

## **Abstract**

FARRELL, MATTHEW J. Sustainable Cotton Dyeing. (Under the direction of Dr. Peter J. Hauser).

Although there are alternative and competitive fiber types, cotton garments remain treasured for their natural feel, look, and comfort. For cotton garments, fiber reactive dyes are the colorant of choice possessing very good wet fastness for laundering, and spreading a wide gamut of achievable colors. However, the use of fiber reactive dyes on cotton is plagued by their historical requirements of large amounts of salt to exhaust the dye, and extensive water use for removing unfixed (hydrolyzed) dye. Waste water (effluent) treatments are costly and do not reduce the amount of raw materials consumed. Modifications of cotton dyeing processes showing significant environmental benefits have been suggested and shown by many researches, but in many cases, there is a financial burden from utilizing these technologies, and/or the methods are not industrially applicable or transferable.

Instead of focusing on process modification of cotton dyeings, much research has focused on direct modification of cotton at a molecular level to impart permanent cationic character. The permanent cationic charge allows salt free dyeing by ionically attracting and bonding anionic dyestuffs. Further, with near complete utilization of applied dyestuffs, it is possible to use much less dye and water for rinsing hydrolyzed dye. Even with all of the promised environmental benefits of cationic cotton, an industry shift towards utilization of cationic cotton has not been seen. The most common cationization reagent is 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC). The lack of industry acceptance of

cationic cotton is attributed to safety concerns regarding CHPTAC, lack of demonstrated bulk scale applications with equivalent performance as conventional fiber reactive dyed cotton, and finally, cost concerns of cationization treatments and subsequent dyeing.

In this work, various aspects of using fiber reactive dyes for cotton are reviewed in terms of properties, processing conditions, environmental and safety considerations, and resulting commercial product specification. The advantages of direct modification of cotton at a molecular level to impart permanent cationic character are reviewed. Use of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) as a cationization agent is reviewed with emphasis on safety, bulk scale applications, and cost and performance compared to conventional fiber reactive dyeing of cotton. This work presents a comprehensive approach for utilization of CHPTAC, including feasible methods of cationization and possible improvements upon existing procedures. Necessary equipment and information for the practical production dyehouse are presented.

Significant improvements in exhaust applications of CHPTAC as well as a new pad bake method for CHPTAC application are presented. Considerable work to find a phase transfer catalyst for exhaust CHPTAC applications is presented, however no commercially feasible process was developed. CHPTAC is successfully applied by foaming at low wet pick up. Models correlating the dyeability of cationized cotton with colorimetric reflectance data are presented which allow a quick and accurate determination of cationized fabric dyeability. Additionally, a method for predicting the amount of cationization, and for predicting a dye recipe conversion from traditionally dyed cotton recipes for cationic cotton are presented.

It was shown that it is a straightforward process to dye level bulk cationic cotton (55 pounds) to near complete dye utilization utilizing traditional textile lubricants, dispersants, and a common textile consumable, carboxymethylcellulose. From 55 pound lots, fastness properties, including lightfastness, of cationic cotton are found to be equal or better than traditionally dyed cotton using fiber reactive dyes. Detailed cost analysis is presented showing that cationic cotton can produce significant financial savings as well as environmental advantages. Results of dyeing experiments and analysis of bulk scale dyeings show that the longstanding premise that cationic cotton may be dyed with any anionic dyestuff may be problematic for the textile dyer. Results showed significant color change when laundered of cationic cotton dyed with reactive dyes without the inclusion of alkali. This color change was attributed to an ion exchange mechanism of dye for suitable anions and was only remedied by covalently bonding applied reactive dyestuffs with the addition of alkali. These results seem to suggest that reactive dyes may be the best suited dyestuff for dyeing cationic cotton as they can impart both ionic and permanent covalent bonding preventing ion exchange during laundering.

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Sustainable Cotton Dyeing

by  
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## **Dedication**

This work is dedicated to my lovely wife Jessica. Words cannot describe my gratitude and love for such a caring, compassionate, hardworking, and overly patient person. Having such a strong, endearing, and enduring partner to fall back on made this possible. Jessica, I don't know what else to say except that I love you endlessly, and thanks for being my wife and putting up with me!

## **Biography**

Matthew Julian Farrell was born April 8, 1982 to Bill and Linda Farrell in Sanford, NC. He has a younger brother Patrick, older sister Kellie, and older brother Will. Matt was married to Jessica in 2010. Matt graduated from Lee County Senior High School in 2001. He obtained his BS degree in Polymer and Color Chemistry from North Carolina State University in 2005. He obtained an MS degree in Textile Chemistry from North Carolina State University in 2007.

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## **1. Introduction**

The coloration of textile goods is plagued with the stigma of an industry that is highly polluting and non-sustainable. The textile industry consumes large amounts of water, chemicals, and energy. Not only is this expensive and costly for the environment, textile processing produces and discharges significant amounts of pollution. Waste treatment is expensive and does not address the problem of raw material consumption or exposure to various processing chemicals. In particular, the coloration of cotton and its colorant of choice, reactive dyes, require vast amounts of salt and water for efficient dye utilization and fastness requirements. Salt is needed to neutralize negative charges produced by cotton in aqueous baths and force the soluble reactive dye out of solution. As a result, large amounts of salt are discharged in the dyebath effluent. Further, because of competing hydrolysis reactions with the reaction of the reactive dye with cellulose, non-trivial amounts of hydrolyzed reactive dyes must be removed from the dyed fabric. In order to sufficiently remove the dye hydrolysate, large amounts of water are required to methodically rinse and remove the hydrolyzed dye. An alternative approach to expensive waste treatments and excessive raw material consumption is through process modification. Processes that consume less raw materials and energy are more sustainable and less polluting. Many academic researchers and industry professionals have developed alternative methods for more sustainable coloration practices of cotton goods. However, many of these improvements have not been commercialized and may require large capital investments, and/or increased processing costs. Additionally, none of these innovations provide a fully

sustainable method for the coloration of cotton goods. However, cationized cotton presents itself as one of the most viable and sustainable alternatives to conventional reactive dye applications to cotton. In order to fully understand and appreciate the opportunities that cationized cotton affords, it is important to review cellulose, conventional reactive dyes and other colorants application to cotton, some of the advancements made in the coloration of textile goods, and finally explore cationized cotton and why it is a sustainable solution for the coloration of cotton goods.

## 2. Literature Review

### 2.1 Cellulosic Fibers

Without a doubt, cellulose is the most abundant and easily renewable resource on the planet. Fundamentally, cellulose is a natural linear polymer composed of beta 1,4 linked glucose units as shown in Figure 2.1 (1). Cellulose possesses three alcohol groups, two secondary and one primary alcohol. The primary alcohol is more easily neutralized and readily available and prominent in chemical reactions of cellulose.

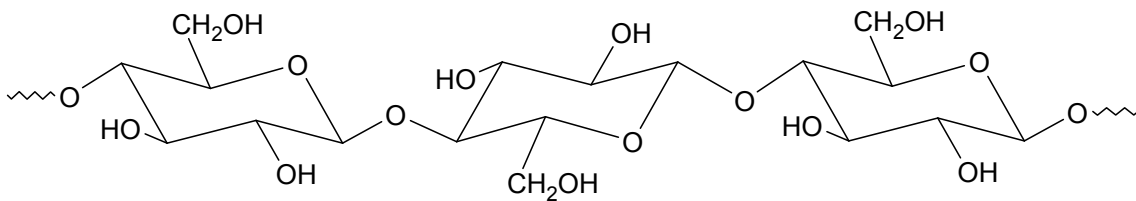


Figure 2.1 - Chemical Structure of Cellulose

There are several highly useful and commercially prevalent chemical derivatives of cellulose including cellulose acetate and carboxymethyl cellulose (CMC). Cellulose acetate is found in such products as a base for photographic film paper, and polymeric films (coatings, wrappers) and fibers. CMC, commonly found as the sodium salt of the acid group, is used in such products as thickeners in food stuffs and sizing agents for textile warps. Starch, shown in Figure 2.2, is a naturally occurring and commercially important relative of cellulose. Starch is very chemically similar to cellulose but different in two major ways. First, starch contains direct alpha bonding of glucose units as compared to the beta 1,4 linkages found in

cellulose. Second, starch incorporates branching of polymeric chains on the primary alcohol of the glucose units.

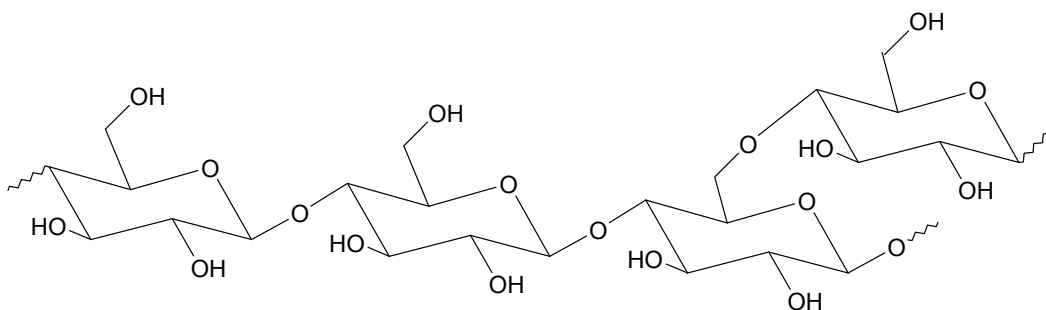


Figure 2.2 - Chemical Structure of Starch

## 2.2 Alkali Cellulose

One of the most important chemical intermediate forms of cellulose is known as alkali cellulose, shown in Figure 2.3. Alkali cellulose is the product of cellulose treated with an alkali to neutralize acidic alcohol groups and ready cellulose as a nucleophile for chemical reactions (2). The degree of deprotonation can be related to the type and amount of base used as well as the temperature of the alkaline application. Alkali cellulose is important because it allows cellulose to readily react with many types of reagents making cellulose, or more importantly, cotton, a commercially important textile fiber.

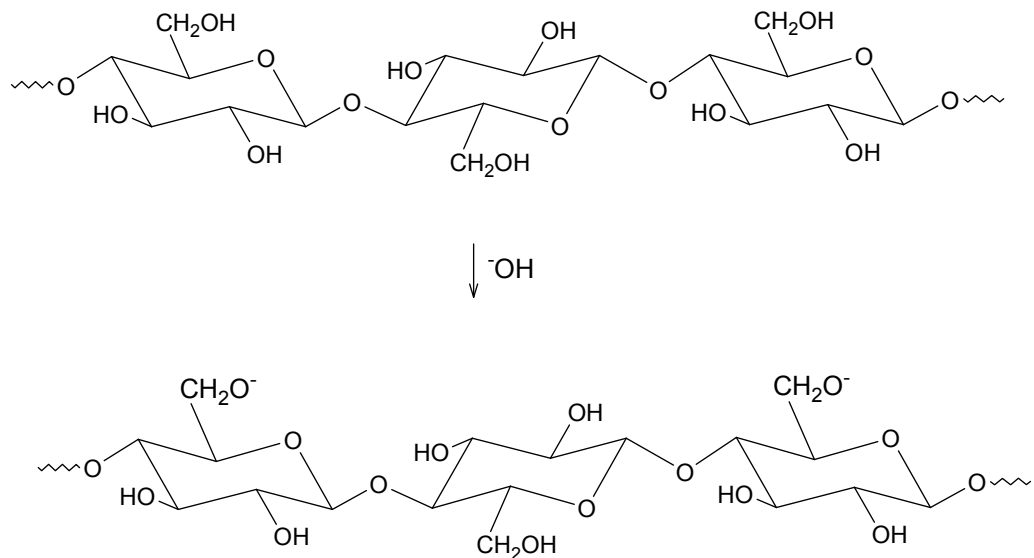


Figure 2.3 - Alkali Cellulose

### 2.3 Coloration of Cellulose

Textile garments have been colored through natural means for thousands of years and synthetic means since the advent of mauvine in 1856 by Perkins over 150 years ago (3,4). Today, the coloration of textiles is a highly competitive but very large segment of the world economy. Synthetic fibers such as polyesters (PET's) and natural fibers such as cotton are in a constant struggle for global dominance in everyday apparel. For a current estimate, cellulose makes up approximately 50% of annual textile fiber production representing about 25 million tons (5). The coloration of PET is fairly straightforward and routinely carried out with disperse dyes with high degrees of utilization of the dyes due to the solubility of disperse dyes inside the PET fiber. Conversely, cotton is routinely colored by varying methods where the colorant utilization efficiency can vary broadly. Cotton fabrics are

cherished by many consumers because of the natural feel and comfort of cotton fabrics compared to the “synthetic” feel of most synthetic fibers and fabrics such as PET. Therefore, it is important to highlight and understand the different coloration mechanisms of cotton goods as well as the drawbacks and advantages of the different mechanisms.

### **2.3.1 Pigments**

Pigmentation of cotton goods is undeniable and unmistakable for the ability to produce washed out and aged goods in new apparel. However, pigments, owing to their definition, are largely insoluble in most ordinary organic solvents and completely insoluble in aqueous application mediums. Hence, for their use as cotton colorants, dispersing agents and binders must be used to adequately apply and fix the pigments. Not only can this process be tedious and expensive, but the application of pigments stains the application equipment and must be cleaned. Further if pigments are released in effluent to water streams, the pigments are almost impossible to break down in waste treatment facilities.

### **2.3.2 Vat Dyes**

Another colorant of choice for cotton goods is vat dyes. The most common vat dye is indigo for blue jeans. Vat dyes are of two types, indigonoid, and anthraquinoid (6). Vat dyes are also largely insoluble in aqueous mediums and for application to cotton must be reduced to their soluble leuco form with a reduction bath. A common reduction bath for vat dyes consists of sodium hydroxide and sodium hydrosulfite. After reduction and application of

vat dyes, the vat dyes need to be reoxidized for fastness properties. As a class, vat dyes give excellent fastness properties but are expensive and have limited hue availability (7). The reduction bath chemicals, especially sodium hydrosulfite, present a safety risk with the hazard of spontaneous combustion of long term storage. As well, reduction baths made from sodium hydrosulfite are also an olfactory pollutant with a distinct foul odor. A typical effluent discharge of a vat dyeing may contain residual dyestuffs, reducing agents, oxidizing agents, detergents, and salt (8).

### **2.3.3 Sulfur Dyes**

Sulfur dyes are an economical colorant for deep black and navy shades on cotton goods but each sulfur dye's composition is a mixture of many structures and are highly unknown (6). Like vat dyes, sulfur dyes must be reduced in order for application to cotton. Similar reduction baths such as those used for vats, sodium hydrosulfite with sodium hydroxide, may be used, but sulfur dyes are also commonly reduced with sodium sulfide (6). Sodium sulfide is a dangerous chemical reagent that may form hydrogen sulfide, a poisonous gas, if acidified. In either case of reduction, both processes produce an olfactory pollutant of rotten eggs as well as effluent pollution. A typical effluent discharge may contain dyestuffs, sodium sulfide, alkali, and salt (8). Finally, the wetfastness obtained with sulfur dyes is only poor to moderate (7).



### **2.3.4 Natural Dyes**

Natural dyes or natural colorants are found in nature and are used to color textile goods such as cotton. Natural colorants were the first colorants used in the coloration of garments dating back prior to 2500 BC (3). Two of the problems with natural colorants are the quantity of colorant obtainable and the expense to obtain because in most cases, natural colorants must be extracted and concentrated from their natural sources. Further, solvents are routinely used to extract and concentrate the natural colorants which to a degree, stains the environmental goals of utilizing natural dyes. Tyrian purple is probably the most infamous naturally derived dye from sea mollusks (9). Because of the limited availability and expense of Tyrian purple, it was illegal for the common man to own or possess clothing dyed with Tyrian purple.

### **2.3.5 Direct Dyes**

Probably two of the most common dyestuffs utilized for the coloration of cotton textile goods are direct and fiber reactive dyestuffs (10). Direct dyes are generally linear large molecules that bind to cellulose by secondary forces such as hydrogen bonding or Van der Waals interactions. Direct dyes are generally only useful on cotton for low-cost goods, or for pale shades, or for goods that are not routinely washed such as curtains or upholstery (especially automotive). Because of the weaker retention mechanism of direct dyes, secondary force bonding, the wash and overall fastness of direct dyes is not very good unless treated with a fixative or resin finished, after which the fastness can be excellent.

Fixation agents may include magnesium chloride or chromium salts, as well as reactive precondensate resins but this increases the cost of the coloration and can release metals into the effluent. On the other hand, because of the large overall size and linearity, near complete exhaustion of direct dyes is common and with little overall salt needed to fully exhaust the dyes. However, direct dyes are quickly becoming considered technologically obsolete except in specialty applications such as automotive upholstery because of their unsurpassed lightfastness (11). A typical effluent discharge of direct dyes may contain dyestuffs, salt, and dye fixing agents (8).

### **2.3.6 Reactive Dyes**

Reactive dyes are the colorant of choice and most widely used colorant for typical cotton textile goods, especially garments. The wide range and brilliancy of available reactive dyes in different reactive chemistries are unparalleled among the other available colorants for cotton goods (12). Because of the very strong and stable ether bonds formed by reaction of alkali cellulose with a reactive dye, the final reactive dyed cotton goods exhibit excellent wet fastness properties. However, light and chlorine fastness in many cases is not good for reactive dyes. Conversely, even with the aforementioned benefits of reactive dyes, the applications of reactive dyes are highly polluting to the environment from the quantities of salt and water used for processing the reactive dyestuffs. Because of the prevalence and amounts of reactive dyes used in the coloration of cotton goods, it is prudent to take a

detailed look at how reactive dyes are applied in terms of chemical reagents, auxiliaries, and the effects on effluent discharge to the environment.

## 2.4 Reactive Dye Chemistry

Since ICI patented the first synthetic reactive dyestuff in 1956 (13), the field of reactive dyes has been highly innovative and highly competitive. When patent protection runs out on patented dyestuffs, cheaper manufacturers as well as competitors are free to synthesize and market the same dye. As a result, dye manufacturers limited the availability of Colour Index classifications to help protect intellectual property, but to remain competitive in a global marketplace, dyestuff manufacturers must constantly innovate to remain a player in the international market. Although it is not the intent to explore all types of reactive dye chemistries, generally however, there still remain two main industrially used types of reactive dyes; halogenic cyclic azine derivatives and sulfato ethyl sulfone type reactive dyestuffs. Figure 2.4 shows the structural features of Reactive Red 11, one of the first types of reactive dyes invented, dichlorotriazines (DCT's) (14).

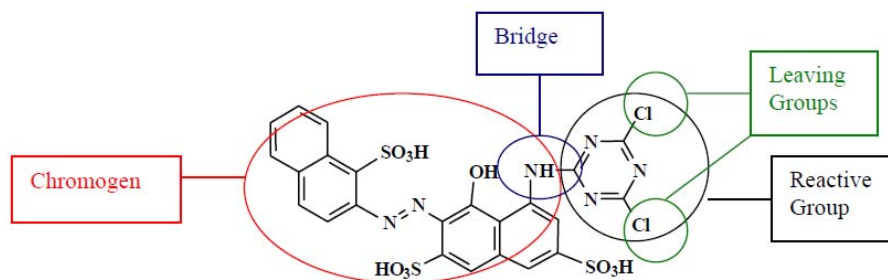


Figure 2.4 – Molecular Features of DCT Type Reactive Dyes

The chromogen of the dye molecule is the color-containing portion of the dye. The chromogen is bridged to the reactive group of the dye molecule through a molecular bridge. The typical bridge is designed to insulate the chromophore from the reactive groups to protect the color of the dye molecule. There are many types of specific reactive groups in reactive dye chemistry. Figure 2.4 shows the DCT reactive group where the chlorine atoms are the leaving groups. In a nucleophilic type substitution reaction, the leaving group leaves so that the cellulosate ion may react with the electron deficient carbon in the azine ring. On the other hand, sulfato ethyl sulfone dyes are unique for reactive dyes in that the actual reactive group is not present in the dye molecule initially. The sulfato ethyl sulfone dye must be activated under basic conditions to yield the reactive vinyl sulfone (VS) group as shown in Figure 2.5. The VS group then undergoes nucleophilic addition with the cellulosate ion.

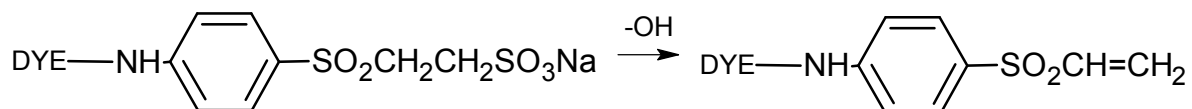


Figure 2.5 – Activation of VS Type Reactive Dyes

In halogenated and VS type dyestuffs, because of alkaline conditions needed to produce alkali cellulose and the reactive form of the VS, there is always a competing hydrolysis reaction of the dye with the fixation of the dye with cellulose. Figures 2.6 and 2.7 show the

competing reactions of a DCT and VS type dyestuff. The hydrolysis reaction renders part, or all, of the reactive groups inactive depending on the specific dye chemistry. As a result, the reactive dye is incapable or limited with its ability to react with cellulose, and the hydrolyzed dye which is incapable of reacting with cellulose must be removed. The removal of hydrolyzed reactive dyestuffs makes up a significant amount of the overall water usage for processing of cotton goods. It should be noted that in the case of the DCT dye that hydrolysis is not reversible but in the case of vinyl addition, in anhydrous heat, the vinyl group can reform.

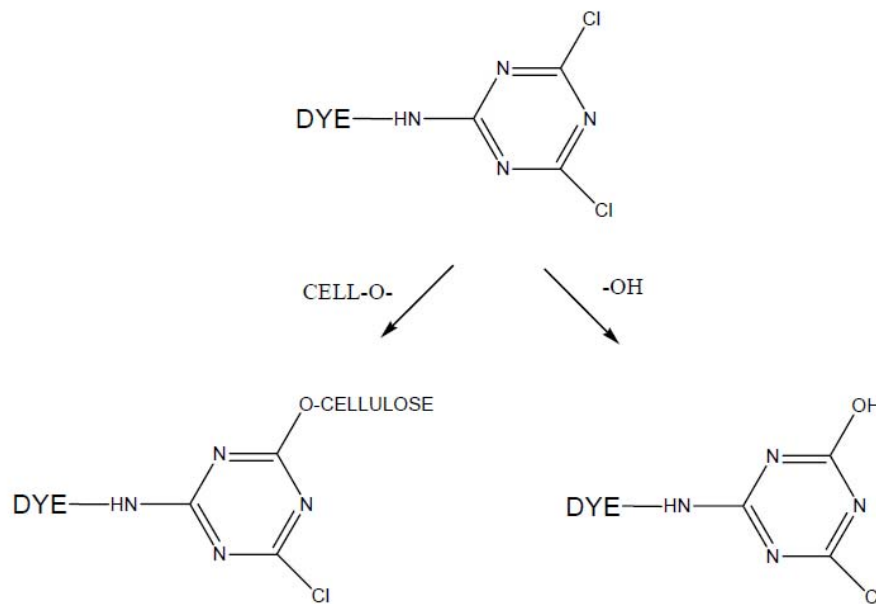


Figure 2.6 – Competing Reactions of DCT Type Reactive Dyes

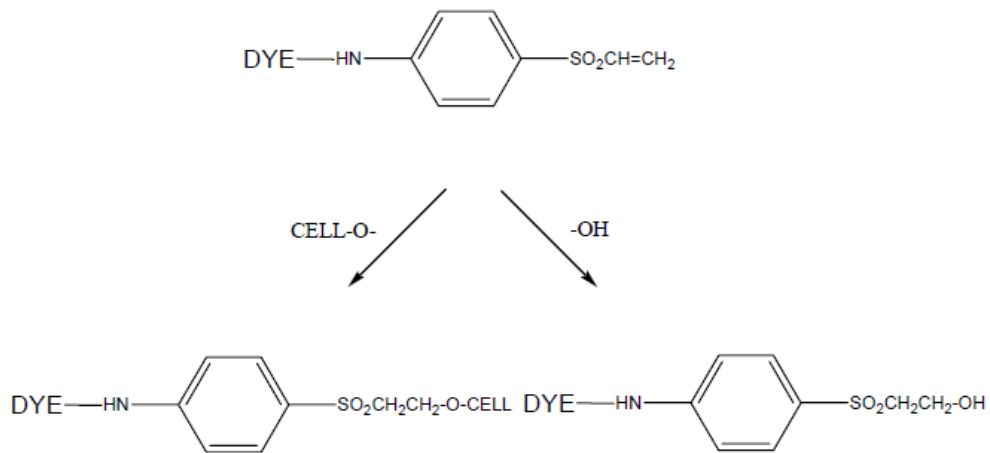


Figure 2.7 – Competing Reactions of VS Type Reactive Dyes

## 2.5 Environmental Problems Associated with Reactive Dyes

Fiber reactive dyes are known for requiring moderate quantities of alkali and large amounts of dye, salt, water, and processing time for depth of shade and fastness requirements as well as the energy required especially in the case of hot dyes. It is important to understand these parameters in the dyeing of traditional fiber reactive dyes on cotton to ascertain how these environmentally unfriendly constraints may be improved upon.

### 2.5.1 Salt

Traditional reactive dye molecules are not as large as direct dye molecules and hence have limited substantivity for cotton goods. Cellulose, when added to water, develops a slightly

negative surface charge referred to as the zeta potential (10, 15). This negative charge on the cellulose tends to repel anionic reactive dyestuffs from the surface of the cotton, although it is of minimal impact. More importantly, the solubility of reactive dyes shifts the reactive dye equilibrium towards staying in the aqueous application medium and not towards the surface of the cotton. In order to sufficiently enhance the substantivity of the reactive dye to the surface of the cotton fiber, large amounts of salt are required to force the reactive dye out of the bath onto the surface of the cellulose. The amounts of salt required for exhaustion and the depth of shade for heavy reactive dye formulations lead to large amounts of salt released in the effluent and discharged to streams and rivers. Salt concentrations may be as high as 100 g/L for dark shades (11, 16). As a result, there is a sufficient threat to aquatic wildlife and an increase in aquatic toxicity (11). Salt may be considered as one of the most toxic chemicals emitted from textile mills because of the quantity released, albeit not necessarily the toxicity of the salt itself (15). Finally, if the effluent must be treated, i.e. desalinated, the additional cost of this processing step makes the desalination unattractive just from an economical point of view.

### **2.5.2 Color**

Another major polluting factor of reactive dye coloration of cotton is the significant amount of color pollution as a result of dye hydrolysis. Color is another example of treatable although expensive waste byproduct of textile processing. Therefore, process modification is the best way to reduce color discharge to the environment. Although estimates of the

amount of hydrolyzed dye will differ depending on the type of reactive dye used as well as the liquor ratio, concentration of salt, etc., in general, anywhere from 20-70% of the dye applied may be hydrolyzed (7, 9, 17-19). When the effluent is discharged into natural water pathways, the hydrolyzed dyestuffs are immediately dispersed because of the high degree of water solubility of the reactive dyestuffs. Methods available to decolorize reactive dye effluent include chemical oxidation. However, the complex resulting mixtures of oxidation may destroy the actual color producing chromogen of the dye molecule but may produce highly toxic molecular fragments of the original dye molecule (13). In other words, the color and visual persistence of the colored effluent discharge may be remedied but may be replaced with molecules that are more toxic to aquatic life than the colored precursor dye compound.

### **2.5.3 Alkali**

Most all reactive dyes require alkali to be added to the reactive dyebath in order to facilitate bonding of cellulose with the reactive dyestuffs. As a result, large amounts of alkaline dyebath solutions are dumped directly into the effluent. In some cases, the fabric is never neutralized and neutralization may only be required in the case of VS dyes. Depending on the reactive chemistry being used, the reactive dye may be very reactive at low temperatures with low amounts of a milder base such as sodium carbonate for DCT dyes, or requiring sodium hydroxide for VS type dyestuffs (6).



#### **2.5.4 Water Usage**

Because of the competing hydrolysis reaction and the resultant hydrolysate that must be removed from reactive dyed cotton goods, profuse amounts of water are required to remove the hydrolysate. It has been approximated that 80% of the water used, 90% of the energy used, and 70% of the time of the total wet processing cycle is contained in the bleach and washing and rinsing processes (20-21). However, as noted in 2.7.2, washing requirements are highly machine dependent. Conventional reactive rinsing falls into a three step process (20-22). First, the salt used for exhausting the reactive dyes must be diluted to a concentration that is virtually zero in the rinsing bath to allow diffusion of the hydrolysate to the surface of the fiber. After the salt has been removed from the fabric and bath, the dyed cotton goods are soaped at high temperature, basically breaking hydrogen bonds to diffuse the hydrolysate. Finally, the diffused hydrolysate is removed from the fabric by a further final rinsing. In the strictest interpretation, the use of water alone in the reactive dyeing process does not have a pollutant effect, however, the reactive dyeing process, i.e. especially the rinsing after the dyeing, utilizes large amounts of a natural resource. Additionally, the amount of water usage and time required to adequately rinse and remove hydrolyzed reactive dye cause the entire dyeing process to be greatly extended. Finally, it is common practice to utilize soaping aids in the removal of hydrolysate, but it has been reported that these soaps do little to improve fastness of the dyed goods but greatly increase organic pollution in the effluent (23).

## **2.6 Why Use Reactive Dyes?**

Even with all the environmental drawbacks of utilizing fiber reactive dyes on cellulose, their use is unparalleled for cotton goods because of the coupling of wide range of colors possible and all around wet fastness properties. To present a viable sustainable alternative to reactive dyes requires that similar colors and similar fastness properties be maintained while improving the ecological aspects of cellulosic coloration. At an academic level, several improvements and technological advancements have been made and suggested, however, the practicality of many of these improvements is questionable.

## **2.7 Major Improvements to Cellulosic Coloration**

### **2.7.1 Process Improvements**

For decades, no one really understood or appreciated the effects of the bath ratio of batch textile dyeing equipment because water, dye, and chemical use were of little concern. The liquor ratio, the mass or volume of water compared to the mass or volume of the fabric is now recognized as a very important and critical variable for processing as well as for the environmental impact of reactive dyed cellulose. Traditionally, liquor ratios ranged upward of 20-40:1 because color yield and salt utilization were not important. Typically, the amount of salt and alkali required for batch reactive dyeings are based on a concentration, therefore in order to maintain that concentration at higher liquor ratios requires much more salt and alkali than the same process run at a lower liquor ratio. Further, at higher liquor ratios, hydrolysis of the reactive dye increases because the dye is not as easily

exhaustible. This requires even more washing at the higher liquor ratio to remove the hydrolysate. Fortunately, this practical knowledge has been well understood and applied in industry such that liquor ratios of 10:1 or less are now common. Reactive dyes applied at a lower liquor ratio will exhibit enhanced efficiency compared to reactive dyes applied at a higher liquor ratio (24). Moreover, improvements in batch equipment technology have produced air jets which instead of relying on water for movement of the fabric rely on jets of air to propel the fabric through the dye machine. This allows the cotton fabric to be dyed effectively at near the wet pick up of the material. The caveat of this technology requires that an existing functioning mill spend a large amount of capital to obtain the up to date technological advancements in the physical processing jets. Many older and established mills are utilizing typical hydraulic jets and because of cost constraints from global competition do not have the capital expenditure to ascertain air jets.

### **2.7.2 Rinsing**

In addition to improvements in reducing the liquor ratios, dyeing equipment manufacturers have studied the efficacy and efficiency of rinsing and have developed rinsing technologies that are very efficient. There are two types of rinsing in jet reactive dyeing processes (20-22). The first type of rinse is the simple drop and fill rinse. The jet is filled with fresh water, the fabric is circulated, the bath is dropped, and the process is repeated. These types of rinses are easy to quantify and model according to Equation 2.1 (21, 25).

$$C_n = C_o * (V_F/V_R)^n \quad \text{Equation 2.1}$$

In Equation 2.1,  $C_n$  is the concentration of dye after  $n$  baths,  $C_o$  is the original concentration of the dye,  $V_F$  is the carry over volume inside the machine after draining, and  $V_R$  is the volume of the freshwater baths plus the carry over volume. Equation 2.1 allows the estimation of dye in the bath after a number of rinses,  $n$ . The second type of rinsing, the overflow rinse, is traditionally highly inefficient because fresh water is continuously pumped into the dye jet and the liquor is “overflowed” out of the overflow port. The efficiency of the overflow will vary depending on the set point of the overflow port, but the liquor is only being slowly diluted and not removed compared to a drop fill type rinse. Additionally, the overflow rinse is more complex to model and requires that the exact volume in the jet and fill rate of the fresh water be known to calculate the efficiency of the overflow rinse according to Equation 2.2 (21, 25).

$$C_t = C_o * e^{-V_t/V} \quad \text{Equation 2.2}$$

In Equation 2.2,  $C_t$  is the concentration of the dye at time  $t$ ,  $C_o$  is the original concentration of dye,  $V_t$  is the volume of water consumed to time  $t$ , and  $V$  is the actual volume of the rinse bath. A pertinent question here is if overflow rinses are so inefficient then why use them? Overflow rinsing is the only way to remove trash or debris from dyed goods such as broken emulsions, lubricants, etc. that may deposit on the surface of the fabric. If none of these

types of issues are present, there is not a need to utilize inefficient overflow rinses but dyers still tend to utilize overflow rinses in the belief that a cleaner fabric is obtained. The dye machinery manufacturer has taken all of these factors into consideration and developed such rinsing processes for the jet as the Aquachron system. Advancements such as Aquachron utilize technology that greatly improves the efficacy of the overflow rinse by limiting the amount of hydrolysate containing liquor mixing with the incoming water, greatly improving the efficiency of the overflow type rinse (20-21). Also, new designs allow cooling water and rinse water to be used interchangeably saving consumed water and time (20). However, once again, in order to obtain these significant processing improvements, the mill would be required to invest capital into new dye machinery whereas an established textile mill already has, maybe inefficient in comparison, but readily available equipment without additional capital expenditure.

### **2.7.3 Synthetic Approaches to Reactive Dyes**

Many researchers have recognized that many textile mills will not embrace new technologies that require extensive capital investment such as state of the art jet dyeing machines when they are already equipped with dyeing equipment. Therefore, investigators have focused on what can be done at the molecular level to optimize reactive dyes to enhance their efficiency. As a precursor, mono reactive dyes, dyes containing one reactive group, typically fix in very low percentages. Bireactive dyes help increase the fixation of reactive dyestuffs by affording two reactive sites. Heterofunctional reactive dyestuffs,

dyestuffs containing different types of reactive groups give the dye molecule a wider range of reactivity compared to a single reactive group. These bifunctional reactive dyestuffs tend to exhibit higher substantivity, exhaustion, and fixation compared to reactive dyes with monofunctional reactivity (7). Reactive groups in general can vary widely in their reactivity depending on the reactive group of the dye employed. Many different variations of reactive dyes resulted from initial patent and global market competition for the reactive dye market. However, for the last few decades, innovations in reactive dye technology have been stunted until the emergence of buzz words such as green, environmentally friendly, and sustainable. In order to make reactive dyes more attractive in an increasingly environmentally-conscious world, dyestuff manufacturers have jumped on board with such innovations as low salt dyestuffs as marketed by Huntsman under the trade name Novacron LS dyes. LS dyes utilize a bridging group to basically bridge two dye molecules together, hence creating a large easily exhaustible dye with a high level of color value due to two chromophores in one dye molecule (26). With lower salt requirements and an increase in dye efficiency because of the high level of exhaustion, dyestuffs such as LS dyes are a valuable alternative in sustainable dyeing of cotton. The caveats to utilizing dyes such as LS dyes are the additional synthesis costs of combining two dye molecules, and the inherent different dyeing properties such as levelness challenges in utilizing more readily exhaustible dyes. Additionally, extensive amounts of research conducted at Leeds and North Carolina State Universities based on patents held by Proctor and Gamble led to the development of Teegafix High Efficiency Reactive Dyes (14, 19, 27-29). Teegafix dyestuffs are similar in

respect to LS dyes in that Teegafix dyes also utilize very low levels of salt in comparison to traditional reactive dyes. Teegafix dyes have been molecularly modeled and designed to be linear and highly planar dyestuffs to allow exhaustion similar to a direct dye. Further, Teegafix dyestuffs are tertiary homofunctional chlorotriazine dyestuffs. With four reactive sites, the probability of dye fixation is highly increased. To date Teegafix dyestuffs have not been commercialized, but the drawback to the use of Teegafix dyestuffs would no doubt be the increased cost of the synthesis and the resulting higher price to the dyer. In comparison to LS dyes, for Teegafix dyes, the synthesis starts from parent DCT dyestuffs, cysteamine bridges are added to the reactive groups, and a mole of cyanuric chloride is added to each bridge. This synthesis is shown in Figure 2.8.

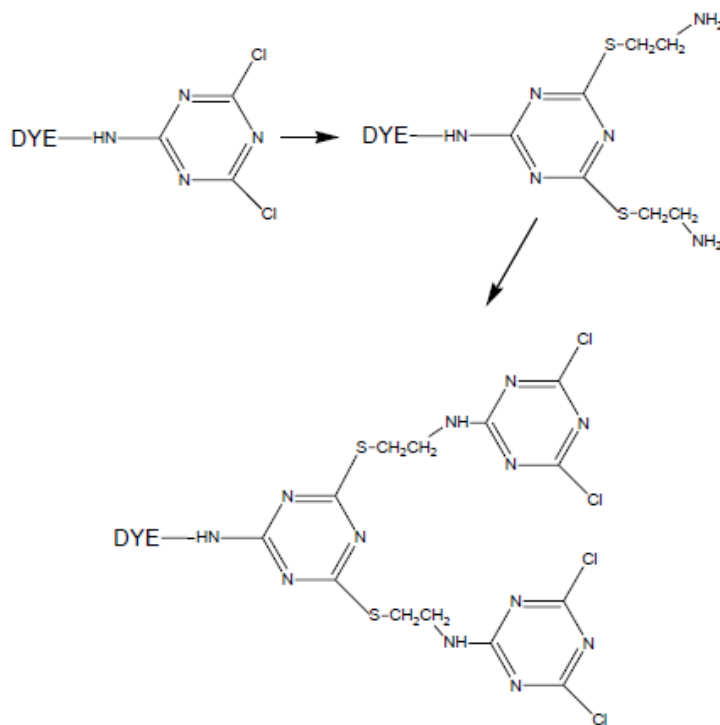


Figure 2.8 – Teegafix Synthesis

From the Teegafix synthesis, the final dye molecule has a lower color value per gram than the parent dye and must make up the loss of color in higher fixation values. This drawback coupled with the projected higher cost of the Teegafix dyestuffs would present an inherent obstacle to utilization even with the vastly superior performance of the dyestuffs. An alternative reactive dye modification has been shown where a reactive dye is provided with a cationized charge to facilitate exhaustion to the surface of cellulose (16, 30). In these dyes, it is possible to utilize near zero salt concentrations and obtain results similar to conventional reactive dyestuffs. Although this technology is also a great step in the right direction, the dyer is still left with hydrolyzed dye which needs to be removed in the same way as with conventional reactive dyes. It has also been suggested and shown that reactive dyes can be applied at a neutral fixation pH. By utilizing higher temperatures to dissociate acidic hydrogen atoms on the cellulose chains instead of alkali, the extent and risk of hydrolysis of the dye molecule is greatly reduced (12). The downside of this approach is that the heat of dyeing, or change in enthalpy, is an exothermic process for exhaustion. The molar heat of dyeing is given by Equation 2.3 (6).

$$\Delta H^{\theta} = \delta H / \delta n \quad \text{Equation 2.3}$$

$\delta H$  represents the amount of heat liberated when an amount of dye,  $\delta n$  (moles), is absorbed onto the surface of a fiber. Because  $\delta H$  is negative for most dyeing systems, the heat of dyeing is negative for most systems. In other words, heating the dye liquor to higher temperatures will result in lower exhaustion levels compared to conventional reactive dyeings unless higher concentrations of salt are used to force exhaustion of the



dye. In a continuing evolution in more sustainable reactive dyeing practices of cotton, many researchers have recognized that the greatest efficiency and utilization of dyestuffs can be obtained by modifying cotton itself at a molecular level to contain a cationized charge and to utilize existing anionic dyestuffs.

## **2.8 Cationized Cotton**

Cationized cotton is the most viable sustainable coloration process for cotton goods. Cationized cotton allows 100% dye utilization when the appropriate amount of cationization and dyestuffs are utilized (31). Further, cationized cotton can be dyed using significantly lower amounts of time, water, and energy (10). Cationized cotton can afford the following benefits with reactive dyes: elimination of salt, increased shade reproducibility, much less rinsing, less susceptibility to liquor ratio variations, and much reduced cycle times (15). As well, with 100% dye utilization, significant reductions in dye required can be obtained compared to traditional fiber reactive dyeings of cotton. Perhaps most importantly, the use of cationized cotton does not require the capital expenditure or high dye synthesis costs dictated by other sustainable technologies.

### **2.8.1 Cationized Cotton Chemistries**

Researchers have looked at many different cationization reagents including polyaminchlorohydrin quaternary ammonium salts (32) Figure 2.9, phenyl monochlorotriazinyl (33) Figure 2.10,

3-methacryloylaminoethyltrimethylammonium chloride (MAPTAC) (34) Figure 2.11, mono-reactive mono-quaternary Figure 2.12, mono-reactive bis-quaternary Figure 2.13, bis-reactive bis-quaternary Figure 2.14, choline chloride with a crosslinker (35) Figure 2.15, acryloyloxyethyl trimethylammonium chloride Figure 2.16, methacryloyloxyethyl trimethylammonium chloride Figure 2.17, methacryloylaminoethyl trimethylammonium chloride Figure 2.18 (36) and other non disclosed tradename materials (37-38). As well, nonpermanent cationized reagents such as cationized starch and block copolymers of polyethylene oxide and quaternary amines can be applied to cotton fabrics in place of salt to enhance the exhaustion of anionic dyestuffs (39-40). All of these different reagents have their pros and cons, but generally speaking, the more complicated the reagent, the more synthesis steps are required resulting in high costs for the reagents. Additionally, vinyl reagents must be free radical polymerized in situ with an initiator. Finally, reagents such as choline chloride with no reactive group require a crosslinker such as DMDHEU and the complications associated with crosslinking such as formaldehyde release and breaking strength of the treated fabric. In terms of volume obtainable for global consumption, cost, and ease of application,

3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC), shown in Figure 2.19, is without a doubt the method of choice for cationization of cellulose.

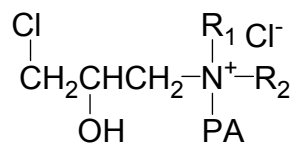


Figure 2.9 – Poly-aminoepichlorohydrin quaternary ammonium salt Cationic Reagent

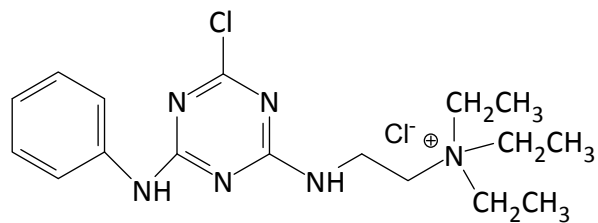


Figure 2.10 - Phenyl monochlorotriazinyl Cationic Reagent

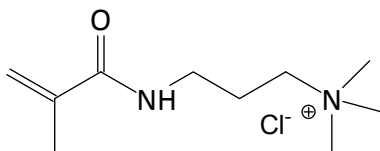


Figure 2.11 – MAPTAC Cationic Reagent

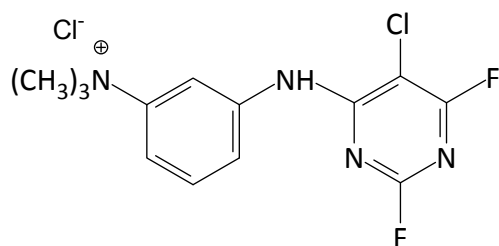


Figure 2.12 - Mono-reactive mono-quaternary Cationic Reagent

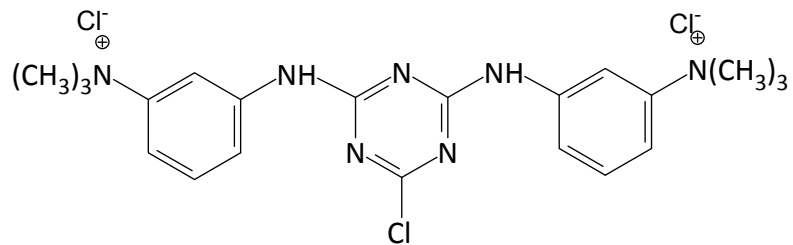


Figure 2.13 - Mono-reactive bis-quaternary Cationic Reagent

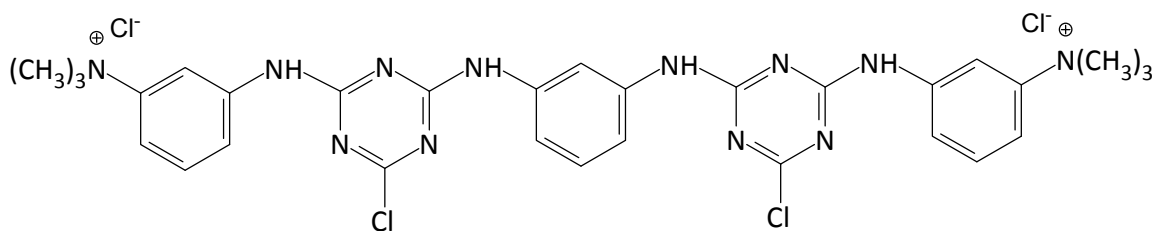


Figure 2.14 - Bis-reactive bis-quaternary Cationic Reagent

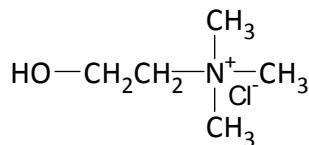


Figure 2.15 – Choline Chloride

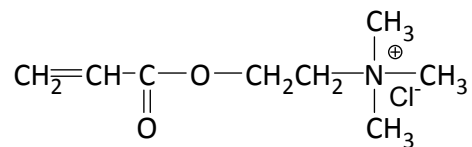


Figure 2.16 - Acryloyloxyethyl trimethylammonium chloride Cationic Reagent

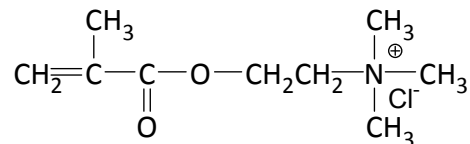


Figure 2.17 - Methacryloxyloxyethyl trimethylammonium chloride Cationic Reagent

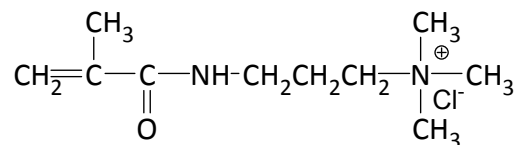


Figure 2.18 - Methacryloylaminopropyl trimethylammonium chloride Cationic Reagent

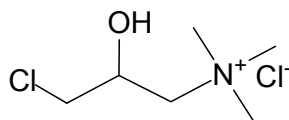


Figure 2.19 – CHPTAC Cationic Reagent

## 2.9 CHPTAC

The utilization of CHPTAC as the reagent of choice for cotton cationization is well documented in the literature (5, 10, 41-52). CHPTAC and its derivatives are the only family of compounds that can be obtained economically and in pure and stable forms for cellulose modification (53). CHPTAC has uses not only for the coloration of cotton goods but also in the cationization of starch (54), ionic wrinkle reduction (44) and the cationization of cotton

for printing (47-51). CHPTAC is formed from the reaction of epichlorohydrin and trimethylamine hydrochloride as shown in Figure 2.20 (54). Table 2.1 shows the typical impurities found in CHPTAC solutions (55).

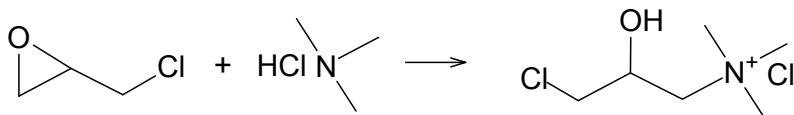


Figure 2.20 – Synthesis of CHPTAC

Table 2.1- Typical Resultant Impurities from CHPTAC Synthesis

| CAS Number | Chemical Name  | Content                        |
|------------|--|--------------------------------|
| 34004-36-9 | 2,2-dihydroxypropyltrimethylammonium chloride (DIOL) | <1.5%                          |
| 55636-09-4 | Bis(trimethylammoniumchloride)-2-hydroxypropane      | 1.3-4%                         |
| 106-89-8   | Epichlorohydrin                                      | <10 ppm                        |
| 96-23-1    | 1,3-dichloro-2-propanol                              | <20 ppm, exceptionally <50 ppm |

### 2.9.1 Reaction of CHPTAC with Cellulose

CHPTAC itself is not reactive with cellulose. In order for CHPTAC to react with cellulose, it must be made into the reactive epoxide form, epoxypropyltrimethylammonium chloride (EPTAC) as shown in Figure 2.21.

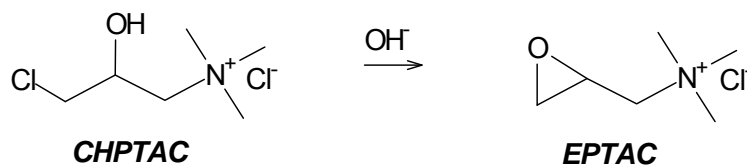


Figure 2.21 – Formation of EPTAC from CHPTAC

Once EPTAC is formed from CHPTAC, EPTAC is reacted with cellulose under alkaline conditions as shown in Figure 2.22 to form stable ether linkages. However, as also shown in Figure 2.22, hydrolysis of EPTAC is also possible under alkaline conditions resulting in an unreactive diol. The first mention of the etherification of cellulose dates back to the early 1920's (56) although there is doubt that the actual reaction was understood to be of epoxide functionality (57). The first reference to epoxy aminated cellulose and improved dye uptake of acid dyes was reported in 1938 (53). Specific studies about the reactivity and stability of alcohols (including cellulose) and epoxide groups have been studied for well over 80 years (58-62). The epoxide group has been described as a spring loaded reactive group, hence its high reactivity (63). With the coupled quaternary ammonium charge on the cellulose chains, the treated cotton goods can now exhaust and bind virtually any anionically charged dyestuff. By virtue of their water solubility through sulfonic acid groups, almost any type of water soluble dyestuff (acid, direct, or reactive) may be utilized to dye cationized cotton.

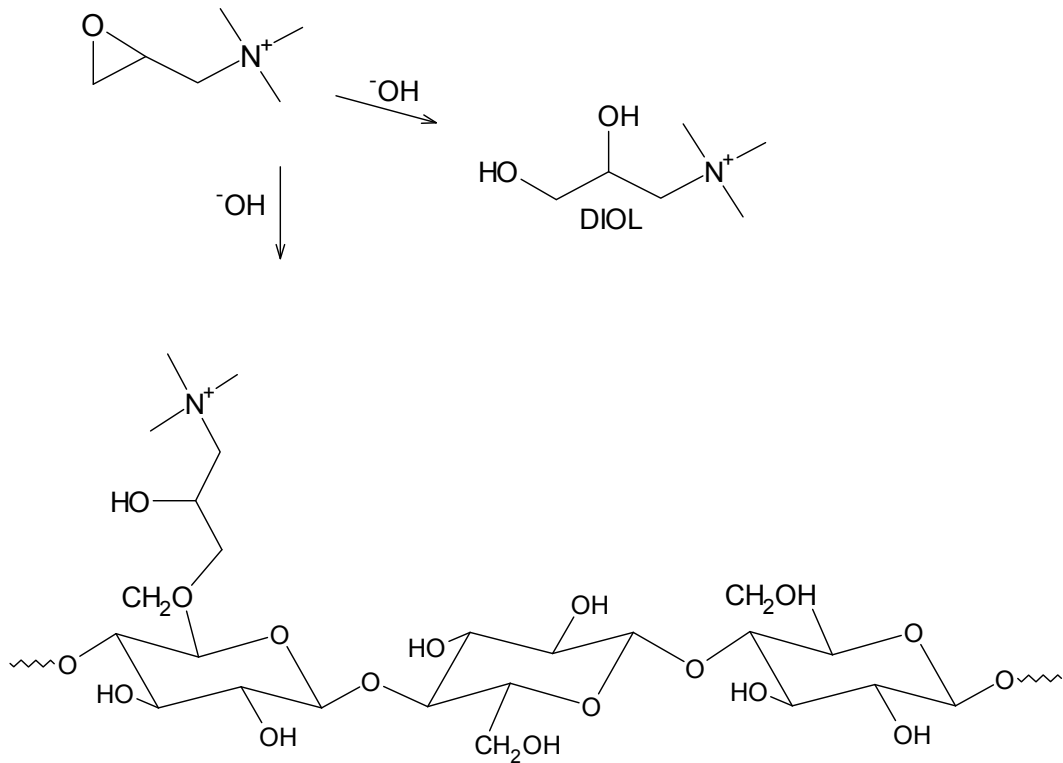


Figure 2.22 – Competing Reactions of EPTAC with Cellulose

### 2.9.2 Application Techniques of CHPTAC

CHPTAC can be applied in the same batch processing techniques as utilized for conventional dyeing and finishing of textile goods. Pad/steam, pad/batch, pad/dry/cure, and exhaustion are all techniques that have been reported in the literature to cationize cotton goods (45). The cold pad/batch method routinely gives the highest percent fixation and utilization of applied CHPTAC, while the exhaustion method typically gives only a few percent fixation of the applied CHPTAC (45). However, it is unlikely that the textile world will accept cold pad batch applications. Moreover, recently it has been suggested that a pad bake application is



better suited for production, but these types of processes require continuous or batch ranges and are best suited for woven fabrics (64). It appears that to date, there is little consensus on the most practical method to cationize cotton in the production mill.

### **3. Project Proposal**

The literature is full of academic examples about the cationization of cotton and the improved and sustainable dyeing of cotton. However, even with all of the reported benefits of cationized cotton, there is very little evidence of an industry shift towards utilizing and dyeing cationized cotton. The following research objectives are designed to help facilitate the spanning of the knowledge gaps in academic work to answer unanswered questions and show the viability of cationized cotton in typical textile mills.

#### **3.1 Safety of CHPTAC**

There is very little data presented in the literature specifically pertaining to the risk and safety of CHPTAC, especially the aquatic toxicity of CHPTAC. A report should be prepared outlining the safety and risks of utilizing CHPTAC in cotton cationization. It doesn't make environmental sense to do away with salts from conventional reactive cotton dyeings and replace them with cationization chemicals such as CHPTAC if CHPTAC is found to be highly toxic for aquatic life, and/or human life. A comprehensive report will outline the synthesis, safe handling, storage, and ecological and toxicological effects of CHPTAC utilization.

#### **3.2 CHPTAC Application Techniques**

There is little agreement for the best method of application of CHPTAC for the production dyer although it is generally agreed upon that the cold pad batch method yields the highest efficiency of the CHPTAC applied. The problem with cold pad batch cationization is that it

requires batching equipment, space for batching, and typically a 16 hour dwell time. The typical textile dyer, the intended user of cationized cotton, needs viable alternative methods to cold pad batch that allow utilization of on hand equipment. Exhaustion results from CHPTAC application have been reported to be very poor, but exhaust application would be the simplest and quickest way to cationize for the textile dyer. A fresh look at exhaustion of CHPTAC should be undertaken as well as verifying some previous reported trends such as cold pad batch being the most efficient cationization process. Percent nitrogen is an analytical method utilized to assess the amount of nitrogen on a cationized sample. However, the percent nitrogen test requires specialized equipment, is costly, and has a lengthy turnaround time if sent to an outside lab. A K/S, percent nitrogen calibration should be made to quickly ascertain an approximate level of the percent nitrogen of a treated sample. The calibration should be made with a readily available dyestuff easily obtainable to allow a researcher or mill to quickly evaluate a cationized sample following a standard dyeing recipe and procedure. This will also allow rapid assessment of experimental processes in the lab as well.

### **3.3 Pilot Scale Application**

Once an optimum application technique has been devised for CHPTAC cationization on an industrial level for typical textile dyers, pilot scale applications should be undertaken. There is no known information in the literature about bulk scale cationizations. Cationizations done in laboratory settings are often atypical in actual production settings. Laboratory

settings typically utilize very high liquor ratios for exhaust cationization and dyeing, 20-40:1, liquor ratios that are highly inconsistent with actual production jets. Further, laboratory studies in the literature have spread a wide gamut of dyestuffs including acids, directs, and reactives. In order for cationization to take hold and be an effective industrial application, research should be focused on utilizing reactive dyes, the dominant colorant being used now for cotton goods in manufacturing. Dyers already have a supply of reactive dyes that they are comfortable with as well as the appropriate supply line. When reactive dyes are used in the literature, they are not used in trichromatic recipes, the typical mixture seen in the textile mill. In order to show cationized cotton as a viable replacement to conventional reactive dyeing, trichromatic reactive dyeing comparisons have to be made at the pilot scale. Finally, it has been suggested that cationized cotton may possess inferior light fastness because it is assumed that the cationization treatment and applied dye are preferentially on the surface of the fabric. Cross sectional micrographs should be taken of treated and dyed samples to examine ring dyeing, as well as performing lightfastness, and wetfastness of cationized and conventional dyeings.

### **3.4 Costing**

Finally, one of the last missing pieces of CHPTAC cotton cationization is actual demonstrated costing examples. There is significant concern in the textile industry about the real cost and sustainable benefits achievable from cationized cotton. To date, the actual costing and attainable sustainable benefits has not been quantified and presented. Therefore, the

results of pilot scale cationization and savings in dye, water, salt, alkali, time, and energy will be recorded and compared to conventional reactive dyeings.

## REFERENCES

1. Cotton Dyeing and Finishing: A Technical Guide. Cotton Incorporated, 1996.
2. Handbook of Fiber Chemistry. Ed. Menachem Lewis. Second ed. New York: Marcel Dekker, Inc., 1998.
3. Smith, Brent. "Dyebath Monitoring and Control: Past, Present, and Future." AATCC Review November 2007, p36.
4. Dawson, T. L. "It Must Be Green: Meeting Society's Environmental Concerns." Coloration Technology 124. (2008): 67-78.
5. Hashem, Mohamed, M. "Development of a One-Stage Process for Pretreatment and Cationization of Cotton Fabric." Coloration Technology 122. (2006): 135-144.
6. The Theory of Coloration of Textiles. Ed. Alan Johnson. Second ed. England: Society of Dyers and Colourists, 1989.
7. Gillingham, Estelle L., et al. "Co-application of Hydroxyalkyl Dyes and Polyphosphonic Acids to Cotton to Achieve Dye-Fibre Covalent Bonding." Coloration Technology. 117. (2001): 318-322.
8. Chavan, R. B. "Environment-Friendly Dyeing Processes for Cotton." Indian Journal of Fibre and Textile Research. 26. (2001): 93-100.
9. Chavez, Felipe Javier Lopez, et al. "Brominated Precursors of Tyrian Purple (C.I. Natural Violet 1) from *Plicopurpura pansa*, *Plicopurpura columellaris* and *Plicopurpura patula*." Dyes and Pigments. 83. (2009): 7-13.
10. Hauser, Peter J. and Adham H. Tabbá. "Improving the Environmental and Economic Aspects of Cotton Dyeing Using a Cationized Cotton." Coloration Technology. 117. (2001): 282-288.
11. Phillips, Duncan. "Environmentally Friendly, Productive and Reliable: Priorities for Cotton Dyes and Dyeing Processes." Journal of the Society Dyers and Colourists. 112. (1996): 183-186.
12. Lewis, David M., et al. "Covalent Fixation of Reactive Dyes on Cotton under Neutral Conditions." AATCC Review. January 2008, p35.

13. Cook, Fred L. "Salt Requirements Put Pressure on Wet Processing Plants." Textile World. 144.8. (1994): 83-86.
14. Farrell, Matthew J. "Color Matching and Utilization of Teegafix High Efficiency Fiber Reactive Dyes in a Production Setting." Master's Thesis, North Carolina State University at Raleigh, 2007.
15. Leonard, Tony M. "Cationized Cotton – 'Fact or Fiction?'"
16. Hinks, David, et al. "Cationized Fiber Reactive Dyes for Cellulosic Fibers." AATCC Review. May 2001, p43.
17. Achwal, W. B. "Washing-off Hydrolysed Reactive Dye – A Common Problem." Colourage. March 1995, p43.
18. George, M. "High Fixation Reactive Dyes – A Review." Man-Made Textiles in India. January 1980, p15.
19. Morris, K. F., et al. "Design and Application of a Multifunctional Reactive Dye Capable of High Fixation Efficiency on Cellulose." Coloration Technology. 124. (2008): 186-194.
20. Bradbury, Mike, et al. "Smart Rinsing: A Step Change in Reactive Dye Application Technology." Journal of the Society of Dyers and Colourists. 116. (2000): 144-147.
21. Rekouniotis, C. "New Approach in Rinsing Process in Overflow-Jet Machines." Melliand Internatinal. 3. (1998): 189-191.
22. Hoffmann, F., et al. "Washing Off Reactive Dyeings in Jets with Bath Change Rinsing and Continuous Rinsing." Melliand International. 4. (1998): 223-226.
23. Anis, Pervin and Huseyin Aksel Eren. "Examining the Effectiveness and the Environmental Impact of Rinsing in Reactive Dyeing." AATCC Review. June 2001, p24.
24. The Dyeing of Cellulosic Fibers. Ed. Clifford Preston. Dyers' Company Publications Trust, 1986.
25. Brenner, E. "Comparison of Different Rinsing Processes in Short-Liquor Piece Dyeing Machines." Melliand English. 6. (1997): 92-94.

26. Cibacron® LS high conc Brochure. Ciba Specialty Chemicals. March 1998.
27. Berger, R. "Fiber Reactive Dyes with Improved Affinity and Fixation Efficiency." Master's Thesis, North Carolina State University at Raleigh, 2005.
28. Carrig, R.J. "Process Development and Optimization for High Efficiency Fiber Reactive Dyes." Master's Thesis, North Carolina State University at Raleigh, 2006.
29. Smith, Brent, et al. "High Affinity, High Efficiency Fibre-Reactive Dyes." Coloration Technology. 122. (2006): 187-193.
30. Lewis, D. M. and L. J. Sun. "Quaternary Reactive Dyes Containing a Thioether-ethylsulphone Group. Part 1: Synthesis of a Trimethylammonium Ethylsulphide-ethylsulphone Dye." Coloration Technology. 119. (2003): 286-291.
31. Thiry, Maria. "Color It Greener." AATCC Review. May/June 2010, p34.
32. El-Shishtawy, Reda M. and S. H. Nassar. "Cationized Pretreatment of Cotton Fabric for Anionic Dye and Pigment Printing with Better Fastness Properties." Coloration Technology. 118. (2002): 115-120.
33. El-Shishtawy, Reda M., et al. "Acid Dyeing Isotherms of Cotton Fabrics Pretreated with Mixtures of Reactive Cationized Agents." Coloration Technology. 120. (2004): 195-200.
34. Srikulkit, Kawee and Patcharee Larpsuriyakul. "Process of Dyeability Modification and Bleaching of Cotton in a Single Bath." Coloration Technology. 118. (2002): 79-84.
35. Stone, Rob L. and Robert J. Harper, Jr. "Cationized Cotton: Approaches and Applications." Book of Papers, AATCC International Conference and Exhibition, 1986.
36. Jang, J., et al. "Investigation of the Improved Dyeability of Cationized Cotton via Photografting with UV Active Cationized Monomers." Coloration Technology. 117. (2001): 139-146.
37. Cai, Y., et al. "A New Method for Improving the Dyeability of Cotton with Reactive Dyes." Textile Research Journal. 69(6). (1999): 440-446.
38. Erdas, Y., et al. "Pretreatment of Cotton with Polmeric Cationized Agents Before Dyeing with Reactive Dyes. Part 1: Quantitative Estimation of Selected Cationized Agents Using Congo Red." Coloration Technology. 119. (2003): 307-309.



39. Han, Shin Young, et al. "Effects of a Cationized Diblock Copolymer Derived from [2-(Methacryloyloxy)-Ethyl]Trimethylammonium Chloride in the Dyeing of Cotton with Reactive Dye." Coloration Technology. 124. (2008): 211-215.
40. Zhang, Shufen, et al. "Continuous Dyeing of Cationized Cotton with Reactive Dyes." Coloration Technology. 121. (2005): 183-186.
41. Cannon, Kristin M. and Peter J. Hauser. "Color Assessment of Cationized Cotton Dyed with Fiber Reactive Dyes." AATCC Review. May 2003.
42. Draper, Sara L., et al. "Characterization of the Dyeing Behavior of Cationized Cotton with Direct Dyes." AATCC Review. October 2002.
43. Grooby, P., et al. "Modification of Cellulosic Fibres with Reactive Quaternary Ammonium Containing Cations; Evaluation by Capillary Zone Electrophoresis and Kjeldahl Nitrogen Determination." Advances in Colour Science and Technology. 6.2. (2003): 39-46.
44. Hashem, M., et al. "Wrinkle Recovery for Cellulosic Fabric by Means of Ionic Crosslinking." Textile Research Journal. 73(9). (2003): 762-766.
45. Hashem, Mohamed, et al. "Reaction Efficiency for Cellulose Cationization Using 3-Chloro-2-Hydroxypropyl Trimethyl Ammonium Chloride." Textile Research Journal. 73(11). (2003): 1017-1023.
46. Hauser, Peter J. and Adham H. Tabba. "Dyeing Cationized Cotton with Fiber Reactive Dyes: Effect of Reactive Chemistries." AATCC Review. May 2002.
47. Hauser, Peter J. and Mehmet Kanik. "Printing of Cationized Cotton with Acid Dyes." AATCC Review. March 2003.
48. Kanik, Mehmet and Peter J. Hauser. "Printing of Cationized Cotton with Reactive Dyes." Coloration Technology. 118. (2002): 300-306.
49. Kanik, Mehmet and Peter J. Hauser. "Ink-jet Printing of Cationized Cotton Using Reactive Inks." Coloration Technology. 119. (2003): 230-234.
50. Kanik, Mehmet, et al. "Effect of Cationization on Inkjet Printing Properties of Cotton Fabrics." AATCC Review. June 2004.

51. Kanik, Mehmet and Peter J. Hauser. "Printing Cationized Cotton with Direct Dyes." Textile Research Journal. 74(1). (2004): 43-50.
52. Morris, Heather and Peter Hauser. "The Effects of a Cationized Reagent on Typical Finishes." AATCC Review. November 2003.
53. Rupin, Michel. "Dyeing with Direct and Fiber Reactive Dyes." Textile Chemist and Colorist. 8. (1976): p139.
54. *European Union Risk Assessment Report, (3-Chloro-2-Hydroxypropyl)Trimethylammonium Chloride*. 2008.
55. *Product Safety Assessment, DOW™ Quat 188 Cationized Reagent*.
56. US Patent #1,502,379. July 22, 1924.
57. McKelvey, John B. "Reaction of Epoxides with Cotton Cellulose in the Presence of Sodium Hydroxide." Textile Research Journal. 29. (1959): 918-925.
58. Alvey, Francis B. "Selectivity of the Epoxide Phenol Reaction." Journal of Applied Polymer Science. 13. (1969): 1473-1486.
59. Scheter, Leon and John Wynstra. "Glycidyl Ether Reactions with Alcohols, Phenols, Carboxylic Acids, and Acid Anhydrides." Industrial and Engineering Chemistry. 48. (1956): 86-93.
60. Tabb, Adham. "Kinetic Works of CHPTAC." Unpublished Data. North Carolina State University at Raleigh, 2001.
61. Schorger, A. W. and M. J. Shoemaker. "Hydroxy Alkyl Ethers of Cellulose." Industrial and Engineering Chemistry. 29. (1937): 114-117.
62. Rowell, Roger M. and W. Dale Ellis. "Reaction of Epoxides with Wood." United States Department of Agriculture, Forest Services, Research Paper FPL 451. December, 1984.
63. Kolb, Hartmuth C. "Click Chemistry: Diverse Chemical Function from a Few Good Reactions." Angewandte Chemie International Edition. 40. (2001): 2004-2021.

64. Wang, Lili et. al. "Preparation of Cationized Cotton with Two-Pad Two-Bake Process and its Application in Salt Free Dyeing." Carbohydrate Polymers. 78. (2009): 602–608.

## 4. Examination of the Safety of CHPTAC

### 4.1 Synthesis (1-3)

CHPTAC is formed from the reaction of epichlorohydrin and trimethylamine hydrochloride as shown in Figure 4.1 (2).

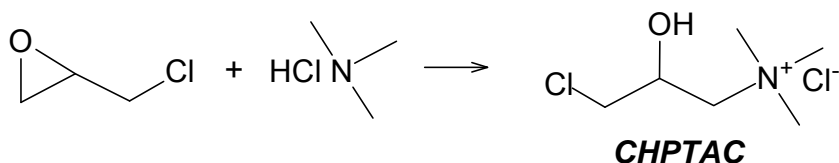


Figure 4.1 – Synthesis of CHPTAC

With the use of epichlorohydrin as a starting reagent, the synthesis of CHPTAC is carried out in a semi-automated or closed process with high levels of engineering controls. The engineering controls minimize the risk of exposure to epichlorohydrin, and hence CHPTAC. Further, the CHPTAC formation product is not washed, so there is not a release to water as a result of CHPTAC synthesis. Unreacted epichlorohydrin and trimethylammonium chloride can be removed by steam distillation, or readily purified by alcohol filtration (4). CHPTAC is typically found as aqueous solutions of 50-70%. The solubility of CHPTAC limits higher concentrations. CHPTAC liquid reagents are clear and odorless and are completely miscible in water and largely insoluble in hydrocarbons. Dow CR2000 solution is a 65% active solution used exclusively in textiles due to its low trimethylamine content and hence low odor. Table 4.1 shows the typical impurities found in CHPTAC solutions (1).

Table 4.1 - Typical Resultant Impurities from CHPTAC Synthesis

| CAS Number | Chemical Name  | Content                              |
|------------|--|--------------------------------------|
| 34004-36-9 | 2,2-dihydroxypropyltrimethylammonium chloride (DIOL) | <1.5%                                |
| 55636-09-4 | Bis/trimethylammoniumchloride-2-hydroxypropane       | 1.3-4%                               |
| 106-89-8   | Epichlorohydrin                                      | <10 ppm                              |
| 96-23-1    | 1,3-dichloro-2-propanol                              | <20 ppm,<br>exceptionally<br><50 ppm |

#### 4.2 Physical and Chemical Properties (1-3)

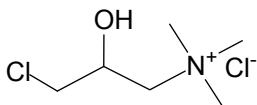
**CAS Number:** 3327-22-8

**EINECS Number:** 222-048-3

**IUPAC Name:** 3-Chloro-2-hydroxypropyltrimethylammonium chloride

**Molecular formula:** C<sub>6</sub>H<sub>15</sub>ONCl<sub>2</sub>

**Structural formula:**



**Molecular weight:** 188.1 g/mol

**Synonyms:** CHPTAC

CHPTAC current classification is Category 3 carcinogen.<sup>1</sup> Tables 4.2-4.3 show specific properties of CR2000 (65% CHPTAC solution) and CHPTAC (1,3).

<sup>1</sup> See Section 4.6.1 on mutagenicity below for further explanation.

Table 4.2- Properties of CR-2000

|                      |              |
|----------------------|--------------|
| Physical State/Color | Liquid/Clear |
| Boiling Point        | 105°C        |
| pH                   | 4-6          |
| Specific Gravity     | 1.17         |
| Flash Point          | None         |
| Precipitation        | -15°C        |

Table 4.3- Properties of CHPTAC

| Property             | Value                   |
|----------------------|-------------------------|
| Physical state       | solid                   |
| Melting Point        | 180.5°C                 |
| Boiling Point        | 190°C-209°C             |
| Specific Gravity     | 1.11                    |
| Vapor Pressure       | $<10^{-3}$ Pa           |
| Water Solubility     | 835.2 +- 9.9 g/L        |
| Autoflammability     | not self ignitable      |
| Flammability         | not highly flammable    |
| Explosive Properties | no explosive properties |
| Oxidizing Properties | not likely oxidizing    |

### 4.3 Uses and Applications (1-2)

Quaternary ammonium cations (quats) are used in the production of many types of industrial and consumer products. The primary use of CHPTAC is in the cationization of starch. With the equivalent mechanism of cellulose and starch cationization and nearly identical chemical structures, the vast amount of data available regarding CHPTAC starch cationization can be readily related to the cationization of cellulose. To cationize starch or cellulose, sodium hydroxide is added to CHPTAC in an aqueous solution. As a product, the reactive epoxypropyltrimethylammonium chloride (EPTAC) is formed. EPTAC is added to alkaline starch or cellulose where the epoxide ring is opened and an ether linkage is formed

principally with the primary hydroxyl group of the starch or cellulose. Finally, the product is neutralized with acid to remove residual alkali. Figure 4.2 shows the cationization of starch using CHPTAC. Attesting to the deemed safety of cationization, cationic starch is used in producing triple layer board used in food packaging of dry goods such as pasta, corn flakes etc. Of course, barrier materials are used when in contact with fatty or aqueous foods, but the allowance of cationized starch in foodstuffs speaks to the acceptable safety of cationized starch. Table 4.4 gives some examples of guidelines regarding food and cationic starches (1). From 2001 European total consumption volume of 23,695 tons of CHPTAC, 95% was used for starch, with the remaining 5% in the synthesis of carnitine salts, guar quaternization, and protein and cellulose modification. This yields an allotment of 1,044 tons of CHPTAC utilized in processing other than starch.

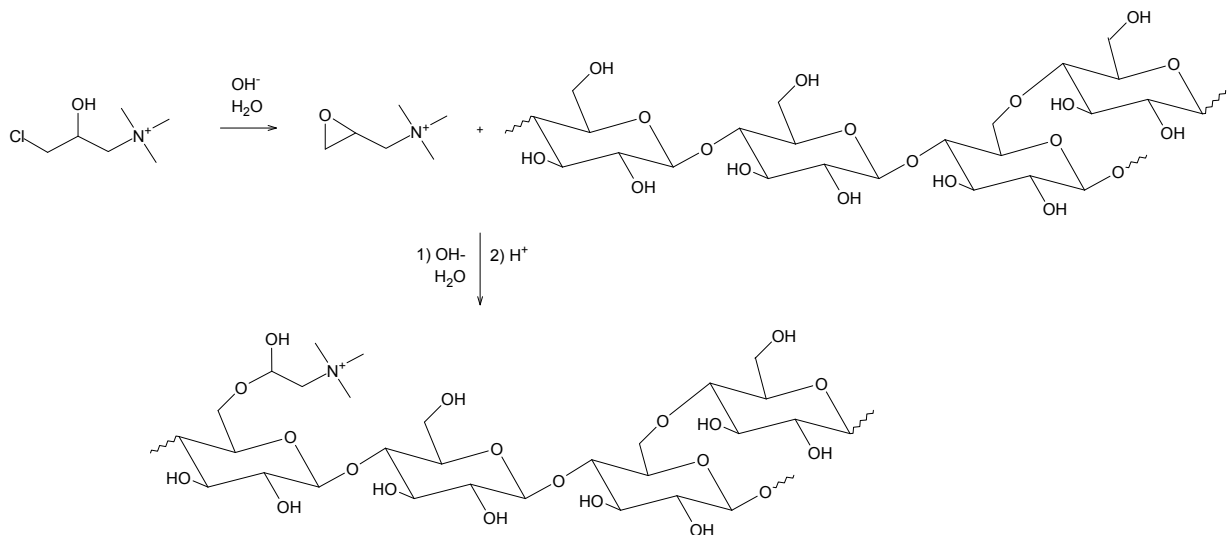


Figure 4.2- Cationization of Starch with CHPTAC

Table 4.4 - CHPTAC/EPTAC Usage in Food Applications

| Country and Agency | Limitation   |
|--------------------|--|
| Germany, BfR       | Maximum nitrogen content in starch ethers: 4%,<br>epichlorohydrin max. 1 mg/kg |
| USA, FDA           | Maximum EPTAC usage 5%   |
| Netherlands        | Maximum EPTAC usage 7%   |

#### 4.4 Stability and Degradation (1)

Figure 4.3 shows the conversion process of CHPTAC to the reactive EPTAC to the non reactive DIOL (1).

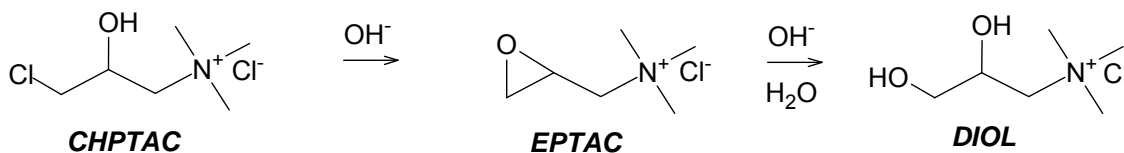


Figure 4.3- CHPTAC Conversion to EPTAC to DIOL

After cationization, the reaction mixture is typically neutralized with strong acid. In this neutralization, EPTAC may be converted back to CHPTAC, however, this reverse reaction is slow and requires heat (>60°C). When dry cationization processes are not used, this leads to a mixture of CHPTAC/EPTAC/DIOL that is potentially released in the waste water. The CHPTAC to EPTAC to DIOL conversion may range from hours to many days depending on temperature and pH. Figure 4.4 shows the time temperature and pH stability of EPTAC from 20-50°C and a corresponding pH of 10.5-12.5 (5).



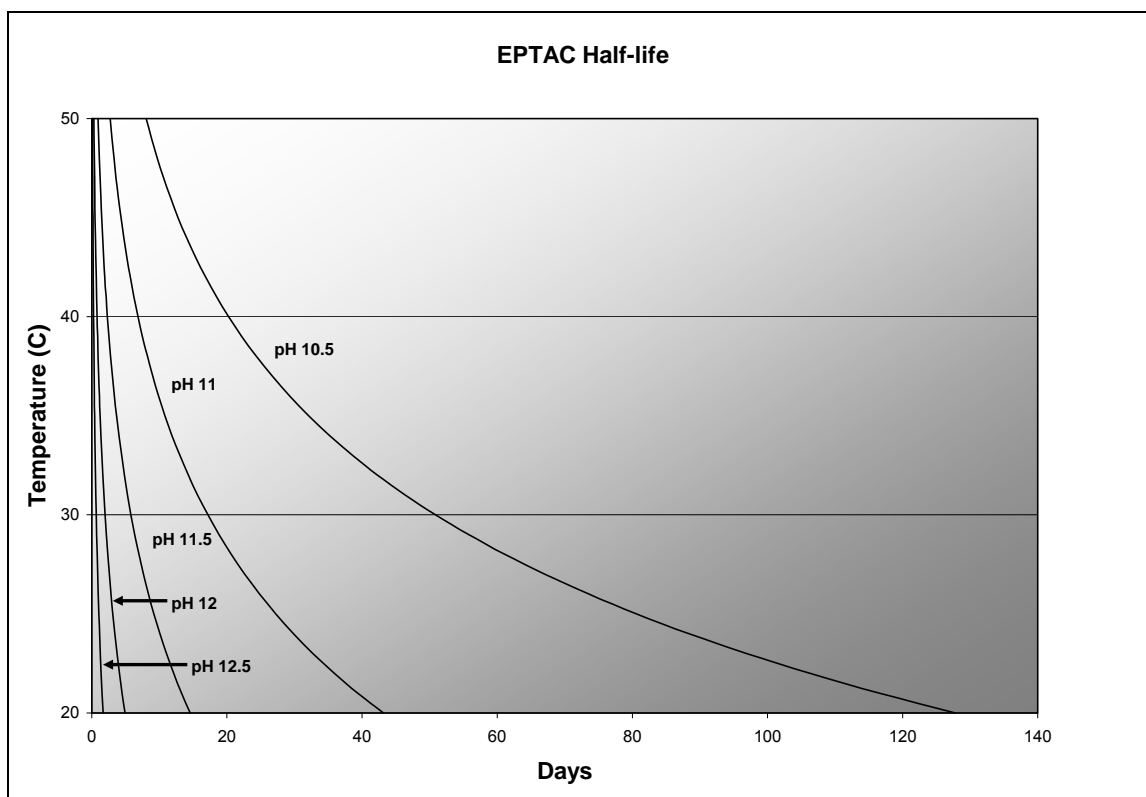


Figure 4.4- EPTAC Half-life

At environmentally applicable conditions of pH 7.8 and a temperature of 12°C the  $\frac{1}{2}$  life conversion of CHPTAC to EPTAC is 21 days.<sup>2</sup> Therefore, practically, the aquatic toxic effects of CHPTAC should be attributed to EPTAC. Table 4.5 shows experimental values of CHPTAC  $\frac{1}{2}$  life at varying pH and temperature (1).

<sup>2</sup> The pH and temperature specified are from European data.  $\frac{1}{2}$  life will vary in different regions according to pH and temperature differences of the surrounding environment, specifically, the aquatic conditions where CHPTAC may be discharged.

Table 4.5- CHPTAC ½ Life

| Temperature | pH  | 1/2 Life  |
|-------------|-----|-----------|
| 12°C        | 7   | 279 days  |
| 12°C        | 7.8 | 21 days   |
| 12°C        | 8.4 | 5.3 days  |
| 25°C        | 4   | >365 days |
| 25°C        | 7   | 27 days   |
| 35.5°C      | 7   | 3.75 days |
| 50°C        | 8.7 | <1 day    |

CHPTAC is not readily biodegradable with a soil ½ life of 300 days, however, CHPTAC is almost 100% transferred to water, minimizing the retention of CHPTAC in soil. In the activated waste water treatment plant, it is estimated that 30.6% of CHPTAC is degraded, 0.779% adsorbed by sludge, there is no volatilization due to the low vapor pressure of CHPTAC, so 68.6% is directed to water (1). CHPTAC is not expected to bioaccumulate because of the high degree of water solubility.

#### 4.5 Toxicity (1)

Acutely, CHPTAC is very slightly toxic to fish and only slightly toxic to micro-organisms. Daphnids are more sensitive to CHPTAC than other organisms that have been tested. The nominal LC<sub>50</sub> is 4128 mg/L for fish (brachydanio rerio). Concerning aquatic invertebrates (daphnia magna), the EC<sub>50</sub> has been found to be between 164 mg/L to 240 mg/L, corresponding to near pure CHPTAC, and a typical 65% solution of CHPTAC. Regarding chronic exposure to CHPTAC, a no effect concentration (NOEC) of 0.51 mg/L has been found for reproduction of daphnia magna. For a 72 hour exposure of algae to CHPTAC, an ErC<sub>50</sub> concentration of >10,000 mg/L has been found. Finally, in respect to the final degradation

product of CHPTAC, DIOL, an LC<sub>50</sub> > 3,200 mg/L (brachydanio rerio), a 48 hour EC<sub>50</sub> of 707 mg/L (daphnia), a 24 hour EC<sub>50</sub> between >1,000 mg/L <3200 mg/L (daphnia), and finally a toxicity threshold of 32 g/L (pseudomonas putida) have all been reported. With the toxicity data available, as well as discharge monitoring and relative risks assigned, Table 4.6 shows predicted no effect concentrations (PNEC) for CHPTAC (1).

Table 4.6 - PNEC for CHPTAC in the Environment

| <b>Freshwater</b>                                     | <b>Soil</b>  | <b>Atmosphere</b> | <b>Marine</b>      |
|---|--------------|-------------------|--------------------|
| 51 ug/L, 1640 ug/L intermittent-fresh water organisms | 0.0608 mg/kg | not applicable    | 5.1 ug/L           |
| 103 ug/L-microorganisms                               | -            | -                 | 11.6 ug/L sediment |
| 0.116 mg/kg-sediment                                  | -            | -                 | -                  |

#### **4.6 Exposure and Human Health (1-3,6)**

CHPTAC is manufactured in closed systems with high levels of engineering controls that prevent the escape of liquid or vapors and minimizes the potential for release to the environment. Occupational exposure to CHPTAC would be possible at production facilities of CHPTAC or at facilities utilizing CHPTAC as cationic reagents. In both instances, the proper use of personal protective equipment (PPE) will greatly reduce occupational exposure. Pragmatically, reputable and responsible facilities that manufacture or employ these products would be expected to have thorough training for personnel regarding the safety, handling, and storage of CHPTAC reagents, as well as providing PPE and safety devices such as chemical showers and eye washes in easily and immediately accessible

locations (administrative controls). Regarding specific exposure to CHPTAC, there are currently no aerosol processes known. Further, exposure to vapors is unlikely due to the very low vapor pressure of CHPTAC. As a result, the main route of exposure to CHPTAC is dermal contact through sampling, lab work, cleaning, and maintenance. Residual levels of CHPTAC in cationized starches average 156 mg/kg with a reasonable worst case (RWC) of 611 mg/kg. With respect to textile application and cationization of cellulose, it would be expected with the abundance of water in the wet processing stages, that through the liquor/fabric interchange of the processing steps, there should be relatively no CHPTAC, EPTAC, or DIOL residue present in the final dyed goods. There are currently no known specific studies regarding CHPTAC, EPTAC, or DIOL residues in cationized cellulose. Table 4.7 shows some methods of human exposure to residual CHPTAC in products utilizing cationic starches (1).

Table 4.7- Examples of Methods of Human Exposure to CHPTAC

| <b>Product</b>            | <b>Scenario</b>                        | <b>Total Exposure</b> |
|---------------------------|--|-----------------------|
| Food Packaging            | Transfer to product from wet packaging | 0.00003 ug/kg bw      |
| Children's books          | Skin exposure and/or ingestion         | 0.06-0.16 ug/kg bw    |
| Copy paper and news paper | Skin exposure                          | 0.6 ug/day            |
| Cosmetics                 | Skin exposure                          | 0.007-0.29 ug/kg bw   |

With CHPTAC possessing a fairly low molecular weight, this property could potentially facilitate absorption of CHPTAC through membranes. However, with CHPTAC possessing low fat solubility and an ionic nature, permeation through skin is not expected to be rapid. As well, mouse skin has been shown to be 43-117 times higher absorptive for CHPTAC than

human skin. Important to note, the pH of most in vitro tests is 7.4 where as shown previously with the ½ life conversions of CHPTAC, considerable EPTAC will be formed in those test conditions. Also, a pertinent question is what happens in the small intestine where a pH 6 would be expected? In other words, the complex human body and pH variations and subsequent conversion or non conversion of CHPTAC in respect to pH and temperature dictates that special consideration and interpretation be given to test and experimental results regarding toxicity and human health effects of CHPTAC exposure. With that precursor given, the dermal lethal dose of CHPTAC has been found repeatedly to be greater than 2000 mg/kg. CHPTAC may be slightly irritating at maximum concentrations, but CHPTAC has not been shown to be a sensitizer. Prolonged skin contact with CHPTAC is not likely to cause significant irritation or result in the absorption of harmful amounts of CHPTAC. It should be noted that in most commercial uses, CHPTAC is converted to EPTAC, which is a potent skin sensitizer. Eye contact with CHPTAC may cause moderate irritation, although corneal injury is unlikely. According to FDA standards, CHPTAC is not considered an eye irritant. Generally speaking CHPTAC has low toxicity if swallowed. Small amounts of CHPTAC swallowed incidental to normal handling operations are not likely to cause injury. Swallowing larger amounts of CHPTAC may cause injury or significant bodily harm. The oral toxicity of CHPTAC is low, with an LD<sub>50</sub> of 2,800 mg/kg or greater. For repeated dose, the lowest observed adverse effect level (LOAEL) of 1,085 mg/kg/day orally has been reported. Generally speaking, the oral toxicity of EPTAC is moderate with an LD<sub>50</sub> of 400 mg/kg - 800

mg/kg. EPTAC is irritating to eyes (corneal damage is likely), skin and mucous membranes and toxic to the kidneys.

#### **4.6.1 Mutagenicity (1-3,6)**

All in vitro mutagenicity tests conducted with CHPTAC have given a positive result, however, as mentioned formerly, these results need to be scrutinized and can be complicated because of the purity (or percent solids of CHPTAC in the test) and the pH of tests. Consequently, even if CHPTAC is not a mutagen, it can convert to EPTAC, a known carcinogen. Concerning in vivo mutagenicity, one study has given a negative in vivo mutagenicity, but because of the lack of further experimental data, there remains some uncertainty about in vivo mutagenicity, and no definite conclusions can be warranted without additional testing. CHPTAC did not produce skin tumors in a two year skin painting study. CHPTAC is not a local carcinogen in mice when administered via skin but there is a possibility that it is a systemic carcinogen based on increased incidence of bronchiolo-alveolar tumors. However, as recurrently mentioned, when carefully scrutinized, the strength of these incidences seems relatively weak. Therefore, CHPTAC is currently classified as a Carcinogen Category 3 compared to EPTAC classified as a Carcinogen Category 2. In addition, in all CHPTAC use scenarios the principal concern is the conversion of CHPTAC to EPTAC. EPTAC is a genotoxic carcinogen and powerful skin sensitizer.

#### **4.6.2 Reproductive Toxicity**

There is very little information on reproductive toxicity regarding CHPTAC exposure. In the absence of reproductive toxicity studies, the only effect of CHPTAC observed in reproductive organs was the decreased testicular weight after long-term dermal exposure in mice with a no observed adverse effect level (NOAEL) of 24 mg/kg/day (1).

#### **4.7 Storage and Handling (2-3)**

CHPTAC must be stored in closed, appropriately lined containers. CHPTAC should not be stored in unlined metal containers or tanks. Phenolic or epoxy lined, carbon steel tanks are recommended. Empty drums should be incinerated. As the physical and chemical properties showed, at temperatures below -15°C precipitation of CHPTAC occurs. As well, copper, brass, and bronze fittings should be used to prevent corrosion. Temperatures in excess of 150°C should be avoided as thermal decomposition may occur where decomposition products may include chloroacetone, hydrogen chloride, methyl chloride, trimethylamine, and other compounds. Contact with amines or ammonia and unintended contact with strong acids and strong bases should be avoided.

#### **4.8 Environmental Releases**

If CHPTAC is spilled, the focus is to safely contain the spill to prevent contamination of soil and surface or ground water. For a small spill, absorbent chemical spill materials can be utilized and collected in suitable and properly labeled containers and in accordance with

applicable government regulations. In the unlikely event of a large spill, first, isolate the area. The area of the spill should be diked to contain the spill. Utilizing PPE and safe handling practices, the spill should be transferred into suitable and properly labeled containers. The spill situation should be handled in accordance with applicable government regulations. Regarding specific regulation, in the USA there are no reporting requirements by CERCLA or SARA Title III regarding CHPTAC. As well, there are no reporting requirements in the EU regarding CHPTAC. However, regulations may exist that govern the manufacture, sale, transportation, use, and/or disposal of CHPTAC. These types of regulations may vary by city, state, country, or geographic region and corresponding statutes. Specific information may be found by consulting the relevant authorities, i.e. CHPTAC supplier, local government, etc.

#### **4.8.1 Fire (3)**

In the event of a fire, the fire should be extinguished with water, foam, dry chemical, or CO<sub>2</sub>. Because of the very likely potential of formation of EPTAC, alkaline extinguishing media should not be used. Fire extinguishing water should be collected and disposed. Protective fire fighting clothing and self-contained breathing apparatus should be used. As thermal degradation products, smoke fumes may contain chloromethane, chloroacetone, trimethylamine, and hydrogen chloride. Any CHPTAC that is in danger of fire should be removed if possible, or have the container cooled by water spray.



#### **4.8.2 PPE (3)**

Although inhalation of CHPTAC is not expected, inhalation exposure may cause chest tightness, cough or an asthmatic reaction. Persons with active asthma may be more susceptible to CHPTAC inhalation risks from cationization processes and should exercise extra vigilance. No respiratory protection should be needed for most applications of CHPTAC. In misty atmospheres, the use of a mist respirator is suggested. The opportunity for accidental ingestion of CHPTAC should be minimized. Food, drinks, tobacco and other items that would present an oral route of entry into the body should be kept out of the work area. The hands and face should be thoroughly washed before eating or smoking. Contamination of non-work areas should be avoided. Exposure of CHPTAC to the eyes should be avoided by wearing chemical goggles, and/or a full face shield. Eye bath and chemical showers should be located in the immediate work area. CHPTAC contact with the skin should be avoided by using impervious clothing as well as nitrile rubber gloves. Gloves should be rinsed with water before removal. Further selection of boots, apron, or full-body suit will depend and vary on the operation of CHPTAC handling or application. Clothing should be laundered before reuse. It is very important to recognize the warning signs of sensitization. When CHPTAC is exposed to the eyes or skin, warning signs of sensitization may include redness, irritation, itching, scaling, burns or blisters.

### **4.8.3 First Aid for Exposure (3)**

For contact with clothing, remove contaminated clothing, use emergency shower, and seek medical attention. For contact with eyes, flush with plenty of clean water for at least ten minutes and seek medical attention. For contact with skin, wash contaminated skin immediately with plenty of water and seek medical advice.

### **4.9 CHPTAC Compared to Sodium Hydroxide**

In comparison to one of the most common textile chemicals frequently used, sodium hydroxide, CHPTAC is far less hazardous. Sodium hydroxide is highly corrosive, highly reactive, causes severe burns, and can readily cause blindness, yet is necessarily used in many textile wet processes including bleaching, dyeing, and mercerization where abundant amounts must be used for full effect. With the dermal and gestational  $LC_{50}/LD_{50}$  both around 500 mg/kg for sodium hydroxide (7-8), compared to over 2000 mg/kg for both dermal and gestational for CHPTAC, it is clear that sodium hydroxide is around four times as acutely poisonous (requiring 1/4 the amount of exposure) to observe 50% lethality in tests subjects compared to CHPTAC. In the interest of further generality, the  $LD_{50}$  of caffeine is around 192 mg/kg and aspirin (acetylsalicylic acid) is around 200 mg/kg (9). Both of these commonly ingested substances are ten times more acutely poisonous (requiring 1/10 the amount of exposure) to observe 50% lethality in test subjects compared to CHPTAC. In short, CHPTAC is less poisonous to humans than many commonly used textile chemicals as well as everyday consumable products.

#### **4.10 Summary of CHPTAC Assessment**

Aspects of physical, chemical, human safety, environmental safety, and safe handling, storage, and disposal of CHPTAC have been examined and reviewed. In general terms, CHPTAC is a high volume chemical (in excess of one million pounds produced per year in the US) (10) that is only slightly toxic to freshwater organisms and has low levels of oral and dermal toxicity for humans. CHPTAC is not a skin or eye sensitizer. With a very low vapor pressure, inhalation risks are not expected. CHPTAC should be stored in sealed, lined, recommended containers. Due to the unique transitioning chemical structures of CHPTAC to EPTAC and/or DIOL from CHPTAC, it is important to understand and specify test conditions (pH, temperature, purity, CHPTAC purity in test) for toxicity, mutagenicity, etc. On the other hand, EPTAC, one of the conversion products of CHPTAC, is a potent skin sensitizer and Carcinogen Class 2. Care and proper PPE should be exercised and utilized in the direct handling and/or processing of both CHPTAC and EPTAC. The half life, degradability, and toxicity to the environment are all dependent on the pH and temperature of the surroundings (water or soil) and the corresponding formation of EPTAC and/or DIOL.

## REFERENCES

1. *European Union Risk Assessment Report, (3-CHLORO-2-HYDROXYPROPYL)TRIMETHYLAMMONIUMCHLORIDE*. 2008
2. *Product Safety Assessment, DOW™ Quat 188 Cationic Reagent*.  
[http://www.dow.com/PublishedLiterature/dh\\_02b6/0901b803802b6d9d.pdf](http://www.dow.com/PublishedLiterature/dh_02b6/0901b803802b6d9d.pdf)
3. *The Safe Handling of CR-2000*. Dow Chemical Company.
4. United States Patent # 4,602,110
5. Quat 188 Epoxide Stability & Half-Life  
[http://dow-answer.custhelp.com/app/answers/detail/a\\_id/9837/](http://dow-answer.custhelp.com/app/answers/detail/a_id/9837/)
6. Scientific Committee on Health and Environmental Risks (SCHER).  
*Risk Assessment Report on (3-CHLORO-2-HYDROXYPROPYL)TRIMETHYLAMMONIUM CHLORIDE*.
7. *MSDS 50% Sodium Hydroxide Solution*. [http://msds.fmc.com/msds/100000010035-msds\\_us-e.pdf](http://msds.fmc.com/msds/100000010035-msds_us-e.pdf)
8. *MSDS Sodium Hydroxide Quickprep Solution*  
[http://www.sargentwelch.ca/pdf/msds/Sodium\\_Hydroxide\\_Quickprep\\_Solution.667.00.pdf](http://www.sargentwelch.ca/pdf/msds/Sodium_Hydroxide_Quickprep_Solution.667.00.pdf)
9. *Median Lethal Dose*. [http://en.wikipedia.org/wiki/Median\\_lethal\\_dose](http://en.wikipedia.org/wiki/Median_lethal_dose)
10. *Chemical Profile for (3-CHLORO-2-HYDROXYPROPYL)TRIMETHYLAMMONIUM CHLORIDE (CAS Number: 3327-22-8)*. [http://www.scorecard.org/chemical-profiles/summary.tcl?edf\\_substance\\_id=3327-22-8](http://www.scorecard.org/chemical-profiles/summary.tcl?edf_substance_id=3327-22-8)

## **5. Methods and Materials**

### **5.1 Methods**

The following methods were used or are referenced for quality control testing of dyed goods where noted.

Lightfastness - AATCC TM 16-2004

Crocking - AATCC TM 8-2007

IIA Wash - AATCC TM 61-2009

Change of Color After Laundering - AATCC TM 124-2009

Cold Water Bleed - AATCC TM 107-2009

Perspiration Fastness - AATCC TM 15-2009

SAS Institutes JMP9 software was used for statistical design and analysis.

The assessed levelness of a fabric is determined by recording the DEcmc of a fabric in a single spot 10 times. Next, 10 readings of the DEcmc are taken at different spots on the fabric. Finally, the standard deviation is found for the instrument and the fabric. The squareroot of the difference of the squares of the standard deviation in the fabric minus the instrument is the final assessed levelness in DEcmc [ $\sigma = (\sigma_{\text{sample}}^2 - \sigma_{\text{instrument}}^2)^{1/2}$ ].

### **5.2 Materials**

Many different reagents and materials were used in these studies and they are described in the experimental sections as they are used. Most reagents if not commonly used are accompanied by a structural drawing for clarity. A standard bleached white twill and

bleached cotton interlock knit were used for the majority of experiments and are noted throughout the experimental section. A tubular knit jersey was used in the 55 pound sample lots. Most importantly, the cationization reagent, CHPTAC was supplied as a 65% solution, tradename CR-2000, by Dow Chemical.

### **5.3 Equipment**

Many different machines, laboratory and pilot scale, were used in these studies including but not limited to: laboratory padders, laboratory can dyeing machines, laboratory curing ovens, small sample jet, large sample jet, along with other machinery. The machinery used is noted in the experimental section when it was utilized.

### **5.4 Percent Nitrogen**

Four different estimates of percent nitrogen are used in these studies. The percent nitrogen determined experimentally refers to the percent nitrogen as determined by Kjeldahl analysis. The predicted percent nitrogen refers to using a model relating the K/S sum from dyeing to the determined percent nitrogen to estimate the percent nitrogen of a sample. A zeroed percent nitrogen is also used, primarily in the context of predicting the amount of nitrogen used for shade matching on cationic cotton. This percent nitrogen is used when noted to zero the K/S sum and determined percent nitrogen model so that the prediction goes through zero percent nitrogen and does not possess a y-intercept. Finally, the amount of zeroed nitrogen predicted needed to match a shade will also be seen. This is

the amount of zeroed nitrogen predicted needed to fully exhaust a dye formula onto a cationized cotton substrate.

## 6. Experimental

### 6.1 Standard twill

Cotton Inc. purchases and has an on hand supply of a standard, bleached, unfinished, 100% cotton twill. A roll of the standard twill cut to ~19 inches wide was obtained that had been Jig washed/scoured and was readily absorbable. With the prepared twill, experiments were carried out by padding water on a Burlington Machinery lab pad at different pad pressures to determine wet pick up (WPU) as a function of pressure as shown in Table 6.1.

Table 6.1 – WPU of Standard Twill

| Sample | PSI | Dry (g) | Wet (g) | % WPU | % WPU Power Prediction |
|--------|-----|---------|---------|-------|------------------------|
| 1      | 10  | 37.8    | 71.8    | 90    | 89.0                   |
| 2      | 10  | 37.8    | 71.9    | 90    | 89.0                   |
| 3      | 20  | 35.9    | 63.1    | 76    | 76.9                   |
| 4      | 20  | 36.6    | 63.9    | 75    | 76.9                   |
| 5      | 30  | 38.1    | 64.8    | 70    | 70.7                   |
| 6      | 30  | 37.2    | 63.8    | 72    | 70.7                   |
| 7      | 40  | 36.7    | 60.9    | 66    | 66.5                   |
| 8      | 40  | 36.7    | 61.4    | 67    | 66.5                   |
| 9      | 50  | 36.7    | 60.4    | 65    | 63.5                   |
| 10     | 50  | 36.7    | 60      | 63    | 63.5                   |

A model was found to correlate well with the PSI of pressure and WPU. This model can be used in conjunction with a K/S and percent nitrogen fixation to assess relative fixation efficiency of padded samples. The WPU as a function of PSI of pressure is shown in Figure 6.1. Compared to a knit, the use of twill woven fabric allows fast sample cutting, easy



chemical padding, and drying/curing in a curing oven for multiple experiments. This WPU model is subsequently used to determine percent add on of applied chemistry.

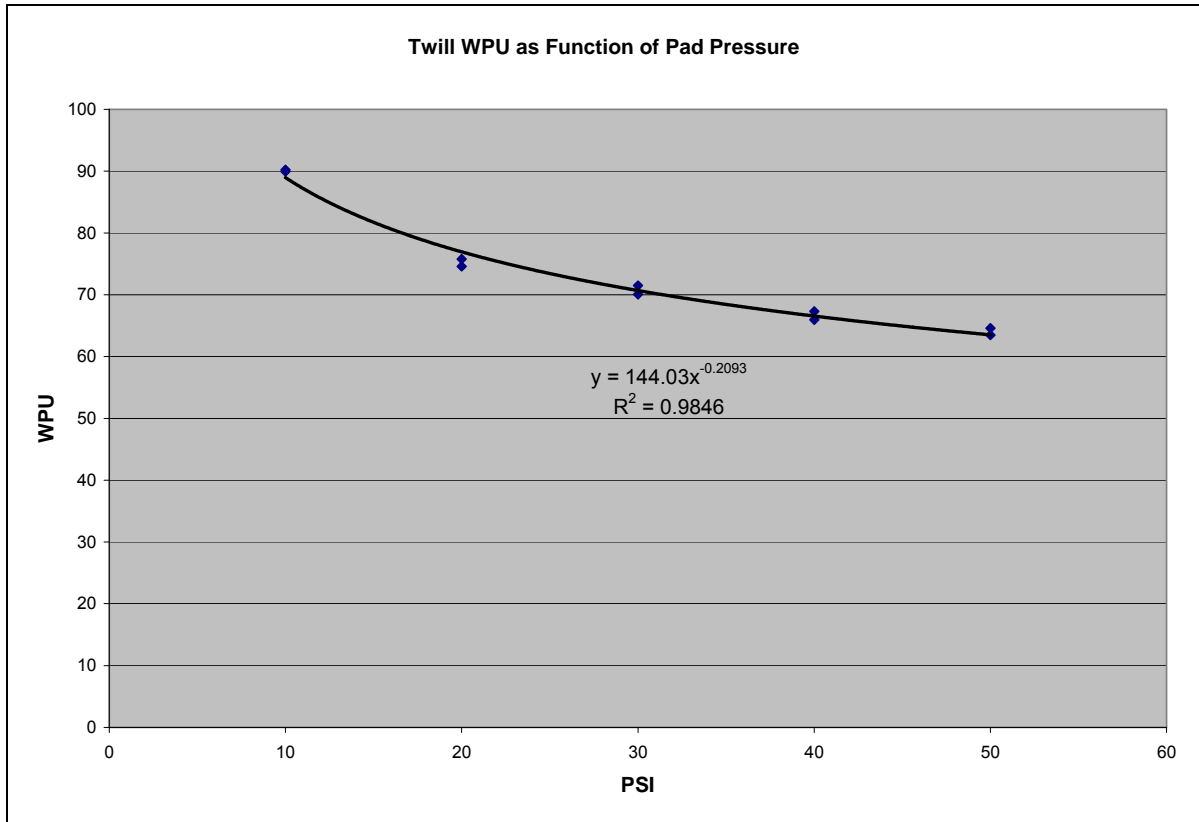


Figure 6.1 – Model of WPU of Standard Twill

## 6.2 K/S Calibration

A simple and easy way to quickly ascertain the percent nitrogen fixed on a sample of cationized cotton is to establish a K/S (utilizing a standard dye and dye procedure) and percent nitrogen relationship. From this model, a treated sample only needs to be quickly dyed with the standard dye and procedure to obtain a reasonable estimate of the nitrogen

fixed on the fabric. Utilizing the model for WPU presented previously, four samples per three different pad pressures of four different baths with varying CHPTAC concentrations at a fixed 2:1 NaOH:CHPTAC mole ratio were padded. Tables 6.2 and 6.3 show the four different application baths and breakdown of the individual samples. Two samples (a and b) were dried for 15 minutes at 40°C in a Despatch laboratory oven and then cured for 15 minutes at 105°C in a separate Despatch laboratory curing oven. Two samples (c and d) were dried only for 30 minutes at 40°C. In this experimental setup, the experiment is performed twice instead of duplicate measurements of the same experiment. The cured samples were hand rinsed for five minutes in a sink, neutralized with 1 g/L acetic acid, further rinsed, and finally dried.

Table 6.2 – Twill Calibration Application Baths

|            | Bath 1 (g/L) | Bath 2 (g/l) | Bath 3 (g/L) | Bath 4 (g/L) |
|------------|--------------|--------------|--------------|--------------|
| 65% CHPTAC | 10           | 25           | 50           | 100          |
| 50% NaOH   | 5.53         | 13.82        | 27.64        | 55.29        |
|            |              |              |              |              |
| mol CHPTAC | 0.035        | 0.086        | 0.173        | 0.346        |
| mol NaOH   | 0.069        | 0.173        | 0.346        | 0.691        |

Table 6.3 – Breakdown of Treated Calibration Samples

| Sample | PSI     | CR2000 (g/L) | NaOH:CHPTAC mole ratio | %WPU | Bath  | %N OWF |
|--------|---------|--------------|------------------------|------|-------|--------|
| 1a     | 10      | 10           | 2 to 1                 | 89.0 | 1     | 0.043  |
| 1b     | 10      | 10           | 2 to 1                 | 89.0 | 1     | 0.043  |
| 1c     | 10      | 10           | 2 to 1                 | 89.0 | 1     | 0.043  |
| 1d     | 10      | 10           | 2 to 1                 | 89.0 | 1     | 0.043  |
| 2a     | 30      | 10           | 2 to 1                 | 70.7 | 1     | 0.034  |
| 2b     | 30      | 10           | 2 to 1                 | 70.7 | 1     | 0.034  |
| 2c     | 30      | 10           | 2 to 1                 | 70.7 | 1     | 0.034  |
| 2d     | 30      | 10           | 2 to 1                 | 70.7 | 1     | 0.034  |
| 3a     | 50      | 10           | 2 to 1                 | 63.5 | 1     | 0.031  |
| 3b     | 50      | 10           | 2 to 1                 | 63.5 | 1     | 0.031  |
| 3c     | 50      | 10           | 2 to 1                 | 63.5 | 1     | 0.031  |
| 3d     | 50      | 10           | 2 to 1                 | 63.5 | 1     | 0.031  |
| 4a     | 10      | 25           | 2 to 1                 | 89.0 | 2     | 0.108  |
| 4b     | 10      | 25           | 2 to 1                 | 89.0 | 2     | 0.108  |
| 4c     | 10      | 25           | 2 to 1                 | 89.0 | 2     | 0.108  |
| 4d     | 10      | 25           | 2 to 1                 | 89.0 | 2     | 0.108  |
| 5a     | 30      | 25           | 2 to 1                 | 70.7 | 2     | 0.086  |
| 5b     | 30      | 25           | 2 to 1                 | 70.7 | 2     | 0.086  |
| 5c     | 30      | 25           | 2 to 1                 | 70.7 | 2     | 0.086  |
| 5d     | 30      | 25           | 2 to 1                 | 70.7 | 2     | 0.086  |
| 6a     | 50      | 25           | 2 to 1                 | 63.5 | 2     | 0.077  |
| 6b     | 50      | 25           | 2 to 1                 | 63.5 | 2     | 0.077  |
| 6c     | 50      | 25           | 2 to 1                 | 63.5 | 2     | 0.077  |
| 6d     | 50      | 25           | 2 to 1                 | 63.5 | 2     | 0.077  |
| 7a     | 10      | 50           | 2 to 1                 | 89.0 | 3     | 0.215  |
| 7b     | 10      | 50           | 2 to 1                 | 89.0 | 3     | 0.215  |
| 7c     | 10      | 50           | 2 to 1                 | 89.0 | 3     | 0.215  |
| 7d     | 10      | 50           | 2 to 1                 | 89.0 | 3     | 0.215  |
| 8a     | 30      | 50           | 2 to 1                 | 70.7 | 3     | 0.171  |
| 8b     | 30      | 50           | 2 to 1                 | 70.7 | 3     | 0.171  |
| 8c     | 30      | 50           | 2 to 1                 | 70.7 | 3     | 0.171  |
| 8d     | 30      | 50           | 2 to 1                 | 70.7 | 3     | 0.171  |
| 9a     | 50      | 50           | 2 to 1                 | 63.5 | 3     | 0.154  |
| 9b     | 50      | 50           | 2 to 1                 | 63.5 | 3     | 0.154  |
| 9c     | 50      | 50           | 2 to 1                 | 63.5 | 3     | 0.154  |
| 9d     | 50      | 50           | 2 to 1                 | 63.5 | 3     | 0.154  |
| 10a    | 10      | 100          | 2 to 1                 | 89.0 | 4     | 0.430  |
| 10b    | 10      | 100          | 2 to 1                 | 89.0 | 4     | 0.430  |
| 10c    | 10      | 100          | 2 to 1                 | 89.0 | 4     | 0.430  |
| 10d    | 10      | 100          | 2 to 1                 | 89.0 | 4     | 0.430  |
| 11a    | 30      | 100          | 2 to 1                 | 70.7 | 4     | 0.342  |
| 11b    | 30      | 100          | 2 to 1                 | 70.7 | 4     | 0.342  |
| 11c    | 30      | 100          | 2 to 1                 | 70.7 | 4     | 0.342  |
| 11d    | 30      | 100          | 2 to 1                 | 70.7 | 4     | 0.342  |
| 12a    | 50      | 100          | 2 to 1                 | 63.5 | 4     | 0.307  |
| 12b    | 50      | 100          | 2 to 1                 | 63.5 | 4     | 0.307  |
| 12c    | 50      | 100          | 2 to 1                 | 63.5 | 4     | 0.307  |
| 12d    | 50      | 100          | 2 to 1                 | 63.5 | 4     | 0.307  |
| 13a    | control |              |                        |      | water | 0.000  |
| 13b    | control |              |                        |      | water | 0.000  |
| 13c    | control |              |                        |      | water | 0.000  |
| 13d    | control |              |                        |      | water | 0.000  |

### 6.2.1 Standard Dyeing

The percent nitrogen for the K/S calibration samples were obtained from Galbraith Laboratories who determined percent nitrogen using the Kjeldahl test. The treated calibration samples were saturation dyed with 6.25% Novacron Red FN-R at a 25:1 liquor ratio at 71°C for 20 minutes in a Roaches laboratory infrared beaker dyeing machine. The dyed samples were rinsed and soaped, dried, conditioned, and evaluated for K/S. This is the standard dyeing and dye process for obtaining K/S information for a treated cationic sample. From the K/S and percent nitrogen of the calibration samples, a K/S vs percent nitrogen model was obtained to predict the percent nitrogen of a cationic sample dyed with the standard method as described above. The model with all of the raw data is shown in Figure 6.2. Table 6.4 shows the percent nitrogen determinations for the treated calibration samples as well as the predicted percent nitrogen from a simple model utilizing the K/S value at  $\lambda_{MAX}$  as shown in Figure 6.2. Utilizing the experimentally determined percent nitrogen, this value is compared to applied percent nitrogen from the dried only samples in Table 6.4 as shown in Figure 6.3. Figure 6.4 shows the percent nitrogen experimentally determined vs percent nitrogen predicted for the pad, dry, cure samples. Figure 6.5 shows percent nitrogen experimentally determined vs the difference in percent nitrogen predicted for the pad, dry, cure samples.

Table 6.4 - Percent Nitrogen Values of Calibration Samples

| Sample | %N Applied | %N Determined | K/S <sub>λMAX</sub> | %N Predicted | %N Difference |
|--------|------------|---------------|---------------------|--------------|---------------|
| 1a     | 0.043      | 0.061         | 3.938               | 0.052        | 0.010         |
| 1b     | 0.043      | 0.064         | 4.879               | 0.056        | 0.008         |
| 2a     | 0.034      | 0.060         | 2.497               | 0.044        | 0.016         |
| 2b     | 0.034      | 0.037         | 3.345               | 0.049        | -0.012        |
| 3a     | 0.031      | 0.057         | 1.905               | 0.041        | 0.015         |
| 3b     | 0.031      | 0.056         | 2.704               | 0.045        | 0.011         |
| 4a     | 0.108      | 0.083         | 10.250              | 0.083        | 0.000         |
| 4b     | 0.108      | 0.084         | 13.323              | 0.098        | -0.014        |
| 5a     | 0.086      | 0.077         | 11.302              | 0.088        | -0.011        |
| 5b     | 0.086      | 0.077         | 11.179              | 0.088        | -0.011        |
| 6a     | 0.077      | 0.082         | 8.031               | 0.072        | 0.010         |
| 6b     | 0.077      | 0.072         | 8.720               | 0.075        | -0.003        |
| 7a     | 0.215      | 0.115         | 15.951              | 0.112        | 0.003         |
| 7b     | 0.215      | 0.106         | 17.345              | 0.119        | -0.013        |
| 8a     | 0.171      | 0.094         | 14.958              | 0.107        | -0.013        |
| 8b     | 0.171      | 0.099         | 13.667              | 0.100        | -0.001        |
| 9a     | 0.154      | 0.098         | 17.983              | 0.122        | -0.024        |
| 9b     | 0.154      | 0.096         | 17.766              | 0.121        | -0.024        |
| 10a    | 0.430      | 0.218         | 25.849              | 0.161        | 0.057         |
| 10b    | 0.430      | 0.176         | 23.699              | 0.150        | 0.026         |
| 11a    | 0.342      | 0.153         | 23.213              | 0.148        | 0.005         |
| 11b    | 0.342      | 0.162         | 24.333              | 0.154        | 0.009         |
| 12a    | 0.307      | 0.116         | 21.143              | 0.138        | -0.022        |
| 12b    | 0.307      | 0.123         | 22.188              | 0.143        | -0.020        |

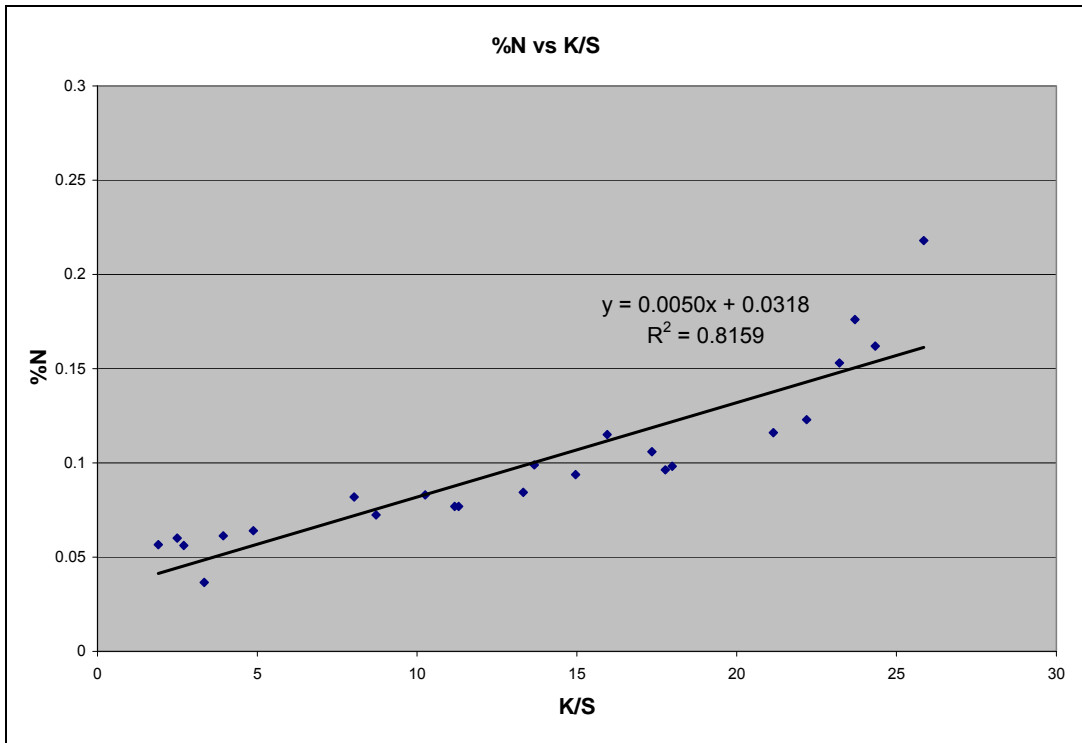


Figure 6.2 – Percent Nitrogen vs K/S at  $\lambda_{MAX}$

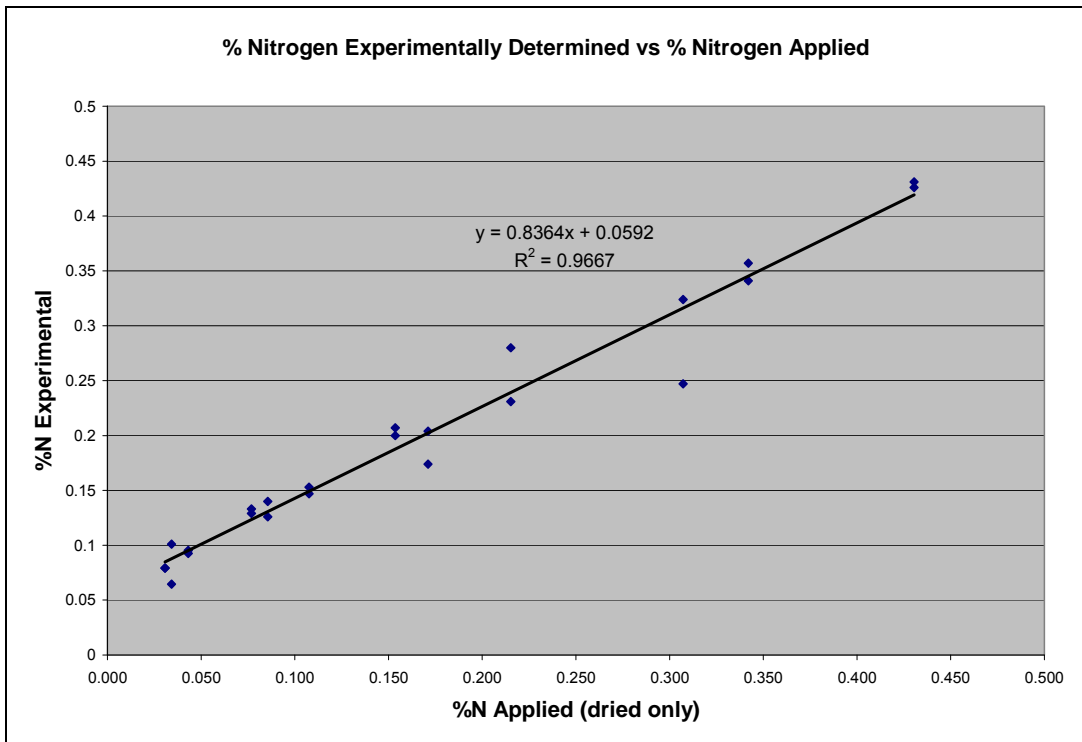


Figure 6.3 – Comparison of Percent Nitrogen Applied and Determined

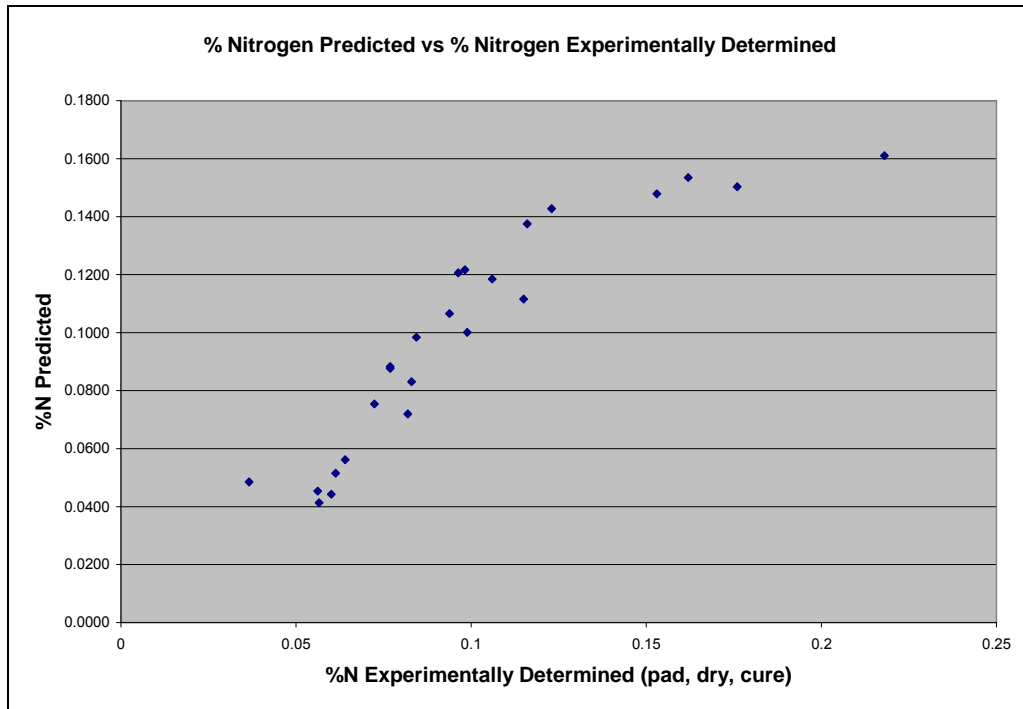


Figure 6.4 - Percent Nitrogen Predicted vs Percent Nitrogen Determined (for pad, dry, cure samples)

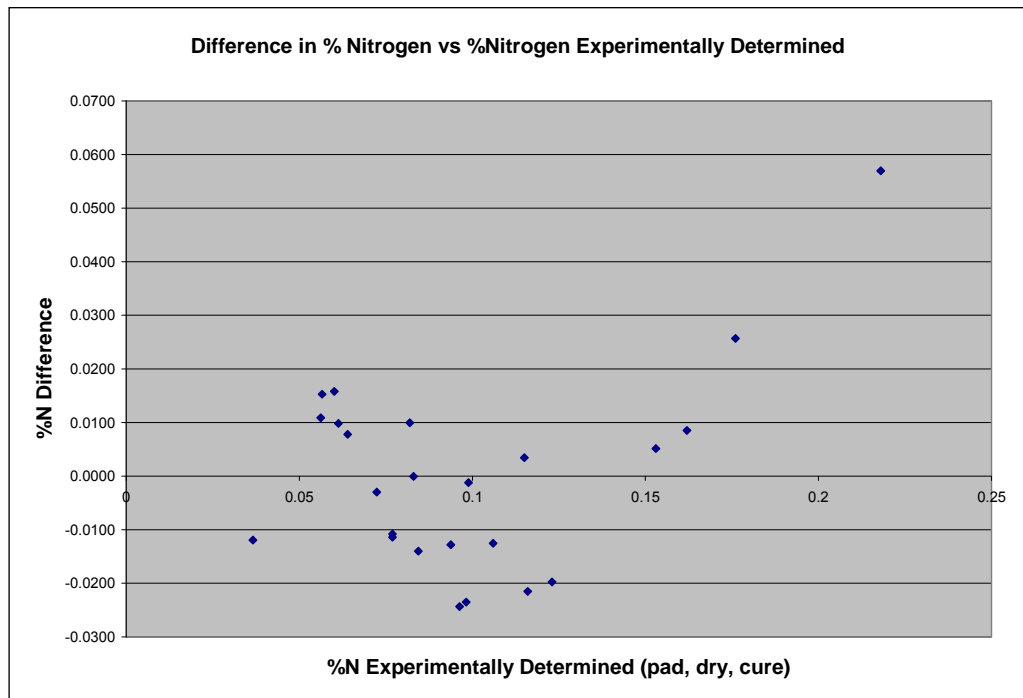


Figure 6.5 - Difference in Percent Nitrogen vs Percent Nitrogen Determined (for pad, dry, cure samples)

As Figure 6.6 shows, if the K/S sum is utilized instead of the K/S at  $\lambda_{MAX}$ , more of the data can be explained and correlated with respect to the experimentally determined percent nitrogen. Further, as Figure 6.7 shows, in the upper range of the percent nitrogen prediction, when utilizing the K/S sum, the predicted values do not flatten as sharply as compared to utilizing the K/S at  $\lambda_{MAX}$ . Finally, as Figure 6.8 shows, the range in the difference of the percent nitrogen predicted is decreased utilizing the K/S sum compared to using the K/S value at  $\lambda_{MAX}$ . The model shown in Figure 6.6 is the basis for the predicted percent nitrogen values that are subsequently shown in further examples and analysis. It should be noted that the models utilizing K/S at  $\lambda_{MAX}$  and K/S sum do not go through a zero value for percent nitrogen. From these K/S at  $\lambda_{MAX}$  and K/S sum models, they both predict the percent nitrogen of an untreated sample to yield 0.03-0.037% nitrogen. When the percent nitrogen of the untreated control is experimentally determined, it has a value of 0.0509% nitrogen. Although each adjustment would have a different impact on the percent nitrogen predictions, instead of forcing the prediction to go through zero or subtracting out the predicted value of the control sample, the percent nitrogen prediction model is left unmodified. This issue will be readdressed in a later section on color and percent nitrogen predictions for color matching, Section 8.2. Further, as Figure 6.3 showed, there was very good agreement in the amount of nitrogen applied and the amount of nitrogen determined for pad and dried only samples.



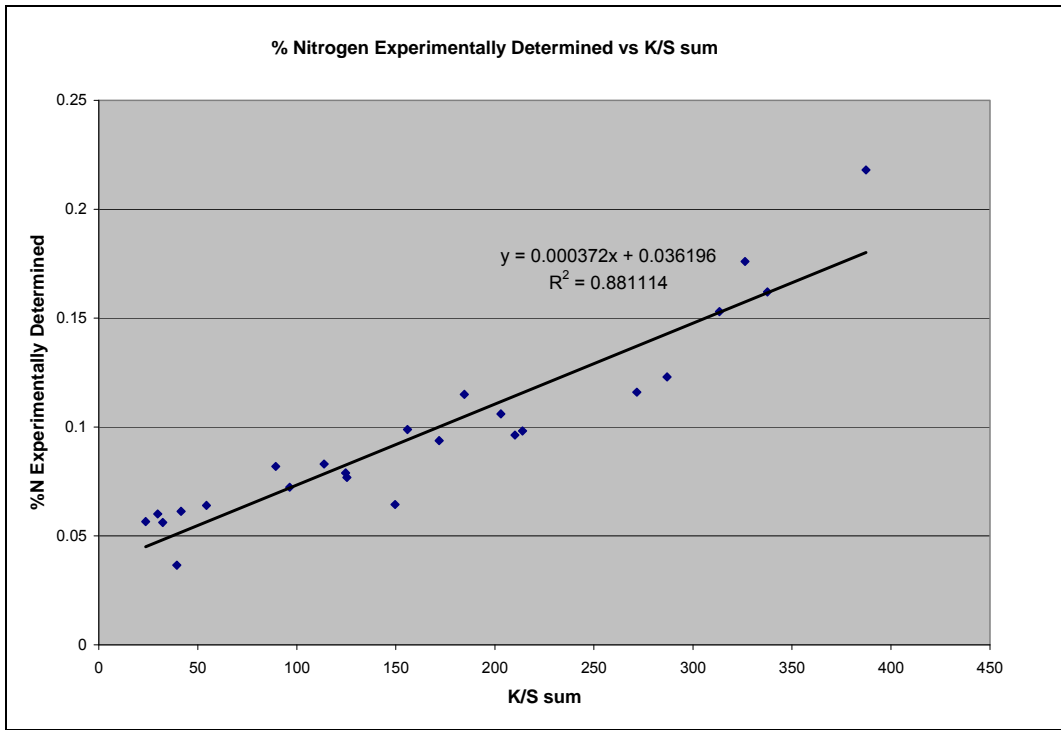


Figure 6.6 – Experimentally Determined Percent Nitrogen vs K/S sum

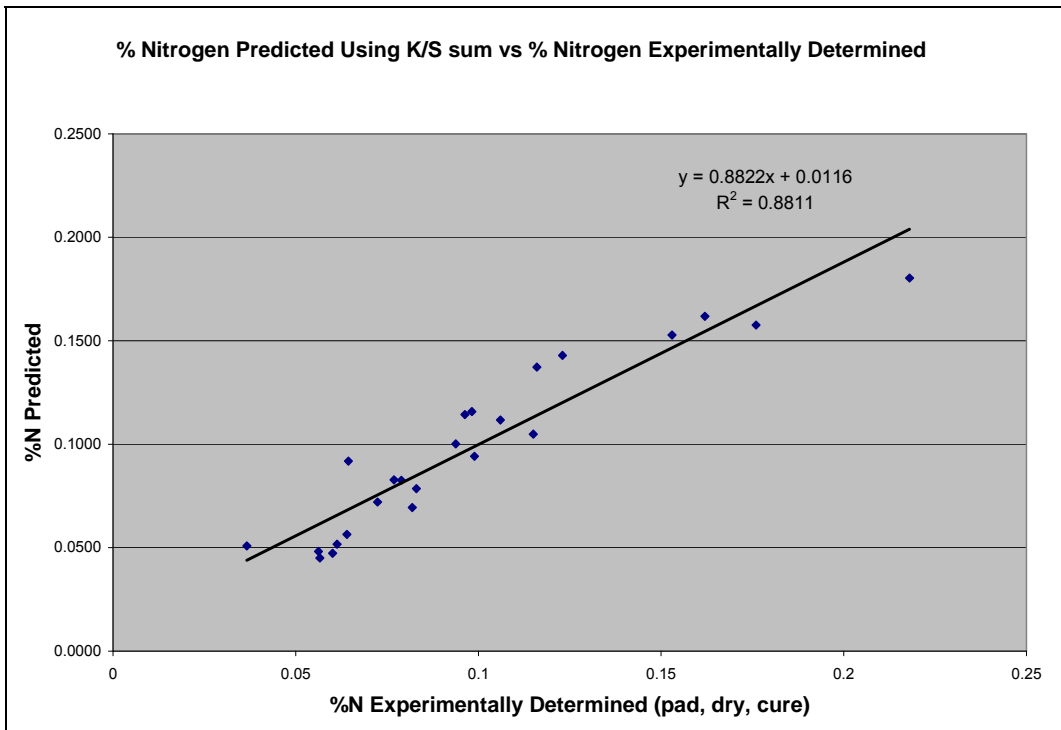


Figure 6.7 - Percent Nitrogen Predicted Using K/S sum vs Percent Nitrogen Determined (for pad, dry, cure samples)

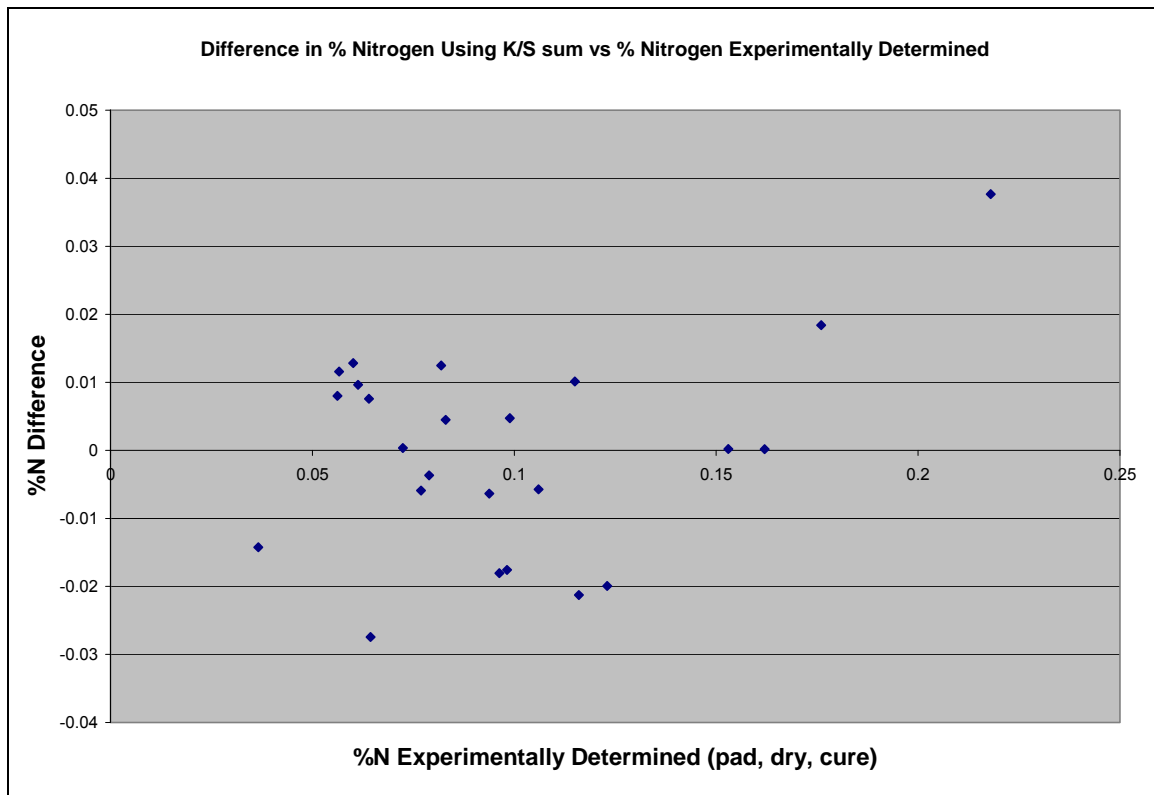


Figure 6.8 - Percent Nitrogen Experimentally Determined vs Difference using K/S sum (for pad, dry, cure samples)

### 6.3 CHPTAC Exhaustion Application Studies

It has been assumed that CHPTAC will not exhaust because of the high degree of water solubility and low molecular weight. However, without a doubt, if CHPTAC can be applied by exhaust methods, this would be the most preferred application method for a typical piece dyer because the dyer can prepare, cationize, and dye all in the same dye machine. As a starting point for the analysis of the exhaustion of CHPTAC, exhaustion samples were prepared at 5% CR2000 owg at a 5:1 liquor ratio on cotton twill in the Roaches dyeing machine. The CR2000 was added first and then the amount of alkali was added and the bath was held at 30C for 30 minutes before being heated to the final reaction temperature.

Samples 22a and 24a were only held for 30 minutes at 70°C. These exhaustion experiments were evaluated by dyeing utilizing the standard dyeing to obtain a baseline for further exhaustion experiments. Results for these experiments are shown in Table 6.5.

Table 6.5 – CHPTAC Exhaustion Experiments

| Sample  | % CR2000 | NaOH:CHPTAC Mole Ratio | Additional g/L Soda Ash | Additional g/L 50% NaOH | Reaction Temperature °C | K/S sum |
|---------|----------|------------------------|-------------------------|-------------------------|-------------------------|---------|
| 15a     | 5        | 0.72                   | 0                       | -                       | 105                     | 3       |
| 16a     | 5        | 1.45                   | 0                       | -                       | 105                     | 47.3    |
| 17a     | 5        | 0.72                   | 0                       | -                       | 105                     | 3.4     |
| 18a     | 5        | 2.00                   | 0                       | -                       | 105                     | 58.1    |
| 19a     | 5        | 1.50                   | 0                       | -                       | 105                     | 49.8    |
| 20a     | 5        | 1.00                   | 0                       | -                       | 105                     | 3.7     |
| 21a     | 5        | 1.00                   | 0.5                     | -                       | 105                     | 9.6     |
| 22a     | 5        | 1.00                   | 0                       | 0.2768                  | 70                      | 5.3     |
| 23a     | 5        | 2.00                   | 0                       | -                       | 30                      | 2.6     |
| 23b     | 5        | 3.00                   | 0                       | -                       | 30                      | 6.2     |
| 24a     | 5        | 1.00                   | 0                       | 0.2768                  | 70                      | 3.1     |
| 24b     | 5        | 2.00                   | 0                       | -                       | 70                      | 34.6    |
| 25a     | 5        | 2.00                   | 0                       | -                       | 70                      | 36.2    |
| 25b     | 5        | 3.00                   | 0                       | -                       | 70                      | 65.5    |
| 26a     | 5        | 2.00                   | 0                       | -                       | 105                     | 55.3    |
| 26b     | 5        | 3.00                   | 0                       | -                       | 105                     | 63.7    |
| CONTROL | -        | -                      | -                       | -                       | -                       | 2.6     |

If the K/S sum values for 5% CR2000 are plotted against the reaction temperature as shown in Figure 6.9, it is clear that the reaction temperature alone is not the determining factor in the exhaustion and fixation of the EPTAC. Similarly, if the K/S sum values for 5% CR2000 are plotted with the ratio of NaOH added as shown in Figure 6.10, it is also apparent that the exhaustion and fixation is not solely determined by the amount of NaOH added.

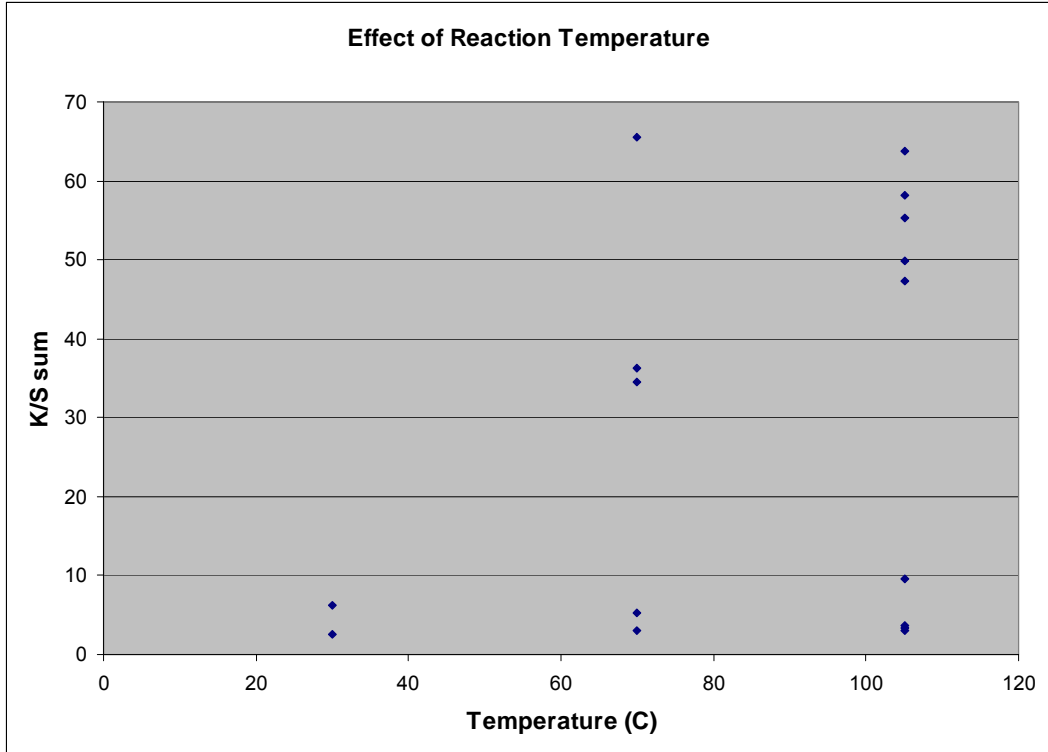


Figure 6.9 – Effect of Reaction Temperature in CHPTAC Exhaust Application

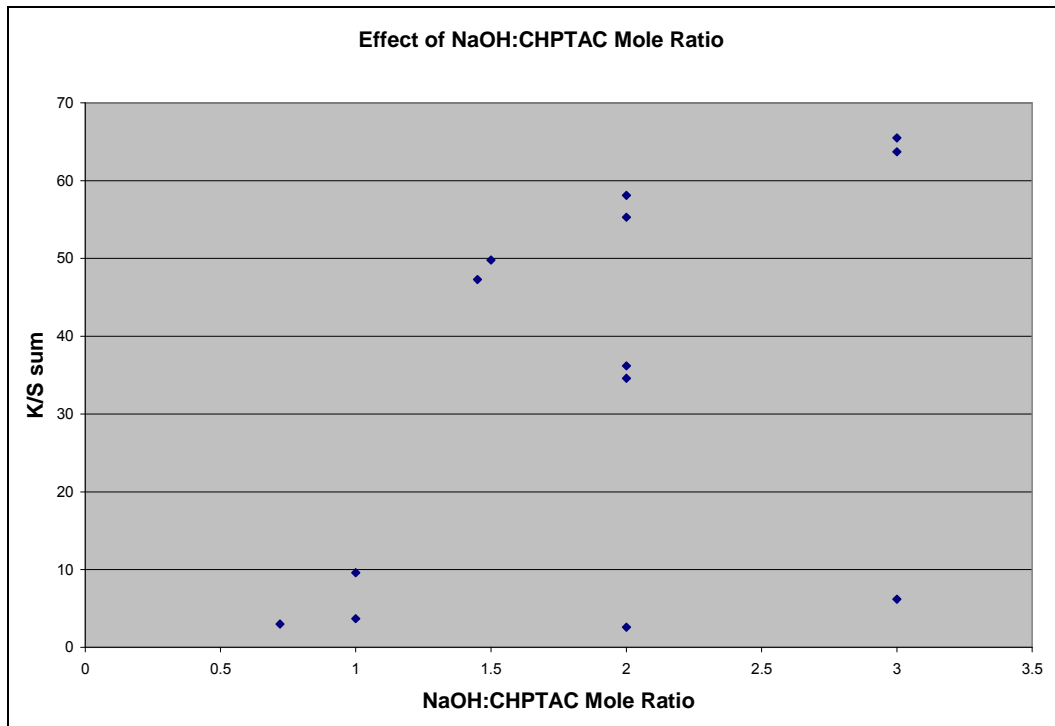


Figure 6.10 – Effect of NaOH:CHPTAC Mole Ratio in CHPTAC Exhaust Application

If the NaOH molar ratio for 5% CR2000 is held constant at 2:1 for NaOH:CHPTAC and the reaction temperature vs K/S sum is plotted, it is clear that the fixation of the EPTAC is temperature dependent when the amount of alkali is held constant. This is illustrated in Figure 6.11. Similarly, if the NaOH ratio for 5% CR2000 is held constant at 3:1 for NaOH:CHPTAC and the reaction temperature vs K/S sum is plotted as shown in Figure 6.12, it is clear that the fixation of the CHPTAC is temperature dependent when the amount of alkali is held constant. However, at a 3:1 ratio, the K/S sum begins to level off and a linear build up is not seen. When the reaction temperature of 105°C is kept constant and the NaOH ratio is plotted against the K/S sum as shown in Figure 6.13, at NaOH ratios of 1:1 or less, no significant fixation is obtained even at high temperature, but with increasing alkali amounts, up to 3:1, the fixation of EPTAC builds and begins to level off.

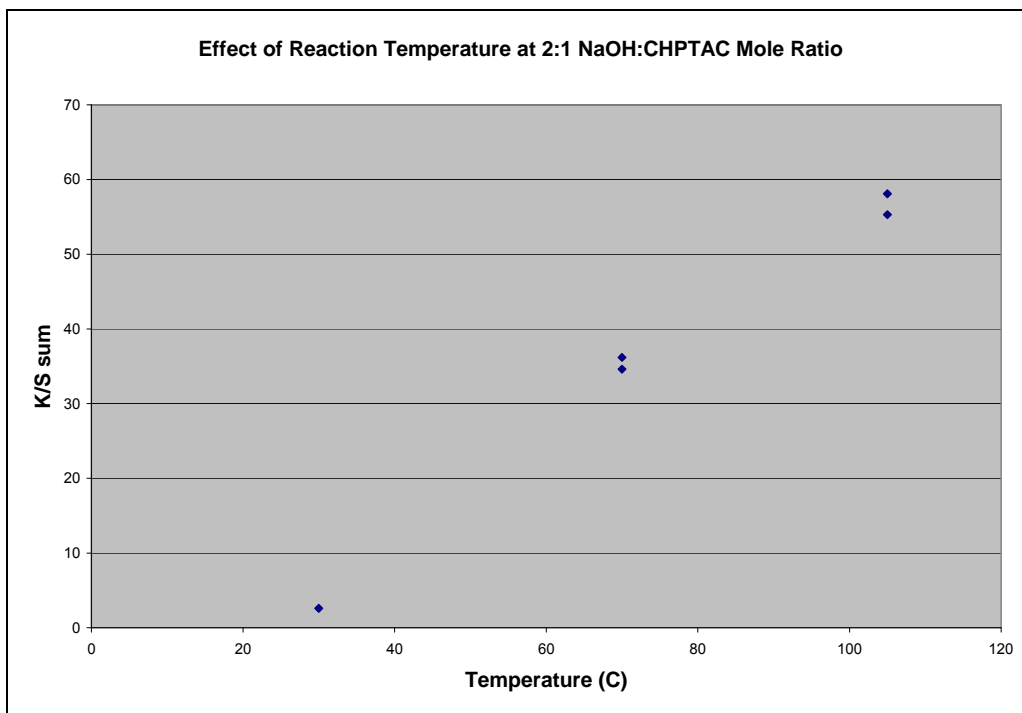


Figure 6.11 – Effect of Reaction Temperature at 2:1 NaOH:CHPTAC Mole Ratio for CHPTAC Exhaust Application

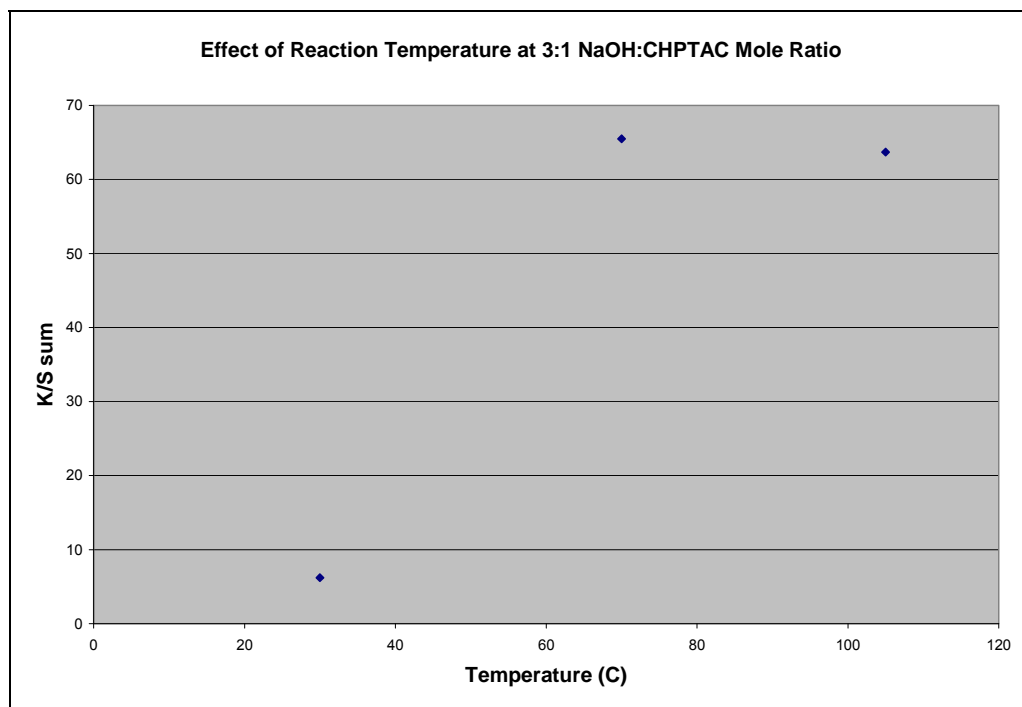


Figure 6.12 – Effect of Reaction Temperature at 3:1 NaOH:CHPTAC Mole Ratio for CHPTAC Exhaust Application

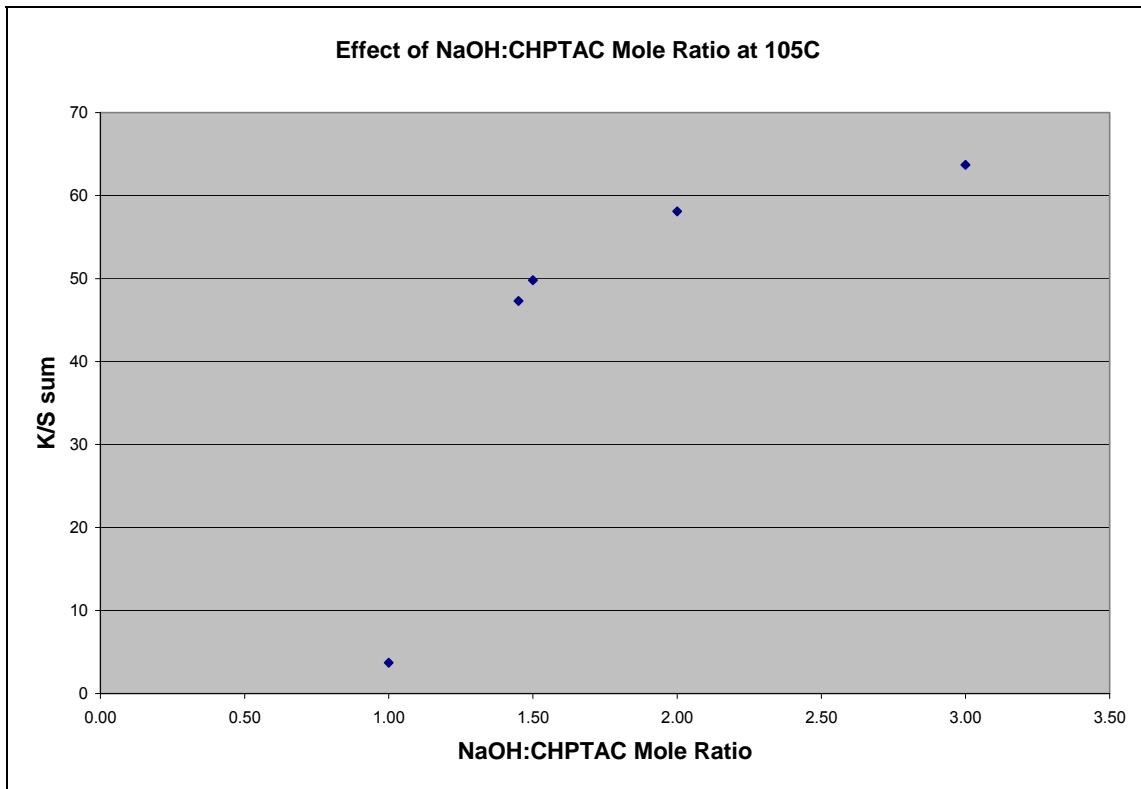


Figure 6.13 – Effect of NaOH:CHPTAC Mole Ratio at 105°C for CHPTAC Exhaust Application

Based on the results obtained, it was recommended to use a 1:1 NaOH:CHPTAC mole ratio to form EPTAC, but utilize a g/L based excess NaOH amount to form alkali cellulose and exhaust EPTAC. At the same time, it was found that if the alkali was added before the CR2000, an increase in fixation of the CHPTAC was observed as shown in Table 6.6. The amounts of NaOH for this recommended procedure and the currently recommended industrial exhaustion procedure of CHPTAC are shown in Tables 6.7-6.8. Tables 6.9-6.10 compare the current suggested industry application of CHPTAC to those of the recommended.

Table 6.6 - Effect of Recommended Procedure in Exhaustion of CHPTAC

| Sample      | % CR2000 | NaOH:CHPTAC Mole Ratio | Additional g/L 50% NaOH | Reaction Temp. °C | K/S sum | Predicted %N | Predicted % Fix |
|-------------|----------|------------------------|-------------------------|-------------------|---------|--------------|-----------------|
| 26b         | 5        | 3:1                    | 0                       | 105               | 63.7    | 0.061        | 25.1            |
| Recommended | 5        | 1:1                    | 5                       | 105               | 90.7    | 0.071        | 29.3            |

Table 6.7 – Amounts of NaOH for Recommended CR2000 Exhaust Procedure

| % CR2000                | 5   | 10   | 15   | 20  |
|-------------------------|-----|------|------|-----|
| NaOH for 1:1 Mole Ratio | 1:1 | 1:1  | 1:1  | 1:1 |
| Excess NaOH g/L         | 5   | 6.67 | 8.33 | 10  |

Table 6.8 – Recommended CR2000 Exhaust Procedure

| Step | Description                 | Time | Temperature |
|------|-----------------------------|------|-------------|
| 1    | add fabric to machine       |      |             |
| 2    | fill machine to volume      |      |             |
| 3    | add NaOH                    |      |             |
| 4    | Heat to 30°C                | 5    |             |
| 5    | add CR2000                  |      |             |
| 6    | circulate                   | 30   | 30°C        |
| 7    | heat 2.0°C/min to 105°C     | 37.5 |             |
| 8    | hold 30 minutes             | 30   | 105°C       |
| 9    | cool to 70°C                | 10   |             |
| 10   | drop bath                   |      |             |
| 11   | rinse well                  |      |             |
| 12   | neutralize with acetic acid |      |             |

Table 6.9 – Reagent Amounts for Current Industry CR2000 Exhaust Procedure

| CR2000 g/L | NaOH #1 (as 100%) g/L | NaOH #2 (as 100%) g/L |
|------------|-----------------------|-----------------------|
| 100        | 14                    | 1.4                   |
| 50         | 7                     | 0.7                   |
| 25         | 3.5                   | 0.35                  |
| 10         | 1.384                 | 0.1384                |



Table 6.10 –Current Industry CR2000 Exhaust Procedure

| Step | Description                 | Time | Temperature |
|------|-----------------------------|------|-------------|
| 1    | add fabric to machine       |      |             |
| 2    | fill machine to volume      |      |             |
| 3    | add CR2000                  |      |             |
| 4    | Circulate                   | 10   | 30°C        |
| 5    | add NaOH #1                 |      |             |
| 6    | Circulate                   | 5    | 30°C        |
| 7    | heat 2.0°C/min to 70°C      | 20   |             |
| 8    | Add NaOH #2                 |      |             |
| 9    | hold 30 minutes             | 30   | 70°C        |
| 10   | cool to 40°C                | 1    |             |
| 11   | drop bath                   |      |             |
| 12   | rinse well                  |      |             |
| 13   | neutralize with acetic acid |      |             |

To compare the new recommended exhaust procedure to the current industry exhaust application, two experiments were carried out in a JFO dyeing machine to cationize 1.2 kg samples of bleached cotton interlock using both procedures. The exhaustion treatments were made at a 6.5:1 liquor ratio utilizing each procedure applying 0.242% nitrogen (5% CR2000). After performing the standard dyeing, the results of the predicted percent nitrogen are shown in Table 6.11.

Table 6.11 - Comparison of Recommended and Current Industrial CHPTAC Exhaustion Processes

|                    | K/S sum | Predicted % Nitrogen | Predicted % Fix |
|--------------------|---------|----------------------|-----------------|
| Recommended        | 53.5    | 0.0570               | 23.5            |
| Current Industrial | 7.5     | 0.0399               | 16.5            |

To better compare the exhaustion processes, a blue shade was formulated using conventional reactive dyes, Levafix Blue E dyes, dichloroquinoxaline reactive group. Utilizing both exhaustion processes, samples were treated at a liquor ratio of 5:1. At a 5:1 LR, 25% CR2000 owg = 50 g/L, likewise, at a 5:1 LR, 12.5% CR2000 owg = 25 g/L. For the new recommended process, in addition to the 1:1 equivalent of sodium hydroxide, 10 g/L and 7.5 g/L were used for the excess amount of alkali. All dyeings were carried out at a liquor ratio of 15:1. Cationic treated samples were dyed with water and dyestuffs only. The control untreated cotton was dyed with a standard recipe of dyes, salt, and alkali for dye fixation as shown below in Table 6.12. The dye procedure for the untreated cotton is shown below in Table 6.13. The cationic samples were also dyed at 60°C for a total of one hour. The color strengths of the dyed samples are given below along with a note on the final dyebath in Table 6.14. %STRENGTH is given as the ratio of the K/S at  $\lambda_{max}$  of the dyed cationic sample compared to the K/S at  $\lambda_{max}$  of the dyed conventional sample.

Table 6.12 - Deck Blue Dye Formula

|                    |        |
|--------------------|--------|
| Levafix Yellow EGA | 0.03%  |
| Levafix Blue EB    | 1.44%  |
| Sodium Sulfate     | 35 g/L |
| Sodium Carbonate   | 9 g/L  |

Table 6.13 - Deck Blue Dye Procedure

|                           |
|---------------------------|
| Add dyes and salt at RT   |
| Heat at 2.0°C/min to 60°C |
| Hold 15 min               |
| Add soda ash over 15 min  |
| Hold 30 min               |
| drop                      |
| rinse                     |
| soap                      |
| dry                       |

Table 6.14 - Color Measurements of Dyed Deck Blue Samples

| Dyed Untreated Cotton as Standard | DEcmc | K/S <sub>λMAX</sub> | %STRENGTH | Final Dyebath   |
|-----------------------------------|-------|---------------------|-----------|-----------------|
| 50 g/L Recommended Exhaust        | 3.44  | 5.803               | 165       | Clear           |
| 25 g/L Recommended Exhaust        | 1.81  | 4.366               | 127       | Very light      |
| 50 g/L Current Industrial Exhaust | 9.3   | 0.996               | 30        | Darker than STD |
| 25 g/L Current Industrial Exhaust | 15.78 | 0.36                | 11        | Darker than STD |

Confident that significant improvements had been made in the exhaust application of CHPTAC, several other experiments were carried out to ascertain the effects of varying the liquor ratio and treatment levels and assessing the improvements in exhaust applications of CHPTAC. These results are shown in Table 6.15.

Table 6.15 - CHPTAC Exhaustion Experiments Varying Treatment Level and Liquor Ratio

| Sample | % CR2000 | Liquor Ratio | Process            | %N Applied | K/S sum | Predicted %N | Predicted %Fixation |
|--------|----------|--------------|--------------------|------------|---------|--------------|---------------------|
| 64     | 25       | 5 to 1       | Recommended        | 1.209      | 258     | 0.133        | 11.0                |
| 65     | 12.5     | 5 to 1       | Recommended        | 0.605      | 147.6   | 0.092        | 15.2                |
| 66     | 25       | 5 to 1       | Current Industrial | 1.209      | 50.3    | 0.056        | 4.6                 |
| 67     | 12.5     | 5 to 1       | Current Industrial | 0.605      | 19.3    | 0.044        | 7.3                 |
| 72     | 50       | 10 to 1      | Current Industrial | 2.418      | 107.7   | 0.077        | 3.2                 |
| 73     | 75       | 15 to 1      | Current Industrial | 3.627      | 73.2    | 0.064        | 1.8                 |
| 74     | 25       | 10 to 1      | Current Industrial | 1.209      | 50.9    | 0.056        | 4.6                 |
| 75     | 37.5     | 15 to 1      | Current Industrial | 1.814      | 5.3     | 0.039        | 2.2                 |
| 76     | 15       | 5 to 1       | Recommended        | 0.725      | 179.8   | 0.104        | 14.3                |
| 77     | 15       | 12 to 1      | Recommended        | 0.725      | 91.4    | 0.071        | 9.8                 |
| 78     | 25       | 5 to 1       | Current Industrial | 1.209      | 51.4    | 0.056        | 4.6                 |
| 79     | 60       | 12 to 1      | Current Industrial | 2.902      | 57.4    | 0.058        | 2.0                 |
| 80     | 15       | 12 to 1      | Recommended        | 0.725      | 103.1   | 0.075        | 10.4                |
| 81     | 20       | 12 to 1      | Recommended        | 0.967      | 129.3   | 0.085        | 8.8                 |
| 82     | 20       | 12 to 1      | Recommended        | 0.967      | 131.7   | 0.086        | 8.9                 |

#### 6.4 Duoprep for Simultaneous Bleaching and Cationization

Foreseeing the usefulness of a preparation process where the bleaching and cationization could be simultaneously carried out, a few experiments were carried out to see if using a traditional bleach cycle and reagents if cotton could also be cationized. A traditional bleach formula is shown in Table 6.16. The results of a duoprep experiment in the Roaches dyeing machine are shown in Table 6.17 where the recommended amount of alkali for exhaustion was added to the amount of alkali required for bleaching. Using a 5:1 liquor ratio on greige cotton interlock, the auxiliaries were added and circulated for five minutes. The alkali was added and heated to 30°C. The CR2000 was added and held at 30°C for 30 minutes. The peroxide was added and the bath was heated to 96°C and held 30 minutes. The bath was cooled, dropped, and the fabric was rinsed and neutralized. Compared to an exhaust

cationization, this test showed that not as much nitrogen was fixed while simultaneously bleaching, but that it is possible to bleach and cationize cotton simultaneously.

Table 6.16 - Bleach Formula

| Reagent/Auxiliary | g/L |
|-------------------|-----|
| Sultafon D        | 2   |
| Marlube CMN       | 1   |
| Marsperse 6000    | 1   |
| Marquest PB       | 1   |
| 50% NaOH          | 4   |
| 35% H2O2          | 4   |

Table 6.17 - Comparison of Exhaust Cationization and Dual Bleach and Cationization

|                          | % CR2000 | %N Applied | K/S sum | Predicted %N | Predicted % Fix |
|--------------------------|----------|------------|---------|--------------|-----------------|
| Recommended Cat. Only    | 15       | 0.726      | 179.8   | 0.104        | 14.3            |
| Bleach and Cationization | 15       | 0.726      | 106.5   | 0.077        | 10.6            |

### 6.5 CHPTAC Exhaustion Application Experimental Design

With the development of an improved exhaustion process for CHPTAC cationization, a statistical experimental design was created with 32 individual randomized experiments to test five variables of the exhaustion process:

- Temperature of exhaustion (T1), time of exhaustion (t1), alkali amount (NaOH), Temperature of fixation (T2), and time of fixation (t2). Tables 6.18-6.22 show the values of the different variables in the designed experiments.

The objective of the experimental design was to center the recommended exhaustion process and pull the different variables in extreme directions to test for optimal parameters and interactions.

Table 6.18 – Values of Variable T1

| T1 |     |
|----|-----|
| -2 | 30C |
| -1 | 40C |
| 0  | 50C |
| 1  | 60C |
| 2  | 70C |

Table 6.19 – Values of Variable t1

| t1 |    |
|----|----|
| -2 | 5  |
| -1 | 20 |
| 0  | 35 |
| 1  | 50 |
| 2  | 65 |

Table 6.20 – Values of Variable NaOH

| NaOH |        |
|------|--------|
| -2   | 1 to 1 |
| -1   | 2 to 1 |
| 0    | 3 to 1 |
| 1    | 4 to 1 |
| 2    | 5 to 1 |

Table 6.21 – Values of Variable T2

| T2 |      |
|----|------|
| -2 | 70C  |
| -1 | 85C  |
| 0  | 100C |
| 1  | 115C |
| 2  | 130C |

Table 6.22 – Values of Variable t2

|    |    |
|----|----|
| t2 |    |
| -2 | 5  |
| -1 | 20 |
| 0  | 35 |
| 1  | 50 |
| 2  | 65 |

Table 6.23 shows the sample numbers and actual run sequence and the variable factors for each run. Once again, the Roaches dyeing machine was used for the exhaust cationizations at a 5:1 liquor ratio on bleached cotton interlock. 15% CR2000 was chosen for the treatment level. Table 6.24 shows the measured response of the designed experiments, K/S, as well as the K/S sum, and predicted percent nitrogen utilizing the K/S sum. Figure 6.14 shows the Predicted vs. Actual for K/S at  $\lambda_{MAX}$  values utilizing the model formed from the experiments in the statistical software.

Table 6.23 – CHPTAC Exhaustion Experimental Design and Run Sequence

| Sample | T1 | t1 | NaOH | T2 | t2 |
|--------|----|----|------|----|----|
| 1      | 1  | -1 | 1    | -1 | -1 |
| 2      | 0  | 0  | 0    | -2 | 0  |
| 3      | 0  | 0  | 0    | 0  | 2  |
| 4      | 1  | 1  | 1    | 1  | -1 |
| 5      | -1 | 1  | -1   | 1  | -1 |
| 6      | 0  | 0  | 0    | 0  | 0  |
| 7      | 0  | 0  | 0    | 0  | 0  |
| 8      | 1  | -1 | -1   | -1 | 1  |
| 9      | 0  | 0  | 0    | 2  | 0  |
| 10     | -1 | 1  | 1    | -1 | -1 |
| 11     | 1  | 1  | 1    | -1 | 1  |
| 12     | 1  | -1 | 1    | 1  | 1  |
| 13     | 0  | 0  | 0    | 0  | 0  |
| 14     | 1  | 1  | -1   | 1  | 1  |
| 15     | 0  | 0  | 0    | 0  | 0  |
| 16     | 0  | 0  | -2   | 0  | 0  |
| 17     | 0  | 0  | 0    | 0  | 0  |
| 18     | 0  | 0  | 2    | 0  | 0  |
| 19     | -1 | -1 | -1   | -1 | -1 |
| 20     | 0  | 0  | 0    | 0  | 0  |
| 21     | 2  | 0  | 0    | 0  | 0  |
| 22     | -1 | -1 | -1   | 1  | 1  |
| 23     | 1  | 1  | -1   | -1 | -1 |
| 24     | -1 | -1 | 1    | -1 | 1  |
| 25     | -1 | 1  | -1   | -1 | 1  |
| 26     | -1 | 1  | 1    | 1  | 1  |
| 27     | -2 | 0  | 0    | 0  | 0  |
| 28     | 0  | 2  | 0    | 0  | 0  |
| 29     | 1  | -1 | -1   | 1  | -1 |
| 30     | 0  | 0  | 0    | 0  | -2 |
| 31     | -1 | -1 | 1    | 1  | -1 |
| 32     | 0  | -2 | 0    | 0  | 0  |



Table 6.24 – Measured Responses from Designed CHPTAC Exhaustion Experiments

| Sample | K/S <sub>λMAX</sub> | K/S sum | %N Predicted |
|--------|---------------------|---------|--------------|
| 1      | 14.6                | 167.0   | 0.099        |
| 2      | 15.7                | 180.1   | 0.104        |
| 3      | 15.4                | 175.3   | 0.102        |
| 4      | 14.8                | 168.5   | 0.100        |
| 5      | 15.5                | 176.8   | 0.103        |
| 6      | 15.2                | 173.5   | 0.102        |
| 7      | 15.4                | 175.3   | 0.102        |
| 8      | 15.5                | 176.7   | 0.103        |
| 9      | 14.5                | 165.7   | 0.099        |
| 10     | 15.5                | 176.9   | 0.103        |
| 11     | 13.8                | 155.9   | 0.095        |
| 12     | 11.6                | 131.2   | 0.086        |
| 13     | 13.6                | 154.7   | 0.095        |
| 14     | 14.5                | 165.9   | 0.099        |
| 15     | 13.7                | 155.2   | 0.095        |
| 16     | 14.9                | 170.5   | 0.101        |
| 17     | 14.6                | 164.9   | 0.098        |
| 18     | 12.2                | 136.2   | 0.088        |
| 19     | 15.7                | 179.3   | 0.104        |
| 20     | 14.4                | 162.7   | 0.098        |
| 21     | 12.4                | 138.1   | 0.089        |
| 22     | 15.5                | 177.4   | 0.103        |
| 23     | 14.9                | 169.1   | 0.100        |
| 24     | 13.4                | 150.8   | 0.093        |
| s25    | 14.8                | 168.4   | 0.100        |
| 26     | 14.5                | 165.1   | 0.099        |
| 27     | 13.9                | 157.3   | 0.096        |
| 28     | 15.0                | 171.0   | 0.101        |
| 29     | 14.3                | 160.4   | 0.097        |
| 30     | 14.8                | 167.4   | 0.099        |
| 31     | 13.1                | 148.2   | 0.092        |
| 32     | 13.5                | 151.9   | 0.094        |

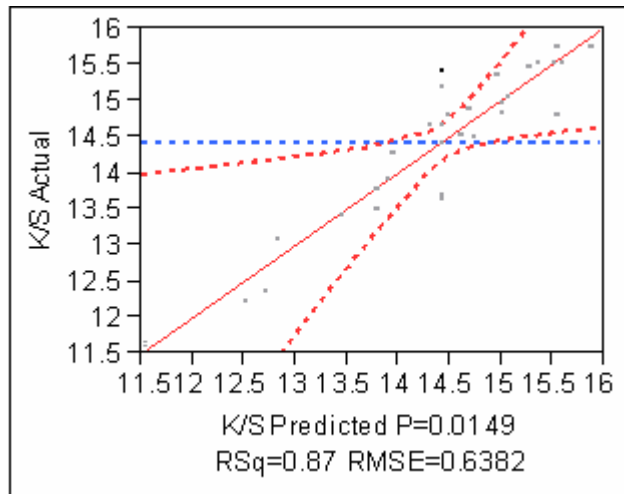


Figure 6.14 –Actual K/S Observed vs K/S Predicted from Statistical Analysis

Tables 6.25-6.27 detail the statistical analysis of the results of the designed exhaustion studies. The important statistic from these tables is the F-ratio or probability of F, which both indicate that the model formed is statistically significant. At 95% confidence, with the value of F at 0.0149, this is lower than 0.05 so the model is statistically significant. Table 6.28 shows the sorted parameter estimates for the variables and interactions between variables. It is clear from Table 6.28 that the amount of sodium hydroxide and the time at the exhaustion temperature,  $t_1$ , are the most important parameters that affect the fixation of CHPTAC. Conversely, the hold time at fixation,  $t_2$ , is the least important of the main five variables. At a p value of 0.05 or 95% confidence, any value of the probability of t in Table 6.28 equal to or less than 0.05 is considered significant. The lower the probability of t, the more significant the factor is and it is less likely to observe a different value than the parameter estimate.

Table 6.25 – Summary of Fit for CHPTAC Exhaustion Experimental Design Results

| Summary of Fit         |          |
|------------------------|----------|
| RSquare                | 0.870614 |
| RSquare Adjusted       | 0.635367 |
| Root Mean Square Error | 0.638151 |
| Mean of Response       | 14.41931 |
| Observations           | 32       |

Table 6.26 – Analysis of Variance for CHPTAC Exhaustion Experimental Design Results

| Analysis of Variance |    |                |             |                    |
|----------------------|----|----------------|-------------|--------------------|
| Source               | DF | Sum of Squares | Mean Square | F Ratio            |
| Model                | 20 | 30.142419      | 1.50712     | 3.7008             |
| Error                | 11 | 4.479602       | 0.40724     | <b>Prob &gt; F</b> |
| C. Total             | 31 | 34.622021      |             | 0.0149*            |

Table 6.27 – Lack of Fit for CHPTAC Exhaustion Experimental Design Results

| Lack of Fit |    |                |             |                    |
|-------------|----|----------------|-------------|--------------------|
| Source      | DF | Sum of Squares | Mean Square | F Ratio            |
| Lack Of Fit | 6  | 1.7208653      | 0.286811    | 0.5198             |
| Pure Error  | 5  | 2.7587368      | 0.551747    | <b>Prob &gt; F</b> |
| Total Error | 11 | 4.4796021      |             | 0.7756             |
|             |    |                |             | <b>Max RSq</b>     |
|             |    |                |             | 0.9203             |

Table 6.28 – Sorted Parameter and Interaction Estimates for CHPTAC Exhaustion Experimental Design Results

| Sorted Parameter Estimates |           |           |         |         |         |
|----------------------------|-----------|-----------|---------|---------|---------|
| Term                       | Estimate  | Std Error | t Ratio | t Ratio | Prob> t |
| [NaOH]                     | -0.622    | 0.130262  | -4.77   |         | 0.0006* |
| Time 1*[NaOH]              | 0.43875   | 0.159538  | 2.75    |         | 0.0189* |
| Time 1                     | 0.3200833 | 0.130262  | 2.46    |         | 0.0318* |
| Temp 1*Temp 1              | -0.279011 | 0.117826  | -2.37   |         | 0.0373* |
| Temp 1                     | -0.30075  | 0.130262  | -2.31   |         | 0.0414* |
| Temp 2                     | -0.286417 | 0.130262  | -2.20   |         | 0.0502  |
| Time 1*Temp 2              | 0.329125  | 0.159538  | 2.06    |         | 0.0635  |
| Temp 2*Temp 2              | 0.2188636 | 0.117826  | 1.86    |         | 0.0902  |
| [NaOH]*Time 2              | -0.291125 | 0.159538  | -1.82   |         | 0.0953  |
| Time 2*Time 2              | 0.2077386 | 0.117826  | 1.76    |         | 0.1056  |
| [NaOH]*[NaOH]              | -0.166386 | 0.117826  | -1.41   |         | 0.1856  |
| Time 2                     | -0.14575  | 0.130262  | -1.12   |         | 0.2870  |
| Temp 1*Temp 2              | -0.17625  | 0.159538  | -1.10   |         | 0.2928  |
| [NaOH]*Temp 2              | -0.1315   | 0.159538  | -0.82   |         | 0.4273  |
| Temp 2*Time 2              | 0.10825   | 0.159538  | 0.68    |         | 0.5115  |
| Temp 1*Time 2              | -0.102875 | 0.159538  | -0.64   |         | 0.5323  |
| Time 1*Time 2              | -0.08125  | 0.159538  | -0.51   |         | 0.6206  |
| Temp 1*[NaOH]              | 0.042125  | 0.159538  | 0.26    |         | 0.7966  |
| Temp 1*Time 1              | -0.039    | 0.159538  | -0.24   |         | 0.8114  |
| Time 1*Time 1              | 0.0033636 | 0.117826  | 0.03    |         | 0.9777  |

Utilizing the statistical analysis software to analyze the various parameter and interaction effects, the software can predict the optimum settings for the different variables to produce the highest response, in this case the highest K/S value. Figure 6.15 shows the prediction profiler and predicted performance of each variable at its predicted optimum value. From the prediction profiler, it predicts the optimum values of the variables as shown in Table 6.29. In practical terms, the optimum procedure for this 15% CR2000 exhaust treatment at a 5:1 liquor ratio would be; add sodium hydroxide (2:1), heat to 45°C, add CR2000, hold 20 minutes, heat to 85°C, hold 50 minutes, rinse and neutralize. Using this optimum procedure, the predicted K/S value of 16.05 was easily verified with K/S values of 16.3 with repeats, and a predicted percent nitrogen of 0.1065% nitrogen. This value corresponds to

14.7% fixation of 15% CR2000 applied, or 0.7254% nitrogen applied. As demonstrated previously, the fixation of exhaust applied CHPTAC will be expected to vary depending on the concentration of CHPTAC applied and the liquor ratio utilized for application.

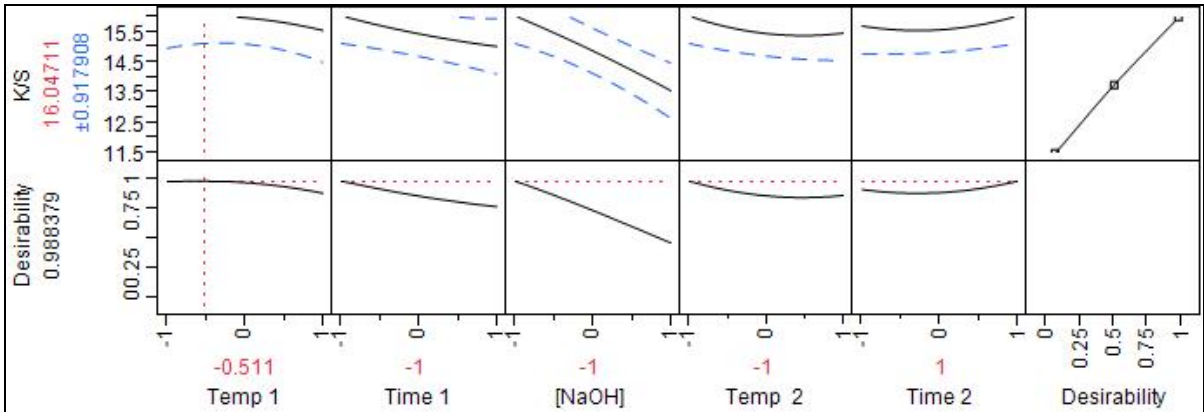


Figure 6.15 – CHPTAC Exhaustion Prediction Profiler

Table 6.29 – Predicted Optimum Exhaust Variable Settings

|      |        |
|------|--------|
| T1   | 45C    |
| t1   | 20 min |
| NaOH | 2:1    |
| T2   | 85C    |
| t2   | 50 min |

## 6.6 Phase Transfer Catalyst for CHPTAC Exhaustion Application

The results of the statistical design exhaustion study showed the predicted effects of the different variables included in the exhaustion and fixation of CHPTAC at a specified liquor ratio and application concentration of CHPTAC. Although the results of the statistical design were statistically significant, the practical significance of the findings of the experimental design did not produce a huge difference in the optimized exhaustion process compared to

the unoptimized exhaustion process as shown in Table 6.8. In other words, the results of the statistical design and analysis for the exhaustion experiments yielded predictions of the effect of varying the five exhaustion parameters, but the analysis does not produce a process with optimal parameters that will produce a “magic bullet” for the exhaustion and fixation of CHPTAC. A seemingly logical next step would be to identify a compatible phase transfer catalyst (PTC) and evaluate the PTC efficacy in improving the fixation of CHPTAC applied in exhaust baths. PTC’s transfer reagents from one phase to another phase in a chemical reaction. This transfer of reagents essentially catalyzes a reaction where the desired reaction takes place in a different phase than where the reagent was formerly found. In the case of the application of CHPTAC, a presumably suitable PTC would be an anionic molecule that would transport the EPTAC formed in the liquor bath (liquid phase) to the cellulose (solid phase) surface for reaction with the cellulosate ion. The anionic molecule would release the EPTAC molecule and return to the liquor bath to repeat the process. This type of mechanism would improve the efficiency of exhaust cationizations because the EPTAC will be brought to the cellulose surface instead of being hydrolyzed or left in the liquor bath. Table 6.30 shows a list of different PTC agents evaluated utilizing the optimized exhaustion process as detailed previously. 15% CR2000 was used on bleached cotton interlock at a 5:1 liquor ratio in the Roaches dyeing machine. Table 6.30 shows the percent nitrogen predicted with each PTC agent and the molarity of the PTC reagent used. Figures 6.16-6.30 show the chemical structure of the PTC agent if known. In the case of the polymeric PTC agents and when the structure was not known, 2.5 g/L of the PTC agent was

used. As seen from table 6.30, only Sarkosyl and sodium decyl sulfate yielded any improvements in the fixation of the applied CHPTAC. All other PTC reagents had a negative or zero impact on the fixation of the applied CHPTAC. Sodium decyl sulfate yielded the highest increase in fixation of applied CHPTAC. Interestingly, in the case of sodium decyl sulfate, similar fixation values were obtained using 1/100<sup>th</sup> the amount of sodium decyl sulfate. It seems possible that some of the evaluated PTC agents may have formed permanent ionic bonds preventing bonding with dyestuffs or that certain PTC agents may have hindered the exhaustion and/or fixation of applied CHPTAC. The range in predicted nitrogen is 0.017% nitrogen between the PTC agents. This corresponds to an increase of about 5.5% in predicted fixed nitrogen utilizing 0.0001 molar sodium decyl sulfate compared to no PTC agent, and a decrease of about 10% in predicted fixed nitrogen utilizing 0.01 molar BTCA or 2.5 g/L of Univadene DFM compared to no PTC agent.

Table 6.30 – PTC Reagents Evaluated

| Sample | K/S <sub>AMAX</sub> | K/S sum | %N Predicted | %Fix | PTC Agent                        | Molarity |
|--------|---------------------|---------|--------------|------|----------------------------------|----------|
| 1      | 16.16               | 186.3   | 0.106        | 14.7 | Sodium Dodecyl Sulfate           | [.01]    |
| 2      | 17.379              | 200.7   | 0.112        | 15.4 | Sodium Decyl Sulfate             | [.01]    |
| 3      | 15.513              | 177.9   | 0.103        | 14.2 | Deoxycholic acid,<br>sodium salt | [.01]    |
| 4      | 16.643              | 191.5   | 0.108        | 14.9 | Sarkosyl                         | [.01]    |
| 5      | 14.577              | 166.6   | 0.099        | 13.7 | BTCA                             | [.01]    |
| 6      | 15.325              | 175.9   | 0.103        | 14.1 | Citric Acid                      | [.01]    |
| 7      | 15.815              | 181.8   | 0.105        | 14.4 | 1,10-Decanedicarboxylic acid     | [.01]    |
| 8      | 14.892              | 169.8   | 0.100        | 13.8 | Succinic acid                    | [.01]    |
| 9      | 16.014              | 184.7   | 0.106        | 14.6 | Suberic acid                     | [.01]    |
| 10     | 16.011              | 184.6   | 0.106        | 14.6 | Adipic acid                      | [.01]    |
| 11     | 15.619              | 181.1   | 0.105        | 14.4 | Low MW sodium alginate           | [.01]    |
| 12     | 15.385              | 177.0   | 0.103        | 14.2 | Polyacrylic acid                 | [.01]    |
| 13     | 15.226              | 176.1   | 0.103        | 14.1 | CMC                              | [.01]    |
| 14     | 15.187              | 175.6   | 0.102        | 14.1 | Domolev PAB                      | [.01]    |
| 15     | 13.948              | 161.7   | 0.097        | 13.4 | Univadene DFM                    | [.01]    |
| 16     | 15.544              | 180.5   | 0.104        | 14.4 | Triton X-100                     | [.01]    |
| 17     | 13.818              | 159.5   | 0.096        | 13.3 | Reserve Salt Flake               | [.01]    |
| 18     | 16.55               | 193.5   | 0.109        | 15.0 | Sodium Decyl Sulfate             | *[.001]  |
| 19     | 17.345              | 203.0   | 0.113        | 15.5 | Sodium Decyl Sulfate             | *[.0001] |
| 20     | 16.061              | 187.8   | 0.107        | 14.7 | Sarkosyl                         | *[.001]  |
| 21     | 16.334              | 189.8   | 0.108        | 14.8 | Sarkosyl                         | *[.0001] |

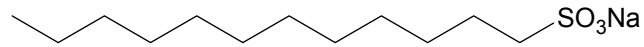


Figure 6.16 - Sodium Dodecyl Sulfate

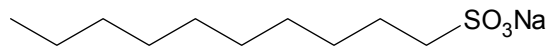


Figure 6.17 - Sodium Decyl Sulfate



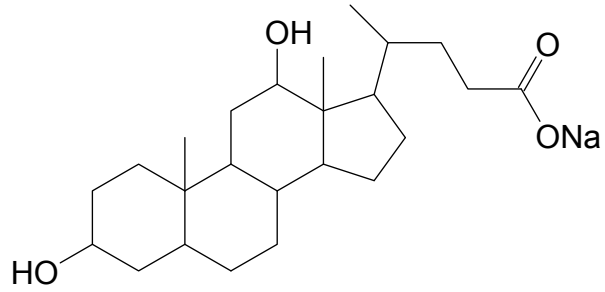


Figure 6.18 - Deoxycholic Acid Sodium Salt

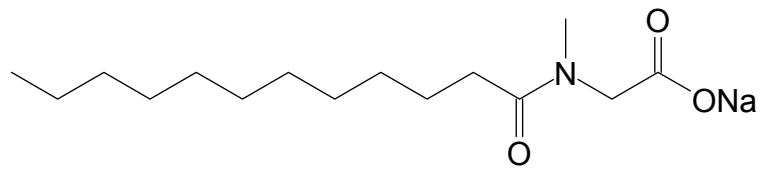


Figure 6.19- Sarkosyl

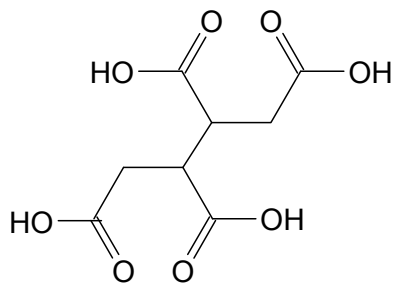


Figure 6.20 - BTCA

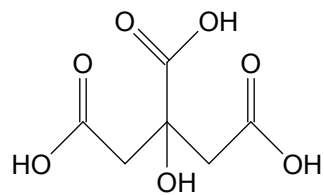


Figure 6.21 - Citric Acid

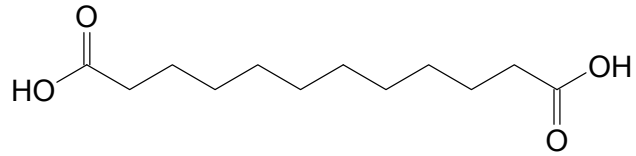


Figure 6.22 - 1,10-decanedicarboxylic acid

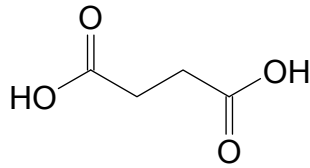


Figure 6.23 - Succinic Acid

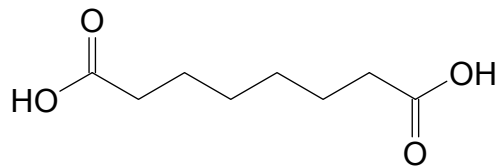


Figure 6.24 - Suberic Acid

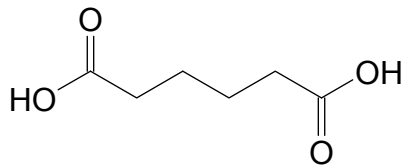


Figure 6.25 - Adipic Acid

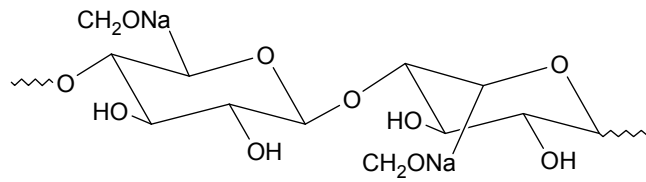


Figure 6.26 - General Structure of Sodium Alginate

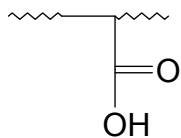


Figure 6.27 - Polyacrylic Acid

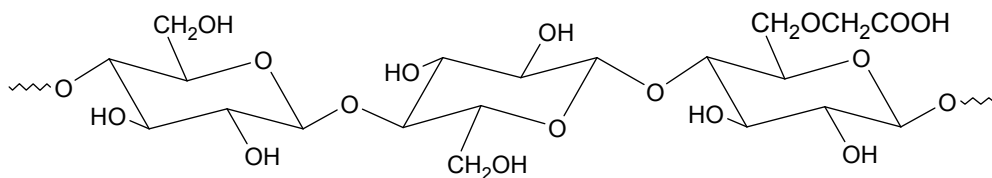


Figure 6.28 - CMC

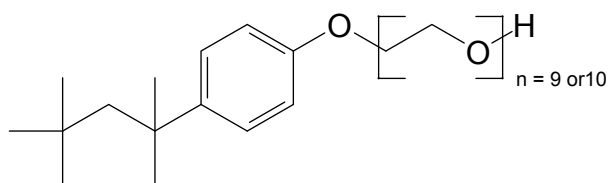


Figure 6.29 - Triton X-100

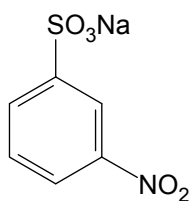


Figure 6.30 - Reserve Salt Flake

## 6.7 Neutral Bake Process for CHPTAC Application

There are different potential processes that may be used for cationizing cellulose including: pad/dry/cure, cold pad/batch, pad/steam, and exhaust for example. Each process has potential benefits and drawbacks including ease of application, time requirements of the application process, and cationization efficiency of the application process. Exhaustion and cold pad batch treatments have emerged as the main modes of realistic industrial cationization. Exhaustion cationization of cotton goods has routinely given very inefficient fixation of the cationic reagent but in relatively short application times utilizing existing batch dyeing equipment. Conversely, cold pad batch applications have routinely given the highest fixation of applied cationic reagent but at typical 16-24 hour application times and require A-frames for batching, (a capital investment if a mill does not possess them). Obviously, an alternative cationization method that would allow high cationization efficiency and throughput would make cationization an even more attractive process. A review of work carried out by Lewis suggests and shows that fixation of reactive dyes can be carried out at neutral pH by heating to high temperatures 100°C or greater (1). With an increase in temperature, the pKa of cellulose decreases such that the amount of cellulose-O<sup>-</sup> increases 100 fold. Analogously, CHPTAC should also theoretically be able to be applied at neutral pH because this reaction also relies on the formation of cellulose-O<sup>-</sup> nucleophiles. However, at a neutral pH, there is not a competing reaction with OH<sup>-</sup> nucleophiles which should theoretically increase the fixation of the CHPTAC when applied by pad baking methods. The premise would be to utilize a 1:1 NaOH:CHPTAC mole ratio with the idea

there is little to no OH<sup>-</sup> left to hydrolyze the epoxide which would allow a high temperature bake, fast throughput, continuous cationization process. Further, there should be little to no odor from this type of cationization process because there is no excess NaOH used. Finally, there would not be a need for neutralization, but a simple rinse may still be required. Some of the limitations of this type of concept are migration and front to back appearances from driving heat in the baking process. As a preliminary step to examine the possibility of neutral fixation, a bath containing 25 g/L of CR2000 and 6.91 g/L of 50% NaOH was prepared and the pH was adjusted to ~7.3. The solution was padded at 90% WPU (0.1088% nitrogen) and baked for 30 minutes at 105°C in a Despatch laboratory oven. The predicted percent nitrogen and fixation were 0.0532% nitrogen and 49% respectively. Although the parameters of this example would be highly unrealistic in an industrial application, these first tests did show that the technique may be a viable alternative cationization technique. Many experiments were carried out examining the neutralization of the initial application bath for a 1:1 ratio. In short, at sodium hydroxide ratios of 1:1 and even down to 0.5:1 ratios of NaOH:CHPTAC, the initial mixed bath pH is alkaline. When attempting to neutralize or adjust the pH of a solution of NaOH and CHPTAC, it becomes apparent that pH adjustment of solutions of NaOH and CHPTAC is not practical. Solutions of NaOH and CHPTAC exhibit very slow response to addition of acid and alkali and make pH adjustments unrealistic. Further, the pH of the initial NaOH and CHPTAC bath varies with time without any attempts at pH adjustment. Essentially, without a repeatable process or confident measurement of the pH of the bath, a neutral bake process cannot be easily

realized. However, through continual experimentation for a neutral bake process, it was found that increasing the alkali amounts beyond a 1:1 ratio and baking at high temperature, that very efficient cationization was realized, leading to the development of a pad bake process.

### **6.8 Pad Bake CHPTAC Application Process**

It was found that high temperatures and concentrations of sodium hydroxide in excess of a 1:1 NaOH:CHPTAC mole ratio readily yielded very high efficiency cationization of cellulose in a pad bake process. From the results found examining a neutral bake process where an increase in alkali at a high fixation temperature yielded better dye retention, Table 6.31 shows the results of an experimental design where time and temperature are the only variables with a fixed 90 second bake. These experiments utilized 50 g/L of CR2000 at a 90% wpu on bleached woven twill (0.218% nitrogen). The samples were padded and baked in a Mathis laboratory conveyor oven. *NOTE: F/B is the strength of the front of the fabric compared to the back of the fabric.*

Table 6.31 – CHPTAC Pad/Bake Experiments

| Sample | Temp. °C | NaOH:CHPTAC Concentration | K/S    | K/S sum | WI-CIE | Predicted %N | Predicted %Fix | F/B  |
|--------|----------|---------------------------|--------|---------|--------|--------------|----------------|------|
| 1      | 177      | 3 to 1                    | 26.127 | 407.8   | 6.24   | 0.189        | 86.6           | 86.0 |
| 2      | 129      | 1.6 to 1                  | 12.902 | 146.3   | 70.46  | 0.092        | 42.0           | 91.1 |
| 3      | 149      | 5 to 1                    | 26.776 | 421.4   | 63.38  | 0.194        | 88.9           | 92.1 |
| 4      | 121      | 3 to 1                    | 16.626 | 197.4   | 69.33  | 0.111        | 50.7           | 92.5 |
| 5      | 149      | 3 to 1                    | 25.338 | 369.3   | 63.82  | 0.175        | 80.0           | 91.3 |
| 6      | 149      | 1 to 1                    | 0.337  | 4.5     | 73.11  | 0.039        | 17.8           | 78.1 |
| 7      | 168      | 1.6 to 1                  | 25.840 | 384.8   | 55.89  | 0.180        | 82.7           | 87.3 |
| 8      | 129      | 4 to 1                    | 25.659 | 392.4   | 66.62  | 0.183        | 84.0           | 93.0 |
| 9      | 168      | 4 to 1                    | 26.812 | 419.9   | 43.24  | 0.193        | 88.7           | 90.8 |
| 10     | 149      | 3 to 1                    | 24.837 | 360.7   | 65.44  | 0.171        | 78.6           | 87.7 |
| 11     | 129      | 4.4 to 1                  | 25.652 | 373.1   | 69.47  | 0.176        | 80.7           | 93.4 |
| 12     | 168      | 4.4 to 1                  | 26.731 | 416.3   | 46.24  | 0.192        | 88.1           | 96.6 |

Statistical analysis of these results suggests that optimal whiteness and fixation can be obtained at 136°C at a 4.4:1 NaOH:CHPTAC mole ratio. However, some levelness and uniformity of treatment issues have been seen using this prediction. Table 6.31 shows that higher fixation values are obtainable with higher temperature and caustic values but that yellowing will result. Also, there are no apparent trends in the F/B levelness of the pad baked samples. However, as a result of the pad bake process, there are resultant “crossovers”, or whiter spots in dyed samples from lack of penetration of the CHPTAC. It should be noted though, that samples treated in a pad bake method do not exhibit ring dyeing as evidenced by microscopic investigation (see Appendix for comparison of CPB and Pad Bake treatments at 0.242% nitrogen applied and standard dyed). Because of the resultant crossovers in the treated pad bake samples, this phenomenon makes the prediction of percent nitrogen of these treated samples harder to determine because the

treatment is preferential and not uniform throughout. The standard dyeing and percent nitrogen model assume that the treatment and dyeing are uniform and equally representative throughout the sample. It should be noted that the crossovers could not be remedied even with high concentrations of alkaline stable penetrants. Simple qualitative tests of observing different cold pad batch and pad baked treatments showed that lower treatment levels of pad baked samples could clear dyebaths compared to higher treatment levels required for cold pad batch treated samples. For a quantitative evaluation however, the percent nitrogen determinations have to be relied upon more heavily than the percent nitrogen predictions. Table 6.32 shows data from Table 6.31 that has been simplified to show the different pad bake experiments with predicted and determined percent nitrogen values. As mentioned before, 0.218 %N was applied to all samples. PBO represents the optimized pad bake procedure for fixation and highest whiteness value. CPB represents a cold pad batch sample for reference.



Table 6.32 – CHPTAC Pad/Bake Percent Nitrogen Values

| Sample | Temp. °C | NaOH:CHPTAC Concentration | Predicted %N | Predicted % Fixation | %N Determined | % Fix Determined |
|--------|----------|---------------------------|--------------|----------------------|---------------|------------------|
| 1      | 177      | 3 to 1                    | 0.189        | 86.6                 | 0.161         | 73.9             |
| 2      | 129      | 1.6 to 1                  | 0.092        | 42.0                 | 0.073         | 33.5             |
| 3      | 149      | 5 to 1                    | 0.194        | 88.9                 | 0.191         | 87.6             |
| 4      | 121      | 3 to 1                    | 0.111        | 50.7                 | 0.089         | 40.8             |
| 5      | 149      | 3 to 1                    | 0.175        | 80.0                 | 0.148         | 67.9             |
| 6      | 149      | 1 to 1                    | 0.039        | 17.8                 | 0.054         | 24.8             |
| 7      | 168      | 1.6 to 1                  | 0.180        | 82.7                 | 0.137         | 62.8             |
| 8      | 129      | 4 to 1                    | 0.183        | 84.0                 | 0.140         | 64.2             |
| 9      | 168      | 4 to 1                    | 0.193        | 88.7                 | 0.174         | 79.8             |
| 10     | 149      | 3 to 1                    | 0.171        | 78.6                 | 0.146         | 67.0             |
| 11     | 129      | 4.4 to 1                  | 0.176        | 80.7                 | 0.128         | 58.7             |
| 12     | 168      | 4.4 to 1                  | 0.192        | 88.1                 | 0.177         | 81.2             |
| PBO    | 136      | 4.4 to 1                  | -            | -                    | 0.131         | 60.1             |
| CPB    | -        | 2 to 1                    | 0.128        | 58.7                 | 0.146         | 67.0             |

Utilizing the parameters for optimal whiteness and fixation, a 5% CR2000 pad bake process was used on bleached cotton interlock to assess the efficacy of an antimigrant in improving the front to back (F and B) levelness of a pad bake treatment. As Tables 6.33 and 6.34 show, an antimigrant can improve the F-B levelness but higher concentrations may reduce the fixation of the applied CHPTAC.

Table 6.33 - Effect of Antimigrant in Levelness of Pad/Bake Process

| Name    | Thermacol MP | K/S sum |
|---------|--------------|---------|
| PBMP1-F | 0            | 339.4   |
| PBMP1-B | 0            | 394.2   |
| PBMP2-F | 1 g/L F      | 356.1   |
| PBMP2-B | 1 g/L B      | 395.6   |
| PBMP3-F | 5 g/L F      | 350.8   |
| PBMP3-B | 5 g/L B      | 375.3   |
| PBMP4-F | 10 g/L F     | 310.5   |
| PBMP4-B | 10 g/L B     | 336.9   |

Table 6.34 - Effect of Antimigrant on Fixation in CHPTAC Pad/Bake Process

| Thermacol MP g/L | %N    | F/B  | %N applied | Predicted % Fix |
|------------------|-------|------|------------|-----------------|
| 0                | 0.174 | 86.1 | 0.242      | 71.8            |
| 1                | 0.177 | 90.0 | 0.242      | 73.2            |
| 5                | 0.172 | 93.5 | 0.242      | 71.2            |
| 10               | 0.158 | 92.2 | 0.242      | 65.1            |

### 6.9 Cold Pad Batch CHPTAC Cationization

Cold pad batch cationizations (CPB) have become the most efficient method of cotton cationization in industrial application. Therefore, any perceived improvements in cationization techniques must utilize a CPB control for comparisons. For the CPB method used here, a solution of sodium hydroxide and CR2000 is mixed at a 2:1 NaOH:CHPTAC mole ratio and padded on a lab padder and batched in a sealed bag for 24 hours unless otherwise noted. Table 6.35 shows results of CPB experiments. Also, because of the simplicity of the CPB method, the CPB method is very simple to model as shown in Figure 6.31 for a 120% WPU. This model can be used to figure out the treatment level of a desired final nitrogen content. Table 6.36 shows some examples demonstrating this concept on bleached cotton interlock.

Table 6.35 - CPB CHPTAC Treatments

| Comment       | CR2000 g/L | NaOH Ratio | % WPU | %N Applied | K/S sum | Predicted %N | Predicted % Fix |
|---------------|------------|------------|-------|------------|---------|--------------|-----------------|
| 24 hrs, twill | 10         | 2 to 1     | 89.0  | 0.043      | 18.2    | 0.044        | 101.9           |
| 24 hrs, twill | 50         | 2 to 1     | 89.0  | 0.215      | 245.0   | 0.128        | 59.6            |
| 24 hrs, twill | 100        | 2 to 1     | 89.0  | 0.430      | 379.7   | 0.178        | 41.4            |
| 24 hrs, knit  | 50         | 2 to 1     | 100.0 | 0.242      | 238.7   | 0.126        | 52.0            |
| 24 hrs, knit  | 100        | 2 to 1     | 120.0 | 0.581      | 366.3   | 0.173        | 29.9            |
| 24 hrs, knit  | 125        | 2 to 1     | 120.0 | 0.726      | 364.9   | 0.173        | 23.8            |
| 24 hrs, knit  | 150        | 2 to 1     | 120.0 | 0.871      | 391.3   | 0.183        | 21.0            |
| 24 hrs, knit  | 10         | 2 to 1     | 120.0 | 0.058      | 15.0    | 0.043        | 73.5            |
| 24 hrs, knit  | 50         | 2 to 1     | 120.0 | 0.290      | 247.1   | 0.129        | 44.4            |
| 24 hrs, knit  | 100        | 2 to 1     | 120.0 | 0.581      | 380.7   | 0.179        | 30.8            |
| 144 hrs, knit | 50         | 2 to 1     | 120.0 | 0.290      | 294.9   | 0.147        | 50.6            |
| 144 hrs, knit | 100        | 2 to 1     | 120.0 | 0.581      | 365.9   | 0.173        | 29.8            |

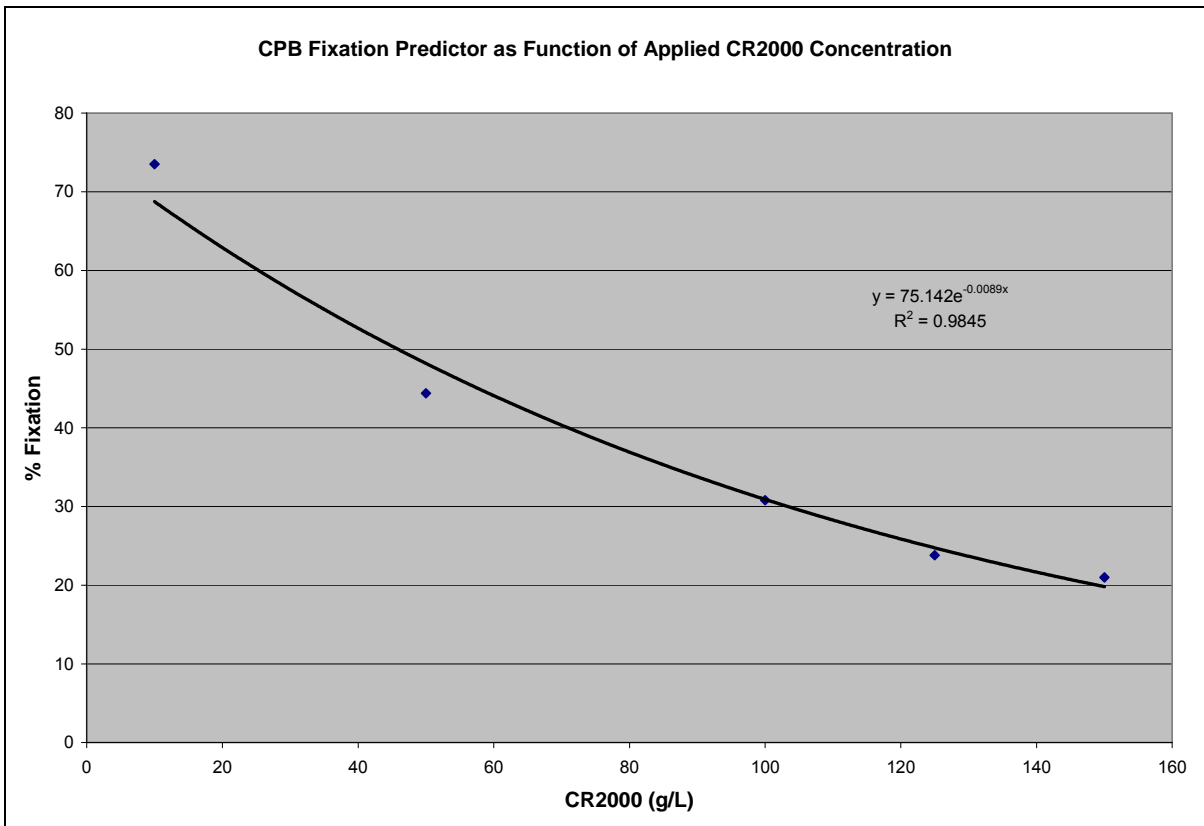


Figure 6.31 - CPB Fixation Prediction

Table 6.36 - Examples of Cold Pad Batch Fixation Prediction

| CR2000<br>g/L | Predicted<br>Fixation<br>from Model | Predicted<br>%N<br>from Model | Actual<br>Predicted %N | Actual Predicted<br>% Fixation |
|---------------|-------------------------------------|-------------------------------|------------------------|--------------------------------|
| 31.5          | 56.8                                | 0.104                         | 0.103                  | 56.4                           |
| 34.65         | 55.2                                | 0.111                         | 0.112                  | 55.5                           |

### 6.10 Foam

As a general trend in the cold pad batch method, lower WPU yielded higher fixation of the applied CHPTAC. This is presumed to be due to lower amounts of water in the application. An emerging, but not new chemical application technology is foaming. When chemistry is foam applied, air is incorporated into a surfactant and chemical solution creating a foam with very high surface area. Utilizing foam, very low WPU, typically 30% WPU, is easily achievable. Several cationization experiments were carried out to see if 1), is cationization by foaming possible, and 2), does lower WPU foaming increase cationization efficiency. Although several foam applications have been tried, the main point of focus is the simple 24 hour cold pad application compared to a 24 hour foam batch application of the same applied percent nitrogen. In this comparison, 0.242% nitrogen is applied to a standard twill fabric by foaming (30% WPU) and padding (100% WPU) on a bleached interlock and batched for 24 hours and then after neutralization standard dyed. The NaOH:CHPTAC mole ratio is 2:1 for the treatments. A Gaston County Lab Foamer was used for the foam application. 30 g/L of Unifroth 1672 was used as the foaming aid. The liquid flow was 0.130 L/min, the airblow ratio was 30:1, the mixer speed was 30%, and the range speed was set to 4.2 m/min. Table 6.37 gives the results of this comparison.

Table 6.37- Foam and Pad Batch Cationization Comparison

|      | %N Applied | %N Predicted | % Fixation Predicted |
|------|------------|--------------|----------------------|
| Foam | 0.242      | 0.126        | 52.1                 |
| Pad  | 0.242      | 0.126        | 52.1                 |

Although the substrates are different, Table 6.37 shows that from this experiment, foaming at a much lower WPU did not seem to have any beneficial effect compared to the higher WPU of the batch application. As mentioned previously, several different foam trials were conducted. Because of the scale and complexity and requirements of the actual foaming process, it is not possible or realistic to run designed experiments as can be done in similar lab applications as padding. However, the batch foam trial that was conducted showed that foaming is just as efficient as padding and that with further experimentation of different foaming aids and fixation techniques (batching, baking) that foam cationization processes may be viable. One important note is that foam baking techniques yielded much better performance in the crossover of yarns than equivalent pad baking cationization treatments. This is presumed to be due to the low WPU limiting migration and abundance of surfactant in the foam treatment.

## REFERENCES

1. Lewis, David M., et al. "Covalent Fixation of Reactive Dyes on Cotton under Neutral Conditions." AATCC Review. January 2008, p35.

## 7. Issues with Dyeing Cationic Cotton

### 7.1 Lightfastness

Traditionally, the lightfastness of cationized cotton has been questioned and has remained a “hanging chad” for cationization acceptance. Concern has been repeatedly expressed that cationized cotton will be ring dyed, resulting in losses of lightfastness. Although this statement may be true with different cationization reagents, especially polymeric cationic reagents that cannot readily diffuse, CHPTAC is a small, easily diffusible cationic reagent that when applied correctly, will not produce ring dyeings. Generally speaking however, even with CHPTAC, the level of treatment is very important for lightfastness (LF) of the dyed shade. The depth of shade desired should coincide with an amount of treatment that yields acceptable LF. If there is too much treatment however, the dye could strike and sit on the surface of the fiber instead of penetrating into the fiber because of the ready availability of dye sites. In this scenario, even if the cationization treatment is uniform throughout, in an extreme case it would be easy to achieve a ring dyed cationic fiber by using more treatment than needed for a light shade. To explore this concept, using bleached cotton interlock, an exhaust cationization was carried out at a liquor ratio of 5:1 using 15% CR2000 (30 g/L) and the recommended exhaust procedure. Similarly, a 5% CR2000 (50 g/L) cold pad batch treatment (0.242% nitrogen), 24 hour batch, was prepared. After the standard dyeing, the CPB treated sample possessed a predicted nitrogen of 0.1259%. The exhaust treated sample possessed a predicted nitrogen of 0.1040%. If the premise is correct that the treatment level is in excess compared to the amount actually needed for a shade and the

lightfastness will suffer, then a noticeable difference in lightfastness should be seen for these treatments. A control green shade was made from the formula seen in Table 7.1 and dyed at a 10:1 liquor ratio with the procedure seen in Table 7.2. The exhaust treated sample and the CPB sample were dyed with dye only at 60°C for one hour at a reduced dye amount to obtain the same depth as the control using the dye formula shown in Table 7.3. Table 7.4 shows the results of the dyeings. Table 7.5 shows the lightfastness results of the control sample, and the CPB and exhaust treated samples at 20 and 40 hours lightfastness.

Table 7.1 – Standard Green Dyeing Recipe

|                        |        |
|------------------------|--------|
| Novacron Yellow FN-2R  | 0.94%  |
| Novacron Red FN-R      | 0.05%  |
| Novacron Br. Blue FN-G | 0.52%  |
| Sodium Sulfate         | 40 g/L |
| Sodium Carbonate       | 12 g/L |

Table 7.2 – Standard Green Dyeing Procedure

|                           |
|---------------------------|
| Add dyes and salt at RT   |
| Heat at 2.0°C/min to 60°C |
| Hold 15 min               |
| Add soda ash over 15 min  |
| Hold 30 min               |
| Drop                      |
| Rinse                     |
| Soap                      |
| Dry                       |



Table 7.3 – Cationic Green Dyeing Recipe

|                        |         |
|------------------------|---------|
| Novacron Yellow FN-2R  | 0.7230% |
| Novacron Red FN-R      | 0.0188% |
| Novacron Br. Blue FN-G | 0.3010% |

Table 7.4 – Green Dyeing Results

| Dyed Untreated Cotton as Standard | DEcmc | % Strength | Final Dyebath |
|-----------------------------------|-------|------------|---------------|
| 50 g/L CPB                        | 1.81  | 106        | Clear         |
| 30 g/L Exhaust                    | 1.54  | 97         | Clear         |

Table 7.5 – Green Dyeing Lightfastness Results

| Dyeing  | 20 hr LF | 40 hr LF |
|---------|----------|----------|
| Control | 4        | 3.5      |
| Exhaust | 4.5      | 3.5      |
| CPB     | 3.5      | 3.5      |

The exhaust treated and CPB treatments cleared the applied dyestuffs, however the exhaust treated sample possessed a significantly lower amount of nitrogen. As can be seen from Table 7.5, the CPB LF was a whole unit lower than the exhaust treatment after 20 hours, representing the effect on LF of over cationization. The exhaust treated LF was better than the control LF at 20 hours illustrating that the LF of cationized cotton can be as good as or better than conventionally dyed cotton with appropriate treatment levels. It becomes apparent that the ability to determine the correct cationization treatment level will be important in dictating the final properties of dyed cationized cotton. This is a topic that will be addressed in Section 8.2

## 7.2 Time and Temperature Requirements

There are two basic dyeing methods to color cationized cotton. One method is to dye cationized cotton to a shade depth and hue where all dye applied is exhausted and the final dye bath is clear. In this method, leveling of the dyes may be a problem, but more sustainable benefits will be seen. An alternative dye method for cationized cotton is to apply more dye than a cationized fabric can handle. In this method, levelness of the treated fabric is much easier to achieve, but the shade is largely dictated by the treatment level and the fabric must be rinsed to remove unfixed dye. In method one, time and temperature are not as important a factor because the goal is to slow down the exhaustion of the dye to help levelness. In method 2, of greater concern are the optimum parameters, if any, for time and temperature to reach a plateau of dye exhaustion where the dyeing can be stopped. It should be reasonably expected if there are dyeability differences from time and temperature that the depth of shade and hue differences should be expected, but also LF differences. There are many types of fiber reactive dyes that are suitable for conventionally dyeing cotton. Although it would be virtually impossible to obtain and test all types of available reactive dyes for optimum time and temperature for application on cationized cotton, an experimental design that examines the extreme types of reactive dyes should draw reasonable conclusions about the types of dyes in between these extreme reactive dye types. Table 7.6 shows the design of a set of experiments using 50 g/L CR2000 cold pad batch treated towels to test the dye ability of two highly different dyestuffs, Procion MX and Drimarene X. Drimarene X (trichloropyrimidine) dyes Figure 7.1 represent some of the

hottest dyes applicable to cotton and Procion MX (dichlorotriazine) Figure 7.2 dyes represent the coolest most reactive dyes for cotton. For fiber reactive dyes applied to cotton, they are generalized by the required reaction temperature. These typically include cool dyes (~40°C), warm dyes (~60°C), and hot dyes (~70-90°C). In the case of forming covalent bonds in the conventional dyeing of cotton, the application temperature is needed to achieve suitable reactivity of the reactive group. The goal of these experiments is to see if the same application temperature is needed when the dyes are applied to cationized cotton and if time will increase shade depth when the dye is used in excess. A stock solution of 1.5 g/L of Procion Yellow MX-3R, Procion Red MX-5B, and Procion Blue MX-R was made up to 3 liters. 400 mL of the stock solution was transferred to Ahiba Texomat dye tubes and 20 gram samples of the towel were cut and placed in the dyetubes. Similarly, a stock solution of 1.5 g/L of Drimarene Yellow X4RN, Drimarene Red XGRN, and Drimarene Navy XNGN was made and utilized in the same manner. Table 7.7 shows the results of the Procion MX dyes. It is clear from the data that time and temperature is relatively unimportant for these cold dyeing dyestuffs. However, as Table 7.8 shows for the Drimarene X dyes, time and temperature are highly important for the final dyed shade and large variances can be expected with modification to the hold time and/or temperature.

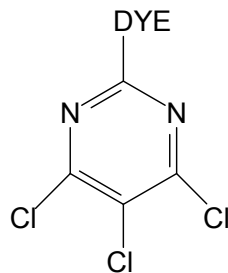


Figure 7.1 - Trichloropyrimidine Dyestuffs

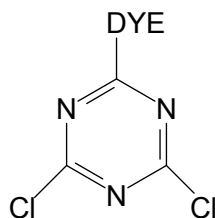


Figure 7.2 - Dichlorotriazine Dyestuffs

Table 7.6 – Dyeability Experiments

|             | Procion MX<br>41°C | Procion MX<br>93°C | Drimarene X<br>41°C | Drimarene X<br>93°C |
|-------------|--------------------|--------------------|---------------------|---------------------|
| 20 min hold | <b>1</b>           | <b>4</b>           | <b>7</b>            | <b>10</b>           |
| 40 min hold | <b>2</b>           | <b>5</b>           | <b>8</b>            | <b>11</b>           |
| 60 min hold | <b>3</b>           | <b>6</b>           | <b>9</b>            | <b>12</b>           |

Table 7.7 – Procion MX CPB Dyeability Results

| Name | L*    | a*    | B*    | C*    | h <sup>o</sup>      |           |
|------|-------|-------|-------|-------|---------------------|-----------|
| 1    | 25.83 | 19.19 | 3.75  | 19.56 | 11.06               |           |
| Name | DEcmc | L*    | A*    | b*    | K/S <sub>λMAX</sub> | %STRENGTH |
| 2    | 0.64  | 26.33 | 18.85 | 3.19  | 16.017              | 95.13     |
| 3    | 0.69  | 26.59 | 19.36 | 3.3   | 15.841              | 94.08     |
| 4    | 2.09  | 26.77 | 20.83 | 2.1   | 16.305              | 96.84     |
| 5    | 2.19  | 27.71 | 21.24 | 2.64  | 15.163              | 90.06     |
| 6    | 1.5   | 26.82 | 20.57 | 2.8   | 16.131              | 95.81     |

Table 7.8 – Drimarene X CPB Dyeability Results

| Name | L*    | a*    | b*     | C*    | h°                  |           |
|------|-------|-------|--------|-------|---------------------|-----------|
| 7    | 28.55 | 6.14  | -11.89 | 13.38 | 297.33              |           |
| Name | DEcmc | L*    | a*     | b*    | K/S <sub>λMAX</sub> | %STRENGTH |
| 8    | 1.65  | 26.12 | 5.96   | -11.2 | 12.568              | 116.88    |
| 9    | 3.17  | 24.76 | 5.72   | -9.37 | 13.963              | 129.85    |
| 10   | 12.51 | 22.42 | 10.45  | -2.51 | 18.308              | 170.26    |
| 11   | 14.3  | 20.82 | 10.45  | -1.09 | 21.103              | 196.25    |
| 12   | 14.59 | 21.22 | 10.77  | -0.9  | 20.386              | 189.59    |

To examine if the cationization treatment makes any difference in the observed dyeability, the same towel fabric was cationized by an exhaust treatment. 730 grams of towel were treated with 30 g/L of CR2000 (1.589% nitrogen) and 35 g/L of 50% NaOH at 70°C for 30 minutes utilizing an 8:1 liquor ratio. The same dyeing experiments as shown in Table 7.6 were repeated with the exhaust treated towel. Table 7.9 shows the results of the exhaust treated towel with Procion MX dyes. Table 7.10 shows the results of the exhaust treated towel with Drimarene X dyes. To a certain extent, similar results as seen with the CPB treated towel are seen with the exhaust treated towel. With the Procion MX dyes, at 41°C, there is minimal difference in strength although with more time, a slight increase in strength is seen. However, at 93°C, the strength is seen to build up to 40 minutes, but holding for 60 minutes resulted in noticeably decreased strength. The same increase in strength and decrease at 60 minutes is seen with the Drimarene X dyes on the exhaust treated towels at 93°C.

Table 7.9 - Procion MX Exhaust Dyeability Results

| Name | L*    | a*    | b*    | C*    | h°                  |           |
|------|-------|-------|-------|-------|---------------------|-----------|
| 1-2  | 35.88 | 22.69 | 4.23  | 23.08 | 10.57               |           |
|      |       |       |       |       |                     |           |
| Name | DEcmc | L*    | a*    | b*    | K/S <sub>λMAX</sub> | %STRENGTH |
| 2-2  | 0.67  | 34.71 | 22.63 | 4.05  | 8.849               | 109.54    |
| 3-2  | 1.16  | 35.31 | 23.91 | 3.35  | 8.705               | 107.76    |
| 4-2  | 2.46  | 34.19 | 23.6  | 1.78  | 9.469               | 117.21    |
| 5-2  | 3.2   | 32.29 | 22.79 | 1.38  | 10.8                | 133.69    |
| 6-2  | 1.9   | 35.04 | 23.01 | 2.17  | 8.637               | 106.92    |

Table 7.10 - Drimarene X Exhaust Dyeability Results

| Name | L*    | a*    | b*     | C*     | h°                  |           |
|------|-------|-------|--------|--------|---------------------|-----------|
| 7-2  | 32.89 | 5.14  | -11.27 | 12.39  | 294.54              |           |
|      |       |       |        |        |                     |           |
| Name | DEcmc | L*    | a*     | b*     | K/S <sub>λMAX</sub> | %STRENGTH |
| 8-2  | 0.49  | 32.27 | 5.43   | -11.55 | 7.776               | 101.98    |
| 9-2  | 2.65  | 31.04 | 6.11   | -9.27  | 8.586               | 112.59    |
| 10-2 | 11.32 | 26.81 | 9.35   | -3.35  | 12.461              | 163.41    |
| 11-2 | 14.01 | 26.31 | 10.89  | -1.85  | 13.369              | 175.32    |
| 12-2 | 14.91 | 28.32 | 11.62  | -1.2   | 11.506              | 150.89    |

### 7.3 Leveling Cationic Cotton Dyeings

When dyeing cationized cotton, anionic dyes, unless retarded, strike immediately on cationic cotton as compared to standard reactive dyeings where the dyes can migrate and level before striking with the addition of alkali. The immediate availability of cationic sites makes leveling cationized cotton very difficult. In contrast to dyeing nylon 6,6 for example where the dyesites available can be controlled with a variety of methods including pH adjustment through dosing and acid derivatives that supply acid as they break down, as well as slow temperature gradients that slow the availability of amorphous regions in the fiber,

cationic cotton dyesites are immediately available. In the case of cationic cotton, cellulose is a natural fiber, i.e. not thermoplastic and dyesites cannot be readily controlled through temperature. As well, the cationic site is permanent and cannot be controlled through pH manipulation in contrast to nylon. Levelness of cationic dyeings are not expected to be a problem with excess dye application because all dye sites are occupied. Conversely however, excess cationization results in a higher risk of unlevelness because there are more than needed dye sites. The correct amount of treatment for a shade lowers the risk of unlevelness by limiting excess dyesites. It is apparent that in order to level cationic dyeings where excessive dye is not applied will require a retarder to slow down the strike of the dye. One complication in developing and evaluating a retarder is the need to visually observe the retarding effect. As a starting point, two commercial dye retarders, Domolev PA-B (anionic) and Domolev H-CDB (cationic) were obtained from MDohmen. Five gram samples of cold pad batch treated cotton interlock with a predicted percent nitrogen of 0.071% nitrogen were cut and placed in small shaker baths. 2 g/L of Domolev PA-B was added to the bath at 10:1 liquor ratio and shaken for five minutes. A control sample with no Domolev was also observed with the retarder. After five minutes, 2 mL of 1.25 g/L of Novacron Red FN-R were added to the baths and heated and shaken to 60°C. With the Domolev PA-B, no visible difference in the slowing of dye strike could be seen by observing the depth of shade building on the fabrics. The same process was repeated with 3 g/L of Domolev H-CDB. Once again, no visible evidence of a slower dye strike could be observed while simultaneously observing the control sample with no dye retarder. On the premise

that commercial nylon retarders may not contain enough ions to fully retard cationic cotton, a sample of carboxymethyl cellulose (CMC) was obtained and evaluated in the same manner using 2 g/L of CMC. In this evaluation, dye retardance was visually evident compared to no CMC. Next, a bleached cotton interlock knit was treated with 100 g/L of CR2000 and 55 g/L of 50% NaOH and batched for 24 hours and contained a predicted percent nitrogen of 0.1783% nitrogen. Two ten gram samples of the highly cationized fabric were cut and placed in separate Ahiba Texomat beakers and filled with water to achieve a final liquor ratio of 22.5:1. In one beaker, 1.5% owg CMC was added. The two baths were heated to 60°C and the dye formula previously shown in Table 7.3 was added. The bath containing the fabric without CMC was cleared of dye in less than one minute. The bath containing the fabric with CMC took approximately eight minutes to clear, demonstrating the ability of CMC to retard applied dyestuffs. Figure 7.3 shows a picture of this comparison. The dyebath on the left contains the CMC and contains a noticeable amount of dye. The dyebath on the right contains no CMC and is cleared of any dye.





Figure 7.3 – Visual Observation of Effect of CMC (Left-with CMC, Right-no CMC)

Next, a cold pad batch treatment with much less nitrogen, 0.103% nitrogen predicted from a 33 g/L cold pad batch treatment using 18.3 g/L of 50% NaOH for 24 hours, was cut in to 10 gram samples. At a 25:1 liquor ratio, 1.5% owg CMC was added to one Texomat beaker and a control without CMC was run in a different Texomat beaker. The two baths were heated to 60°C where the dye formula shown in Table 7.3 was added. Without CMC, the dyebath was clear in 10 minutes as compared to 14 minutes with CMC. To observe if the

temperature of CMC addition made any difference, a cold pad batch treatment with 0.0925% nitrogen predicted from a 33 g/L cold pad batch treatment using 18.3 g/L of 50% NaOH for 24 hours, was cut in to 10 gram samples. Using the same 25:1 liquor ratio, the CMC was added at 30°C and held for 5 minutes and then the dye formula shown in Table 7.3 was added and the dye liquor was heated to 60°C at 2°C/min. Without CMC, the dyebath was clear at 18 minutes and with CMC the dyebath was clear at 19 minutes. This collective set of experiments clearly demonstrates the need for the appropriate amount of cationization for a dye shade as evidenced by the slowing in exhaustion with decreasing treatment amounts. As well, CMC is an effective retarder but only when the CMC is applied and allowed to bind with the cationic sites with time and temperature before the dye is applied. To serve as a more realistic test of the ability of CMC to retard and level cationic dyeings, 55 pounds of bleached tubular knit was padded at 120% WPU using 33 g/L CR2000 (0.1915% nitrogen) and 18.3 g/L of 50% NaOH and batched for 24 hours. The fabric was rinsed and neutralized at an 8:1 liquor ratio in a Fong's sample jet. The jet was filled for the 8:1 liquor ratio, 1.5% owg CMC was added and the liquor was heated to 60°C. The dye formula from Table 7.3 was added at a 70% curve over 20 minutes and the jet was held for 30 minutes. At the end of the dyeing, the dyebath was not clear but had a minimal amount of color. The fabric was level except for some areas of unlevelness and clear marks of no color caused by roping in the jet. From this trial it was apparent that dyeing cationic cotton will require a lubricant, especially in the case of cold pad batch treated goods. Further, even with excess dye in the bath, this method of dyeing will not ensure a level cationic

dyeing. To develop a combination of a leveling package for cationized cotton, experiments were conducted utilizing a textile lubricant, Marlube CMN, a textile dispersant, Marsperse 6000, and the dye retarder CMC. A bleached lightweight woven fabric was obtained that had been cold pad batch treated with 50 g/L of CR2000 and a predicted percent nitrogen of 0.0905% nitrogen. 900 grams of fabric was cut and added to a JFO laboratory dyeing machine with water to achieve a final liquor ratio of 8:1. At 60 inches wide, and approximately 18 feet long, the fabric is approximately 90 square feet of fabric in the machine. Although this is unrealistic of any practical dyeing application, this setup makes a very good test for the leveling ability of cationized fabric see Figure 7.4. In other words, if cationic cotton can be reasonably leveled in this extreme setup, then good levelness results would be expected in more typical dyeing setups.



Figure 7.4 – Demonstration of Setup of Leveling Experiments in JFO

After heating to 60°C, 0.3% each of Drimarene Yellow K-2RC2G, Drimarene Red K-4BL, and Drimarene Blue K-2RL (diflourochloropyrimidine dyes as shown in Figure 7.5) was added to the JFO over a 30 minute period. This process was repeated several times with different levels of the lubricant, dispersant, and CMC.

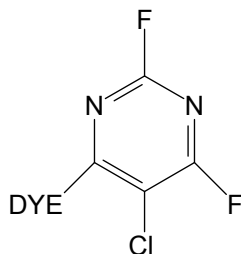


Figure 7.5 - Difluorochloropyrimidine Dyestuffs

Without any of the leveling combination, the dyebath was clear of dye at the end of the dye addition and possessed an assessed levelness of 9.24 DEcmc. With a combination of 3% CMC, 2% Marlube CMN, and 2% Marsperse 6000, the bath cleared approximately 15 minutes after the finish of the dye addition and possessed an assessed levelness of 0.68 DEcmc, a huge improvement in the levelness of the dyed fabric. Table 7.11 shows the experiments and resulting levelness of these experiments. For a conventional dyeing comparison, 40 g/L of sodium sulfate and 12 g/L of soda ash were used with the same dye amounts. For the conventional dyeing process, the salt was added and the bath was heated to 60°C, held for 15 minutes, the soda ash was added over 15 minutes and held for 30 minutes.

Table 7.11 – Assessed Levelness of Leveling Experiments

| <b>Dyeing</b>                         | <b>Levelness (DEcmc)</b> |
|---------------------------------------|--------------------------|
| Dye only                              | 9.14                     |
| 0.134% CMC, 0.16% disp., 0.107% lubr. | 4.25                     |
| 2% CMC, 1.17% disp., 1.17% lubr.      | 0.81                     |
| 3% CMC, 2% disp., 2% lubr.            | 0.68                     |
| <i>Conventionally Dyed</i>            | <i>0.19</i>              |

The combination of lubricant, dispersant, and CMC clearly showed the ability to produce improved levelness of cationized cotton dyeings and were used in the dyeings of the 55 pound loads presented in Chapter 9.

## 8. Making Cationization More Appealing

### 8.1 Anionic Softening Agents

While experimenting with the PTC reagents, an improved softened hand was noticed with the fabrics treated with sodium dodecyl sulfate. It was assumed that the alkyl tail could function as a hand modifier and remain permanently bound to the cationic site through ionic bonding with the sulfate head. Using a surfactant molecule as a hand modifier would certainly be a challenge because of the foaming nature of the surfactant but a fatty acid when neutralized could be an optimal candidate for a softener for cationized cotton. Further, in premise, the softener should remain permanent through ionic bonding. This also means that an appropriately applied fatty acid could be added at the end of an exhaust dyeing and utilized to near 100% efficiency, similar to a suitable anionic dyestuff. Three potential softener candidates, stearic acid sodium salt (mixture of stearic and palmitic fatty chain) 96%, linoleic acid (technical) 60%, and palmitic acid 98%, were obtained from Acros Organics. These structures are shown in Figures 8.1-8.3.

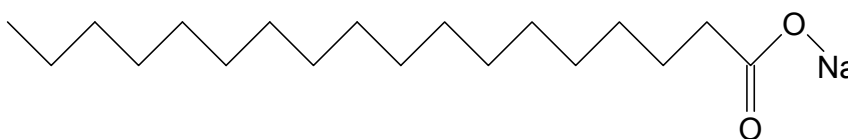


Figure 8.1 Sodium Stearate

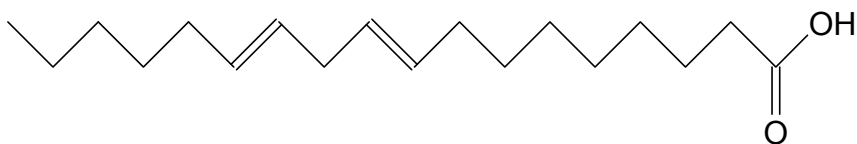


Figure 8.2 – Linoleic Acid



Figure 8.3 – Palmitic Acid

As Figures 8.1-8.3 show, stearic and palmitic acid are saturated fatty acids and are waxy solids. Linoleic acid is a liquid possessing two unsaturated double bonds in the alkyl chain. As a starting point, five gram samples of a highly cationized cotton interlock knit, 0.1783% nitrogen predicted, and another very low amount of cationization cotton interlock knit, 0.0439% nitrogen predicted were cut. The stearic acid as supplied is already neutralized to the sodium salt. A 10 g/L solution/dispersion was prepared by adding 0.5 grams of sodium stearate to 50 mL of water. The fabrics were added and heated to 46°C for 5 minutes and rinsed thoroughly. From these two treated samples and an untreated control, it was very easy for small hand panels to pick out the control untreated fabric as the harshest hand and the fabric with the higher amount of nitrogen as the softest or best hand. In order for these potential softeners to be utilized in true experiments however, they had to be emulsified first to make usable emulsions. 10 g/L solutions of each reagent were prepared in 1 L flasks



without filling to the 1 L mark. To the linoleic and palmitic acid, the appropriate amount of NaOH was added to neutralize 10 grams of the softener. Sodium dodecyl sulfate although not a very good emulsifier, was used to emulsify the waxes because if the sodium dodecyl sulfate became incorporated or bonded with the cationic sites on the cotton, its softening affect had already been observed. 0.5 g/L of sodium dodecyl sulfate was efficient in emulsifying/dispersing the already liquid linoleic acid. The palmitic and stearic acid required heating to 71°C, adding emulsifier, and flash cooling in an ice bath repeatedly until the wax was emulsified. The stearic acid required 19.5 g of sodium dodecyl sulfate to achieve a usable emulsion. The palmitic acid required 29.5 g of sodium dodecyl sulfate to form a usable emulsion. With emulsions of the three waxes, the experiments laid out in Table 8.1 were performed at a 10:1 liquor ratio by adding the amount of reagent required, heating to 60°C, and holding for 15 minutes. The fabric used for these experiments was the same 0.0439% nitrogen predicted used in the initial tests with stearic acid. After these samples were treated, small hand panels were asked to evaluate the samples for best hand and rank best to worst. These results are shown in Table 8.2.

Table 8.1 – Softener Experiments 1

| Sample # | Sodium Stearate | Linoleic Acid | Palmitic Acid |
|----------|-----------------|---------------|---------------|
| S1       | 0.50%           |               |               |
| S2       | 2%              |               |               |
| S3       | 5%              |               |               |
| S4       |                 | 0.50%         |               |
| S5       |                 | 2%            |               |
| S6       |                 | 5%            |               |
| S7       |                 |               | 0.50%         |
| S8       |                 |               | 2%            |
| S9       |                 |               | 5%            |

Table 8.2 – Results of Small Hand Panel 1

| Person 1 | Person 2 | Person 3 | Person 4 |
|----------|----------|----------|----------|
| s7       | s6       | s6       | s6       |
| s6       | s5       | s5       | s4       |
| s3       | s3       | s3       | s5       |
| s2       | s4       | s1       | s3       |
| s5       | s1       | s2       | s2       |
| s1       | s2       | s4       | s1       |
| s4       | s9       | s9       | s7       |
| s8       | s8       | s7       | s8       |
| s9       | s7       | s8       | s9       |

The results of the hand panel were used to weight and rank the samples such that the softest sample obtained nine points, and if the sample was rated worst it received one point. These results are seen in Table 8.3 where it can be seen that linoleic acid was the most preferred hand agent from this set of experiments.

Table 8.3 – Rank of Treated Samples in Hand Panel 1

| Rank            | Sample | Weighted Points |
|-----------------|--------|-----------------|
| 1 <sup>st</sup> | s6     | 35              |
| 2 <sup>nd</sup> | s5     | 28              |
| 3 <sup>rd</sup> | s3     | 27              |
| 4 <sup>th</sup> | s4     | 21              |
| 5 <sup>th</sup> | s2     | 20              |
| 6 <sup>th</sup> | s1     | 18              |
| 7 <sup>th</sup> | s7     | 15              |
| 8 <sup>th</sup> | s8     | 8               |
| 9 <sup>th</sup> | s9     | 7               |

In a second set of experiments seen in Table 8.4, the same amount of softening agent is used with the same liquor ratio and time and temperature as before but the fabric now is highly cationized. A 40% CR2000 exhaust treated bleached cotton interlock was prepared at a 6.5:1 liquor ratio using the optimized exhaust procedure with a final predicted percent nitrogen of 0.1523% nitrogen. The results of another small hand panel for these experiments are shown in Table 5.40. *Note: nd means that the person could not differentiate any difference between the samples. Sample s19 is a control untreated fabric. It should also be noted that the 0.5% owg of all three softening agents had clear final application baths.*

Table 8.4 – Softener Experiments 2

| Sample # | Sodium Stearate | Linoleic Acid | Palmitic Acid |
|----------|-----------------|---------------|---------------|
| S10      | 0.50%           |               |               |
| S11      | 2%              |               |               |
| S12      | 5%              |               |               |
| S13      |                 | 0.50%         |               |
| S14      |                 | 2%            |               |
| S15      |                 | 5%            |               |
| S16      |                 |               | 0.50%         |
| S17      |                 |               | 2%            |
| S18      |                 |               | 5%            |

Table 8.5 - Results of Small Hand Panel 2

| Person 1 | Person 2 | Person 3 | Person 4 |
|----------|----------|----------|----------|
| nd       | s18      | nd       | s11      |
| nd       | s11      | nd       | s18      |
| nd       | s17      | nd       | s17      |
| nd       | s14      | nd       | s16      |
| nd       | s15      | nd       | s12      |
| nd       | s16      | nd       | s13      |
| nd       | s12      | nd       | s10      |
| nd       | s10      | nd       | s14      |
| nd       | s13      | nd       | s15      |
| s19      | s19      | s19      | s19      |

Table 8.6 - Rank of Treated Samples in Hand Panel 2

| Rank             | Sample | Weighted Points |
|------------------|--------|-----------------|
| 1 <sup>st</sup>  | s11    | 31              |
| 2 <sup>nd</sup>  | s18    | 31              |
| 3 <sup>rd</sup>  | s17    | 28              |
| 4 <sup>th</sup>  | s16    | 24              |
| 5 <sup>th</sup>  | s12    | 22              |
| 6 <sup>th</sup>  | s14    | 22              |
| 7 <sup>th</sup>  | s15    | 20              |
| 8 <sup>th</sup>  | s10    | 19              |
| 9 <sup>th</sup>  | s13    | 19              |
| 10 <sup>th</sup> | s19    | 4               |

Tables 8.5-8.6 show that with a higher nitrogen level it is much harder to distinguish between different anionic softening agents as well as different amounts of those applied reagents.

## 8.2 Dye and Nitrogen Prediction for Cationized Cotton Total Formulation

The importance of appropriate cationization levels has been demonstrated especially for leveling dyeings of cationized cotton as well as achieving acceptable lightfastness. One way to obtain an appropriate treatment level for a dye shade is time consuming trial and error. A simpler way to determine the treatment level needed for a shade is if the percent nitrogen needed for a specified dye amount of a specified dye in a dye formula can be predicted. If the dye formula for cationized cotton can also be predicted simultaneously, the result would be an invaluable tool for industrial application. Most, if not all dye Houses and color labs possess and utilize color match software and spectrophotometers. These

applications and hardware allow a user to predict a match to a fabric swatch utilizing a specified dye set and substrate. Although this process is not guaranteed to give absolute matches, the process usually predicts a color that can be adjusted by a seasoned shade matcher to achieve a match in a few attempts. The software used for these purposes is Xrite's Color iControl along with an Xrite Color i7 benchtop spectrophotometer. Because the method of dyeing is different with conventional reactive dyeing as compared to dyeing cationized cotton, the same primaries and color shade predictions cannot be used interchangeably. In traditional reactive dyeings, the dyeing mechanism is exhaustion and covalent fixation of the applied reactive dye. In the dyeing of cationic cotton, the dyeing mechanism is a combination of almost simultaneous exhaustion and fixation. The fixation can be ionic as well as covalent if alkali is used in the dyeing. For the purpose of developing a color and nitrogen prediction scheme, the dyeing method is taken and assumed to be full exhaustion of the applied dye and ionic bonding only. With these assumptions, very good color predictions should be expected because all dye applied will be fixed and there are not blocking or hydrolysis effects that can alter the shade as seen in traditional fiber reactive dyeings. The first step in developing colorant primaries is to dye different percentages of single dyes on cationized cotton. Two cold pad batch treated samples of bleached cotton interlock were prepared at 50 g/L and 100 g/L with final predicted percent nitrogen of 0.129% nitrogen and 0.178% nitrogen respectively. These two cationized fabrics were used as shown in Table 8.7 for creating the primaries for color matching and relating the K/S sum to percent dye. To ensure levelness, the primaries were made by shaker bath at a 50:1

liquor ratio with gentle heating until the dyebath cleared. Tables 8.8-8.10 show the K/S sum obtained with the applied percent dye. Figures 8.4-8.6 show the graphs of these data and the linear fit of the K/S sum with applied percent dye.

Table 8.7 – Percent Dye and Substrates Used for Primary Dyeings

| % Dye | %N Predicted of Substrate Used |
|-------|--------------------------------|
| 0.10% | 0.129                          |
| 0.25% | 0.129                          |
| 0.50% | 0.129                          |
| 1%    | 0.129                          |
| 1.50% | 0.178                          |
| 2%    | 0.178                          |
| 3%    | 0.178                          |

Table 8.8 – K/S sum and Percent Dye for Novacron Blue FN-R

| Name           | K/S sum | % Dye |
|----------------|---------|-------|
| Nov. Blue FN-R | 13.8    | 0.1   |
| Nov. Blue FN-R | 14.0    | 0.1   |
| Nov. Blue FN-R | 32.4    | 0.25  |
| Nov. Blue FN-R | 31.6    | 0.25  |
| Nov. Blue FN-R | 61.2    | 0.5   |
| Nov. Blue FN-R | 59.3    | 0.5   |
| Nov. Blue FN-R | 134.5   | 1     |
| Nov. Blue FN-R | 133.4   | 1     |
| Nov. Blue FN-R | 206.6   | 1.5   |
| Nov. Blue FN-R | 202.0   | 1.5   |
| Nov. Blue FN-R | 277.0   | 2     |
| Nov. Blue FN-R | 271.3   | 2     |
| Nov. Blue FN-R | 398.4   | 3     |
| Nov. Blue FN-R | 387.2   | 3     |

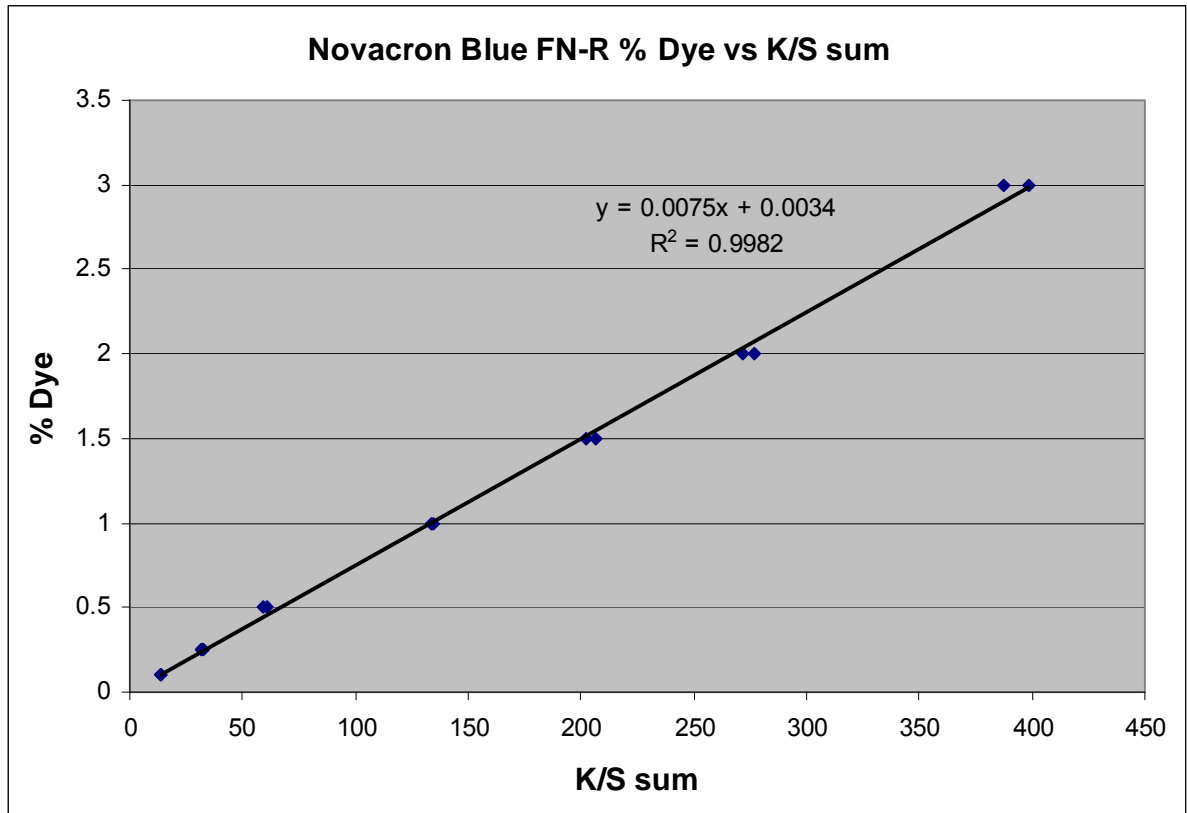


Figure 8.4 – Percent Dye vs K/S sum for Novacron Blue FN-R

Table 8.9 - K/S sum and Percent Dye for Novacron Yellow FN-2R

| Name              | K/S sum | % Dye |
|-------------------|---------|-------|
| Nov. Yellow FN-2R | 12.7    | 0.1   |
| Nov. Yellow FN-2R | 12.4    | 0.1   |
| Nov. Yellow FN-2R | 33.6    | 0.25  |
| Nov. Yellow FN-2R | 33.9    | 0.25  |
| Nov. Yellow FN-2R | 61.1    | 0.5   |
| Nov. Yellow FN-2R | 61.0    | 0.5   |
| Nov. Yellow FN-2R | 108.5   | 1     |
| Nov. Yellow FN-2R | 110.4   | 1     |
| Nov. Yellow FN-2R | 206.5   | 2     |
| Nov. Yellow FN-2R | 204.2   | 2     |
| Nov. Yellow FN-2R | 329.1   | 3     |
| Nov. Yellow FN-2R | 329.1   | 3     |



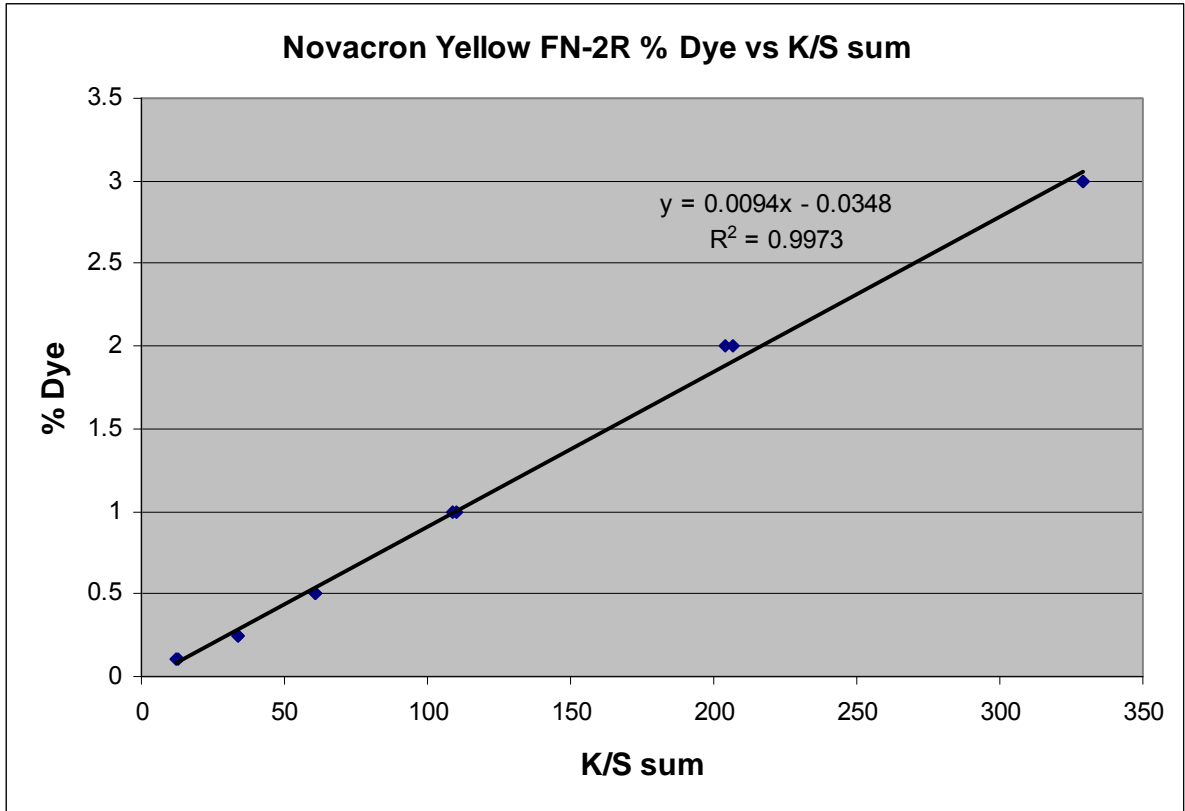


Figure 8.5 – Percent Dye vs K/S sum for Novacron Yellow FN-2R

Table 8.10 - K/S sum and Percent Dye for Novacron Red FN-R

| Name          | K/S sum | % Dye |
|---------------|---------|-------|
| Nov. Red FN-R | 13.2    | 0.1   |
| Nov. Red FN-R | 12.2    | 0.1   |
| Nov. Red FN-R | 24.3    | 0.25  |
| Nov. Red FN-R | 24.9    | 0.25  |
| Nov. Red FN-R | 47.0    | 0.5   |
| Nov. Red FN-R | 46.1    | 0.5   |
| Nov. Red FN-R | 124.4   | 1     |
| Nov. Red FN-R | 120.8   | 1     |
| Nov. Red FN-R | 162.3   | 1.5   |
| Nov. Red FN-R | 156.4   | 1.5   |
| Nov. Red FN-R | 267.8   | 3     |
| Nov. Red FN-R | 265.7   | 3     |

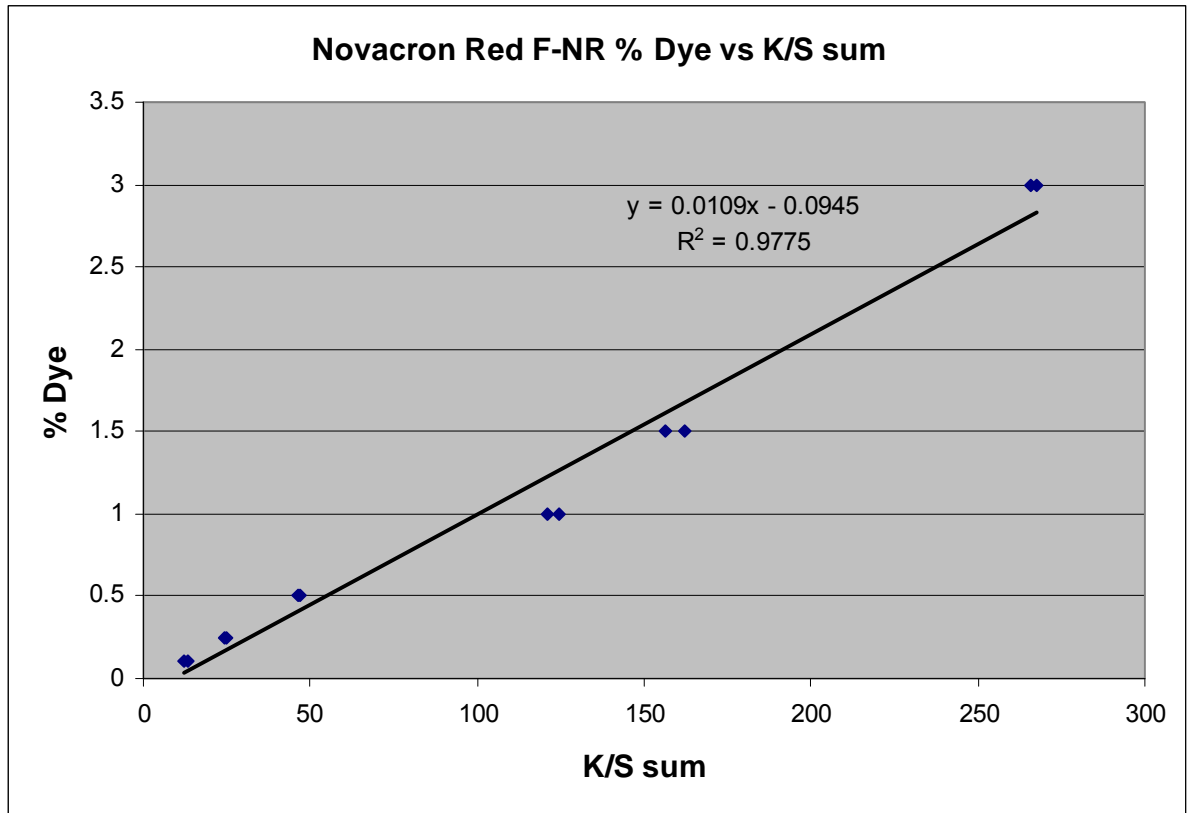


Figure 8.6 – Percent Dye vs K/S sum for Novacron Red FN-R

With models and equations relating the K/S sum and percent dye for each dye, models and equations are needed to relate the K/S sum to the percent nitrogen required for that K/S sum and percent dye as found in a dye formula. Along with the 50 g/L and 100 g/L CR2000 used in making the primaries, a 10 g/L CR2000 cold pad batch treated sample of bleached cotton interlock was prepared with a final predicted percent nitrogen of 0.0427 % nitrogen. These three treatments were saturated dyed with the three Novacron dyes using the standard dyeing procedure as previously described. The K/S sum obtained for each dye

with the different nitrogen levels are shown in Table 8.11. The percent nitrogen vs K/S sum for the three Novacron dyes are shown in Figures 8.7-8.9.

Table 8.11 – Percent Nitrogen and K/S sum Relationships for Primary Dyes

| Dye               | %N    | K/S sum |
|-------------------|-------|---------|
| Nov. Blue FN-R    | 0.043 | 22.647  |
| Nov. Blue FN-R    | 0.129 | 277.577 |
| Nov. Blue FN-R    | 0.178 | 461.39  |
| Nov. Yellow FN-2R | 0.043 | 26.579  |
| Nov. Yellow FN-2R | 0.129 | 265.887 |
| Nov. Yellow FN-2R | 0.178 | 363.756 |
| Nov. Red FN-R     | 0.043 | 15.016  |
| Nov. Red FN-R     | 0.129 | 244.287 |
| Nov. Red FN-R     | 0.178 | 372.479 |

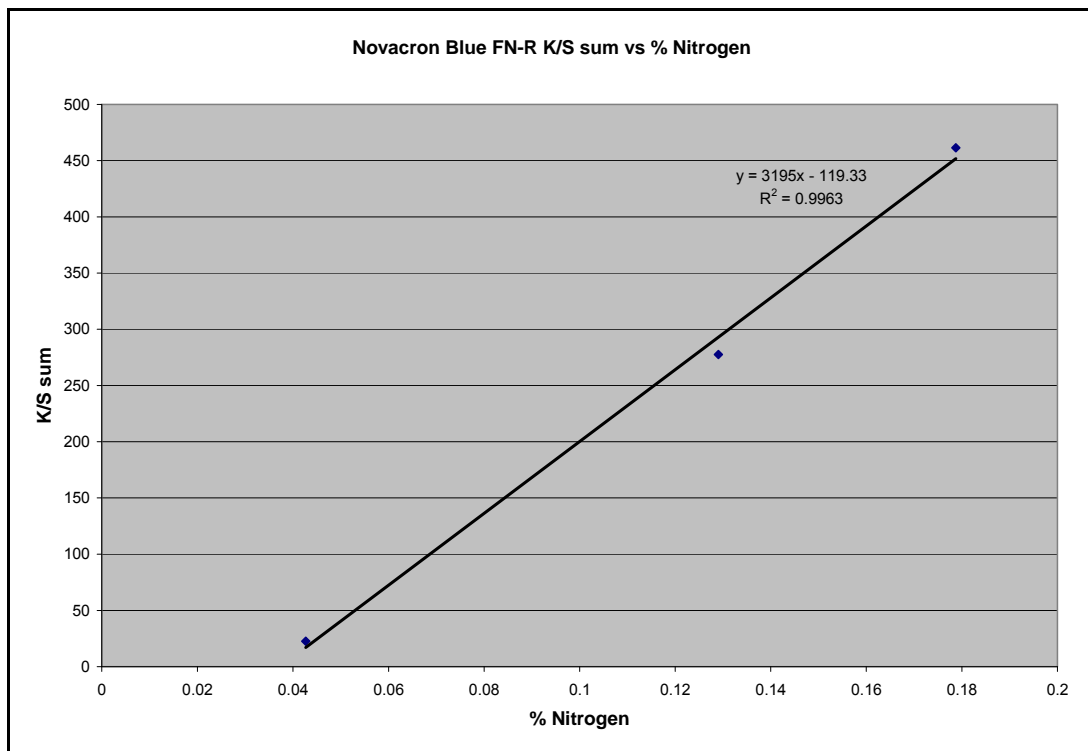


Figure 8.7 – Novacron Blue FN-R K/S sum vs Percent Nitrogen

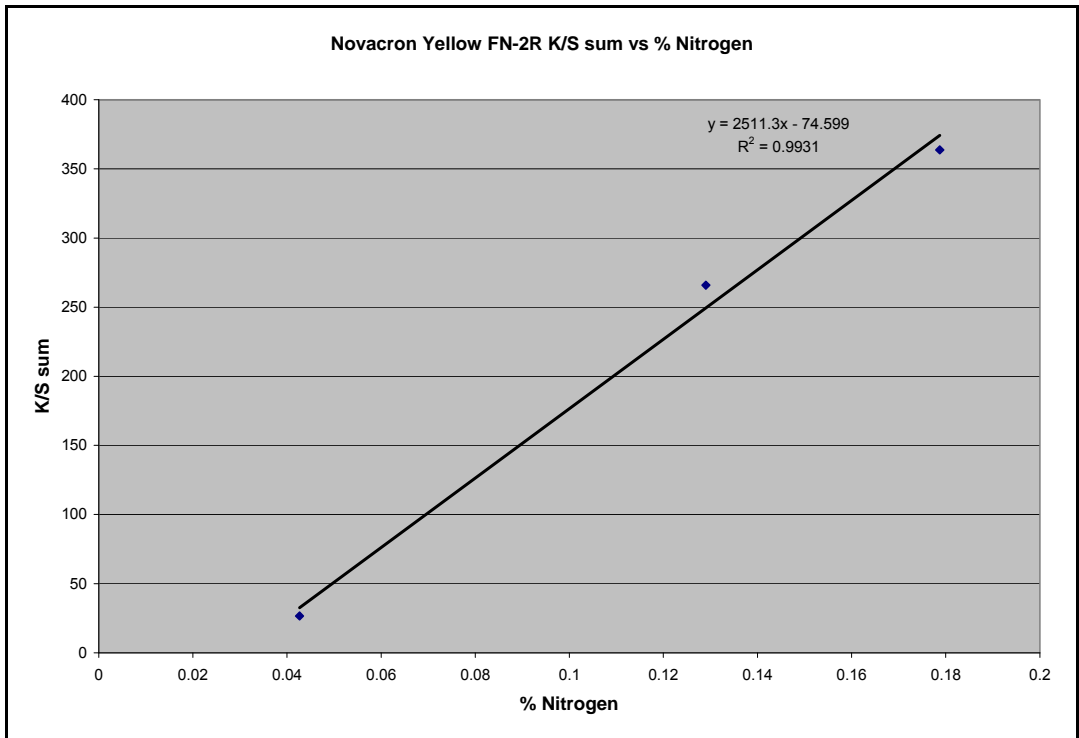


Figure 8.8 - Novacron Yellow FN-2R K/S sum vs Percent Nitrogen

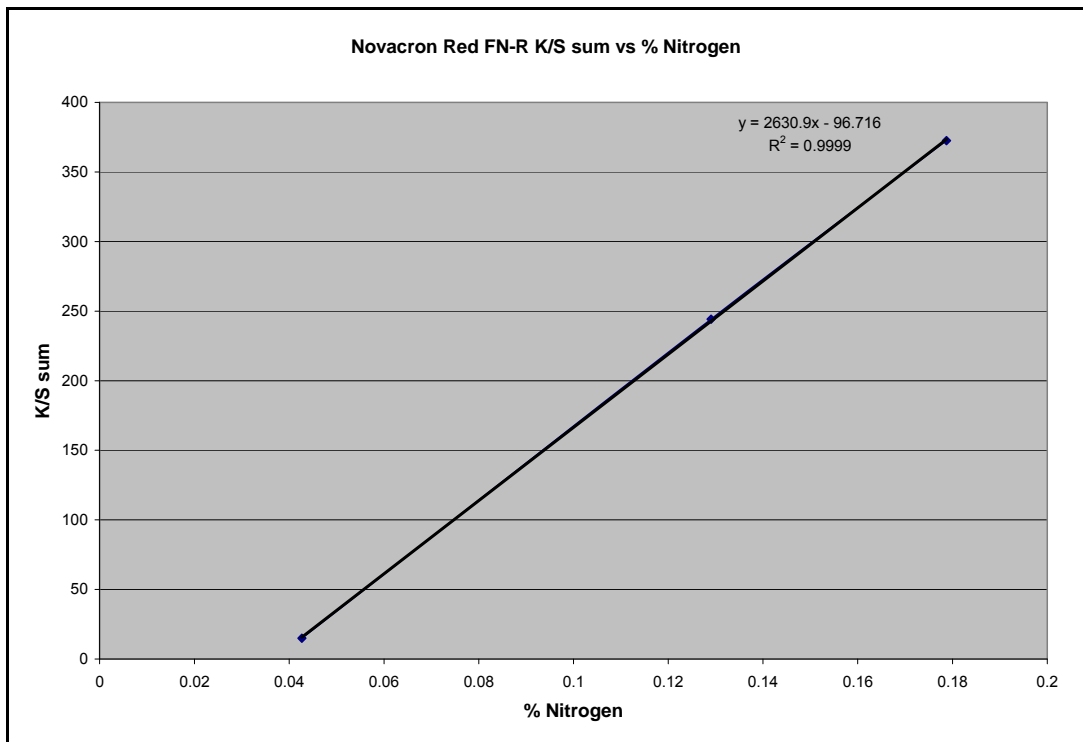


Figure 8.9 - Novacron Red FN-R K/S sum vs Percent Nitrogen

With equations and relationships relating the percent dye and K/S sum and the dyed cationic cotton primaries input into the color match software, it was possible to predict a formula for a shade and predict the required amount of percent nitrogen. When dyed, the final dyebath should become clear. After initial trials, it became clear rather quickly that the original percent nitrogen prediction causes inaccurate predictions in the level of treatment because the model used for predicting percent nitrogen did not go through zero percent nitrogen. In other words, no matter what percent dye was predicted to be used in a dyebath for cationic cotton, the same amount of nitrogen would always be added even if the formula used 0.01% dye or 1.00% dye. To remedy this, the original percent nitrogen prediction model was modified to pass through zero. Although the percent nitrogen of the control fabric was determined and predicted to be between 0.05-0.06% nitrogen, for purposes of zeroing the percent nitrogen model, 0.037% nitrogen is subtracted (the percent nitrogen predicted for no treatment) from the samples used to form the original percent nitrogen model and form the new model shown in Figure 8.10. As a result, new K/S sum vs percent nitrogen models are needed. These new models for K/S sum vs Zeroed Percent Nitrogen are shown in Figures 8.11-8.13. The same models for correlating the K/S sum with percent dye can still be used as they are not affected by changing the relationships in percent nitrogen and K/S sum.

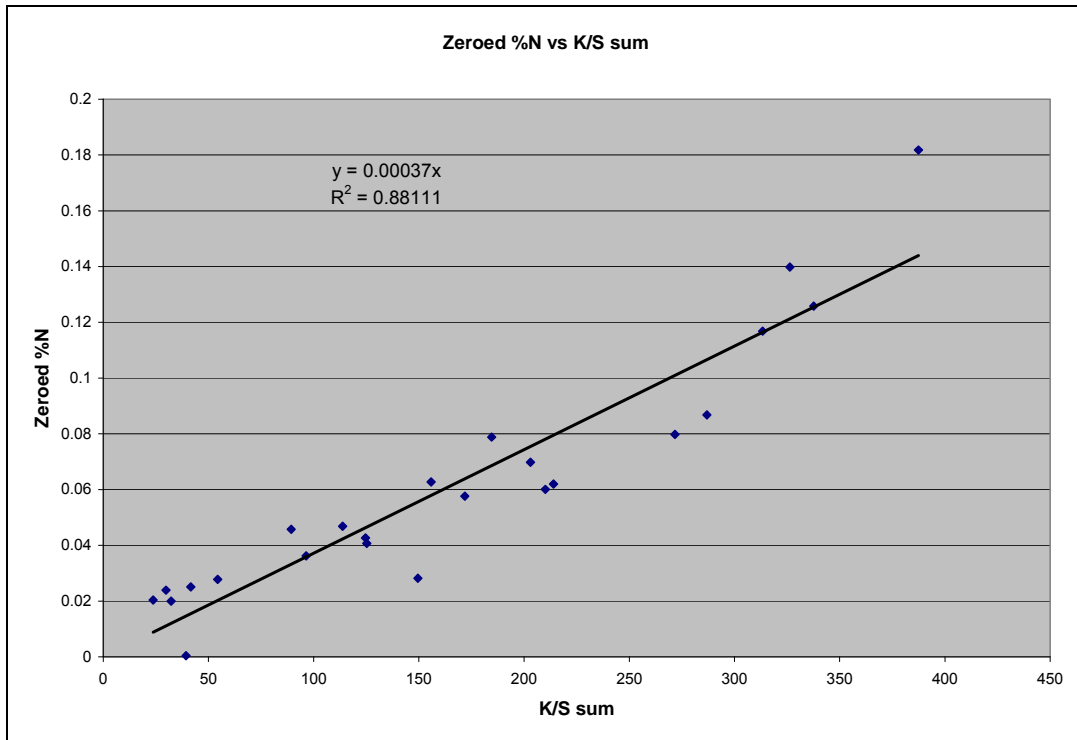


Figure 8.10 – Zeroed Percent Nitrogen vs K/S sum

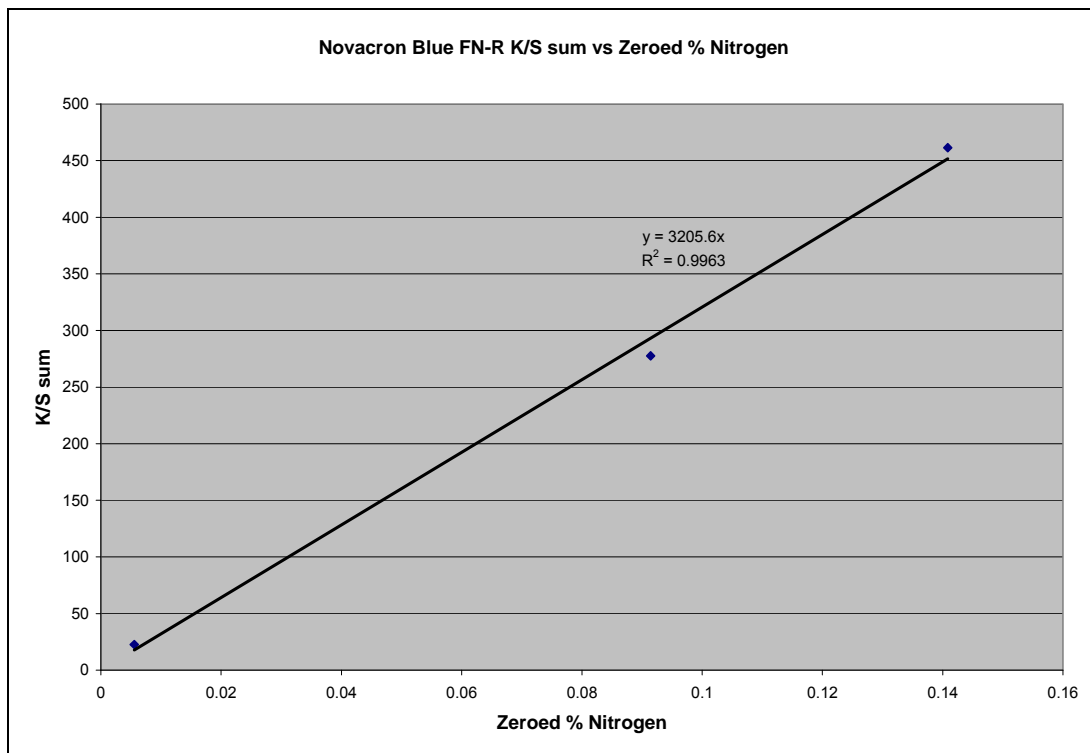


Figure 8.11 – Novacron Blue FN-R K/S sum vs Zeroed Percent Nitrogen

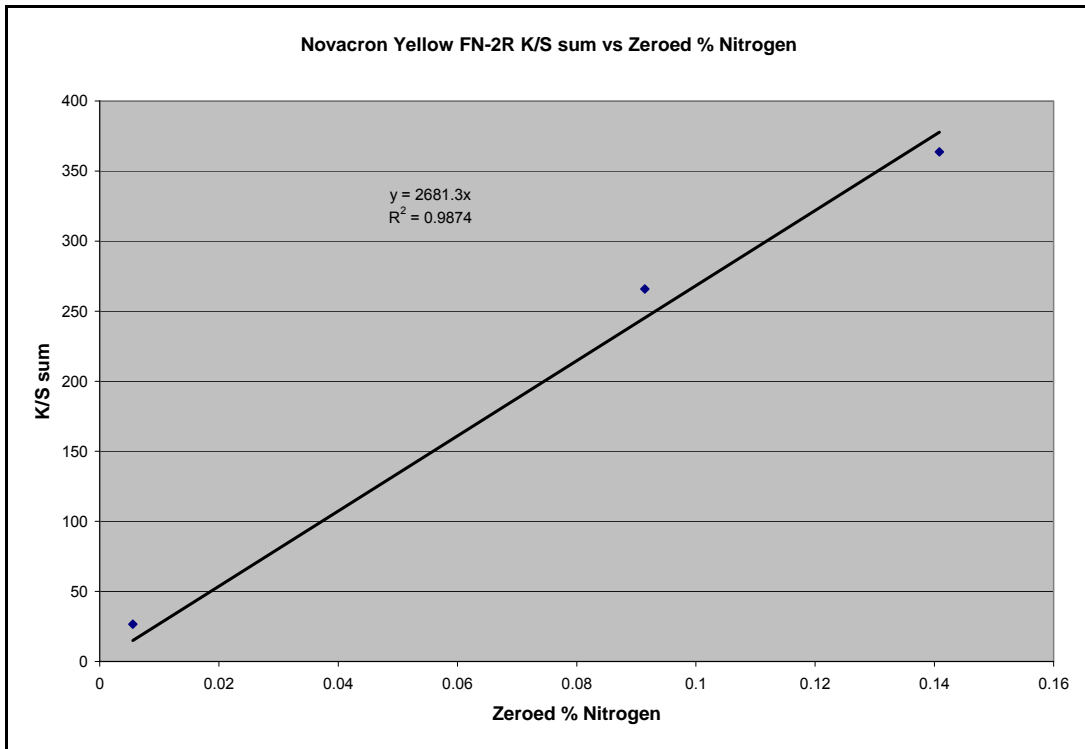


Figure 8.12 – Novacron Yellow FN-2R K/S sum vs Zeroed Percent Nitrogen

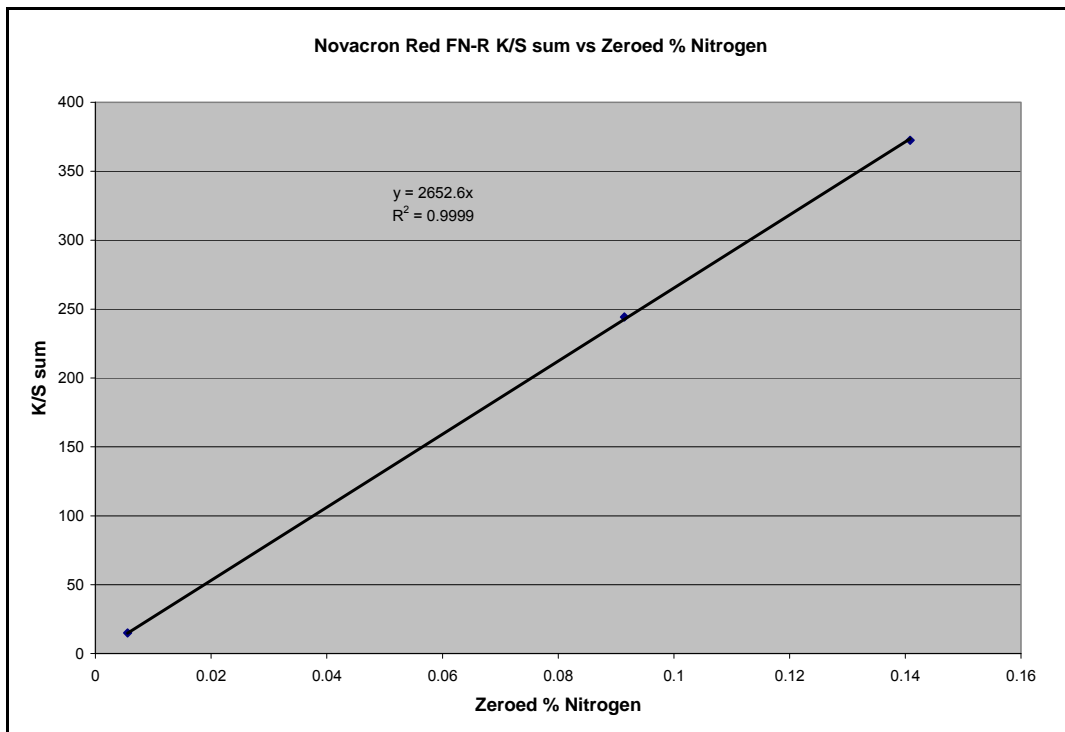


Figure 8.13 – Novacron Red FN-R K/S sum vs Zeroed Percent Nitrogen

Using the zeroed nitrogen model and new relationships for K/S sum and percent Nitrogen, the logic for determining the K/S sum for a predicted dye amount is shown below in Table 8.12. From a predicted color match dye formula on cationic cotton, the percentage of dye is turned into a predicted K/S sum utilizing the equation derived from the graph for a single dye relating the percent of dye and expected K/S sum. The predicted K/S sum is then turned into a predicted amount of zeroed percent nitrogen required to form that K/S sum utilizing the equation derived from the graph for a single dye relating the K/S sum and predicted amount of zeroed nitrogen required to obtain that K/S sum. Finally, the zeroed percent nitrogen for all three dyes is added up to form the required zeroed nitrogen level.

Table 8.12 - K/S sum Prediction Logic

|   |
|---|
| To determine K/S sum for Yellow, IF % Yellow=0, then K/S sum =0, if % Yellow is not = 0, then K/S sum = $(\% \text{ Yellow} + 0.0348) / 0.0094$ |
| To determine K/S sum for Red, IF % Red=0, then K/S sum =0, if % Red is not = 0, then K/S sum = $(\% \text{ Red} + 0.0945) / 0.0109$             |
| To determine K/S sum for Blue, IF % Blue=0, then K/S sum =0, if % Blue is not = 0, then K/S sum = $(\% \text{ Blue} - 0.0034) / 0.0075$         |

In order to predict the percent nitrogen from a predicted K/S sum for a given dye amount, the following logic is used as shown below in Table 8.13. For clarity, a flow chart depicting the color matching and percent nitrogen needed predictions processes is shown in the Appendix, Figure A3.



Table 8.13 - Percent Nitrogen Prediction Logic

|  |
|--|
| To determine the % nitrogen needed for Yellow, IF K/S sum =0, then % nitrogen needed =0, if K/S sum is not = 0, then % nitrogen = (K/S sum/2681) |
| To determine the % nitrogen needed for Red, IF K/S sum =0, then % nitrogen needed =0, if K/S sum is not = 0, then % nitrogen = (K/S sum/2652)    |
| To determine the % nitrogen needed for Blue, IF K/S sum =0, then % nitrogen needed =0, if K/S sum is not = 0, then % nitrogen = (K/S sum/3205)   |

## 8.2.1 Dye and Nitrogen Prediction Examples

### 8.2.1.1 Orange Shade

For simplicity, a conventional reactive orange shade was made up using two of the three dye primaries as shown in Table 8.14 and dyed on bleached cotton interlock by an all in procedure at 60°C for one hour at a 10:1 liquor ratio. A sample of the final dyebath was saved.

Table 8.14 – Conventional Orange Shade

|                   |        |
|-------------------|--------|
| Nov. Yellow FN-2R | 0.75%  |
| Nov. Red F-NR     | 0.20%  |
| Sodium Sulfate    | 35 g/L |
| Soda Ash          | 10 g/L |

From the conventionally dyed orange shade, a dye formulation prediction was made using the Color iControl software using the cationic cotton primaries. The amount of dye predicted to match the shade from Table 8.14 on cationized cotton is shown in Table 8.15. The corresponding zeroed percent nitrogen predicted required for this shade is shown in

Table 8.16. A previously treated sample of woven cotton was predicted to have a similar amount of percent nitrogen, 0.0318% zeroed nitrogen, and it was used with the formula in Table 8.15 and dyed with the same procedure for the conventional dyeing. A sample of this bath was saved as well. The color differences between the two dyed samples are shown in Table 8.17 and a picture of the final dyebaths are shown in Figure 8.14. As Figure 8.14 shows, the cationic cotton dyebath possesses much less dye than the conventional dyebath. As Table 8.17 showed, the strength of the conventional to the cationic sample is 102% with a DEcmc of nearly 3. The L\* and b\* numbers are very close for the standard and cationic sample, but the a\* number shows that the cationic sample is greener, presumably due to the inclusion of a small amount of blue that was not present in the conventional dyeing.

Table 8.15 – Cationic Cotton Orange Formula Prediction

|                   |         |
|-------------------|---------|
| Nov. Yellow FN-2R | 0.5160% |
| Nov. Red FN-R     | 0.1213% |
| Nov. Blue FN-R    | 0.0017% |

Table 8.16 – Percent Nitrogen Prediction for Cationic Cotton Orange Shade

| Dye               | % Dye  | K/S sum Predicted                       | %N Predicted  |
|-------------------|--------|---|---------------|
| Nov. Yellow FN-2R | 0.516  | 58.60                                   | 0.0219        |
| Nov. Red FN-R     | 0.1213 | 19.80                                   | 0.0075        |
| Nov. Blue FN-R    | 0.0017 | -0.23                                   | -0.0001       |
|                   |        |   |               |
|                   |        | <b>Total zeroed %N predicted needed</b> | <b>0.0292</b> |

Table 8.17 – Orange Color Comparisons

| Conventional Orange | L*    | a*    | b*   |       |            |
|---------------------|-------|-------|------|-------|------------|
|                     | 64.61 | 35.5  | 48.7 |       |            |
|                     |       |       |      |       |            |
|                     | DL*   | Da*   | Db*  | DEcmc | % Strength |
| Cationic Orange     | 0.13  | -3.04 | 0.89 | 2.96  | 101.8      |



Figure 8.14 - Final Dyebaths (L-R) Conventional and Cationic Orange Dyeings

### 8.2.1.2 Purple Shade

Similar to the orange shade, a purple shade was made up using two of the three primaries as shown in Table 8.18. The conventional purple shade was dyed using the same method as for the orange shades. After the purple shade was dyed, a color prediction was obtained using the Color iControl software as shown in Table 8.19. The corresponding percent zeroed nitrogen prediction for this purple shade on cationized cotton is shown in Table 8.20. As with the orange shade, a previously treated woven sample was found to have a

predicted percent nitrogen of 0.0204% zeroed nitrogen, the exact amount predicted needed. Table 8.21 compares the color differences between the two samples and Figure 8.15 shows a picture of the final dyebaths of the two samples. As Figure 8.15 shows, near complete exhaustion of the cationic cotton was achieved. Further, as Table 8.21 shows, the strength of the cationic sample compared to the conventional dyeing is 97% with a DEcmc of 1.66. These results clearly show the effectiveness of the color and nitrogen prediction methodology, but, the tool also needs to work for traditional three dye combinations and predicting dye formulations when the dye class used is not known or is different than the primary dyes.

Table 8.18– Conventional Purple Shade

|                |        |
|----------------|--------|
| Nov. Red FN-R  | 0.27%  |
| Nov. Blue FN-R | 0.41%  |
| Sodium Sulfate | 30 g/L |
| Soda Ash       | 9 g/L  |

Table 8.19 – Cationic Cotton Purple Formula Prediction

|                   |         |
|-------------------|---------|
| Nov. Yellow FN-2R | 0.0046% |
| Nov. Red FN-R     | 0.1296% |
| Nov. Blue FN-R    | 0.2703% |

Table 8.20 – Percent Nitrogen Prediction for Cationic Cotton Purple Shade

| Dye               | % Dye  | K/S sum Predicted                       | %N Predicted  |
|-------------------|--------|---|---------------|
| Nov. Yellow FN-2R | 0.0046 | 4.19                                    | 0.0016        |
| Nov. Red FN-R     | 0.1296 | 20.56                                   | 0.0078        |
| Nov. Blue FN-R    | 0.2703 | 35.59                                   | 0.0111        |
|                   |        |   |               |
|                   |        | <b>Total zeroed %N predicted needed</b> | <b>0.0204</b> |

Table 8.21 – Purple Color Comparisons

|                     |       |      |        |       |            |
|---------------------|-------|------|--------|-------|------------|
| Conventional Purple | L*    | a*   | b*     |       |            |
|                     | 49.98 | 8.96 | -25.87 |       |            |
|                     |       |      |        |       |            |
|                     | DL*   | Da*  | Db*    | DEcmc | % Strength |
| Cationic Purple     | 0.29  | 1.05 | 1.92   | 1.66  | 97.4       |



Figure 8.15 - Final Dyebaths (L-R) Conventional and Cationic Purple Dyeings

### 8.2.1.3 Additional Prediction Examples

Using a shade card with colors that had been conventionally dyed with reactive dyes on mercerized cotton, several shades were picked out that used the three primary dyes for coloration. From the swatch in the shade card book, matches were predicted using cationic cotton and the zeroed percent nitrogen needed for the shade was predicted. Table 8.22 shows the conventional formulas on mercerized cotton. Table 8.23 shows the cationic formulas for use on cationic cotton with the predicted amount of zeroed nitrogen needed

for the shade as well as the percent zeroed nitrogen actually used in the dyeing. After dyeing the cationic cotton at a 10:1 liquor ratio at 60°C for one hour, Tables 8.24-8.26 show the color differences for these samples compared to the conventional standard. Figure 8.16 shows a picture of the final dyebaths for these three shades on cationic cotton. It should be noted that when using mercerized yarn, much less dye is required as compared to non mercerized cotton. Therefore, there is not a noticeable reduction in dyestuffs required for cationized cotton. However, the intent of these experiments is to see if a conventionally dyed color can be matched onto cationic cotton, the amount of nitrogen needed can be predicted, and the final dyebath is nearly 100% exhausted. Indeed, as Figure 8.16 shows, in each cationic dyeing, nearly complete exhaustion was realized while obtaining DEcmc values of 1.5-3.2. Although the strengths of the cationic dyeings are significantly less than the controls, this is attributed to the use of mercerized cotton in the controls.

Table 8.22 – Conventional Color Forecast Formulas on Mercerized Yarn

|                   | Savannah | Cocoon | Silver Crest |
|-------------------|----------|--------|--------------|
| Nov. Yellow FN-2R | 1.50%    | 0.41%  | 0.086%       |
| Nov. Red FN-R     |          | 0.36%  | 0.1%         |
| Nov. Red FN-3G    | 0.05%    |        |              |
| Nov. Blue FN-R    | 0.40%    | 0.27%  | 0.225%       |
| Sodium Sulfate    | 55 g/L   | 50 g/L | 30 g/L       |
| Soda Ash          | 13 g/L   | 12 g/L | 8 g/L        |

Table 8.23 – Cationic Cotton Prediction Formulas for Color Forecast Shades

|                     | Savannah | Cocoon  | Silver Crest |
|---------------------|----------|---------|--------------|
| Nov. Yellow FN-2R   | 1.9677%  | 0.4541% | 0.1066%      |
| Nov. Red FN-R       | 0.0852%  | 0.3082% | 0.1015%      |
| Nov. Blue FN-R      | 0.3367%  | 0.2231% | 0.2159%      |
| Predicted Zeroed %N | 0.0995   | 0.0425  | 0.0212       |
| Zeroed %N Used      | 0.1091   | 0.0487  | 0.0212       |

Table 8.24 – Savannah Color Differences

| Savannah          | L*    | a*   | b*    |       |            |
|-------------------|-------|------|-------|-------|------------|
|                   | 40.91 | 2.35 | 33.64 |       |            |
|                   |       |      |       |       |            |
|                   | DL*   | Da*  | Db*   | DEcmc | % Strength |
| Cationic Savannah | 3.18  | 2.48 | 3.19  | 2.9   | 87.8       |

Table 8.25 - Cocoon Color Differences

| Cocoon          | L*    | a*    | b*    |       |            |
|-----------------|-------|-------|-------|-------|------------|
|                 | 42.39 | 10.69 | 12.45 |       |            |
|                 |       |       |       |       |            |
|                 | DL*   | Da*   | Db*   | DEcmc | % Strength |
| Cationic Cocoon | 1.92  | 0.59  | 1.39  | 1.55  | 90.5       |

Table 8.26 - Silver Crest Color Differences

| Silver Crest          | L*    | a*   | b*    |       |            |
|-----------------------|-------|------|-------|-------|------------|
|                       | 51.15 | 1.20 | -4.39 |       |            |
|                       |       |      |       |       |            |
|                       | DL*   | Da*  | Db*   | DEcmc | % Strength |
| Cationic Silver Crest | 3.34  | -1.5 | 1.82  | 3.17  | 82.2       |

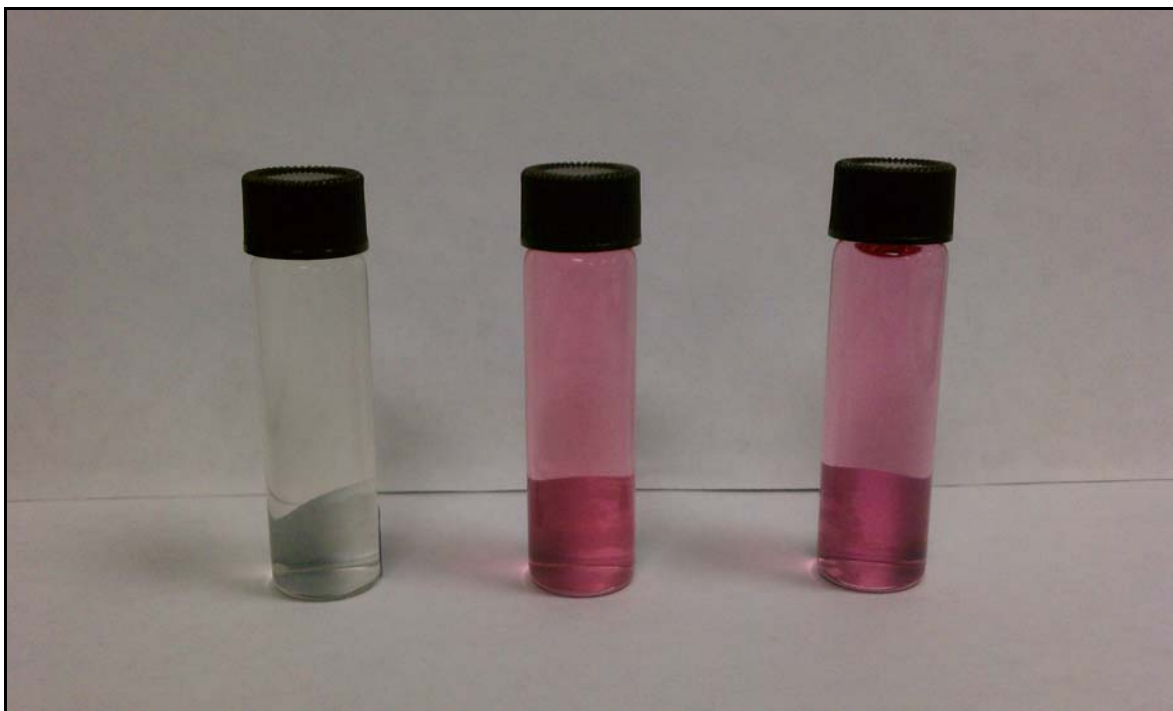


Figure 8.16 - Final Dyebaths (L-R) for Savannah, Cocoon, and Silver Crest on Cationic Cotton

As a final test, one of the shades from the color forecast that was not formulated with the three primary dyes was selected. The formula for this conventionally dyed shade is shown in Table 8.27. The predicted formula for the shade on cationic cotton, the predicted zeroed percent nitrogen for the shade, and the actual predicted zeroed percent nitrogen used to make the shade are shown in Table 8.28. The color difference for the cationized sample compared to the conventionally dyed is shown in Table 8.29. A picture of the final dyebath for the cationized cotton marzipan is shown in Figure 8.17. As Figure 8.17 shows, very good exhaustion was obtained and only a small amount of red dye is visibly left. This example is interesting because the control dyeing utilized vinyl sulfone dyes at 3.5% owg while the cationic cotton utilized only 2.39% owg of Novacron FN dyes. Previous examples showed



that because of the use of mercerized cotton, the cationic cotton dyeings did not show decreases in the amount of dye used. However, with vinyl sulfone dyes on mercerized cotton, the cationic cotton sample matched with Novacron FN dyes shows a significant reduction in dyestuffs even though the standard was on mercerized cotton. This preliminarily suggests that it may be possible to save significant amounts of dye by switching from conventionally dyed vinyl sulfone cotton to cationic cotton dyed with Novacron FN dyes. This would need to be evaluated with many shades to be proven.

Table 8.27 - Color Formula for Marzipan on Mercerized Yarn

|                    |          |
|--------------------|----------|
|                    | Marzipan |
| Rem. G. Yellow RGB | 1.80%    |
| Rem. Red RGB       | 1.70%    |
| Rem. Navy RGB      | 0.029%   |
| Sodium Sulfate     | 40 g/L   |
| Soda Ash           | 13 g/L   |

Table 8.28 Cationic Cotton Prediction Formula for Marzipan

|                     |          |
|---------------------|----------|
|                     | Marzipan |
| Nov. Yellow FN-2R   | 1.9677%  |
| Nov. Red FN-R       | 0.0852%  |
| Nov. Blue FN-R      | 0.3367%  |
| Predicted Zeroed %N | 0.0646   |
| Zeroed %N Used      | 0.0665   |

Table 8.29 - Marzipan Color Differences

|                   |       |       |       |       |            |
|-------------------|-------|-------|-------|-------|------------|
| Marzipan          | L*    | a*    | b*    |       |            |
|                   | 42.92 | 42.64 | 25.71 |       |            |
|                   |       |       |       |       |            |
|                   | DL*   | Da*   | Db*   | DEcmc | % Strength |
| Cationic Marzipan | 1.77  | -4.34 | 1.89  | 3.25  | 88.5       |



Figure 8.17 - Final Dyebath for Marzipan on Cationic Cotton

## 9. Bulk Scale Cationization and Dyeing

### 9.1 Costing

55 pound sample lots of a traditional fiber reactive dyeing, and an exhaust cationized and cold pad batch cationized cotton were prepared and dyed for the same depth of shade and color. The total costs of dyes, chemicals, auxiliaries, and consumables were used to get a single cost per pound for each total process. These results are presented in the tables below. The dyeings were carried out in a Fongs sample jet at an 8:1 liquor ratio. The exhaust treated cationic sample was treated in the same jet at the same liquor ratio. The cold pad batch sample was padded at 120% WPU and batched 24 hours before loading into the jet. The cationized samples were neutralized in the jet prior to dyeing. See Appendix for complete jet processing procedures for bleaching, neutralization, cationization, and dyeing and rinsing. The fabric used was a lightweight tubular cotton knit that was bleached before cationization and slit in the case for the cold pad batch. Cost numbers shown are for pound of fabric. Table 9.1 shows the chemical costs for bleaching. The bleaching cost is the same for each lot. Table 9.2 shows the cationization treatment costs for cold pad batch and exhaust applications. Table 9.3 shows the standard dyeing cost. Table 9.4 shows the cationic dyeing cost. Table 9.5 shows the consumables used during the processes. Table 9.6 shows process consumables used per pound of fabric. Table 9.7 shows the estimated consumable costs used. Table 9.8 shows the process consumable costs per pound of fabric. Table 9.9 shows the total cost of each lot from bleach to dyeing. *Note: the costs of*

consumables will vary with location in the world. These values were estimated from private correspondences and presentations for an average value.

Table 9.1 – Bleach Cost

| Bleach                            | g/L                | Grams | Price  |
|-----------------------------------|--------------------|-------|--------|
| Sultafon D                        | 2                  | 400   | 2.0264 |
| Marlube CMN                       | 1                  | 200   | 0.3656 |
| Marsperse 6000                    | 1                  | 200   | 0.5815 |
| Marquest PB                       | 1                  | 200   | 0.4626 |
| 50% NaOH                          | 4                  | 800   | 1.7741 |
| 35% H <sub>2</sub> O <sub>2</sub> | 4                  | 800   | 1.6308 |
| 56% Acetic                        | 1                  | 100   | 0.1872 |
|                                   |                    |       |        |
| <b>Bleach/lb</b>                  | <b>\$0.1278/lb</b> |       |        |

Table 9.2 - Cationization Treatment Costs

| CPB-Treat           |                    | Grams    | Price   |
|---------------------|--------------------|----------|---------|
|                     |                    | 40L (g)  |         |
| CR2000              | 36 g/L             | 1440     | 3.9648  |
| 50% NaOH            | 19.9 g/L           | 776      | 1.7209  |
|                     |                    |          |         |
| EXH-Treat           |                    |          |         |
|                     |                    | 200L (g) |         |
| CR2000              | 16.5%              | 4125     | 11.3574 |
| 50% NaOH            | 2 to 1             | 2281     | 5.0577  |
|                     |                    |          |         |
| Neutralization      |                    |          |         |
| EXH Acetic          | 1 g/L              | 200      | 0.3745  |
| CPB Acetic          | 0.75 g/L           | 150      | 0.2809  |
|                     |                    |          |         |
| <b>CPB treat/lb</b> | <b>\$0.1085/lb</b> |          |         |
| <b>EXH treat/lb</b> | <b>\$0.3053/lb</b> |          |         |

Table 9.3 – Standard Dyeing Cost

| Dyeing STD           |                    | Grams | Price  |
|----------------------|--------------------|-------|--------|
| Nov. Yellow FN2R     | 0.94%              | 235   | 4.5551 |
| Nov. Red FN-R        | 0.05%              | 13    | 0.2327 |
| Nov. Br. Blue FN-G   | 0.52%              | 130   | 6.7491 |
| Sodium sulfate       | 40 g/L             | 8000  | 7.8537 |
| Soda ash             | 12 g/L             | 2400  | 2.4026 |
|                      |                    |       |        |
| Marsperse 6000       | 1.5 g/L            | 300   | 0.8722 |
| Marlube CMN          | 1 g/L              | 200   | 0.3656 |
|                      |                    |       |        |
| <b>STD dyeing/lb</b> | <b>\$0.4187/lb</b> |       |        |

Table 9.4 – Cationic Dyeing Cost

| Dyeing CAT           |                    | Grams | Price  |
|----------------------|--------------------|-------|--------|
| Nov. Yellow FN2R     | 0.708%             | 177.0 | 3.4308 |
| Nov. Red FN-R        | 0.018%             | 4.5   | 0.0838 |
| Nov. Br. Blue FN-G   | 0.286%             | 71.5  | 3.7120 |
|                      |                    |       |        |
| Marsperse 6000       | 1.5 g/L            | 300   | 0.8722 |
| Marlube CMN          | 1 g/L              | 200   | 0.3656 |
| CMC                  | 1%                 | 250   | 2.4229 |
|                      |                    |       |        |
| <b>CAT dyeing/lb</b> | <b>\$0.1980/lb</b> |       |        |

Table 9.5 – Consumables Used During 55 Pound Processes

|                       | Time (mins) | Water Used (L) | Steam Used (lbs) | Power Used (KWH) |
|-----------------------|-------------|----------------|------------------|------------------|
| Standard              | 193         | 5111           | 102              | 12               |
| Pad Batch Application | 1595        | 3831           | 48               | 9                |
| Exhaust Application   | 240         | 3432           | 132              | 14               |
| Bleach                | 174         | 12340          | 749              | 12               |

Table 9.6 – Process Consumables Used Per Pound of Fabric

|                       | Time (mins)/lb | Water (L)/lb | Steam (lb)/lb | Power (KWH)/lb |
|-----------------------|----------------|--------------|---------------|----------------|
| Standard              | 3.51           | 92.9         | 1.85          | 0.22           |
| Pad Batch Application | 29.00          | 69.7         | 0.87          | 0.16           |
| Exhaust Application   | 4.36           | 62.4         | 2.41          | 0.25           |
| Bleach                | 3.16           | 224.36       | 13.63         | 0.22           |

Table 9.7 – Estimated Consumable Costs

|             |              |
|-------------|--------------|
| Steam       | 0.0418 \$/lb |
| Water       | 0.00027 \$/L |
| Waste Water | 0.0004 \$/L  |
| Electricity | 0.15 \$/KWH  |

Table 9.8 – Consumable Costs Per 55 Pound Process

|                       |        |
|-----------------------|--------|
|                       | \$/lb  |
| Standard              | 0.1724 |
| Pad Batch Application | 0.1076 |
| Exhaust Application   | 0.1806 |
| Bleach                | 0.2123 |

Table 9.9 – Total Processing Cost

|                               |               |
|-------------------------------|---------------|
| <b>Total Cost</b>             | <b>\$/lb</b>  |
| <b>Standard</b>               | <b>0.9312</b> |
| <b>Exhaust Treated</b>        | <b>1.0238</b> |
| <b>Cold Pad Batch Treated</b> | <b>0.7541</b> |

## 9.2 Quality Control

In order to validate the environmental and financial savings found in Section 9.1, quality control tests for dyed cationized cotton must perform as well as conventional fiber reactive dyed cotton. Typical color assessment quality control tests were conducted on the three 55 pound sample lots. The results of these QC tests are shown in Tables 9.10-9.15. In general, for every QC test except change of color, the dyed cationic cotton exhibited equivalent or increased performance. Figures 9.1-9.4 show the absorbance spectra of the fabric, ending dyebaths, and pictures of the final dyebaths.

Table 9.10 - Color Properties of 55 Pound Lots

| STD | L*    | a*     | b*    |       |            |
|-----|-------|--------|-------|-------|------------|
|     | 46.91 | -13.82 | 24.17 |       |            |
|     |       |        |       |       |            |
|     | DL*   | Da*    | Db*   | DEcmc | % Strength |
| EXH | 0.64  | -0.23  | 1.1   | 0.67  | 97.4       |
| CPB | -1.37 | -0.43  | 1.64  | 1.11  | 114        |

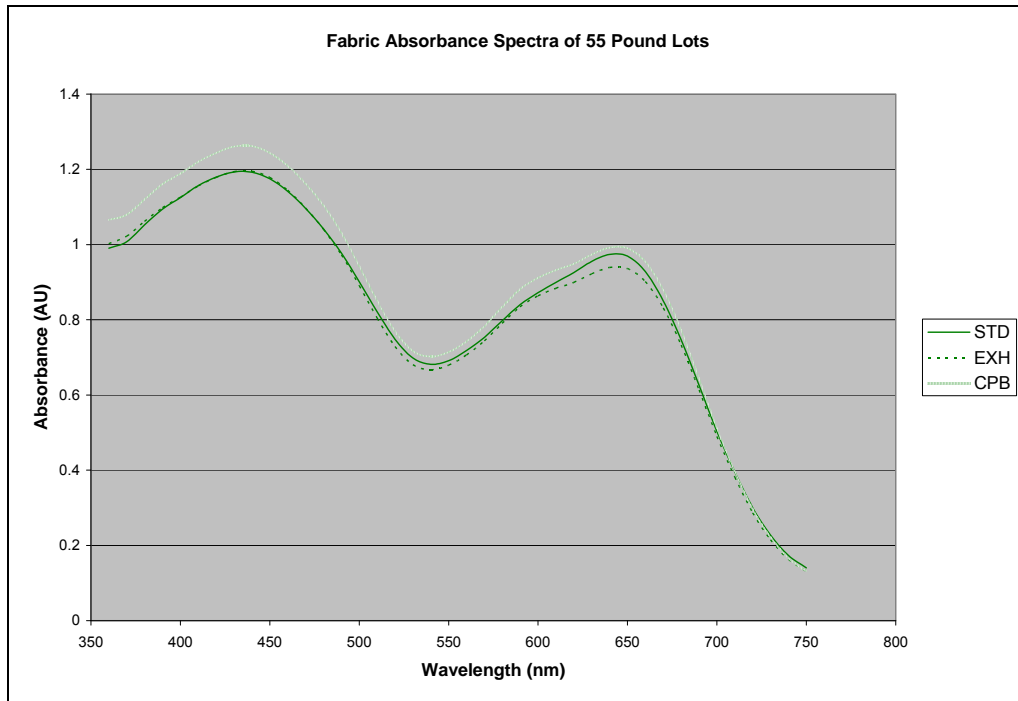


Figure 9.1 - Fabric Absorbance Spectra of 55 Pound Lots

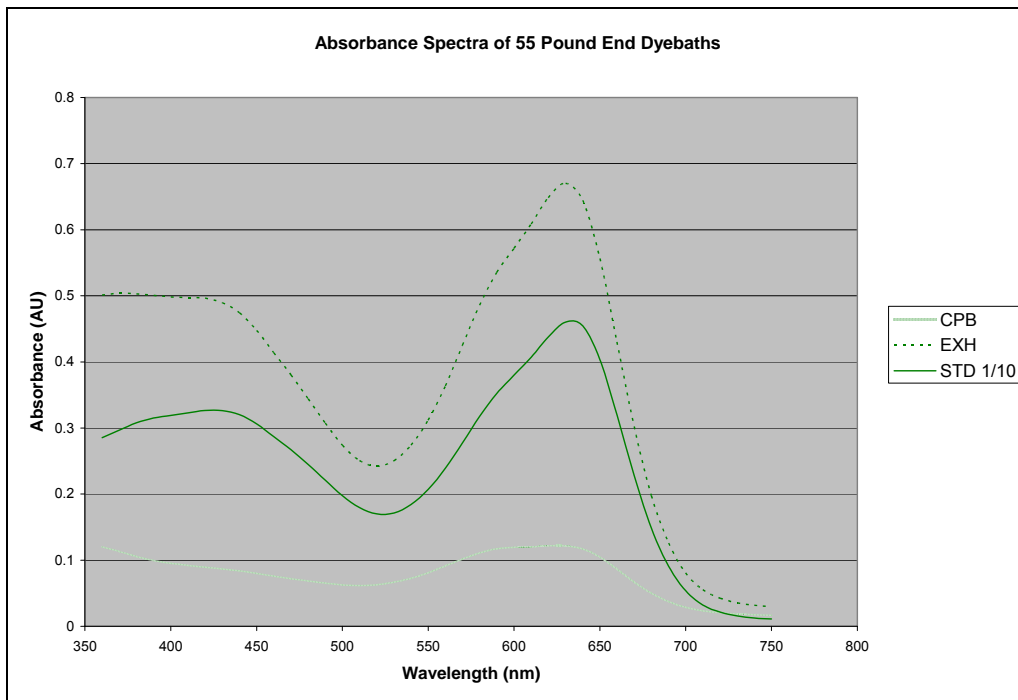


Figure 9.2 - Absorbance Spectra of 55 Pound End Dyebaths, 1/10<sup>th</sup> Standard



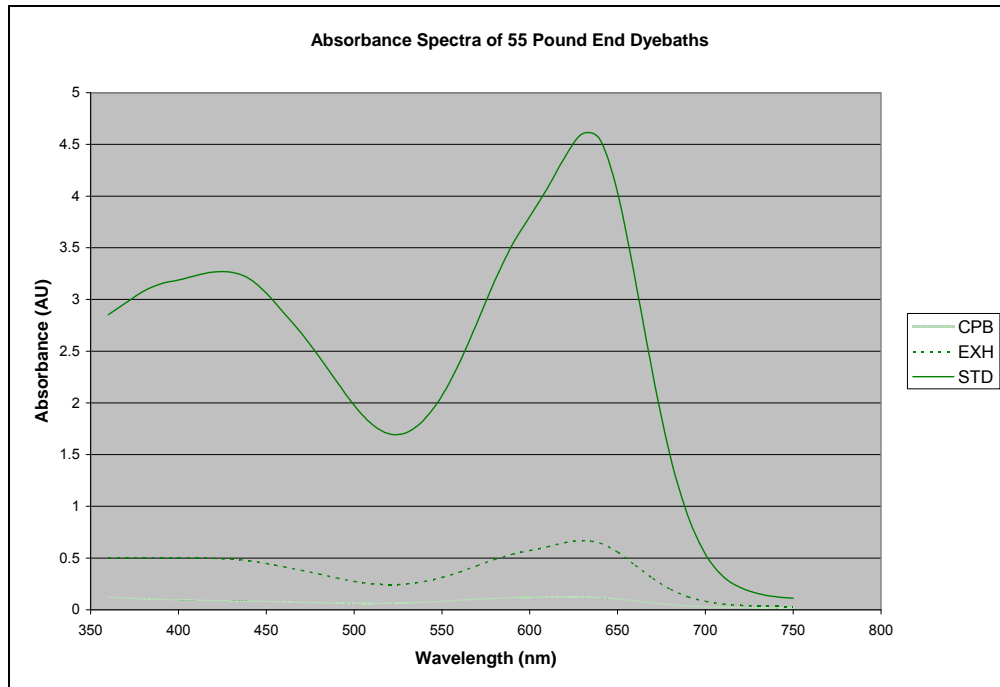


Figure 9.3 - Absorbance Spectra of 55 Pound End Dyebaths

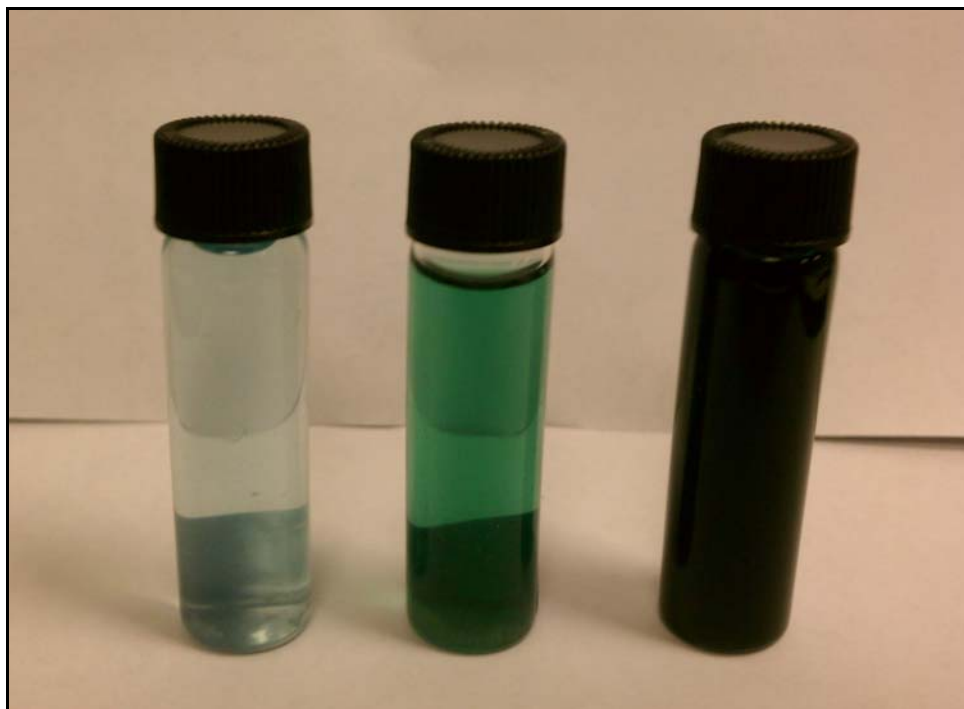


Figure 9.4 - Picture of Final Ending Dyebaths of 55 Pound (L-R) CPB, Exhaust, Standard

Table 9.11 - Assessed Levelness of 55 Pound Lots

| 55 lb. Lot | Levelness (DEcmc) |
|------------|-------------------|
| CPB        | 0.27              |
| EXH        | 0.21              |
| STD        | 0.12              |

Table 9.12 - Crocking and Lightfastness of 55 Pound Lots

|     | Wet | Dry | 20 hr LF | 40 hr LF |
|-----|-----|-----|----------|----------|
| CPB | 4.5 | 5   | 5        | 4.5      |
| STD | 4   | 4.5 | 4.5      | 4.5      |
| EXH | 4.5 | 5   | 5        | 4.5      |

Table 9.13 - Staining from IIA Wash Tests of 55 Pound Lots

|     | IIA Cotton | IIA Nylon | IIA Polyester |
|-----|------------|-----------|---------------|
| CPB | 3.5        | 3.5       | 3.5           |
| STD | 3.5        | 3         | 3             |
| EXH | 3          | 3         | 3.5           |

Table 9.14- Staining from Cold Water Bleed Tests of 55 Pound Lots

|     | Cold Water Bleed Cotton | Cold Water Bleed Nylon | Cold Water Bleed Polyester |
|-----|-------------------------|------------------------|----------------------------|
| CPB | 4                       | 4.5                    | 4.5                        |
| STD | 4.5                     | 4                      | 4.5                        |
| EXH | 4.5                     | 4                      | 4.5                        |

Table 9.15 - Change of Color Results of 55 Pound Lots

|     | CoC IIA | CoC 5X Wash |
|-----|---------|-------------|
| CPB | 4       | 4           |
| STD | 4.5     | 5           |
| EXH | 3.5     | 3.5         |

### 9.3 Change of Color

The dyed cationic cotton lots exhibited failures in color fastness when exposed to laundering yet excelled in fastness testing such as crocking. If unfixed dye or surface dye were a problem and showed up in laundering, then fastness issues in crocking would be expected but were not observed. If dyed cationic cotton loses color when washed as the IIA and CoC laundering demonstrate, then the environmental and financial savings found in Section 9.1 are essentially meaningless because the quality of the dyed cationic cotton does not measure up to conventionally dyed cotton. To investigate the change of color, it was noted that the laundering tests utilize a standard alkaline detergent. Five gram samples of the dyed exhaust treated cationic samples were cut and placed in 100 mL of distilled water. In one bath, 0.25 g of soda ash was added. In a second bath 1 g of AATCC liquid detergent was added. In a third bath, no additive was included. The baths were brought to a boil for 10 minutes. With distilled water only, no dye was removed suggesting that there was not evidence of any unfixed dye. With soda ash a significant amount of dye was removed. With the detergent, a noticeable amount of dye was also removed. A picture of the baths after these experiments is shown in Figure 9.5.

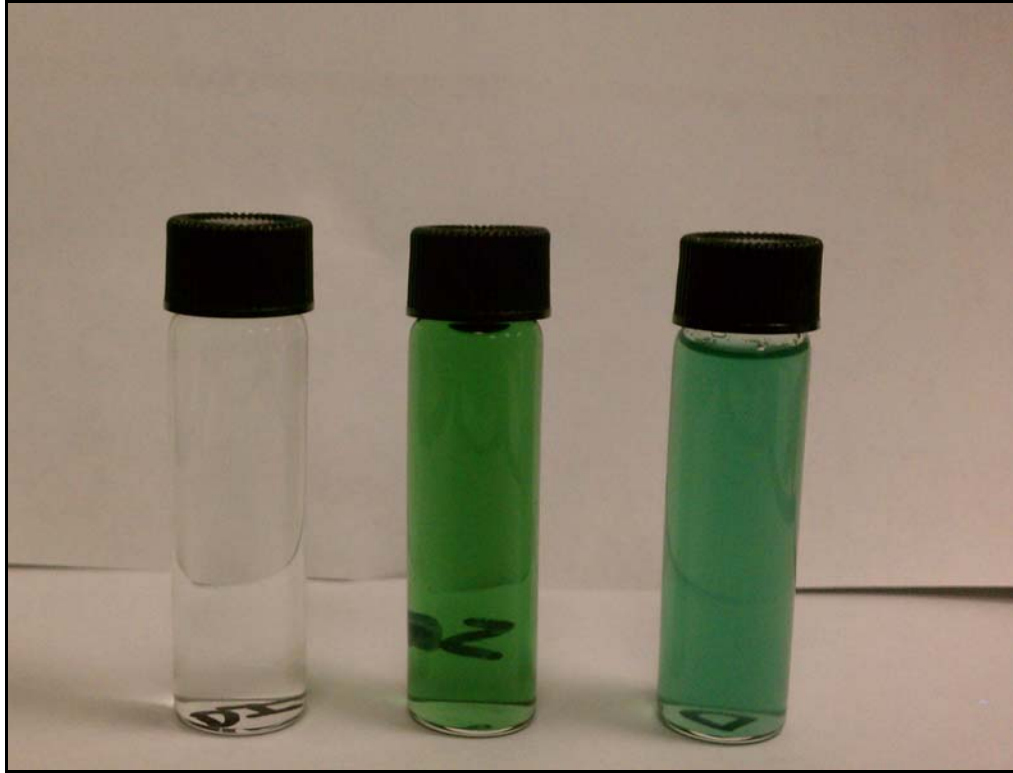


Figure 9.5 - (L-R) Distilled Water, Soda Ash, AATCC Detergent Boiling Tests

Working on the premise that carbonate and/or anionic surfactant molecules bind with cationic sites in an exchange for dye (ion exchange), experiments were carried out to try to remedy the change of color issue. A bleached cotton knit that had been cold pad batch treated with 50 g/L of CR2000 was obtained. Utilizing the standard dyeing, the zeroed percent nitrogen was predicted to be 0.0887% nitrogen. Using the percent nitrogen predictor for a dyeing formula, a formula was made using the three primary dyes that should approximately 100% exhaust for the predicted percent nitrogen. This formula and zeroed percent nitrogen prediction is shown in Table 9.16. Using a split bath technique, the dye formula was made up and two samples of the knit were prepared at a 10:1 liquor ratio.

The dye was added and the bath was heated to 60°C. To one sample 30 g/L of soda ash was added and the baths were held for one hour. A picture of the end dyebaths are shown in Figure 9.6. The absorbance spectra of the end dyebaths are shown in Figure 9.7. A plot of the absorbance spectra of the dyed fabrics are shown in Figure 9.8. The color difference between the two dyed samples was 1.25 DEcmc.

Table 9.16 - Dye Formula Composed to Fully Exhaust on Obtained Treated Knit

| Dye               | % Dye | K/S Sum Predicted                       | %N Predicted  |
|-------------------|-------|---|---------------|
| Nov. Yellow FN-2R | 0.5   | 56.89                                   | 0.0212        |
| Nov. Red FN-R     | 0.4   | 45.37                                   | 0.0171        |
| Nov. Blue FN-R    | 1.1   | 146.21                                  | 0.0456        |
|                   |       |   |               |
|                   |       | <b>Total zeroed %N predicted needed</b> | <b>0.0839</b> |



Figure 9.6 - Effect of Soda Ash Ending Dyebaths (L-no soda ash, R-with Soda Ash)

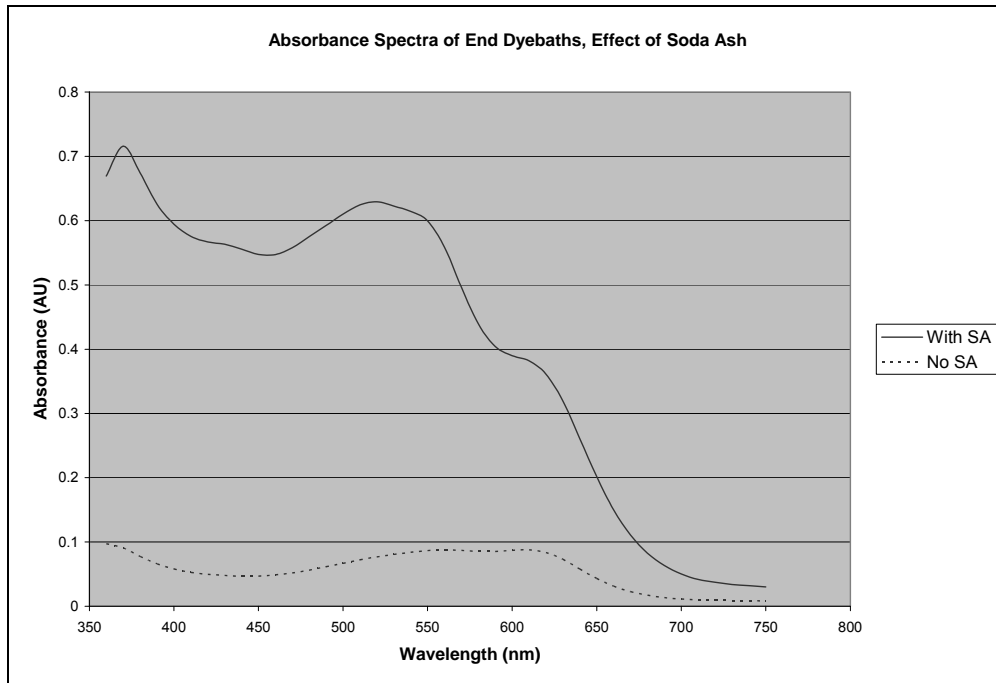


Figure 9.7 - Absorbance Spectra of Ending Dyebaths - Effect of Soda Ash

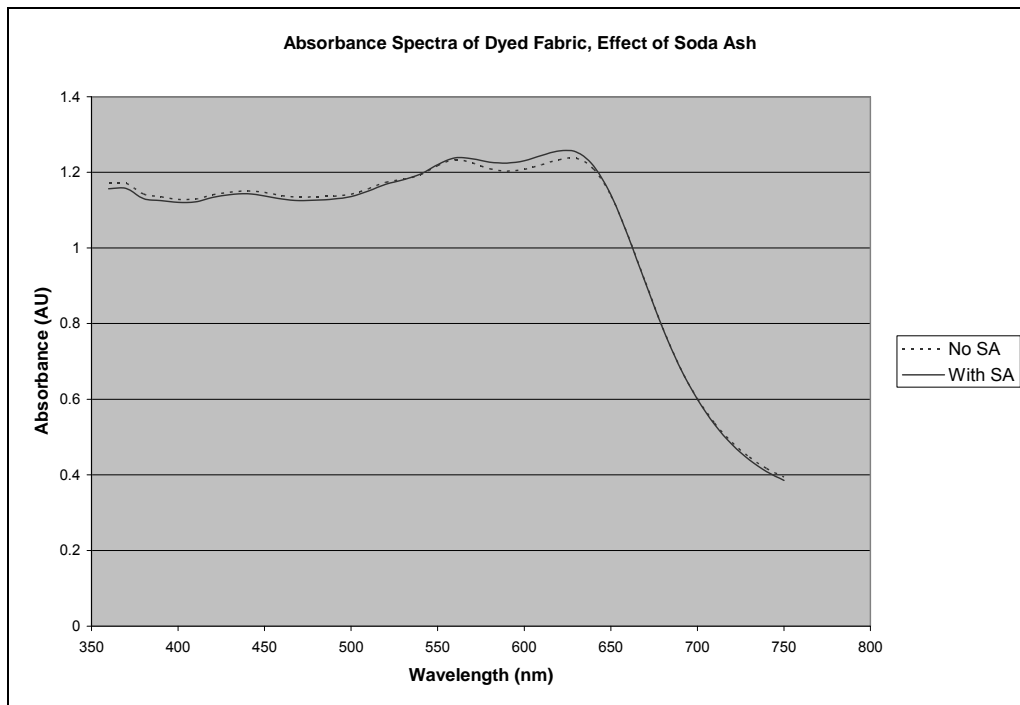


Figure 9.8 - Absorbance Spectra of Dyed Fabric - Effect of Soda Ash

Although there is minimal difference in the color of the dyed fabric and the dyeing with soda ash left more dye in the bath, the dyeing with soda ash should possess ionic and covalent bonding. If the former premise regarding ion exchange is correct, then accordingly, covalent bonding should prevent the removal of dye in laundering. IIA wash tests were performed on the dyed samples. A picture of the ending IIA wash baths are shown in Figure 9.9. As well, the absorbance spectra of the ending IIA wash test baths are shown in Figure 9.10. The greyscale for color change after IIA wash is shown in Table 9.17. With soda ash, there was no dye removed in the IIA wash and the grey scale after washing was greatly improved.



Figure 9.9 - IIA Wash Test Baths (L-Soda Ash Dyeing, R-No Soda Ash in Dyeing)

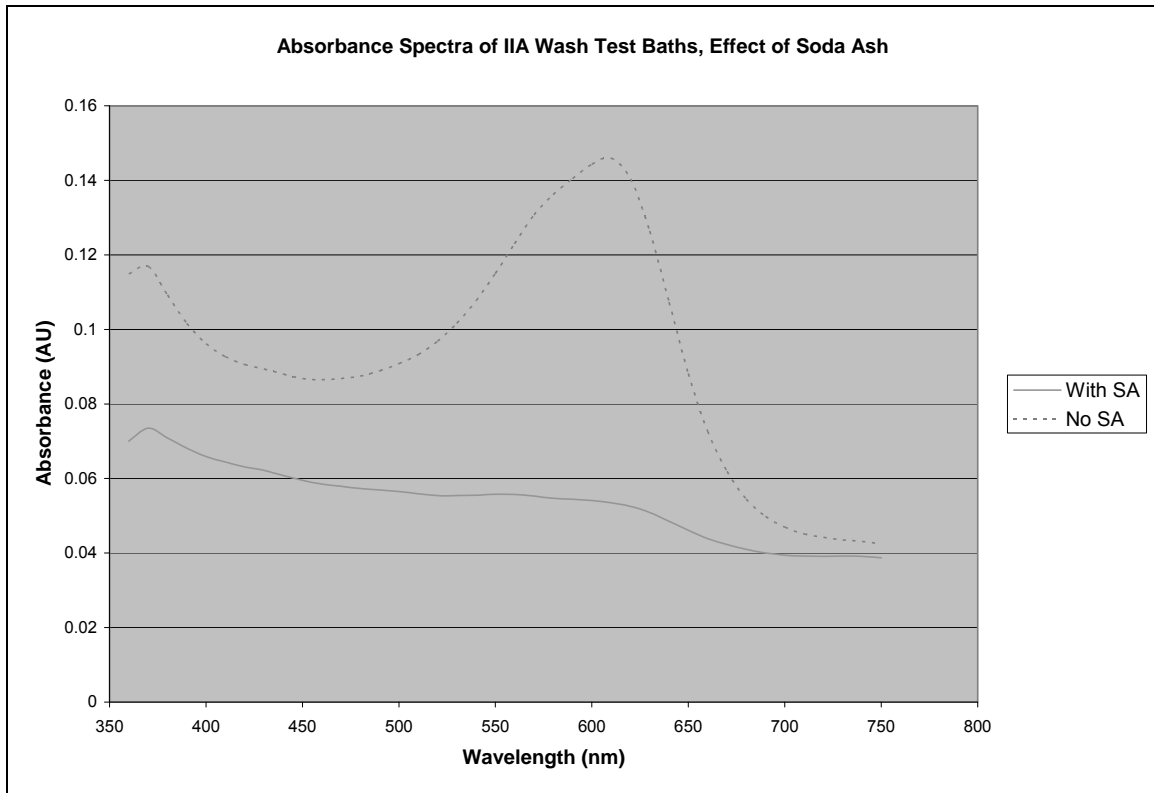


Figure 9.10 - Absorbance Spectra of IIA Wash Test Baths - Effect of Soda Ash

Table 9.17 - Grey Scale for Color Change after IIA Wash Test

|         |     |
|---------|-----|
| With SA | 4.5 |
| No SA   | 3.5 |

#### 9.4 Verification of Color Change Improvement for Dyed Cationic Cotton

In order to establish the relevance of the significant environmental and financial savings found in Section 9.1, the failure in the change of color of the dyed cationic cotton needed to be proved remedied on the same shade and application as the 55 pound trials. 2.2 pounds of the same tubular knit used in the 55 pound trials was treated at an 8:1 liquor ratio in a laboratory JFO dyeing machine. In anticipation of a decrease in dye retention by utilizing



soda ash, the CR2000 treatment level was increased from 16.5% to 17.5% using a 2:1 NaOH:CHPTAC ratio and the optimized exhaust cationization procedure. After cationization, the same cationic green dye shade and auxiliaries as the 55 pound lots was applied with 12 g/L of soda ash. At an 8:1 liquor ratio, after adding CMC, heating to 60°C and adding the dye over 20 minutes, the soda ash was added over 10 minutes and the bath was held for 30 minutes. Figure 9.11 shows a picture of the final dyebath. Figure 9.12 shows the absorbance spectrum of the final dyebath compared to the final dyebath of the 55 pound exhaust treated cationic cotton dyebath. Table 9.18 shows the color difference of the JFO dyed sample with soda ash compared to the conventionally dyed 55 pound sample. The assessed levelness of the JFO treated and dyed cationic cotton was 0.17 DEcmc. Finally, the same QC tests as performed on the 55 pound lots were performed on the JFO dyeings as shown in Tables 9.18-9.22. In general, the QC tests improved with the addition of soda ash in the dyeings, especially the change of color after washing.



Figure 9.11 Ending Dyebath of JFO Cationization and Dyeing with Soda Ash

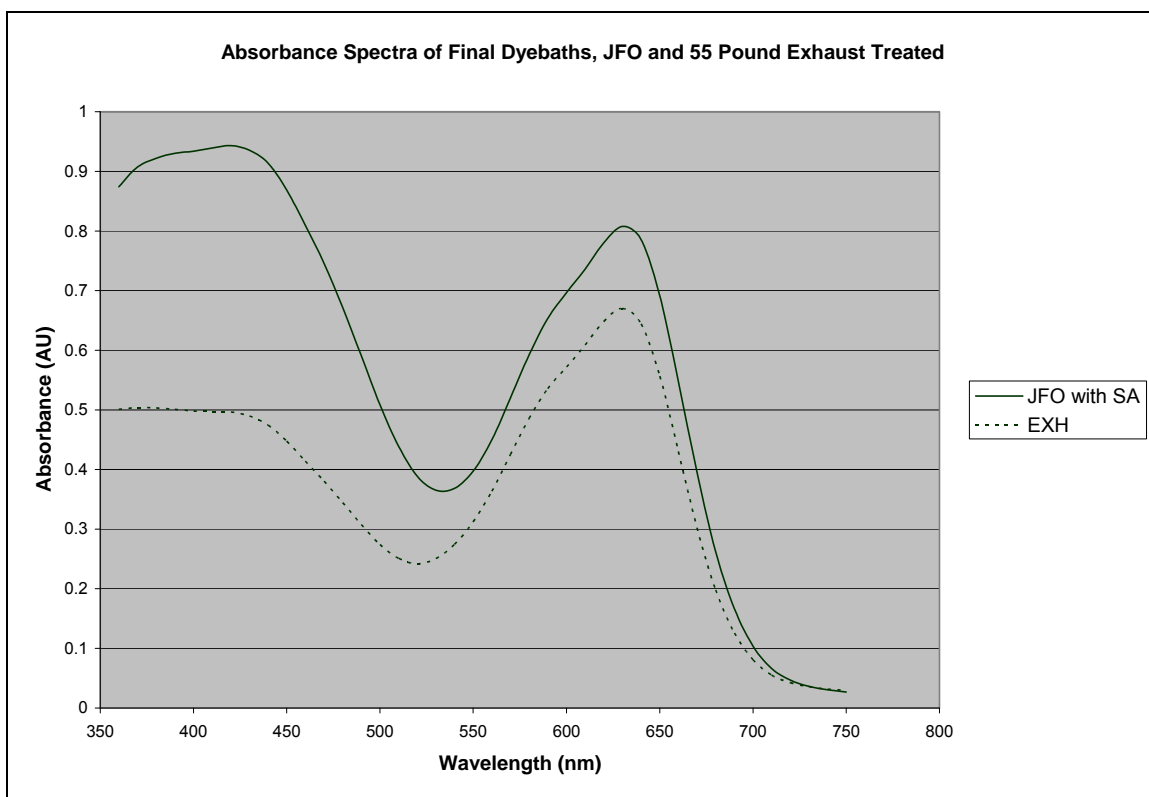


Figure 9.12 - JFO Cationic Green Final Dyebath Absorbance Spectrum

Table 9.18 - JFO Cationic Green Compared to Conventional 55 Pound Dyeing

|                   |       |        |       |       |            |
|-------------------|-------|--------|-------|-------|------------|
| STD               | L*    | a*     | b*    |       |            |
|                   | 46.91 | -13.82 | 24.17 |       |            |
|                   |       |        |       |       |            |
|                   | DL*   | Da*    | Db*   | DEcmc | % Strength |
| JFO with soda ash | -0.68 | -2.38  | -1.27 | 1.95  | 102.8      |

Table 9.19 - Crocking and Lightfastness of JFO Cationic Green

|     |     |     |          |          |
|-----|-----|-----|----------|----------|
|     | Wet | Dry | 20 hr LF | 40 hr LF |
| JFO | 4.5 | 4.5 | 4.5      | 4.5      |

Table 9.20 - Staining from IIA Wash Tests of JFO Cationic Green

|     |               |              |                  |
|-----|---------------|--------------|------------------|
|     | IIA<br>Cotton | IIA<br>Nylon | IIA<br>Polyester |
| JFO | 4.5           | 4.5          | 4.5              |

Table 9.21- Staining from Cold Water Bleed Tests of JFO Cationic Green

|     |                               |                           |                               |
|-----|-------------------------------|---------------------------|-------------------------------|
|     | Cold Water<br>Bleed<br>Cotton | Cold Water<br>Bleed Nylon | Cold Water<br>Bleed Polyester |
| JFO | 4                             | 4.5                       | 4.5                           |

Table 9.22 - Change of Color Results for JFO Cationic Green

|     |         |               |
|-----|---------|---------------|
|     | CoC IIA | CoC<br>5 Wash |
| JFO | 4       | 4             |

## **10. Discussion**

Cationic cotton has been around for many years with no discernible large scale industrial acceptance in spite of much work showing the ecological benefits of utilizing cationized cotton. Initially, three major issues were attributed to this lack of acceptance.

- 1) Questions about the safety of the preferred cationization chemistry CHPTAC
- 2) No large scale demonstration of successful cationizations and dyeings possessing the same quality as conventional fiber reactive dyed cotton
- 3) Worries about the true cost of cationization from preparation to dyed goods

During these studies, it became apparent that there are at least two other major issues involved with utilizing cationic cotton that come from addressing the three presumed issues. Those issues are what method and dyes are appropriate for dyeing cationic cotton without losses in quality, and how to match a conventional reactive dyed shade using cationic cotton with an appropriate amount of nitrogen.

### **10.1 Safety of CHPTAC**

It seems that the cationization of cotton has been given notoriety for being a toxic chemical process utilizing a carcinogenic chemical reagent. To anyone investigating the cationization of glucose based polymers, it becomes apparent that the cationization of other materials such as starch utilize CHPTAC extensively and have so for many years. In fact, it was reported that 95% of CHPTAC utilization in Europe is used in starch modification leaving 5% CHPTAC usage for other materials such as cellulose. Modified starches are even

incorporated in to barrier materials for foodstuffs, demonstrating the deemed safety of cationized starch. It also becomes apparent that the final cationized product is not the recipient of safety concerns, but rather the product formed in situ from adding sodium hydroxide to CHPTAC. As a result from adding sodium hydroxide, CHPTAC is converted to EPTAC. EPTAC is a carcinogen and highly irritating reagent. However, the base reagent for cationization, CHPTAC, is fairly non toxic as outlined in Section 4.5. CHPTAC is the reagent that is manufactured, transported, handled, and utilized for cationization of cellulose. The EPTAC formed from CHPTAC is not present until sodium hydroxide is added to the CHPTAC where the CHPTAC is almost simultaneously converted to EPTAC. It is clear as in all cases of handling chemical reagents, that care should be exercised when handling CHPTAC, but that carcinogenic danger is not immediately imminent from utilizing CHPTAC unless and when sodium hydroxide is added forming the reactive epoxide. The EPTAC can then in turn react with nucleophiles such as cellulose. In terms of safety and occupational exposure, exhaust cationization of cellulose would be the safest method of cationization carried out in a closed dyeing machine. In this method the sodium hydroxide and CHPTAC are introduced separately, forming the EPTAC in solution, and the worker is not routinely exposed to EPTAC. One of the downsides however of exhaust cationization is the relatively low efficiency of cationization even with improvements made in the exhaustion process. Cold pad batch processes as well as the developed pad bake process give much higher fixation of applied cationic reagent but require padding of EPTAC solutions. In these cases, occupational exposure should be limited by not premixing, handling, or transporting EPTAC

solutions. Instead, sodium hydroxide and CHPTAC should be piped to the mix tank or pad trough so that EPTAC is formed right before padding, reducing the risk for occupational exposure. Finally, it should be noted that extra care and vigilance must be used when analyzing results of ecological and toxicological studies because of the unique transitioning nature of the primary chemical reagent CHPTAC. In the presence of alkali, CHPTAC is almost instantaneously converted to EPTAC, a carcinogen. As well, CHPTAC is limited to solubility in solutions which are commonly supplied for cationization processes. Taken together, when examining studies regarding ecological or toxicological studies, the purity and concentration of the CHPTAC needs to be taken into account and more important, the pH of the test. Even though CHPTAC is not a proven carcinogen or highly toxic chemical, in some test methods CHPTAC may be converted to EPTAC and the effects of EPTAC may inappropriately be attributed to CHPTAC.

## **10.2 Cationization Treatments**

Before attempting to cationize and cost large scale cationization and dyeing, studies were undertaken to see if there were any opportunities in improving the application and efficiency of commonly used industrial cationization methods. Very high fixations of CHPTAC have been reported in the past but because of the methods and parameters used, pad dry cure for example, it presumably cannot translate into industrially realistic processes. Exhaustion and cold pad batch methods have emerged as the two main modes of industrial cationization. Exhaust application allows a typical textile dyer to utilize their on

hand equipment and cationize very quickly but with low fixation efficiency. On the other hand, cold pad batching requires a padding range and A-frames for batching. If the dyer has neither it will require a capital investment. Further, because of the batching time 16-24 hours, throughput is significantly lower. However, the direct chemical costs of cationization are much lower for CPB as shown in 9.1. At an attempt to create a process allowing high throughput and cationization efficiency, a pad bake application was shown to allow the fastest throughput and highest fixation of these three processes but is probably only suitable for woven cationization because of dimensional stability. The three treatment methods are discussed below.

### **10.2.1 Exhaust Cationization**

Figure 10.1, adapted from the Dow Chemical Company shows the  $\frac{1}{2}$  life in days of EPTAC at different temperatures and pH. As can be seen from Figure 10.1, the utilization of EPTAC is covariant dependent with respect to temperature and pH, the same trends found in the exhaustion and fixation of CHPTAC. If Figure 10.1 is extrapolated to 105°C in Figures 10.2-10.3 (1), it becomes clear that the utilization of EPTAC is greatly increased. Also, with the results of the exhaustion studies, by arranging the alkali addition before addition of the CHPTAC, it is proposed that alkali cellulose is formed allowing ionic exhaustion of the CHPTAC/EPTAC molecule. When this change in order of addition was made, an increase of 16% in fixed percent nitrogen was seen. A proposed mechanism of the recommended and optimized exhaust processes are thought to proceed by neutralization of alcohol groups by

addition of alkali followed by the simultaneous formation of EPTAC when CHPTAC is added to the bath. The EPTAC exhausts to the surface of the cellulose where it is ionically attracted to the cellulosate ion and held until the epoxide can react with the cellulosate ion.

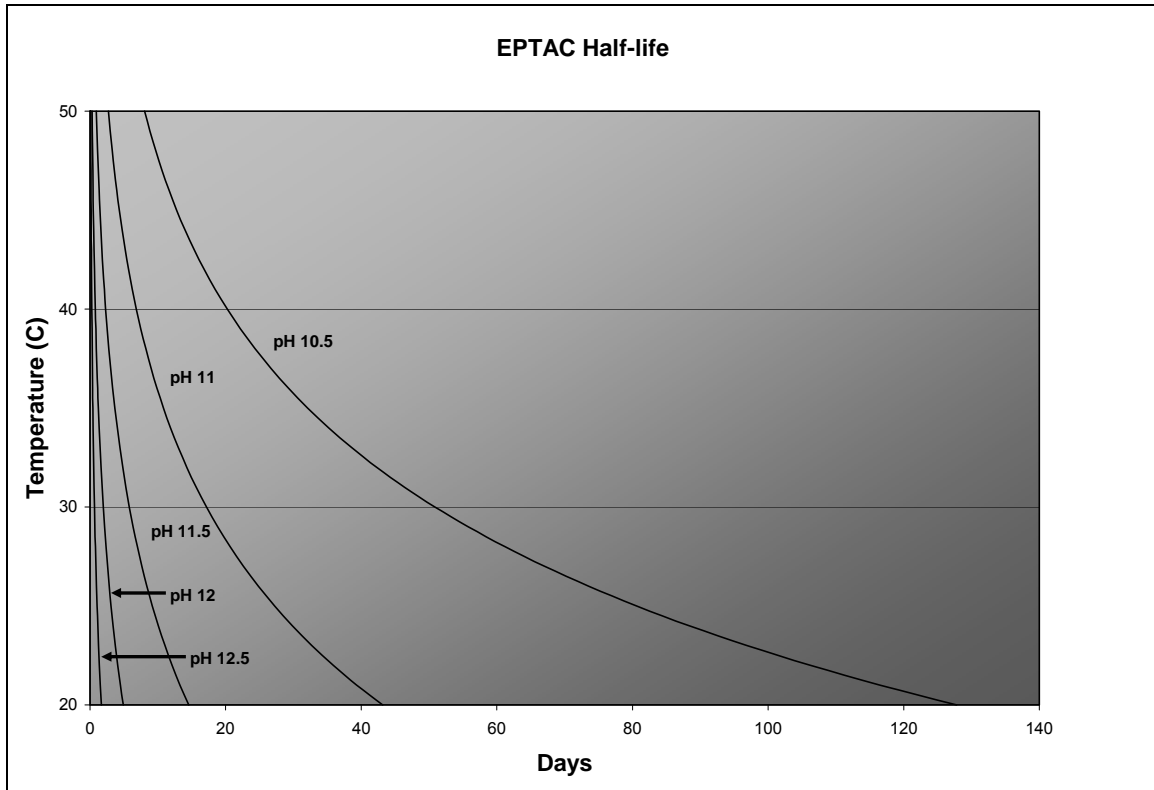


Figure 10.1 – ½ Life of EPTAC Solutions



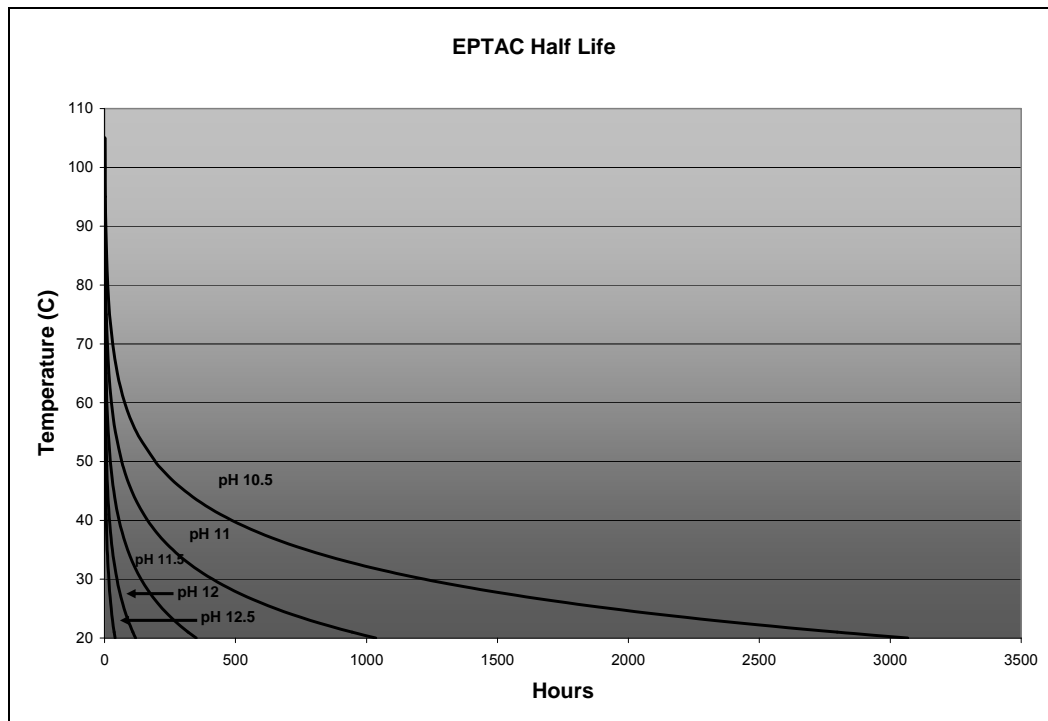


Figure 10.2 – ½ Life of EPTAC Extrapolated to 105°C

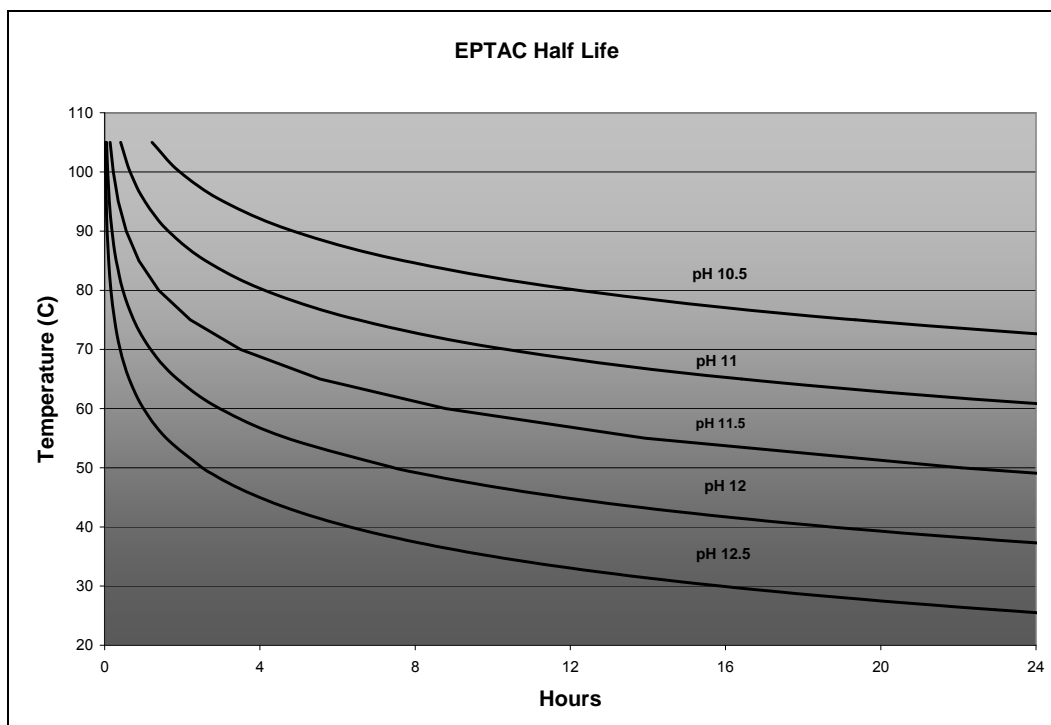


Figure 10.3 – Zoomed Extrapolated ½ Life of EPTAC to 105°C

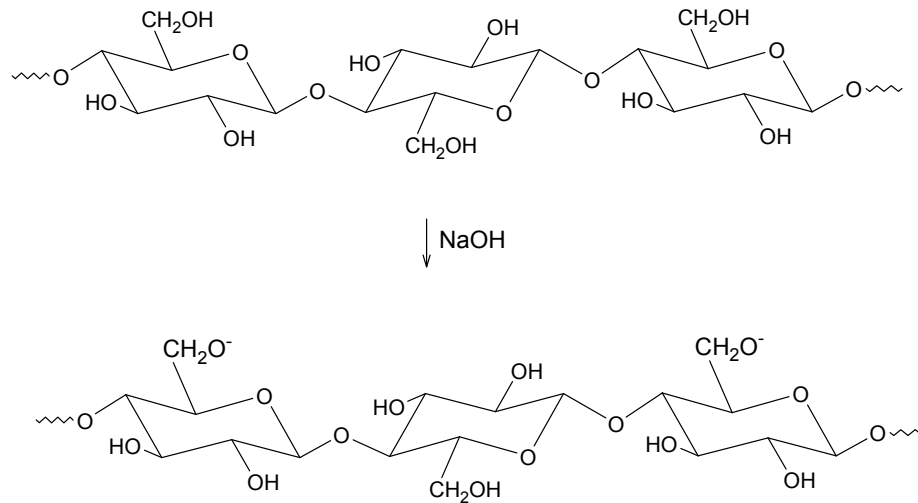


Figure 10.4 - Formation of Alkali Cellulose

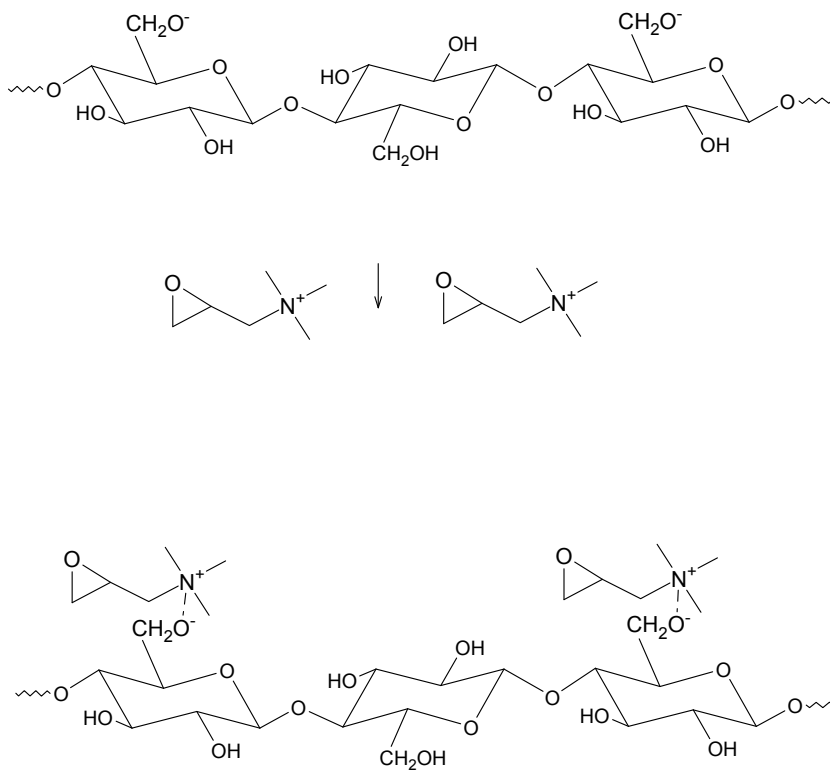


Figure 10.5 - Ionic Attraction of EPTAC to Alkali Cellulose

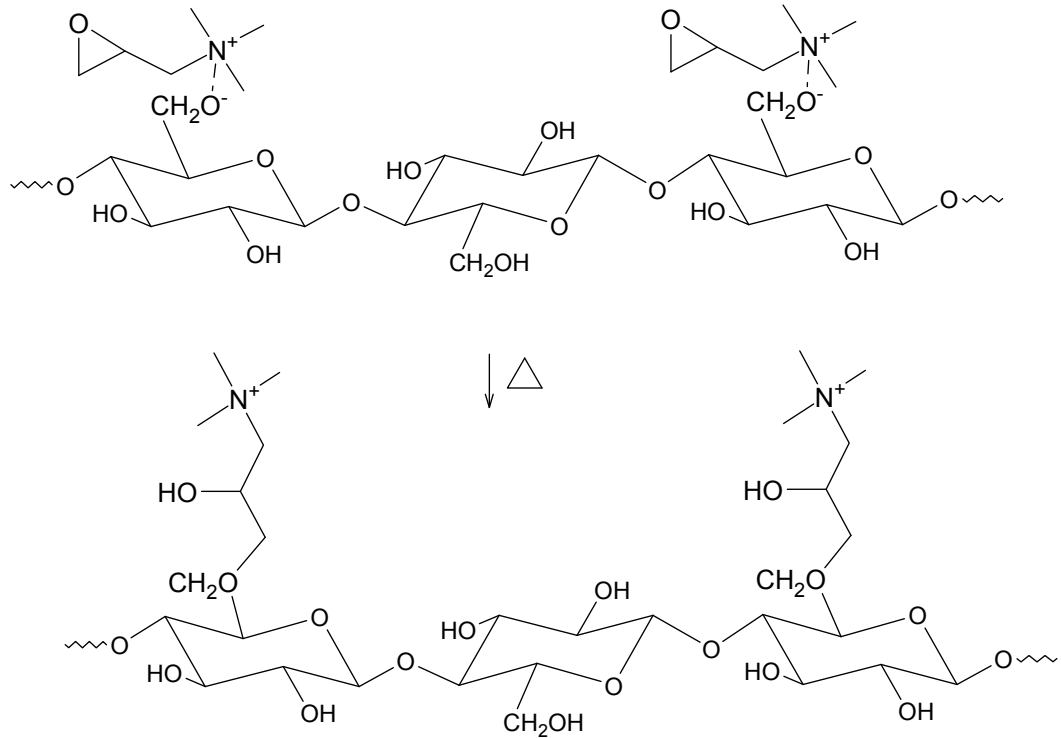


Figure 10.6 - Covalent Fixation of EPTAC

When comparing the gains in fixation of CHPTAC compared to the current recommended exhaust procedure, it is clear that more sodium hydroxide is key in improving the fixation of exhaust applied CHPTAC. This was verified in the statistical design analysis which found sodium hydroxide to be the most important variable in the exhaust process followed by time given for the EPTAC to exhaust to the cellulose surface, seemingly in agreement with the presumption made regarding ionic exhaustion of EPTAC. Further, from the initial exhaustion experiments it was clear that even with substantial amounts of alkali that little fixation occurred without increasing temperature. Compared to the currently used

industrial exhaust application, approximately double the amount of fixed nitrogen is present utilizing the recommended exhaust process and this would be expected to improve slightly using the optimized process. Although it was clearly demonstrated that the recommended exhaust process could be improved by optimizing the variables using statistical design, the gain in fixation of nitrogen, 0.104% nitrogen to 0.1065% nitrogen (from 15% CR2000 application) is rather small. Regardless of if the recommended or optimized exhaustion process is used, these improvements in exhaust application of CHPTAC will undoubtedly make exhaustion applications of CHPTAC more cost efficient and beneficial because the CHPTAC can be applied in typical textile dyeing machinery. Fixation efficiency should be expected to decline with increases in liquor ratio and increases in concentration of applied CHPTAC, trends that are also seen in cold pad batch applications. Taking the exhaust application a step further, experiments were carried out to see if a suitable phase transfer catalyst (PTC) could be found to increase the fixation efficiency of the exhaust application. The results of the PTC experiments show that certain PTC agents may improve the fixation of CHPTAC, but that most PTC reagents negatively affect the fixation of CHPTAC. This is presumably due to the formation of permanent ionic bonds between CHPTAC and the PTC agent that do not allow ionic bonding of applied dyestuffs. In other words, a PTC agent may affectively greatly improve the fixation of CHPTAC, but if permanent ionic bonds are formed between the CHPTAC and PTC reagent, the improvement in fixation of CHPTAC would not be realized by dyeing, or the predicted percent nitrogen. It would be possible to realize an increase in percent nitrogen through

nitrogen analysis, but even these results would be problematic to interpret, especially in the case of reserve salt flake that contains nitrogen. In short, if a PTC agent was confirmed to increase the fixation of CHPTAC but this increase in fixation did not yield an increase in dye retention, then the benefit of utilizing a PTC agent is not achieved. The results of Table 6.30 do show that it is possible to increase fixation of applied CHPTAC and that it may be possible to find a more effective PTC reagent by evaluating additional PTC candidates.

### **10.2.2 Cold Batch Cationization**

Cold pad batch cationization has routinely yielded the highest level of fixation of applied CHPTAC utilizing an industrially realistic process. As such, cold pad batch cationization treatments are used in these studies as a control for comparison, especially in the case of the pad bake method where increases in cationization efficiency were found. It was noted and found that modeling cold pad batch cationizations are very straightforward and allow the calculation of an expected fixed amount of nitrogen, an invaluable tool for determining appropriate treatment levels. It was observed in the cold pad batch applications and it is not known to have been reportedly previously that increases in fixation were observed with decreases in the WPU of applied CHPTAC. Presumably, the higher the amount of water in the batch processes, similar to the exhaustion process, causes more hydrolysis of the EPTAC and an observed resultant decrease in fixation efficiency. With this in mind, several foam trials were conducted to judge the efficacy of foam cationization as well as if the decrease in WPU (approximately 30% WPU typical) would drastically increase the fixation of applied

CHPTAC. Because of the complexity of the setup and running of the foaming machinery, repeated trials and experiments are unrealistic as compared to typical lab scale equipment. The one foam trial of importance, comparing the cold pad batch and foam batch with the same amount of applied nitrogen and batch times resulted in equivalent final predicted nitrogen levels. Even though this is only one experiment and utilized different substrates, the findings of this experiment are very encouraging. It seems possible that if foaming parameters such as blow ratio, fabric speed, head pressure, and foaming aid can be optimized that it may be possible to improve the fixation utilizing a lower WPU. Further, this experiment showed that indeed, foam cationization is possible and at least as efficient as cold pad batch methods. One important note is that the foaming aid more than likely needs to be non ionic so it will not bind with the cationic sites of the CHPTAC molecule and prevent dye uptake even if the lower WPU greatly increases the fixation efficiency of cationization.

### **10.2.3 Pad Bake Cationization**

The pad bake process will allow a continuous process with a very high throughput with a very high efficiency. A resultant issue when utilizing pad bake processes are crossovers. Resultant crossovers could not be rectified in the pad bake process and the inclusion of crossovers makes nitrogen predictions by dyeing of this type of process problematic. As expected, the percent nitrogen predicted from dyeing is overestimated for every sample except one. However, the determined percent nitrogen verifies that the pad bake

treatment method offers an alternative cationization treatment with higher percent fixation than the cold pad batch method. The only foreseeable drawback of this cationization technique would presumably be losses in lightfastness. Even though the treatment is not ring dyed as evidenced by microscopic examination, the treatment does produce crossovers presumably similar to some continuous dyeing applications such as continuous vat dyeing of cotton. The pad bake method would be the most efficient practical method to date for cationizing cotton goods. This is presumably due to high baking temperatures driving off applied water resulting in lower chances of hydrolysis. Even though not presented within these studies, the pad bake method has been carried out on a full scale tenter frame using slit cotton knit where it is possible to overfeed the fabric. It should be noted that presumably the pad bake method would be better suited for woven fabrics because of a higher degree of dimensional stability.

### **10.3 Dyeing Cationized Cotton**

#### **10.3.1 Dyeing Method**

There are two basic methods of dyeing cationized cotton. Method one is the complete exhaustion of applied dyestuffs leaving a practically clear dyebath. This method realizes the most significant environmental and cost savings potential because the dye is fully utilized and as such, significant reductions in the amount of dye required can be reduced from conventional dyeing recipes while utilizing zero salt and significant reductions in rinsing. The downside of this method is that all dye will be taken up by the fabric and it requires a

leveling strategy to slow down dye strike and maintain levelness of the dyed fabric. This is the method that has been widely used in these studies. On the other hand, a second dyeing method for cationized cotton is to saturate dye the cationized cotton. In this method, more dye is applied than the cationization treatment can ionically bond with. This allows the dyeing saturation limit to be reached more quickly as compared to a conventional dyeing, but does not realize the full environmental and cost savings benefits as compared to method one. Further, the final shade obtained is dictated by the cationization level and not predominately by the amount of dye put into the dyeing. As well, with method two, blocking effects caused by different dye substantivities will be a problem because of the limited number of dyesites. Specifically concerning time and temperature requirements for method two dyeings, although a generalization is not warranted by the experiments conducted in Section 7.2 regarding exact dye type and needed time and temperature requirements, the results do suggest that other reactive dyes for cellulose should fall somewhere in between the extreme data points presented for time and temperature dependency when dyeing cationic cotton. For that reason, it is suggested that as a starting point, the dye manufacturer's recommendation for time and temperature be followed and optimized from there if needed for dyeing cationic cotton. The results of the exhaust treated towels do seem to suggest that extended hold times actually result in decreased shade depth. This suggests that with increased hold time, dye may be removed in exhaust treated cationizations being dyed with excess dyestuffs, but only at high temperature applications, i.e. 93°C from these experiments. When method one is utilized to dye



cationized cotton, the down sides are appropriately determining the amount of nitrogen needed for the shade and utilizing an effective dye retarder and leveling system as discussed in 7.3. It should be noted that method one and two can also utilize alkali in the dyeing process. As found in these studies, it seems that alkali will be required for maintaining fastness properties of dyed cationized cotton using reactive dyes.

### **10.3.2 Cationic Cotton Dye Leveling System**

Because cationic cotton possesses permanent cationic charges in a fiber that is not thermoplastic, the cationic dyesites are immediately and instantaneously available for applied anionic dyestuffs. In the case of method two dyeings where excess amounts of dye are used, this is not expected to be a problem for levelness but a benefit because the dyeing can be completed in much shorter time compared to traditional dyeings. However, in method one dyeings, the dye must be retarded to prevent the rapid dye strike and a lubricant to significantly lube the cationic cotton to allow movement of the fabric, especially cold pad bath treated fabrics. In traditional fiber reactive dyeings in the jet, the fabric is typically tubular knit where the ends are circular sewn. This allows the tube to “balloon” with air inside the sewn fabric and helps minimize rope marks and streaking. For cold pad batch treated cationized cotton dyeings, the tubular knit is slit for padding and batching so it cannot balloon like a tubular knit. Further, the width of the fabric going through the venturi nozzle of the jet is essentially doubled. This makes the cold pad batch treated cationization treatments the hardest to level. As well, in traditional reactive dyeings, the

dyes can migrate. Anionic dyestuffs on cationized cotton will not migrate readily so the fabric in any method of treatment will benefit from lubrication to allow easier application of the dyestuffs on cationic cotton. Therefore, a lubricant is necessary to lubricate the cationized fabric, especially cold pad batch treated fabric so that dye is easily accessible to all areas of the fabric since it is not likely to migrate and level like traditional reactive dyeings. CMC is used as a dye retarder and was shown to sufficiently retard the strike of applied dyestuffs. When the lubricant and CMC are utilized with a dispersant, the package was found to greatly improve levelness in method one dyeings as shown in 7.3. The leveling combination was used in 55 pound dyeings of cationized cotton and produced level dyeings of all dyed cationic cotton lots.

### **10.3.3 Appropriate Dye Types for Cationized Cotton**

It has been widely assumed that any type of anionic dyestuff will dye cationic cotton. This premise is fundamentally true, however, problems have been seen in some fastness tests, specifically laundering tests that utilize a standard alkaline detergent. In these studies when reactive dyes were ionically bound only, significant failures were seen in change of color after laundering. This problem was significantly improved by dyeing with alkali and inducing both covalent and ionic bonding. In the case of other anionic dyestuffs without reactive sites the washfastness would be expected to suffer. However, the presumption presented here is that in the absence of covalent bonding, that significant ion exchange may occur when laundered in anionic detergent between dyestuffs and surfactant molecules as well as

any other suitable anion. Without knowing the exact dye structure in advance of dye application it would be hard to predict fastness properties. However, it would be expected if the premise regarding ion exchange is true that dyes such as monosulfonated acid dyes would fail change of color after laundering and multisulfonated dyestuffs such as direct dyes would excel in change of color after laundering on cationic cotton. Examining two previously published studies by Hauser et al. specifically regarding acid and direct dyestuffs, the exact trend is seen (2,3). In the case of multisulfonated dyestuffs such as Direct Yellow 106 (6 sulfonate groups), Direct Red 80 (6 sulfonate groups), and Direct Blue 78 (4 sulfonate groups), for the Yellow and Red direct dyes with six sulfonate groups, the change of color was as good or better on cationic cotton. With the highest cationization treatment, the Direct Blue dye had a half unit lower than conventional cotton but on a lower cationization treatment level the color change was equal to the conventional. In the case of acid dyes, disulfonated acid dyes Acid Yellow 79 and Acid Red 260 yielded perfect ratings of 5 on color change tests while monosulfonated dyes ranged from 2.5 to 3 and one rating of 4.5 for a metallized acid dye. The results of the studies presented in this text and other previously published studies seem to suggest that the dye chemistry or reactive group itself is not as important as the number of sulfonate groups available to anchor the dye molecule ionically to as many cationic dye sites as possible to prevent ion exchange when reactive dyes are not used. This presents a problem for non reactive dyes because in order to ensure washfastness by utilizing dyes with multisulfonation, the shade depth obtained would be expected to go down because more dye sites will be occupied by fewer dyes. To build the

same depth of shade as say a reactive dye that can ionically and covalently bond may require higher treatment levels of cationization, significantly increasing the cost of dyeing cationized cotton. It seems that reactive dyes may be the most practical and beneficial dyes for dyeing cationic cotton. In terms of dyeing cationic cotton, there is only one major difference between most reactive dyes that needs to be addressed. Many if not most reactive dye types are based on cyclic azines and possess permanent reactive sites for reaction with cellulose. The immediate exceptions to this generalization are the widely used vinyl sulfone dyes. Sulfato ethyl sulfone groups undergo an elimination reaction when exposed to alkali forming the reactive vinyl sulfone group. This presents a challenge for dyeing cationic cotton because without knowing the exact dye structure in advance it would be very hard to predict washfastness properties. A vinyl sulfone may possess three sulfonate groups when applied that can ionically bond with cationic cotton. On addition of alkali, two of those sulfonate groups may be associated with sulfato ethyl sulfone groups and undergo elimination to form two vinyl groups. Now the sites available for ionic bonding have been drastically reduced. Take for example Reactive Black 5 as shown in Figure 10.7. In a neutral bath the dye would possess four sites for ionic bonding. Upon addition of alkali, as shown in Figure 10.8, two of the sulfonate groups would be converted to vinyl groups and cannot ionically bond but may undergo covalent bonding. As a result of reduction in the number of sulfonate sites, the total achievable dye depth would be expected to increase through ionic bonding, because now the dye molecule will only occupy two cationic sites at most. Although unpublished, this has been confirmed by other researchers

for dyeing vinyl sulfone dyes with and without soda ash. As a side, a seemingly interesting experiment would be to boil Reactive Black 5 in alkali fully hydrolyzing all reactive sites and apply a similar depth of non hydrolyzed Reactive Black 5 at a neutral pH and see if the shade observed in the case of the hydrolyzed dye is double the depth of the neutrally applied dye. Because of the unique transitioning structure of vinyl sulfone dyes, the issue with vinyl sulfone type dyes becomes should they be bound ionically utilizing all sulfonate sites or dye under alkaline conditions. If dyed with alkali should the soda ash be added directly in the beginning of the dye cycle to immediately convert all sulfato ethyl sulfone groups to vinyl sulfones or should the alkali be added after the dyes are exhausting? If the alkali is added in the beginning of the dyeing does the likelihood of dye hydrolysis increase preventing the dye from covalently fixing and suffer fastness issues? If the soda ash is added after the dyes are exhausted does that mean that dye will be removed from the cationized cotton because the anionic dye site has been lost? Because of these questions, vinyl sulfone type dyes were not chosen to work with. Instead, workhorse Novacron FN dyes were chosen as used in the 55 pound studies. Although the structures of the Novacron dyes used are not known or readily available, they are thought to be heterobifunctional fluorotriazine vinyl sulfone type. When the Novacron dyes were used in ionic bonding only, the change of color was poor after laundering. When soda ash was included in the dyeing the change of color was improved but more dye was left in the dyebath. With vinyl sulfone dyes the fastness should also improve but less dye should be left in the bath as compared to dyeing without soda ash because of the elimination of ionic bonding sites. In general in the case of reactive dyestuffs

for cationic cotton, the dyer needs to understand the difference between vinyl sulfone and non vinyl sulfone type dyestuffs and how utilizing alkali in the dyeing will affect the dyeability and final outcome of the dyed cationic cotton. Because of the elimination in vinyl sulfone dyes, it would be unreasonable to expect vinyl sulfone type dyes to dye similarly to non vinyl sulfone dyes even though with conventional dyeing the dye processes are very similar. In short, it seems that at least preliminarily, it would be much easier for the textile dyer to utilize non vinyl sulfone type dyes or heterobifunctional dyes where they do not have to worry about the effect of soda ash on the ionic bonding character of the applied dyestuffs. It also seems that some types of anionic dyestuffs other than reactive dyes may be suitable for cationic cotton but they will be required to be multisulfonated. If a dye is multisulfonated it may be required bind to more cationic sites and thus a higher level of treatment may be required to build deeper shades.

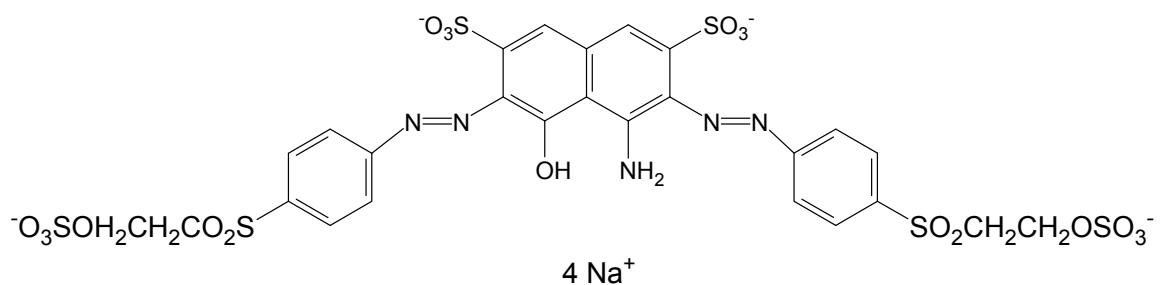


Figure 10.7 - CI Reactive Black 5

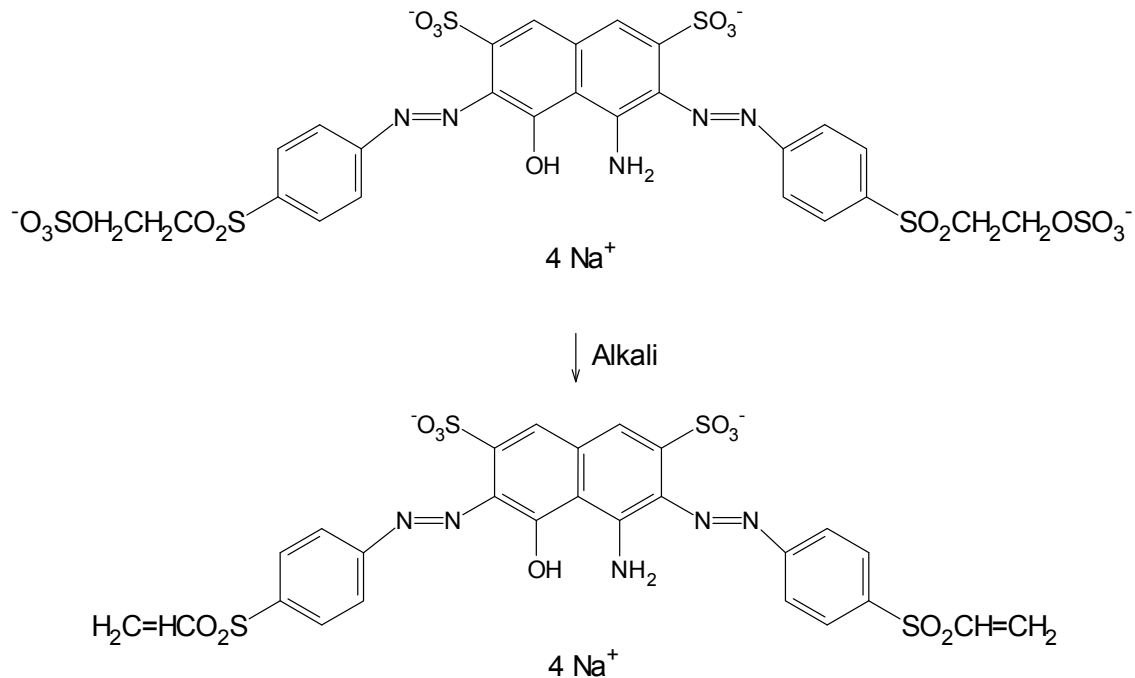


Figure 10.8 - Activation of Vinyl Groups of Reactive Black 5

#### 10.3.4 Anionic Softeners

In an effort to make cotton cationization more attractive, experiments were carried out to see if fatty acids could be used as hand modifiers, softeners, for cationic cotton. This would theoretically allow complete softener utilization in the same exhaust bath as the dyeing. When linoleic acid, stearic acid, and palmitic acid were emulsified and applied at 0.5%, 2%, and 5% to a very low level of cationic cotton, 0.0439% nitrogen, linoleic acid at 5% was the preferred hand. This seems odd at first because the linoleic acid is only 60% solid whereas the palmitic and stearic acids were supplied at 96%+ solid. On closer analysis however, the

results do show a trend where with increasing use of emulsifier, the harsher the hand was deemed. This makes sense if the softening agent is highly emulsified it will be very hard to get the softening agent out of emulsion onto the cationic site. The results of linoleic acid in liquid form and very little emulsifier seemed to satisfy this assumption with this set of experiments. When a highly cationized cotton substrate was used, 0.1523% nitrogen, and the experiments were repeated, it was much harder for small hand panels to discern differences in hand. These experiments in sample set two suggest a few encouraging trends. One, it is possible to fully exhaust an anionic softening agent onto cationized cotton as observed by clear final application baths at 0.5% application level. Two, at a certain level of cationization and applied anionic softening agents, it is hard to discern between increases in amount of the softening agent and between softening agents. In sample set one with a very low percent nitrogen on the fabric, linoleic acid was clearly more effective. This was presumed to be because of the very low amount of emulsifier used and ready prevalence of the softening agent as compared to the high amounts of emulsifier required to emulsify the palmitic and stearic acids. With a high degree of cationization, the linoleic acid was not preferred which seems to suggest with a high enough degree of cationization it is possible to soften the cationized fabric even with a high amount of emulsifier. All of the experiments positively suggest that cationized cotton can be easily softened with readily available fatty acids but that more than likely a specialty emulsifier would need to be found in order to release the fatty molecule to bind with the cationic site.



### **10.3.5 Color and Nitrogen Prediction for Shade Matching Cationic Cotton**

When attempting to match a shade conventionally reactive dyed on cotton onto cationic cotton, the appropriate amount of treatment is required for shade depth and ensuring acceptable lightfastness. It was shown in Section 8.2 that it is possible to build dye primaries consisting of different dye percentages on cationic cotton for color prediction in a color prediction software package. Further, it was shown that the K/S sum for a certain dye could be predicted from the percent dye required for a shade. From the K/S sum the amount of nitrogen required to make that K/S sum could be predicted. By adding the amount of nitrogen required for all dyes in a predicted dye formula on cationized cotton, an appropriate treatment level can be used to attempt near complete exhaustion of applied dyestuffs and a near match to the conventional standard. This package of color matching and percent nitrogen prediction was shown to work very well while nearly exhausting all dyebaths and obtaining a near match to the conventionally dyed standard. The dyeing method utilized in making the primary dyeings and lab dips was method one where all dye was exhausted and no soda ash was used. As shown in the 55 pound dyeings, without soda ash, the change of color after washing was unacceptable. When soda ash was added to the dyeing the change of color was improved. Although the color and nitrogen prediction worked very well, because of the dyeing method used in the preparation of the primaries and lab dips, the predictions would be expected to fail in laundering. The experiments did show it is possible to predict formulas for cationic cotton as well as the percent nitrogen required for the shade. In order for this type of prediction process to be useful, the process

would need to be repeated utilizing a dyeing method where soda ash is included in the dyeings and near complete exhaustion is obtained. As shown in Section 9.3, inclusion of soda ash changed the color of the final dyed sample as well as left more dye in the bath as compared to without soda ash for Novacron FN dyes. Therefore it would be highly beneficial if this process could be repeated with more reactive dyes utilizing soda ash and proven to work as an effective tool for predicting colors for shade matching and the appropriate nitrogen level.

#### **10.4 Large Scale Cationization Costs and Savings**

Cationic cotton has promised to yield savings in salt, dye, and dyeing consumables such as water, power, and steam. However, these presumptions have never been substantiated with any large scale demonstrations. Further, there has been concern about increases in cost from utilizing CHPTAC before dyeing. Three 55 pound sample lots were made by dyeing a conventional dyeing with salt and soda ash, a cationic cotton exhaust treated dyeing, and a cationic cotton cold pad batch treated dyeing, all to the same shade depth and color. From the 55 pound sample lots, the amounts of time, water, steam, and power were monitored for each lot as well as the chemicals and auxiliaries used for each process. From all of these consumables, costs were determined for a total cost of each process from start to finish. The bleach cost for all lots is the same and does not change. The cost for the exhaust cationization was \$0.3053/lb and the cold pad batch treated cost was \$0.1085/lb. As expected from lower fixation in the exhaust application, the exhaust application cost

about 2.8 times more than the cold pad batch application. The standard dyeing utilized 1.5% dye owg including 40 g/L salt with a cost of \$0.4187/lb. The cationic dyeing for both cationic lots utilized only 1.102% dye owg including 1% CMC and cost \$0.1980/lb. The cationic dyeings cost less than half the amount of the standard dyeing, utilized no salt, and saved nearly 1/3 the amount of dye. Excluding the bleaching which is the same for all lots, compared to the standard dyeing, even with the neutralization baths required after cationization, the entire exhaust application utilized only 67% of the amount of water as the standard and the entire CPB process used only 75% of the amount of water. Further, steam requirements were more than cut in half for the CPB application total process and required about 30% more steam for the exhaust application total process. Power savings were also observed for the CPB process utilizing only about 75% the amount as the standard dyeing while the full exhaust process required approximately 16% more power than the standard. Concerning steam usage, the CPB utilized only 47% of the amount of steam as the standard while the exhaust treat cycle utilized about 30% more steam. Still excluding the consumables used in the bleach process, the cost for the standard dyeing consumables was \$0.1724/lb, the CPB was \$0.1076/lb, and the exhaust treatment consumables were \$0.1806/lb, only slightly more than the standard dyeing cost. Including the bleach costs, the total cost for the conventional dyeing from preparation to dyeing was \$0.9312/lb. Similarly, for the total exhaust treat process, the cost was \$1.0238/lb, an increase of approximately 10%. For the CPB total process, the cost was \$0.7541/lb, decreasing the cost to approximately only 73% the cost of the conventional dyeing while cutting all consumables

of the dyeing process, water, steam, and power. Although the exhaust treatment caused an increase in the total cost of producing the dyed goods, as shown previously in Section 6.4, it appears that it will be possible to combine the bleaching and exhaust cationization processes. If this is possible, the consumables costs for the separate cationization process can be excluded. If it is assumed that a similar fixation efficiency can be obtained with optimization of the duoprep process, then the \$0.1806 can be subtracted from the \$1.0238/lb and the new cost would be \$0.8432/lb and would likewise save extensive consumables as well as money. Further, as previously shown in Table 6.15, when increasing the liquor ratio of exhaust application the efficiency of the cationization goes down. If the exhaust application can be made in a low liquor ratio jet such as an air jet at 5:1 or lower, then significant reductions in needed CHPTAC can be expected. This would also decrease the cost of exhaust applications. The liquor ratio utilized for the 55 pound cationic exhaustion was 8:1. Regardless of the experimental costs of the complete cationization and dyeing processes, if losses in quality of the dyed cationic cotton are observed, then the bulk scale demonstrations and costing are useless.

### **10.5 Quality Control of 55 Pound Lots**

In general, for every QC test except change of color, the dyed cationic cotton exhibited equivalent or increased performance. In the 55 pound cationic cotton dyeings no soda ash was utilized. As a result, it was found that without covalent bonding, that dye was easily removed with the addition of soda ash or standard AATCC detergent. It is thought that an

ion exchange can explain the loss of color with ionic bonding only. This is depicted in Figure 10.9. In the case of adding soda ash to ionically dyed cationic cotton, the anion could be the divalent carbonate ion, hydroxide ion, or the monovalent protonated carbonate ion. In the case of an alkaline detergent, the exact alkali used would need to be known to predict possible ions for exchange but the anionic detergent could also be the anion. AATCC detergent is known to contain anionic surfactants as well as sodium borate, an alkali and candidate for ion exchange with dye. When alkali was used in the dyeing and covalent bonding was formed, no removal of dye was seen after IIA wash and an improvement in color change after five launderings was also seen as well as improvement in the staining of other fibers. Further, crock fastness and lightfastness were not significantly affected by utilizing soda ash in the cationic dyeing. If other anionic dyes besides reactive dyes are used, then ion exchange and removal of dye would be expected. Therefore, it is predicted that anionic dyes with multisulfonation will have to be used to improve the change of color when laundered. It would also be expected that other QC tests that utilize reagents that could tend to act in the same method of ion exchange would cause failures for cationic cotton dyed without soda ash. In a report by Cotton Inc. where many dyes were dyed on cationic cotton without soda ash, it was found that the dyed cationic cotton suffered very poor perspiration fastness (4). The synthetic perspiration used in the tests contains lactic acid as well as dibasic sodium phosphate, both perfect anionic candidates for ion exchange. It was found that with an alkaline wash after dyeing that the perspiration ratings could be improved significantly. A quick test was made with the 55 pound exhaust treated and dyed

without soda ash green and the JFO green dyed with soda ash. Three gram samples of the two fabrics were cut and placed in 30 mL of DI water and 0.1 g of dibasic sodium phosphate was added and brought to a boil. A significant amount of dye was removed from the sample dyed without soda ash while only a minimal amount of dye was removed from the dyeing with soda ash as shown in Figure 10.10. This seems to verify the findings in the Cotton Inc. report and further support an ion exchange mechanism of dye removal. However, it should be noted that the boiling aspect of all of the quick tests with alkali more than likely also causes some degradation of the fixed CHPTAC as witnessed by the aroma of trimethyl amine in all experiments where dyed samples were boiled with alkali. This degradation of the cationic head would seem to also remove dye from the surface of the fiber if dye was ionically bound to the cationic trimethyl amine head. With verification of the QC testing of the 55 pound sample lots, the cost analysis are verified. If soda ash is included into the costing of the cationic dyeings as will be required, the cost of the cationic dyeings and overall total cost will increase by \$0.0437/lb.

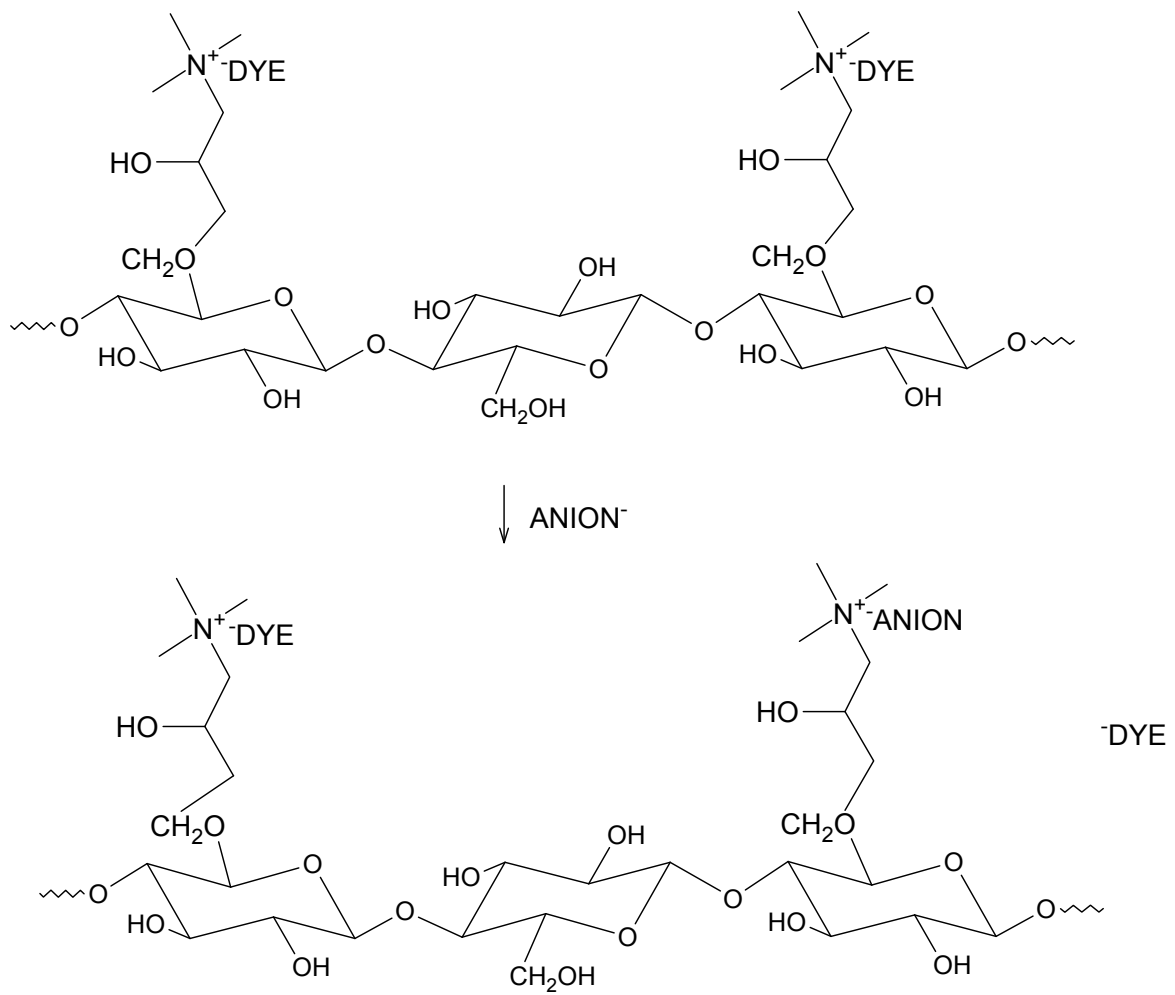


Figure 10.9 - Proposed Ion Exchange Mechanism for Cationic Cotton Dyed with Fiber Reactive Dyes without Utilizing Soda Ash



Figure 10.10 - Green Dyeings Boiled in Dibasic Sodium Phosphate (L-without soda ash, R-with soda ash in the dyeing)

### **10.6 A Note on Percent Nitrogen**

When cotton has been cationized, the quantitative measurement of the fixed cationic reagent is determined by percent nitrogen of the sample. There are two commonly used methods including Kjeldahl and combustion. In the Kjeldahl test, the test is quite laborious and involves digestion with sulfuric acid to finally measure the amount of ammonia formed from the sample. In the combustion technique, the sample is combusted and analyzed for formed nitrogen gas. The combustion technique is much faster and allows more samples to be tested quickly but utilizes very small samples. This requires that samples such as cationized cotton be entirely uniform and may produce unrealistic nitrogen determinations



if not completely uniform. Regardless of the method chosen to measure the percent nitrogen of cationized cotton, the values obtained for cationic cotton in the experiments presented ranged primarily from 0.05-0.25% nitrogen. An explanation of the bias and expected error in percent nitrogen determinations has been reported and predicted to be around 0.02% nitrogen (5). This 0.02% nitrogen would represent almost 40% relative error in the value obtained for low treatment levels, around 0.05%. Further, if auxiliary chemicals such as urea or surfactants with nitrogen were utilized in cationization processes and still remained after processing, this nitrogen would show up and be perceived as cationic reagent. As well, different cotton substrates should naturally be expected to contain different amounts of nitrogen in the cotton. For these reasons, the percent nitrogen determinations become rather laborious to analyze and form absolute values for fixation. It seems to make more sense to correlate the dyeability of a cationic cotton sample to an increase in the percent nitrogen of a sample. In this method, only the nitrogen in the dyeability of the cationic cotton is assessed and not the total nitrogen content present in the fabric. This is the method used throughout these studies. Of course the drawback to this method assumes uniform treatment and dyeing which as seen with the pad bake process was not the case and yielded over predictions for fixation. However, standard dyeing methods such as the one in these studies will allow different researchers to compare cationization processes by dyeability without the uncertainty of nitrogen determinations. No matter what the percent nitrogen is determined or assigned to be as in the case of

zeroing the percent nitrogen for color predictions, the dyeability of the sample will stay the same.

## REFERENCES

1. Quat 188 Epoxide Stability & Half-Life  
[http://dow-answer.custhelp.com/app/answers/detail/a\\_id/9837/](http://dow-answer.custhelp.com/app/answers/detail/a_id/9837/)
2. Draper, Sara L., et al. "Characterization of the Dyeing Behavior of Cationized Cotton with Direct Dyes." AATCC Review. October 2002.
3. Hauser, Peter J. and Mehmet Kanik. "Printing of Cationized Cotton with Acid Dyes." AATCC Review. March 2003.
4. Technical Bulletin, TRI3016-"Dyeing of Cationic Pretreated Cotton," 2003.
5. Hashem, Mohamed, et al. "Reaction Efficiency for Cellulose Cationization Using 3-Chloro-2-Hydroxypropyl Trimethyl Ammonium Chloride." Textile Research Journal. 73(11). (2003): 1017-1023.

## 11. Conclusions

The textile industry is notorious for its gross use of precious commodities such as water, consumption of power, raw materials, and extensive waste discharge. Cotton garments, cherished for their natural look and feel are historically very environmentally unfriendly because of the use of reactive dyes in the coloration process. As a result of reactive dyeings, abundant quantities of salt are consumed and discharged into effluent as well as color pollution through unfixed dyestuffs. An alternative and environmentally attractive approach to cotton dyeing is through cotton modification using 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) rendering cotton with a permanent positive charge. The permanent positive charge allows the uptake of suitable anionic dyestuffs without the need for salt and with sustainable environmental and financial savings. Even with the promised benefits of cationized cotton, the textile industry has not made an evident shift towards its utilization. It is thought that the main reasons for the lack of cationization acceptance can be attributed to safety concerns about CHPTAC, lack of quantified and demonstrated large scale cationization results, and worries of increased processing costs utilizing CHPTAC. These issues as well as other issues that become apparent when demonstrating the feasibility and practicality of cotton cationization have been explored and addressed.

The safety and utilization of CHPTAC has been extensively reviewed and summarized. CHPTAC, the cationic chemical reagent for cellulosic and other glucose polymers is relatively non-toxic, is not an irritant or skin sensitizer, and is a high volume

chemical. CHPTAC becomes inappropriately associated with the effects of epoxypropyltrimethylammonium chloride (EPTAC), a carcinogen class 2 and potent skin sensitizer. EPTAC is formed in situ from CHPTAC in the presence of alkali. It is important that the differences between EPTAC and CHPTAC be recognized and realized and associated correctly. Further, textile wet processing can be designed for cationization utilizing existing equipment for minimal potential occupational exposure to EPTAC.

In published research, many methods have been shown and used for the cationization of cotton but exhaustion and cold pad batch (CPB) methods have emerged as industrially relevant. Traditionally, exhaustion methods have yielded very low fixations of CHPTAC. Significant improvements in the fixation of exhaust applied CHPTAC have been realized, approximately double the amount of current industrial process recommendations. Experimental design has predicted the importance and effect of the main variables associated with the exhaustion of CHPTAC. Further, attempts at identifying a phase transfer catalyst were not successful in identifying an industrially significant agent, but, some reagents did show slight improvements in the fixation of exhaust applied CHPTAC. A pad bake process that can easily be industrially adopted has been suggested and shown to realize CHPTAC fixations greater than those found with the CPB method. Results do suggest that utilizing ultra low wet pick up techniques such as foaming should increase the fixation of applied CHPTAC. An initial foaming test albeit successful was identical in fixation to a CPB control. Although the foaming process is somewhat complex, positive initial findings prove

that foam cationization is possible and that optimization and further studies of foam application may yield promising results for cotton cationization.

In an effort to realize, prove, or disprove some of the concerns and issues encountered when dyeing cationized cotton, several different areas involving the dyeing of cationic cotton have been addressed. Concerning lightfastness, indeed, with inappropriate treatment levels, i.e. over cationization, lightfastness of dyed cationic cotton can fail because of surface dyeing. However, with correct amounts of cationization, dyed cationic cotton can perform better in lightfastness than the same shade dyed using conventional methods. Concerning correct treatment levels for a traditionally dyed shade, logic has been shown and used to simultaneously predict a shade match on cationic cotton and predict the corresponding required nitrogen level for near complete exhaustion of applied dyestuffs. In an effort to make cationic cotton more appealing, initial experiments have shown that it is possible to efficiently soften cationic cotton in an exhaust bath utilizing neutralized fatty acids.

Specifically concerning the dyeability of cationic cotton, there appears to be two methods of dyeing. Method one is the complete exhaustion and utilization of applied dyestuffs. This method is challenging because the treatment level for complete exhaustion needs to be identified and the applied dyes are very hard to level. As already mentioned, an effective color match and nitrogen prediction scheme has been developed and demonstrated with examples. Further, a very efficient leveling package for cationic cotton has been developed and demonstrated utilizing a lubricant, dispersant, and carboxymethyl

cellulose as a dye retarder. The second method of dyeing cationic cotton utilizes a saturation dyeing technique for saturating the dyesites with more dye than they can hold. This ameliorates leveling issues and the shade can be dyed in significantly less time. However, this method does not realize the same level of environmental savings as method one and the color will be heavily dictated by the level of cationic treatment and not necessarily by the amounts of dye added. Experiments showed huge differences in temperature and hold times for depths of shade obtained utilizing this method. As a result, it has been suggested that the dye manufacturer's recommendations for time and temperature be followed and optimized from there.

Specifically regarding acceptable dye types for the coloration of cationic cotton, it appears preliminarily that reactive dyes may be the best contenders because they allow ionic and covalent bonding. Fabrics dyed utilizing ionic bonding only with certain reactive dyes showed failures in washfastness presumably resulting from a suggested ion exchange mechanism. With alkali included in reactive dyeings, color change ratings were greatly improved. It may be possible to dye cationic cotton with other anionic dyes possessing multiple sulfonate groups but it is envisioned that these dyes would require many sulfonate groups to prevent ion exchange and as result the shade depth achievable will go down because of dye site utilization. As a result, other acceptable dyestuffs may require higher degrees of cationization to allow the building of shade depth with highly sulfonated dyestuffs. Further, because of the uniqueness of vinyl sulfone dyes, the vinyl reactive group is not present in the initial dye molecule and only is formed when alkali is added. This

presents challenges to the dyer in achieving shade depth and covalent bonding by taking into the account the number of dye sites available in the vinyl sulfone dyes and when that number will change when alkali is added.

Concerning the cost of cationization and dyeing of cationic cotton, 55 pound lots of CPB methods have shown tremendous financial savings and demonstrated the ease of large scale cationizations and successful dyeings. Further, with quantified consumables used during processing, remarkable ecological savings have also been found with CPB cationization and dyeing. With exhaust treated cationization of 55 pound lots, a slight increase in cost has been observed but this would be expected to be cheaper than conventional cotton dyeings if a dual bleach and cationization process can be realized as suggested. Further, with lower liquor ratio exhaust applications the costs observed would also be expected to decrease. The exhaust cationizations did show savings in the precious commodity water. Finally, quality control testing showed that with inclusion of soda ash in reactive dyeings of cationized cotton compared to conventionally dyed cotton, fastness was as good or better for dyed cationic cotton.



## 12. Recommendations for Future Work

These studies have shown that cationization chemicals are not inherently toxic and explained the differences in CHPTAC and EPTAC. Further, it was shown that bulk cationizations and subsequent dyeings are straightforward and that fastness properties can even be improved compared to conventional dyeings. As well, cationized cotton was shown to achieve financial savings paired with environmental savings. This work also provided information, suggestions, and a very valuable tool for shade matching and corresponding cationization treatment levels required. With this work as well as the work of previous researchers, typical textile dyeing mills should have a very good opportunity for success in utilizing cationic cotton. However, this work suggests that there are additional opportunities in further developing cationic cotton tools and methods.

As shown in the cost analysis, the exhaust cationization treatment resulted in a slight increase in processing costs compared to conventionally dyed cotton. It is suggested that if the bleaching and cationization can be completed simultaneously, then the overall cost of the exhaust cationization and dyeing will be significantly lower than the conventional dyeing process. Although an initial trial showed that this is possible, a complete study on simultaneous bleaching and cationization would be highly beneficial in terms of cost savings utilizing exhaust applied CHPTAC.

It was shown that by developing cationic cotton primaries for individual dyes and inputting into color prediction software, it is possible to predict cationic cotton formulations. By relating the K/S values and percent nitrogen, it is possible to predict the

amount of cationization required for the dye formula. Although this methodology was shown to work very well, the dyeing method used did not use alkali in the dyeing which proved to be detrimental in fastness properties. This process would prove highly beneficial if it can be repeated with many dyestuffs as well as using reactive dyes with alkali.

Finally, an ion exchange mechanism was proposed for cationic cotton dyed with ionic bonds only. This suggests that suitable dyestuffs for cationic cotton will be reactive dyes and polysulfonated anionic dyes that have a higher chance of staying permanently bound. It is suggested that different dyes and dye classes be examined for stability to ion exchange through laundering processes. It is suggested that the solubility product constant ( $K_{sp}$ ) be determined, if any, in water only. In a closely related study using methyl viologen and alkyl sulfates,  $K_{sp}$  were found using different chain lengths and found to decrease with increasing chain length (1). In other words, it may be found that at certain molecular weights of dyes, that the  $K_{sp}$  is negligible or non-existent. These studies should also determine equilibrium constants for ion exchange of dye ( $K_{ie}$ ) in the presence of different anions. By determining these constants for many dyes, the most suitable dyes for cationic cotton can be identified for fastness properties when laundered.

## REFERENCES

1. Engelman, E. Eric and Dennis H. Evans. "Treatment of the Electrodeposition of Alkyl Sulfate Salts of Viologen Radical Cations as an Equilibrium Process Governed by a Solubility Product." Analytical Chemistry. 66 (9). May 1994: 1530-1534.

## APPENDIX

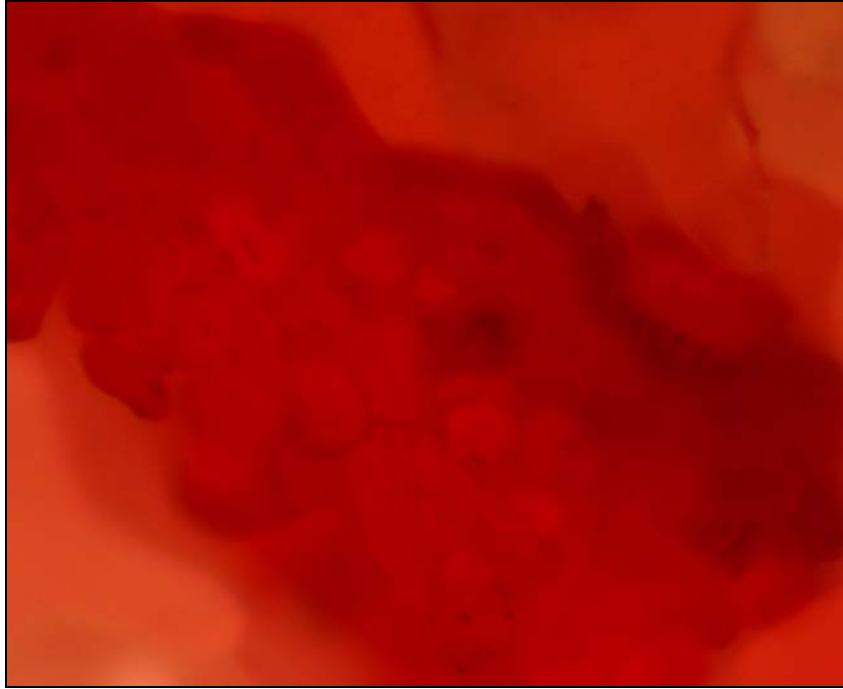
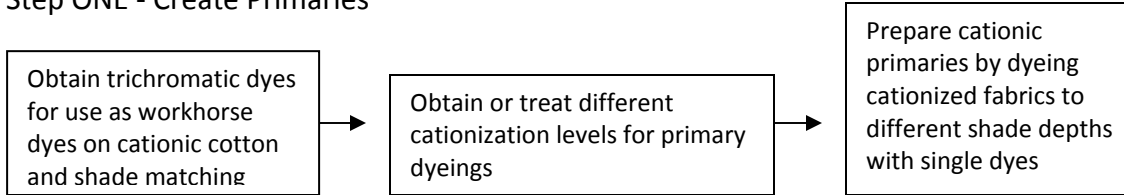


Figure A1 - Micrograph of CPB Treated Cotton - 50X

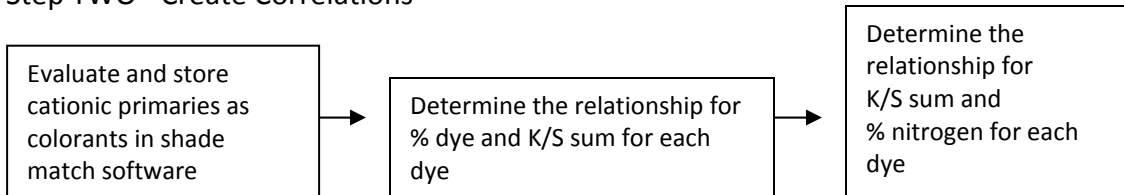


Figure A2 - Micrograph of Pad Bake Treated Cotton - 50X

### Step ONE - Create Primaries



### Step TWO - Create Correlations



### Step THREE - Predict Dye Formula and Percent Nitrogen

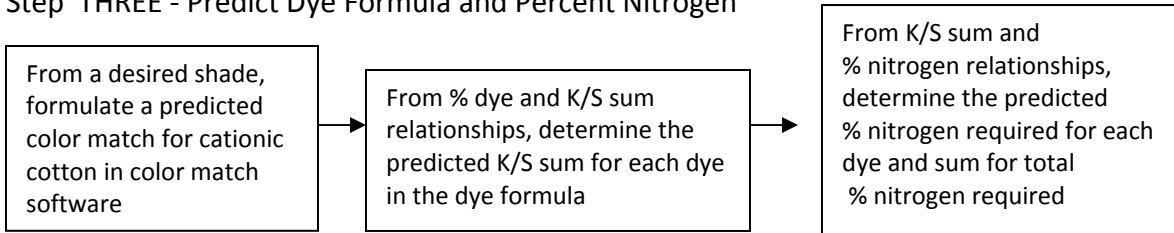


Figure A3 - Flowchart for Cationic Cotton Dye Formula and Nitrogen Prediction

Table A.1 - 55 Pound Bleach Jet Procedure

| Command        | Parameters             |
|----------------|------------------------|
| Insert Program | 600 - Batch Weight     |
| Fill           | at 080F to 100%        |
| Add Fill       | Lev:10% From:1         |
| Add Prepare    | Prompt:00              |
| Add Dose       | 00m C:0                |
| Load Fabric    |                        |
| Add Prepare    | Prompt:00              |
| Add Fill       | Lev:10% From:1         |
| Add Dose       | 00m C:0                |
| Add Prepare    | Prompt:00              |
| Add Fill       | Lev:10% From:1         |
| Add Dose       | 00m C:0                |
| Heat           | 9.9 TO 225F            |
| Run            | 35mins                 |
| Cool           | 5.0 TO 160F            |
| Drain          | to 000%                |
| Fill           | at 120F to 100%        |
| Rinse          | 160F 70% 10mins        |
| Drain          | to 000%                |
| Fill           | at 120F to 100%        |
| Rinse          | 160F 70% 10mins        |
| Drain          | to 000%                |
| Fill           | at 120F to 100%        |
| Add Fill       | Lev:10% From:0         |
| Add Prepare    | Prompt:00              |
| Add Dose       | 00m C:0                |
| Temperature    | 9.9 TO 140F            |
| Run            | 10mins                 |
| Drain          | to 000%                |
| Fill           | at 160F to 100%        |
| Rinse          | 100F 70% 10mins        |
| pH Check       | Low:06.0 High:07.0 B:0 |
| Unload Machine | Drain? 0/1:0           |
| Drain          | to 000%                |

Table A.2 - 55 Pound Conventional Reactive Dyeing Jet Procedure

| Command         | Parameters         |
|-----------------|--------------------|
| Insert Program  | 600 - Batch Weight |
| Fill            | at 080F to 100%    |
| Temperature     | 9.9 TO 100F        |
| Add Fill        | Lev:20% From:1     |
| Add Prepare     | Prompt:01          |
| Load Fabric     |                    |
| Add Dose        | 00m C:0            |
| Run             | 05mins             |
| Heat            | 4.0 TO 140F        |
| Add Recirculate |                    |
| Add Heat        | to 140F            |
| Add Prepare     | Prompt:00          |
| Run             | 15mins             |
| Add Dose        | 00m C:0            |
| Add Fill        | Lev:10% From:0     |
| Add Prepare     | Prompt:10          |
| Run             | 10mins             |
| Add Dose        | 20m C:0            |
| Add Fill        | Lev:25% From:0     |
| Add Prepare     | Prompt:07          |
| Run             | 15mins             |
| Add Dose        | 20m C:0            |
| Run             | 45mins             |
| Drain           | to 000%            |
| Fill            | at 080F to 075%    |
| Rinse           | 120F 70% 10mins    |
| Drain           | to 000%            |
| Fill            | at 160F to 075%    |
| Temperature     | 9.9 TO 160F        |
| Heat            | 9.9 TO 200F        |
| Run             | 10mins             |
| Cool            | 9.9 TO 160F        |
| Drain           | to 000%            |
| Fill            | at 080F to 075%    |
| Rinse           | 100F 25% 10mins    |
| Find Seams      |                    |
| Drain           | to 000%            |
| Unload Machine  | Drain? 0/1:0       |



Table A.3 - 55 Pound Cationic Exhaust Treatment Jet Procedure

| Command        | Parameters         | Notes  |
|----------------|--------------------|--------|
| Insert Program | 600 - Batch Weight |        |
| Fill           | at 000F to 100%    |        |
| Add Prepare    | Prompt:00          |        |
| Add Fill       | Lev:15% From:1     |        |
| Add Dose       | 00m C:0            | NaOH   |
| Add Prepare    | Prompt:00          |        |
| Add Fill       | Lev:15% From:1     |        |
| Heat           | 5.0 TO 112F        |        |
| Add Dose       | 10m C:0            | CR2000 |
| Run            | 20mins             |        |
| Heat           | 5.0 TO 185F        |        |
| Run            | 50mins             |        |
| Cool           | 5.0 TO 160F        |        |
| Drain          | to 000%            |        |

Table A.4 - 55 Pound Cationic Neutralization Jet Procedure

| Command        | Parameters             | Notes       |
|----------------|------------------------|-------------|
| Insert Program | 600 - Batch Weight     |             |
| Batch Weight   | 040 Lbs                |             |
| Liquor Ratio   | 08.0:1                 |             |
| Flow Rate      | 100%                   |             |
| Reel Speed     | 100YPM                 |             |
| Fill           | at 100F to 100%        |             |
| Run            | 06mins                 |             |
| Drain          | to 000%                |             |
| Fill           | at 000F to 100%        |             |
| Add Fill       | Lev:00% From:1         |             |
| Add Prepare    | Prompt:00              |             |
| Add Dose       | 00m C:0                | Acetic Acid |
| Run            | 06mins                 |             |
| pH Check       | Low:05.0 High:07.0 B:1 |             |
| Drain          | to 000%                |             |
| Unload Machine | Drain? 0/1:0           |             |

Table A.5 - 55 Pound Cationic Dyeing Jet Procedure

| Command        | Parameters         | Note           |
|----------------|--------------------|----------------|
| Insert Program | 600 - Batch Weight |                |
| Fill           | at 000F to 100%    |                |
| Add Fill       | Lev:10% From:1     |                |
| Add Prepare    | Prompt:00          |                |
| Add Dose       | 00m C:0            | CMC and aux.'s |
| Add Fill       | Lev:10% From:1     |                |
| Add Prepare    | Prompt:00          |                |
| Heat           | 2.0 TO 135F        |                |
| Add Dose       | 20m C:7            | Dye            |
| Run            | 30mins             |                |
| Drain          | to 000%            |                |
| Unload Machine | Drain? 0/1:0       |                |

Table A.6 - 55 Pound Cationic Dyeing After Rinse Jet Procedure

| Command        | Parameters         |
|----------------|--------------------|
| Insert Program | 600 - Batch Weight |
| Fill           | at 000F to 100%    |
| Rinse          | 115F 70% 10mins    |
| Drain          | to 000%            |
| Unload Machine | Drain? 0/1:0       |