \right)^{1/2}
\]

Equation 9

4.1.3 Results and Discussion

4.1.3.1 Calibration of Everzol and Evercion Dyes Using Hue-Metrix Monitor

With the calibration method described in experimental session, all six dyes were calibrated using the Hue-Metrix Monitor. The details of the calibration information for each dye are summarized in Table 19, including the wavelength of maximum absorbance, the slope coefficient between concentration (g/L) and absorbance (Absorbance = Slope coefficient * Conc.), and the coefficient of determination (R-squared) of the calibration curve.
Table 19 Calibration information of Everzol and Evercion dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>Color Index (C.I.)</th>
<th>Wavelength of Max Absorption ($\lambda_{\text{max}}$)</th>
<th>Slope Coefficient</th>
<th>R-squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everzol Red 3BS</td>
<td>Reactive Red 239</td>
<td>550 nm</td>
<td>0.6971</td>
<td>0.9998</td>
</tr>
<tr>
<td>Everzol Yellow 3RS</td>
<td>Reactive Yellow 176</td>
<td>426 nm</td>
<td>0.4656</td>
<td>0.9996</td>
</tr>
<tr>
<td>Everzol Blue BRF</td>
<td>Reactive Blue 221</td>
<td>620 nm</td>
<td>0.4094</td>
<td>0.9995</td>
</tr>
<tr>
<td>Evercion Red H-E7B</td>
<td>Reactive Red 141</td>
<td>552 nm</td>
<td>0.5758</td>
<td>1.0000</td>
</tr>
<tr>
<td>Evercion Yellow H-E4R</td>
<td>Reactive Yellow 84</td>
<td>415 nm</td>
<td>0.3931</td>
<td>1.0000</td>
</tr>
<tr>
<td>Evercion Blue H-ERD</td>
<td>Reactive Blue 160</td>
<td>626 nm</td>
<td>0.2889</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

In Table 19, the R-squared values of all dyes are higher than 0.999, which indicates that all calibration curves fit the data very well and the response variations were fully explained by the linear calibration models. Thus, all the calibration models obtained are valid.

4.1.3.2 Evaluation of Cationization Degree: Nitrogen Content Analysis

As an indication of cationization degree, nitrogen content of the cationized cotton fabrics was measured after sufficient washing and scouring. The percentage of nitrogen fixed on the cationized cotton fabric is 0.27%. By referring to previous research on cationization of cotton using CHPTAC\textsuperscript{24}, this level of cationization equals the application of 100 to 150 g/L CHPTAC (65% commercial product) using a cold pad-batch method with fixation rate around 50%.
4.1.3.3 Determination of Dye Concentration for Monitoring

To find out the appropriate dye concentration to be applied on cationized cotton fabrics for monitoring, various concentrations of Everzol Red 3BS were applied on cationized cotton fabrics using the sample dyeing procedure (Figure 52). After dyeing, colorimetric values of dyed cotton fabrics were measured using a reflectance spectrophotometer. The dye concentrations of left dyebath solutions were measured using the HueMetrix monitor based on the calibration curve obtained. All the data are listed in Table 20 and the final dyebaths are presented in Figure 54 (from left to right: increase of initial dye concentration).

Table 20 Colorimetric data and dyebath concentrations of cationized cotton dyed with different amount of Everzol Red 3BS

<table>
<thead>
<tr>
<th>Applied dye conc. (% owf)</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h°</th>
<th>Dye conc. after dyeing (g/L)</th>
<th>Dye uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>45.71</td>
<td>57.57</td>
<td>-3.66</td>
<td>57.69</td>
<td>356.37</td>
<td>0.005</td>
<td>98.5%</td>
</tr>
<tr>
<td>1</td>
<td>40.42</td>
<td>58.2</td>
<td>0.58</td>
<td>58.2</td>
<td>0.57</td>
<td>0.012</td>
<td>98.2%</td>
</tr>
<tr>
<td>1.5</td>
<td>38.18</td>
<td>57.91</td>
<td>2.9</td>
<td>57.99</td>
<td>2.87</td>
<td>0.018</td>
<td>98.2%</td>
</tr>
<tr>
<td>2</td>
<td>36.84</td>
<td>57.9</td>
<td>4.71</td>
<td>58.1</td>
<td>4.65</td>
<td>0.027</td>
<td>98.0%</td>
</tr>
<tr>
<td>2.5</td>
<td>35.23</td>
<td>57.48</td>
<td>6.71</td>
<td>57.87</td>
<td>6.66</td>
<td>0.054</td>
<td>96.8%</td>
</tr>
<tr>
<td>3</td>
<td>34.32</td>
<td>56.94</td>
<td>8.17</td>
<td>57.52</td>
<td>8.17</td>
<td>0.092</td>
<td>95.4%</td>
</tr>
</tbody>
</table>

Figure 54 Final dyebaths for different concentrations of Everzol Red 3BS
As presented in Table 20 and Figure 54, with the increase of applied dye concentration, the concentration of dye in the final dyebath also increased. When less than 2% of the dye was added, there is very little dye left in the solution. As previously mentioned, if dyes can be fully exhausted by cationized cotton, the problem in levelness of dyeing is more significant. It is more difficult to control the dye strike rate and levelness of dyeing when lower concentration of dyes was applied on the same cationized cotton fabric. Thus, 1% of dye was selected for further monitoring in order to find an efficient way which can be applied to most situations to slow down the exhaustion of dyes and help obtain level dyeing on cationized cotton.

4.1.3.4 Repeatability of Dyebath Monitoring Using HueMetrix

To examine the repeatability of the dyebath monitoring method, 1% of the Everzol Red 3BS was applied on the cationized cotton fabric for three times (Figure 55). All of the monitorings were conducted at 37°C with 15:1 liquor ratio and 15 g/L soda ash was added at the beginning of dyeing.
4.1.3.5 Dyeing of Everzol and Evercion Dyes on Cationized Cotton

In this section, prepared cationized cotton fabrics were dyed with Everzol and Evercion dyes at 37°C. This temperature was selected since it is usually the lowest applicable dyeing temperature in industry. For all dyeings, 1% owf of dye was applied with 15:1 liquor ratio. Also, 15 g/L soda ash was added into the bath before the dye was added. The dye exhaustion monitoring of all six dyes at 37°C are presented in Figure 56.
In the figure, small differences can be noticed for the exhaustion curves of different dyes. Generally, Everzol dyes have slightly faster dye strike rate than Evercion dyes. The difference in dye strike rates are expected to be related to the structure of the dyes. As presented in Figure 50 and Figure 51, both Everzol dyes and Evercion dyes are bifunctional dyes. Everzol dyes are heterobifunctional dyes with a monochlorotriazine and a vinylsulphone group while Evercion dyes are monobifunctional dyes with two monochlorotriazine groups. Thus, Everzol dyes require a reaction temperature around 60°C and Evercion dyes require at least 80°C to enable the reaction with cellulose. Since the monitoring temperature is 37°C which is much lower than the reaction temperature of both kinds of dyes, the difference in reactive groups should have no influence on dyeing kinetics of the dyes.
In another aspect, the overall molecule structure of the dye, such as the molecular size and number of sulfonate groups, are more important factors for the exhaustion kinetics of the dyes. Before monitoring, Evercion dyes are expected to have higher dye strike rate since all of them are larger dye molecules with higher number of negatively charged groups, such as sulfonate group. However, the monitoring curves in Figure 56 indicate that the anionic groups on reactive dyes are not the only key factor on dyeing kinetics of reactive dyes on cationized cotton. Since the monitoring curves of all six dyes are relatively close and the influence of dye structures on dyeing kinetics on cationized cotton are complex, more experiments using dyes with different structures are needed before firm conclusions can be made.

As an indication of levelness of dyed fabrics, overall standard deviation for $\Delta E_{cmc}$ ($\sigma$) of each fabric was measured and presented in Table 21 with other colorimetric data. A higher $\sigma$ value indicates worse levelness of the dyed fabric. Based on previous research, the $\sigma$ of conventionally dyed cotton fabric with good levelness is around 0.2. Usually, a $\sigma$ lower than 0.5 is required for acceptable dyeing levelness.

<table>
<thead>
<tr>
<th>Dye</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h°</th>
<th>Levelness ($\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everzol Red 3BS</td>
<td>40.91</td>
<td>55.29</td>
<td>-1.62</td>
<td>55.31</td>
<td>358.32</td>
<td>0.617</td>
</tr>
<tr>
<td>Everzol Yellow 3RS</td>
<td>64.50</td>
<td>27.11</td>
<td>68.31</td>
<td>73.49</td>
<td>68.35</td>
<td>0.969</td>
</tr>
<tr>
<td>Everzol Blue BRF</td>
<td>35.54</td>
<td>-1.55</td>
<td>-27.04</td>
<td>27.08</td>
<td>266.72</td>
<td>1.423</td>
</tr>
<tr>
<td>Evercion Red H-E7B</td>
<td>41.72</td>
<td>54.17</td>
<td>-1.50</td>
<td>54.19</td>
<td>358.41</td>
<td>0.516</td>
</tr>
<tr>
<td>Evercion Yellow H-E4R</td>
<td>65.13</td>
<td>22.44</td>
<td>63.49</td>
<td>67.34</td>
<td>70.53</td>
<td>0.637</td>
</tr>
<tr>
<td>Evercion Blue H-ERD</td>
<td>42.43</td>
<td>-4.15</td>
<td>-24.86</td>
<td>25.20</td>
<td>260.52</td>
<td>1.000</td>
</tr>
</tbody>
</table>
As presented in the table, all six dyeing resulted in relatively poor levelness on cationized cotton, especially for Everzol Blue BRF, Evercion Blue H-ERD, and Everzol Yellow 3RS. By combining the levelness data and the dye exhaustion curves in Figure 56, it was found that the levelness of dyeing is not directly correlated with the dye strike rates. The three Everzol dyes have very close exhaustion curves but very different levelness performance. Thus, dye structure also plays an important role in levelness of dyed cationized cotton fabrics.

For all six reactive dyes evaluated, the amount of dye applied has been fully exhausted in 5 to 10 minutes and the levelness of dyed cationized fabrics are relatively poor. Thus, control of exhaustion rate is necessary for obtain level dyeing on cationized cotton with the evaluated reactive dyes.

4.1.3.6 The Effect of Temperature on Dye Strike Rate and Levelness

To evaluate the effect of temperature on dyeing kinetics and levelness, dye strike rates of all three Everzol dyes were monitored at 30°C, 37°C, and 60°C since 30°C is the lowest temperature that can be run in the lab and 60°C is the reaction temperature of Everzol dyes. Other conditions including dye concentration (1%), liquor ratio (15:1), and soda ash concentration (15 g/L) were all controlled the same as previous experiments. Figure 57 shows the monitoring curves of Everzol Red 3BS at 30°C, 37°C, and 60°C.
As the figure shows, with the increase of temperature, the dye strike rate was increased. It indicates that the control of dyeing temperature can help reduce the exhaustion rate of dyes on cationized cotton in some degree. However, even with a dyeing temperature as low as 30°C, the dyes were fully exhausted in around 10 minutes, which is still too fast.

As presented in Figure 58 and Figure 59, Everzol Yellow 3RS and Everzol Blue BRF were also monitored at the same temperatures. As proved by the exhaustion curves, the influences of temperature on dye exhaustion of all three Everzol dyes are similar. The exhaustion rate of the dyes was slightly reduced by lowering the dyeing temperature but the effect is relatively small.
For Evercion dyes, instead of single dye monitoring, the mixture of the same amount of all three Evercion dyes was monitored at different temperatures. Since the reaction temperature
of Evercion dyes is 80°C, the temperatures selected are 30°C, 37°C, and 80°C. The dye mixture for monitoring contains 0.35% of each Evercion dye, including Evercion Red H-E7B, Yellow H-E4R, and Blue H-ERD. Thus, the total amount of dye applied is 1.05%, which is close to the single dye concentration (1%) applied in previous experiments. Other dyeing conditions such as liquor ratio and soda ash concentration were also kept the same. The obtained exhaustion curves are presented in Figure 60.

![Exhaustion Curves](image)

**Figure 60** The influence of temperature on exhaustion of Evercion dyes

Similar to Everzol dyes, the exhaustion of the Evercion dye mixture on cationized cotton was slightly slowed down by lowering the dyeing temperature. Since the mixture of the same
amount of three Evercion dyes was used for monitoring, it is easy to compare the affinity for
the cationized cotton of the three Evercion dyes. In the figure, with a lower dyeing
temperature, the difference in exhaustion curves between the dyes is more significant. It is
clear that at 30°C the dye strike rate of Red H-E7B is faster than Blue H-ERD, which is
faster than Yellow H-E4R.

To evaluate the influence of dyeing temperature on levelness of dyed cationized cotton
fabric, overall standard deviation for $\Delta E_{cmc}$ ($\sigma$) of each fabric was measured as an indication
of levelness and presented in Table 22.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Temperature (°C)</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>$h^\circ$</th>
<th>Levelness ($\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everzol Red 3BS</td>
<td>30</td>
<td>40.29</td>
<td>54.23</td>
<td>-1.65</td>
<td>54.26</td>
<td>358.26</td>
<td>0.596</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>40.91</td>
<td>55.29</td>
<td>-1.62</td>
<td>55.31</td>
<td>358.32</td>
<td>0.617</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>38.10</td>
<td>55.01</td>
<td>0.08</td>
<td>55.01</td>
<td>0.08</td>
<td>0.994</td>
</tr>
<tr>
<td>Everzol Yellow 3RS</td>
<td>30</td>
<td>65.30</td>
<td>28.02</td>
<td>69.19</td>
<td>74.65</td>
<td>67.95</td>
<td>0.881</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>64.50</td>
<td>27.11</td>
<td>68.31</td>
<td>73.49</td>
<td>68.35</td>
<td>0.969</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>63.29</td>
<td>28.02</td>
<td>69.20</td>
<td>74.66</td>
<td>67.96</td>
<td>1.072</td>
</tr>
<tr>
<td>Everzol Blue BRF</td>
<td>30</td>
<td>35.79</td>
<td>-1.02</td>
<td>-28.13</td>
<td>28.15</td>
<td>267.92</td>
<td>0.884</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>35.54</td>
<td>-1.55</td>
<td>-27.04</td>
<td>27.08</td>
<td>266.72</td>
<td>1.423</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>32.45</td>
<td>0.16</td>
<td>-29.04</td>
<td>29.04</td>
<td>270.32</td>
<td>2.400</td>
</tr>
<tr>
<td>Evercion Dye Mixture</td>
<td>30</td>
<td>36.97</td>
<td>14.21</td>
<td>1.41</td>
<td>14.28</td>
<td>5.67</td>
<td>0.779</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>36.82</td>
<td>14.72</td>
<td>1.70</td>
<td>14.82</td>
<td>6.59</td>
<td>1.618</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>36.51</td>
<td>14.35</td>
<td>2.85</td>
<td>14.63</td>
<td>11.23</td>
<td>3.263</td>
</tr>
</tbody>
</table>
For all dyes applied, including single Everzol dyes and Evercion dye mixture, the decrease of dyeing temperature improved the levelness of dyed cationized cotton. However, for different dyes, the influence of dyeing temperature on levelness is different. For example, when applied at 30°C, the levelness of the fabrics dyed with Everzol Yellow 3RS and Everzol Blue BRF are very close (σ around 0.88). With application temperature increased to 60°C, the cationized fabric dyed with Everzol Yellow 3RS has much better levelness than the fabric dyed with Everzol Blue BRF.

Even though the effect of dyeing temperature on dye exhaustion rate is not very significant, better levelness for all dyes applied was obtained by lowering the dyeing temperature. In consideration of levelness, reactive dyes should be applied on cationized cotton at low temperature. However, the selection of dyeing temperature is limited by the application conditions and in industry it is hard to use a dyeing temperature lower than 37°C. Thus, only controlling the dyeing temperature is not sufficient enough to obtain level reactive dyeing on cationized cotton.

4.1.3.7 The Effect of Soda Ash on Dye Strike Rate and Levelness

In conventional reactive dyeing, alkali such as Na₂CO₃ or NaOH is required to create alkaline conditions and enable the fixation of dyes on cotton. Previous research indicate that compared with conventional reactive dyeing, the concentration of alkali for dyeing cationized cotton can be reduced but a certain amount alkali is still needed in the dyeing process of cationized cotton to ensure good color yield and colorfastness properties, especially for vinyl sulfone dyes²⁴. For the monitoring conducted in the previous section, all dyeings were
conducted with soda ash added in the bath initially. In this section, to evaluate the effect of soda ash on exhaustion kinetics and levelness of dyeing, monitoring with no soda ash was conducted for both Everzol and Evercion dyes.

The exhaustion of 1% Everzol Red 3BS on cationized cotton with no soda ash added at the beginning was monitored and compared to the exhaustion with 15 g/L soda ash added initially (Figure 61). For both dyeings, the initial monitoring temperature was controlled as 37°C while other dyeing conditions were kept the same as previous experiments. In Figure 61, the red arrows indicate the time period of increasing the dyeing temperature from 37°C to 60°C. For the monitoring without soda ash in initial bath (the dotted line), the blue arrow indicates the addition of 15 g/L of soda ash to enable the dye fixation, while no additional alkali is needed for the exhaustion with soda ash in initial bath.

![Figure 61 The influence of soda ash on exhaustion of Everzol Red 3BS](image)
By comparing the two curves, it was noticed that the influence of soda ash on dyeing kinetics of Everzol Red 3BS is relatively small. With soda ash added initially, the dyes exhausted slightly faster than the one without soda ash. However, without the addition of soda ash, the dyes exhausted more completely on the cationized fabric, as indicated by the slightly higher exhaustion percentage. This is because the sulfatoethyl sulfone groups on Everzol dyes have ionic interactions with the cationic sites on treated cotton while the addition of soda ash eliminates sulfate ions from the sulfatoethyl sulfone groups and convert them into vinyl sulfone groups.

The effects of soda ash on dyeing kinetics of Everzol dyes were also evaluated by using the mixture of all three Everzol dyes. The dye mixture for monitoring contains 0.35% of each Everzol dye, including Everzol Red 3BS, Yellow 3RS, and Blue BRF. The exhaustion curves of the dye mixture on cationized cotton with and without soda ash in initial dyebath were presented in Figure 62.
The results indicate that the addition of soda ash in initial dyebath slightly increased the dye strike rate of Everzol dyes on cationized cotton, which agrees with the single dye exhaustion of Everzol Red 3BS in Figure 61. Thus, both figures suggest that the presence of soda ash has relatively small influence on the dyeing kinetics of Everzol dyes. With the addition of soda ash, the Everzol dyes were exhausted slightly faster but the difference is not significant.

Similarly, the effect of soda ash on dyeing kinetics was also evaluated for Evercion Red H-E7B (Figure 63) and Evercion dye mixture (Figure 64). For both monitoring, the initial dyeing temperature is 37°C and other dyeing conditions were kept the same as previous experiments. As presented in Figure 63, the addition of soda ash has significant influence on the dyeing kinetics of Evercion Red H-E7B. Without soda ash in the initial dyebath, the dye...
strike rate of Evercion Red H-E7B on cationized cotton is very slow. This is different from the performance of Everzol dyes. Thus, the influence of soda ash on dyeing kinetics of reactive dyes on cationized cotton is highly related to the structure of the dye. From the exhaustion curve of Evercion Red H-E7B without soda ash added initially, it was also noticed that with the dyeing temperature increased to 80°C (as indicated by the red arrows) the dye strike rate increased significantly. Thus, the dyeing kinetics of Evercion Red H-E7B can be effectively controlled by controlling the dyeing temperature and addition of soda ash.

Figure 63 The influence of soda ash on exhaustion of Evercion Red H-E7B

Also, the dye mixture of three Evercion dyes was monitored with and without soda ash in the initial dyebath (Figure 64). The dye mixture for monitoring contains 0.35% of each Evercion dye, including Evercion Red H-E7B, Yellow H-E4R, and Blue H-ERD.
Clearly, for all three Evercion dyes, adding soda ash changes the dyeing kinetics on cationized cotton. Eliminating the addition of soda ash in initial dyebath significantly slowed down the exhaustion speed of the Evercion dyes. The exhaustion curves, especially the curves without soda ash added, also indicate that the affinity of Evercion Red H-E7B and Evercion Blue H-ERD for the cationized cotton is higher than Evercion Yellow H-E4R.

Appropriate dye strike rate on cationized cotton can be obtained for all three Evercion dyes by controlling the dyeing temperature and the time for adding soda ash. Thus, for both Everzol and Evercion dyes, colorimetric values (Table 23) of the dyeing were also measured to further evaluate the influence of soda ash on levelness and other dyeing performance.
Table 23 The influence of soda ash on colorimetric values and levelness of dyed cationized cotton

<table>
<thead>
<tr>
<th>Dye</th>
<th>Addition of soda ash</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h°</th>
<th>Levelness (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everzol Red 3BS</td>
<td>Initially</td>
<td>40.91</td>
<td>55.29</td>
<td>-1.62</td>
<td>55.31</td>
<td>358.32</td>
<td>0.617</td>
</tr>
<tr>
<td></td>
<td>After temperature increased</td>
<td>40.71</td>
<td>54.68</td>
<td>-1.47</td>
<td>54.70</td>
<td>358.46</td>
<td>0.678</td>
</tr>
<tr>
<td>Everzol dye mixture</td>
<td>Initially</td>
<td>33.59</td>
<td>11.96</td>
<td>0.96</td>
<td>12.00</td>
<td>4.59</td>
<td>0.842</td>
</tr>
<tr>
<td></td>
<td>After temperature increased</td>
<td>34.36</td>
<td>12.62</td>
<td>0.73</td>
<td>12.64</td>
<td>3.31</td>
<td>1.012</td>
</tr>
<tr>
<td>Evercion Red H-E7B</td>
<td>Initially</td>
<td>41.72</td>
<td>54.17</td>
<td>-1.50</td>
<td>54.19</td>
<td>358.41</td>
<td>0.516</td>
</tr>
<tr>
<td></td>
<td>After temperature increased</td>
<td>43.04</td>
<td>52.22</td>
<td>-2.58</td>
<td>52.28</td>
<td>357.17</td>
<td>0.276</td>
</tr>
<tr>
<td>Evercion dye mixture</td>
<td>Initially</td>
<td>36.82</td>
<td>14.72</td>
<td>1.70</td>
<td>14.82</td>
<td>6.59</td>
<td>1.618</td>
</tr>
<tr>
<td></td>
<td>After temperature increased</td>
<td>39.17</td>
<td>13.78</td>
<td>3.16</td>
<td>14.14</td>
<td>12.92</td>
<td>0.392</td>
</tr>
</tbody>
</table>

As presented in the table, for the cationized cotton fabrics dyed with Everzol Red 3BS and Everzol dye mixture, the overall standard deviation for $\Delta E_{cmc}$ ($\sigma$) was not reduced by eliminating soda ash from the initial dyebath, which indicates comparable or even slightly worse dyeing levelness compared with the fabric dyed with soda ash added initially. This agrees with the previous monitoring curves, indicating that soda ash has relatively small influence on dyeing kinetics and levelness of Everzol dyes on cationized cotton. In comparison, eliminating soda ash from the initial dyebath significantly improved the levelness of cationized cotton fabrics dyed with Evercion Red H-E7B and Evercion dye mixture, as reflected by the reduced overall standard deviation for $\Delta E_{cmc}$ ($\sigma$). Thus, level dyeing with Evercion dyes can be obtained on cationized by controlling the dyeing temperature and the time for adding soda ash.
To evaluate whether the effect of soda ash on dyeing kinetics of Evercion dyes is caused by the alkaline condition or the addition of electrolyte, more dyeing were conducted for Evercion dyes. In this part, small sample dyeings were conducted using an Ahiba Spectradye Plus lab dyeing machine and the dyebath solutions at 10, 20 and 30 min of dyeing are presented to demonstrate the rate of dye exhaustion. The dyeing temperature was kept as 37 °C and the liquor ratio is 15:1. As presented in Figure 65, four samples with 1% Everzol Red H-E7B and different other chemicals were prepared to evaluate the effect of alkali and electrolyte on the dyeing kinetics of the dye. In the figure, sample 2 (with Na₂CO₃) and 3 (with Na₂SO₄) have much faster dye strike rate compared with sample 1 (with only the dye) and 4 (with NaOH). This indicates that the dye strike rate of Evercion Red H-E7B on cationized cotton was not influenced by the alkalinity of the dyebath but significantly increased with the addition of electrolyte.

1: With only 1% of Evercion Red H-E7B, pH: 7.4
2: With 1% of Evercion Red H-E7B and 15 g/L Na₂CO₃, pH: 11.3
3: With 1% of Evercion Red H-E7B and 15 g/L Na₂SO₄, pH: 7.3
4: With 1% of Evercion Red H-E7B and 0.5 g/L NaOH, pH: 11.3

Figure 65 The effect of electrolyte and alkaline on the dyeing kinetics of Evercion Red H-E7B
The same experiment was also conducted on Evercion Yellow H-E4R (Figure 66) and Evercion Blue H-ERD (Figure 67). As presented in the figures, the addition of Na$_2$CO$_3$ and Na$_2$SO$_4$ accelerated the exhaustion of both dyes, which agrees with the results of Evercion Red H-E7B. In contrast, the increase of pH has little influence on the dye exhaustion process of Evercion dyes. Since soda ash is the only kind of electrolyte to be added for dyeing cationized cotton with Evercion dyes, the time for adding soda ash should be carefully selected to control the dye strike rate and levelness of dyeing. This might be applicable for some other reactive dyes as well.

1: With only 1% of Evercion Yellow H-E4R, pH: 7.0
2: With 1% of Evercion Yellow H-E4R and 15 g/L Na$_2$CO$_3$, pH: 11.3
3: With 1% of Evercion Yellow H-E4R and 15 g/L Na$_2$SO$_4$, pH: 7.1
4: With 1% of Evercion Yellow H-E4R and 0.5 g/L NaOH, pH: 11.3

Figure 66 The effect of electrolyte and alkaline on the dyeing kinetics of Evercion Yellow H-E4R
1: With only 1% of Evercion Blue H-ERD, pH: 7.2
2: With 1% of Evercion Blue H-ERD and 15 g/L Na$_2$CO$_3$, pH: 11.3
3: With 1% of Evercion Blue H-ERD and 15 g/L Na$_2$SO$_4$, pH: 7.5
4: With 1% of Evercion Blue H-ERD and 0.5 g/L NaOH, pH: 11.4

Figure 67 The effect of electrolyte and alkaline on the dyeing kinetics of Evercion Blue H-ERD

4.1.4 Conclusions

After comparing the exhaustion curves of the six commercially significant reactive dyes on cationized cotton, small differences in dyeing kinetics of different dyes were noticed. Generally, when dyed at 37°C and soda ash added in the initial dyebath, Everzol dyes have slightly faster dye strike rate than Evercion dyes. With this dyeing condition, all dyes evaluated have been fully exhausted in 5 to 10 minutes and the dyed cationized cotton fabrics have relatively poor levelness, especially for Everzol Blue BRF, Everzol Yellow 3RS, and Evercion Blue H-ERD.

The monitoring at varying temperatures demonstrated that decreasing the temperature only slightly reduced the dye exhaustion rate for both Everzol and Evercion dyes. However, for most of the dyes applied, significantly better levelness on dyed cationized cotton fabric was
obtained by lowering the dyeing temperature. Thus, a low initial dyeing temperature should be used for dyeing cationized cotton with reactive dyes.

In another aspect, the addition of soda ash has different effects on dyeing kinetics and levelness for different dyes. For Everzol dyes, the addition of soda ash has relatively small influence on the dye strike rate and levelness of dyed cationized cotton fabric. In comparison, eliminating the addition of soda ash in initial dyebath significantly reduced the dye strike rate of the Evercion dyes and improved the levelness of dyeing. The influence of soda ash on dyeing kinetics of Evercion dyes is from its function as an electrolyte rather than the change in alkalinity. Thus, for Evercion dyes, level dyeing on cationized can be obtained by controlling the dyeing temperature and the time of adding soda ash. However, the dye strike rate and dyeing levelness of Everzol dyes should be better controlled through other methods such as the use of leveling agents.
4.2 Real-Time Dyebath Monitoring of Reactive Dyeing on Cationized Cotton for Levelness Control—Part 2: Effects of Leveling Agents

Abstract: Cationization of cotton brings advantages in the reactive dyeing process, such as the elimination of electrolytes and increase of color yield. In another aspect, high dye strike rates resulted from electronic attractions between anionic dyes and cationized cotton may cause problems in levelness of dyeing, especially for light shades. For some reactive dyes (e.g. Evercion dyes), the selection of dyeing temperature and elimination of soda ash in initial dyebath can effectively control the dye strike rate and improve the levelness of dyeing. However, for some other dyes (e.g. Everzol dyes), the use of leveling agents is necessary to slow down the dye exhaustion process. In this study, a variety of anionic, cationic, and amphoteric leveling agents were applied to control the dye strike rate and levelness of Everzol dyes on the cotton fabric cationized using 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC). The leveling effect of adding dyes in portions was also evaluated and it was used in combination with leveling agents to better control the dye exhaustion process and levelness of dyeing.

Keywords: Cationized cotton, Reactive dye, Dyeing kinetics, Real-time monitoring, Levelness, Leveling agents

4.2.1 Introduction

Introduction of cationic sites on cotton fibers brings a variety of advantages in reactive dyeing process, such as the elimination of electrolytes, increase of dye exhaustion and color
yield and improvement in fastness properties. At the same time, with cationic groups
attached, adsorption of anionic reactive dyes happens rapidly through an ionic exchange
mechanism, which makes it difficult for dyes to migrate. This is different from a
conventional reactive dyeing process, which the adsorption and diffusion of dyes are
reversible. Thus, the dyeing kinetics of reactive dyes should be carefully controlled to obtain
level dyeing on cationized cotton, especially for pale dyeing.

In the previous study, the influence of dyeing temperature and addition of soda ash on dyeing
kinetics of cationized cotton were evaluated for six commercial reactive dyes (Everzol dyes
and Evercion dyes). For Evercion dyes, the control of dyeing temperature and soda ash are
effective in reducing dye strike rate and improving levelness of dyed cotton. However, the
dye strike rate of Everzol dyes should be better controlled through other ways such as the
addition of leveling agents.

Similar to dyeing nylon fibers, leveling agents for dyeing cationized cotton are either fiber
substantive (anionic) or dye substantive (cationic)\textsuperscript{13}. Since anionic leveling agents are
substantive towards the cationized cotton fiber, they initially block or compete with the
anionic dye molecules for the cationic sites within and on the surface of the substrate\textsuperscript{158,159}. The decrease of initial rate of dye adsorption promotes level dyeing while the blocking effect
is temporary and the more substantive dye molecules will displace the anionic surfactant
eventually\textsuperscript{13}. The anionic leveling agents can be either monomeric or polymeric. With small
molecular size, monomeric leveling agents such as sulfates or sulfonates have good
penetration performance but relatively low affinity\textsuperscript{19}. 
The retarding mechanism of cationic leveling agents is different: cationic agents form complexes with anionic dyes in the dyebath to prevent the adsorption of dyes. Then, with the increase of temperature, the dye-cationic agent complexes become unstable and will gradually release the dye molecules for adsorption on to the fiber\textsuperscript{158}. To solubilize the anionic dye-cationic agent complex and prevent precipitation in dyebath, a non-ionic component in the leveling agent is needed. There are also some amphoteric leveling agents, with both anionic and cationic groups present. Clearly, to ensure good leveling effect and uninfluenced final exhaustion rate, the leveling agent needs to be carefully selected\textsuperscript{13}.

In this study, a selection of anionic, cationic, and amphoteric leveling agents were applied to control the dye strike rate of Everzol dyes on cationized cotton. The retarding and leveling performance of the leveling agents as well as their influence on the final dye exhaustion were compared. Also, the addition of leveling agents can be applied in combination of adding dyes in portions to better control the dye strike rate and levelness of dyeing.

4.2.2 Experimental

4.2.2.1 Materials

Cotton yarns cationized with 3-chloro-2-hydroxy propyltrimethylammonium chloride (CHPTAC) were provided by ColorZen, USA. As described in the experimental section of Part 1, the yarns were knitted into jersey fabric with the density of 107 g/m\textsuperscript{2} and mild scouried with soda ash. After neutralizing and rinsing, final pH of the fabric was controlled as 6 to 7. The percentage of nitrogen fixed on the cationized cotton fabrics is 0.27%. Three Everzol dyes (Everzol Red 3BS, Everzol Yellow 3RS, Everzol Blue BRF) were obtained from
Everlight Chemical Inc., Taiwan. Leveling agents used in the experiments include Chromabond S-100 dye-complexing polymer from Ashland Inc., USA, Migroassit WWB from LANXESS Corporation, USA, Albafix ECO and INVALON® DAM 50% Liq dispersing agent from Huntsman Corporation, USA, and Sodium 1,5-naphthalenedisulfonate dibasic and lignosulfonic acid sodium salt from Sigma-Aldrich, USA. The nonionic dispersing agent NOVADYE NT-9 was obtained from Boehme Filatex, USA. Other chemicals used, including anhydrous sodium acetate, glacial acetic acid, sodium carbonate, and Triton X-100 were supplied by Fisher Scientific, USA and Sigma-Aldrich, USA.

4.2.2.2 Dyebath Monitoring Using the Hue-Metrix Monitor System

A HueMetrix Dye-It-Right system was used for monitoring dye exhaustion rate on cationized cotton. First, a validated calibration plot of concentration vs. absorbance was generated for each dye. To enable real-time dyebath monitoring, the Mathis JFL dyeing machine interfaces with the HueMetrix Monitor through a circulation loop to facilitate the flow of dyebath. During the dyeing process, the HueMetrix Monitor automatically collects a microsample (0.1 ml) in every 90 seconds to measure the absorbance value using the integrated UV–Vis spectrophotometer and calculate the dye concentration in bath. The percentage of dye exhaustion at certain time was calculated from $100 \times (1 - \frac{C_t}{C_0})$ where $C_0$ and $C_t$ are the concentrations of the dye in the dyebath at the beginning of dyeing and at time t, respectively. The details for obtaining calibration curves and operating the HueMetrix system were described in the experimental section in Part 1.
In this part, all monitorings were conducted at 37°C initially. With the selected leveling agent added, the solution was circulated for 5 minutes before the addition of dyes. To avoid interactions between soda ash and leveling agents, which may influence dye exhaustion rate, the initial dye bath contained no soda ash. After certain point of dye exhaustion, the dyeing temperature was increased from 37°C to 60°C (reaction temperature of Everzol dyes) and soda ash was added to enable dye fixation. After dyeing, all samples were rinsed thoroughly with both warm and cold water to remove unfixed dyes and air dried at room temperature.

4.2.2.3 Color Measurement and Determination of Levelness

Colorimetric values of all dyed fabrics were measured using an X-Rite® Datacolor Spectraflash 600X spectrophotometer equipped with iControl software from X-Rite. While testing, each sample was folded two times and the following settings were selected: illuminant D65, 10° supplemental standard observer, specular included, UV included. Each sample was measured ten times by changing the measuring point randomly to calculate the average value.

As an indication of dyeing levelness, overall standard deviation for $\Delta E_{cmc}$ ($\sigma$) can be calculated based on Equation 9, in which $\sigma_{\text{instrument}}$ is the standard deviation of the instrument and $\sigma_{\text{sample}}$ is the standard deviation of the sample.
4.2.3 Results and Discussion

4.2.3.1 Chromabond S-100 (Amphoteric)

Chromabond S-100 dye-complexing polymer (Figure 68) is a vinylpyridine-based polymer that contains betaine functionality. The molecular weight of the polymer is around 35,000.

![Figure 68 Structure of Chromabond S-100 dye-complexing polymer](image)

The monitorings of Everzol Red 3BS with different concentrations (1%, 5%, and 10%) of Chromabond S-100 are presented in Figure 69. All monitorings were conducted at 37°C and without adding soda ash initially. In the figure, the red arrows indicate the time of heating to increase the dyeing temperature to 60°C and the blue arrow indicates the addition of 15 g/L soda ash into the dyebath solution.
First, for the dyeing without leveling agent, dyes were fully exhausted in 5 to 10 minutes and adding soda ash only slightly reduced the dye exhaustion rate. With 1% of Chromabond S-100 added, the initial dye exhaustion speed was not influenced and 90% of the dye was exhausted in around 5 minutes. However, adding 1% of the leveling agent slightly reduced the dye exhaustion percentage at equilibrium. Also, after soda ash was added into the dyebath, some of the dyes were detached from the fabric and went back to the dyebath again.

This situation is more significant for the monitoring with 5% and 10% of Chromabond S-100. With a high concentration of Chromabond S-100 in bath, the initial dye exhaustion was
slowed down but the exhaustion percentage at equilibrium was also significantly reduced. Even though increasing the temperature to 60°C increased the exhaustion percentages, after the addition of soda ash, around 20% of the dyes were detached from the fabric and the final dye exhaustion is relatively low. Thus, Chromabond S-100 is not an applicable leveling agent for reactive dyeing with cationized cotton since it can hardly release the dye molecule after bonding and will influence the final dye uptake.

As reflected by the colorimetric data in Table 24, the increase of Chromabond S-100 concentration in dyebath significantly increased the L* value of dyed fabrics, indicating a decrease in color depth. Even though the addition of a high concentration of Chromabond S-100 improved the levelness of the dyed fabric (reduced overall standard deviation for $\Delta E_{\text{cmc}}$, $\sigma$), the leveling agent is not applicable in practical reactive dyeing due to the decrease of dye uptake and loss in color yield.

<table>
<thead>
<tr>
<th>Conc. of Chromabond S-100</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>$h^\circ$</th>
<th>Levelness ($\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No leveling agent</td>
<td>40.71</td>
<td>54.68</td>
<td>-1.47</td>
<td>54.70</td>
<td>358.46</td>
<td>0.678</td>
</tr>
<tr>
<td>1%</td>
<td>43.35</td>
<td>54.27</td>
<td>-2.50</td>
<td>54.33</td>
<td>357.36</td>
<td>0.691</td>
</tr>
<tr>
<td>5%</td>
<td>44.92</td>
<td>51.17</td>
<td>-4.52</td>
<td>51.37</td>
<td>354.95</td>
<td>0.598</td>
</tr>
<tr>
<td>10%</td>
<td>48.60</td>
<td>47.46</td>
<td>-6.60</td>
<td>47.92</td>
<td>352.08</td>
<td>0.326</td>
</tr>
</tbody>
</table>
4.2.3.2 Albafix ECO (Cationic)

Albafix ECO is an aqueous solution based on polyethylene polyamine. The major component of Albafix ECO is cyanoguanidine polymer with diethylenetriamine. The polymer contains numerous amines, which carry positive charges under acid conditions. Thus, after mixing with acid, the positively charged polymer can bond with reactive dyes to slowdown the exhaustion rate. To release the dye from the dye-leveler complex, soda ash or other alkali can be dosed to neutralize the solution.

However, the positively charged Albafix ECO forms small precipitates with the negatively charged Everzol Red 3BS dye molecules. Even with up to 30 g/L of the nonionic dispersing agent NOVADYE NT-9 added, there are still some particles of the dye-agent complex in the mixed dye solution. With precipitates in dye solution, the HueMetrix system cannot be used to monitor the dyeing process. Thus, sample dyeings in beakers were conducted using an Ahiba Spectradye Plus lab dyeing machine. The dyeing conditions were kept the same as the dyebath monitoring. With 1% of Everzol Red 3BS applied, different concentrations of Albafix ECO including 1%, 5%, and 10% were added.

After dyeing, it was found that adding Albafix ECO changed the shade of the cationized cotton dyed with Everzol Red 3BS. Also, with soda ash added during dyeing, free amines were emitted and can cause a bad smell. In another aspect, precipitates formed between the dye and Albafix ECO will cause problems during dyeing. Thus, Albafix ECO is not an appropriate leveling agent for dyeing cationized cotton.
4.2.3.3 Migrassist WWB (Cationic)

The major components of Migrassist WWB include 25%-35% quaternary ammonium compounds, ethylbis(hydroxyethyl)tallow alkyl, ethoxylated, Et sulfates (salts) and 20%-30% ethoxylated stearylamine. Figure 70 shows the exhaustion curves of 1% Everzol Red 3BS at 37°C with different concentrations of Migrassist WWB.

![Exhaustion curves of Everzol Red 3BS with different concentrations of Migrassist WWB](image)

As the figure shows, the addition of 1% of Migrassist WWB has relatively small influence on dye strike rate of Everzol Red 3BS. With the concentration of Migrassist WWB increased to 5%, the exhaustion curve of the dye was changed significantly. In the initial exhaustion stage (0 to 10 minutes), the dye strike rate is still fast and around 65% of the dye was exhausted in 10 minutes. However, the rest of the dye in bath exhaust very slow and even with
temperature increased and soda ash added, there is still around 10% of the dye left in bath after 65 minutes of exhaustion. With 10% of the leveling agent added, the dye strike rate has been further reduced and it takes too long to fully exhaust the dyes. The exhaustion curves with 5% and 10% of Migrassist WWB indicate very strong retarding and leveling performance of it for Everzol Red 3BS. However, with temperature increased to 60°C, the dye strike rate is still very slow, indicating that the dye-leveling agent complex formed is very stable and the dye molecules were released too slow for adsorption.

The fast exhaustion of free dyes in bath and too slow exhaustion rate of the dye-leveling agent complex makes the dye exhaustion process hard to be controlled. The improved levelness of the dyeing with Migrassist WWB (Table 25) proves the good leveling performance of the agent. However, the increased L* value of the samples indicates a reduction in dye uptake and a decrease in color yield. Thus, other leveling agents were tried to better control the dye exhaustion process.

Table 25 The effect of Migrassist WWB on colorimetric data and levelness of dyed cationized cotton fabrics

<table>
<thead>
<tr>
<th>Conc. of Migrassist WWB</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h°</th>
<th>Levelness (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No leveling agent</td>
<td>40.71</td>
<td>54.68</td>
<td>-1.47</td>
<td>54.70</td>
<td>358.46</td>
<td>0.678</td>
</tr>
<tr>
<td>1%</td>
<td>40.84</td>
<td>54.02</td>
<td>-2.23</td>
<td>54.07</td>
<td>357.64</td>
<td>0.424</td>
</tr>
<tr>
<td>5%</td>
<td>42.72</td>
<td>53.38</td>
<td>-2.87</td>
<td>53.46</td>
<td>356.92</td>
<td>0.430</td>
</tr>
<tr>
<td>10%</td>
<td>43.16</td>
<td>52.92</td>
<td>-3.91</td>
<td>53.06</td>
<td>355.77</td>
<td>0.328</td>
</tr>
</tbody>
</table>
4.2.3.4 Naphthalene Sulfonate (Anionic)

Sodium 1,5-naphthalenedisulfonate dibasic (Figure 71) carries a negative charge in water and are theoretically substantive towards the cationized cotton fiber to initially block or compete with the reactive dyes for the cationic ammonium ion sites on the surface of the substrate. This may decrease the initial rate of dye adsorption and promotes level dyeing.

![Figure 71 Sodium 1,5-naphthalenedisulfonate dibasic](image)

Figure 72 shows the exhaustion curves of 1% Everzol Red 3BS with different concentrations of naphthalene disulfonate. Same as previous experiments, the dyeing starts at 37°C and the red arrows in the figure indicates the increase of temperature to 60°C and the blue arrow indicates the addition of 15 g/L soda ash into the dyebath solution.
As the figure shows, the effect of the naphthalene disulfonate on the exhaustion of Everzol Red 3BS is relatively small. In Table 26, the overall standard deviation for $\Delta E_{cm}$ ($\sigma$) of all samples is higher than 0.5, further proves that the sodium 1,5-naphthalenedisulfonate dibasic has very limited leveling performance.

Table 26 The effect of sodium 1,5-naphthalenedisulfonate dibasic on colorimetric data and levelness of dyed cationized cotton fabrics

<table>
<thead>
<tr>
<th>Conc. of naphthalene disulfonate</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h°</th>
<th>Levelness ($\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No leveling agent</td>
<td>40.71</td>
<td>54.68</td>
<td>-1.47</td>
<td>54.70</td>
<td>358.46</td>
<td>0.678</td>
</tr>
<tr>
<td>1%</td>
<td>41.04</td>
<td>54.49</td>
<td>-2.04</td>
<td>54.53</td>
<td>357.86</td>
<td>0.730</td>
</tr>
<tr>
<td>5%</td>
<td>40.29</td>
<td>54.11</td>
<td>-1.72</td>
<td>54.14</td>
<td>358.18</td>
<td>0.667</td>
</tr>
<tr>
<td>10%</td>
<td>42.00</td>
<td>58.27</td>
<td>-0.44</td>
<td>58.27</td>
<td>359.57</td>
<td>0.512</td>
</tr>
</tbody>
</table>
To evaluate whether increasing the number of sulfonate group can increase the leveling performance of naphthalene sulfonate, the naphthalene-1,3,6-trisulfonic acid trisodium salt hydrate (Figure 73) was also tried. However, a similar result as the naphthalene disulfonate was obtained for the naphthalene trisulfonate.

![Figure 73 Naphthalene-1,3,6-trisulfonic acid trisodium salt hydrate](image)

Both the monitoring curves and levelness data of the naphthalene sulfonates indicates that their affinity for cationized cotton is not strong enough to slow down the exhaustion of Everzol Red 3BS. Thus, polymeric leveling agents with higher affinity should be applied.

4.2.3.5 Lignin Sulfonate (Anionic)

The lignosulfonic acid sodium salt (Figure 74) is a polymeric anionic leveling agent with an average molecular weight of 52,000. Figure 75 shows the exhaustion curves of 1% Everzol Red 3BS with different concentrations of lignin sulfonate added.

![Figure 74 Lignosulfonic acid sodium salt](image)
As presented in Figure 75, monitorings with 5% and 10% of lignin sulfonate have slightly reduced exhaustion rates than the dyeing with no leveling agent added. Even though the effect of lignin sulfonate on dye exhaustion rate is more significant than the naphthalene sulfonate, the levelness (Table 27) of all dyed samples are still relatively poor. Leveling agents with higher efficiency should be tried.
Table 27 The effect of lignin sulfonate on colorimetric data and levelness of dyed cationized cotton fabrics

<table>
<thead>
<tr>
<th>Conc. of lignin sulfonate</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h°</th>
<th>Levelness (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No leveling agent</td>
<td>40.71</td>
<td>54.68</td>
<td>-1.47</td>
<td>54.70</td>
<td>358.46</td>
<td>0.678</td>
</tr>
<tr>
<td>1%</td>
<td>41.34</td>
<td>54.91</td>
<td>3.66</td>
<td>55.03</td>
<td>3.81</td>
<td>0.581</td>
</tr>
<tr>
<td>5%</td>
<td>41.72</td>
<td>54.17</td>
<td>3.98</td>
<td>54.32</td>
<td>4.20</td>
<td>0.634</td>
</tr>
<tr>
<td>10%</td>
<td>41.32</td>
<td>53.52</td>
<td>4.39</td>
<td>53.70</td>
<td>4.69</td>
<td>0.505</td>
</tr>
</tbody>
</table>

4.2.3.6 INVALON® DAM (Anionic)

The INVALON® DAM 50% Liq dispersing agent is an aqueous solution of formaldehyde condensate of naphthalene sulfonic acid. Since the activity of the product is 50%, the concentrations of the leveling agent were increased. In Figure 76, different concentrations (2%, 10% and 20% owf) of INVALON® DAM were added into the dyebath respectively to evaluate its effect on dye exhaustion rate. The concentration of Everzol Red 3BS and other dyeing conditions were kept the same as previous experiments.
As presented in Figure 76, the addition of INVALON® DAM significantly reduced the exhaustion rate of Everzol Red 3BS. Also, with higher concentration of the leveling agent added, the more significant effect on exhaustion was obtained. When dyeing without leveling agent, 90% of the dye in bath was exhausted in 5 to 10 minutes. While with high concentrations of INVALON® DAM added, the exhaustion time for 90% of the dye was extended to longer than 30 minutes. Also, the addition of INVALON® DAM has relatively small influence on the final dye exhaustion and all of the dyeing reached around 95% of final dye uptake. Thus, with reduced exhaustion rate and comparable final dye uptake, INVALON® DAM is an effective leveling agent for dyeing cationized cotton with Everzol Red 3BS.
The effect of INVALON® DAM was further examined by dyeing with Everzol dye mixture, which includes 0.35% owf of each Everzol dye (Red 3BS, Yellow 3RS, and Blue BRF). As the figure shows, the leveling agent is also effective on the Everzol dye mixture. In another aspect, with the leveling agent added, the Everzol Red 3BS exhaust slower than the other two components in the dye mixture, indicating slightly lower affinity compared with Everzol Yellow 3RS and Everzol Blue BRF.

![Figure 77 The effect of INVALON® DAM on exhaustion of Everzol dye mixture](image)

For the levelness of dyeing (Table 28), with both dye recipes (Everzol Red 3BS and Everzol dye mixture), the overall standard deviation for ΔEcme (σ) of dyed cationized cotton was reduced to lower than 0.5 by using INVALON® DAM. In another aspect, the L* value of
dyed cationized cotton was slightly increased by adding the leveling agent, indicating a small decrease in color depth. However, in consideration of both dye strike rate and levelness of dyeing, the formaldehyde condensate of naphthalene sulfonic acid (INVALON® DAM) is an effective leveling agent for dyeing cationized cotton with Everzol dyes.

Table 28 The effect of INVALON® DAM on colorimetric data and levelness of dyed cationized cotton fabrics

<table>
<thead>
<tr>
<th>Dye</th>
<th>Conc. of INVALON® DAM</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h°</th>
<th>Levelness (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everzol Red 3BS</td>
<td>No leveling agent</td>
<td>40.71</td>
<td>54.68</td>
<td>-1.47</td>
<td>54.70</td>
<td>358.46</td>
<td>0.678</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>41.87</td>
<td>56.28</td>
<td>2.68</td>
<td>56.34</td>
<td>2.71</td>
<td>0.488</td>
</tr>
<tr>
<td></td>
<td>10%</td>
<td>42.05</td>
<td>56.91</td>
<td>1.86</td>
<td>56.94</td>
<td>1.87</td>
<td>0.390</td>
</tr>
<tr>
<td></td>
<td>20%</td>
<td>42.59</td>
<td>56.87</td>
<td>1.91</td>
<td>56.90</td>
<td>1.92</td>
<td>0.318</td>
</tr>
<tr>
<td>Everzol dye mixture</td>
<td>No leveling agent</td>
<td>34.36</td>
<td>12.62</td>
<td>0.73</td>
<td>12.64</td>
<td>3.31</td>
<td>1.012</td>
</tr>
<tr>
<td></td>
<td>20%</td>
<td>36.98</td>
<td>13.35</td>
<td>3.51</td>
<td>13.80</td>
<td>14.73</td>
<td>0.427</td>
</tr>
</tbody>
</table>

4.2.3.7 Adding Dye in Portions

Besides the use of leveling agents, dosing of dye or adding dye in portions can also help reduce the dye strike rate. In this part, the effect of adding dye in 4 portions on dyeing kinetics and levelness were evaluated for the dyeing with 1% Everzol Red 3BS. Also, adding dye in portions was used in combination with the leveling agent INVALON® DAM. The exhaustion curves are presented in Figure 78 and the levelness data are listed Table 29.
By comparing the blue curves in the figure, it was found that even though adding the dye in portions extended the total exhaustion time, the dye strike rate for each portion of dye is still very high. In comparison, with 20% INVALON® DAM added, the strike rates of all portions of dyes were significantly reduced. The exhaustion curves indicate that, by combining the use of the leveling agent and addition of dye in portions, the exhaustion process of Everzol Red 3BS on cationized cotton can be well controlled.

Also, without the use of the leveling agent, adding dye in portions is not beneficial for the levelness of the dyed fabric (Table 29). In contrast, the combined use of these two methods significantly improved the dyeing levelness of the cationized cotton with Everzol Red 3BS.
Table 29 The effect of adding dyes in portions on colorimetric data and levelness of dyed cationized cotton fabrics

<table>
<thead>
<tr>
<th>Addition of dye</th>
<th>Conc. of INVALON DAM</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h°</th>
<th>Levelness (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add in all</td>
<td>No leveling agent</td>
<td>40.71</td>
<td>54.68</td>
<td>-1.47</td>
<td>54.70</td>
<td>358.46</td>
<td>0.678</td>
</tr>
<tr>
<td></td>
<td>20%</td>
<td>42.59</td>
<td>56.87</td>
<td>1.91</td>
<td>56.90</td>
<td>1.92</td>
<td>0.318</td>
</tr>
<tr>
<td>Add in 4 portions</td>
<td>No leveling agent</td>
<td>40.31</td>
<td>55.36</td>
<td>-0.07</td>
<td>55.36</td>
<td>359.93</td>
<td>0.796</td>
</tr>
<tr>
<td></td>
<td>20%</td>
<td>41.80</td>
<td>52.90</td>
<td>-2.54</td>
<td>52.96</td>
<td>357.25</td>
<td>0.217</td>
</tr>
</tbody>
</table>

4.2.4 Conclusions

In the previous study, the selection of dyeing temperature and elimination of soda ash in dyebath effectively controlled dye strike rate and improved levelness of cationized cotton dyed with Evercion dyes. However, to obtain level dyeing with Everzol dyes, the use of leveling agents is necessary.

Among the applied anionic, cationic, and amphoteric leveling agents, the formaldehyde condensate of naphthalene sulfonic acid (INVALON® DAM 50% Liq) has the best performance in consideration of dye strike rate, final dye uptake, and levelness of dyeing. Also, the addition of leveling agents can be applied in combination of dye dosing or adding dyes in portions to better control the dye exhaustion process and further improve the levelness of dyeing. The suggested chemicals and process are also applicable for dyeing cationized cotton with other reactive dyes.
CHAPTER 5 ENVIRONMENTAL ASSESSMENT OF DEEP DYED COTTON FABRICS: CATIONIZATION DYEING VS. CONVENTIONAL REACTIVE DYEING

Abstract: Dyeing is an essential process to produce commercially acceptable cotton products but it has the potential to cause significant environmental impacts. The objective of this study is to compare the environmental impacts of deep dyed cotton using cationization dyeing procedure with conventionally dyed cotton. The study followed the life-cycle assessment (LCA) methodology outlined in ISO 14040 and systems investigated mainly focused on the dyeing process of cotton fabrics (system “gate-to-gate”). The chosen functional unit is 1000 kg of cotton fabrics dyed in a deep black shade using reactive dyes. The environmental impact categories assessed in the analysis were global warming potential, acidification, eutrophication, ecotoxicity, and human health (carcinogenic and non-carcinogenic) effects. We found that the conventional reactive dyeing system has higher impacts in half of the impact categories, including global warming, acidification, and ecotoxicity, mainly because of its large consumption of energy. The chemicals used for cationization caused high impacts in eutrophication and human health effects of the cationization dyeing system. Finally, toxicity of the two systems was further discussed and suggestions for cleaner production were made for both conventional and cationization dyeing system.

Keywords: Life-cycle assessment, Environmental impacts, Cotton, Dyeing, Reactive dye, Cationization
5.1 Introduction

In the textile industry, dyeing is an essential process to add value to the product and produce aesthetically appealing textiles. As one of the dominant materials in the textile market, cotton can be dyed with fiber reactive dyes, direct dyes, sulfur dyes, vat dyes, and azoic dyes. Although a wide range of dyes can be used for cotton coloration, it is difficult to obtain ultra-deep shades on cotton with good colorfastness in an environmentally responsible way\textsuperscript{24}. As the most commonly used dye class for cotton coloration, reactive dyes have advantages in wet colorfastness compared with other dye classes, especially for deep dyeing. However, due to the poor affinity of reactive dyes for cotton and their limited reaction efficiency, there are high concentrations of dyes and electrolytes remaining in the wastewater when reactive dyes are applied on cotton in conventional dyeing procedures. Also, the substantial level of unfixed and hydrolyzed dyes on the fabric requires heavy water consumption for multiple soaping and rinsing. All of these may cause serious environmental problems.

Since cationized cotton produces ionic attractions to negatively charged dyes like reactive and direct dyes, cationization of cotton has been widely researched in recent years to eliminate the use of salt and improve the dyeability and colorfastness properties of cotton\textsuperscript{60,61,105,112}. Among the variety of cationic reagents for cotton and other cellulosic products\textsuperscript{70,80}, 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC) is one of the most commonly used agents due to its high reaction efficiency and relatively low cost\textsuperscript{63}. Before application to cellulosic fibers, CHPTAC is converted to 2,3-epoxypropyl trimethylammonium chloride (EPTAC) by reacting with alkali. Then EPTAC can react with the hydroxyl groups on cotton under alkaline conditions to make cotton fibers positively
charged\textsuperscript{59,61}. The application methods for cationization of cotton include exhaustion, cold pad-batch, pad-steam and pad-dry-cure\textsuperscript{63}. It is well accepted that deep dyeing of cationized cotton is more environmentally benign at the dyeing stage compared with the conventional method\textsuperscript{112,113}, but no full life-cycle assessment with the cationization process included has been conducted to evaluate the environmental impact of applying cationization before dyeing.

Since one of the motivations for applying cationization on cotton is to reduce environmental impact, it is important to determine whether applying cationization is environmentally beneficial for obtaining ultra-deep shades on cotton fabrics. In this study, the relative environmental performance of the innovative cationization dyeing process was analyzed and compared with conventional reactive dyeing using life-cycle assessment (LCA). Data from industry, pre-published research, and lab-scale experiments was used to generate the life-cycle inventory (LCI) for both innovative and conventional dyeing process. By using the openLCA software with ecoinvent 2.2 database\textsuperscript{212}, both processes were modeled and six impact categories from TRACI\textsuperscript{213}, USETox\textsuperscript{214}, and IPCC 2007\textsuperscript{215} were selected as the criteria for evaluating the environmental impacts. After the impacts of the two dyeing methods were compared, the limitations of our study were explained and potential improvements for future work were suggested. The outcomes of this study can provide decision support to both researchers in this field and manufacturers in the textile industry.
5.2 Methodology

5.2.1 Goal and Scope

The goal of this study is to evaluate the environmental impacts of the innovative cationization dyeing process and compare it with conventional reactive dyeing for obtaining deep shades on cotton fabrics. The target audiences are researchers in this field, textile manufacturers, and eco-conscious consumers. This comparative LCA will support researches and decisions related to the development of textile dyeing for high efficiency and low environmental impacts.

5.2.1.1 Functional Unit

To ensure the validity of the comparison, the functional unit of this study was defined as 1000 kg of cotton fabrics dyed in a deep black shade using reactive dyes at a facility in US.

5.2.1.2 System Boundaries

The study mainly focused on the dyeing process of cotton. For the conventional dyeing system, only the dyeing and the subsequent soaping and rinsing process were included in the system boundary (Figure 79). Since cationization was applied on cotton before dyeing to enable the application of no salt dyeing process, cationization and subsequent rinsing and neutralizing were also included in the system boundary of the innovative dyeing system (Figure 80).
Figure 79 System map of conventional reactive dyeing process

Figure 80 System map of innovative cationization dyeing process
For both systems, wastewater treatment was included in the system boundary since the volume and content of the wastewater in the two systems are different. Also, water, energy (electricity and steam), dyes and other chemicals were indicated as inputs for each process. Since the consumption of cotton fabric for both systems is the same, cotton fabric was not included as an input of either system. The life-cycle analyses for both systems are gate-to-gate partial LCA looking at only the dyeing and its related process in the entire production chain. Thus, the environmental impacts associated with cotton cultivation, fabric production, product usage and disposal, or any other process that was not influenced by replacing conventional reactive dyeing with innovative cationization dyeing method were not considered. In both scenarios, transportation of cotton products, chemicals, and water were excluded. In the foreground system of this study there are no co-products.

5.2.2 Data Collection and LCI Analysis

In this analysis, different sources and collection methods were used. First, data regarding the production process, including dyeing procedures, dyeing recipes, and water usage were obtained from the industrial textile enterprise. Based on the information of the procedures and machinery, the consumption of water, dyes, and other chemicals were estimated. Also, data from scientific reports, previously published literature, as well as on-going research were mainly used to determine the product flows for the innovative cationization dyeing system.

Background processes and product flows were modeled in the openLCA using ecoinvent v2.2. Data sets in ecoinvent were verified and updated as necessary using published
literature\textsuperscript{217-223}. For example, the wastewater treatment process was modeled based on the “treatment, sewage, to wastewater treatment, class 3” process provided in ecoinvent\textsuperscript{224,225}. Since the effluent from cotton wet processing has a different chemical composition from sewage, modifications on product and elementary flows have been applied by referring to published life-cycle assessments of cotton dyeing\textsuperscript{218,222}. The electricity consumption and other inputs of the wastewater treatment process were only related to the volume of the wastewater but the final emissions after treatment were estimated based on the chemical contents of the original effluent.

For both scenarios, one of the critical factors on environmental impact is the consumption and emission of chemicals. However, for some chemicals such as reactive dyes and the cationic reagent (CHPTAC), no background processes and information were found in the ecoinvent database. Thus, synthesis processes of these chemicals from the available background products were first modeled using the ecoinvent database. Inputs for the chemical and dye synthesis were estimated theoretically based on literature or the information provided by the supplier\textsuperscript{226,227}. If synthesis information was not found, intermediates or available chemicals with similarities were used as proxies for the unfound chemicals\textsuperscript{99,228,229}.

5.2.3 Impact Assessment

For impact assessment, the Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI)\textsuperscript{213} and USEtox\textsuperscript{214} methods were mainly used. Based on the fact that in this assessment the environmental impacts of the US textile industry were
evaluated, TRACI was used since it is a methodology tailored specifically to US conditions. The USEtox impact assessment methodology is a current method specifically developed to assess the toxicity effect.

Three main impact categories were considered for this analysis. The first category is atmospheric impacts, which include Global Warming Potential (GWP) and Acidification Potential (AP). The second impact category is water impacts, measured by Eutrophication Potential (EP). The third impact category, toxicity, consists of three subcategories: Ecotoxicity Potential (ETP), Human Health-Carcinogenic (HH-C), and Human Health-Non-Carcinogenic (HH-NC). The toxicity potentials were selected from USETox and other categories were selected from the TRACI. Also, the out-of-date impact factors for GWP in TRACI were updated based on IPCC 2007\textsuperscript{215}. Midpoint impacts (Table 30) were utilized, which are considered to possess lower level of uncertainty compared with endpoint impacts\textsuperscript{230}. For all included environmental impact categories, 95% of the overall impacts are included.

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global Warming</td>
<td>Kg CO\textsubscript{2}</td>
<td>Converts inventory amounts to CO\textsubscript{2} equivalents</td>
</tr>
<tr>
<td>Acidification</td>
<td>Mole of H\textsuperscript{+}</td>
<td>Converts inventory amounts to moles of H\textsuperscript{+} equivalents</td>
</tr>
<tr>
<td>Eutrophication</td>
<td>Kg N</td>
<td>Converts inventory amounts to nitrogen equivalents</td>
</tr>
<tr>
<td>Ecotoxicity</td>
<td>CTU</td>
<td></td>
</tr>
<tr>
<td>Human Health Carcinogenic</td>
<td>CTU</td>
<td>Converts inventory amounts to Comparative Toxicity Units (CTU)</td>
</tr>
<tr>
<td>Human Health Non-Carcinogenic</td>
<td>CTU</td>
<td></td>
</tr>
</tbody>
</table>
One of the limitations of the impact assessment is that the USEtox method is not complete for textile chemicals\textsuperscript{217,218,220}. To convert the inflows and outflows from the inventory to potential environmental impacts, characterization factors (CFs) must be provided for all chemicals. Due to the relative small coverage of chemicals used in the textile industry, especially for detergents and dyestuffs, some articles on LCA of textiles exclude toxicity impacts\textsuperscript{218}. In this research, USEtox CFs were developed for the missing textile chemicals by combining the life cycle perspective with chemical risk information\textsuperscript{220,231}. However, the assessment of chemicals is still a weak point for the life-cycle impact assessment of this project. Also, the USEtox mainly focused on characterizing the toxicity of the actual emitted substances while the human toxicity in a working environment was not addressed. In another aspect, the current LCA methodologies do not yet cover the salinization of local water system, which is an important impact for conventional reactive dyeing system.

Normalization was used to assist in the interpretation of the life-cycle impact assessment (LCIA) results. To identify the key impact categories for this assessment, the atmospheric and water impacts were normalized to person equivalents based on the normalization factors for TRACI\textsuperscript{232} and the toxicity impacts were normalized using the normalization reference for USEtox\textsuperscript{233}. The normalization factors used for all categories are presented in Table 31.
Table 31 Normalization factors for all impact categories analyzed

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Normalized value per capita</th>
<th>Normalized unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global Warming</td>
<td>2.45×10⁴</td>
<td>CO₂ equiv/yr/capita</td>
</tr>
<tr>
<td>Acidification</td>
<td>7.44×10³</td>
<td>H⁺ equiv/yr/capita</td>
</tr>
<tr>
<td>Eutrophication</td>
<td>1.80×10¹</td>
<td>N equiv/yr/capita</td>
</tr>
<tr>
<td>Ecotoxicity</td>
<td>5.12×10³</td>
<td>CTU/yr/capita</td>
</tr>
<tr>
<td>Human Health Carcinogenic</td>
<td>1.02×10⁻⁴</td>
<td>CTU/yr/capita</td>
</tr>
<tr>
<td>Human Health Non-Carcinogenic</td>
<td>4.54×10⁻⁴</td>
<td>CTU/yr/capita</td>
</tr>
</tbody>
</table>

5.3 Results

5.3.1 LCI Results

For the conventional reactive dyeing process, knitted cotton fabrics dyed using a conventional jet dyeing machine using exhaustion method was assumed. A liquor ratio of 10:1 was chosen as typical for cotton fabric dyeing. Batchwise dyeing of cotton fabrics using airflow jet machines involves repeated heating and cooling cycles. Since cooling water is typically provided from rivers and is returned to the respective river catchment, it is not considered for water consumption. The conventional dyeing process consists of the following stages:\(^{218}\):

- Exhaustion of dyes from an aqueous bath containing a high concentration of electrolyte, normally under neutral conditions.
- Addition of alkali to promote further dye uptake and fixation of absorbed dyes with cotton fibers at optimal pH and temperature.
- Washing-off the dyed material to remove electrolyte, alkali and unfixed dye.
Since ultra-deep black dyeing on cotton fabrics was obtained using C.I. Reactive Black 5 (vinyl sulfone fiber reactive dye), a dyeing temperature of 60°C was selected. To obtain a comparable deep black shade on both fabrics, 7% of C.I. Reactive Black 5 was assumed to be applied for conventional reactive dyeing while only 5% of the dye is required for cationized cotton fabrics. Table 32 compares the dyeing and following washing procedure of conventional and cationized cotton\textsuperscript{112,218}.

Table 32 Dyeing procedure of conventional reactive dyeing and innovative cationization dyeing

<table>
<thead>
<tr>
<th>Conventional process</th>
<th>Time (min)</th>
<th>Cationized cotton process</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load machine</td>
<td>15</td>
<td>Load machine</td>
<td>15</td>
</tr>
<tr>
<td>Dyeing at 60°C</td>
<td>160</td>
<td>Dyeing at 60°C</td>
<td>90</td>
</tr>
<tr>
<td>Rinse at 50°C</td>
<td>15</td>
<td>Rinse &amp; neutralization at room temp</td>
<td>15</td>
</tr>
<tr>
<td>Rinse at 50°C</td>
<td>15</td>
<td>n/a</td>
<td>-</td>
</tr>
<tr>
<td>Rinse &amp; neutralization at 50°C</td>
<td>20</td>
<td>n/a</td>
<td>-</td>
</tr>
<tr>
<td>Scour at 90°C</td>
<td>30</td>
<td>n/a</td>
<td>-</td>
</tr>
<tr>
<td>Rinse at 60°C</td>
<td>15</td>
<td>n/a</td>
<td>-</td>
</tr>
<tr>
<td>Rinse at room temp</td>
<td>15</td>
<td>n/a</td>
<td>-</td>
</tr>
<tr>
<td>Unload machine</td>
<td>15</td>
<td>Unload machine</td>
<td>15</td>
</tr>
</tbody>
</table>

For the cationization process of cotton fabrics, the cold pad-batch method was selected. The concentration of CHPTAC (65%) applied for cationization is 100 g/L while the alkali added to enable the reaction is 55 g/L of 50% NaOH. Sufficient rinsing and neutralizing are required before the dyeing of cationized cotton fabrics but drying of the fabrics is not necessary. For dyeing cationized cotton, the addition of Na\textsubscript{2}SO\textsubscript{4} was eliminated and the concentration of Na\textsubscript{2}CO\textsubscript{3} can also be reduced.
Based on the estimated procedures and chemical recipes, the product flows for the manufacture of cotton fabrics dyed in deep black through conventional reactive dyeing and the innovative cationization dyeing process are shown in Table 33. In the inventory, wastewater treatment was considered as an input rather than a separate foreground process since wastewater treatment was modeled based on a treatment in ecoinvent database and it involves relatively complex product flows. Detailed information about the material and energy inputs of wastewater treatment were drawn from the “treatment, sewage, to wastewater treatment, class 3” process provided in ecoinvent.

Table 33 Product flows for the manufacture of cotton fabrics dyed in deep black through conventional and innovative dyeing process

<table>
<thead>
<tr>
<th>Input</th>
<th>Unit</th>
<th>Quantity per producing 1000 kg products</th>
<th>Conventional</th>
<th>Innovative</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Electricity</td>
<td>MJ</td>
<td></td>
<td>1500</td>
<td>1800</td>
</tr>
<tr>
<td>Steam</td>
<td>kg</td>
<td></td>
<td>8500</td>
<td>1400</td>
</tr>
<tr>
<td>Tap water</td>
<td>kg</td>
<td></td>
<td>70000</td>
<td>61000</td>
</tr>
<tr>
<td>NaOH 50%</td>
<td>kg</td>
<td></td>
<td>18</td>
<td>55</td>
</tr>
<tr>
<td>Acetic Acid (56%)</td>
<td>kg</td>
<td></td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>kg</td>
<td></td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Reactive dye (C.I. Reactive Black 5)</td>
<td>kg</td>
<td>70</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>kg</td>
<td></td>
<td>800</td>
<td>0</td>
</tr>
<tr>
<td>Detergent</td>
<td>kg</td>
<td></td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>CHPTAC (65%)</td>
<td>kg</td>
<td></td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Wastewater Treatment</td>
<td>m³</td>
<td></td>
<td>70</td>
<td>61</td>
</tr>
</tbody>
</table>

As presented in the table, since the cationization process was applied before dyeing using the cold pad-batch method, slightly higher amounts of electricity were consumed for the
innovative cationization dyeing system. However, due to the much shortened dyeing process and minimized after-washing cycles, significant amount of steam was saved for using cationized cotton. In general, applying cationization saves a significant amount of energy. In consideration of water consumption, the soaping and washing process after conventional dyeing consumes a large amount of water while for the innovative system the process that consumes the most water is the rinsing stage after cationization. Using the innovative dyeing system saves around 13% of water usage. The volume of wastewater to be treated is proportional to the water consumption in the wet processing stages. For chemical usage, due to the elimination of salt during dyeing and the increased dye uptake, less dye, Na₂SO₄, and detergent were consumed for the innovative system. However, the application of cationization requires a large amount of CHPTAC (cationic reagent) and alkali.

5.3.2 LCIA Results

Based on the results of life cycle inventory, life cycle impacts of both conventional reactive dyeing and innovative cationization dyeing process were calculated using openLCA. The data presented is for producing 1000 kg dyed cotton product, which is the functional unit. Also, process contributions were analyzed to identify the key processes. Normalization was applied to help compare the impacts across categories.

5.3.2.1 Impact Results

The LCIA results for both the conventional and cationization dyeing systems of all the impact categories are listed in Table 34. As the data demonstrates, the conventional dyeing process contributed higher impacts than the cationization dyeing process in Global Warming
Potential (GWP), Acidification Potential (AP), and Ecotoxicity Potential (ETP). While for the other impact categories, including Eutrophication Potential (EP), Human Health-Carcinogenic (HH-C), and Human Health-Non-Carcinogenic (HH-NC), the cationization dyeing process has higher impacts.

Table 34 Comparative LCIA results associated with conventional and cationization dyeing process

<table>
<thead>
<tr>
<th>Impact Category</th>
<th>Unit</th>
<th>Quantity per producing 1000 kg products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Conventional</td>
</tr>
<tr>
<td>Global Warming</td>
<td>kg CO₂</td>
<td>3,333</td>
</tr>
<tr>
<td>Acidification</td>
<td>mole of H⁺</td>
<td>549.1</td>
</tr>
<tr>
<td>Eutrophication</td>
<td>kg N</td>
<td>1.357</td>
</tr>
<tr>
<td>Ecotoxicity</td>
<td>CTU</td>
<td>1,757</td>
</tr>
<tr>
<td>Human Health Carcinogenic</td>
<td>CTU</td>
<td>6.232×10⁻⁵</td>
</tr>
<tr>
<td>Human Health Non-Carcinogenic</td>
<td>CTU</td>
<td>9.579×10⁻⁵</td>
</tr>
</tbody>
</table>

5.3.2.2 Contribution Analysis

Processes contributions to each impact category for both conventional reactive dyeing and cationization dyeing process are shown in Figure 81. For both systems, wastewater treatment was not considered as a separate process for evaluating the environmental impacts. Since all processes in the systems produce wastewater, wastewater treatment was taken as an input and the impacts of the inputs and emissions were attributed to each processing stage based on the volume and chemical contents of the effluent produced in the process.
Figure 81 Results of contribution analysis for the conventional and cationization dyeing (innovative) process
For the conventional reactive dyeing process, the use of large amounts of steam and electricity during dyeing and washing has high contributions to most of the impact categories: 76% of GWP, 64% of AP, 21% of EP, 53% of ETP, 50% of HH-C, and 44% of HH-NC. This is because the conventional reactive dyeing requires long dyeing times and intensive washing and scouring processes after dyeing to remove the unfixed and hydrolyzed dyes, especially for deep black shades. Besides the use of steam and electricity, the other hot spot of the conventional reactive dyeing is the consumption and emission of the reactive dye, C.I. Reactive Black 5.

As Figure 81 shows, compared with conventional reactive dyeing, the dyeing stage of cationized cotton contributed less impact for all categories. This agrees with previous research that if the cationization process was not considered, the dyeing of cationized cotton is more environmentally benign compared with conventional reactive dyeing process\textsuperscript{59,112,205}.

However, due to the emissions of trimethylamine, ammonia, and other nitrogenous compounds during the production and application of CHPTAC, the cationization process and the following rinsing have high contributions to EP. Also, since CHPTAC is synthesized from epichlorohydrin (category 2 carcinogen) and trimethylamine hydrochloride and it can convert to EPTAC (category 2 carcinogen), the cationization process contributed to 54% impacts for HH-C and 68% impacts for HH-NC of the cationization dyeing system. While for the categories that were dominated by energy consumption (GWP, AP, and ETP), the cationization dyeing system has lower impacts than the conventional reactive dyeing system.
5.3.2.3 Normalization

Based on the normalization factors provided in Table 31, impacts of all categories were normalized to person equivalents (the annual contribution of an average person in US) and the results are presented in Figure 82.

![Normalized impacts of all evaluated categories for the conventional reactive dyeing and cationization dyeing systems](image)

Figure 82 Normalized impacts of all evaluated categories for the conventional reactive dyeing and cationization dyeing systems

As the figure shows, due to the large consumption of organic chemicals in both systems, the Human Health-Carcinogenic potential has the highest impact after normalized to person equivalent. For the three most important impact categories after normalization, the cationization dyeing system has higher contributions in HH-Carcinogenic and HH-Non-
Carcinogenic while its impact on Ecotoxicity is significantly lower than the conventional dyeing system.

5.4 Discussion

5.4.1 Toxicity and Salinity Impacts

As mentioned previously, the three toxicity categories have highest impacts after normalized to person equivalent. For human health impacts (carcinogenic and non-carcinogenic), the higher contributions of the cationization dyeing system is mainly due to the high consumption of cationic reagents and chemical emissions to wastewater. Even though the production and application of CHPTAC also have significant impacts on Ecotoxicity, the Ecotoxicity impact of the cationization dyeing system is still less than 50% of the conventional reactive dyeing system due to the large reduction of steam requirements during dyeing and after-washing.

The USEtox impact assessment methodology does not address the exposure of chemicals in the working environment and the related toxicity impacts. However, in both systems, large quantities of hazardous chemicals and dyes were handled by workers, especially for the cationization process using a cold pad-batch method. In another aspect, conventional reactive dyeing uses large amounts of electrolytes (Na₂SO₄), which is disposed in large quantities through wastewater in local water bodies in spite of some efforts of recovery²¹⁸,²²⁵. The salinization of local drinking and agricultural water may also cause serious environmental problems. However, the current LCA methodologies do not yet cover this impact category thus it was not reflected on the LCIA results. Since one of the motivations for using
cationized cotton is to eliminate the use of salt during dyeing, the benefit of the cationization dyeing system on reducing water salinization should also be considered.

5.4.2 Feasible Cleaner Production Proposal

From the previous analysis, it was found that the energy (steam and electricity) consumption is crucial for cleaner production of deep dyed cotton using conventional reactive dyeing. In the conventional dyeing process, a significant amount of reactive dyes were hydrolyzed and need be removed by repeated scouring and washing after dyeing. This consumes extra amount of dyes, increases chemical emissions, and above all, requires for a large amount of energy for heating. Thus, if the conventional reactive dyeing system is used, reactive dyes with modified structure and higher fixation efficiency should be applied to lower the environmental impacts.

For the innovative cationization dyeing system, the major concern is the use of the toxic and carcinogenic cationic reagent EHPTAC. Large impacts in Human Health, both carcinogenic and non-carcinogenic is from the synthesis and application of the cationic reagent. Thus, the application method for cationization should be carefully selected to minimize the exposure of workers during handling at the same time of increase application efficiency. For the cold pad-batch application method, it was suggested that NaOH and CHPTAC should be piped to the mix tank or pad trough so that EPTAC is formed right before padding, reducing the risk for occupational exposure. Furthermore, closed spray-padding systems can be utilized to minimize the human contact of the chemicals. Also, wastewater containing unfixed and hydrolyzed cationic reagents should be carefully controlled to avoid the emissions to
freshwater systems. To more effectively reduce the toxicity impacts of cationization, environmentally benign cationic agents, such as chitosan can be used as a substitute for improving cotton dyeability\(^9_{2,236}\).

5.4.3 Uncertainties and Outlook

For both scenarios, one of the important factors on environmental impact is the consumption and emission of chemicals. However, for some chemicals, such as reactive dyes and the cationic reagent (CHPTAC), background processes and characterization factors are unavailable. Even though alternatives were used or CFs were developed for missing chemicals, the assessment of chemicals is still a weak point for this assessment, especially for toxicity impacts. Also, there are some uncertainties on the emissions and degradations of the chemicals after wastewater treatment since most of the results are based on theoretical estimations rather than real measurements in local water system.

Since human toxicity in the working environment and salinization of water were not included in the current LCA methodologies, no firm conclusion can be addressed for the toxicity impacts of the systems. The missing of chemicals and weakness in the currently available LCIA methods regarding toxicity issues is crucial for both dyeing and other processes in the textile industry. Since a biased LCA can be misleading for textile researchers, manufacturers, and eco-conscious consumers, it is important that the LCA methodology is developed further to enhance its relevance and reliability as a methodology for the textile industry\(^220\).
5.5 Conclusions

In conclusion, the conventional reactive dyeing system has higher impacts in Global Warming Potential, Acidification Potential, and Ecotoxicity Potential than the cationization dyeing system due to the large consumption of energy during conventional reactive dyeing and repeated after-washing. The use of quaternary ammonium based cationic reagents and the emissions of nitrogenous compound during cationization resulted in the higher Eutrophication Potential of the cationization dyeing system. Since the cationic reagent is synthesized from epichlorohydrin and can convert to carcinogenic EPTAC, the cationization process has large impacts on Human Health, both Carcinogenic and Non-Carcinogenic.

Based on the LCA results and the limitations of the toxicity methodology, no firm conclusion on which dyeing system is more environmentally beneficial can be generated. For conventional reactive dyeing, modified reactive dyes with higher fixation rates should be applied to lower the environmental impacts. For cationization dyeing, the toxicity impacts of cationization should be reduced by careful selection of cationic agent, modification of application method, and control of chemical emissions. It is also necessary to complete the chemical inventory in LCA database and toxicity assessment methodology to help provide more accurate environmental assessments for the textile industry.
CHAPTER 6 CONCLUSIONS

This study mainly focused on three aspects on cotton cationization: ultra-deep dyeing on mercerized cationized cotton, real-time dyebath monitoring of cationized cotton for levelness control, and a comparative life-cycle assessment of cationization dyeing versus conventional reactive dyeing of cotton.

First, the effect of mercerization and cationization degrees on dyeing performance and colorfastness properties of cotton fabrics were evaluated. Considering both dyeing performance and cost effectiveness, the optimum treatment conditions were 21% NaOH for mercerization (barium number around 130) and 125 g/L CHPTAC for cationization. Both color yield and dye uptake leveled out with further increases in chemical concentrations. Compared with untreated cotton dyed with a conventional dyeing procedure, the well mercerized cationized cotton fabrics dyed without electrolytes have improved colorfastness to laundering, higher color durability, slightly reduced colorfastness to dry crocking and comparable performance on other colorfastness properties.

The influence of liquor ratio and dyestuff amount on producing ultra-deep black dyeings on mercerized cationized cotton was also evaluated. For mercerized only cotton fabric, nearly equivalent depth of shades were obtained independent of the liquor ratio and the amount of CI Reactive Black 5 applied (from 7% to 10% owf). For mercerized cationized cotton, the liquor ratio also had a negligible effect on the depth of shade obtained, but increasing the amount of dye resulted in an increased in shade depth. In conclusion, the ultra-deep black
shade obtained on mercerized cationized cotton was not obtainable using mercerized uncationized cotton, even with very low liquor ratio and drastically increased dye amounts.

In another aspect, for obtaining level light to medium reactive dyeings on cationized cotton, the influence of temperature, dye structure, addition of soda ash, and leveling agents on dyeing kinetics and levelness of cationized cotton were evaluated. Lowering the dyeing temperature only slightly reduced the dye exhaustion rate of the reactive dyes but significantly improved the levelness of dyed cationized cotton fabrics. The addition of soda ash has relatively small influence on dye strike rate and levelness of cationized cotton dyed with Everzol dyes. In comparison, eliminating the addition of soda ash in the initial dyebath significantly reduced the dye strike rate of the Evercion dyes and improved the levelness of dyeing. Thus, for Evercion dyes, level dyeing on cationized cotton was obtained by controlling the dyeing temperature and the time of adding soda ash. However, the dye strike rate and dyeing levelness of Everzol dyes should be better controlled using leveling agents.

Among the variety of anionic, cationic, and amphoteric leveling agents applied, the formaldehyde condensate of naphthalene sulfonic acid (INVALON® DAM 50% Liq) has the best performance in consideration of dye strike rate, final dye uptake, and levelness of dyeing. Also, the addition of leveling agents can be applied in combination of dye dosing or adding dyes in portions to better control the dye exhaustion process and further improve the levelness of dyeing.
In the last part of this research, the environmental impacts of deep dyed cotton using cationization dyeing procedure were compared with the cotton fabrics dyed using conventional reactive dyeing. Among the six environmental impact categories assessed, the conventional reactive dyeing system has higher impacts in global warming, acidification, and ecotoxicity potential, mainly caused by its high consumption of energy during dyeing and washing off process. For the cationization dyeing system, the large amount of CHPTAC used for cationization caused high impacts in eutrophication and human health effects, both carcinogenic and non-carcinogenic. Since no firm conclusion on which dyeing system is more environmentally beneficial was generated, feasible cleaner production proposal of both dyeing systems were suggested.
CHAPTER 7 RECOMMENDATIONS FOR FUTURE WORK

In this research, the ultra-deep black dyeing was obtained using CI reactive black 5, which is a vinyl sulfone based bifunctional dye. For further experiments, dyeing performance and colorfastness properties of other classes of reactive dyes on mercerized cationized cotton fabrics should also be investigated. Also, the mercerization, cationization, and dyeing process of cotton fabrics should be fully optimized by statistically designed experiments and pilot trials should be run to validate their commercial applicability.

In another aspect, future work on real-time dyebath monitoring of cationized cotton can be focused on evaluating the dyeing kinetics and levelness of cationized cotton using other reactive dyes to further investigate the influence of dye structure. After finding the relationships between the dyeing kinetics, levelness, and dye structure, suggestions on dyeing procedure and chemical recipe can be made for different kinds of dyes to help obtain level dyeing on cationized cotton. Direct and acid dyes can also be applied on cationized cotton and monitored for dye strike rate and levelness since these anionic dyes may suffer from the same levelness problem as reactive dyes.

For the comparative life-cycle assessment, background processes and characterization factors are missing for important chemicals. Also, human toxicity in the working environment and salinization of water were not included in the current LCA methodologies. Thus, to obtain a more accurate environmental assessment, it is necessary to re-do the analysis in the future after the LCA database and methodology are further developed.
REFERENCES


115. C.Rowe, K. (1994). *Effects of sodium hydroxide solution temperature in the mercerization process on dye uptake and physical properties of 100% cotton fabric.* Institute of Textile Technology, Charlottesville, VA.


