

ABSTRACT

ZHANG, NANSHAN. Anionization of Cotton with 3-Chloro-2-hydroxy-1-propanesulfonic Acid Sodium Salt Hydrate (CHPSAS). (Under the direction of Dr. Peter Hauser and Dr. Melissa Pasquinelli.)

Cotton, the most typical natural cellulosic fiber, has exceptional affinity for various dyes and therefore can be dyed with a great deal of dye-classes. Basic dyes, or called cationic dyes are well-known as it can produce bright shades with high color intensity. However such dye-classes are not used in dyeing cotton since its structure is non-planar as well as not large enough for appropriate affinity. To give cotton a negative charge, a variety of chemicals such as citric acid, chloroacetic acid and 1,2,3,4-butanetetracarboxylic acid (BTCA) have been applied. In the current work, a novel anionic agent, 3-chloro-2-hydroxy-1-propanesulfonic acid sodium salt hydrate (CHPSAS) was used to impart negative charges to cotton in order to form strong ionic bonds with basic dyes. A one-step process, cold pad batch was employed to apply anionic feature to cotton fibers which made the whole experiment environmental friendly. An improved color yield and fair fastness properties have been acquired though CHPSAS fixations were not that ideal. Two basic dye structures which showed superior fastness properties were studied in detail. Sulfur fixation, color strength, washfastness and crockfastness properties of anionic cotton have been investigated.

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Anionization of Cotton with 3-Chloro-2-hydroxy-1-propanesulfonic Acid Sodium Salt Hydrate (CHPSAS)

by
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DEDICATION

This work is dedicated to my family for their unselfish love and encouragement in all my endeavors.

BIOGRAPHY

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1. INTRODUCTION

Cotton is considered as the most popular textile in the world today for its natural comfort, versatility in use and it is eco-friendly. Basic dyes, are called cationic dyes as cations existed in the dye molecule, are primarily used for dyeing acrylic and cationic dyeable polyester fibers. This group of dyes is unique due to the brilliant colors it can produce. Since it carries positive charges, it has an affinity for diverse fibers with varied colorfastness. Cellulose fibers are usually not dyed with such kind of dyes as the positively charged dye cannot form strong bonds with these fibers. To solve this problem, a series of anionic agents including 1,2,3,4-butanetetracarboxylic acid (BTCA), polymaleic acid and citric acid have been discovered to impart negative charges to cotton [1].

A new dyeing system which aims to maximize basic dye fixation on cellulosic fibers and to make the process eco-friendly at the same time has been investigated in the current work. The cold pad batch was the process to apply anionic character to cotton fibers as it was a one-step process and it saved energy and water together. The novel anionic reagent, 3-chloro-2-hydroxy-1-propanesulfonic acid sodium salt hydrate (CHPSAS) was reacted with cellulose chains to impart negative charges on cotton. As it can form strong ionic bonds with basic dyes which carry positive charges, CHPSAS-treated cotton will have an affinity to such cationic dyes which helps to expand the range of available dyes for cotton. The superiority of this new system covers reduction in dye use and chemical waste as well as shorter dyeing times. Thus it involves less environmental impact and higher dyeing efficiency. In particular, the current work paid special attention to optimize dye yield of the anionic cotton treated

with CHPSAS dyed with basic dyes. Moreover, dyeing behavior and colorfastness properties of basic dyes with anionically modified cotton were studied in detail.

2. LITERATURE REVIEW

2.1 The nature of cotton

Cotton, one of the oldest natural fibers which dates back to more than 7000 years ago, is harvested naturally from cotton plant. Moderate strength, color retention and capability to be washed and dyed enable its numerous end-uses such as apparel and home fashion.

The world uses this white fibrous product more than any other natural fibers and it is primarily grown and used to make cloth. As cotton can be woven, knitted and blended with other existing natural fibers such as flax, it is regarded as ‘the fabric of our lives’ by the American Cotton Council [2]. Cotton is noted for its versatility, appearance, performance and above all, its natural comfort. In today's fast-moving world, it is still nature's wonder fiber, providing thousands of useful products and supporting millions of jobs as it moves year after year from field to fabric [3]. As for cotton, the primary end uses include apparel and home fashion such as active wear and table cloths. According to data provided by National Cotton Council, 5 million bales of cotton have been spun from American textile mills annually during 2006 to 2008, which can be used to make more than a billion pairs of jeans. [4].

The benefits of purchasing cotton clothes are considerable, such as hypoallergenic and dust mite resistance, softness and good body moisture absorbency [5].

What's more, cotton has other outstanding characteristics such as environmentally friendly and durable. Not only is cotton biodegradable, it is also a renewable resource. Many people who are concerned with the environment choose to get clothes that are made with organic cotton. This is the cotton that is grown without the use of pesticides. As for durability, cotton-made clothes usually have a moderate tensile strength which makes it relatively strong. Cotton clothing is especially good for intractable children, who are hard on clothing. Clothes made with cotton still look good after they have been worn hard [5]. Micronaire, fiber strength and length are regarded as three important physical properties of cotton. The micronaire range is 3.0 to 5.5 for upland cotton, which is an indication of fiber fineness and ripeness related to the performance of processing and the end product. Length and strength of cotton fiber varies inherently and fiber lengths range from 1.0 to 1.25 inches for American upland cotton.

2.2 Chemistry of cellulose

Cellulose is a polymer of glucose which has a ring structure with five carbon atoms and an oxygen atom. α -Glucose and β -glucose are widely accepted as two types of dextrorotary glucose, where the difference rests with the location of the hydroxyls above or below the ring structure. In the β -glucose structure, two hydroxyl groups are distributed oppositely on the ring, however in α -glucose both hydroxyl groups either locate at the top or the bottom of the pyranose ring [6]. Cellulose is a macromolecule — a natural polymer with a long chain of β -D-glucose links. Figure 1 below indicates two unlinked β -D-glucose molecules and they

become integrated with each other via combining the highlighted grey part with elimination of water. A cellobiose or a disaccharide, comprising two β -D-glucose joined in 1:4 positions, is then formed in this way and comes the repeating unit of the cellulose polymer chain. This β -glucose structure determines that adjacent units should invert by 180° if hydroxyl groups are connected in the 1:4 positions. Theoretically, fiber can be formed feasibly only if β -linkage exists, by orienting polymers in a line. The number of the repeating units is referred to as the 'degree of polymerization'. Adjacent cellulose chains are held together by hydrogen bonding where takes place between hydroxyl groups of molecules (Fig.2). Crystalline regions occupy around 70% in cotton, while amorphous regions which absorb dyes and chemicals are distributed therein. Each cellobiose unit has a total amount of three chemically reactive hydroxyl groups (one primary and two secondary) where substitution reactions and water absorption occur, however the hydrogen bonding tends to be weak in water as hydrogen bonds would break quickly.

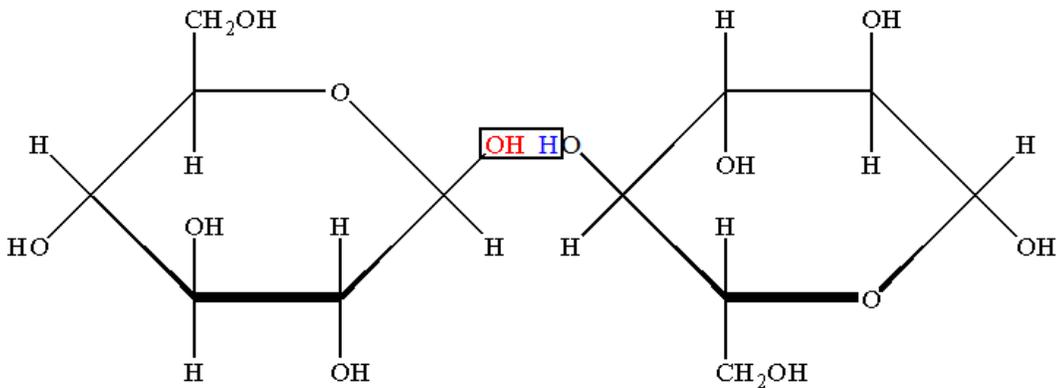


Figure 1. Two unlinked molecules of β -D-glucose

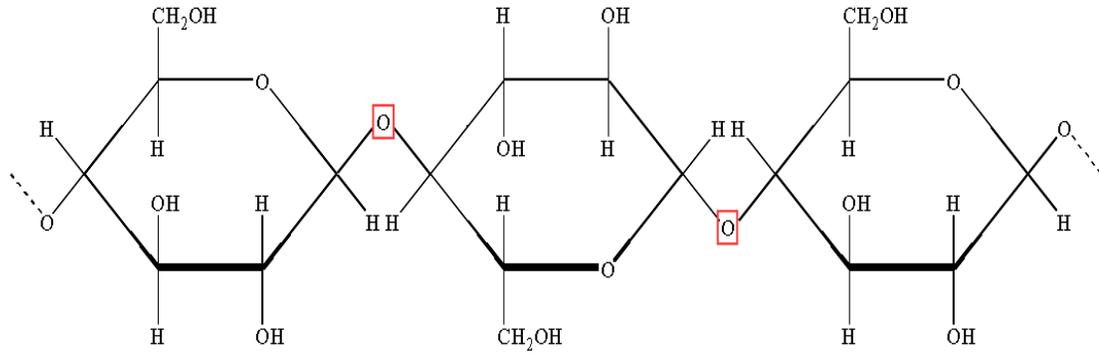


Figure 2. How polysaccharide is formed from disaccharide

Single cotton fiber, with ribbon-like structure, has twists and convolutions longitudinally at regular intervals. The cross-section of cotton fiber is of kidney shape, which may be caused by non-uniform mechanical strains in the drying process.

From outside to inside a normal cotton fiber is made of these six parts: cuticle, primary wall, winding layer, secondary wall, lumen wall and lumen, the structure of which is schematically illustrated in Figure 3 below. The innermost passage of cotton is known as lumen, a hollow canal which carries nourishment during the growth of cotton. The secondary wall embodies the main part of the fiber and takes up most of fiber weight. It is consisted of irregular-sized fibrils where the cellulose chains are well lined up. The fibrils which generally oriented at an angle of 23° to the fiber axis are accumulated reversely in helical form along the fiber length [7]. Such reversed points are particular for cotton, offering the ability of prolongation.

Winding layer is also included in the secondary wall with micro fibrils at about 70° to fiber axis. The less crystalline layer, primary wall, appears in the outer layer which gives a

firmer structure. Cuticle, with a thickness of a few molecules, is the outermost layer of the fiber. It comprises waxes and resins which work to prevent water and dyes from the cotton fiber.

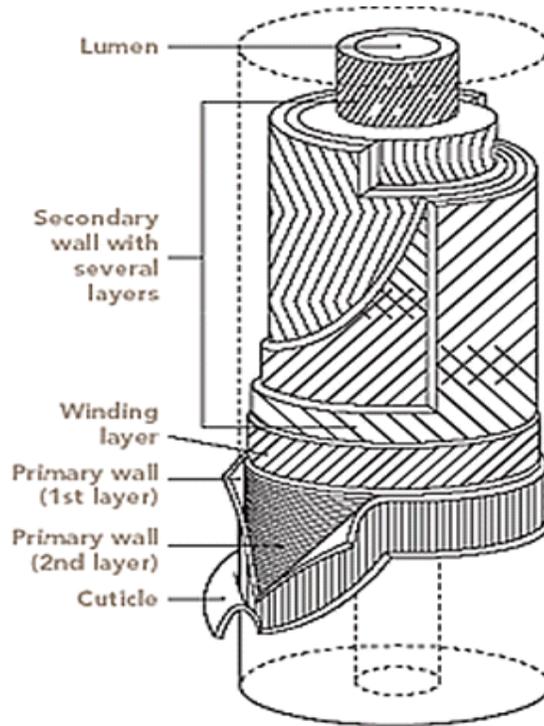


Figure 3. The structure of cotton layers [7]

Cotton fiber contains chemical components including cellulose, protein, ash, wax, sugar, acids and other chemical compounds. Non-cellulose chemicals such as ash and wax are usually located in the cuticle of the fiber. The chemical composition of cotton is displayed as follows in Table 1.

Table 1. Chemical composition of cotton [8]

Chemical composition	Percentage
Cellulose	91.00%
Water	7.85%
Protoplasm and pectins	0.55%
Waxes and fatty substances	0.40%
Mineral salts	0.20%

2.3 Dyes for cotton

In dyeing with non-cellulosic fibers, one certain class of dyes dominating the substrate is the most general case. For instance, basic dyes are often used in dyeing acrylic fibers and acid dyes are usually utilized to dye wool or nylon fibers. However, cotton has exceptional affinity for a variety of popular dyes which satisfies spending limitation, practicability and fastness demand, including dye types such as natural dyes, direct dyes, fiber reactive dyes, vat dyes and sulfur dyes. This universality in dyeing property is a result of a long-term research in cotton dyeing since early civilizing process. Besides, the stable nature of cotton fiber under the presence of various chemicals in aqueous condition enables the application of many classes of dyes. In addition there is no single kind of dye which can meet the demand of all uses.

In days of old, cotton was dyed by natural dyestuffs which needed to be treated with mordants first. However, such kinds of dyes encountered issues as restricted color range and unsatisfied color fastness properties. Direct dyes, with immediate attraction to cotton,

accessed to market after natural dyes and became the first dye class which had no need of mordants. By modifying direct dyestuffs with copper and other metals, fastness properties of cotton have been enhanced. Although this dye class only had limited brightness, poor fastness to chlorine and some aromatic amines used as raw materials were recognized as carcinogens, advantages of such dyes involve extensive color shades, easy operation and economical procedures. Several dye species were discovered in the first years of the last century, including azoic dyes, sulfur dyes and vat dyes. Azoic dyes appeared on the market with the commercial name 'Para Red' in the 1880s, by combining amines with β -naphthol to form an insoluble pigment in the fiber [9]. It has been widely accepted that dyeing cellulose with azoic dyes is the least costly way to attain heavy color shades such as red and scarlet, yet there is quite a limited shade range which can be reached by azoic dyes. Sulfur dyes are generally used on cellulosic fibers and their blends due to their adequate wet fastness and light fastness features. In 1873, the first ever commercialized sulfur dye named 'Cachou de Laval' was made from sawdust and even up to today its structure is mostly unknown except for containing disulfide linkages. Vat dyes are nonionic, possessing at least two reducible carbonyls. Such kind of structure enables high fixation as there is oxidation-reduction reaction of the insoluble form and is especially suitable for continuous dyeing, nevertheless there are concerns with vat dyes' complicated application procedure and poor abrasion resistance. Indigo, a naturally occurring vat dye, was made synthetically in 1883 and commercialized by BASF in 1897. As a dye, it has no affinity for cotton with poor fastness properties to laundering and crocking but these deficiencies make no difference to its

popularity. It has been praised as ‘King of Dyes’ for its fascinating worn look and styling potential. To deal with wash fastness problem of direct dyes, the idea of forming covalent bonds between dyes and cellulose was being commercialized in the 1960’s. Under alkaline conditions, reactive groups can form covalent bonds with hydroxyl groups on cellulose chains. By forming covalent bonds with cellulose fibers, dye molecules become integrated with the cellulose molecule and therefore enhancing colorfastness of a garment. Even though this dye class possesses extraordinary wet fastness qualities and broad span of vivid color shades, incomplete dye up-take and environmental matters remain to be solved. What’s more, most of the reactive dyes are not fast to hypochlorites so that there will be potential problems during chlorine bleaching.

Basic dyes, also called as cationic dyes are commonly referred to hydrochlorides of organic bases. They are considered as the first synthetic dyes in the history and basic dyes such as Malachite Green and Magenta are widely applied even until today. Such kind of dyes can provide colored cations when immersed in water and the process of salt formation is displayed in Figure 4 below [10]:

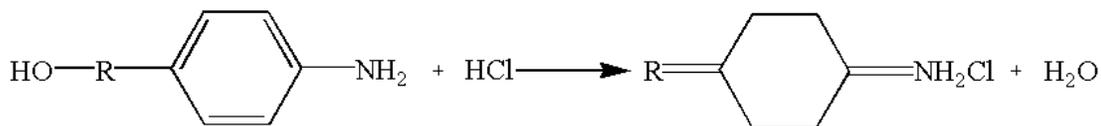


Figure 4. Salt-formation process of basic dyes

The main use of basic dyes is to dye protein fibers such as acrylic and cationic dyeable polyester, for the reason that ionic bonds can be formed with fibers that contain anionic groups. The most prominent nature of basic dyes is their brilliance and vividness of color, while level dyeing and lightfastness properties remain to be improved. As basic dyes might be dissipated into colorless bases under alkaline condition, hard water and alkaline solutions should be kept away. With the development of modified basic dyes, much better fastness properties have been investigated on hydrophobic fibers such as polyacrylonitrile fibers. There are three general types of modified basic dyes [10]:

1. Basic dyes with a delocalized positive charge (Figure 5).

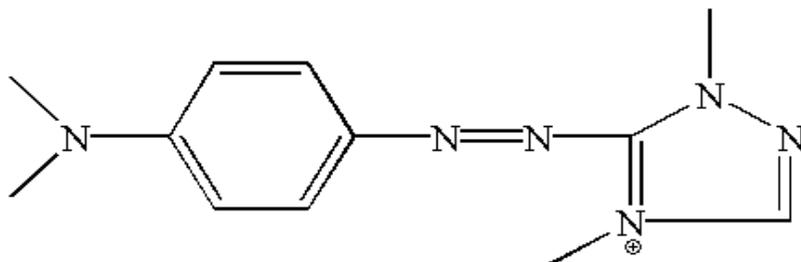


Figure 5. C.I. Basic Red 22

2. Basic dyes having a heterocyclic ring with a quaternary nitrogen atom (Figure 6).

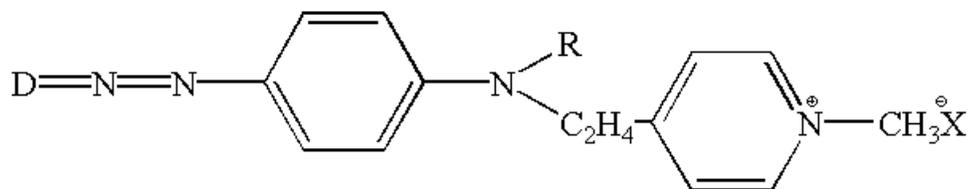


Figure 6. C.I. Basic Orange 14

3. Basic dyes comprising a cation in a branched chain (Figure 7)

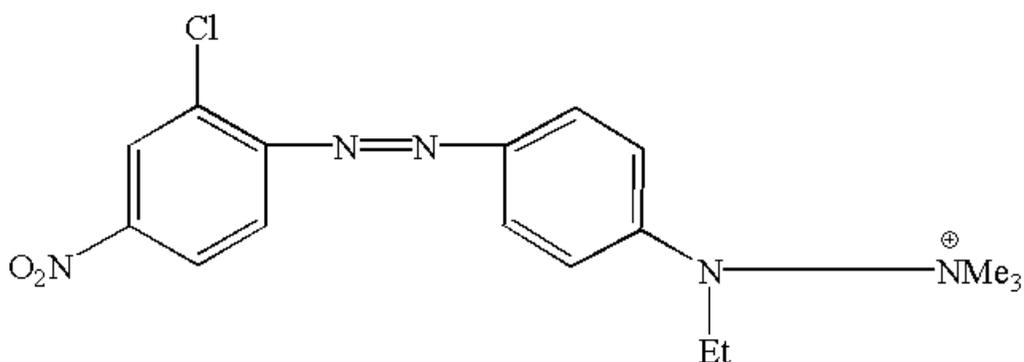


Figure 7. C.I. Basic Red 18

However these dyes have no affinity for cellulose, nylon and regular polyester without mordants as such fibers do not have anionic groups. Based on the structure of cotton fibers, the types of interaction between cotton fibers and dyes include covalent bonds and secondary valency forces. Once giving cotton a charge, the range of dyes used has been expanded and a new type of fiber has been created.

2.4 Anionization of cotton

Imparting positive or negative charges to cotton fibers could potentially improve the dyeability to certain kinds of dyes which carry the opposite charges. By offering fiber a positive charge, it is capable of forming ionic bonds with anionic groups in acid dyes so that such kind of dyes can be applied in dyeing cotton. This enables fair light fastness and full range of bright color of dyeing cotton with acid dyes. By making fiber anionic, basic dyes become chemically attractive to cotton fibers via forming ionic bonds with the anionic groups on the cellulose chains. Applying basic dyes on cotton provides a full range of brilliance at the same time.

N-methylol crosslinking agents have been previously recognized to impart unique characteristics such as wrinkle-free properties by forming covalent bonds with hydroxyl groups of cellulose. However, the mutagenic effect of formaldehyde has attracted much concern and eco-friendly textiles are urgently needed by today's industry. With the discovery of underlying human carcinogenicity brought by formaldehyde, researches have been focused on substitutes as crosslinking agents for cotton in order to replace the conventional N-methylol reagents [11].

Cotton cellulose can be given negative charge through diverse routes, including treatment with chloroacetic acid or chlorosulphonic acid (Figure 8) [12]. The product after anionization of cellulose with chloroacetic acid is termed as carboxymethylcellulose (CMC) (Figure 9), which can be also called cellulose glycolic or cellulose glycolate acid.

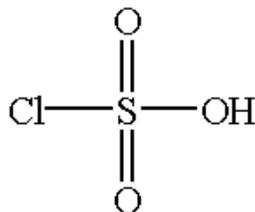


Figure 8. Chlorosulphonic acid

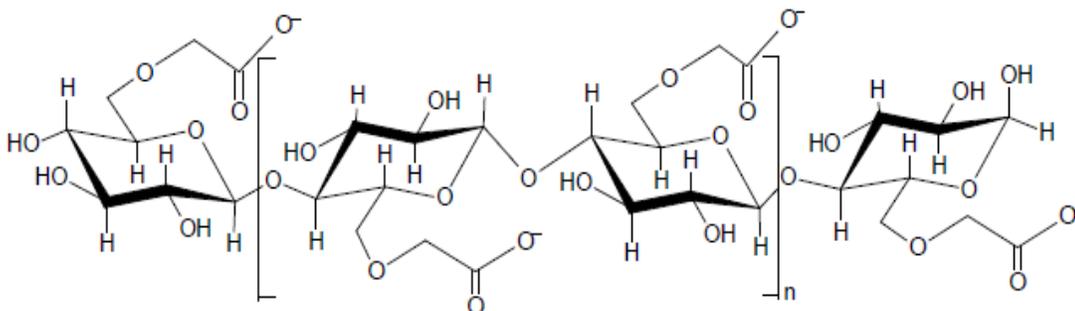
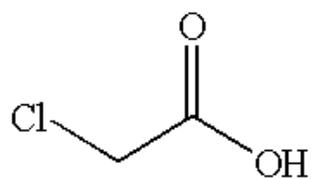


Figure 9. Carboxymethylcellulose (CMC)

The main purpose of the carboxymethylation reaction is to form anionic cotton by grafting negative charges onto the cellulose chain. This process mainly happens in amorphous regions rather than crystalline regions, making a non-homogeneous distribution of carboxymethyl groups at the early stage. With reaction time, such reagents go through into much more ordered areas and become more evenly distributed [1].

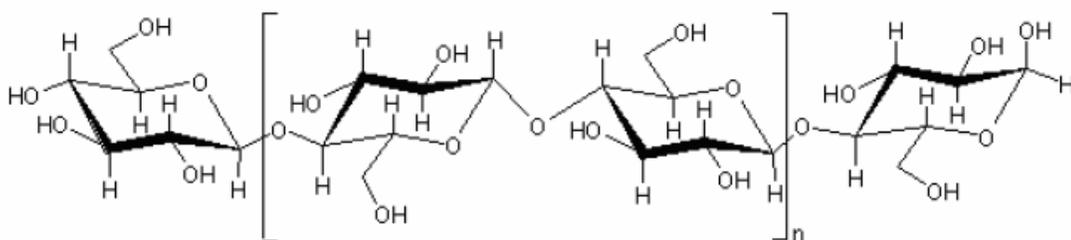
The process of carboxymethylation involves soaking and padding of cellulosic fabric with sodium hydroxide as well as drying to promote further reaction. During this procedure, hydroxyl groups in cellulose chains have undergone a chemical reaction where the hydrogen atom is removed and the oxygen becomes negatively charged. After that the cellulose is

called soda cellulose, which has affinity for reacting with sodium chloroacetate. Treating soda cellulose with sodium chloroacetate can be achieved either by being soaked and padded through the blending of sodium hydroxide and sodium chloroacetate, or by passing through chloroacetate solution straightforwardly. The hydroxyl groups on the cellulose chains are replaced by stable ether linkages, forming anionic cellulose as shown in Figure 10 below:



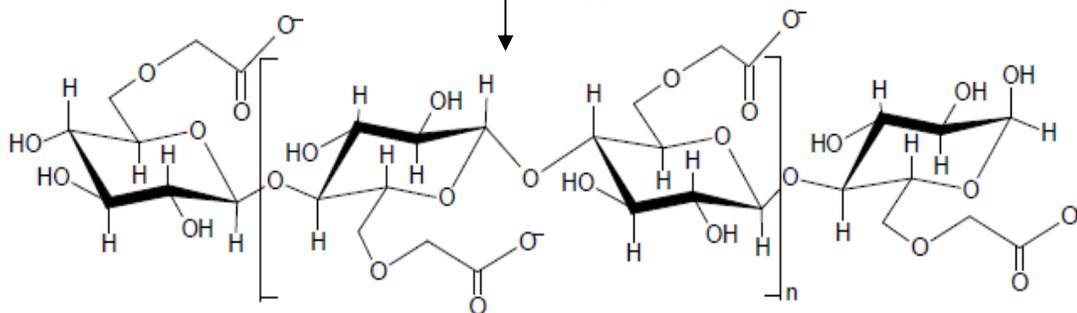
Chloroacetic acid

+



Cellulose

↓
NaOH



Anionic cellulose

Figure 10. Carboxymethylation reaction of cotton cellulose

It is well-accepted that polycarboxylic acids can impart anionic character to cellulose via forming ester bonds with such fabrics [13]. Welch determined that a lower temperature

was needed for a cis-type maleic acid than that of a trans-type fumaric acid to react with cellulose [14]. Research for such anionic agents started in the 1960s and it had been recognized that polycarboxylic acids had advantages such as good strength retention and capability for durable press over other nonformaldehyde crosslinkers. By studying the esterification mechanism between polycarboxylic acids and cotton cellulose, Yang and his colleagues found that a five-membered cyclic anhydride intermediate was formed during the esterification process [15].

Since Welch found 1,2,3,4-butanetetracarboxylic acid (BTCA) (Figure 11) worked well in imparting anionic character to cotton fabrics in 1988, a related study focused on the use of multifunctional carboxyl acids due to their formaldehyde-free property. In the presence of sodium hypophosphite catalyst, ester bonds are formed between an anhydride and the hydroxyl groups on cellulose. Choi and his coworkers explored a particular type of BTCA as the most effective agent of polycarboxylic acids in 1994, though it has less durability than N-methylol compounds as the tendency to be hydrolyzed [16].

Yang and coworkers studied the effectiveness of BTCA as a cross linking agent and it was found out that a better bridging performance could be observed with an increase in acid concentration and curing temperature [15]. When heated at high temperature, a nucleophilic substitution reaction will take place by reacting an anhydride intermediate form of BTCA with the hydroxyl group on cellulose. Sodium hypophosphite (SHP) works to promote the formation of this intermediate and has been widely accepted as a useful catalyst for the esterification reaction. To improve shade change and aquatic contamination problems, Lee

and coworkers investigated a nonphosphorous catalyst for BTCA which had comparable catalysis to SHP. Sodium propionate, the novel catalyst, appeared to have superior strength retention than SHP and can be regarded as an appropriate substitute for this conventional catalyst [13]. Kang and coworkers studied dyeability of cotton treated with BTCA in 2004. Anionic cotton fabrics dyed with direct dyes and fiber reactive dyes showed a substantial reduction in color strength, while in contrast enhanced tinctorial strength and color fastness features were observed when applying basic dyes [17].

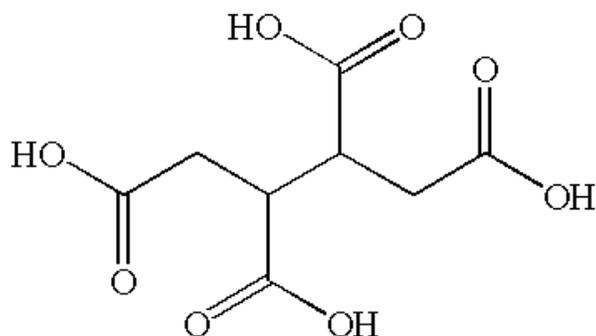


Figure 11. 1,2,3,4-butanetetracarboxylic acid (BTCA)

However, limitations of using BTCA such as risky impact of phosphorus catalyst, mechanical strength loss and high price made it important to find other substitutes for such a crosslinking agent. Other anionic reagents with lower cost have been explored to replace BTCA, including citric acid, maleic acid, polymaleic acid, polyacrylic acid and their derivatives [18]. As the application of BTCA involves the problem of high cost, a trifunctional carboxylic acid — citric acid was put into use in 1990 by the research of

Andrews and his coworkers [19]. In 2001, Ibrahim et al. applied citric acid (Figure 12) as a formaldehyde-free anionic agent in order to investigate the optimized condition and formulation for the manufactured product [11]. It turned out that citric acid worked well as a crosslinking agent for cellulosic fabrics with sodium hypophosphite as a catalyst.

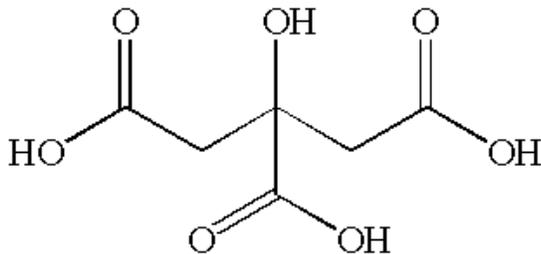
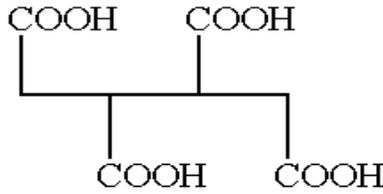
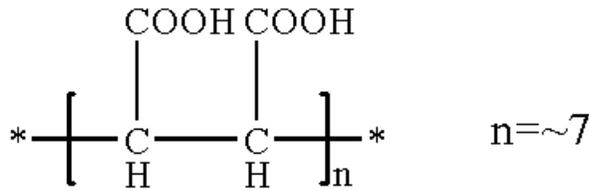


Figure 12. Citric acid

However, the cross-linking performance between citric acid and cellulose was not satisfactory as the hydroxyl of citric acid was believed to hinder the esterification of citric acid with cellulose [20]. Two polymers of maleic acid — the homopolymer (PMA) and the terpolymer (TPMA), with the benefit of low cost, had also been tried as crosslinking agents due to their analogous structure to BTCA (Figure 13), nevertheless the low accessibility of the anhydride intermediates to cellulosic hydroxyls made them less applicable when compared with BTCA.



BTCA

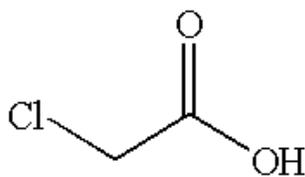


PMA

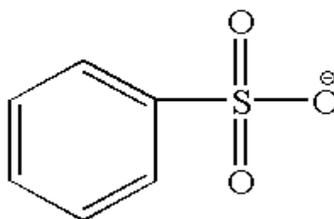
Figure 13. Structure of BTCA and PMA

Yang and Xu investigated the combination of citric acid and polymeric carboxylic acid (PMA or TPMA), observing citric acid converted from a trifunctional acid to a tetrafunctional acid. Specifically, the TPMA/CA group appeared to have better performance than PMA/CA combination which might be attributed to the formation of more flexible crosslinking networks under the treatment of the first set [19].

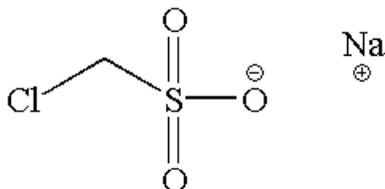
Various routes have been investigated to manufacture anionic cellulose, including reacting cellulose with vinyl sulfone or chlorotriazine compounds with a negative charge [12], by treating cellulosic fabrics with chloroacetic acid or by adding sodium chloromethyl sulfonate (CMSA) to cellulose as well [20] (Figure 14).



Chloroacetic acid



Anionic vinyl sulfone



Sodium chloromethyl sulfonate

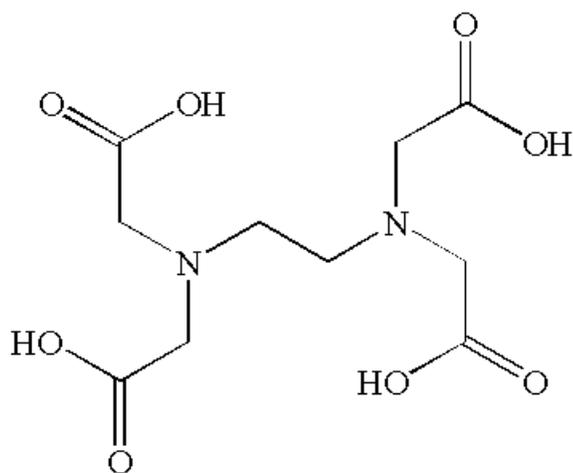
Figure 14. Structures of several anionic agents

In 2010, Haji and Shoushtari introduced a novel method to improve the dyeability of cellulosic fibers with cationic dyes. Cotton fibers were first treated with air plasma followed by grafting with acrylic acid to create anionic groups on the fiber surface. Natural dyes, with

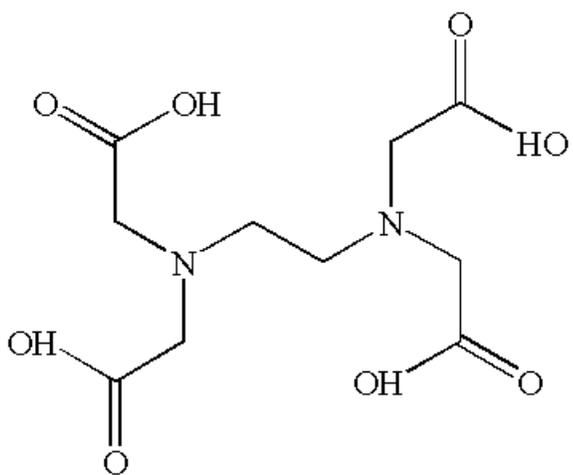
positive charges which extracted from berberis vulgaris were applied to dye the grafted samples [22].

According to Bilgen's research, anionic cellulose can be produced by the application of polyanions, containing ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), trisodium salt, monohydrate, ethylenediamine di(o-hydroxyphenylacetic acid (HEDTA), oxalic acid or maleic acid [23] (Figure 15). Besides, compounds of certain acids have also been tried to impart negative charges to cellulose. Mixtures of citric acid and maleic acid/itaconic acid with phosphorous catalyst have been investigated, showing reduced strength loss [14]. Citric acid, coupled with a terpolymer of maleic acid, acrylic acid and vinyl alcohol exhibited better performance and durability than most of other polycarboxylic acids [24]. In addition, researchers examined that chain length was relevant to strength loss of fabrics. Polycarboxylic acids with short chain received strength loss on the same level with formaldehyde while in contrast long-chain polycarboxylic acids achieved little or no strength loss at all. Treating cellulose with a combination of citric acid and chitosan revealed an improvement in tensile and tear strength, which might due to the esterification process both between citric acid and cellulose and between citric acid and chitosan [25].

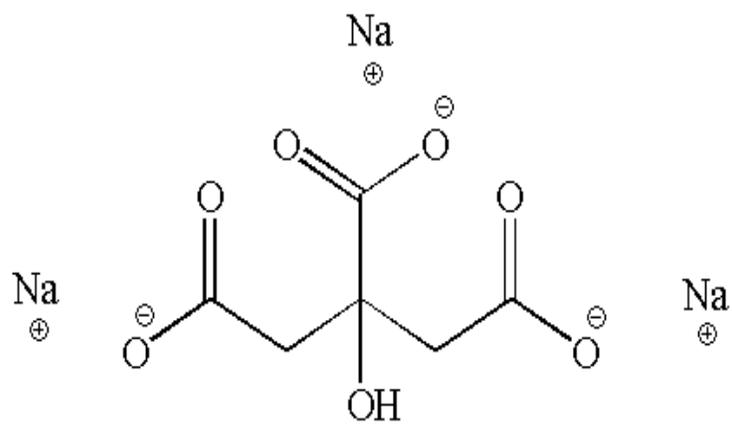
Figure 15. Structure of some polyanions



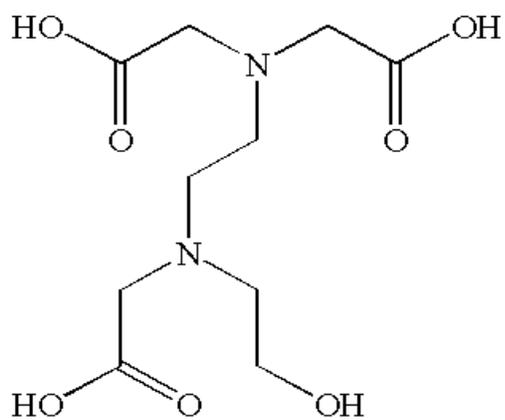
EDTA



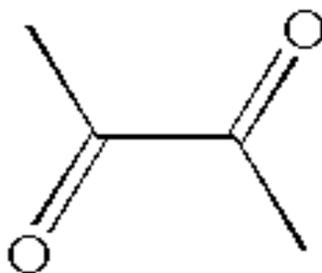
Nitrilotriacetic acid



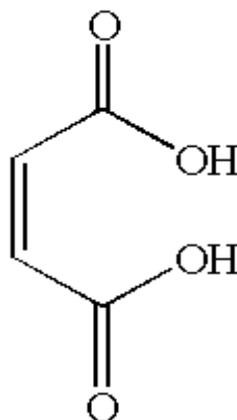
Citric acid trisodium salt anhydrous



HEDTA



Oxalic acid



Maleic acid

Although the use of multifunctional carboxylic acids prevents the emission of formaldehyde, problems including tensile strength loss and yellowing issues block the application of polycarboxylic acids in finishing process of cellulosic fabrics. Such chemical treatments might change the properties (both physical and chemical) of cotton, thus influence dye absorbency of various classes [26]. All these issues talked above make it difficult to replace formaldehyde finishes in commercial use today.

2.5 A novel anionic reactant — CHPSAS

3-Chloro-2-hydroxy-1-propanesulfonic acid sodium salt hydrate (CHPSAS) is known as an important reactant in polymer modification due to a reactive halogen atom and hydroxyl groups and hydrophilic sulfonic groups in its molecular structure (Figure 16). It can be also used in preparing surfactants, modified starch and drilling fluid loss additive. CHPSAS is synthesized from epichlorohydrin reacting with sodium bisulfite in the mixed solvent of methyl formate and water, as shown in Figure 17 [27].

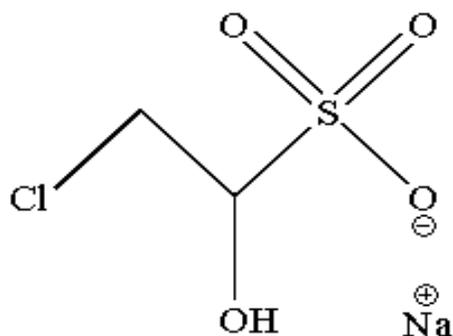


Figure 16. Chemical structure of CHPSAS

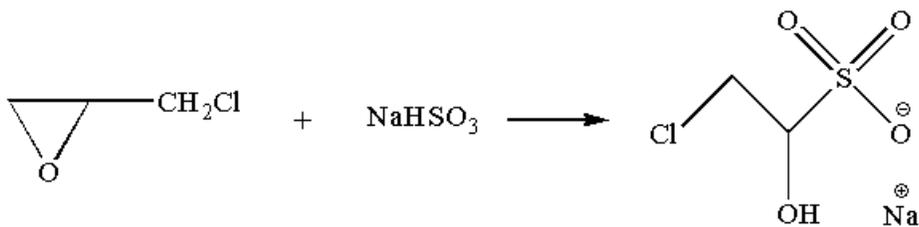


Figure 17. Synthetic route of CHPSAS

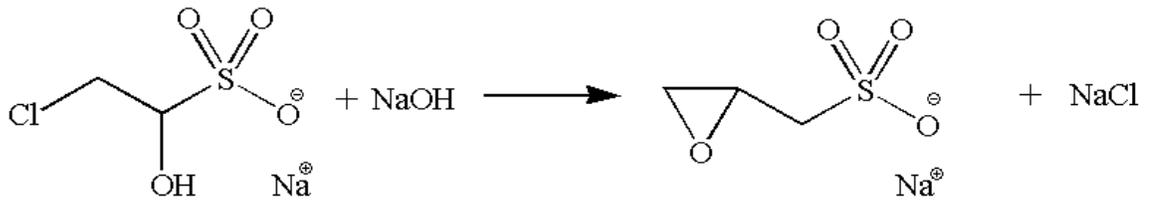
It is a chloralkane containing hydroxyl and sulfonic groups, which can be reacted with imidazole to make amphoteric surfactants via an alkylation reaction. Under alkaline conditions CHPSAS can have an etherification reaction with starch to manufacture starch derivatives with sulfonic groups, which work as excellent drilling fluid loss additive. The epoxy intermediate, oxiranemethanesulfonic acid sodium salt, is widely accepted as a useful multifunctional reactant with its ability to prepare many commonly used materials with unique properties via copolymerization and ring-opening reaction [27].

CHPSAS is used in the manufacture of ion exchange resins for water purification treatments and can easily react with hydroxyl groups to form permanent anionic sites on a material. Reaction of cellulose with CHPSAS depends on time, pH and temperature in alkaline aqueous solution which operates as a base catalyst. The anionization process comprises several reactions simultaneously [28]:

1. In the presence of sodium hydroxide, CHPSAS forms an epoxy intermediate (oxiranemethanesulfonic acid sodium salt) which acts as the anionic reactant for fiber modifications among a series of reactions (equation 1).
2. The epoxy intermediate then reacts with cellulose chains (equation 2).
3. The intermediate can also be hydrolyzed, forming a non-reactive product (2, 3-dihydroxy derivatives) (equation 3).

Hydrolysis of the epoxy intermediate starts immediately when CHPSAS and sodium hydroxide are mixed and the epoxy intermediate is formed. This hydrolyzed byproduct has

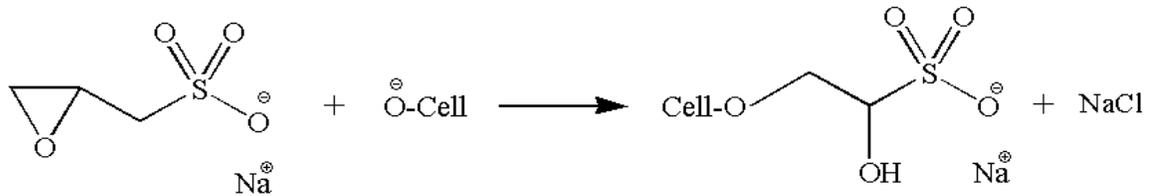
no affinity for cellulose and therefore cellulose fabric should be treated immediately after CHPSAS and NaOH are mixed. The anionization reaction is shown in Figure 18.



3-Chloro-2-hydroxy-1-propanesulfonic acid sodium salt hydrate (CHPSAS)

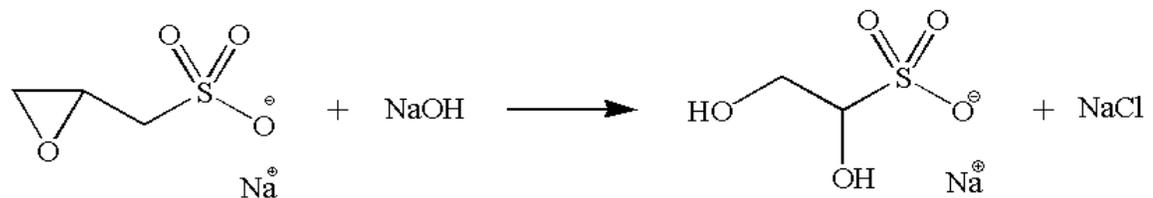
Oxiranemethanesulfonic acid sodium salt

Equation 1



Equation 2

Anionic cellulose



Equation 3

Hydrolyzed CHPSAS

Figure 18. Anionization of cotton cellulose with CHPSAS

Through giving cotton a negative charge by CHPSAS, cotton fibers can potentially be imparted with absolutely novel properties, leading to using such fibers in unexpected fields [28].

2.6 Research objectives

For a long time, the textile industry has been looking for ways to expand the dye range for cellulose fabrics. By giving cotton fibers a negative charge, previously unused dyes such as basic dyes are able to be applied on cotton. The objective of the current work was to apply basic dyes on cotton which was pretreated with a novel anionic agent — CHPSAS. Color strength, sulfur content analysis, fastness to laundering, staining and crocking have been evaluated and the optimized ratio of CHPSAS and sodium hydroxide has been found.

In the work presented here, anionization of cotton fabrics was achieved by the formation of covalent bonds between the cellulose chains and CHPSAS via the cold pad batch method.

It is widely recognized that dyeing cotton with a cold pad batch process enables the lowest water and energy consumption, meanwhile the amount of salt could be reduced or eliminated. Cold pad batch provides the most economical way for padding anionic agent to cotton, thus this procedure is eco-friendly. Besides, the one-step process makes it more convenient and attractive to pretreatment of cotton [29].

The cold pad batch route was studied in detail and process parameters in producing anionic sites were adopted from previous research [28]. To find out the optimized ratio of CHPSAS and NaOH, fixed amounts of CHPSAS were applied with a series of ‘CHPSAS-

NaOH' ratios. In the following step, by keeping the mole ratio of CHPSAS and NaOH obtained above, a series of samples with different CHPSAS concentrations had been generated for sulfur analysis. Moreover, sulfur content has been determined to indicate the degree of combination between CHPSAS and fabric. Cotton pretreated with CHPSAS has been dyed with a series of commercially available basic dyes, with untreated cotton being dyed as control groups at the same time. The color strength, washfastness and crockfastness of the dyed fabrics were determined.

3. EXPERIMENTAL PROCEDURES AND DESIGNS

Experimental materials, chemical reagents and analytical methods applied in the current work are introduced in this section, including the description and manufacturers of equipment, and chemicals and detailed information on fabrics. All materials and chemicals are economical, environmentally friendly and commercially available in mainstream textile industries.

3.1 Materials and chemicals

Related information such as name and chemical constitution of materials and chemicals used in this work are listed in Table 2 below. Cotton fabric, the substrate which is bleached desized cotton print cloth with basis weight of 102g/m^2 , is manufactured by Test Fabrics Incorporation. Each cotton sample was $6'' \times 10.2''$ with weight of 10 grams. The anionic agent used is 3-chloro-2-hydroxy-1-propanesulfonic acid sodium salt hydrate (CHPSAS), white

powder from Sigma-Aldrich with 100% purity. Sodium hydroxide of 50% w/w aqueous solution acted as the base, which was made by Fisher Scientific. The materials and chemicals used in the current work are listed in Table 2.

Table 2. Materials and chemicals

Name or Group	Description	Manufacturer
Cotton Fabric	Bleached desized print cloth, style 400, 102g/m ² , 44"/45", 78×76, ISO 105/F02	Testfabrics, Inc.
Anionic Agent	3-Chloro-2-hydroxy-1-propanesulfonic acid sodium salt hydrate (CHPSAS), 100% purity	Sigma-Aldrich Products
Alkali	Sodium hydroxide, 50% w/w aqueous solution	Fisher Scientific
Acid	Acetic acid, 90% aqueous solution	Arcos Organics
Surfactant	ApolloScour SDRS	Apollo Chemical Company

3.2 Equipment

The process involved with fabric treatment was completed in the Pilot Plant of College of Textiles at North Carolina State University. The padding machine was the product of Werner Mathis AG, which enabled padding fabric up to 18 inches in width. The trough of the

padder could hold one liter volume of water. Furthermore, running speed and pressure between two padding rolls were able to be adjusted. To dry the cotton fabric, samples were first centrifuged in a Bock Centrifugal Extractor with 10 lbs. maximum load and then dried in a Yamato Mechanical Convection Oven DKN 810 with a corrosion-resistant stainless steel interior. Time of centrifugation for extractor and temperature of drying could be controlled. Cotton samples were placed flat on metal frames in the convection oven. After the chemicals were mixed together, solutions were heated and stirred with Corning stirrer/hot plates. The pH values of solutions were measured accurately by using a Fisher Scientific Accumet Model 15 pH meter with a standard combination pH electrode.

An Ahiba Nuance Top Speed Infrared Lab Dyeing Machine (rotary dyeing machine) was employed to exhaust the dye onto the fabric. Infrared heating and water cooling made it possible to control the program precisely. The dyeing machine enabled uniform temperature inside each dyeing beaker and level dyeings were easily achieved. Dyeing parameters such as temperature, rotation speed and dyeing time of the machine were able to be regulated and monitored constantly. A Datacolor i7 Xrite was used to measure parameters such as color strength and chromatic aberration, with the aid of Color iControl software. CIE whiteness index, L* a* b* color scale and CMC color difference and other related parameters were able to be determined through the software.

3.3 Application procedures

This section contains experimental steps and methods of treating cotton anionically, including solution preparation and pad batch procedures. Dye formulation and dyeing techniques are also discussed below. To find out the optimized ‘CHPSAS-NaOH’ ratio, a design of experiment (DOE) has been carried out with fixed amount of anionic agent. In the following part, a number of samples with different concentrations of CHPSAS have also been generated for sulfur content analysis by keeping the constant ‘CHPSAS-NaOH’ ratio found above.

3.3.1 Design of experiment

An optimized ‘CHPSAS-NaOH’ ratio was investigated first. A series of ten different mole ratios were set to explore the best formula for anionization of cotton, including a group without CHPSAS treatment (No. 11) as a control group. Total solution was 50 grams containing a fixed amount of 5 grams CHPSAS for each experimental group. The chemical formulas are displayed in Table 3 below.

Table 3. Optimization of 'CHPSAS-NaOH' ratio

Sample No.	Mole Ratio	CHPSAS (g)	CHPSAS (mol)	NaOH* (g)	NaOH* (mol)	Solution (g)
1	1:1	5	0.0254	2.03	0.0254	50
2	1:1.25	5	0.0254	2.54	0.0318	50
3	1:1.375	5	0.0254	2.79	0.0349	50
4	1:1.5	5	0.0254	3.05	0.0381	50
5	1:1.625	5	0.0254	3.30	0.0413	50
6	1:1.625	5	0.0254	3.30	0.0413	50
7	1:1.75	5	0.0254	3.56	0.0445	50
8	1:1.875	5	0.0254	3.81	0.0476	50
9	1:2	5	0.0254	4.07	0.0508	50
10	1:2.25	5	0.0254	4.58	0.0572	50
11	N/A	0	0	0	0	50

*concentration of NaOH in the current work was 50%

After obtaining the optimized mole ratio of CHPSAS and NaOH, the next step was to generate a series of samples treated with different concentration of CHPSAS by keeping the mole ratio constant. A series of anionic treatment involved CHPSAS concentrations of 0.10, 0.25, 0.50, 1.0, 2.5, 5.0 and 10.0 percent to total solution volume.

3.3.2 Anionization

3.3.2.1 Pad batch route (PB)

Pad batch is one of the widely used techniques for semi-continuous treatment of cellulosic fibers. In the pad batch process, treatment is done at room temperature, therefore it offers a series of unique advantages in simplicity, flexibility and a great reduction in capital investment. It is also termed as ‘cold pad batch’ since it’s primarily a room temperature method. Exceptional features of the pad batch route are various, including significant reductions in waste and lower costs as compared to other padding processes, exclusion of leveling agents which are required in conventional baths. Besides, since lower temperatures and lower bath ratios are needed for pad batch processes, significant savings in energy and water usage can be realized.

CHPSAS and NaOH were mixed together with a series of mole ratios displayed in Table 3 and volume was made up to the required mark by adding water and stirring continuously for a few minutes. Samples of approximately 6×10 inches were padded through the mixture to a wet pick up of 95%. Then the wet samples were put into plastic bags, sealed and held for

20 hours at room temperature. Samples were rinsed with warm water and acetic acid until neutral. To dry the fabric, samples were put into the convection oven at 45°C for 20 minutes.

3.3.3 Dyeing with the Ahiba Nuance and basic dyes

Sevron Blue BGL, a commercially available basic dye was used to dye all the CHPSAS treated samples and a control. Liquor ratio was 20:1 in preparing dye solution. To increase the solubility of basic dye, a paste was made by mixing dye particles with three milliliters acetic acid. Water was heated in the kettle to around 90°C and the paste was added into it. The dye solutions were then stirred continuously for one hour with a magnetic bar on a stirring hot plate.

The dyeing program was divided into three steps which will be described in detail below. Firstly in the preheating process, the temperature was raised to 25°C at the ramp rate of 1°C/min and this was kept constant for another 5 minutes. Secondly in the dyeing procedure, the beakers were heated up to 75°C 1°C/min and were held for 15 minutes. The final step was to cool the beakers to a relatively low temperature quickly in order to take out the beakers conveniently. All working parameters are listed in Table 4. During the whole program, the rotation speed was remained at 25 rounds per minute (rpm). Samples were rinsed with warm water (50°C) twice after being extracted from the nuance. The dyed cotton samples were then centrifuged in the extractor for 30 seconds and dried in the convection oven at 45°C for 20 minutes. Flow of work of the dyeing process is displayed below in Figure 19.

Table 4. Working parameters of the dyeing process

Step	Parameters			
	Temperature	Ramp rate	Minute	Speed
1	25°C	1°C/min	5min	25rpm
2	75°C	1°C/min	15min	25rpm
3	45°C	-2°C/min	0min	25rpm

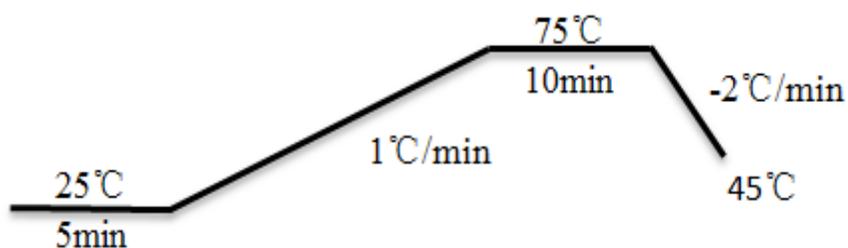


Figure 19. Schematic representation of working parameters of the dyeing process

3.3.4 Dyeing CHPSAS treated samples with a series of commercially used basic dyes

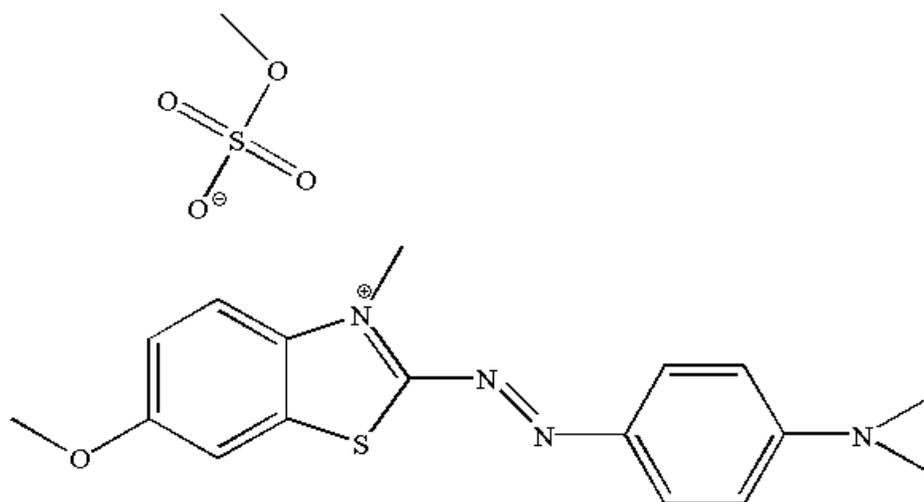
To verify the improvement in the dyeing effect of anionic cotton, nine commonly used basic dyes were applied to dye CHPSAS treated and untreated cotton, including three basic blue dyes, two basic red dyes and one basic dye of green, yellow, orange and violet each. Descriptions of these basic dyes are listed in Table 5 below and their chemical structures are shown in Figure 20. To avoid the confusion for naming dyes, the Society of Dyers and

Colourists and the American Association of Textile Chemists and Colorists identify individual dyes by giving a five digit-Color Index number to each dye [30].

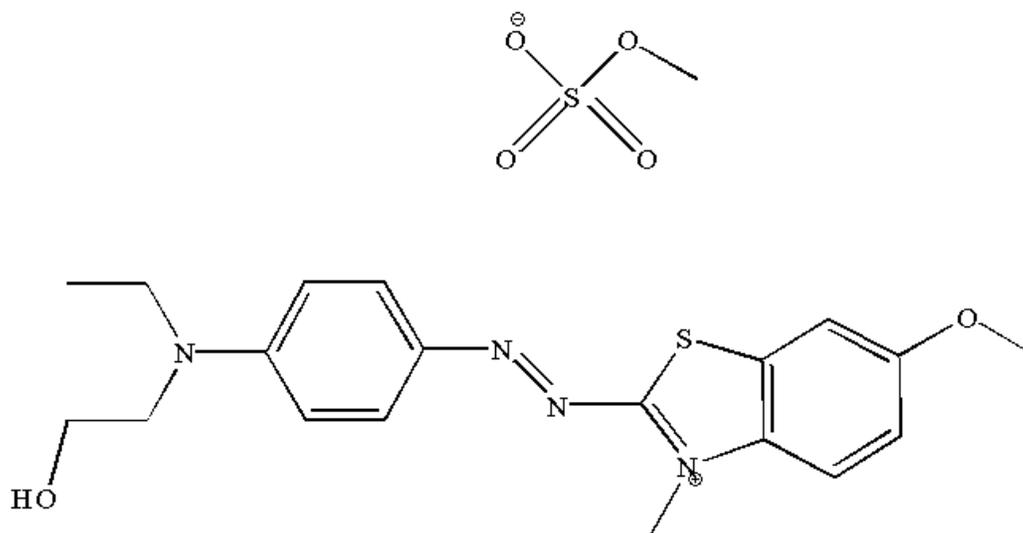
Table 5. Descriptions of nine basic dyes

No.	Name	Generic Name	CI No.	Molecular Formula
1	Sevron Blue GLK	Basic Blue 54	11052	$C_{18}H_{22}N_4O_5S_2$
2	Sevron Fast Blue RL	Basic Blue 41	11154	$C_{20}H_{26}N_4O_6S_2$
3	Sevron Blue 5GMF	Basic Blue 3	51004	$C_{21}H_{26}IN_3O$
4	Atlantic Rhodamine 5G	Basic Red 1	45160	$C_{28}H_{31}N_2O_3 \cdot Cl$
5	Sevron Red CBL	Basic Red 22	11055	$C_{12}H_{17}N_6$
6	Malachite Green Liquid	Basic Green 4	42000	$2(C_{23}H_{25}N_2) \cdot 2(C_2HO_4) \cdot C_2H_2O_4$
7	Basacryl GLDN YELL X-GFL 200%	Basic Yellow 28	N/A	$C_{20}H_{24}N_3O \cdot CH_3O_4S$
8	Sevron Orange G 200%	Basic Orange 21	48035	$C_{22}H_{23}ClN_2$
9	Calcozine New Fuchsine Cyanamid	Basic Violet 2	42520	$C_{22}H_{24}ClN_3$

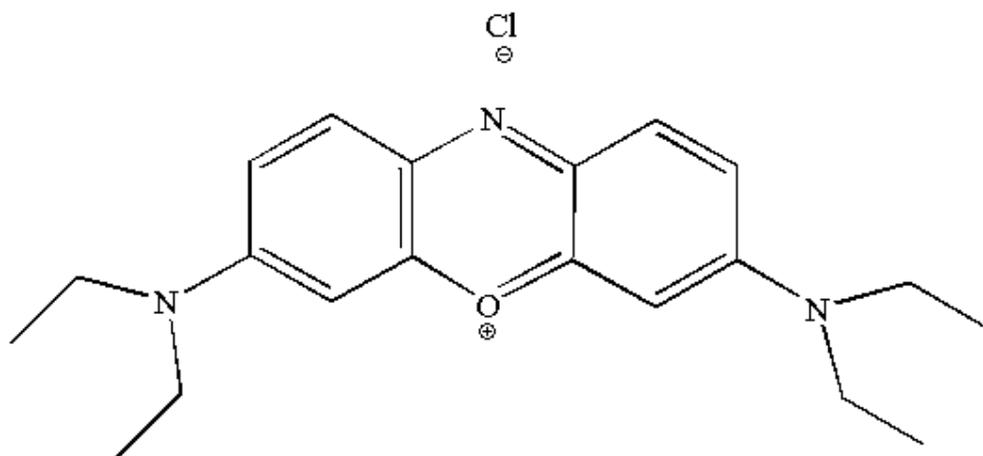
Figure 20. Chemical Structures of nine basic dyes



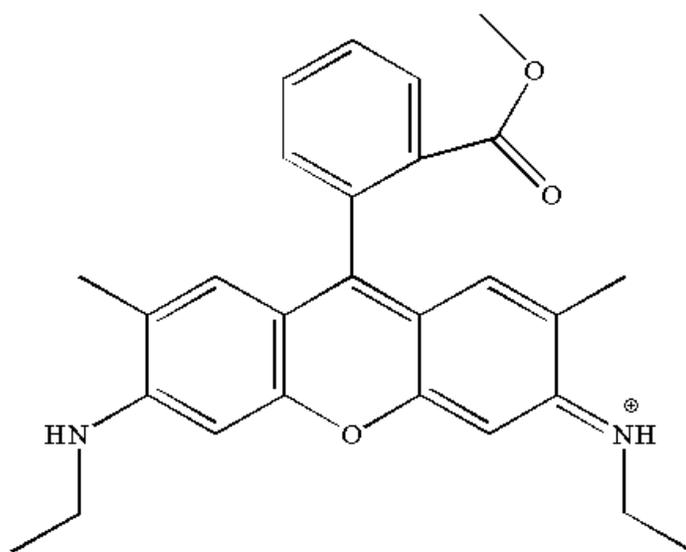
Basic Blue 54



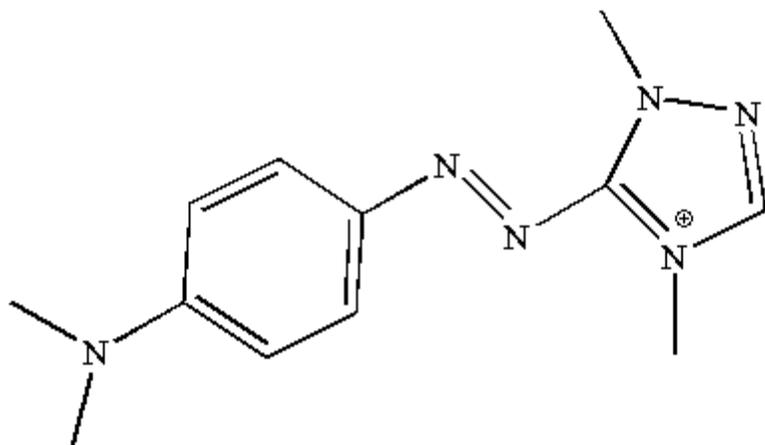
Basic Blue 41



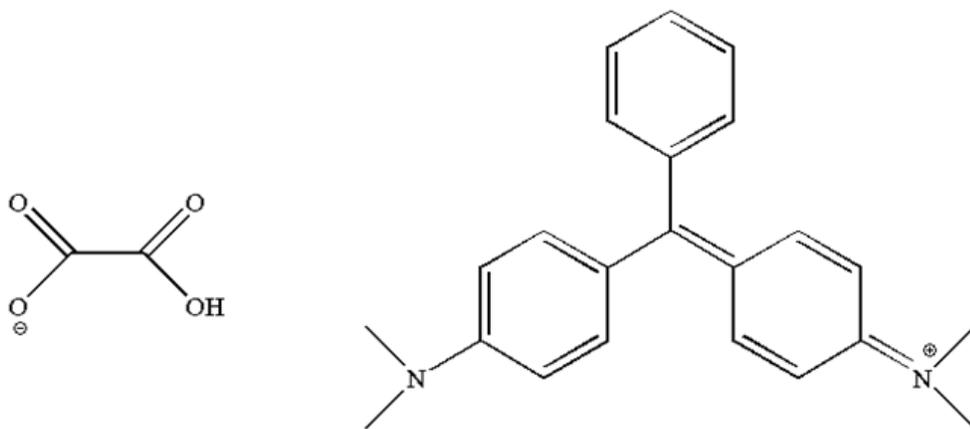
Basic Blue 3



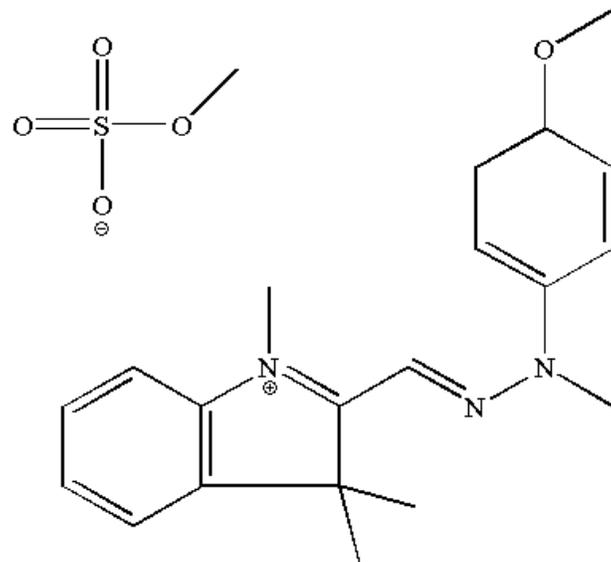
Basic Red 1



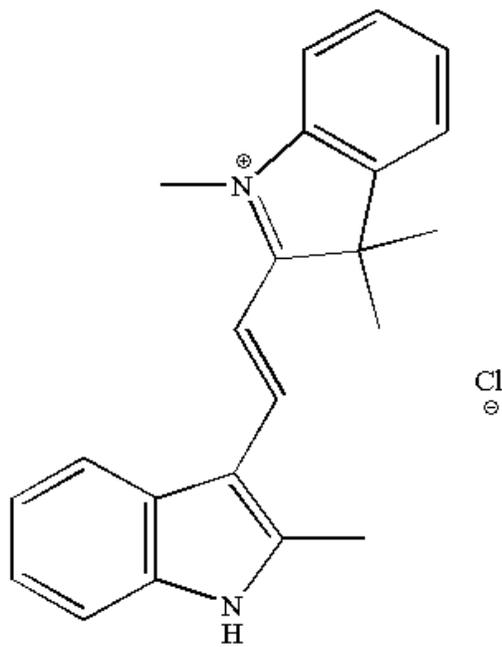
Basic Red 22



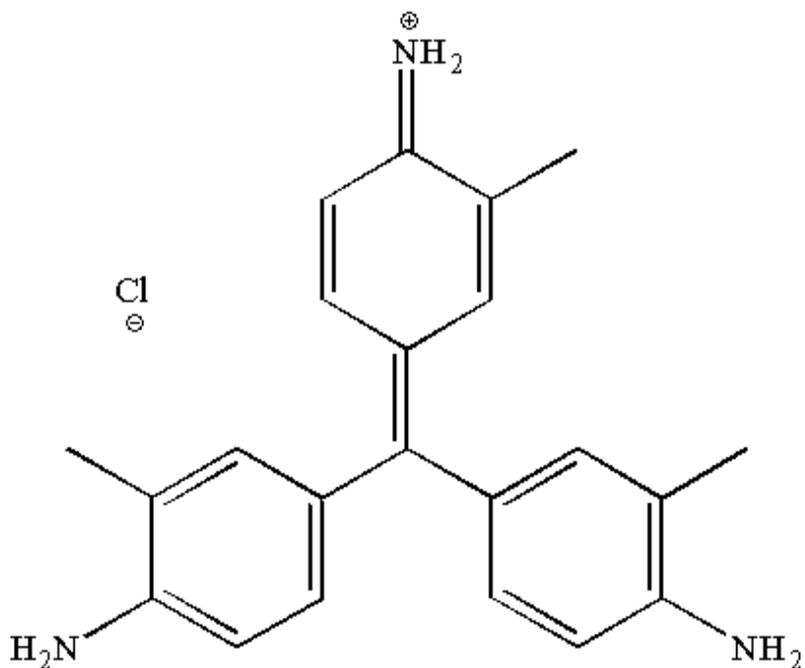
Basic Green 4



Basic Yellow 28



Basic Orange 21



Basic Violet 2

Nine cotton samples (Sample No. 20, 21, 22, 23, 24, 25, 26, 27, 28) were treated with the optimized formula found in the above experiment and were padded to 95% wet pick up. Another nine blank samples (Sample No. 29, 30, 31, 32, 33, 34, 35, 36, 37) were also prepared as control groups respectively for further analysis. Detailed descriptions of sample treatment are shown in Table 6.

Following the instructions of 'Sevron Cationic Dyes for Acrylic Fibers' [31], liquor ratio was controlled at 20:1. Basic dyes were predissolved at 90°C and then mixed with one-half their solution weight of 56% acetic acid (only 90% acetic acid was available in the lab, so the amount of acid needed to be recalculated). The pH value of the dyebaths was adjusted

to 4.0-5.0 (in the current experiment pH was regulated to 5.0) with 90% acetic acid. Since the weight of each sample was 10 grams and the amount of dye was set to 1% on fabric weight, 0.1 gram of basic dye was used for dyeing each cotton sample. Since 0.05 gram of 56% acetic acid was needed to mix each basic dye, 0.03 gram of 90% acetic acid was necessary for each dye mix. All working parameters are listed in Table 7 and flow of work of the dyeing process is displayed below in Figure 21.

Table 6. Descriptions of sample treatment in the dyeing processes

No.	Name	Generic Name	Formula	
			CHPSAS:NaOH	Conc. of CHPSAS
21	Sevron Blue GLK	Basic Blue 54	1:1.875	10%
22	Sevron Blue GLK	Basic Blue 54	N/A	N/A

No.	Name	Generic Name	Formula	
			CHPSAS:NaOH	Conc. of CHPSAS
23	Sevron Fast Blue RL	Basic Blue 41	1:1.875	10%
24	Sevron Fast Blue RL	Basic Blue 41	N/A	N/A

Table 6 Continued

No.	Name	Generic Name	Formula	
			CHPSAS:NaOH	Conc. of CHPSAS
25	Sevron Blue 5GMF	Basic Blue 3	1:1.875	10%
26	Sevron Blue 5GMF	Basic Blue 3	N/A	N/A

No.	Name	Generic Name	Formula	
			CHPSAS:NaOH	Conc. of CHPSAS
27	Atlantic Rhodamine 5G	Basic Red 1	1:1.875	10%
28	Atlantic Rhodamine 5G	Basic Red 1	N/A	N/A

No.	Name	Generic Name	Formula	
			CHPSAS:NaOH	Conc. of CHPSAS
29	Sevron Red CBL	Basic Red 22	1:1.875	10%
30	Sevron Red CBL	Basic Red 22	N/A	N/A

Table 6 Continued

No.	Name	Generic Name	Formula	
			CHPSAS:NaOH	Conc. of CHPSAS
31	Malachite Green Liquid	Basic Green 4	1:1.875	10%
32	Malachite Green Liquid	Basic Green 4	N/A	N/A

No.	Name	Generic Name	Formula	
			CHPSAS:NaOH	Conc. of CHPSAS
33	Basacryl GLDN YELL X-GFL 200%	Basic Yellow 28	1:1.875	10%
34	Basacryl GLDN YELL X-GFL 200%	Basic Yellow 28	N/A	N/A

No.	Name	Generic Name	Formula	
			CHPSAS:NaOH	Conc. of CHPSAS
35	Sevron Orange G 200%	Basic Orange 21	1:1.875	10%
36	Sevron Orange G 200%	Basic Orange 21	N/A	N/A

Table 6 Continued

No.	Name	Generic Name	Formula	
			CHPSAS:NaOH	Conc. of CHPSAS
37	Calcozine New Fuchsine Cyanamid	Basic Violet 2	1:1.875	10%
38	Calcozine New Fuchsine Cyanamid	Basic Violet 2	N/A	N/A

Table 7. Working parameters of the dyeing process

Step	Parameters			
	Temperature	Ramp rate	Minute	Speed
1	25°C	1°C/min	5min	25rpm
2	100°C	1°C/min	60min	25rpm
3	45°C	-2°C/min	0min	25rpm

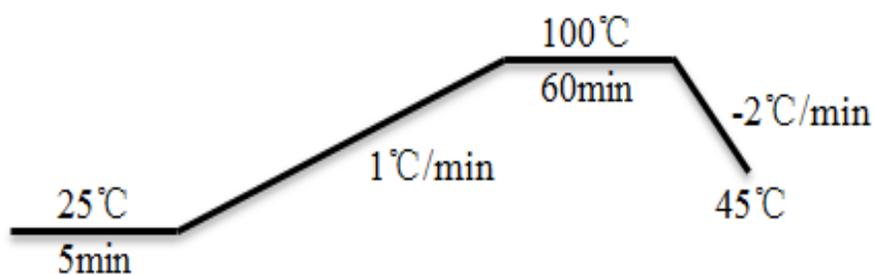


Figure 21. Schematic representation of working parameters of the dyeing process

After being dyed in Nuance machine, the cotton samples were rinsed twice with warm water (60°C) containing 1g/L surfactant ApolloScour SDRS. This soaping agent was an excellent choice for removing unfixed dyes from the cotton surface. Samples were then centrifuged in the extractor for 30 seconds and dried in the convection oven at 45°C for 20 minutes.

3.4 Analysis methods

Methods for data analysis and experimental techniques were used for characterization of CHPSAS-treated and untreated samples. Color strength measurements were used to determine color yields on fabrics through K/S values. The accelerated laundering test (AATCC TM 61-2010) was used to assess colorfastness to laundering of textiles which were desired to be laundry resistant. Colorfastness to crocking (AATCC TM 8-2007) was designed to find out how much color shifted from the surface of dyed samples to other surfaces by rubbing. In addition, sulfur content analysis was employed in the current work to evaluate the extent of reaction between CHPSAS and cotton fabric.

3.4.1 Sulfur content analysis

The percentage of sulfur from sulfonate groups in the anionized fabric is an indication of the degree of chemical reaction between CHPSAS and cotton. Results of sulfur analysis are reported in the dimensions of ppm (parts per million). After the optimized ‘CHPSAS-NaOH’ ratio and amount of CHPSAS were investigated, sulfur content analysis was applied

to evaluate how much CHPSAS reacted with cellulose. After being padded and washed to neutral pH, original cotton samples were cut in half to small pieces (3''×10''). One half was used for dyeing with basic dyes, while the other one was sent to the Environmental and Agricultural Testing Service in the Department of Soil Science at North Carolina State University for sulfur analysis.

3.4.2 Color strength test

The purpose of colorant formulation is to compute how much each dye is required to match the desired color shade. In recent times instrumental color measurement has largely replaced conventional match prediction methods which depended on visually contrasting color differences between dyed samples and the desired shade. The reflection spectrum of a sample decides the coordinates for its color for a certain CIE illuminant and an observer. The principle of spectrophotometric matching is to reproduce the reflection spectrum with a suitable mixture of colorants, whose color coordinates should be the same as the target. Kubelka and Munk put forward a two-flux theory which simplified the conventional complicated models by dropping the fluorescence phenomenon [32]. In this equation, only absorption and scattering of light are considered to exist inside the media. Considering K and S representing the absorption and scattering coefficients respectively, the reflectance R_{∞} can be written as Equation (4) when the thickness is sufficient:

$$R_{\infty} = 1 + (K/S) - [(K/S)^2 + 2(K/S)]^{1/2} \quad \text{(Equation 4)}$$

where K and S are absorption and scattering coefficients of the reflecting medium.

Rewriting the above equation, leads to the famous form of Kubelka-Munk Equation (5):

$$F(R_{\infty}) = \frac{K}{S} = \frac{(1-R_{\infty})^2}{2R_{\infty}} \quad (\text{Equation 5})$$

$F(R_{\infty})$ here is widely known as the Kubelka-Munk function, which can also be written as $F(R)$. The equation is valid for monochromatic light and R_{∞} is measured at absolute opacity. In textiles, this condition can be acquired through folding the fabric until the reflectance does not depend on the number of folds. Different from the reflectance measured by the instrument, the Kubelka-Munk function has a direct relationship to colorant concentration since the theory postulates the ratio of absorption and scattering coefficients have a straightforward correlation with colorant concentration. If C_i stands for the concentration of each colorant and n is the number of colorants in a mixture, $F(R)$ can be expressed as follows based on the single constant formulation in Equation (6) [10].

$$F(R) = F_s + \sum_{i=1}^n b_i c_i \quad (\text{Equation 6})$$

where F_s is the additive function value of the substrate

b_i is the specific additive function value of colorant i , i.e. $[F(R)_i - F_s]/c_i$

c_i is the concentration of colorant i

n is the number of colorants in the mixture

A Color i7 Benchtop Spectrophotometer was used to measure color parameters such as K/S values in the current work. The built-in NetProfiler system together with auto-configure functions and self-diagnostic techniques gives it persistent and accurate performance [33].

Color iControl software was used in the current project, worked as the application software for the spectrophotometer. Information such as the size of the sample port, the type of illumination, whether or not reflectance or transmittance data are included in the 'calibration mode properties dialog box'. Calibration is the necessary step before measurements are taken, which is reached by clicking 'Calibrate' button under 'Spectro' menu and then following the instructions. The next step is to calibrate the sensor, which verifies that the instrument calibration was successful. The black tile and the white tile are placed on the instrument port to finish the standardization of the sensor.

Calibration is recommended every eight hours of spectrophotometer operation. Firstly, calibration process should be launched from the software interface. Then the black trap is prepared before removing the calibration tile. Once the calibration process is complete, the Calibrated LED becomes lit. When the reflectance measurements are taken, the sample is folded for three times and then presented at the view port. Samples can be viewed from the preview monitor on computer screen. After each reading, the cotton sample is taken off the door and another measurement targeting area should be tested. Parameters such as DEcmc and %Strength can be read from the software and a total of four readings are required for each specimen. Functions of 'Measure Standard' or 'Measure Trial' from the software interface are designed to trigger the measurement, followed by presenting the relevant data in the software.

In the experiment of investigating the optimized 'CHPSAS-NaOH' ratio, sample No.11 (the blank group) was set as the standard and % strength of the other ten CHPSAS-treated

samples were read based on the control group. Likewise, in the experimental series of finding the optimized concentration of CHPSAS, sample No.19 (the blank group) was relegated as the standard of this set of fabrics. The % strength of the other seven fabrics with different concentration of CHPSAS were measured to find out the sample with the deepest color shade, indicating the highest level of CHPSAS reaction.

3.4.3 Colorfastness to laundering

Colorfastness is the ability of a material to resisting color change when exposed to any environment during the processing, testing and other usage.

The accelerated washing tests are designed to measure colorfastness of textiles to laundering. A running test of 45 minutes which investigated color loss from detergent and abrasion of five typical home launderings was applied in the current project. Specifically, the abrasive action is caused by friction between fabric and canister, low liquor ratio and interaction of steel balls on the fabric. Frequently a compromise can be reached between the cost of attaining a certain color and acceptable fastness properties.

The washfastness test was performed by following AATCC Colorfastness to Laundering: Accelerated (AATCC Test Method 61-2010 2A) [34]. The test was designed to evaluate colorfastness of textiles to washing under low temperature laundering at home. Test specimens of 2”×6” were cut and then put into different canisters. Multifiber test fabric was used in determining staining properties. A piece of 2”×2” test fabric cloth was sewn along

one edge of the specimen. Test conditions such as experimental temperature, amount of detergent solution and number of steel balls are listed in Table 8.

Table 8. Conditions of the laundering test [34]

Test No.	Temp		Total Liquor Volume (ml)	Percent Powder Detergent of Total Volume	Percent Liquid Detergent of Total Volume	Percent Available Chlorine of Total Volume	No. Steel Balls	No. of Rubber Balls	Time (min)
	°C(±2)	°F(±4)							
2A	49	120	150	0.15	0.23	None	50	0	45

Preheating the canisters to the test temperature in the laundering machine was needed before the program started. At least two minutes were required to finish the preheating process. The program of the laundering machine was running at 40 rpm and the whole washing process lasted for 45 minutes. After being extracted from the laundering machine, each specimen was kept in a separate beaker. They were rinsed in beakers with deionized water at around 40°C for three times. In the following step, samples were put in the extractor to remove excess water. All cotton fabrics were then dried in a convection oven at 50°C for 20 minutes.

3.4.3.1 Evaluation of color change

Color change of the dyed specimens was judged by comparison with ‘Gray Scale for Color Change’ (AATCC Evaluation Procedure 1-2007) [35], which adopted a visually assessing method to evaluate color changes from colorfastness tests by using gray scale ratings. Gray change expressed the amount of color alteration with washing. By comparing the color difference between the treated and untreated specimens in gray scale ratings, colorfastness results could be reported.

The levels of fastness are dependent on the color difference before and after the test. Such degrees are presented numerically — with 5 indicating the highest (next to no color was lost) and 1 showing the lowest (most color was lost). Between the integers, intermediate numbers such 4-5, 1-2 could also be expressed as the fastness grading. Fading of color using the gray scale ratings is measured by comparing five pairs of gray standards similar to those shown below (Figure 22). As for each standard, one side is considered as the exact chroma to the specimen before test. The other side varies from the beginning chroma (no color loss) to white (total color loss). Degree of color change before and after the experiment is corresponded to one of the standard pairs, thus the matched gray scale rating.

Gray scale ratings could be transformed to CIELAB color difference values using the colorimetric tolerance data defined for the standards as shown in Table 9 [36].

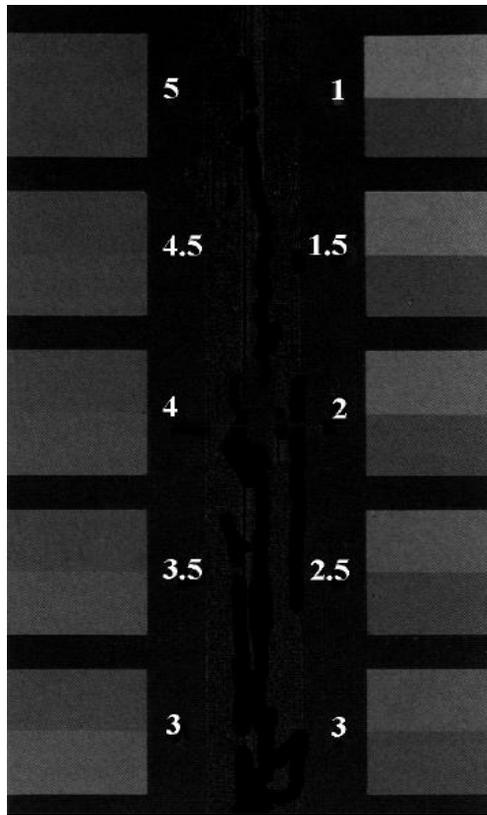


Figure 22. Gray scale for color change [36]

Table 9. Gray scale grades corresponding with CIELAB color difference

Gray Scale Grade	CIELAB Color Difference	Description
5	0.0	Equal
4-5	0.8 ± 0.2	
4	1.7 ± 0.3	Slight
3-4	2.5 ± 0.3	
3	3.4 ± 0.4	Noticeable
2-3	4.8 ± 0.5	
2	6.8 ± 0.6	Considerable
1-2	9.6 ± 0.7	
1	13.6 ± 1.0	Much

The original fabric and its corresponding test specimen were laid abreast in the same plane and same orientation. A sharp junction was expected to be made between these two fabrics and the gray scale should be placed along the edges of the specimens with the junctions of the fabric and the scale pair arrayed (Figure 23). Conditions for observing included illumination level of 1080-1340 lx, 45° incident light upon the surfaces and viewing direction of 90° to the surface plane.

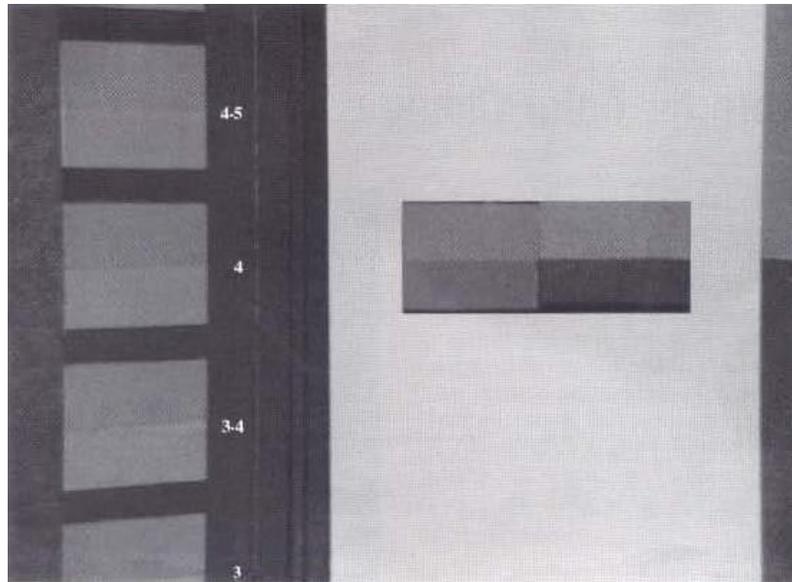


Figure 23. Illustration of how to use scale [36]

3.4.3.2 Evaluation of staining

Colorant staining is the unintended transference of the colorant from the substrate when being exposed to the environment. Staining effects were assessed by comparison with ‘Nine-step Chromatic Transference Scale’ (AATCC Evaluation Procedure 8-2007) [37].

Sixty color chips of five hues: red, yellow, green, blue and purple make up the scale. The neutral chip (row number 5) and the neutral gray chips (row number 1) are other expression forms of gray chips on the gray scale for staining. Ten rows are aligned in a way that each color shows a gradual change in a line. From top to the bottom, the colors range from the lightest to the darkest. The top rows indicated with number 5 represents no color and row number 1 at the bottom illustrates the darkest colors (Figure 24). Illumination parameters of this experiment are the same as those of evaluating gray scale for color change.

The specimen to be evaluated was observed under the chips behind the card. To grade staining, numerical levels were rested with row numbers on the scale. The corresponding relation between grades and colorant staining is shown below in Table 11.



Figure 24. Nine-step chromatic transference scale [37]

Table 10. Rating method given in the scale [37]

Colorant Staining	Grade
No transfer	5
Transfer equal to Row 4.5	4.5
Transfer equal to Row 4	4
Transfer equal to Row 3.5	3.5
Transfer equal to Row 3	3
Transfer equal to Row 2.5	2.5
Transfer equal to Row 2	2
Transfer equal to Row 1.5	1.5
Transfer equal to Row 1	1

Evaluation of 9-step chromatic transference scale was expected to give the same results as either the gray scale ratings for staining or the 5-step chromatic transference scale ratings, which was believed to improve grading precision especially for those less-experienced raters.

Gray scales for color change and staining were measured by two experimenters with color science experience twice at different times. Here the mean values of gray scale ratings were adopted.

3.4.3.3 Colorfastness to crocking

AATCC Test Method 8-2007 (Colorfastness to crocking: AATCC Crockmeter Method) [38] was employed to evaluate the crockfastness properties of the dyed CHPSAS-treated

samples. The objective of this test method is to measure how much color transferred from textile surface to other surfaces with rubbing. During the experiment, a test fabric with color was rubbed with a white cloth under certain conditions and color transference from the test specimen to the white cloth was evaluated by comparison with the gray scale for staining in the form of a certain grade.

The white test cloth was 50 mm in square and specimen size was cut in 2.0”×5.1”. The test specimen was placed on the base of the flat with the long direction being rubbed. In the following step, the specimen was covered by the specimen holder to prevent slippage. The test cloth was then mounted with the direction of rubbing and the covered finger was lowered onto the specimen. Before the test started, the finger was placed at the front end. The running program of the motorized tester was set to 10 complete turns at the rate of one turn per second. After the program ended, white cloth was removed, waiting to be evaluated after conditioning.

3.4.3.4 Evaluation of staining

The quantity of color transfer from the dyed specimen to the white cloth was rated by the gray scale of staining. To grade dry crocking fastness, reference standard was the same as mentioned in Table 11. AATCC Evaluation Procedure 2-2007 [39] provided the method of using the gray scale to assess textile staining from colorfastness tests.

Gray scale consists of pairs of non-glossy neutral grey color chips. These pairs are placed on adjacent sides of a black board, demonstrating sensed color changes in accordance

with either integral fastness ratings or half-number ratings. Gray stains show the amount of staining of adjacent materials which undergo washing. Color transference from the test specimen to an adjacent specimen is assessed in a similar way to that of gray change. There are ten standard pairs in total just as the gray change standard pairs mentioned above. But one thing being different is that instead of black, one side of each standard is white and the other half alters from white (generally no staining) to a gray with the chroma value of the test samples (much staining) (Figure 25). Specifically, a gray scale grade 5 represents two same white reference chips on the scale, with no color difference between the pair and a tolerance of ± 0.2 . As for staining ranks 4.5 to 1, a white reference chip paired with darker neutral gray chips of similar gloss. Half-step staining grade pairs stand for intermediate values between those integral grade pairs. Sample placement and illumination parameters are similar to that mentioned in Gray Scale for Color Change and how to use the scale is displayed below in Figure 26. The grade of the test specimen is obtained by comparison with color difference between the original and tested ones visually with that of the standard pairs on the scale. The rating number is the pair that is mostly in accordance with the contrast of the unstained and stained specimens. Particularly, a gray scale rating of 5 shows there is no color difference between the two pieces in the pair.

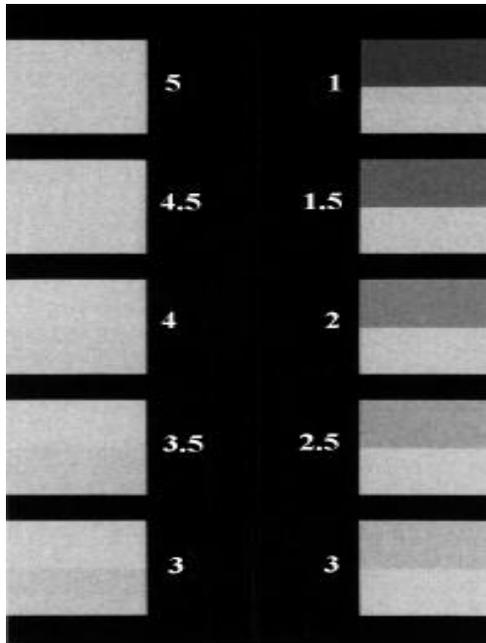


Figure 25. Gray Scale for staining [39]

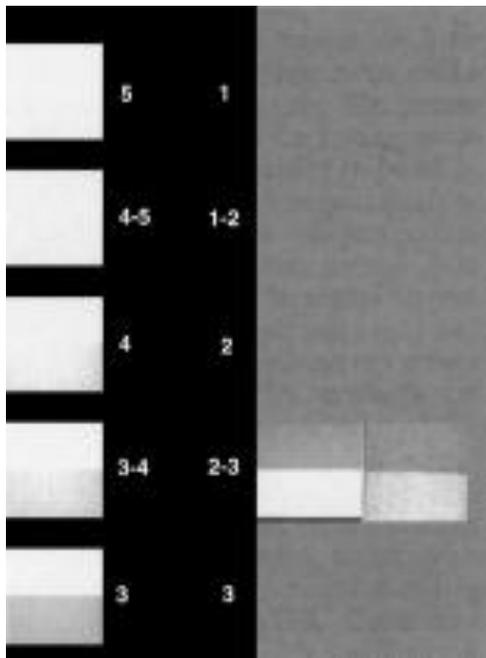


Figure 26. Illustration on how to use scale [39]

Gray scale for staining was measured by two experimenters with color science experience twice at different times. Here the mean values of gray scale ratings were adopted.

4. RESULTS AND DISCUSSION

In this results and discussion part, outcomes of the analytical methods mentioned in the last section will be presented and analyzed in detail, including sulfur content analysis of CHPSAS-treated samples, color strength tests of both treated and untreated fabrics being dyed with a series of nine basic dyes and colorfastness to laundering, staining and crocking tests.

4.1 An optimized formula of NaOH and CHPSAS

In order to find out the optimal formula of anionization of cotton fabrics with CHPSAS, the most important factor is to study the appropriate proportion of NaOH and CHPSAS in the bath. To determine this, samples treated with a series of recipes were dyed with basic dye Sevron Blue BGL. Through measuring color strength of each sample, the one with the highest K/S value (or had the deepest color shade) was regarded as the sample with the optimal 'NaOH-CHPSAS' ratio.

A set of experiment with ten different mole ratios of NaOH and CHPSAS was designed and the solutions pad applied. As the volume of solution was 50 ml and generally the chemical concentration should not exceed 10g/100ml, the amount of CHPSAS was fixed to 5

grams. The ingredients of the ten recipes are listed in detail in Table 3. Particularly the mole ratio of 1.625:1 was repeated in order to verify the previous research [28].

By using the Color i7 Benchtop Spectrophotometer and Color iControl software, the K/S value of each specimen was measured three times and mean K/S values and their corresponding mole ratios are shown in Table 12. Sample No.11 was the untreated sample and acted as a control group here.

Table 11. K/S values of specimens treated with different 'NaOH-CHPSAS' ratios

Sample No.	Mole ratio of NaOH : CHPSAS	K/S value
1	1.000	2.73±0.33
2	1.250	4.94±0.22
3	1.375	5.46±0.25
4	1.500	5.59±0.33
5	1.625	5.89±0.38
6	1.625	5.74±0.27
7	1.750	6.77±0.32
8	1.875	7.63±0.27
9	2.000	7.03±0.25
10	2.250	6.86±0.26
11[Blank]	0.000	2.51±0.16

To better viewing the tendency of K/S values with increased ‘NaOH-CHPSAS’ ratios, a plot was made to illustrate the effect of mole ratios on color strength tests. Results are seen below in Fig. 27.

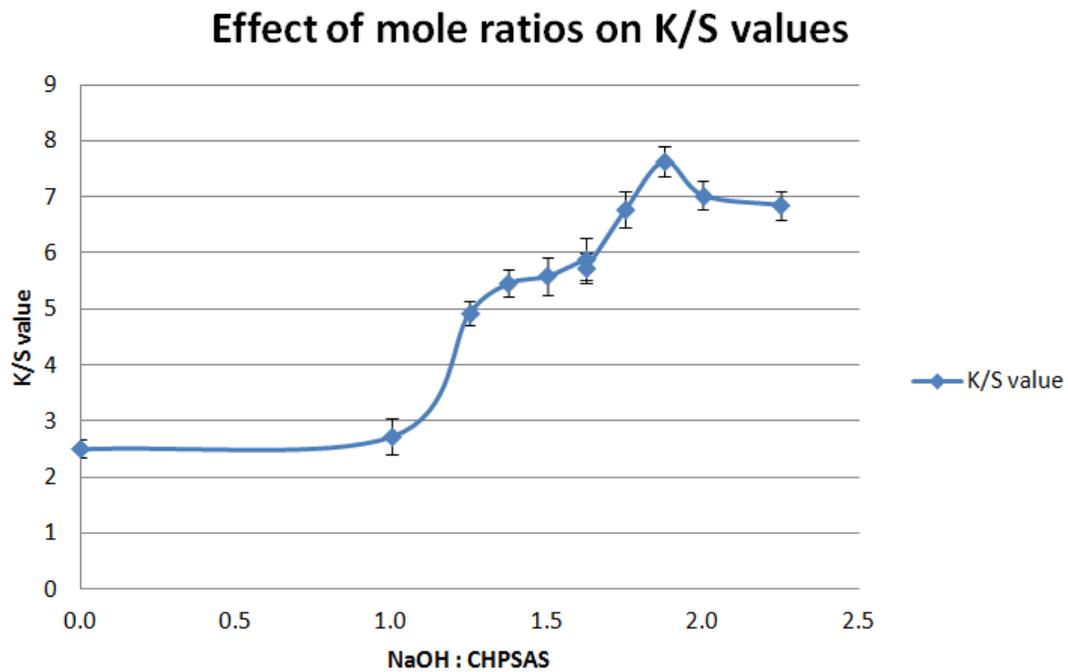


Figure 27. K/S values of specimens with different ‘CHPSAS-NaOH’ ratios

Blank samples did not go through padding process and therefore contained no NaOH or anionic agent. The K/S value of the blank fabric was around 2.500 and was the lowest compared with those CHPSAS-treated samples, which indicated that the anionic treatment indeed created bonds between cellulose and CHPSAS, thus made anionic cotton chemically attractive to basic dyes. For an individual sample, standard deviation of each measurement is

displayed in the table and it demonstrates the accuracy between each test. From the standard deviation of each measurement and error bars shown in the graph, it's seen that the uncertainty in the reported measurement is acceptable, thus differences between K/S values of various 'NaOH-CHPSAS' ratios are statistically significant.

When the mole ratio of NaOH and CHPSAS was 1:1, K/S value did not show an evident enhancement compared with the control group, while the K/S number started to ascend quickly at a mole ratio of 1.25:1. This was probably because in the former case, not enough NaOH was existed to react with CHPSAS which obstructed the formation of oxiranemethanesulfonic acid sodium salt, the epoxy intermediate (Equation 1). While in the latter condition, the amount of sodium hydroxide enabled the processing of reaction in Eqn. 2. K/S value under this situation was 4.936, nearly twice as much as that of a mole ratio 1:1. Within a certain range, color strength values went up as the mole ratio increased. The reason why Group 5 and 6 were designed to repeat the mole ratio 1.625 was that previous researchers claimed that mole ratio 1.60:1 of NaOH and CHPSAS was the best ratio to achieve the greatest yield of CHPSAS on cotton [28]. However in our experiment, it could be seen that when the mole ratio was greater than 1.60, the color yield of the fabrics still improved. For example, sample 7 with the mole ratio of 1.75:1 gave a K/S value of 6.776, which is a 20% increase over the ratio previously thought to be the best.

Color yields maximized at a ratio of 1.875:1, which had a K/S value of 7.633. After that point, mole ratios greater than 1.875 showed a decrease in dye yield. For instance, Group 9 and 10 with mole ratios of 2.0:1 and 2.25:1 respectively had 8% and 10% less color yield

than Group 8. This was likely because the intermediate epoxy form, oxiranemethanesulfonic acid sodium salt, was prone to be hydrolyzed with excess sodium hydroxide. As base was being added, there was potential for hydrolysis. The hydrolyzed product would not form covalent bonds with cellulose chains and therefore did not assist in anionic treatment. This kind of byproduct was unwanted and hence should be avoided. From the color strength results it is seen that with a fixed CHPSAS amount at mole ratio of 1.875:1, more bonds were created between the anionic agent and cellulose than any other ratios. Therefore 1.875:1 was the optimized mole ratio of sodium hydroxide and CHPSAS and this ratio would be used in the following experiment to explore the percentage of sulfur fixation on fabrics.

4.2 Determine percentage of sulfur by K/S measurements

After an optimized mole ratio of NaOH and CHPSAS had been found, a set of samples were generated for the sulfur analysis. By measuring K/S values, the percentage of sulfur was able to be determined.

By keeping the mole ratio of NaOH and CHPSAS constant at 1.875:1, cotton samples were treated with a series of different concentrations of CHPSAS: 0.25%, 0.50%, 1.00%, 2.00%, 4.00%, 8.00% and 10.00%. Eight cotton fabrics with various CHPSAS proportions were generated at a constant NaOH-CHPSAS ratio to get fabrics for a calibration curve of %S versus K/S values.

As mentioned before, the pad batch process was applied and each sample was padded to 95% wet pick up with formulas shown below in Table 13.

Table 12. Recipes of different concentrations of CHPSAS

Sample No.	CHPSAS(g)	CHPSAS(mol)	NaOH*(g)	NaOH*(mol)	Solution(g)
12	0.25	0.0013	0.19	0.0024	100
13	0.5	0.0025	0.38	0.0047	100
14	1	0.0051	0.76	0.0096	100
15	2	0.0102	1.53	0.0191	100
16	4	0.0204	3.05	0.0383	100
17	8	0.0407	6.10	0.0763	100
18	10	0.0509	7.63	0.0954	100
19 [Blank]	0	0	0	0	100

*concentration of NaOH in the current work was 50%

4.2.1 Sulfur content analysis

The anionic agent, 3-chloro-2-hydroxy-1-propanesulfonic acid sodium salt hydrate (CHPSAS), contains sulfur. Therefore the sulfur content of the treated fabrics is proportional to covalent bonds formed between CHPSAS and cellulose chains. Thus anionic cotton was analyzed for percent sulfur content.

The untreated fabric contained no sulfur and was regarded as a control group. On the other hand, anionic cotton samples treated with CHPSAS exhibited a presence of diverse levels of percent sulfur fixation.

K/S values after samples were dyed with basic dye Sevron Blue BGL were also included. Sulfur concentrations of unit ppm (parts per million) which obtained from the Environmental and Agricultural Testing Service are listed in Table 14 below.

Table 13. Calculation of sulfur content for samples treated with different concentration of CHPSAS

Sample No.	CHPSAS (g/100ml)	Conc. of S (ppm)
12	0.25	1
13	0.5	8
14	1	18
15	2	93
16	4	271
17	8	1007
18	10	1416
19 [Blank]	0	0

To determine the anionization efficiencies at the optimal ratio, the percentage of sulfur fixation on each sample was calculated at different CHPSAS concentrations. For example, a sample padded with 4% CHPSAS concentration i.e, 40g/L CHPSAS solution with a wet pickup (wpu) of 95%, gave a sulfur content of 0.0271% on weight of fabrics. The theoretical percentage sulfur under this situation for 40g/L CHPSAS padded fabric was 0.6185% (95% wpu). Therefore the percent of sulfur fixation is calculated by 0.0271% divided by 0.6185% or 4.38%.

Table 14. Percent of sulfur fixation at different CHPSAS concentrations

Sample No.	CHPSAS(g/100ml)	Theoretical %	Actual %	CHPSAS fixation %
12	0.25	0.0407	0.0001	0.26
13	0.5	0.0814	0.0008	1.03
14	1	0.1628	0.0018	1.16
15	2	0.3256	0.0093	3.01
16	4	0.6511	0.0271	4.38
17	8	1.3022	0.1007	8.14
18	10	1.6278	0.1416	9.16
19[Blank]	0	0	0	0

*theoretical% is calculated by assuming wet pick up is 100%

Anionization efficiencies at different CHPSAS concentrations are shown in Table 15. Fixation percents showed an ascending tendency from 0.25g/100ml all the way to 10g/100ml CHPSAS concentrations. From the table it is clear seen that as the CHPSAS concentration increased, a higher fixation of CHPSAS is obtained. Specifically, the amount of sulfur detected in sample No.12 to No.14 was too small (under 20 ppm) to be valid. This trend is against the theory in Hashem and Hausers' research which argued that a decrease in fixation with ascending treatment level was expected [40]. However, as they mentioned in the same paper, at lower concentrations the trend they found was not significantly comparable to the experimental error although fixation might seem higher. Besides, as pad batch method used

in the current project inevitably allowed the existence of moisture, which led to the hydrolysis reaction of the epoxy intermediate. At lower concentrations, it is believed that hydrolysis might influence the percent of CHPSAS more significantly than that of higher concentrations.

For better viewing the variation tendency of percent CHPSAS fixation with CHPSAS concentration, Figure 28 showed a nearly linear relationship between these two parameters, with the coefficient of determination (R^2) of 0.9846.

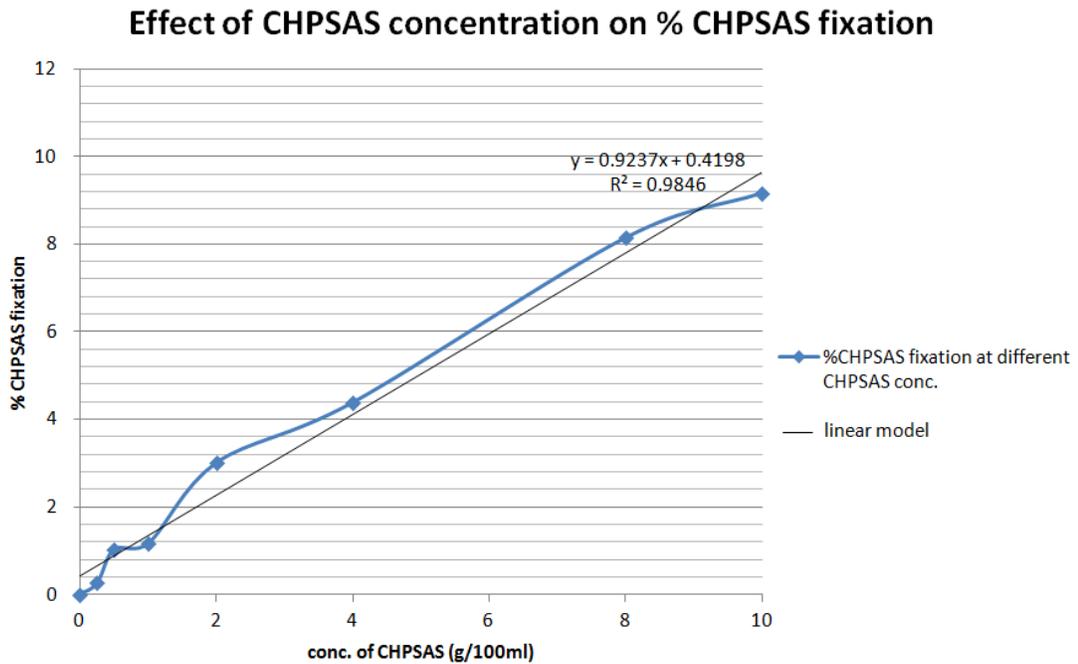


Figure 28. Effect of CHPSAS concentration on percent CHPSAS fixation

Although the results indicated that 10% CHPSAS gave the highest percent CHPSAS fixation among all the other CHPSAS concentrations, 9.16% was not a satisfying fixation

percent. From previous research, several methods might be responsible to improve efficiency of cellulose anionization [40]. Methods such as adding additives in the bath as well as adjusting the sequence of chemicals could affect the distribution coefficient. Furthermore, reducing liquor ratio via using less water per unit of cellulose could help to enhance the anionization efficiency as there will be fewer solvents reacted with the epoxy intermediate. Inert solvents such as acetone could possibly provide higher efficiencies of anionization by getting rid of water. As pad batch process was applied in the current experiment, instead of an one-stage padding by mixing CHPSAS and sodium hydroxide together, padding fabric with NaOH first and then with CHPSAS might be a better choice to get preferable fixations. In addition, using pad batch but not other methods such as pad-dry-cure might be another reason for the low fixation of CHPSAS on the fabric. According to the analysis by Goli, the lower sulfur contents in the pad batch process were ascribed to the lower reaction efficiency compared with that of the pad-dry-cure method. The main difference between these two processes was the presence of water or not. As water could not be completely eliminated in the pad batch method, the intermediate product was more likely to be hydrolyzed [41].

Also it was assumed that the same NaOH:CHPSAS ratio was correct for all CHPSAS concentrations, this may not be true. The amount of NaOH at low CHPSAS concentrations may not have been high enough for the desired reaction.

The rest of the padding procedures and the dyeing process were the same as previously mentioned in section 3.3.2.1 and 3.3.3. Results of color strength values were measured using Color iControl software and are displayed below in Table 16.

Table 15. Color strength tests of different CHPSAS concentrations

Sample No.	CHPSAS (%)	% S	K/S values
12	0.25	0.0001	2.22±0.31
13	0.5	0.0008	2.23±0.21
14	1	0.0018	2.28±0.25
15	2	0.0093	2.44±0.22
16	4	0.0271	3.38±0.23
17	8	0.1007	5.38±0.29
18	10	0.1416	7.06±0.34
19[Blank]	0	0	2.17±0.36

To clearly and concisely recognize the change law of K/S values with varied sulfur content, a plot (Figure 29) had been drawn of percent of sulfur on K/S values.

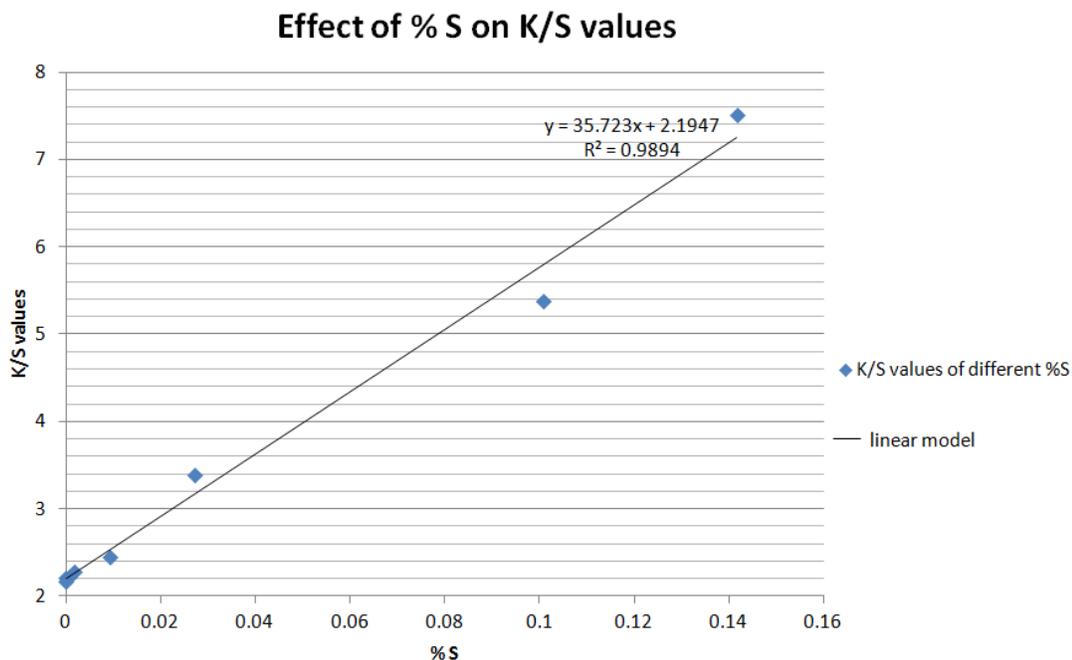


Figure 29. Effect of % S on K/S values

From the chart above, it could be seen that the general trend of K/S value was ascending. As percentage of sulfur mounted up, color yield of the dyed fabric was proved to be higher. Results showed that color strength of % S under 0.0018% did not change much. For instance, K/S value of sample 14 (with % S of 0.0018%) was only 3% higher than that of sample 13 (with % S of 0.0008%). It had merely 5% more color yield even compared with the control group. This might be interpreted by only a very few covalent bonds had been formed between cellulose chains and the anionic reagent at that time. As not enough linkages were created between them, cotton fabrics did not carry sufficient negative ions. Therefore color yield of these samples had not improved evidently when dyed with basic dyes.

After % S reached 0.0271%, K/S values grew by a large margin. This could possibly attribute to more and more covalent bonds were formed as CHPSAS content increased, which made anionic cotton more attractive to cationic dyes. At percent sulfur of 0.1416%, K/S was found to have its highest value. One linear model of $y = 35.723x + 2.1947$ was calculated by Excel to fit the tendency of the plots. From this equation, a linear relation between K/S value and concentration of CHPSAS could be observed. The coefficient of determination (R^2) of 0.9894 was calculated for this model, which showed a good reliability in fitting. This set of experiment proved that CHPSAS does increase the affinity between cellulose fabrics and basic dyes and even a low fixation of CHPSAS on cotton can improve the dyeability of cotton with basic dyes to a high level.

4.3 Dyeing CHPSAS-treated and untreated cotton samples with a series of nine basic dyes

To further evaluate the improvement in dyeability after the anionic treatment, nine commercially available basic dyes were applied to dye the anionic and blank samples under the same dyeing conditions. Detailed information on the dyes was listed previously in Table 5 and their chemical structures were shown in Figure 20. Pretreatment and dyeing procedures have been described in the earlier section.

4.3.1 Color strength results of anionic and untreated samples dyed with nine basic dyes

To explore the effect of CHPSAS in dyeing cotton with basic dyes, nine pairs of cotton samples were dyed with nine different kinds of basic dyes in the Ahiba Nuance. Results of color strength tests were listed in Table 17.

Table 16. K/S values of nine pairs of CHPSAS-treated and untreated samples

Group No.	Basic Dyes	Sample No.	K/S value
1	Basic Blue 54 [Treated]	20	5.44±0.19
	Basic Blue 54 [Untreated]	29	2.16±0.21
2	Basic Blue 41 [Treated]	21	4.26±0.21
	Basic Blue 41 [Untreated]	30	0.94±0.07
3	Basic Blue 3 [Treated]	22	2.10±0.22
	Basic Blue 3 [Untreated]	31	1.33±0.13
4	Basic Red 1 [Treated]	23	9.54±0.79
	Basic Red 1 [Untreated]	32	3.37±0.32
5	Basic Red 22 [Treated]	24	1.21±0.14
	Basic Red 22 [Untreated]	33	0.28±0.01
6	Basic Green 4 [Treated]	25	1.48±0.13
	Basic Green 4 [Untreated]	34	0.68±0.06
7	Basic Yellow 28 [Treated]	26	1.13±0.14
	Basic Yellow 28 [Untreated]	35	0.38±0.01
8	Basic Orange 21 [Treated]	27	12.28±0.89
	Basic Orange 21 [Untreated]	36	2.81±0.18
9	Basic Violet 2 [Treated]	28	17.99±0.99
	Basic Violet 2 [Untreated]	37	5.90±0.24

Eighteen samples were divided into nine groups and basic dyes were also numbered one to nine. Each pair of fabrics was dyed with the basic dye of the corresponding number.

For example, Group one being consisted of sample No.20 and No.29 was dyed with basic dye No.1, Sevron Blue GLK. To directly realize the contrast of color yield between anionic and control samples, a histogram of K/S values is drawn in Figure 30.

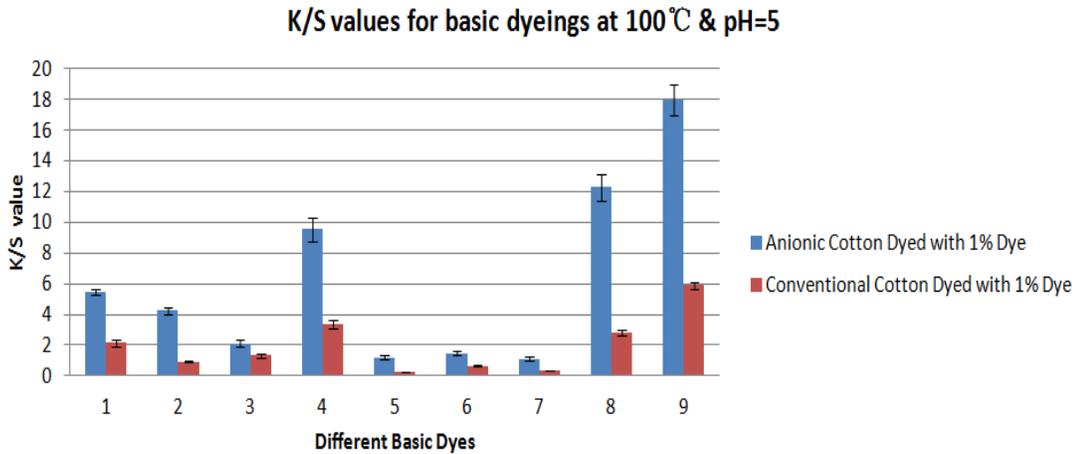


Figure 30. K/S values for fabrics dyed with nine basic dyes at 100°C & pH=5

Desirable dyeing was acquired on anionically modified cotton fabrics which had been dyed with nine kinds of basic dyes at high temperature (100°C) without electrolytes at pH~5.

From the histogram it is seen that the blue column was taller than the red one in each pair, which indicated that anionic cotton was prone to be dyed with basic dyes and had higher color yields than untreated cotton. Specifically, the CHPSAS-treated samples in Group 2 and 8 had higher mean K/S values of 4.55 times and 4.38 times than untreated samples

respectively. Such huge contrast between the anionic and blank samples is attributed to the difference in affinity to basic dyes. Getting a deep color shade with basic dyes could not be achieved economically on conventional cotton, while this could become commercially available for cotton with pretreatment with anionic reagents. Basic dyes in general carry positive charges for quaternary nitrogen cations are present in the dye molecules. As a result, there were electrostatic attraction forces between the anionic cotton and dye molecules. The enhancement in color yield of the anionic cotton could be interpreted as the formation of ionic bonds between the cationic nitrogen and the anionic groups on modified cotton. After dyeing with basic dyes, level dyeing was achieved with the anionic cotton, indicating cotton could be dyed evenly after pre-treating with CHPSAS by a cold pad batch process. Although basic dyes are normally applied to dye fibers with negative charges such as acrylic fibers, anionic cotton can be dyed with these of dyes efficiently as well. No electrolyte was needed for dyeing anionic cotton with basic dyes because of the chemical attraction between the anionic dye sites and basic dyes with positive charges.

4.3.2 Colorfastness to laundering of anionic and untreated samples dyed with nine basic dyes

In the test of colorfastness to laundering, several significant parameters were taken into consideration to examine the effect of CHPSAS in dyeing cotton with cationic dyes. The assessment evaluated color change and staining level before and after the washing test.

4.3.2.1 Evaluation of color change of CHPSAS-treated and untreated samples after the laundering test

4.3.2.1.1 Evaluation of color change in gray scale

Following the procedure of AATCC Evaluation Procedure 1-2007 — Gray Scale for Color Change, gray scale ratings before and after laundering of eighteen samples were determined and are displayed below in Table 18.

Table 17. Colorfastness to laundering of nine pairs of CHPSAS-treated and untreated samples in gray scale

Group No.	Basic Dyes	Sample No.	Gray Scale ratings
1	Basic Blue 54 [Treated]	20	2.4±0.14
	Basic Blue 54 [Untreated]	29	2.7±0.36
2	Basic Blue 41 [Treated]	21	1.7±0.22
	Basic Blue 41 [Untreated]	30	2.0±0.37
3	Basic Blue 3 [Treated]	22	2.4±0.16
	Basic Blue 3 [Untreated]	31	2.8±0.50
4	Basic Red 1 [Treated]	23	2.2±0.29
	Basic Red 1 [Untreated]	32	2.3±0.36
5	Basic Red 22 [Treated]	24	2.2±0.16
	Basic Red 22 [Untreated]	33	3.0±0.51
6	Basic Green 4 [Treated]	25	4.7±0.14
	Basic Green 4 [Untreated]	34	2.6±0.29
7	Basic Yellow 28 [Treated]	26	2.2±0.08
	Basic Yellow 28 [Untreated]	35	2.4±0.22
8	Basic Orange 21 [Treated]	27	2.7±0.14
	Basic Orange 21 [Untreated]	36	2.9±0.36
9	Basic Violet 2 [Treated]	28	3.0±0.29
	Basic Violet 2 [Untreated]	37	2.6±0.45

A histogram was made to concisely compare the colorfastness to laundering of nine pairs of samples. From the results of gray scale ratings shown in Figure 31, even untreated fabrics have relatively higher mean values in gray scale ratings than anionic ones, since the ratings of different measurements vary greatly, colorfastness to laundering of anionic and untreated cotton are at the same level.

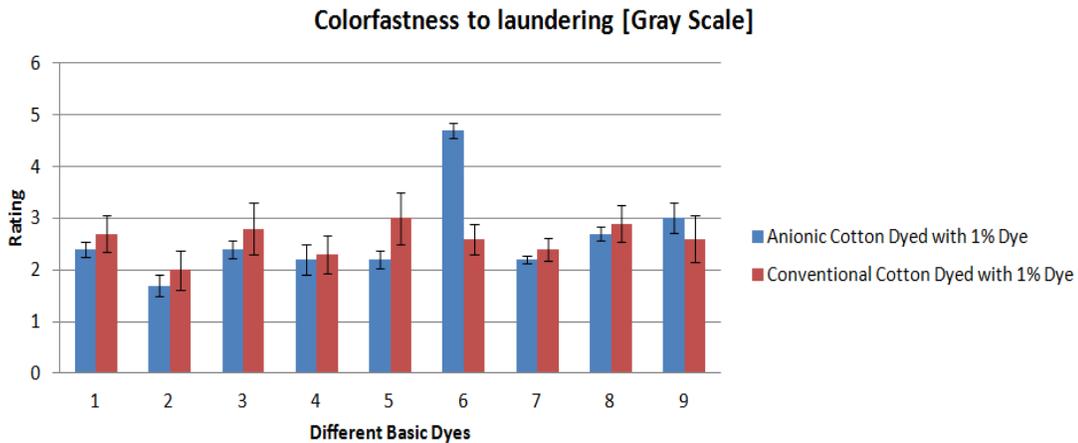


Figure 31. Colorfastness to laundering of eighteen samples in gray scale

The data illustrated treating cotton with anionic agent did not impair washfastness properties of samples dyed with basic dyes. It seemed that even the percent fixation of CHPSAS is low, anionic dyes sites are still able to bind basic dyes to a certain extent without the addition of other chemicals during the laundering test.

Overall, anionic cotton showed colorfastness to laundering with gray scale ratings comparable to untreated ones (especially CHPSAS-treated sample No.6 had a gray scale rating of 4.7).

4.3.2.1.2 Evaluation of colorfastness in DE_{cmc}

Although the evaluation in gray scale was rated six times by observers at different time periods in total, color difference of samples before and after laundering was assessed in DE_{cmc} as gray scale ratings were potentially influenced by subjective factors.

DE_{cmc} is a color-difference formula being applied in industrial pass/fail decisions since 1984. It is in token of an ellipsoidal volume in the axes of lightness (DL*), chroma (DC*) and hue (DH*) which is standard-centered. Here we used DE_{cmc} as an alternative approach to judge the color aberration between the unwashed samples and those after the laundering test. Delata E values of these nine pairs were illustrated below in Table 19.

Table 18. Colorfastness to laundering of nine pairs of CHPSAS-treated and untreated samples in DE_{cmc}

Group No.	Basic Dyes	Sample No.	DE _{cmc}
1	Basic Blue 54 [Treated]	20	8.18±0.24
	Basic Blue 54 [Untreated]	29	7.56±0.78
2	Basic Blue 41 [Treated]	21	9.26±0.17
	Basic Blue 41 [Untreated]	30	8.56±0.86
3	Basic Blue 3 [Treated]	22	7.62±0.34
	Basic Blue 3 [Untreated]	31	7.35±0.75
4	Basic Red 1 [Treated]	23	8.12±0.30
	Basic Red 1 [Untreated]	32	7.24±0.84
5	Basic Red 22 [Treated]	24	8.26±0.14
	Basic Red 22 [Untreated]	33	5.32±0.81
6	Basic Green 4 [Treated]	25	0.74±0.13
	Basic Green 4 [Untreated]	34	6.83±0.68
7	Basic Yellow 28 [Treated]	26	8.84±0.33
	Basic Yellow 28 [Untreated]	35	7.98±0.71
8	Basic Orange 21 [Treated]	27	7.01±0.32
	Basic Orange 21 [Untreated]	36	6.52±1.06
9	Basic Violet 2 [Treated]	28	7.62±0.41
	Basic Violet 2 [Untreated]	37	6.02±0.86

As exhibited in the histogram (Figure 32), the trend of DE_{cmc} values was opposite to that of gray scale ratings, which could make sense. For almost all experimental groups displayed in Figure 31 (except Group No.6), anionic cotton samples had lower gray scale ratings in mean values compared with its corresponding untreated ones. However, variations in DE_{cmc} of untreated samples are much larger than that of anionic ones, indicating both two kinds of samples are at the same level in color change.

In addition to this, conventional cotton had a Delta E value of 6.83 prior and posterior to the washing test in the sixth pair. While in comparison that value of the sixth anionic sample was 0.74, implying there was almost no color change after the fastness test. Results of DE_{cmc} were in accordance with what we had got in gray scale measurement, which verified the laboratory conclusion that pretreatment of CHPSAS did not damage washfastness properties of cellulosic fabrics.

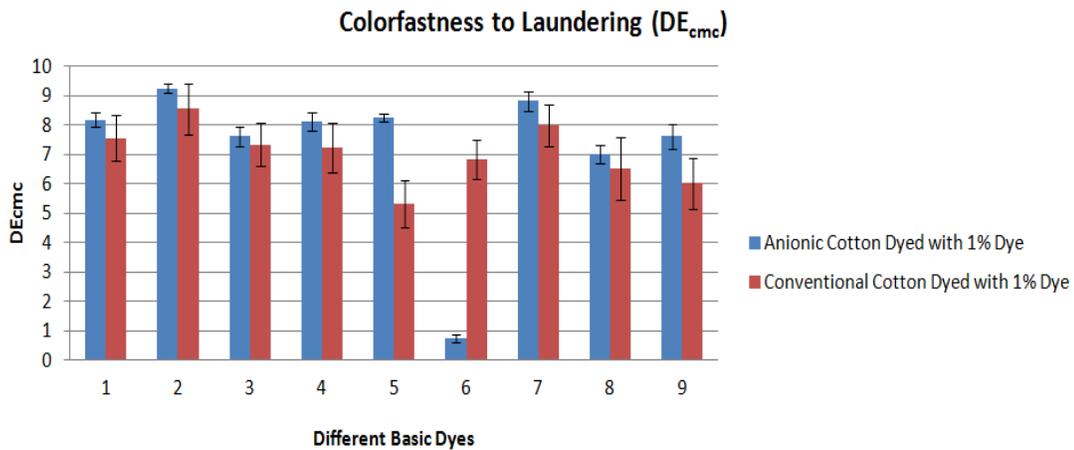


Figure 32. Colorfastness to laundering of eighteen samples in DE_{cmc}

4.3.2.2 Evaluation of color staining of CHPSAS-treated and untreated samples after the laundering test

To check staining status on other fiber types such as bleached cotton, nylon 6.6 and polyester, multifiber fabric strips have been used. Such kind of strip contained yarns which were made of various generic kinds of fibers. The multifiber strip used in the current experiment was MFF #43A, which was made of thirteen types of fibers, including acetate, modacrylic, triacetate and so on. The level of colorfastness to staining was evaluated in gray scale according to ‘Nine-step Chromatic Transference Scale’ (AATCC Evaluation Procedure 8-2007) and the rating for each sample was presented below in Table 20. Gray scale ratings were determined by two experienced observers at two different time periods.

Table 19. Colorfastness to staining of nine pairs of CHPSAS-treated and untreated samples in gray scale

Group No.	Basic Dyes	Sample No.	Gray Scale ratings
1	Basic Blue 54 [Treated]	20	2.5±0.22
	Basic Blue 54 [Untreated]	29	2.7±0.45
2	Basic Blue 41 [Treated]	21	2.2±0.24
	Basic Blue 41 [Untreated]	30	2.4±0.57
3	Basic Blue 3 [Treated]	22	2.4±0.29
	Basic Blue 3 [Untreated]	31	2.6±0.37
4	Basic Red 1 [Treated]	23	2.2±0.25
	Basic Red 1 [Untreated]	32	2.4±0.59
5	Basic Red 22 [Treated]	24	2.4±0.14
	Basic Red 22 [Untreated]	33	2.7±0.22
6	Basic Green 4 [Treated]	25	4.4±0.24
	Basic Green 4 [Untreated]	34	2.5±0.22
7	Basic Yellow 28 [Treated]	26	2.3±0.22
	Basic Yellow 28 [Untreated]	35	2.4±0.43
8	Basic Orange 21 [Treated]	27	2.6±0.08
	Basic Orange 21 [Untreated]	36	2.8±0.41
9	Basic Violet 2 [Treated]	28	3.2±0.22
	Basic Violet 2 [Untreated]	37	2.7±0.24

As demonstrated in Figure 33, the mean gray scale ratings of untreated ones were just a little bit higher than the anionic ones. However, as larger standard deviations were found on untreated samples, fastness to staining of anionic and conventional cotton was still on the same class, meaning that treatment with CHPSAS did not impair staining fastness. In particular, the anionic sample had a rating of 4.4, which was much higher than that of the conventional one in Group No.6. Besides, similar to Group 6, untreated cotton had more severe staining problem than anionic cotton in Group 9.

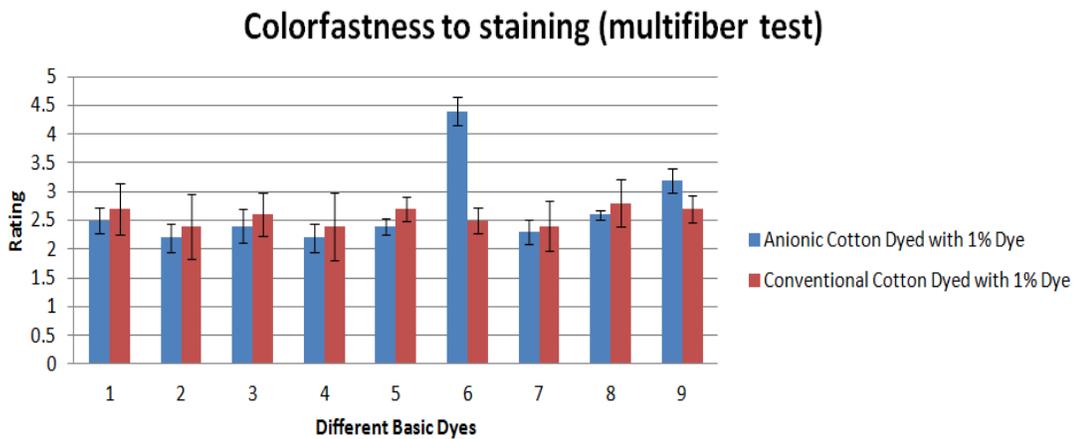


Figure 33. Colorfastness to staining of eighteen samples in gray scale

4.3.2.3 Evaluation of K/S values for eighteen samples after the laundering test

To judge the amount of color loss of eighteen samples during the washing test, K/S values had been measured after the laundering experiment and were exhibited in Table 21. Sample No.20, 21, 22, 23 all the way to No.37 were labeled as original eighteen cotton

samples, including nine anionic treated and nine control groups dyed with basic dyes. While the sample '20 prime' referred to sample 20 which experienced the laundering test. The remaining labels are in the same manner.

Table 20. K/S values of nine pairs of CHPSAS-treated and untreated samples before and after the laundering test

Group No.	Sample No.	Basic Dyes	K/S value
1	20'	Basic Blue 54 [Treated]	1.87±0.26
	29'	Basic Blue 54 [Untreated]	1.05±0.22
2	21'	Basic Blue 41 [Treated]	0.73±0.11
	30'	Basic Blue 41 [Untreated]	0.38±0.06
3	22'	Basic Blue 3 [Treated]	0.61±0.10
	31'	Basic Blue 3 [Untreated]	0.23±0.03
4	23'	Basic Red 1 [Treated]	2.28±0.26
	32'	Basic Red 1 [Untreated]	1.08±0.11
5	24'	Basic Red 22 [Treated]	0.10±0.02
	33'	Basic Red 22 [Untreated]	0.04±0.01
6	25'	Basic Green 4 [Treated]	1.30±0.12
	34'	Basic Green 4 [Untreated]	0.37±0.09
7	26'	Basic Yellow 28 [Treated]	0.26±0.03
	35'	Basic Yellow 28 [Untreated]	0.12±0.04
8	27'	Basic Orange 21 [Treated]	1.88±0.09
	36'	Basic Orange 21 [Untreated]	0.70±0.16
9	28'	Basic Violet 2 [Treated]	7.59±0.34
	37'	Basic Violet 2 [Untreated]	2.92±0.16

*sample 20' stands for sample 20 which went through laundering

Thirty-six samples were divided by nine groups, in order to make it easier for comparison and analysis, as shown in Figure 34. As was mentioned earlier, there was no doubt that cotton that had been treated with anionic agent had higher color strength before the washing test in each group. By observing K/S values after the test, it was not hard to find that the modified cotton still possessed higher color yield compared with the corresponding untreated one. Generally, K/S values of cotton treated with CHPSAS were twice as high as conventional cotton. In particular, color strength of anionic cotton was more than three times better than that of the control sample in Group No.9.

In other words, the relatively lower K/S value in each group belonged to the untreated cotton which went through the washing test. However, in most cases (seven groups except No.6 and No.9), dyed conventional cotton before washing had more color strength than the dyed anionic one which endured the washing test.

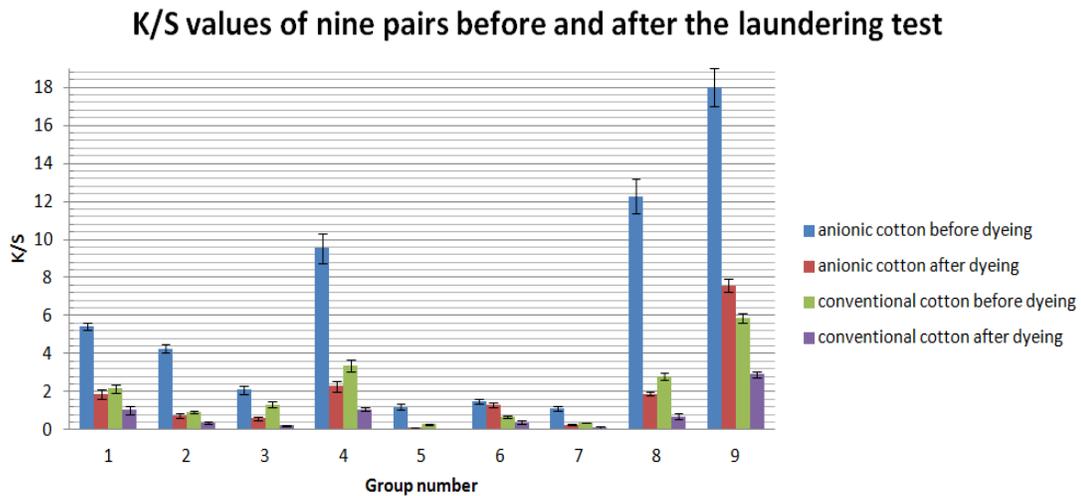
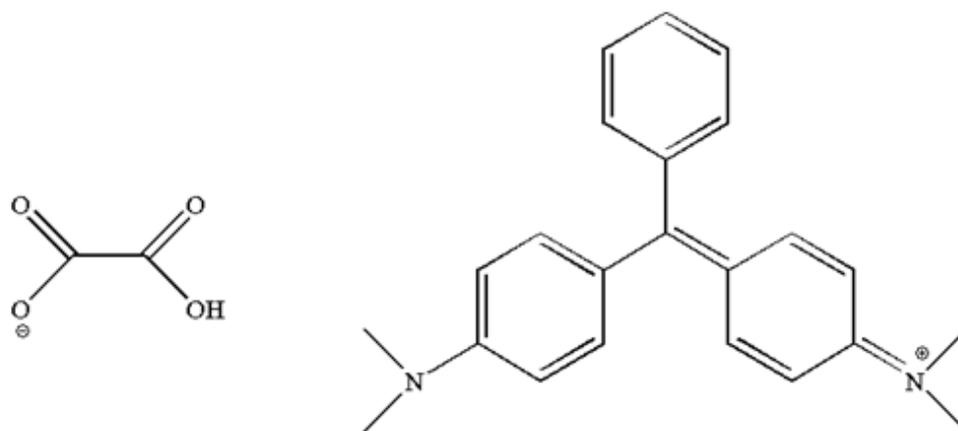
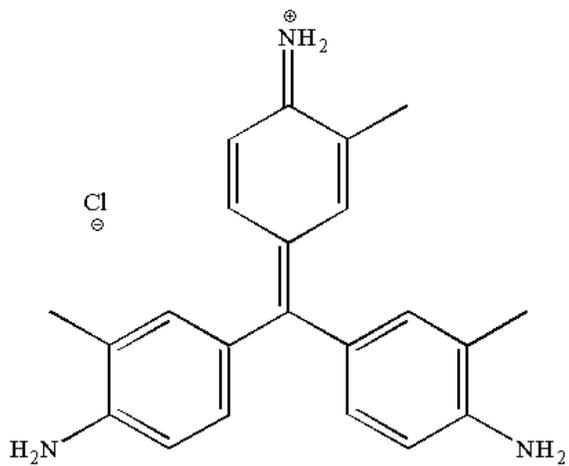


Figure 34. K/S values for fabrics before and after the laundering test

The basic dyes which had been used in Group 6 and 9 were Basic Green 4 and Basic Violet 2 respectively in Figure 35:



Basic Green 4



Basic Violet 2

Figure 35. Chemical Structures of two basic dyes

To consider the affinity between basic dyes and anionic cotton, several factors including the stability of cations in the dye structure and steric hindrance should be taken into consideration. For Basic Violet 2, the cations are located outside aromatic rings and this makes it easier for quaternary nitrogen to create ionic bonds with anionic cotton, small linking groups around the cation also show less steric hindrance. What's more, amino groups existed in the dye structure can also form covalent bonds with cellulose which help to bind basic dyes to anionic cotton. Although the conjugated structure is inclined to make the positive charge distributed homogeneously in the whole system thus lessen its affinity to anionic fabric, from the fastness results it seems that this factor is not as dominant as those two factors discussed above. As for the structure of Basic Green 4, the quaternary nitrogen is also exocyclic which is more readily to react with negative ions. The two methyl groups linked with the cation can donate electrons to it, making the positive charge more stable and more promptly to react with anions in CHPSAS-treated cotton. This might explain the reason why anionic cotton withstood the washing test had higher color yield than those corresponding untreated cotton even before washing. In a word, although sulfur fixation was not satisfying, anionic cotton samples being dyed with Basic Green 4 and Basic Violet 2 showed superior performances in color strength and fastness properties than dyed with other seven basic dyes.

4.3.3 Colorfastness to crocking of anionic and untreated samples dyed with nine basic dyes

Crockfastness test evaluates the level of color transfer from textile surface to other surfaces. In our experiment, only dry crock test was taken for all eighteen samples. Like previous gray scale assessment, ratings were made by two trained experimenters for four times in total. The average rating of four gray scale values for each sample was shown in Table 22.

Table 21. Colorfastness to crocking of nine pairs of CHPSAS-treated and untreated samples in gray scale

Group No.	Basic Dyes	Sample No.	Gray Scale ratings
1	Basic Blue 54 [Treated]	20	5.0
	Basic Blue 54 [Untreated]	29	5.0
2	Basic Blue 41 [Treated]	21	5.0
	Basic Blue 41 [Untreated]	30	5.0
3	Basic Blue 3 [Treated]	22	5.0
	Basic Blue 3 [Untreated]	31	5.0
4	Basic Red 1 [Treated]	23	4.2±0.16
	Basic Red 1 [Untreated]	32	4.0±0.22
5	Basic Red 22 [Treated]	24	5.0
	Basic Red 22 [Untreated]	33	5.0
6	Basic Green 4 [Treated]	25	4.6±0.08
	Basic Green 4 [Untreated]	34	4.2±0.14
7	Basic Yellow 28 [Treated]	26	5.0
	Basic Yellow 28 [Untreated]	35	5.0
8	Basic Orange 21 [Treated]	27	5.0
	Basic Orange 21 [Untreated]	36	5.0
9	Basic Violet 2 [Treated]	28	4.7±0.16
	Basic Violet 2 [Untreated]	37	4.0±0.22

Both gray scale ratings of treated and untreated cotton fabrics were relatively high, basically above 4.0 and there were as many as six groups whose grades reached 5.0. Results in Figure 36 portrayed that treatment with anionic agent did not affect the crockfastness properties of dyed samples, which showed the evidence that anionic treatment improved color yield of cotton without harming the fastness properties of fabrics dyed with basic dyes. Furthermore, anionic cotton in Group 4, 6 and 9 even had better behavior in crockfastness than that of conventional cotton in each group, showing that pre-treating cotton with CHPSAS could maintain or even improve the fastness properties to crocking.

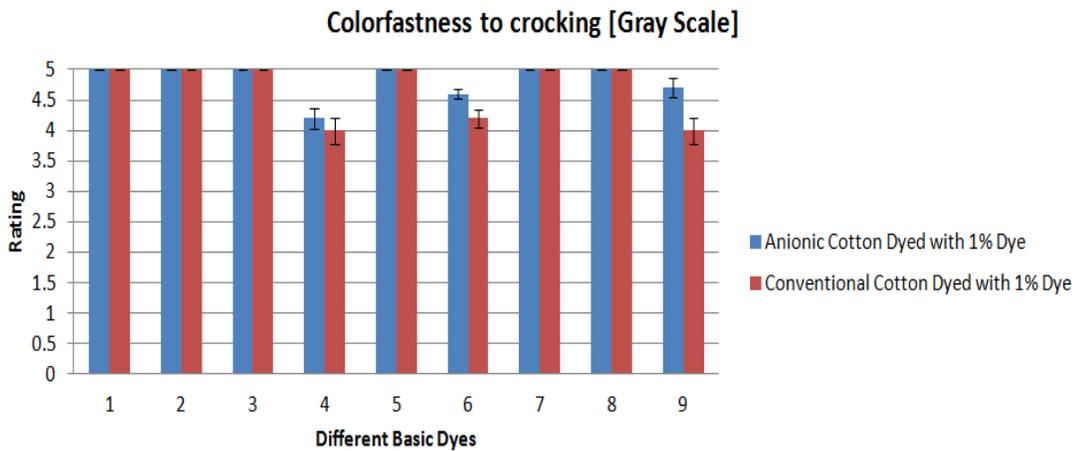


Figure 36. Colorfastness to crocking of eighteen samples in gray scale

4.3.4 Fastness testing results of each sample

The results of washfastness and crockfastness tests for anionic and conventional cotton fabrics which were dyed with 1% basic dye were shown below in Figure 37 – 45 for every sample individually. In these figures, “2A CC” referred to the test followed AATCC Test

Method 61-2A (Colorfastness to Laundering: Accelerated). “2A Stain” represented color transfer to undyed cotton during the laundering 2A procedure. ‘Dry Crock’ was colorfastness to crocking (AATCC Test Method 8). In the following figures, colorfastness results of nine basic dyes used in the current project would be displayed and discussed.

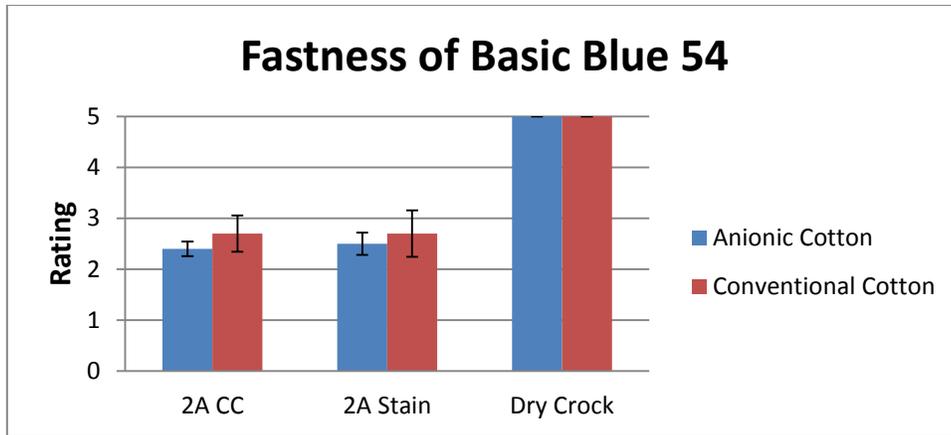


Figure 37. Colorfastness of Basic Blue 54 of conventional cotton and anionic cotton

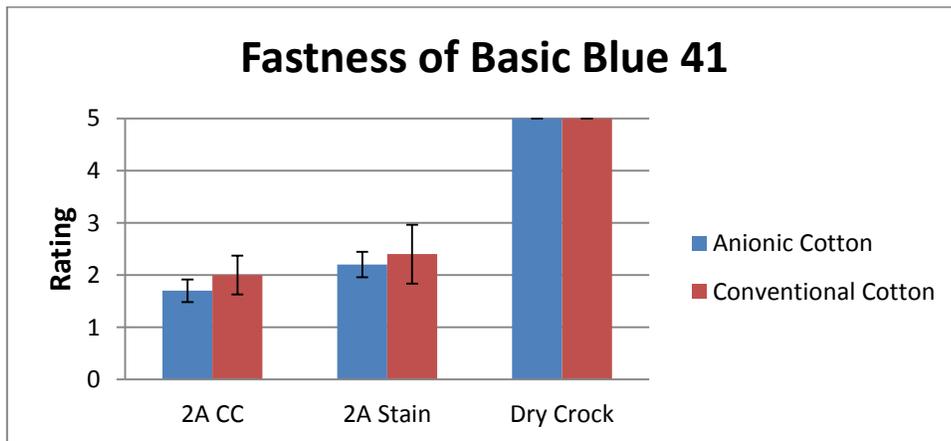


Figure 38. Colorfastness of Basic Blue 41 of conventional cotton and anionic cotton

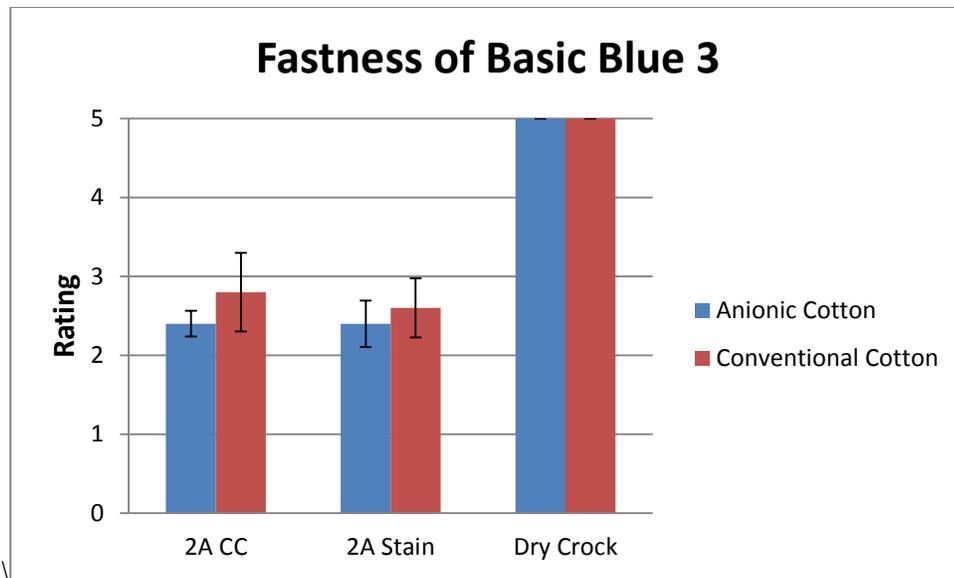


Figure 39. Colorfastness of Basic Blue 3 of conventional cotton and anionic cotton

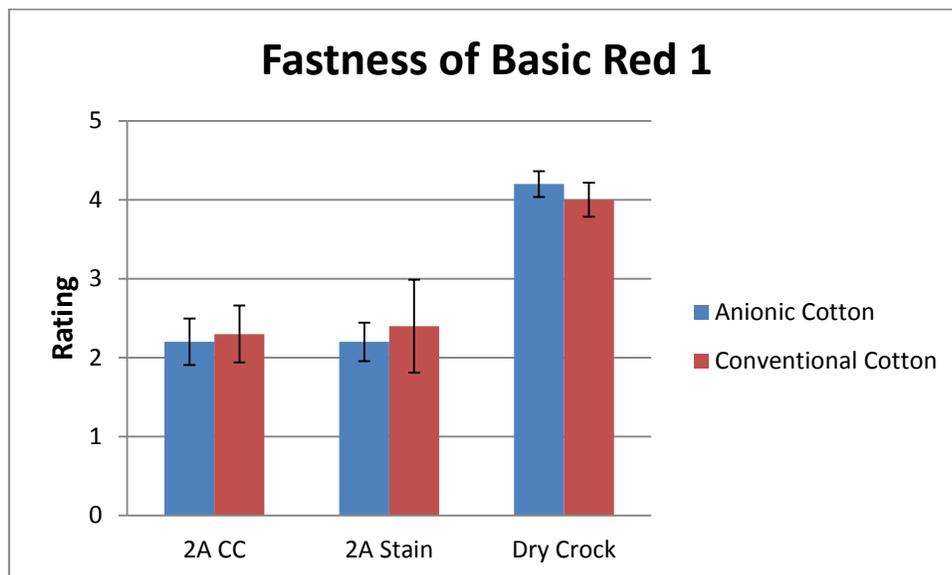


Figure 40. Colorfastness of Basic Red 1 of conventional cotton and anionic cotton

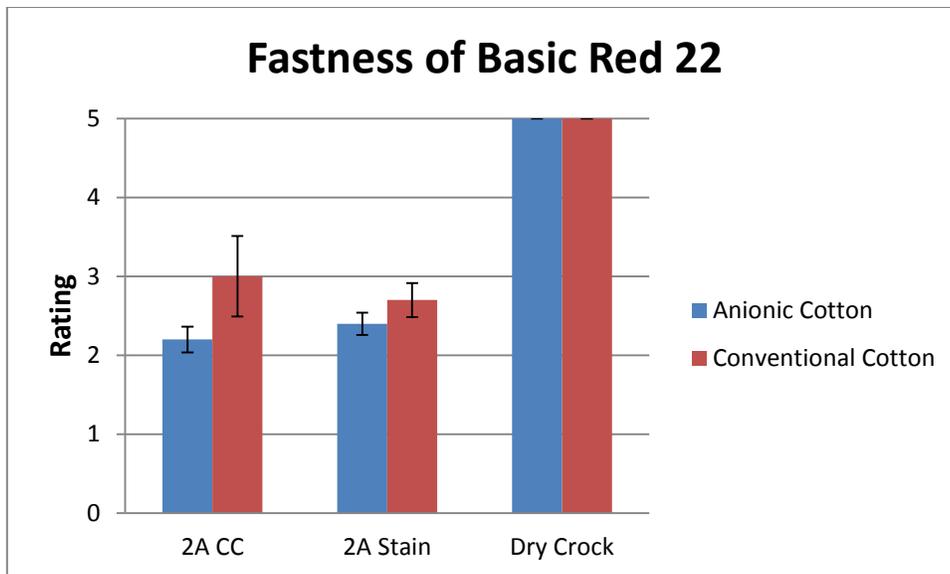


Figure 41. Colorfastness of Basic Red 22 of conventional cotton and anionic cotton

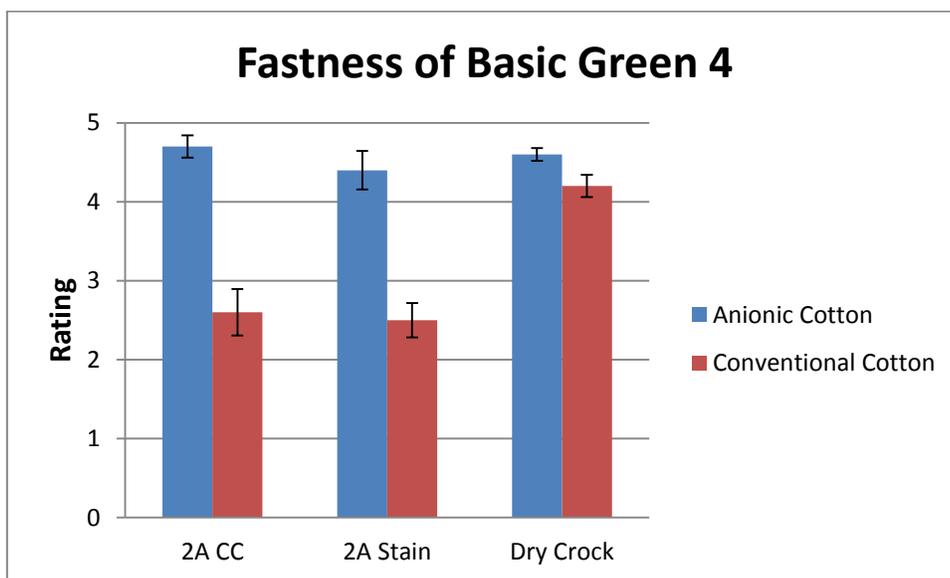


Figure 42. Colorfastness of Basic Green 4 of conventional cotton and anionic cotton

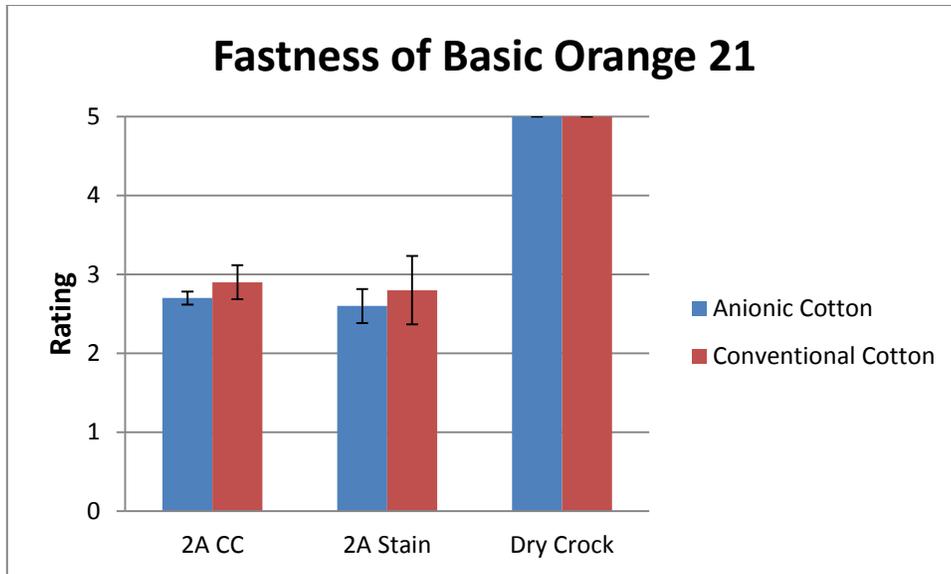


Figure 43. Colorfastness of Basic Orange 21 of conventional cotton and anionic cotton

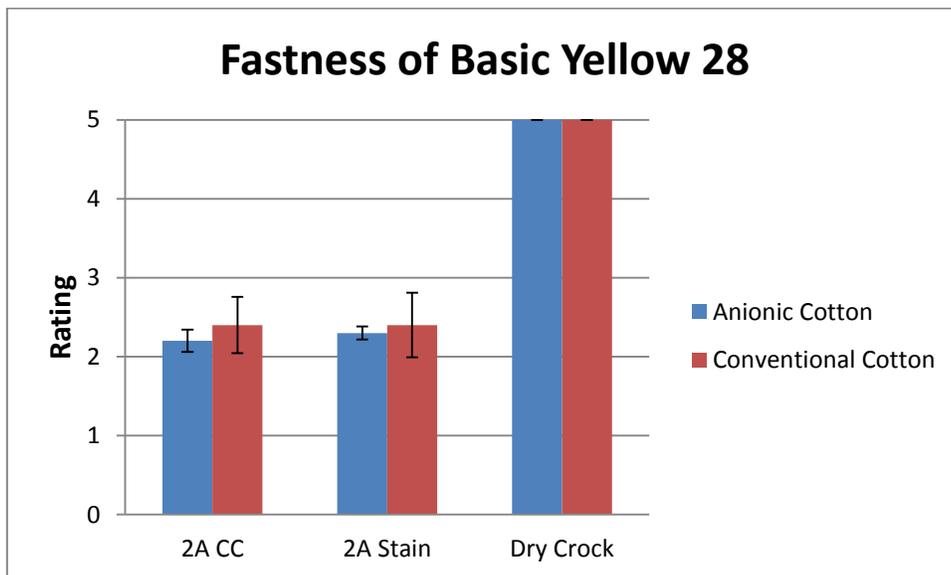


Figure 44. Colorfastness of Basic Yellow 28 of conventional cotton and anionic cotton

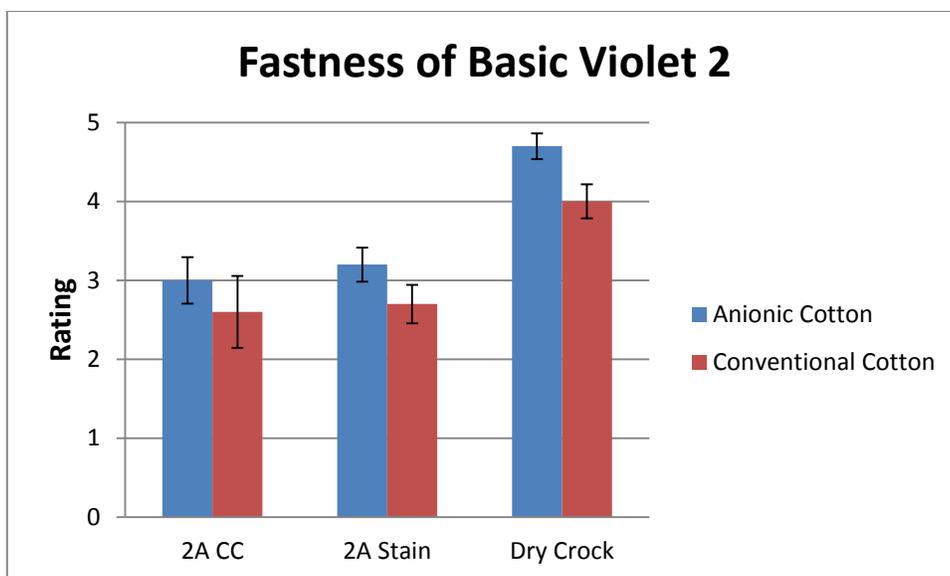


Figure 45. Colorfastness of Basic Violet 2 of conventional cotton and anionic cotton

As discussed earlier, CHPSAS improved the color yield of samples dyed with every basic dye to a high level and therefore enhanced the dyeability of cotton with cationic dyes. Meanwhile, fastness properties almost remained the same for anionic sample in each group. Generally cotton treated with CHPSAS had comparable colorfastness to washing and rubbing with conventional ones, indicating that anionic treatment could provide an ascending color yield without damaging fastness properties. Particularly, as for Group No.6 which was dyed with Basic Green 4, CHPSAS-treated fabric showed superior fastness properties in all washing, staining and crocking tests. What's more, anionic sample in Group 9 also exhibited better fastness in staining and crocking, with gray scale ratings higher than 4.0 and excellent color yield even after washing. To sum up, all these nine groups demonstrated that cotton could be dyed with basic dyes by anionically modified with CHPSAS since the color yield

had been improved to a high content. Particularly, Basic Green 4 and Basic Violet 2 exhibited the best overall properties including excellent color strength and fastness properties, possibly for the reason that they had more stable cations in the dye structure as well as less steric hindrance, which could promote the linkage between dye molecules and anionic dye sites on modified cotton.

4.4 Conclusions

The cold pad batch process enables the anionic cotton to be dyed evenly and therefore provides superbly uniform treatment of cotton with CHPSAS. Besides, by using this method, uniform and level dyeing is achieved with the absence of electrolytes, which simplifies the whole procedures. Although sulfur fixations were not very satisfying which might attribute to inherent deficiencies of pad batch procedures, from the analysis to the results, an improved color yield and fair fastness properties to laundering, staining and crocking after dyed with basic dyes has been obtained. In addition, anionic cotton being dyed with Basic Green 4 and Basic Violet 2 shows even better fastness properties than the conventional one in the same group for more stable cations in the dye structure as well as lower steric hindrance than other basic dyes. The new system not only allows dyeing cotton with basic dyes to a high color yield, but also uses fewer basic dyes to achieve equal depth of shade compared with the conventional cotton. To enhance anionization efficiencies, some feasible ideas include using inert solvents instead of water or reducing liquor ratio to weaken hydrolysis reaction and in

place of pad batch method, pad-dry-cure is believed to provide higher sulfur fixations as less water existed after such process.

5. THESIS CONCLUSIONS

The current work has focused on finding out an optimized formula for CHPSAS and sodium hydroxide to maximize the anionization reaction yield. Our project also concerns about exploring dye yields and colorfastness of basic dyes on anionic treated cotton fabrics with 3-Chloro-2-hydroxy-1-propanesulfonic acid sodium salt hydrate. Cold pad batch was chosen to apply this anionic reagent to cotton as its incomparable advantages in saving energy and water and reducing preparation procedures. From the results we can see the anionic pretreatment increases the color yield and crockfastness properties of dyed cotton while maintains wetfastness properties on cotton dyed with basic dyes. Even for two basic dyes, exceptional colorfastness to washing, staining and crocking has been obtained, which may contribute to their low steric hindrance and high reactivity of cations existed in the dye molecules. Such kind of treatment is considered to be a promising way to dye cotton with basic dyes, a dye type which has no affinity for cotton originally. Meanwhile the process is eco-friendly, which diminishes the impact to the environment, including energy and water during the whole process. Although the percent of sulfur fixations seem not high enough, a series of practical suggestions such as using inert solvents in place of water and using other methods such as pad-dry-cure procedures have been proposed to improve anionization efficiencies.

6. FUTURE PROSPECTS

Cotton pre-treating with CHPSAS in a cold pad batch process has shown prospects to be dyed with basic dyes, which carry positive charges. CHPSAS could potentially become a substitute for conventional anionic agents such as BTCA and citric acid in crosslinking cotton. However, such treatment is still far from mass application as fastness problems for dyeing anionic cotton with basic dyes, though dyeability of cotton for such kind of dyes has been enhanced evidently.

Poor washfastness properties of dyed CHPSAS-treated samples are mainly due to the low CHPSAS fixations on the fabric. To increase chemical bonding between the anionic agent and cellulosic fabric, several promising attempts could be focused on

1. Adding electrolytes (such as sodium lauryl sulfate and sodium chloride) of various amounts in the bath to get higher reaction efficiencies thus acceptable wetfastness performance.
2. Adjusting temperature or pH, or altering the sequence when adding CHPSAS and NaOH. For instance, padding the fabric through sodium hydroxide first and then through CHPSAS solution might offer better fixation.
3. Other application methods such as pad-dry-cure process can be used to substitute cold pad batch process in order to increase the fixation of CHPSAS on cotton since water could be eliminated during this procedure. Reducing the liquor ratio, i.e. less water usage per amount of cellulose, might help to reduce the hydrolysis effect.

To check whether anionic pretreatment impair mechanical properties of cotton samples or not, parameters such as tensile strength and elongation at break of treated and untreated fabrics remain to be evaluated.

Furthermore, evaluation with confocal microscopy may help to confirm the occurrence of reaction inside the fiber and the distribution of anionic dye sites throughout the fiber diameter. By combining SEM images together with confocal microscopy, the oval cross-sectional shape of the treated fabrics could be explored in depth.

An evident improvement in dyeability of cotton with basic dyes has been shown by the use of CHPSAS to add anionic dye sites.

Additional work is needed to enhance the durability of dyeing anionic cotton with basic dyes. By increasing CHPSAS fixation on fabrics with the possible solutions mentioned above, it is believed that higher color yield and better fastness properties could be obtained.

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