ABSTRACT

GOLI, KIRAN KUMAR. Use of Modified Cellulose for the Improvement of Water Repellency. (Under the direction of Dr. Peter Hauser).

A novel method is developed for imparting durable water repellency to cotton cellulosic fabrics based on ionic interactions. Most of the traditional water repellent finishing chemicals such as paraffin waxes, pyridinium compounds, formaldehyde based N-methylol crosslinkers, siloxanes and fluoro-carbon polymers are either non-durable to washing or environmentally unsafe or expensive. Our method includes cationization of cotton fabric with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC) followed by subsequent treatment with a salt of stearic acid to form ionic attractions between cationic groups of cationized cotton fabric and anionic groups of stearate anion. These ionic interactions hold the stearate or hydrophobic molecules on the surface of cotton fabric outwards giving durable water repellency without releasing any hazardous chemicals present in almost all other durable water repellent treatments for textiles.

Use of Modified Cellulose for the Improvement of Water Repellency

by

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

Textile Chemistry

Raleigh, North Carolina

2008

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DEDICATION

This work is dedicated to my parents, Anjali Devi and Venkata Rao, my brothers Ashok Babu and Leela Krishna and Dr. Peter Hauser and Dr. Brent Smith.

BIOGRAPHY

Kiran Kumar Goli was born in Epurupalem, Andhra Pradesh, India. He completed his high school education from Bharathi Junior College in 2002. Later, he joined Mumbai University Institute of Chemical Technology, Mumbai, India and completed the Bachelor of Technology program in Fibers and Textile Processing in May 2006. He was admitted to Master of Science program in Textile Chemistry and started his research work under the guidance of Dr. Peter Hauser and Dr. Brent smith in College of Textiles at North Carolina State University.

ACKNOWLEDGEMENTS

I would like to thank Dr. Peter Hauser for his advice, encouraging words and support throughout my graduate research and dissertation preparation. I am also extremely thankful to Dr. Richard Spontak and Dr. David Hinks for their willingness to serve on my graduate committee. I am also indebted to Dr. Mohamed Hashem, Dr. Eunkyoung Shim and Dr. Mehdi Afshari for their help during the research.

I wish to acknowledge the financial support of National Textile Centre for this research. Special thanks to Mr. Jeff Krauss, Ms. Angie Brantley, Ms. Judy Elson, Ms. Shane Jarvis, Ms. Vicki Stocksdale and Ms. Birgit Andersen. I would also like to thank all my friends and colleagues who have helped me in my work and made my stay enjoyable at graduate school.

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1. INTRODUCTION

Water repellent treatment of cotton fabric is an important finishing process which prevents penetration of water through the fabric without destroying comfort of the fabric[1]. Water repellent fabrics are used in rain-wear, sportswear, medical bandages, upholstery fabrics for automobiles, headliners, cover tapes for adhesive plasters, and outdoor activities. In the early 1930's, there was an increased interest in achieving durable water repellency and it has been playing an important role in the apparel industry ever since[1-3].

The existence of intermolecular attractive forces of polarity and hydrogen bonding are imperative in providing strength, heat resistance and dry-cleaning resistance to the textile fabric. However, these forces enhance easy wetting of fiber by water offering little resistance to snow and rain for outerwear garments. This problem could be overcome by adding various water repellent chemicals to the fabric either chemically or with mechanical coating. The water repellent compounds cover the outer surface of the fabric with hydrophobic groups. These hydrophobic groups repel water molecules forming a low energy surface. The treatments in which mechanical forces or secondary valences bond the water repellent chemical onto the fabric suffer from durability or wash away during dry-cleaning. The formation of permanent covalent bonds between the fiber and water repellent chemical are necessary to produce durable water repellency[4]. The chemical nature of the bond between fiber and water repellent chemical prevents the removal of the water repellent chemical during laundering or dry-cleaning[5].

Pyridinium compounds, chromium based metal complexes and N-methylol based products accomplish the durable chemical bond formation. These products provide durable water repellent performance. Unfortunately, these compounds are hazardous and toxic to the environment limiting their production.[6] Polysiloxanes can also be applied to textile fabrics based on hydrogen bonding and mechanical interactions between the fabric and the –Si-O-Si- bonds of the silicone compound along with network cross-link formation within the polysiloxane compound itself. This finish gives semi-durable water repellency. Fabric treated with fluorocarbon chemicals exhibit excellent water repellency. However, this finish is expensive and needs a heat treatment after washing to retain repellency[7].

A method has been developed in this work in which ionic interactions between oppositely charged cationic cellulose fabric and anionic stearate ions, i.e., cationization of cellulose followed by exhaustion with a stearate anion, gave durable water repellency to cotton cellulose fabric. The ionic interactions are strong enough to overcome harsh hot washings and are durable to 20 hot wash laundry cycles. The chemicals used are economical and environmentally safe. The process does not require any special equipment and no curing is required. A similar approach can also be followed in anti-microbial finishing.

2. BACKGROUND

This chapter gives an overview of the cellulose, its structure and a brief discussion of water repellents in the textile industry.

2.1. Chemistry of cellulose

The knowledge of chemical composition, structure, and morphology of cellulose molecule in fibrous form is very important in understanding physical and chemical properties of cotton cellulose. For instance, the presence of functional groups, size of crystallites, orientation of polymer chains, degree of polymerization and presence of inter and intra-molecular interactions dictates the physico-mechanical properties of resultant fabric[8, 9]. The textile industry consumes the major part of cellulosic polymers in the form of cotton. Cotton fiber is obtained from fibers that grow around the seeds of cotton plants. The length of cotton fiber ranges from 10 to 35 mm depending upon the quality and type of fibers. The color of the raw cotton fiber varies from creamy white to dirty grey depending on climatic conditions and the environment under which it is grown[10]. Raw cotton contains impurities in the form of wax, protein, ash, pectin, etc. ranging from 4-12 % placed on the outer side of the fiber[11]. Scouring and bleaching processes remove most of the impurities of cotton fiber to obtain 99% pure cellulose[8].

Cellulose is a linear condensation polymer described chemically as poly (1,4-β–D-anhydroglucopyranose). The repeating unit of cellulose polymer is the cellobiose unit consisting of two glucose units each with six carbon atoms joined by a glucosidic linkage as shown in Figure 2.1.[8, 11] The cotton cellulose consists of 6000-10000 cellobiose units, depending upon the nature and quality of the fiber.[10]

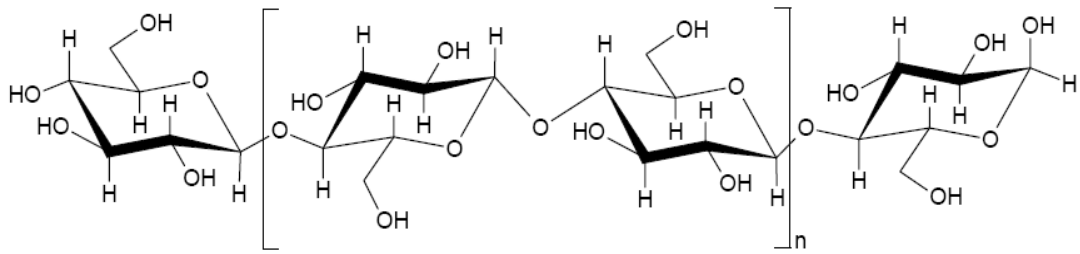


Figure 2.1. Molecular structure of cellulose [8]

Three hydroxyl groups, one primary (-CH_2OH) and two secondary hydroxyl groups, present in each glucose unit are the most important chemical groups. These hydroxyl groups are the reacting sites which will undergo substitution reactions, such as etherification and esterification with many chemicals allowing the modification of cotton or imparting finish to the fabric.[9,10] The primary hydroxyl group has relatively higher reactivity than secondary hydroxyl groups because of its higher acidity.[12,13] For reversible reactions and higher molecular weight reagents, primary hydroxyl groups react faster than secondary hydroxyl groups. In the case of irreversible William syntheses involving smaller molecular weight reagents, the secondary hydroxyl groups at the C-2 positions are more reactive in nature[14]. The polarity of these hydroxyl groups also results in hydrogen bonding between the oxygen atom positioned between the rings and the secondary hydroxyl groups of adjacent parallel cellulose polymers[10, 15]. The strength of the cotton fiber is enhanced with the increase of the moisture content resulting from increased hydrogen bonding from adsorbed moisture[13].

The crystallinity of cotton cellulose fiber ranges between 65-70 %, leaving the remaining portion as amorphous in nature. In native cellulose, polymer chain molecules are parallel to each other along with close packing of cellobiose units in crystalline regions[11]. Cotton fiber also contains about 20-41 % of unoccupied space because of lumen and spaces between fibrils. This spacing also enhances the modification of cotton fabrics by enhancing accessibility of chemical reagents. To a smaller extent, Vanderwaal's forces also exist between the polymer chains.[10, 15]

2.2. Water repellent finishing

Water repellent finishing is a treatment applied to textile substrates that does not allow passage of water droplets through the fabric but allows passage of water vapor [2]. In other words, it should prevent spreading of water droplets on the surface of textile and should not wet the fabric[7]. Water repellent fabrics find applications for clothing, home, rain-wear, medical bandages, etc[2]. The intermolecular forces of polarity or attraction and hydrogen bonding forming capability present in cotton fibers and other most common fibers renders strength, heat resistance and dry-cleaning resistance. At the same time, these forces are responsible for easy wetting of fabric by liquid water rendering less resistance to wettability of outerwear garments from rain and snow. Water resistance is normally achieved through two methods:

1. A rubber or polyvinyl chloride forms a continuous flexible coating over the entire fabric making it completely resistant to water (water proof). This finish prevents permeation of water vapor from the body of the wearer to the outside causing it to be uncomfortable.

2. Hydrophobic surface treatment is given in such a way that individual fibers are covered with a water repellent chemical making them resistant to wetting and allowing passage of water vapor. Water vapor passage makes a fabric more comfortable to wear than the fabric with a continuous coating.

A water repellent fabric with permanent resistance to dry-cleaning is desired. This can be achieved by attaching the hydrophobic chemicals to the individual fibers by permanent covalent bonding.[4]

2.3. Principle of repellency

Repellency is obtained by reducing the free energy of a fiber surface by using various chemicals which have lower surface energies. These lower surface energy bodies have lower adhesive interactions between the fiber and the liquid than the internal cohesive interactions within the liquid. This prevents spreading of liquid droplets on the surface of the textile fabric. For any liquid, the critical surface energy or tension (γ_c) of the solid surface must be lower than the surface tension of the liquid for the liquid to be repelled[7]. Surface tension is defined as the force per unit length (dynes/cm) acting on the surface of a liquid which resists wetting on a surface.[16] It is also important to understand critical surface tension. For a given homologous series of organic liquids, the contact angle (Θ) is measured on a low surface energy solid. The plot of cosine of the contact angle measured versus the surface tension of the liquid gives a straight line. The intercept of this line at $\cos \Theta = 1$ (contact angle = 0) is defined as the critical surface tension (γ_c).[3] Some of the surface tensions of selected surfaces are shown in Table 2.1. [3, 17]

Table 2.1. Critical surface tensions of different substrates[3, 17]

Surface constitution	γ_c (dynes/cm)
Oriented perfluoroalkanes ($-CF_3$)	6
$-CF_2H$	15
PTFE ($-CF_2-$)	18
Oriented alkanes ($-CH_3$)	23
Silicone	24
PE ($-CH_2-$)	31
-CH- (benzene ring edge)	35
$=CCl_2$	43
PVC	39
Polyester	43
Cotton	44
Wool	45
Polyamide	46

2.3.1. Water repellency of textile fabrics

The chemical and physical properties of fiber, yarn and the chemicals used for finishing determine the water repellency of the resulting fabric. Wenzel proposed that water repellency of a textile fabric involves the same principles as in capillary tubes and applied the fundamental principles of wetting to textile materials to design a better water repellent fabric[18].

2.3.1.1 Some theoretical aspects of water repellency [18]

The following physico-chemical aspects are important in understanding the mechanism of water repellency of textile materials:

1. Adhesion (W) between solid and liquid directly measures the ability of a given liquid to wet a particular solid.

$W = \gamma (1 + \cos \Theta)$ where, W = Adhesion or wettability,

γ = Liquid to air surface tension

Θ = Contact angle between solid and liquid

For a given value of surface tension (γ), adhesion (W) of a solid is a function of contact angle Θ. For small values of Θ, W is large resulting in a ready wetting of any given solid by the liquid.

2. The nature of the liquid and the solid which are in contact with each other also decides the magnitude of contact angle. If the liquid which adsorbs on solid contains any dissolved substance, the contact angle varies depending on the dissolved substance as compared to the contact angle of the original liquid. Coating the solid surface with another substance also results in decrease or increase of contact angle.

3. Contact angle also depends on the nature of the surface. For $\Theta < 90$, rougher surface lowers contact angle, while for $\Theta > 90$, roughness increases the contact angle.

4. The contact angle between the liquid and the wall of a capillary tube and the size of the capillary determine the motion of the liquid into a capillary tube. Equilibrium contact angles less than 90^0 ($\Theta < 90^0$) between the liquid and the wall of capillary tube result in rise of the liquid through the tube by surface forces, as shown in Figure 2.2. In contrast,

these surface forces acting on the liquid exercise in such a direction to oppose the movement of the liquid in capillary tube at larger contact angles ($\Theta > 90^0$) between the liquid and the wall of the capillary tube. Therefore, stress must be applied to force the movement of liquid into the capillary tube.

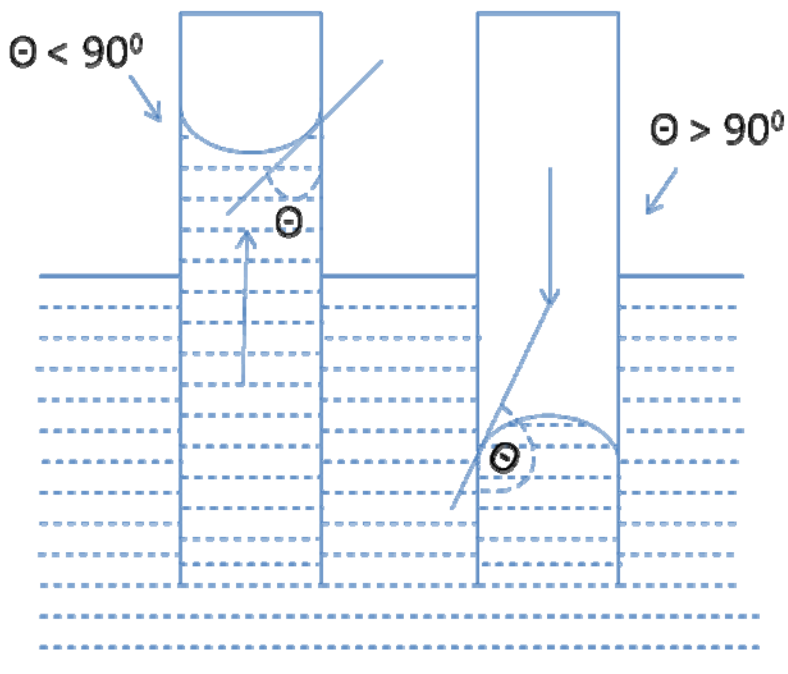


Figure 2.2. Flow of liquid through capillary tube

Fabrics consist of pores resembling these small capillaries. The fibers in the twisted yarn lie side by side and form very narrow openings which serve as micro channels for the movement of liquid. The spaces between warp and weft yarns form larger openings that serve as macrochannels. These micro and macro channels are functions of fabric construction parameters, such as tightness, nature of the weave and rigidity of the twist in the yarn. A low contact angle between the fabric material and water results in penetration of water through both micro and macro channels to completely wet the fabric.

Modifying the capillary wall or treating the fabric chemically or physically in such a way that results in higher contact angle between the liquid and the wall of the capillary tube or between the liquid and the fiber surface may prevent capillary action or the penetration of liquid through microchannels placed on the surface of the fabric. But, water penetrates through fabric to some extent via macrochannels without wetting the fibers and the degree of penetration depends on several following factors. Schematically consider the cross-section of a set of parallel yarns in a fabric as circles as shown in Figure 2.3. At higher contact angles ($\Theta > 90^0$), the extent of penetration of the water through the fabric is low and the equilibrium position of the water level follows a line similar to AA and the fabric works as an efficient water repellent material. If stress is applied to force the water through openings, the equilibrium position of the water level may vary in accordance to the stress applied and the contact angle may decrease. At contact angle $\Theta = 90^0$, water partially penetrates through the fabric and the equilibrium position of water level will be represented as BB. Upon application of slight pressure at ($\Theta = 90^0$), the liquid is forced to penetrate through the fabric and result in the formation of droplets on the other side of the fabric as shown by line CC. The surface forces which act at the meniscus oppose the penetration of liquid through the fabric until this stage. Disturbing the equilibrium state at this stage may result in coalescence of droplets and is represented as DD. At this stage individual liquid droplets lose their meniscus and the surface forces will not resist the passage of liquid through the fabric. After this incident, Θ, between the fabric and the liquid will not affect the passage of liquid through the fabric and the treatment given to the fabric will not matter much. Abrading the interior part of the tent during rain to achieve a dripping of water is common example of this effect.

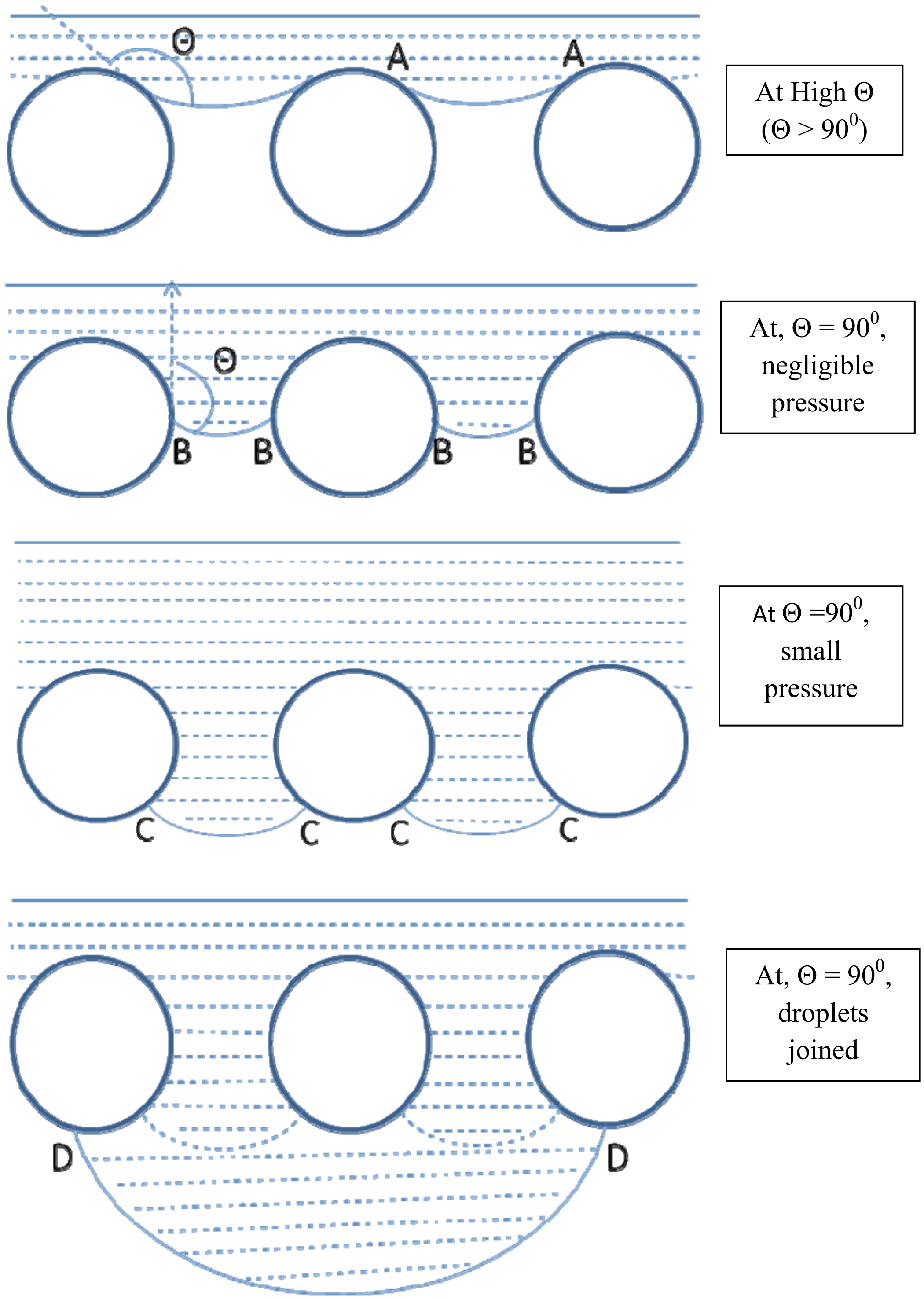


Figure 2.3. Movement of liquid through macrochannels upon application of stress[18]

At higher contact angles ($\Theta > 90^0$), there is always some force which resists the capillary action of water which acts at the circumference of water meniscus. The pressure needed to overcome this resisting force in a small round capillary tube is shown in Figure 2.4.

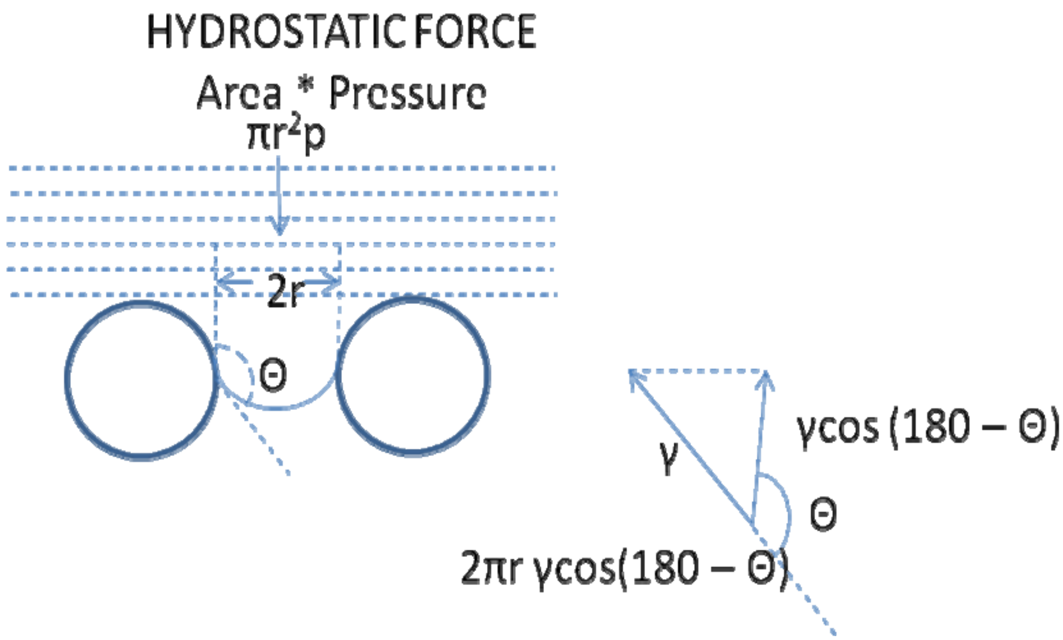


Figure 2.4. Relationship between contact angle and hydrostatic pressure[18]

The total force which resists the motion of liquid through a round capillary tube of radius r is given by $2\pi r\gamma\cos(180 - \Theta)$. At equilibrium, an equal amount of hydrostatic force $\pi r^2 P$, P is the pressure, opposes the resisting motion of liquid. Therefore, at equilibrium,

$$2\pi r\gamma \cos(180 - \Theta) = \pi r^2 P$$

$$-2\pi r\gamma \cos\Theta = \pi r^2 P \quad \text{(Since, } \cos(180 - \Theta) = -\cos\Theta\text{)}$$

$$P = \frac{-2\pi r\gamma \cos\Theta}{\pi r^2} = \frac{-2\gamma \cos\Theta}{r}$$

From the above equation, it can be understood that a water repellent treatment should increase the contact angle or the fabric should be designed or woven to give a smaller channel size to prevent water penetration. The above models reflect an ideal case of a smooth uniform tube but the results are in good agreement with the values obtained from real fabrics using hydrostatic pressure test results.

When a drop of water hits the surface of the water repellent fabric, the impact pressure (P) is calculated by assuming that the kinetic energy of the falling drop is not dissipated by spreading, i.e., $P = mv/ta$, where, m is the mass of water drop, a is the area over which an impact pressure is exercised when a drop hits the fabric, and v is the velocity which changes within time, t, from the moment at which the drop first contacts the fabric and the moment at which final part of the drop strikes the fabric. In reality, the whole kinetic energy of the falling drop does not contribute to impact pressure since part of it is dissipated in spreading of the drop when it hits.

In general, rain drops have higher kinetic energy since drops fall from higher altitude with considerable velocity with greater mass. Generally performance of water repellent fabric can be improved by a double layered fabric with soft cushion backing. For effective water repellency both layers of the fabric should be water repellent. The soft cushion backing absorbs the energy of falling drops and increases the extent of impact (t) reducing the effective pressure. Any drop penetrated though the outer fabric gets locked in between the outer fabric and cushion and most of its kinetic energy dissipates within this duration of time. If the cushion is water repellent, the drop remains in between the outer layer and cushion until evaporation takes place. If the cushion is not water repellent, then drops after penetrating through the outer fabric will saturate the cushion and will spread the water to surroundings and coalescence of droplets takes place under the cushion[18].

2.4. Water repellent agents

2.4.1. Aluminium and zirconium Compounds[6, 19]

Aluminium and zirconium compounds are two of the oldest water repellent agents having hydrocarbon hydrophobes. The fabric has to be soaked in alkaline aluminum acetate for 9-20 hours followed by drying, which leaves insoluble aluminium acetate on the fabric imparting repellency. Aluminium acetate could also be applied by padding the fabric with aluminium acetate followed by treating with alkali which leaves precipitated alumina on fabric. Precipitation of aluminium acetate on the fabric is a two step process. The major disadvantage of the route is poor adhesion of repellent and dusting of the fabric. The above process was improved by using water soluble soaps such as stearic acid salt, instead of alkali to produce aluminium soap in the fiber.

$$3\ C_{17}H_{35}COONa + (HCOO)_3\,Al \longrightarrow (C_{17}H_{35}COO)_3\,Al + 3\ HCOONa$$

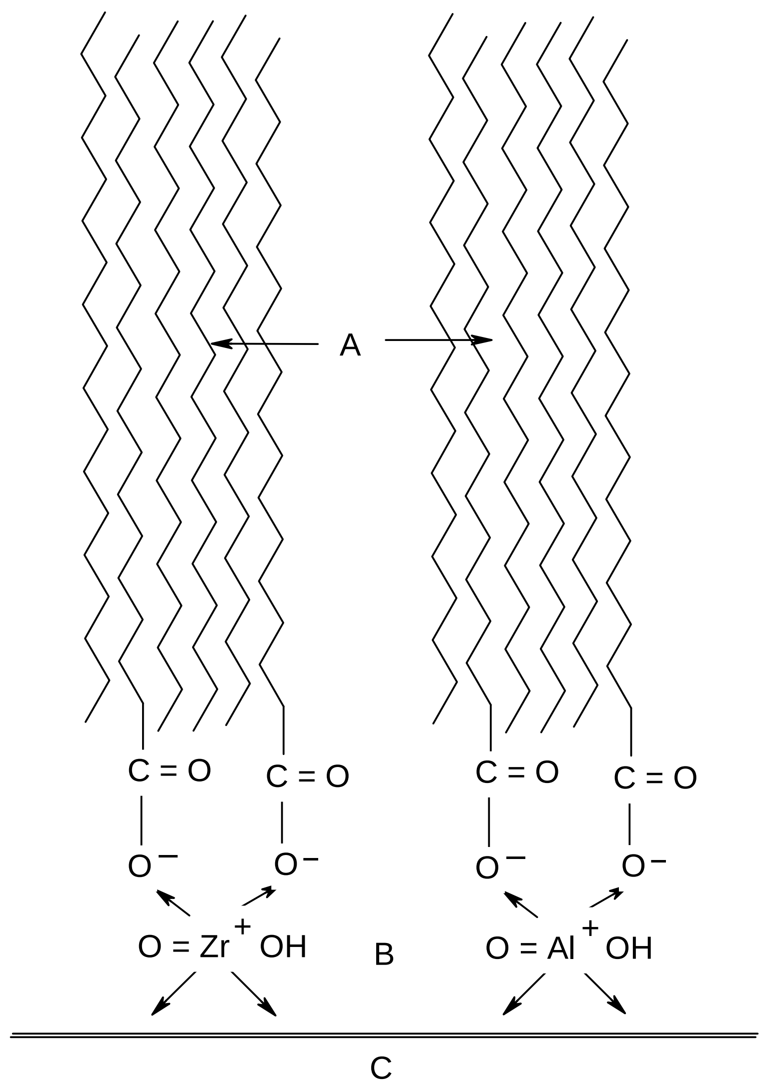
Equation 2.1. Reaction of stearic acid salt and aluminium acetate

Aluminum soaps such as aluminium stearate and palmitates are not soluble in water but are soluble in alkaline detergent solution by converting into soluble sodium and potassium soaps resulting in poor wash fastness of the water repellent fabric. Aluminium is replaced by zirconium to improve fastness to laundering since zirconium soaps are more hydrophobic and are more resistant to alkali than aluminium soaps. Treatment can also be given in a single step process by padding the fabric in aluminum soap solution by using a suitable organic solvent.[6, 19]

2.4.2. Paraffin repellents

Coating of the fabric with hydrophobic substances such as paraffin wax alone or in combination with other waxes such as beeswax, carnauba wax and vaseline were some of the earliest and economical ways of preparing water repellent fabric. Wax is applied to the fabric by rubbing a solid wax into the fabric or as a solution in a suitable organic solvent such as benzene or by spraying wax in the molten state onto the fabric. The most generally used method was preparing aqueous emulsions from wax which were then padded onto fabric. Wax-aluminium processes were applied to cotton fabric in a two step process where fabric was first padded with wax emulsion followed by drying and then treating with aluminium acetate.[6, 19] This process was modified into a single bath process with the development of stable emulsions containing aluminium or zirconium salts of fatty acids. Padding or exhaustion method can also be used with these emulsions.

The adhesion of the repellent chemical or finish to the fiber surface increases due to polar interactions between carboxyl groups of fatty acids and metal salts (metal salts are held on the fiber surface) and non-polar interactions between hydrocarbon groups of fatty acids as shown in Figure 2.5. These compounds can be used along with other finishing chemicals. The advantages include low cost and uniform water repellency. The resulting water repellent fabric is less durable to dry cleaning and laundering with lower air and vapor permeability levels. Their non-durability resulted in limited use of these paraffin based water repellents.



A - Hydrophobic Interactions, B – Polar Interactions, C – Fiber Surface

Figure 2.5. Fatty acid metal salt and fiber surface interactions[7]

The durability can be increased by preparing wax dispersions with polymers such as polyvinyl alcohol, polyethylene, polybutylacrylate, acrylic polymers, etc. The durability can also be increased by incorporating cross-linking agents in wax-polymer emulsions.[7,19]

2.4.3. Proteins[19]

Glue, gelatin and casein are some of the protein substances used in conjunction with aluminium salts. The principle is based on insolubilising the protein at the last stage of application by the action of aluminum compounds, formaldehyde, tannin and bichromates. Fabrics were treated with gum arabic followed by an after treatment of steeping in a weak solution of formaldehyde to insolubilise the gelatin. An acetic acid solution of glue or gelatin protein with aluminium acetate can be applied onto the fabric to impart water repellency. Glycerine was added to the above water repellent solution to reduce stiffness of the fabric. Mystolene K.P is a protein/aluminium complex and can be applied on to fabric by padding with 5-10 percent solution depending on the repellency and handle desired.

2.4.4. Metal complexes[6]

A Quilon Werner type chrome complex marketed by DuPont contains hydrocarbon hydrophobic groups such as stearic acid groups coordinated with chromium. These compounds are available in isopropyl alcohol solutions.

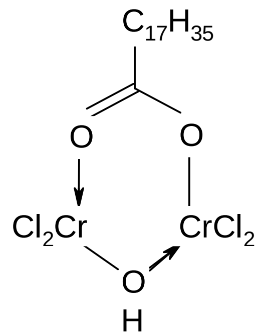


Figure 2.6. Quilon water repellent compound[6]

In the presence of small amounts of water, the chrome complex ionizes into chloride groups and the stearic chrome molecule acquires a positive charge as shown in Figure 2.7.

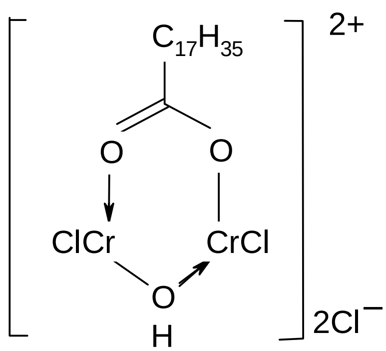


Figure 2.7. Quilon in ionised form[6]

When this complex is dissolved in water, more ionization of chloride groups takes place and the chromic ions becomes more basic leading to polymerization with oxygen group bridges between two chromium atoms. Increase of temperature of the solution also leads to polymerization. Thus this premature polymerization should be avoided by careful monitoring of pH and temperature during application. Fabric is treated with a chrome complex solution followed by drying to remove water molecules and curing at

150–170^{0}C at which complete polymerization of complex occurs as – Cr – O – Cr - linkages and covalent bonds formed with polar groups (-OH, -COOH, -CONH$_2$) or negatively charged groups of fiber surface as shown in Figure 2.8.

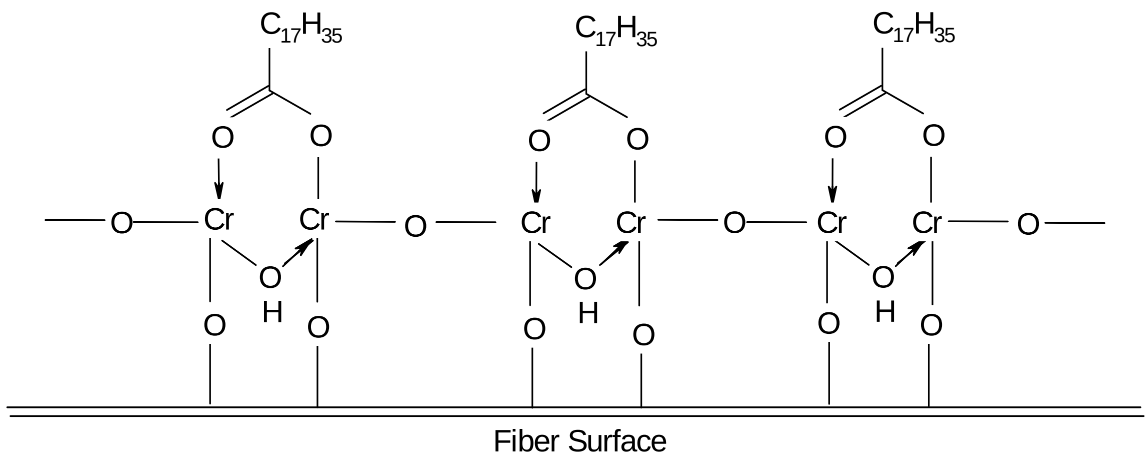


Figure 2.8. Polymerization of Quilon compound onto the fabric surface[6]

Since the chromium part of the complex is covalently linked to the fiber surface, the fatty acid portion i.e., the stearate group, is oriented outward from the fiber surface. The oriented stearic acid group imparts water repellency to the resulting product. Quilon complex solutions are acidic which might degrade fiber materials such as cellulose, which are sensitive to acidic conditions. Quilon treatment leaves a blue-green coloration on the fabric. It gives semi-durable water repellency to cotton fabrics [6, 20]

2.4.5. Pyridinium compounds[6, 21]

In this type of water repellents, a hydrocarbon hydrophobic chain such as fatty acid derivatives is attached to a pyridinium ring. When heated to higher temperatures like 149 ^{0}C, quaternary ammonium pyridinium compounds react with cellulose forming an ether linkage between the hydrophobic part of the pyridinium compound and cellulose.

Stearamidomethylpyridinium chloride reacts with cellulose to produce water repellent fabric with the attachment of hydrophobic stearyl groups to cellulose. The reaction releases a byproduct, pyridine hydrochloride as shown in Figure 2.9. ICI markets this product under the trade name Velan PF.

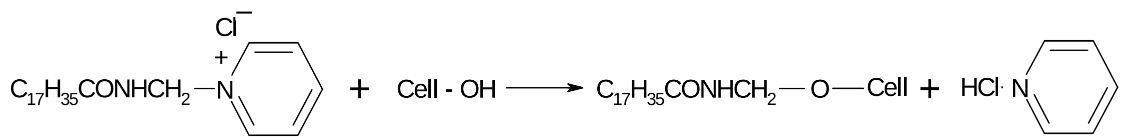


Figure 2.9. Reaction of cellulose with stearamidomethyl pyridinium chloride

Another reaction mechanism was suggested by Davis where cellulose reacts with methylolstearamide, an intermediate formed from stearamidomehtylpyridinium chloride compound in presence of water[6]. A pad-dry-cure process is used to apply stearamidomethylpyridinium chloride to the fabric. Fabric is padded in a solution of stearamidomethylpyridinium chloride followed by drying at low temperatures and cured at around 149 ^{0}C for several minutes. Due to the formation of pyridine, an unpleasant odor develops on the surface of the fabric, which can be removed by scouring the cured fabric.

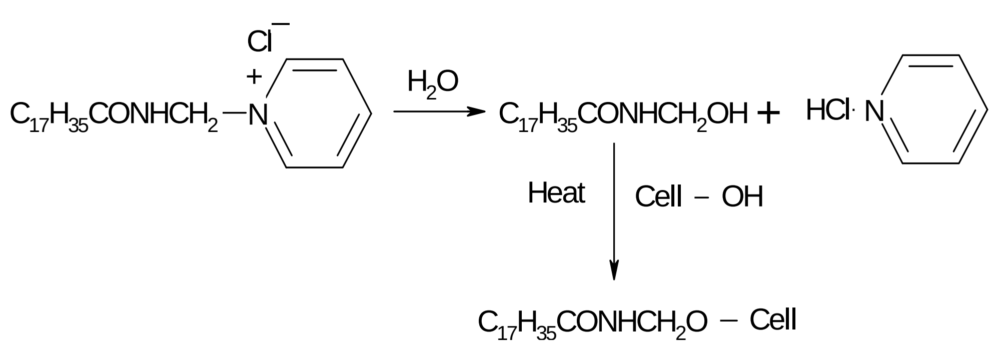


Figure 2.10. Proposed reaction of cellulose with stearamidomethyl pyridinium chloride[6]

To avoid the tendering of fabric due to HCl formed in the reaction, sodium acetate buffer is added (Muller reaction mechanism) and the reaction takes place as shown in Figure 2.11.[6, 21].

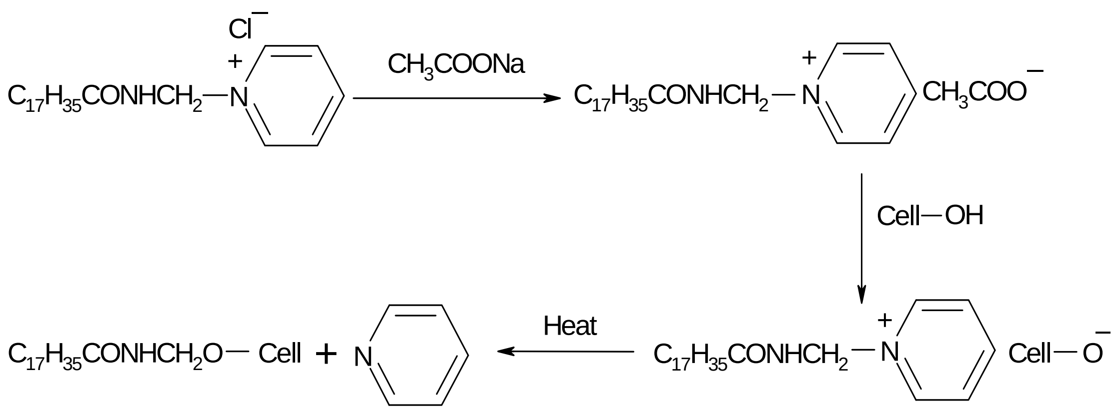


Figure 2.11. Muller reaction mechanism of stearamidomethyl pyridinium chloride with cellulose

In another process developed by Baldwin et al. octadecoxymethyl pyridinium cellulose is prepared by reacting chloromethyl alkoxy ethers and pyridine in the presence of the fabric. Fabric is treated in a solution of chlormethyl alkoxy ether and pyridine and heated together in toluene solvent followed by padding, drying and curing.

Quaternary pyridinium water repellents showed synergistic effects in combination with fluorochemical repellents giving excellent durability to laundering. However, the use of quaternary pyridinium compounds is limited due to the release of the toxic chemical pyridine during processing.

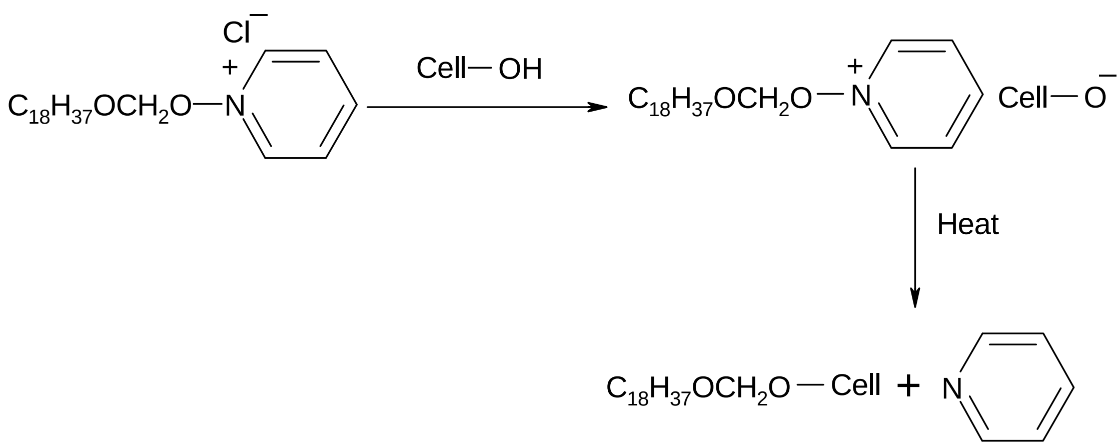


Figure 2.12. Reaction of chloromethyl alkoxy ether and pyridine

2.4.6. Stearic acid -methylol compounds[6, 7]

N-methylol compounds are used for crosslinking of cotton fabrics to impart durable wrinkle resistance. This crosslinking could also be used to impart durable water repellency to cellulose fabrics by modifying N-methylol compounds. N-methylol compounds can be reacted with hydrophobic compounds containing an active hydrogen atom such as alcohols, amines and carboxylic acids to form a methylol compound containing a hydrophobic alkyl chain. The resulting methylol compound reacts with the primary hydroxyl group of cellulose under acidic conditions and at high temperatures to form an ether linkage between cellulose and the methylol compound imparting durable water repellency to cellulosic fabrics. Methylol compounds also react by self-condensation to produce a resin or crosslinked cellulose fabric giving durable water repellent cellulosic fabrics.

2.4.6.1. Stearamide – formaldehyde water repellent [6]

Stearamide reacts with formaldehyde to produce a methylol compound containing a stearyl chain. This compound reacts with the hydroxyl group of cellulose producing water repellent fabric due to stearyl group attachment which gives water repellency.

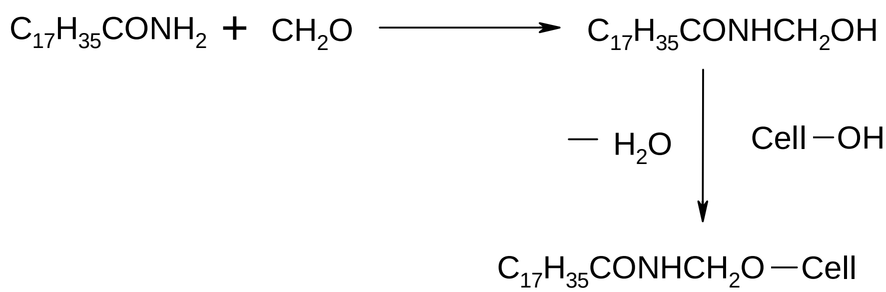


Figure 2.13. Reaction of cellulose with stearamide-formaldehyde

2.4.6.2. Stearyl urea – formaldehyde water repellent [6]

Stearyl urea also reacts with formaldehyde followed by cellulose to give durable water repellent cellulosic fabric.

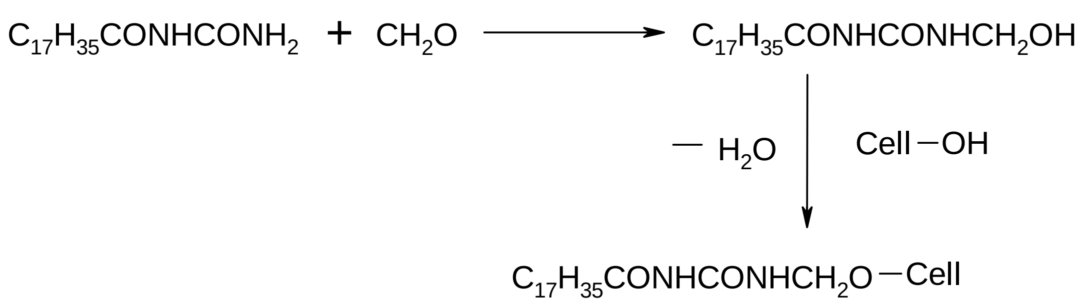


Figure 2.14. Reaction of cellulose with stearyl urea-formaldehyde

The fabric can also be treated with stearylamide or stearyl urea followed by treating with formaldehyde to form methylol compounds. The resulting methylol compounds react with cellulose or with each other to form a resin giving permanent water repellency.

2.4.7. Melamine and stearyl based water repellents[6, 7, 22]

Melamine reacts with 6 moles of formaldehyde to give hexamethylol melamine as shown in Figure 2.15. These hexa methylol melamine products react with stearamide to give the possible stearamide-melamine derivative below. This stearamide-melamine derivative contains methylol groups that react with cellulose or react with each other to form resinous products giving durable water repellency.

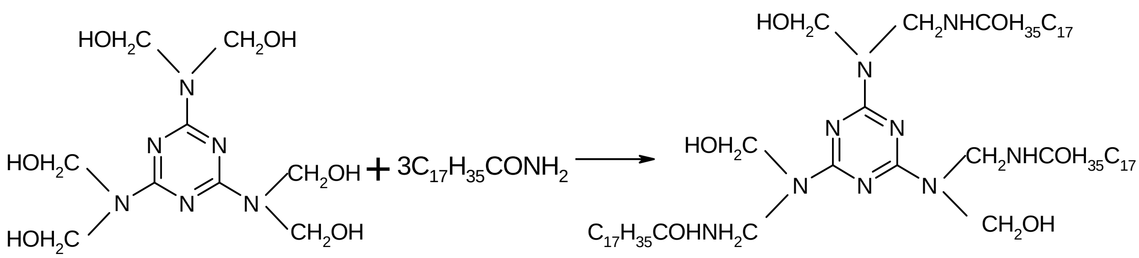


Figure 2.15. Reaction of melamine and stearamide

These alkylated methylol melamine compounds can be applied by treating textile fabrics with their aqueous dispersions followed by drying at room temperature and curing at given temperature range.[6, 7]

A patent by Grim[22], claimed the method of treating cotton fabric with a solution of methylated methylol melamine and octadecyl alocohol dispersion at 27-38 ^{0}C followed by padding to remove excess solution and provide uniform application of the chemical. The padded fabric was dried and then cured at 143 ^{0}C for seven minutes to form a water insoluble resinous product on the fabric. The product expected from the solution of methylated methylol melamine and octadecyl alcohol acts as a water repellent chemical. The octadecyl group imparts water repellency to textile fabric while the methylated methylol groups react with cellulose and themselves releasing methyl alcohol.

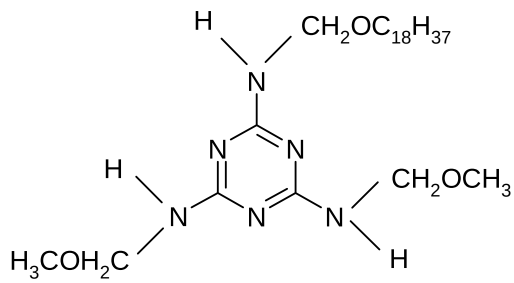


Figure 2.16. Reaction product of methylated methylol melamine and octadecyl alcohol

A catalyst, oxalic acid or diammonium hydrogen phosphate, can be added to the dispersion to reduce the curing time and temperature. Decrease in tensile strength, abrasion resistance, shade change of dyed fabrics and release of potential carcinogen formaldehyde limits the use of methylol compounds as water repellents.[6, 7, 22]

2.4.8. Silicone water repellents

Silicone compounds are found to be good water repellents. Patnode[23] observed water repellency by using silicon compounds, when he exposed fabrics to a mixture of dichlorotrimethylsilane and trichloromethylsilane in vapor form followed by neutralizing with ammonia. The resultant fabric showed water repellency. Thereafter, several developments took place in using silicone chemistry with textile fabrics. Silicone compounds show high resistance to a broad range of temperatures ranging from low to high temperatures along with good electrical properties. Generally, mixtures of dimethyl polysiloxane and methyl hydrogen polysiloxane are used to impart water repellency to textile fabrics.[19, 24, 25] These are produced in the following steps: a) Silicon tetrachloride is prepared from sand, coke and brine,

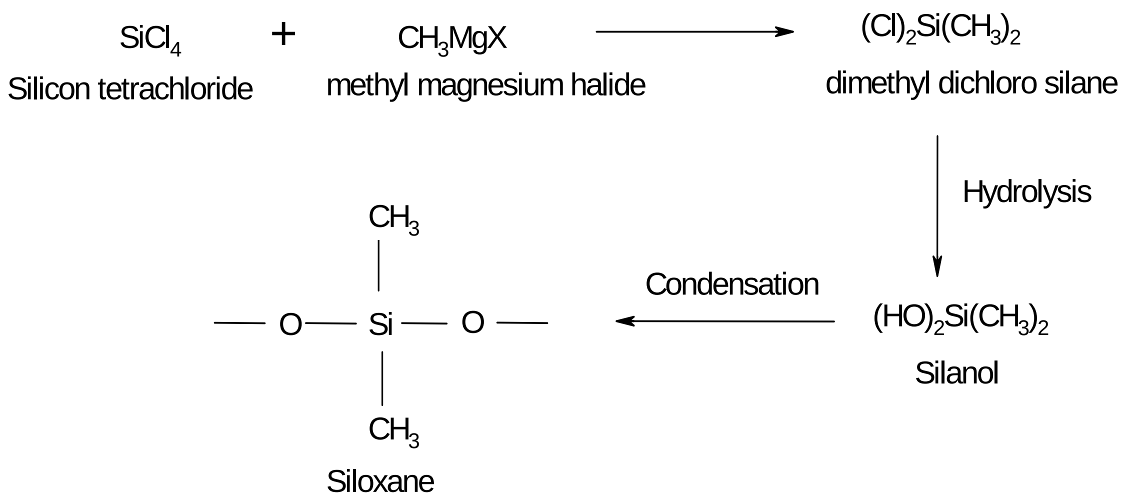


Figure 2.17. Preparation of siloxanes from silicon tetrachloride[19]

b) Silicon tetrachloride is reacted with Grignard reagent to replace some of the chlorine groups with alkyl groups giving alkyl silicon halides (generally, methyl silicon chloride), c) Silanol is the resulting product from hydrolyzing alkyl silicon chloride, d) Silanols are not stable and undergo condensation to give siloxanes. Two –SiOH groups of silanol undergo condensation to give a siloxane polymer with -O-Si-O- backbone[19].

Siloxane polymer chain length, type of alkyl group (e. g., methyl, ethyl, propyl, butyl) attached to silicon and degree of cross-linking determines the performance of water repellency. Normally polysiloxanes are represented as follows:

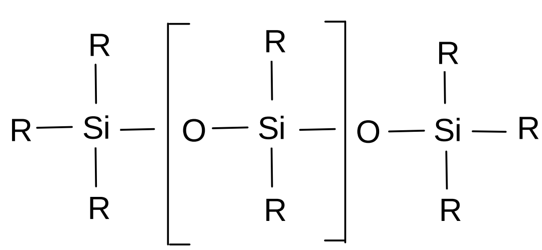


Figure 2.18. Polysiloxane

Where, R is either methyl or hydrogen group. The substituent 'R' in the given polymer chain can be methyl or hydrogen or can be a mixture of both.[6, 7]

Polydimethylsiloxanes (PDMS) have a typical '–Si-O-Si-' backbone structure with methyl side groups. The oxygen atom of the backbone forms hydrogen bonding with polar surface of the fiber whereas the hydrophobic methyl groups are oriented outwards i.e., away from fiber surface giving water repellency, as shown in Figure 2.19[7]. Polydimethylsiloxanes form a flexible sheath-like layer around the fiber giving soft hand comfort.

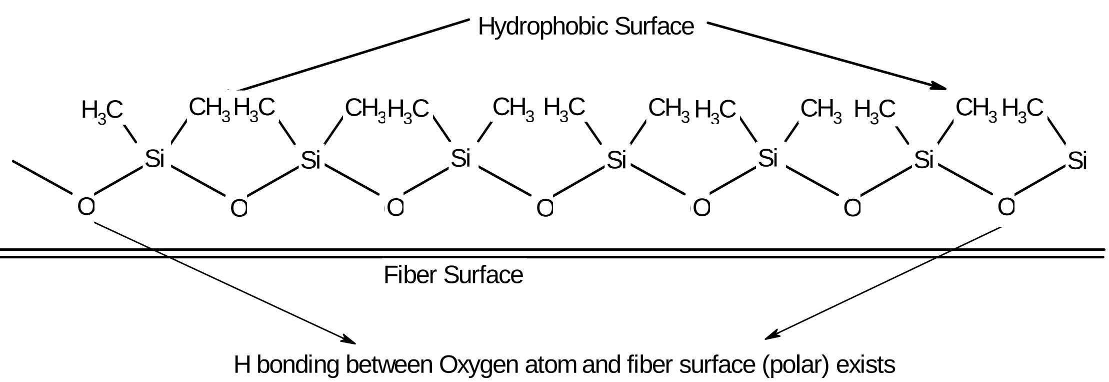


Figure 2.19. Formation of thin film on the cellulose fabric surface by polysiloxanes[7]

Since H bonding holds PDMS layer on the fiber surface, the durability of the finish to laundering and dry cleaning is less. To improve durability and lower temperatures required for curing, silane and a catalyst, tin octoate, are used along with the silanol. The catalyst also facilitates the proper orientation of the methyl groups outwards imparting good repellency. Silanol, silane and tin octate constitute the components of a silicone water repellent. Fabric is padded with the silicone water repellent system followed by drying at low temperatures and curing at 120-150^{0}C. During curing a reaction between silanol and silane takes place forming crosslinked three dimensional structures surrounding the fiber. Hydrolysis of Si–H bond takes place in basic or strongly acidic medium. To prevent hydrolysis, organic additives buffered at pH 3-4 are added to stabilize the bonds. The reaction between silanol and silane is shown in Figure 2.20.

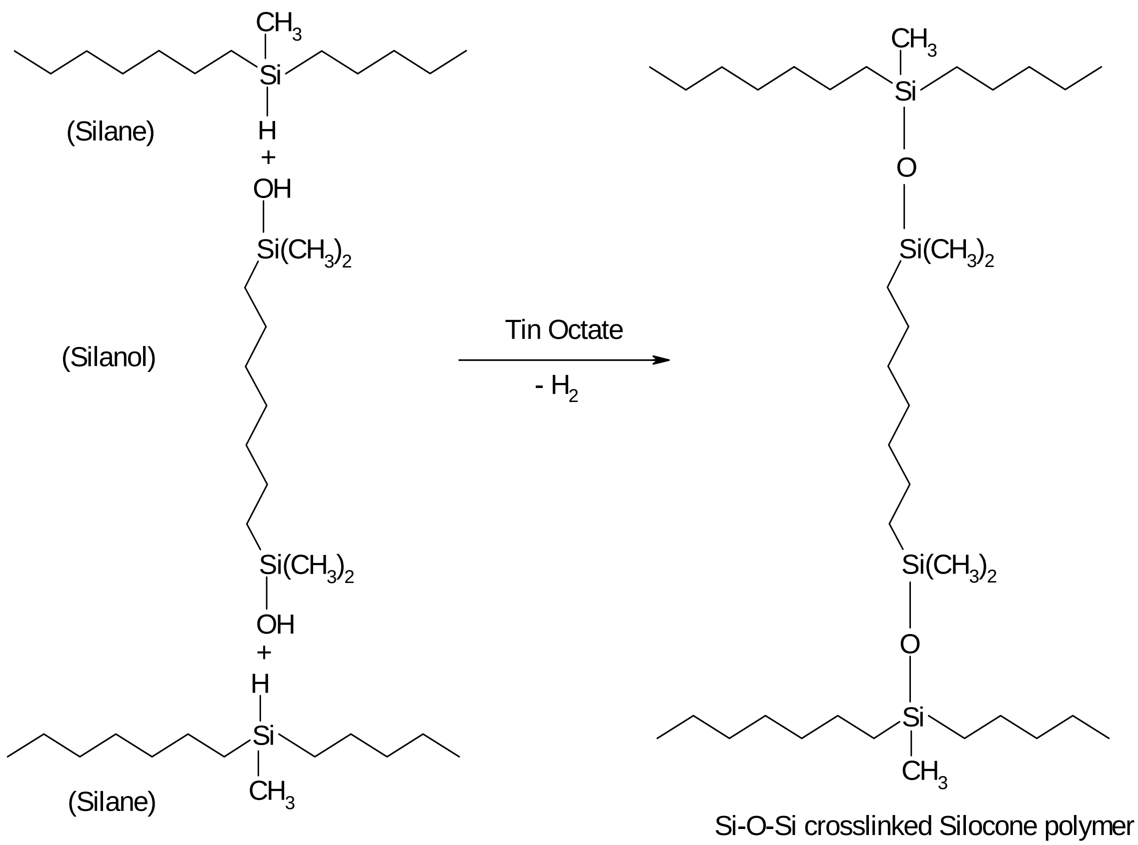


Figure 2.20. Reaction of silanol and silane[7]

Exhaustion methods can also be employed to apply silicone water repellents. Silicone repellents give high water repellency at lower concentrations along with soft hand, resistant to UV irradiation and hydrolysis and improved resistance to wet and dry wrinkling behavior. Cotton swelling during laundering breaks the silicone sheath layer resulting in a decrease of water repellency resulting in moderate durability to dry cleaning and laundering [6, 7, 26, 27].

2.4.9. Fluorochemical repellents

Fluorochemical repellents have much lower surface energies than hydrophobic and silicone repellents imparting both water repellency and oil repellency together. Hydrocarbon and silicone repellents offer only water repellency. Uniform distribution, packing, proper orientation, structure and length of the fluorocarbon segment, amount of fluorocarbon chemical applied on the fiber, composition and geometry of fabric determines repellency of fluorocarbon finishes.[3,6,7] The $–CF_3$ end group should be present in any fluorochemical to form a low energy surface[3]. Generally, seven fluorinated carbon atoms along with trifluoromethyl as terminal group is sufficient enough to form a dense layer on the outer side of the fabric to cover inner non-fluorinated segments achieving good repellency.[6] If the inner non-fluorinated atoms are not covered with fluorinated atoms, wettability of the material increases significantly.

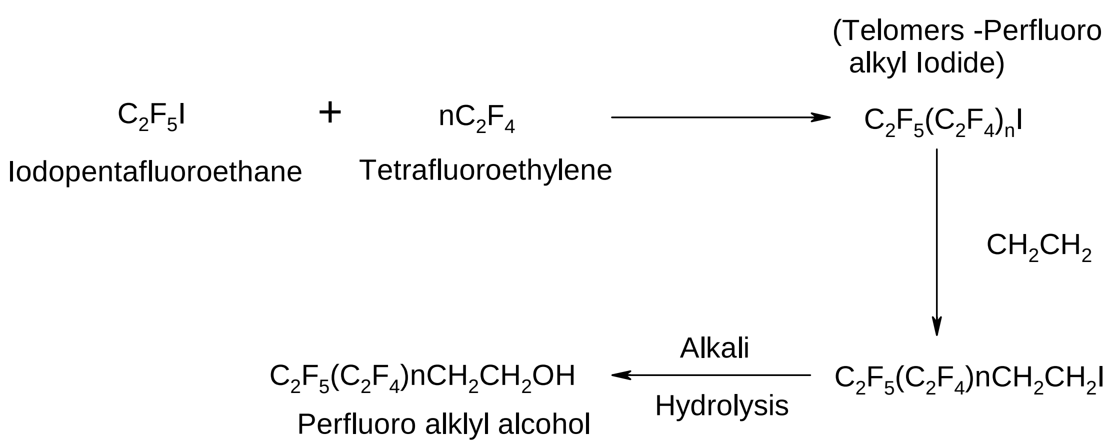


Figure 2.21. DuPont telomerisation process for the preparation of fluoroalkyls[6]

Grajeck and Petersen suggested fluorinated carbon atoms of four atoms along with $–CF_3$ are sufficient enough to provide good repellency and that the repellency increases with increase of chain length of perfluoroalkyl groups. Perfluoro acrylic copolymers are commonly used as water and oil repellents. Perfluoro alkyl compounds are produced by electrochemical fluorination or telomerization of tetrafluoroethylene.[3,6] DuPont telomerisaiton process is shown in Figure 2.21. These perfluoro alkyl alcohol groups are reacted with acrylic acids or methacrylic acids to produce corresponding esters followed by polymerization to give perfluoro acrylic copolymers as shown in Figure 2.22.[7]

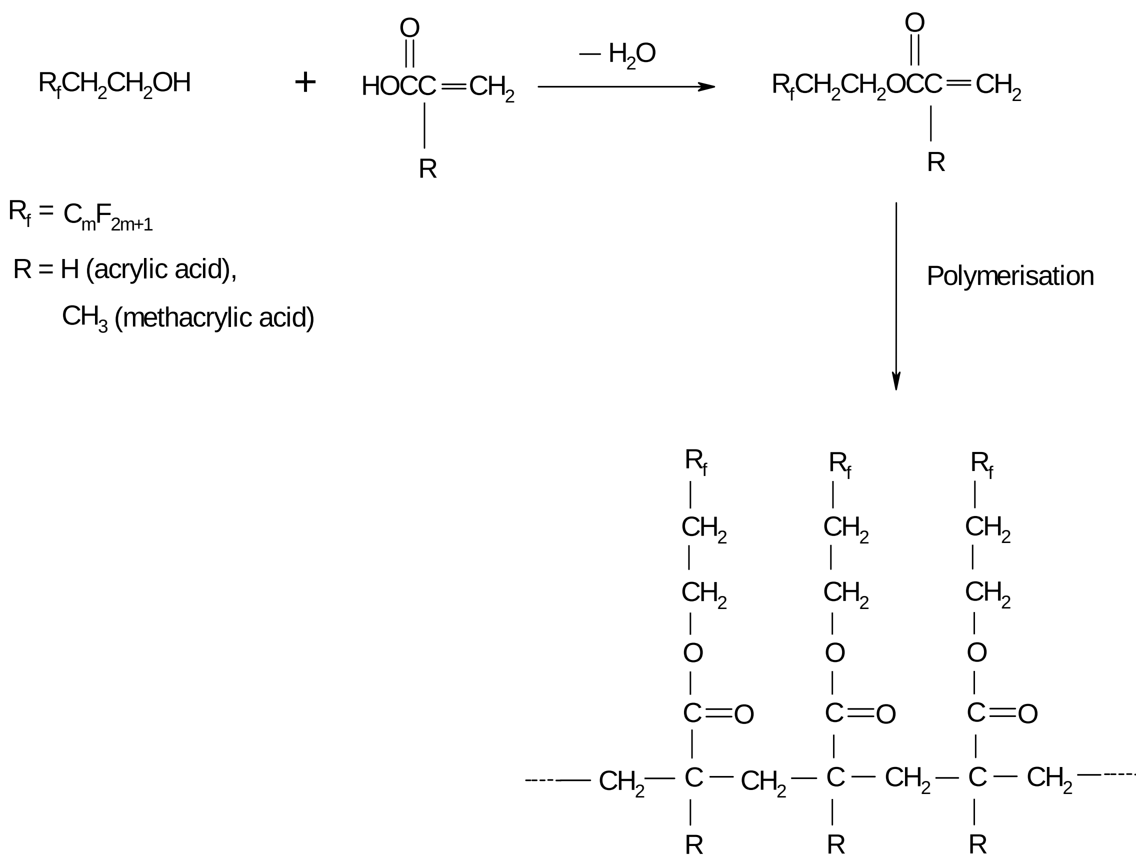


Figure 2.22. Preparation of fluoroalkyl acrylic polymer from acrylic acids[7]

Generally, fluorocarbon polymers are applied to textile fabrics as copolymers by using various co-monomers containing long chain fatty alcohol acrylates such as lauryl or stearyl methacrylate, butylacrylate, vinyl chloride, vinylidene chloride and acrylonitrile to improve the fabric hand, film formation, durability and reduce the cost associated with fluoro chemicals. The presence of these co-monomers also increases water repellency without affecting oil repellency. Sometimes, siloxanes such as polydimethylsiloxanes are incorporated into the fluoroacrylates to impart soft handle to the fabric[17]. Surfactants used in the preparation of flurochemical polymer emulsions affect water repellency, oil repellency, and durability to laundering and drycleaning. The charge on the latex particles should be opposite or neutral as compared to the charge on the fabric surface. Perfluro alkyl molecules in the form of polyacrylates and in the form of chromium complexes offer different performance levels of water or oil repellency and durability. The perfluro alkyl group is connected to a molecule having a functional group, which forms a physical or chemical bond between the fluoro groups and substrate. Strength, nature and type of this bond decide durability to dry cleaning, durability to laundering, repellency and abrasion resistance of the resulting fabric. The degree of orientation and packing of the perfluoro groups depends mostly on the type of the bonding elements present in it. A hydrophilic bonding group may decrease the inherent water repellent characteristic of the fluorocarbon repellent[3, 17].

Most of the fluorocarbon chemicals are applied by the pad-dry-cure method[28]. The fluoropolymers can also be applied by exhaust and spray methods. The fabric is impregnated with fluoropolymer followed by drying at around 110^0C or higher to remove water and moisture depending on the nature of the chemical and cured at 150-182^{0}C for 1-3 mins[6]. Heat treatment orients the perfluoro groups on the fabric surface forming a dense fluorocarbon layer providing optimal repellency. Washing decreases water repellency of the fluorochemical treated fabric, but repellency recovers with a following heat treatment[29]. During washing, cellulosic fibers swell allowing cellulose molecule segments to travel in the fiber. Because of this movement, cellulose molecules treated with hydrophobic perfluoro groups orient or rotate into inner parts of the fabric to stay away from hydrophilic conditions of washing[30]. In some of the recent fluorocarbon (Laundry-air-dry (LAD)) products, orientation of the fluorocarbons on the surface is regenerated by air drying after laundering without the need of heating such as ironing, pressing or tumble drying. This can be achieved by incorporating a booster such as isocyanate as blocking groups into the fluoro polymers during polyacrylate polymer-ization. These boosters stabilize the fluorine side chains during washing, preventing the orientation of the perfluoro groups into inner parts of the fabric. The water repellency and oil repellency are retained for repeated washings without heat treatments. The use of boosters decreases the curing temperatures thus preventing any fiber damage that occurs at high temperatures[7, 31].

The decrease in water repellency after washing can also be decreased by using crosslinking agents such as 1,2,3,4-butanetetracarboxylic acid (BTCA). Xu et al. suggested that fabric finished with fluorocarbon resin and 8% BTCA showed improved water repellency after several washings than fluorocarbon resin alone[29]. For all fluorochemical finishes, concentrations of 1% or less solids on the fabric are sufficient enough to impart water repellency to the fabric. But, the durability of these finishes to washing can be improved by increasing the concentration of active solids on fabric[3]. Higher cost, release of hazardous aerosols during drying and curing processes and fabric greying during laundering are general disadvantages of flurorocarbon chemicals[7].

2.5. Reaction between cotton cellulose and CHTAC

Many studies have been contributed extensively towards cationization of cellulose using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC). CHTAC is available commercially from Dow Chemical as a 65 % aqueous solution under the trade name CR-2000 [13]. The active cationic agent which reacts with the cellulose polymer is 2,3-epoxypropyl trimethyl ammonium chloride (EPTAC). This reactive material is prepared in-situ by reacting CHTAC with alkali and sodium hydroxide (NaOH), as shown in Figure 2.23.

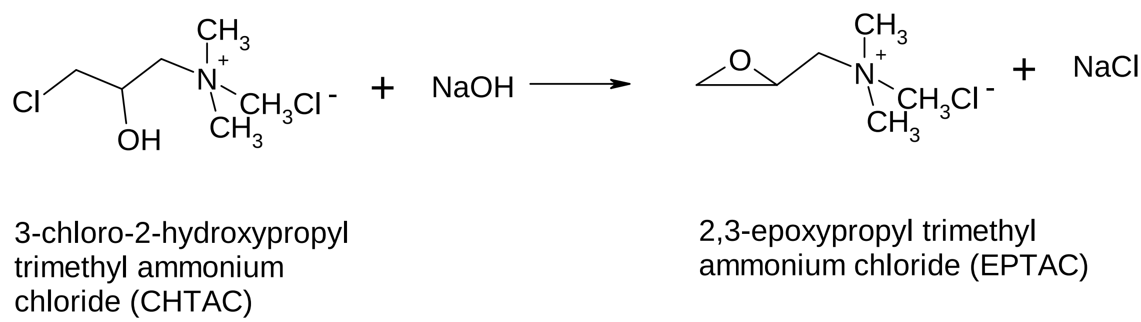


Figure 2.23. Reaction of CHTAC with sodium hydroxide

The resultant EPTAC reacts with alcohols under alkali conditions forming ethers. Hence hydroxyl groups of cellulose react with EPTAC to form cationized cellulose cotton as shown in Figure 2.24. At the same time EPTAC also reacts slowly with water to form a hydrolyzed waste material as shown in Figure 2.25. The hydrolysis reaction is unavoidable and decreases the utilization efficiency of the cationizing agent to less than perfect.

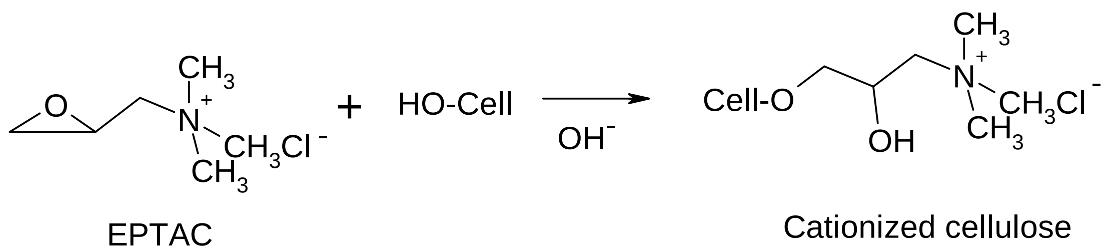


Figure 2.24. Reaction of EPTAC with cellulose

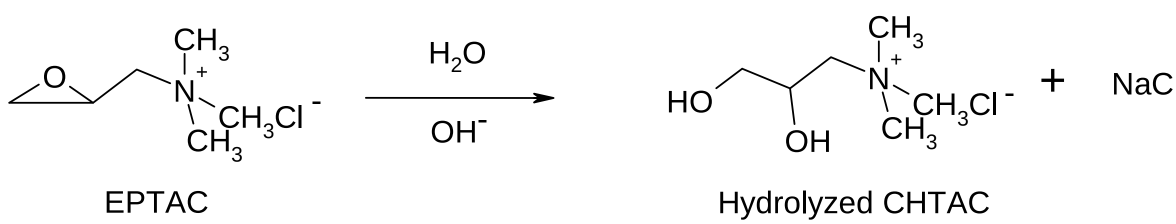


Figure 2.25. Hydrolysis reaction of EPTAC

EPTAC also reacts with carboxyl groups and amine groups in the presence of basic conditions as shown in Figures 2.26 and 2.27[32].

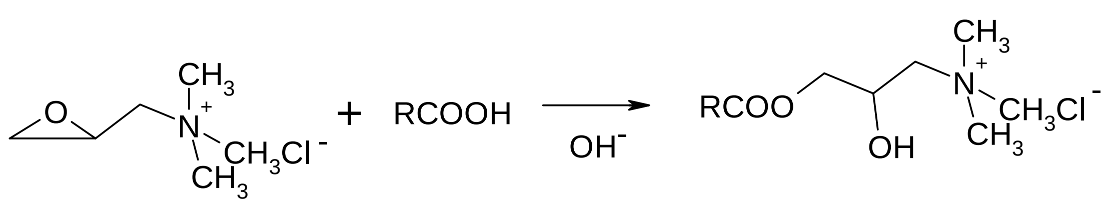


Figure 2.26. Reaction of EPTAC with carboxylic acids

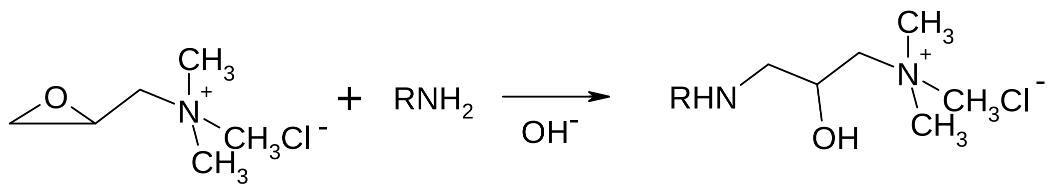


Figure 2.27. Reaction of EPTAC with amines

The cationization of cotton fabric can be carried out by pad-batch, exhaust, pad-steam or pad-dry-cure methods. Each and every process has different reaction and fixation efficiencies. In the pad batch process, the fabric is padded with a solution mixture of NaOH and CHTAC at 100 % wet pickup followed by batching at room temperature for 24 hours[13, 33, 34]. The padded fabric should be wrapped in a plastic bag to avoid migration of chemical due to evaporation of water and to eliminate carbon dioxide since the carbon dioxide reacts with sodium hydroxide forming sodium carbonate[35,13]. The exhaustion process utilizes exhaustion liquor at a bath ratio of 20:1 with fabric, at a temperature of 75^0C for 90 minutes. Acetone emerged as the best solvent system among water, ethanol, isopropanol and methanol solvents, obtaining higher cationization levels. The pad steam application process involves padding of fabric with a solution mixture of CHTAC and NaOH followed by steaming at 100^0C for 30 minutes. The pad-dry-cure method emerged as the best application process among the above other processes giving higher fixations of around 85 %[33]. This process was studied at different drying and curing temperatures and times along with different concentration ratios of NaOH and CHTAC. The optimum conditions involves padding of fabric with NaOH:CHTAC solution mixture at a mole ratio of 1.8:1 or higher at which maximum obtainable efficiency is achieved followed by drying at a temperature of around 40^0C or below for 5 min or longer periods of time to remove water and curing at a temperature of 110^0C or higher for 5 min or more at which reaction between EPTAC and cellulose occurs efficiently. Higher temperatures of drying result in hydrolysis of EPTAC giving hydrolyzed waste material. At lower drying temperatures, if water is not removed completely, the residual water remaining on the fabric reacts with CHTAC; a competing reaction decreases the extent of cationization.

Hence, removal of water at low temperatures is very important before curing of the fabric. The exhaust method gives a cationization fixation of around 10%, while pad-batch, pad-steam and pad-dry-steam processes gives fixations of about 25%, 25% and 50% respectively. As mentioned earlier, the pad-dry-cure method gave higher fixations of about 85 %. It is also observed that the percent of fixation of CHTAC is higher at lower concentrations and decreases with increase of CHTAC concentration[33]. Cationized fabrics showed some yellowing of the fabric. This yellowing may be due to the presence of the nitrogen containing cationic agent [54].The chemical structure of cationized cellulose is shown in figure 2.28.

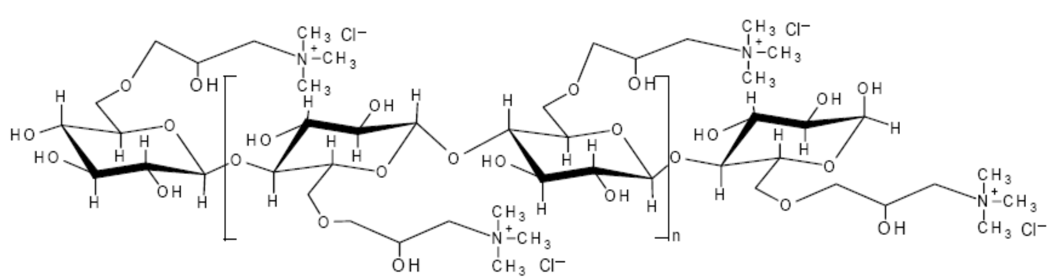


Figure 2.28. Structure of cationized cellulose[13]

Cellulosic fabrics can also be treated with several other materials such as chloropropionyl chloride (CPC), N-methylol-acrylamide (NMA) etc., to impart cationic character. Cellulose can be esterified with chloropropionyl chloride (CPC), which contains terminal β-chloro groups as shown in Figure 2.29. These β-chloro groups can be replaced by quaternary amine groups by reacting CPC cotton with trimethylamine as shown in Figure 2.29[36]. Treating cotton with NMA at 150^0C, using $ZnCl_2$ as catalyst gives modified cellulose with pendant double bond which can undergo reaction by the mechanism of Michael addition as shown in Figure 2.30[37].

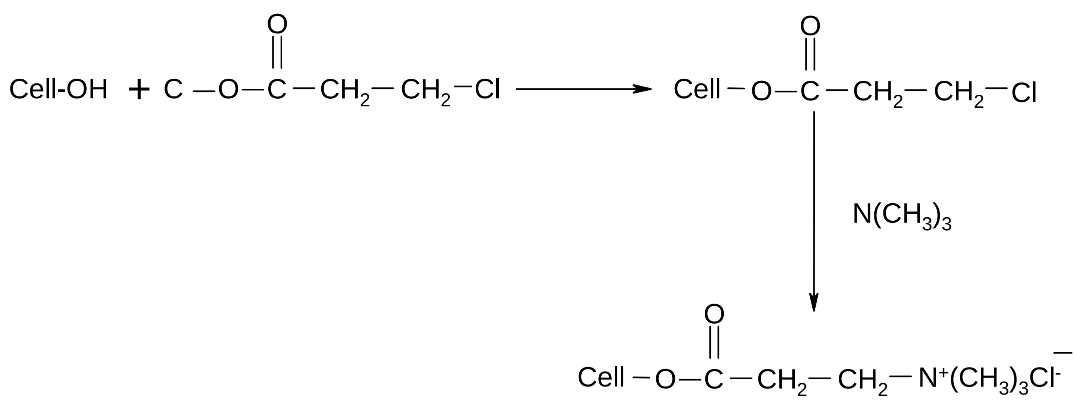


Figure 2.29. Reaction of cellulose and chloropropionyl chloride

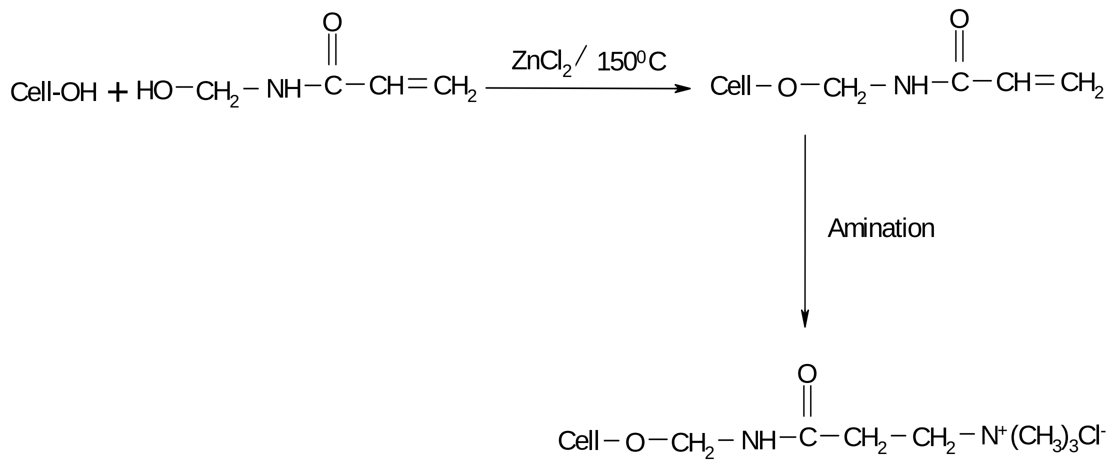


Figure 2.30. Reaction of cellulose and NMA

2.6. Prior research on ionic interactions

Most of the earlier work using cationized cellulose contributed towards improving the dyeability of anionic acid and reactive dyes. Dyeing of cotton fabrics with reactive dyes requires higher concentration of salts NaCl or Na_2SO_4, (40-100 g/l) and gives only moderate efficiency of dye usage due to 50-90 % fixation. The fixation of dye depends on the application process, dye type and depth of color desired. The presence of high amounts of sodium chloride and sodium sulfate attacks stainless steel vessel and concrete pipes. The accumulation of sulfate ions also increases the acidity of streams, lakes and rivers. Dyeing of cellulosic fabrics with reactive dye at neutral or slightly acidic conditions in the absence of salt lowers the environmental problems by increasing fixation efficiency of dye and reducing hydrolysis of reactive dye. Use of cationized cellulose facilitates reactive dyeing at neutral or slightly acidic conditions thus reducing environmental concerns and increases dye fixation by decreasing hydrolysis of dye [36, 38].

Cellulose fibers develop slightly negative charges in aqueous solutions. Thus anionic dyes have to overcome this charge barrier to be adsorbed onto the cellulose fiber. Generally large amounts of salts are added to the dye bath to neutralize this negative charge. In addition to this, the non-planar structure of acid dyes makes them non-substantive. Modifying the cellulose fiber by the incorporation of cationic groups results in higher substantivity for anionic dyes[38]. The cationic or positive charges strongly attract anionic dyes increasing their affinity and forming ionic bonds[39]. As positive charges are always present, dyeing can be carried out without addition of salts and independent of pH. Draper et al. showed an enhanced dyeing rate, improved dye uptake and significant increase in K/S values for cationized cotton compared to untreated cotton fabric. There was also significant improvement in fastness to laundering and light implying ionic attractions between dye and the fiber [40, 41].

2.7. Research objective

Achieving laundry durable water repellency for cellulosic fabrics without releasing hazardous chemicals and at the same time being economical is an important goal of textile treatment. Most of the present water repellent treatments are either non-durable or expensive or a threat to environment. The research objective of this work was to develop a new process to obtain a durable water repellent treatment by solving the above-mentioned limitations.

This method of invention imparts durable water repellency for 100% cotton fabric using stearic acid. Due to the absence of significant interactions between cotton fiber and stearic acid, durable water repellency cannot be achieved. However by incorporating cationic groups into the cellulose fiber, the negatively charged stearate anions (head) can be attracted by these cationic groups forming ionic bonds. The strength of the electrostatic bond is 5 kcal/mole which is 10-20 times less than the strength of covalent bond[63]. The hydrophobic part of the stearic acid salt aligns outward on the surface of the fabric. These outward oriented stearyl groups gives water repellency. The ionic interactions existing between cellulose cotton fiber and stearic acid hold lower surface energy stearate molecules on to the surface of the fabric imparting durable water repellency. This process was carried out in two steps.

Step 1 - Pretreatment of cotton fabric – Cationization of cotton with CHTAC by pad-dry-cure method (described in Section *2.5*)

Step 2 – Treatment of cationized cotton fabric with oppositely charged anionic stearic acid salt by exhaustion method.

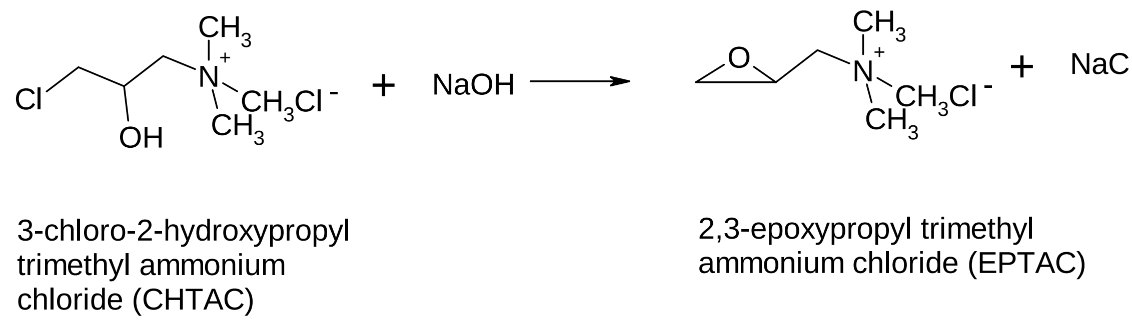


Figure 2.31. Reaction of CHTAC with alkali

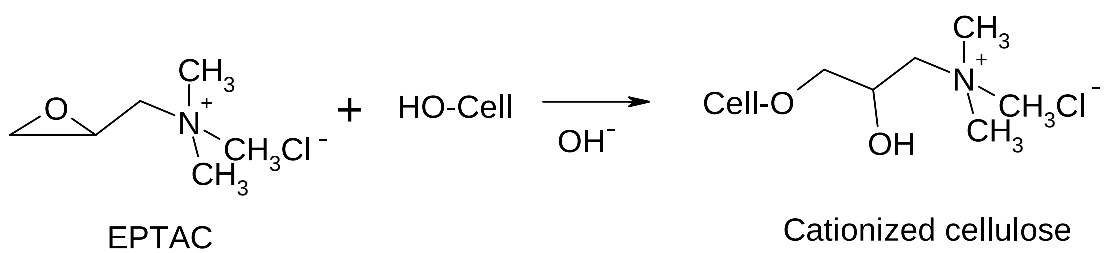


Figure 2.32. Reaction of EPTAC with cellulose – step 1

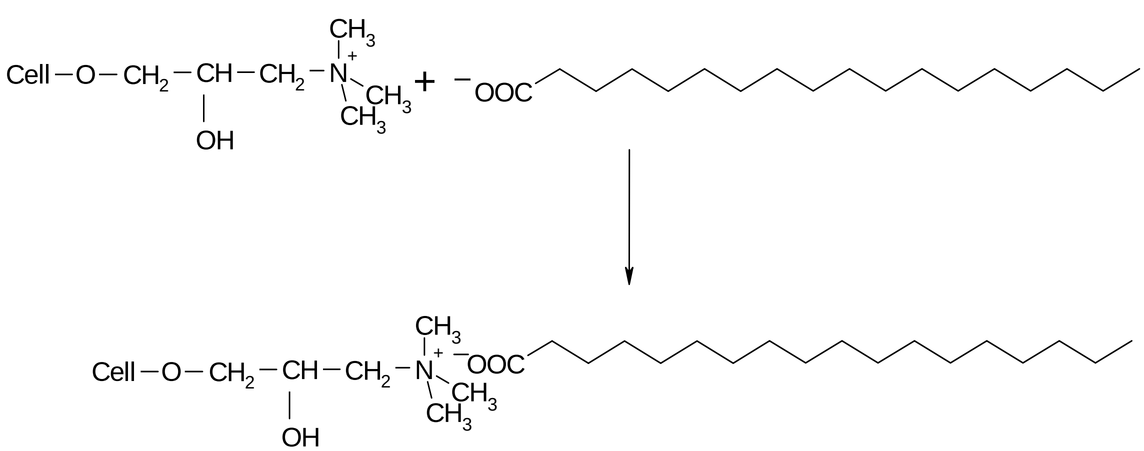
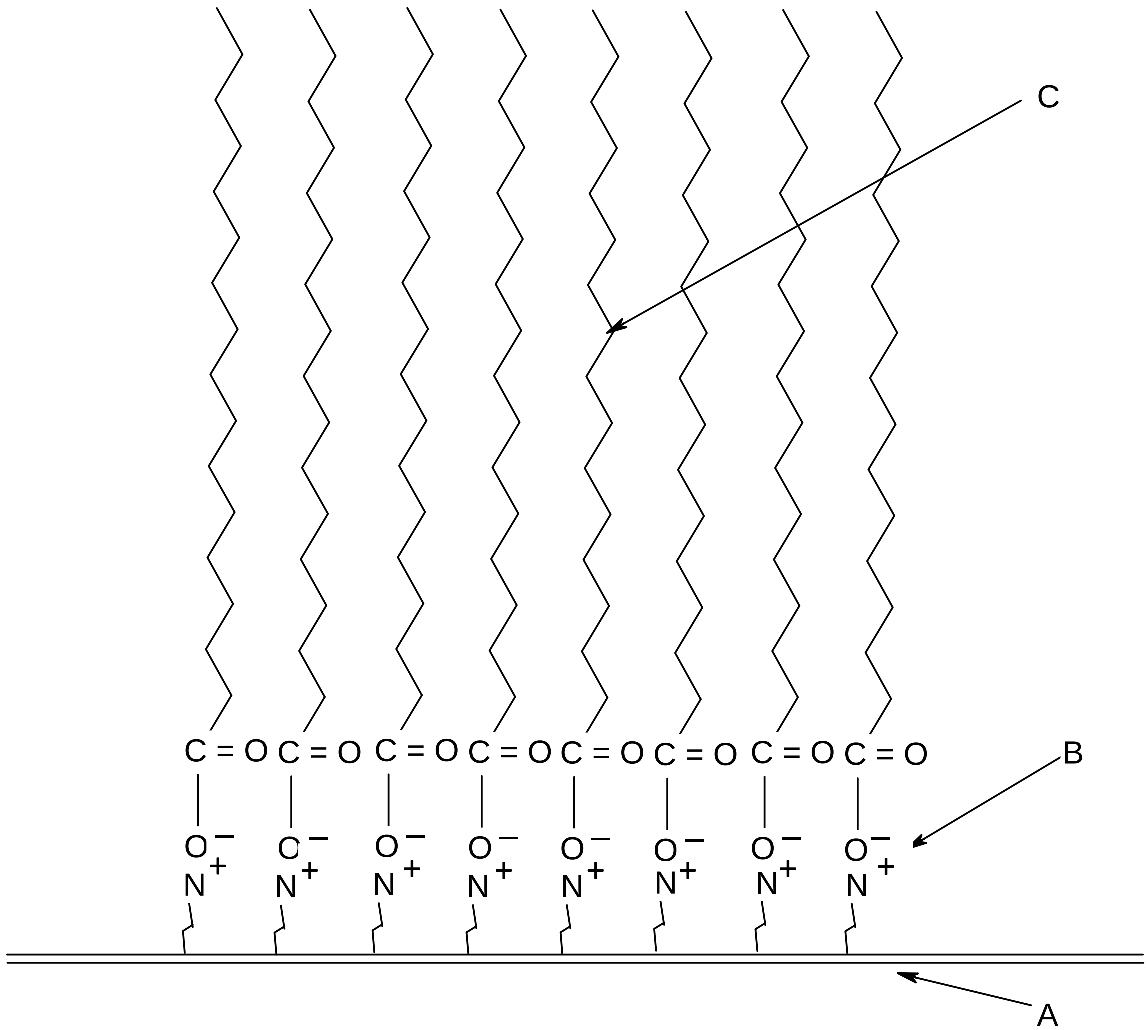


Figure 2.33. Reaction of cationized cellulose with stearic acid salt – step 2



A - Fabric substrate, B - Ionic interactions, C - Hydrophobic groups

Figure 2.34. Formation of ionic interactions between stearate ions onto cationized cellulose fabric

This process is based on the principle of improving dyeing behavior of acid dyes by modifying cellulose as cationic cellulose by quaternary ammonium salts. Existing equipment was utilized for the treatment and the chemicals used for the treatment were economical and environmentally safe. The behavior of cationization with CHTAC was studied in detail. Confocal microscopy was used to evaluate distribution of cationic sites and observed the cross-sectional geometry of the fiber. X-ray diffraction technique was used to study the changes of structure in modified cellulose and stearic acid treated fabric. The resultant treated fabrics were evaluated for durable water repellency, tensile strength, elongation at break, air permeability and stiffness to obtain optimum conditions.

3. EXPERIMENTAL PROCEDURES

Materials, chemicals and the experimental techniques used in this research work are available in most of the textile industries. Since cost is a major concern in developing this process, raw materials, chemicals and experimental techniques used are easily available, environmentally safe and economical. The fabric, chemicals and equipment names, details and their manufacturers are listed in this section. The synthesis of the resulting experimental products and their application methods are explained.

3.1. Materials

The materials and chemicals used in the research work are listed in Table 3.1 including their names, descriptions and manufacturers. The fabric received from Test Fabrics was washed with 2 g/l Na_2CO_3 to remove any impurities present in the fabric. The weight of the fabric after washing was 112 g/m^2. The washed fabric had 84 warp yarns per inch and 77 weft yarns per inch.

Table 3.1. Materials and Chemicals

Substrate or Chemical name	Description	Manufacturer
Cotton Fabric	Bleached desized cotton print cloth, style 400, 102 g/m^2, 44”/45”, 78X76, ISO 105/FO2	Test Fabrics Inc.
Cationic Agent	3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC), 65 % solution	Dow Chemical Company

Table 3.1. continued.

Substrate or Chemical name	Description	Manufacturer
Acid	Stearic Acid, Reagent grade 95 %	Sigma-aldrich, Inc.,
Base	Ammonium Carbonate, for analysis ACS, M.W = 96.09	Acros Organics
Surfactant	Aerosol OT 75 % (Sodium dioctyl sulfosuccinate in mixture of ethanol and water)	Cytec Industries Inc.,

3.2. Equipment

Solutions were prepared by simultaneous heating and stirring by using Corning stirrer/hot plates. A Fisher Scientific Accumet® model 15 pH meter was used to measure the pH of the solutions prepared. The fabric finishing processes were carried out in the North Carolina State University College of textiles pilot plant. A Werner Mathis AG padding machine was used for padding textile fabrics. A fabric width of up to 18 inches can be used in this padding machine. The wet pick up of the fabric was controlled by adjusting the pressure and speed of the pad rolls. The fabric samples of about 12x15 inches were mounted on metal pin frames and dried and cured in Werner Mathis AG forced air oven. Datacolor Ahiba Nuance Top Speed Infrared Lab dyeing machine (rotary dyeing machine) was used for exhausting water repellent chemical onto the fabric. The temperature, rotation speed and the time of the dyeing machine were controlled.

3.3. Application procedures

This section lists procedures for the treatment of cotton fabric with water repellent chemical and lists the experimental methods in detail. The water repellent chemical was applied to cotton fabric in two steps. First, bleached cotton fabric was cationized with 3-chloro-2-hydroxypropyltrimethyl ammonium chloride. The cationization process was carried out in alkaline medium (NaOH) using alkali to CHTAC molar ratio of 2:1. The cationized fabric was washed with cold water several times, neutralized with dil. acetic acid (2g/l), washed with water and air-dried. Second, cationized cotton fabric was treated with neutralized stearic acid using an exhaustion technique at 85 ^{0}C for 30 min. The material to bath ratio was adjusted at 1:13. The sample was then squeezed to wet pick-up of 100 %, and dried at 105^{0}C for 10 min followed by curing at different temperatures of 105^{0}C, 118^{0}C or 118^{0}C for 5 minutes. A schematic representation of the application process is shown in Figure 3.1.

3.3.1 Cationization

The cationization of cellulose fabric was previously optimized by Hashem et al[33]. The same procedure was adopted in this work. For cationizing cellulose, an aqueous solution consisting of CHTAC and NaOH in the molar ratio of 1:2 was prepared. While mixing the CHTAC solution with NaOH, the temperature was kept constant by cooling the mixture with ice/cold water. The prepared cationizing solution can be applied to textile fabric by pad-dry-cure and pad-batch methods.

3.3.1.1. Pad-dry-cure method

Fabric samples of dimensions 12x15 were soaked in the prepared cationizing solution mixture of CHTAC and NaOH and padded to 100% wpu. The padded samples were then dried at 35^0C for 12 min, and finally cured at 120^0C for 15 min in forced air oven. The cured fabrics were washed with cold water, neutralized with dil. acetic acid (2g/l), washed with cold water, centrifuged and air-dried.

3.3.1.2. Pad-batch method

The same size fabric samples used in pad-dry-cure methods were used in this method. The fabric samples were soaked in the prepared cationizing solution mixture consisting of CHTAC and NaOH in the molar ratio of 1:2 and padded to 100 % wpu. Then the wet fabrics were placed in polyethylene bags, and air was removed before sealing. The sealed bags were stored for 24 hours at room temperature followed by washing with cold water, neutralized with dil. acetic acid (2g/l), washed with cold water, centrifuged and air-dried.

3.3.2. Preparation of neutralized stearic acid

Stearic acid (95 %) was added slowly with continuous stirring (Corning heater/stirrer) to water pre-heated to 85^0C. Then the calculated amount of ammonium carbonate ($(NH_4)_2CO_3$) required to neutralize the stearic acid was added slowly at regular intervals with continuous stirring at 85^0C. The resulting emulsion was stabilized by adding 0.5 ml of 10% Aerosol OT 75% anionic surfactant to a 2% ammonium stearate emulsion and allowed to cool. The anionic surfactant was added accordingly to the remaining 2%, 4% and 6% ammonium stearate emulsions.

3.3.3. Application of neutralized stearic acid to cationized cellulose

Prepared neutralized stearic acid was applied to cationized cotton fabrics by exhaustion method after which the fabric was dried at 105^0C for 10 min and finally cured at different temperatures of 105^0C, 118^0C or 130^0C for 5 min to study the effect of curing temperatures followed by washing with cold water and dried at ambient conditions.

3.3.3.1. Exhaustion method

The cationized fabric samples were taken into 500 mL beakers filled with neutralized stearic acid. The beakers were loaded into the rotary dyeing machine. The material to liquor ratio was maintained at 1:13. The temperature of beakers was raised to 85 ^{0}C with a rate of 4^0C/min and was held at this temperature for 30 min. Finally, the samples were removed and squeezed to 100% wpu.

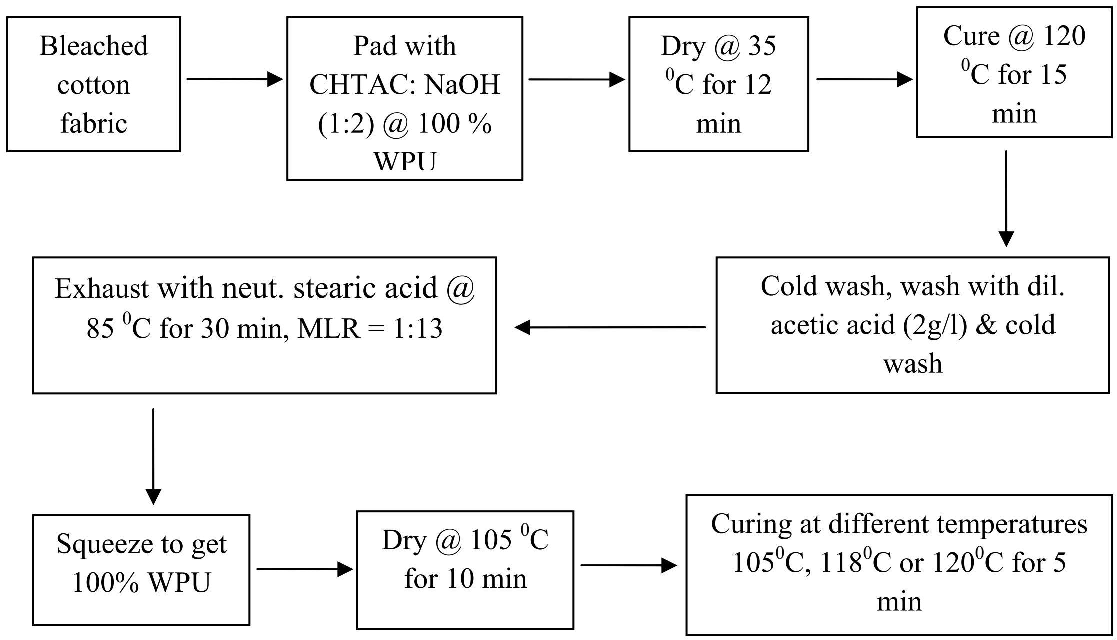


Figure 3.1.Schematic representation of the cationization of fabric by pad-dry-cure method followed by exhaustion of ammonium stearate

3.4. Analysis and testing methods

This section describes analytical and test methods used in this work for characterizing pre-treated and final finished fabrics. Confocal microscopy was used to characterize the uniformity of the cationization treatment. X-ray diffraction was used to evaluate the crystallinity of treated and untreated materials. The untreated and treated cellulosic fabrics were tested for water repellency, tensile strength, stiffness and air permeability.

3.4.1. Nitrogen content

The percent of nitrogen present in quaternary ammonium compound in the cationized fabric was used an indicator to estimate the amount of CHTAC reacted with cellulose[42]. This nitrogen analysis was accomplished using a Perkin-Elmer PE 2400 CHN Elemental analyzer (manufactured by Perkin-Elmer Corporation, Norwalk, CT, USA). Soybean leaves were used to calibrate the instrument. Internal standards, NBS 1572-citrus leaves and NBS 1564-wheat flour were used to ensure proper functioning of the equipment. The sample analyzer is based on the classical methods of Pregal and Dumas. The samples were combusted in a pure oxygen environment resulting in the formation of combustion gases. These gases were passed through the separation zone and the thermal conductivity detector column to separate the combustion gas mixture and to measure the amount of nitrogen content in an automated fashion[13].

3.4.2. Confocal microscopy

Confocal microscopy is an imaging technique which gives qualitative information on the distribution of the chemicals or additives within the cross-section of the fiber, yarn or the fabric. This technique also gives a three dimensional view of the fiber with good geometric resolution and high quantum yield. The three dimensional image is obtained by optical sectioning, which avoids fiber destruction. The series of x,y dimension optical section patterns obtained are put together to obtain a three dimensional image. This technique utilizes a wavelength in the visible region to provide information and requires the fiber to be dyed with a fluorescent dye, which absorbs energy from the laser radiation and emits fluorescence. The fluorescence emitted from the scanned specimen gives details of the structure of the cross-section and whether the cationization reaction occurs only on the surface or inside the fiber diameter[13, 43, 44]. Fabrics cationized with 1.25 M CHTAC solution by the pad-dry-cure method and untreated control samples were examined using this technique.

The samples for this technique were prepared by staining the fabric with Acid Yellow 73 Fluorescein, a water soluble dye. The cationized and blank samples were dyed at 0.1 % shade in a hot water bath incorporated with a mechanical shaker at 70 ^{0}C for 16 hours. Dye beakers should be agitated with the mechanical shaker at a speed of 140 strokes / min. Above 120 strokes/min, the uptake of the dye doesn't depend on the shaking factor. Staining was carried out a material to liquor ratio of 1:40. The samples after dyeing were removed and rinsed with cold water and warm water to remove the loose dye present on the surface of the fabric and dried at ambient conditions[45]. The dyed samples were scanned with Leica TCS SP1 confocal laser scanning microscope with a Leica DM IRBE inverted microscope attached. The fluoroscent stained samples were observed with a 40x PL APO 1.25 N.A. oil immersion objective and excited with the 488 nm line of an argon laser. The resultant emission from the specimen was collected from 504 to 548 nm.

3.4.3. Wide-angle X-ray diffraction

The X-ray diffractograms of untreated, cationized and finished samples were measured using an Omni Instrumental Siemens X-ray diffraction unit, operated at 35 kV and 25 mA. The radiation generated from Cu-Kα (λ =1.54 A^{0}) source filtered by Be was allowed to interact with the sample. The fabric samples were prepared manually and placed on a sample holder. The samples were scanned from $2\theta = 5^{0} - 40^{0}$ with a step size of 0.1 perpendicularly[46].

3.4.4. . Percent add-on

Percent add-on gives the amount of ammonium stearate bound to the fabrics by exhaustion method and is calculated as shown below

$$\% \, add - on = \frac{Final\ weight\ of\ the\ fabric - Initial\ weight\ of\ the\ fabric}{Initial\ weight\ of\ the\ fabric} * 100$$

Initial weight – Weight of the untreated control or cationized fabrics before the exhaustion of ammonium stearate

Final weight – Weight of the untreated control or cationized fabrics after the treatment with ammonium stearate[47]

It is also important to understand the term “exhaustion”. Exhaustion refers to the proportion of chemical in the bath taken up by a substrate to the original amount of chemical available in the bath[47]. During exhaustion the chemical species moves into the fibrous structure due to hydrogen bond interactions or polar interactions or ionic interactions or van der Waals interactions[42]. In this research, ionic interactions play a major role in the exhaustion of the negatively charged chemical onto the positively charged cotton substrate. Conditioning of the fabrics before measuring their weights is essential to reduce the moisture regain deviations associated with cotton fabric. Percent add-on was measured for the Series 5-10 as shown in Table 3.6. The weights of blank and cationized samples were measured before the application of the ammonium stearate. However, the add-on values measured have errors due to the yarns coming out of the fibers during exhaustion in the rotary dyeing machine.

3.4.5. Air permeability

ASTM D 737-04 Standard Test Method for Air Permeability of Textile Fabrics was used to determine the air permeability of the samples. A high pressure differential air permeability machine - 5179 manufactured by The Frazier Precision Instrument Company, USA was used for evaluation. This method measures the rate of air flow passing through a given area of fabric perpendicularly. Thus, the resultant rate of air flow gives the air permeability of the textile fabric[48].

3.4.6. Water repellency test

AATCC Test Method 22-2001 Water Repellency: Spray Test was used to evaluate the repellency of the fabric. The samples were conditioned for 24 hours at $21^0 \pm 1^0$C at a relative humidity of 65±2% prior to testing. The specimens were stretched on a hoop, which was held at angle of 45^0 and 250mL of water was poured though a spray nozzle. Any wetting or spotted pattern observed was compared with the photographic rating chart. A fabric with complete non-wetting was given a "100" rating, while a fabric with complete wetting was assigned a "0" rating[49, 50].

3.4.7. Durability to washing

The washing and drying conditions listed in AATCC Test Method 124-2001 Appearance of Fabrics after Repeated Home Laundering, Table III & Table IV for Cotton Sturdy were used to evaluate the durability of water repellent fabrics. The experiments were performed as described in the test method[51].

3.4.8. Tensile strength

ASTM Test Method D5035-06 Standard Test Method for Breaking Force and Elongation of Textile Fabrics was used to determine the tensile strength and elongation at break of the treated and untreated fabrics using a Q-Test™ /5 tensile tester manufactured by MTS systems corporation using Testworks 4 software. The specimen of one inch by six inch was prepared in the warp direction by raveling. The sample loaded into the machine with a gauge length of 3 inches and was pulled with a constant crosshead speed of 12 inches/min. The tensile tests were carried out only in the warp direction by using four specimens[52].

3.4.9. Basis Weight and Flexural Rigidity

ASTM D 1388-96 Standard Test Method for Stiffness of Fabrics was used to determine the basis weight and bending rigidity of the treated and untreated fabric. A Stiffness of Cloth Tester Motorized – S0015 manufactured by IDM Instruments, Australia was used. Bending rigidity was obtained from basis weight and overhang length. Samples of dimension 1 inch by 8 inch were prepared and their basis weights were measured. Four specimens in the warp direction were used to measure basis weights.

ASTM D 1388-96 Standard Test Method for Stiffness of Fabrics – Option A: Cantilever Test was used to determine bending rigidity of the samples. Fabric specimen of 1 inch by 8 inch was placed on the horizontal platform and movable slide was moved automatically by automatic tester. The distance was recorded at which the leading edge of the specimen touches the inclined surface. This is called overhang length. Four specimens for a warp direction were tested in four orientations to obtain average value of bending rigidity[53].

3.5. Cationization

This section provides the labeling system used to assess the effect of concentration of CHTAC solution on the amount of nitrogen fixed on the fabric. This section also compares pad-dry-cure and pad-batch methods and soaking time of the cationization solution required to get effective fixation of CHTAC onto the fabric.

3.5.1. Effect of concentration of CHTAC on mmoles of nitrogen by Pad-dry-cure method

The first set of experiments (Series 1) was done to measure variation of concentration of CHTAC on the amount of nitrogen fixed on the fabric (mmol N/100g fabric). The cationized solutions of various concentrations of CHTAC and alkali mixture in the molar ratio of 1:2 were prepared. Each column in Table 3.2 represents the samples prepared on a particular day using the same procedure for all samples by the pad-dry-cure method with a soaking time of 2 min.

Table 3.2. Sample identification for the effect of CHTAC concentration variation on mmol N/ 100 g cotton using pad-dry-cure method

Concentration of CHTAC (M)	Day 1	Day 2	Day 3	Day 4
0.75	1A	1F	1K	1P
1	1B	1G	1L	1Q
1.25	1C	1H	1M	1R
1.5	1D	1I	1N	1S
1.75	1E	1J	1O	1T

3.5.2. Effect of soaking time of samples in cationizing solution by pad-dry-cure method

The effect of variation in soaking times of the fabric samples in cationizing solution on the amount of nitrogen fixed on the fabric (mmol N/100g fabric) was measured in Series 2. Cationizing solutions consisting of 1.25M CHTAC and 2.5 M NaOH were prepared. Samples were soaked for different time periods of 0, 2, 4, 6 min and padded through the solution mixture to get 100 % wpu as shown in Table 3.3.

Table 3.3. Sample identification for the effect of variation of soaking time on mmol N/ 100 g cotton at 1.25 M CHTAC using pad-dry-cure method

Soaking time in solution mix. of 1.25:2.5 M CHTAC: NaOH solution mixture (min)	Day 1	Day 2	Day 3	Day 4
0	2A	2E	2I	2M
2	2B	2F	2J	2N
4	2C	2G	2K	2O
6	2D	2H	2L	2P

3.5.3. Effect of concentration of CHTAC on mmoles of nitrogen by pad-batch method

These sets of experiments (Series 3) were done to measure variation of concentration of CHTAC on the amount of nitrogen fixed on the fabric (mmol N/100g fabric) by the pad batch method. The cationizing solutions of various concentrations of CHTAC and alkali mixture in the molar ration of 1:2 were prepared. Each column in Table 3.4 represents the samples prepared on a particular day using the same procedure for all samples by the pad-batch method with a soaking time of 2 min.

Table 3.4. Sample identification for the effect of CHTAC concentration variation on mmol N/ 100 g cotton using pad-batch method

Concentration of CHTAC (M)	Day 1	Day 2	Day 3	Day 4
0.75	3A	3F	3K	3P
1	3B	3G	3L	3Q
1.25	3C	3H	3M	3R
1.5	3D	3I	3N	3S
1.75	3E	3J	3O	3T

3.5.4. Comparison of pad-dry-cure and pad-batch method on amount of the mmol of nitrogen fixed on the fabric

Fabric samples prepared by pad-dry-cure (Series 1) and pad-batch (Series 3) methods were compared to select the route which gives the higher cationization. The cationizing solutions consisted of varying 0.75M, 1.0M, 1.25M, 1.5M and 1.75M CHTAC solutions.

3.5.5. Effect of multiple cationization treatments on cotton fabric

Fabric samples in Series 4 were given multiple cationization treatments by the pad-dry-cure method. During day 1, seven fabrics were cationized with a cationization solution of 1.25 M CHTAC. Out of these seven fabrics, one of the fabrics were put aside and remaining six cationized fabrics were cationized again using 1.25 M CHTAC solution. In the next step, one of the six fabrics was put aside and remaining fabrics were again cationized by treating with 1.25 M CHTAC. The same approach was followed with remaining five fabrics to give multiple treatments. Each column in Table 3.5 represents the samples prepared on a particular day using the same procedure for all samples. Pad-dry-cure method and a soaking time of 2 min were used for the Series 4.

Table 3.5. Sample identification for the effect of multiple cationization treatments on cotton fabric by pad-dry –cure method.

No. of CHTAC treatments (1.25 M)	Day 1	Day 2
1	4A	4H
2	4B	4I
3	4C	4J
4	4D	4K
5	4E	4L
6	4F	4M
7	4G	4N

3.6. Ionic interactions

This section describes procedures for the development of water repellent fabric with ionic interactions between positively charged cationized cellulose fabric and negatively charged stearyl ions.

3.6.1. Cationization of cellulose fabrics followed by exhaustion with neutralized stearic acid

Fabric samples of dimensions 12x15 were used for this treatment. From the above experiments, it was observed that maximum cationization was obtained by the pad-dry-cure method as compared to pad-batch methods with a soaking time of 2 min (see Section

4.1). So, all fabrics were cationized by the pad-dry cure method. In this section, the effect of cationization, the effect of curing temperature and the effect of stearic acid concentration on the performance of water repellency of the fabric were studied. The experimental design for the cationization of cellulose fabrics followed by exhaustion with neutralized stearic acid is shown in Table 3.6.

Table 3.6. Experimental design for cationization of cellulose fabric followed by exhaustion of neutralized stearic acid.

	Conc. of ammonium Stearate (% 0wb)								
	2.0 %			4.0 %			6.0 %		
Curing Temperature (^{0}C)	105	118	130	105	118	130	105	118	130
CHTAC conc. (M)									
0 (Series 5)	5A	5B	5C	5D	5E	5F	5G	5H	5I
0.75 (Series 6)	6A	6B	6C	6D	6E	6F	6G	6H	6I
1.0 (Series 7)	7A	7B	7C	7D	7E	7F	7G	7H	7I
1.25 (Series 8)	8A	8B	8C	8D	8E	8F	8G	8H	8I
1.5 (Series 9)	9A	9B	9C	9D	9E	9F	9G	9H	9I
1.75 (Series 10)	10A	10B	10C	10D	10E	10F	10G	10H	10I

The cotton fabrics were cationized with an aqueous solution mixture of CHTAC and NaOH in the molar ratio 1:2 with varying concentrations of 0.75M, 1.0M, 1.25M, 1.5M, and 1.75M respectively. Nine fabrics were prepared for each concentration of CHTAC. The fabrics were impregnated in different concentrations of CHTAC solutions for 2 min, padded to 100 % wpu and dried at 35^0C for 12 min. The samples were then cured at 120^0C for 15 min, rinsed with water, washed with 2 g/L acetic acid, washed with water again and centrifuged and dried under ambient conditions. The nitrogen content of each fabric was analyzed after cationization.

The cationized samples were conditioned overnight at 65% RH at a temperature of 21^0C. The above cationized samples including untreated cellulosic fabrics were then subjected to exhaustion using 2%, 4%, 6% owb ammonium stearate solutions as shown in Table 3.6. Ammonium stearate solutions were prepared as described in the Section *3.3.2*. The beakers of the exhaust machine were filled up with ammonium stearate solutions at a material to liquor ratio of 1:13. The temperatures of the solutions were raised to 85^0C with a rise of 4^0C/min. The samples were held at this temperature for 30 min followed by cooling for 2 min. The samples were removed from the machine and squeezed to 100% wpu using a pad roller and then dried at 105^0C for 10 min and cured at 105^0C, 118^0C or 130^0C for 5 min and washed with cold water and dried.

For 0.75M CHTAC, nine cationized samples were prepared represented by 6A, 6B, 6C, 6D, 6E, 6F, 6G, 6H, 6I. The nine cationized samples were divided into three groups, thus each group had three cationized samples. The three groups were exhausted with different ammonium stearate emulsion concentrations of 2% (6A, 6B & 6C), 4% (6D, 6E & 6F) and 6% (6G, 6H & 6I) (owb) respectively. Hence, 6A, 6B & 6C were treated with 0.75 M

CHTAC and exhausted with an ammonium stearate emulsion concentration of 2 % owb. These three fabrics were dried at 105^0C and cured at 105^0C (6A), 118^0C (6B) and 130^0C (6C) for five minutes. This helped in studying the effect of curing temperature on water repellency. In the same way, Series 5, 7, 8, 9, 10 were prepared.

4. RESULTS AND DISCUSSION

This section discusses the data obtained for the experiments in Section *3* and gives the possible reasons for the particular behavior or trend observed in the experiments.

4.1. Nitrogen content analysis

The concentration of the cationic agent attached to the fiber was measured as percent nitrogen content on a quaternary amine[39]. Nitrogen content of samples treated with CHTAC from Series 1-4 were determined. The un-cationized cellulose cotton fabric contains approximately 0.02% of nitrogen content due to the presence of natural impurities such as proteins, ash, pectin and waxes. The nitrogen content of the fabrics varied with change in the CHTAC concentration. Pad-batch and pad-dry cure methods also affected the amount of nitrogen content present in the CHTAC treated fabrics. Nitrogen analyses were done after complete treatment as explained in the Section *3.4.1.* Nitrogen content analyses were obtained in percent values from the Perkin-Elmer PE 2400 CHN Elemental analyzer. The percent values were converted into mmol N/100 g of the fabric by using the formula

$$\text{mmol N/100 g of cotton} = (\%\ \text{N X } 1000) / 14$$

4.1.1. Cationization – Pad dry cure method

In Series 1, samples were cationized by the pad-dry-cure method as explained in Section *3.5.1* using varying concentrations of CHTAC. The results showed an increase in % N content (% Nitrogen content) or mmol N/100 g of the fabric with an increase in CHTAC concentration from 0.75M to 1.25M and thereafter it decreased as shown in Figure 4.1 and in Table 8.1 of the appendix. Up to 1.25 M CHTAC concentration, the reaction of EPTAC (a reactive species derived from CHTAC under alkaline conditions) with cellulose is more favored than hydrolysis of the EPTAC. The increase of CHTAC concentration in the padding liquor results in the availability of more CHTAC species which will produce more EPTAC reactive species for the same amount of the fabric between 0.75-1.25 M CHTAC concentrations. The resultant increased EPTAC molecules with the increase of CHTAC concentration react with more hydroxyl groups of cellulose to increase the nitrogen content of the fabric from 0.75 M to 1.25 M CHTAC concentration.

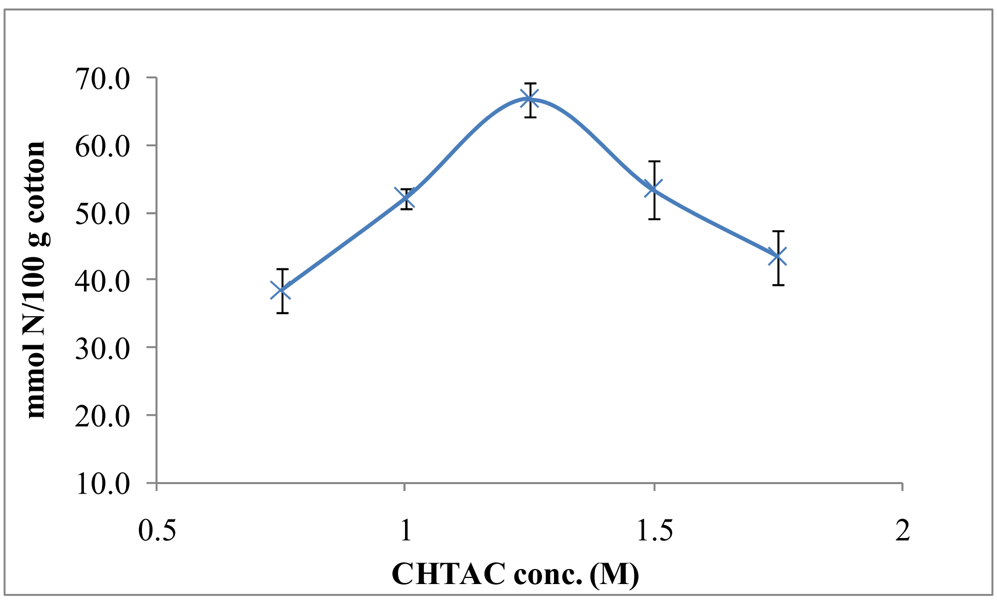


Figure 4.1. Effect of CHTAC concentration on mmol N/100 g of fabric by pad-dry-cure method

For further increase in CHTAC concentration i.e., above 1.25 M CHTAC concentration, the hydrolysis of EPTAC is more favored than the reaction of EPTAC with cellulose in the presence of cellulose. The increase in the amount of CHTAC also resulted in the increase of NaOH concentration relatively in the padding liquor, since the padding liquor contains CHTAC and NaOH in the molar ratio of 1:2. One part of NaOH is required to convert CHTAC to EPTAC and the same amount of NaOH is required to facilitate the reaction of EPTAC with hydroxyl groups of cellulose. Above 1.25 M CHTAC, the increase in the concentration of alkali is considerable enough to favor hydrolysis of EPTAC reaction as compared to cationization reaction. This might be the reason responsible for the decrease of mmol N/100 g fabric after 1.25 M CHTAC.

The cationization efficiencies (percent Nitrogen fixation) at different CHTAC concentrations were calculated. For example, a sample padded with 0.75 M CHTAC concentration i.e, 141 g/L CHTAC solution at a wet pickup (wpu) of 100%, gave a nitrogen content of 0.537 % on weight of goods. The theoretical nitrogen content for 0.75 M CHTAC padded fabric should contain 1.05 %, so the cationization efficiency or the percent fixation is given by 0.537/1.05 or 51.2 %.

Table 4.1. Percent nitrogen fixation for pad-dry-cure samples at different concentrations

CHTAC concentration (M)	Fixation percent/ Cationization efficiency
0.75	51.2 %
1	52.1 %
1.25	53.4 %
1.5	35.6 %
1.75	24.8 %

Fixation percents or cationization efficiencies at different CHTAC concentrations are shown in Table 4.1. The cationization efficiency showed an indication of increase in the fixation efficiency from 0.75-1.25 M CHTAC concentrations, and reduced considerably thereafter. This shows that above 1.25 M CHTAC, the cationization reaction was less favored than hydrolysis of EPTAC.

4.1.2. Effect of soaking time of samples in cationization solution mixture – pad dry cure method

The effect of soaking time of the fabric in a constant solution mixture of CHTAC and NaOH (molar ratio 1.25:2.5 respectively), before padding for different time intervals 0 min, 2 min, 4 min and 6 min was studied in Series 2 as described in Section *3.5.2*. The results in Figure 4.2 and Table 8.2 of the Appendix, show no significant change in the amount of nitrogen fixed on the fabric, within the time limits employed.

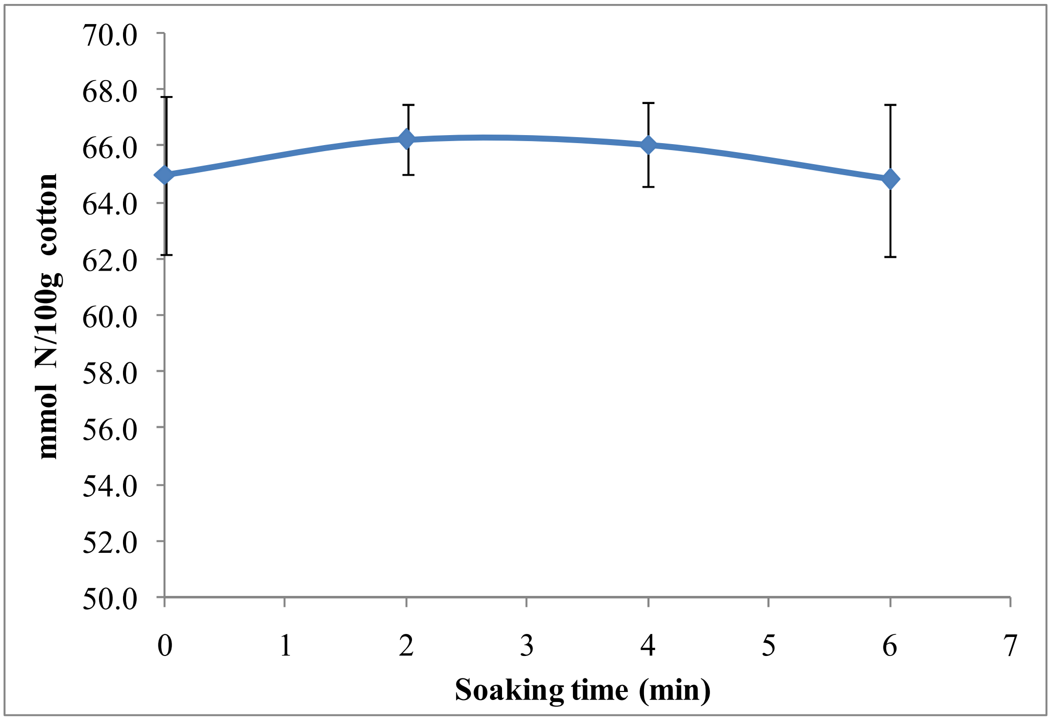


Figure 4.2. Effect of soaking time on % N content of the fabric by pad-dry-cure method

However, data scattering was less at a soaking time of 2 min as compared to other time intervals. Padding of the fabric without soaking may not give sufficient time for the uniform distribution of the CHTAC molecules on the fabric resulting in more scattering of the data. At time intervals of 6 min, there is a possibility of the hydrolysis of EPTAC reaction competing at a faster rate than cationization reaction. A soaking time range of 2-4 minutes before padding was chosen as the distribution of the CHTAC chemical on to the cellulose fabric is optimum. For all further experiments, a soaking time of 2 min before padding was used.

4.1.3. Cationization – Pad batch method

In Series 3, samples were cationized by the pad-batch method as explained in Section *3.5.3* using varying concentrations of CHTAC.

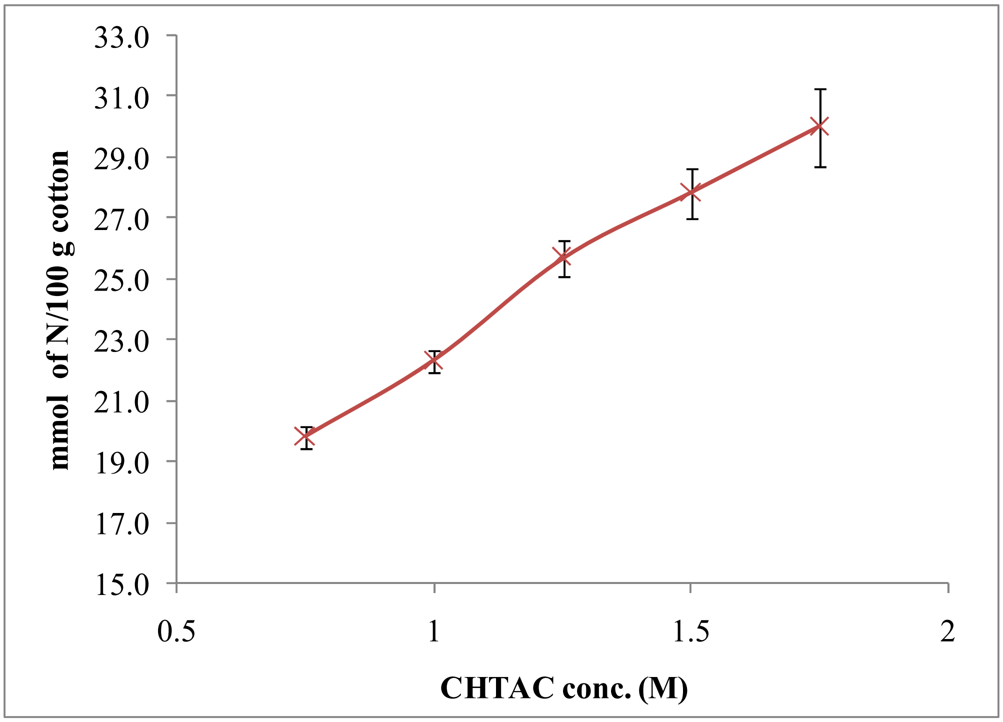


Figure 4.3. Effect of CHTAC concentration on mmol N/100 g of fabric by pad-batch method

The results show an increase in % N content or mmol N/100 g of the fabric with an increase in CHTAC concentration as shown in Figure 4.3 and in Table 8.3 of the Appendix. The increase of CHTAC concentration in the padding liquor results in the availability of more CHTAC species which will produce more EPTAC reactive species for the same amount of the fabric. The resultant increased EPTAC molecules with increase of CHTAC concentration react with more hydroxyl groups of cellulose to increase the nitrogen content of the fabric. The fixation percent or cationization efficiencies at different CHTAC concentrations were calculated as described for pad-dry-cure methods. Fixation percents or cationization efficiencies calculated are tabulated in Table 4.2. The low cationization efficiency values obtained for the pad-batch method as compared to pad-dry-cure methods resulted in lower amounts of % N content in the pad-batch treated fabrics.

Table 4.2. Percent nitrogen fixation for pad-batch samples at different concentrations

CHTAC concentration (M)	Fixation percent/ Cationization efficiency
0.75	26.4
1	22.3
1.25	20.6
1.5	18.6
1.75	17.1

4.1.4. Comparison of pad-dry-cure and pad-batch methods – cationization

Cationization treatments carried out by pad-dry-cure and pad-batch methods at different CHTAC concentrations were compared as shown in Figure 4.4. The results show that at all the CHTAC concentrations employed pad-dry-cure methods gave higher nitrogen contents.

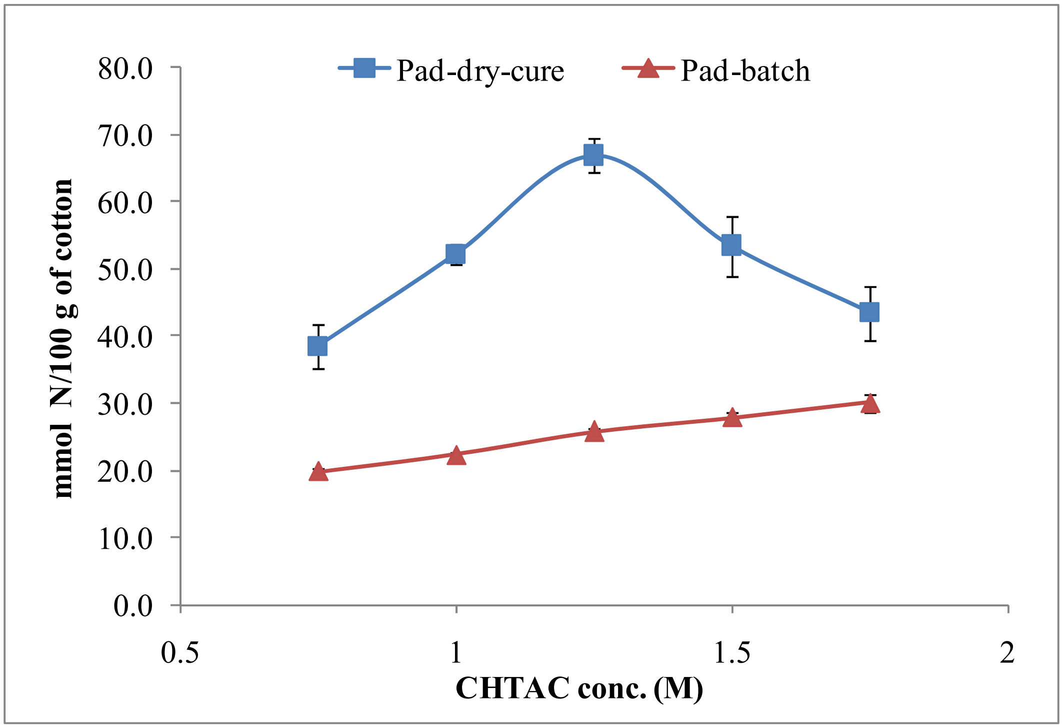


Figure 4. 4. Comparison of cationization treatments by pad-dry-cure and pad-batch methods

It is evident from Figure 4.5, the reaction efficiency or percent nitrogen fixation is greater in the pad-dry-cure method as compared to the pad-batch method at all concentrations. The lower nitrogen contents in the pad-batch method are due to the lower reaction efficiency. The presence of water during pad-batch methods favors the hydrolysis of EPTAC reaction more as compared to cationization reaction. In the case of the pad-dry-cure method water is eliminated completely during the drying step to suppress hydrolysis of EPTAC[33]. Thus for all further experiments, samples prepared by pad-dry-cure methods were used.

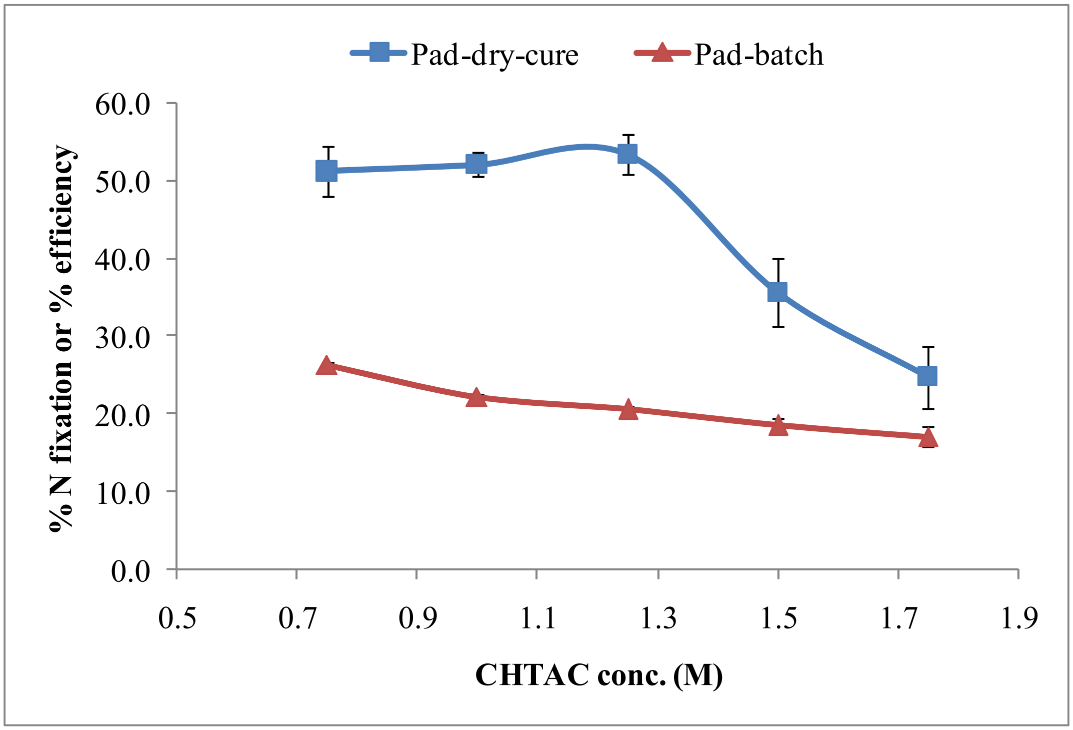


Figure 4. 5. Comparison of % N fixations of cationization treatments by pad-dry-cure and pad-batch methods

4.1.5. Multiple Cationization treatments of cotton fabric – Pad dry cure method

Higher nitrogen content was obtained for the cotton fabric cationized at 1.25 M CHTAC concentration by the pad-dry-cure method. In order to study the extent to which a given fabric could be saturated with nitrogen content, multiple cationization treatments were given to the fabric with 1.25 M CHTAC concentration at molar ratio of CHTAC and NaOH 1:2 respectively by the pad-dry cure method as explained in Sections *3.3.1.1* and *3.5.5.* The results are tabulated in Table 8.4 of the Appendix. Figure 4.6 shows an increase in N content of the sample with increase of the multiple treatments of the fabric. However, the N content curve becomes flatter with the increase of the multiple cationization treatments suggesting that the extent of nitrogen content added decreased in each cationization step. Table 4.3 shows the extent of nitrogen content added in each treatment.

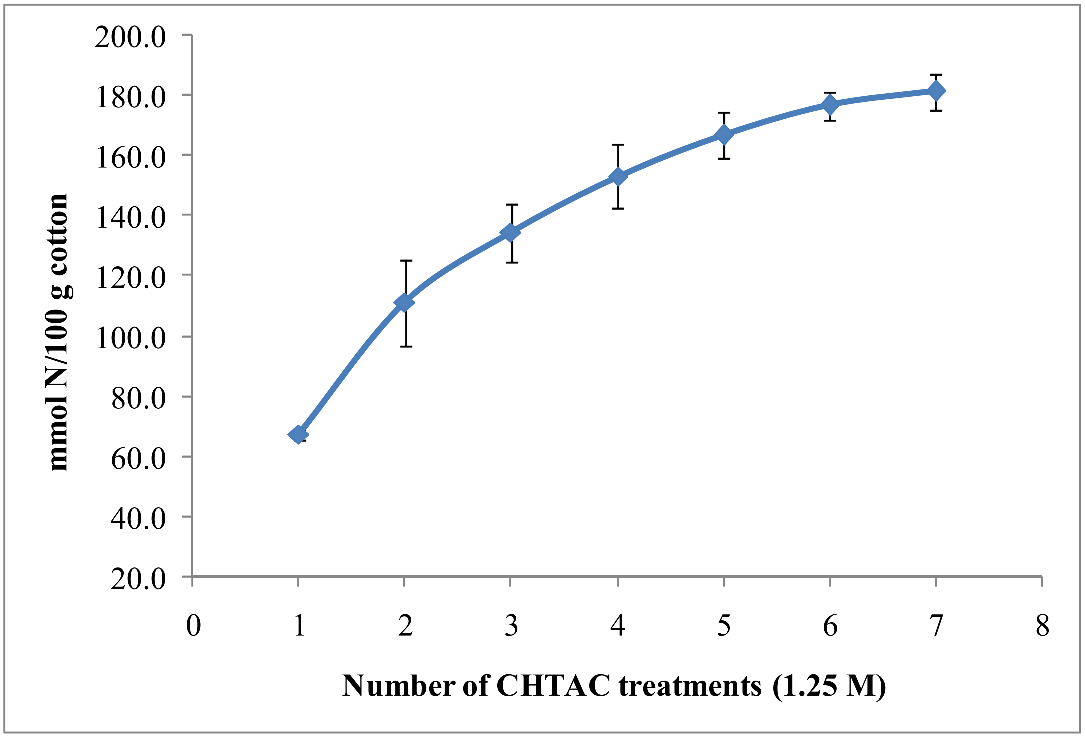


Figure 4.6. Effect of multiple cationization treatments on mmol N/100 g cotton by pad-dry-cure method

After treatment 1, the number of available hydroxyl groups of cellulose to react with EPTAC molecules decreases and also the cationizing groups already present in the cellulose repels cationic charged EPTAC molecules in the padding liquor. The latter effect becomes more significant with the increase of the number of the multiple treatments contributing to the lower addition of N content to the fabric from treatment 1 to treatment 7.

Table 4.3. Amount of nitrogen content (mmol N/100 g cotton) added in each cation-ization step of multiple cationization treatments

Multiple CHTAC treatments	N content (mmol N/100 g cotton) added in each treatment
Treatment 1	67.5
Treatment 2	43.9
Treatment 3	23.2
Treatment 4	18.6
Treatment 5	13.6
Treatment 6	10
Treatment 7	4.6

4.2. Analysis of confocal microscopy images of untreated and cationized samples

In order to determine if the cationization reaction occurs uniformly or evenly across the cross-section of the cellulose fiber, cationization samples prepared by pad-dry-cure method at 1.25 M CHTAC were analyzed qualitatively by confocal microscopy. The samples were prepared as described in Section *3.4.2.* The cationized sample was dyed more evenly and deeper as compared to untreated control sample at the same % of shade. This gives a clear idea about the presence of the positively charged quaternary ammonium compound in the cationized fabric. A confocal microscopy image of the cross-section of the untreated control sample is shown in Figure 4.7. The morphology of the cross-section of the fiber is kidney shaped. From Figure 4.7 uneven dyeing is observed occurring across the cross-section of the untreated fiber. The slight staining of the sample was due to the natural substantivity of the fiber towards the acidic dye.

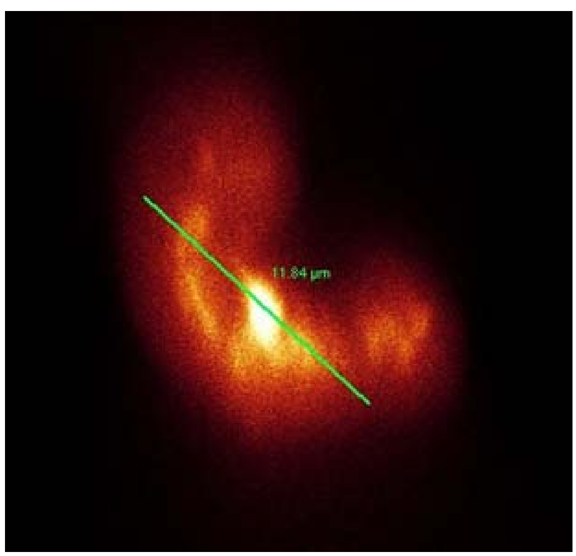


Figure 4.7. Confocal image of the dyed untreated control cross-section

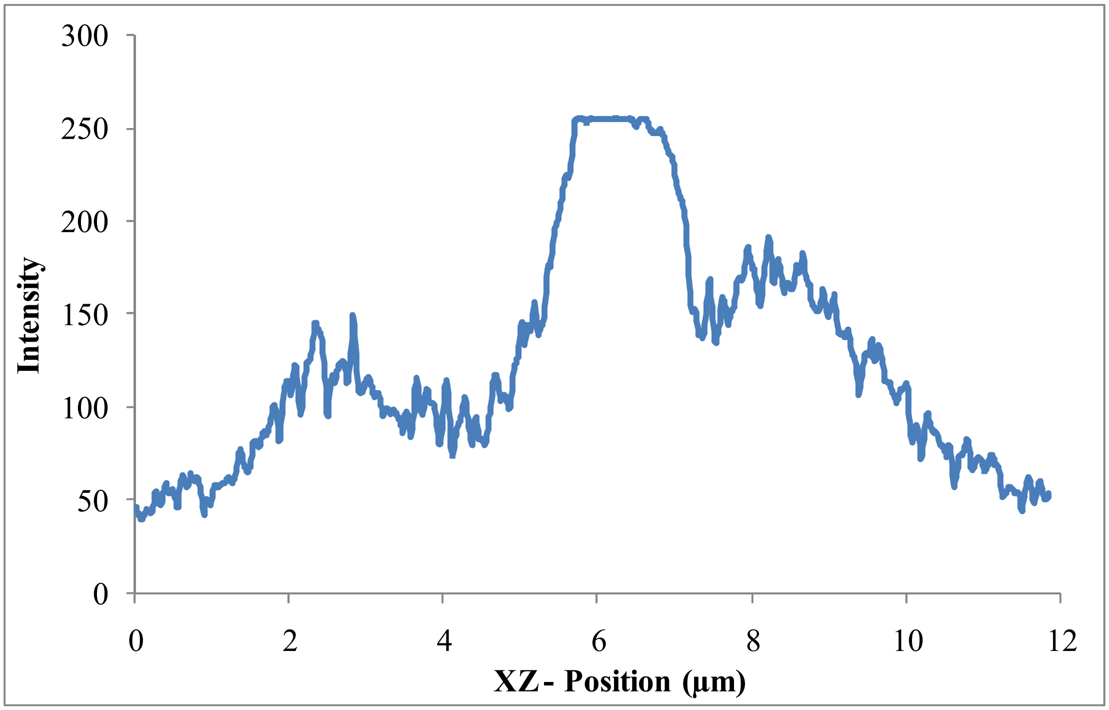


Figure 4.8. Intensity profile over the cross-section of the untreated control (untreated cotton) sample

Quantitative analysis of intensity across the cross-section of the untreated control sample is shown in Figure 4.8. The intensity varied all across the XZ direction. The 3-dimensional image of the untreated fiber in Figure 4.9 showed the presence of convolutions which occurs naturally in cotton[13]. Figure 4.9 also clearly shows the uneven dyeing of cotton fiber. Figure 4.10 shows the confocal cross-sectional image of the cationized sample prepared by the pad-dry-cure method. The image shows that the dyeing occurred uniformly all across the cross-section of the fiber which implies that the cationization reaction also occurred inside the fiber evenly.

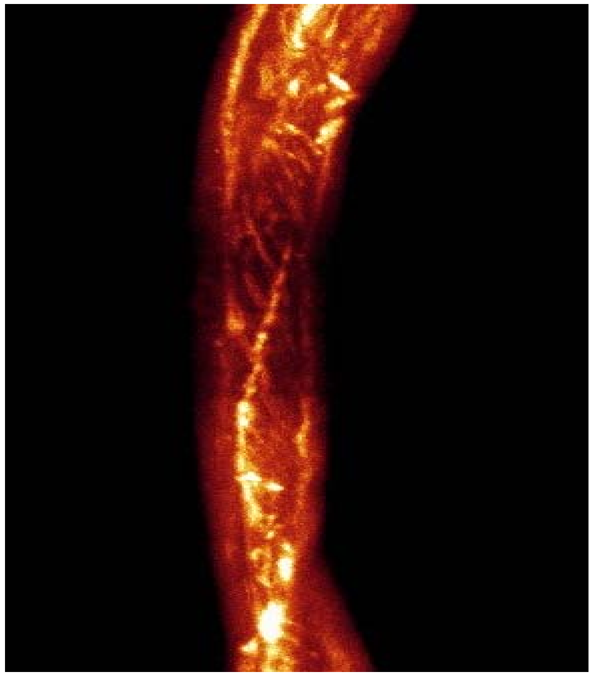


Figure 4.9. 3- Dimensional confocal image of the untreated control (100 % cotton) sample

Quantitative analysis of intensity across the cross-section of the cationized sample is shown in Figure 4.11. The intensity is almost constant all across the XZ-direction i.e, across the cross-section of the fiber as compared to the untreated fiber. This implies that the cationization reaction had occurred throughout the fiber in a uniform manner. The geometry of the fiber cross-section of the cationized fiber is similar to the untreated fiber, but it is flatter than untreated fiber.

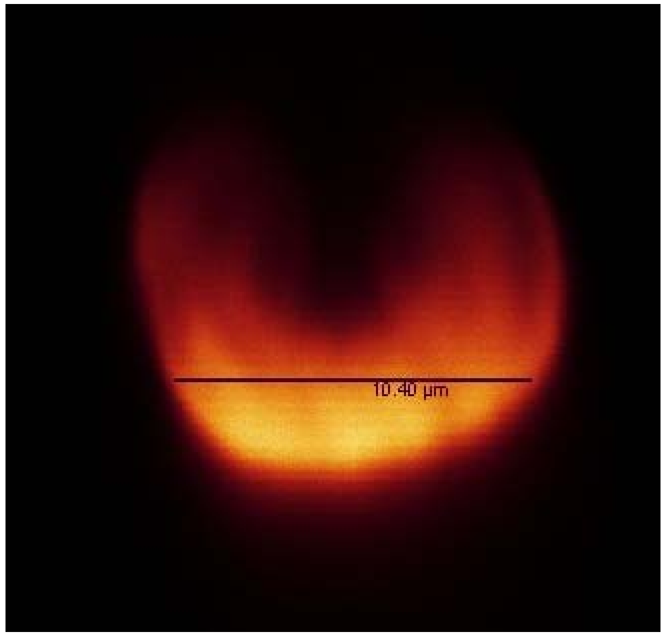


Figure 4.10. Confocal cross-sectional image of cationized fiber

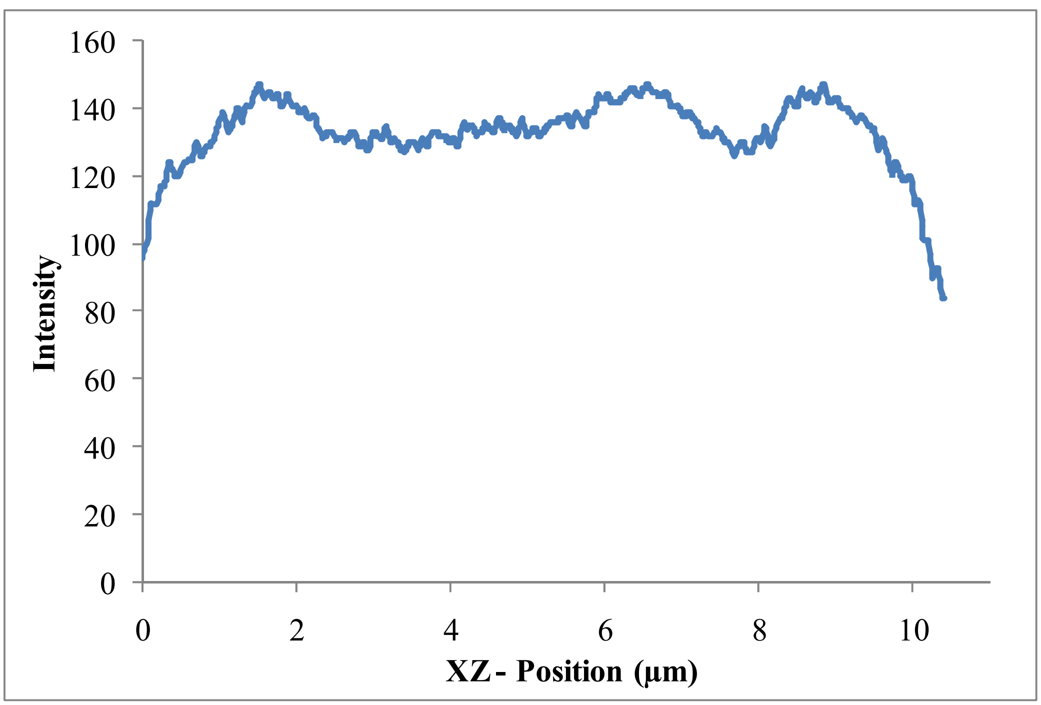


Figure 4.11. Intensity profile over the cross-section of the cationized sample

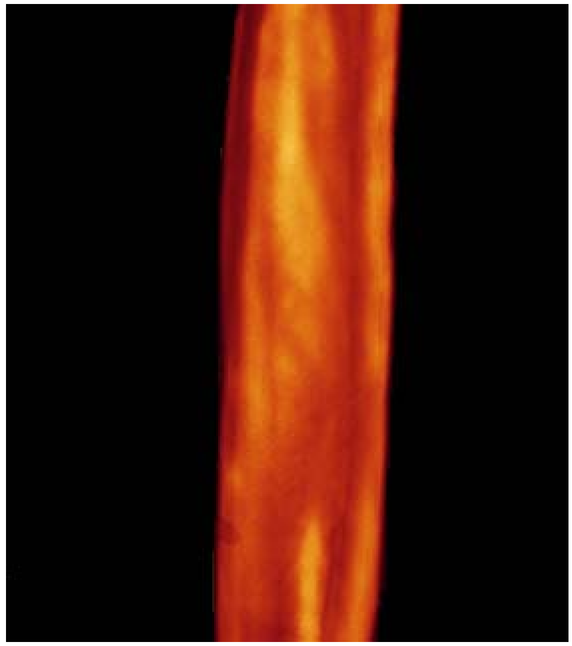


Figure 4.12. 3- Dimensional confocal image of the cationized fiber

The 3-dimensional confocal image of the cationized fiber is shown in Figure 4.12. In comparison with untreated sample, the convolutions were less apparent in the cationized sample. The presence of sodium hydroxide in the cationized solution mixture appears to be responsible for the loss of the convolutions[12].

4.3 Analysis of X-ray diffractograms of untreated and cationized samples

Wide-angle X-ray diffraction measurements were carried out to observe if any structural changes occurring in the cationized samples in comparison with the blank untreated samples as described in Section *3.4.3.* In X-ray diffractograms, pure cotton contains peaks at diffraction angles (2θ) 14.8, 16.3 and 22.6 corresponding to diffraction planes of $1\bar{1}0$, 110 and 020[55]. The above diffraction planes correspond to cellulose I polymorph, a signature of native cotton. Figures 4.13 and 4.14 contain X-ray diffractograms of untreated pure cotton sample and cationized samples prepared by pad-dry-cure and pad-batch methods respectively.

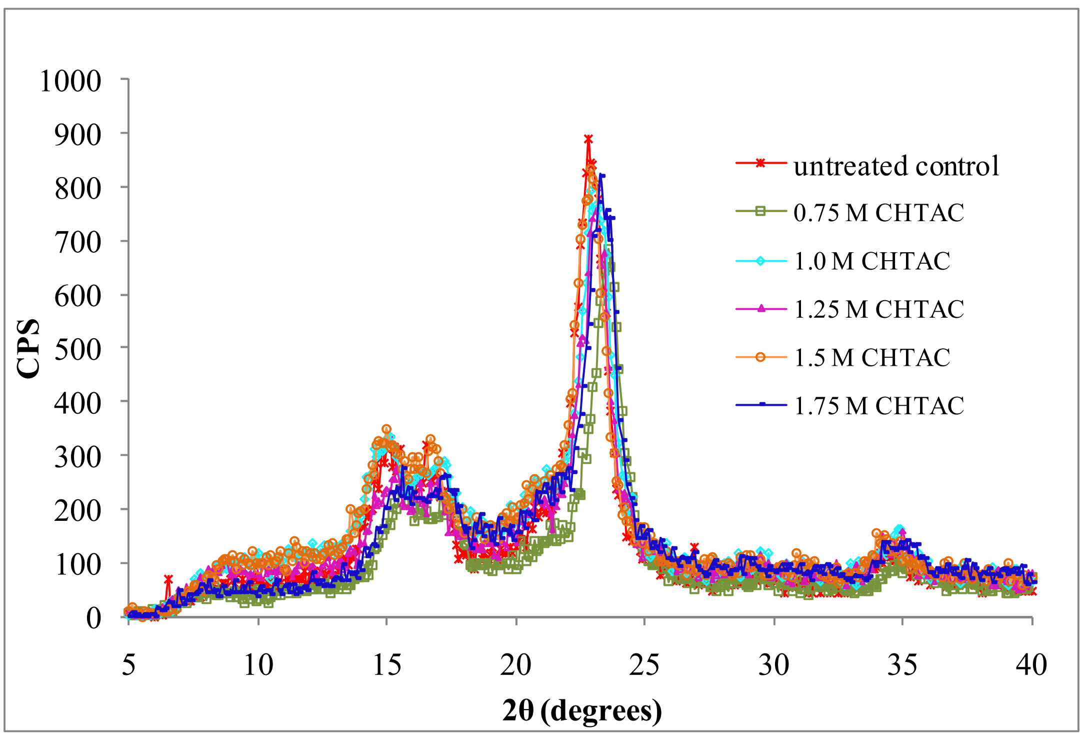


Figure 4.13. X-ray diffractogram of untreated control and cationized fabrics (pad-dry-cure)

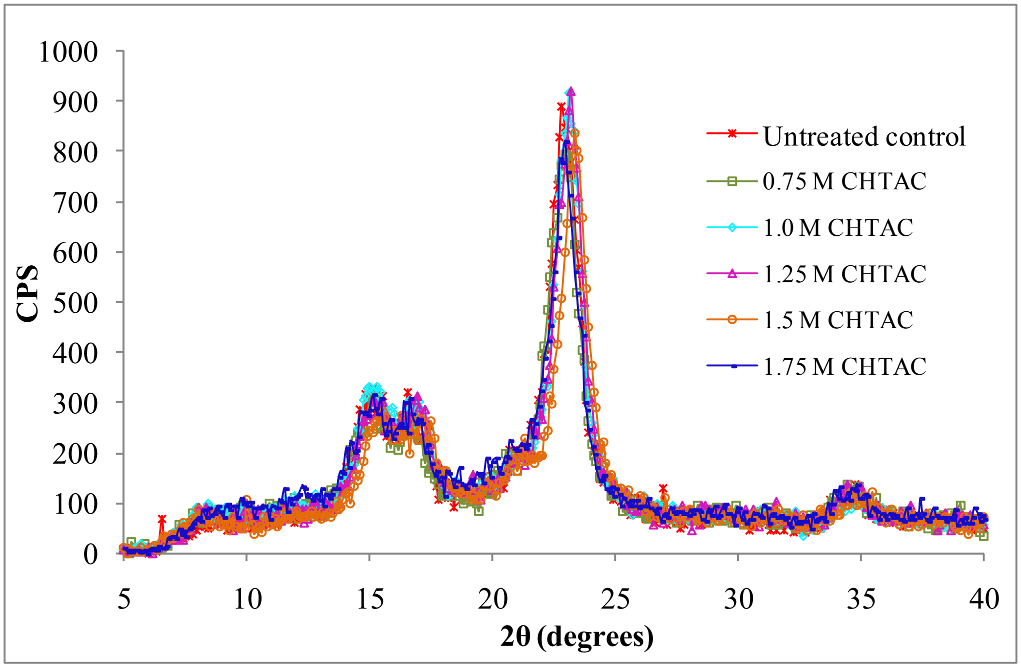


Figure 4.14. X-ray diffractogram of untreated control and cationized fabrics (pad-batch)

In Figures 4.13 & 4.14, untreated control and CHTAC treated samples at 0.75 M, 1.0 M, 1.25 M, 1.5 M, and 1.75 M concentrations have three diffraction peaks corresponding to $(1\bar{1}0)$, (110) and (020) planes representing cellulose-I polymorph. The data show that the diffraction peaks of cationized samples coincide with the untreated control sample. From Figure 4.13 and 4.14, it is evident that the CHTAC treatment does not change the cellulose-I polymorph or crystalline structure present in the untreated control. In the cationization process, the highest concentration of NaOH used for 1.75 M CHTAC is 3.5 M NaOH. Conversion of CHTAC to EPTAC utilizes 1.75 M of NaOH. However, for the conversion of cellulose-I to cellulose – II requires 8.0 M NaOH[56] or 20 to 25% NaOH solution[57]. Hence, the amount of NaOH available in the cationization used in this work is insufficient to cause any noticeable morphological changes.

4.4. Analysis of percent add-on values of ammonium stearate exhausted cationized samples

The percent add-on values for ammonium stearate treatment were measured for the Series 5 to 10 as detailed in Section *3.4.4.* The percent add-on gives the amount of the ammonium stearate retained within the cationized and blank fabric after the completion of the exhaustion. Due to the moisture regain value deviations with cellulose fabrics and the loss of some of the yarns coming out of the fabric during exhaustion with ammonium stearate at higher temperatures errors may have resulted in measuring the values of add-on. The percent add-on values corresponding to ammonium stearate chemical for untreated and cationized fabrics are shown in Table 8.5 of the Appendix. From Figure 4.15, it is observed that at all the concentrations of the CHTAC and ammonium stearate employed, the curing temperatures have no effect on the percent add-on of the ammonium stearate. At all the curing temperatures, the percent add-on values lies within one standard deviation. It is also evident that the percent add-on of the uncationized i.e, 100 % cotton fabric is negligible as compared to the cationized samples. This suggests that the negatively charged ammonium stearate chemical is barely adsorbed when positively charged groups are not present in the fabric[39]. In contrast, adsorption of the negatively charged ammonium stearate is observed in the positively charged cationized fabric. The negatively charged ammonium stearate molecules in the liquor bath are attracted by the positively charged cationized fabric by forming electrostatic bonds. Ionic attractions play a major role in the exhaustion of the ammonium stearate onto cationized fabric.

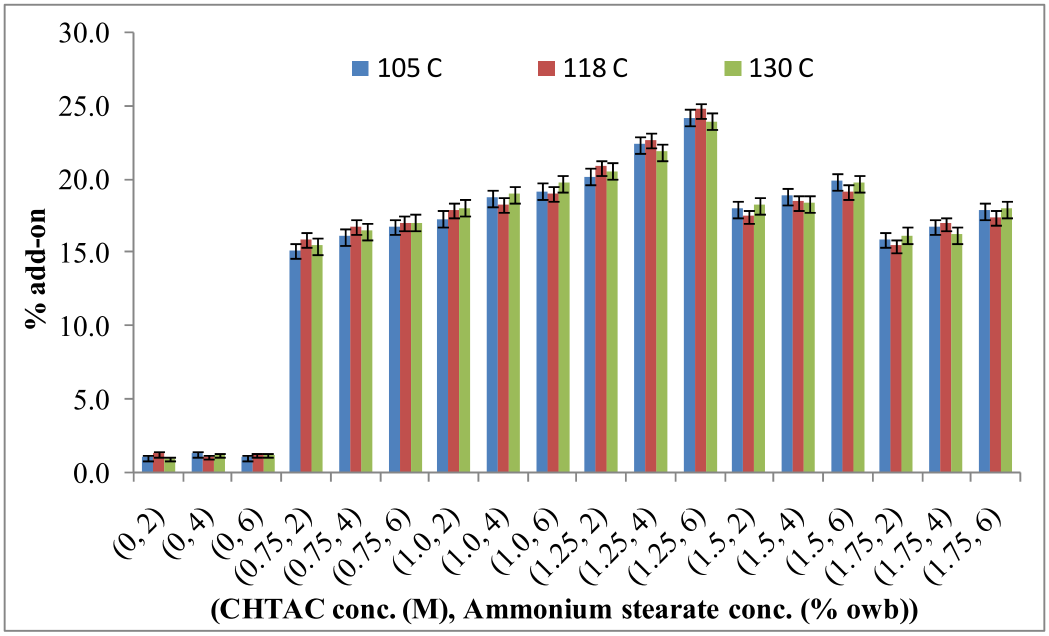


Figure 4.15. Effect of curing temperature on percent add-on of untreated and cationized fabrics treated with ammonium stearate.

From Figure 4.16, an increase in percent add-on values of ammonium stearate is observed with the increase of the positively charged groups (% N content increases from 0.75 M to 1.25 M CHTAC and therafter it decreases for 1.5 and 1.75 M CHTAC) up to 1.25 M CHTAC and thereafter it decreased due to the decrease of positively charged groups. Figure 4.16 represents the results at a curing temperature of 105^0C. This behavior is analogous to the process of dyeing wool with acid dyes in acidic solutions. The absence of acidic solutions during dyeing results in a negligible adsorption due to the absence of the positively charged amino group. Adding acid to the dyeing system protonates the amino group and an electrostatic bond forms between negatively charged acid dye group and positively charged amino group of the wool[58].

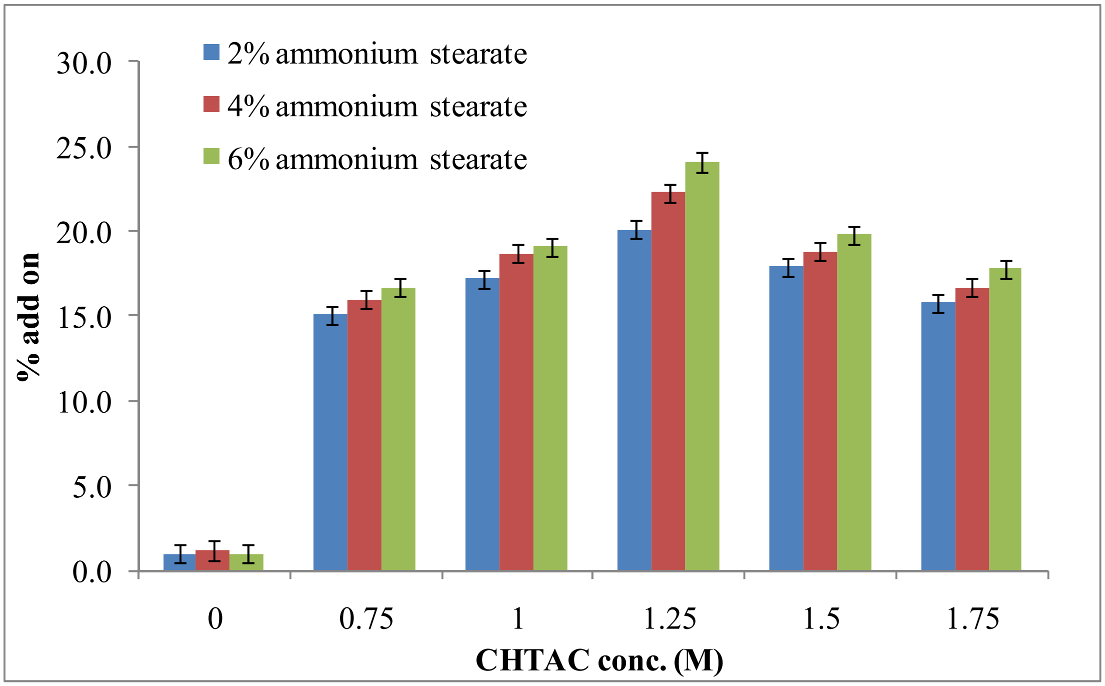


Figure 4.16. Effect of CHTAC and ammonium stearate concentrations on percent add-on at $105^{0}C$

At all the CHTAC concentrations, an increase in ammonium stearate concentrations (% owb) from 2% to 6% showed an increase in the percent add-on values. Higher add-on values were obtained for 1.25 M CHTAC cationized samples which has higher % N content or higher cationic charges followed by 1.5 M, 1.0 M, 1.75 M and 0.75M cationized fabrics. The difference in percent add-on values of 1.5 & 1.0 M and 1.75 & 0.75 M cationized fabrics is almost negligible due to the presence of almost same amount of % N contents. A similar trend was observed at curing temperatures of $118^{0}C$ and $130^{0}C$ and the data is shown in Table 8.5 of the Appendix. Cationization of cotton fabrics greatly improved the exhaustion of the water repellent chemical, since percent add-on values obtained for 0.75 M -1.75 M cationized fabrics are in the range of approximately

15% - 25%. Hence, cationization increases adsorption of stearyl anions from the bath due to increased substantivity as compared to untreated cotton[39].

Nine cationized fabrics at a CHTAC conc. of 1.25 M were exhausted and dried at 105^0C and these nine fabrics were divided into three sets and a set of three of fabrics were cured at 105^0C, 118^0C and 130^0C followed by other two sets in the same manner. The plus or minus one standard deviation value calculated from the 1.25M samples cured at 105^0C was assigned to all the fabric cured at 105^0C. Similar calculations were applied for fabrics cured at 118^0C and 130^0C.

4.5. Analysis of air permeability values of untreated, cationized and ammonium stearate exhausted cationized samples

Air permeability is normally used as an indicator to study the breathability of water repellent fabrics. Breathability is one of the most important factors of the clothing which decides comfort of the fabric. Air permeability was measured for the untreated cotton sample, cationized samples of Series 1 and ammonium stearate exhausted samples from Series 5 to 10 as described in Section *3.4.5*. Five readings were taken for each specimen at different positions of the fabric and the data were averaged. Air permeability results are shown in Table 8.6 of the Appendix. Figure 4.17 shows the air permeability values of untreated and cationized samples of Series 1. Cationized samples showed reduction in air permeability with the increase of the % N content in the sample. The cationized sample of 1.25 M CHTAC concentration showed the largest reduction in air permeability of about 63.26% as compared to the uncationized sample. The shrinkage of the fabric during cationization resulted in a decrease of air permeability apart from the solids add-on on the fabric due to the closer packing of yarns. The number of warp and weft yarns per inch were measured by using a pick glass for untreated fabric, cationized fabrics, and 1.25 M cationized fabric exhausted with 6 % ammonium stearate cured at 105^0C. Table 4.4 shows that the number of weft yarns per inch increased after cationization with the increase of % N content on the fabric. However, the number of warp yarns per inch remained almost unchanged. Due to the shrinkage of the warp yarns, the weft yarns came closer together. The exhaustion of ammonium stearate on the cationized fabric showed an indication of increase in the number of weft yarns per inch from 86 to 90 whereas the number of warp yarns per inch decreased from 83 to 81. This results shows that cationization and ammonium stearate treatments caused the fabric shrinkage.

Table 4.4. Warp and weft yarn measurements for untreated and finished fabrics

Substrate	No. of warp yarns / inch	No. of weft yarns / Inch
Untreated fabric	84	77
0.75 M CHTAC	83	82
1.0 M CHTAC	83	84
1.25 M CHTAC	83	86
1.50 M CHTAC	82	84
1.75 M CHTAC	84	82
1.25 M CHTAC + 6 % stearic acid	81	90

During cationization samples were dried and cured in an oven with weft ends mounted on pin frames. Thus, tension was applied only in weft direction leaving warp yarns unrestrained. The un-restrainment in warp direction during drying and curing have led to the shrinkage of the fabric in warp direction during the reaction, increasing the number of wefts per inch and reducing the air permeability. The results from Table 4.4 confirm the shrinkage of the fabric in warp direction after cationization. The presence of higher amounts of alkali in the cationization of 1.25 M CHTAC resulted in greater swelling

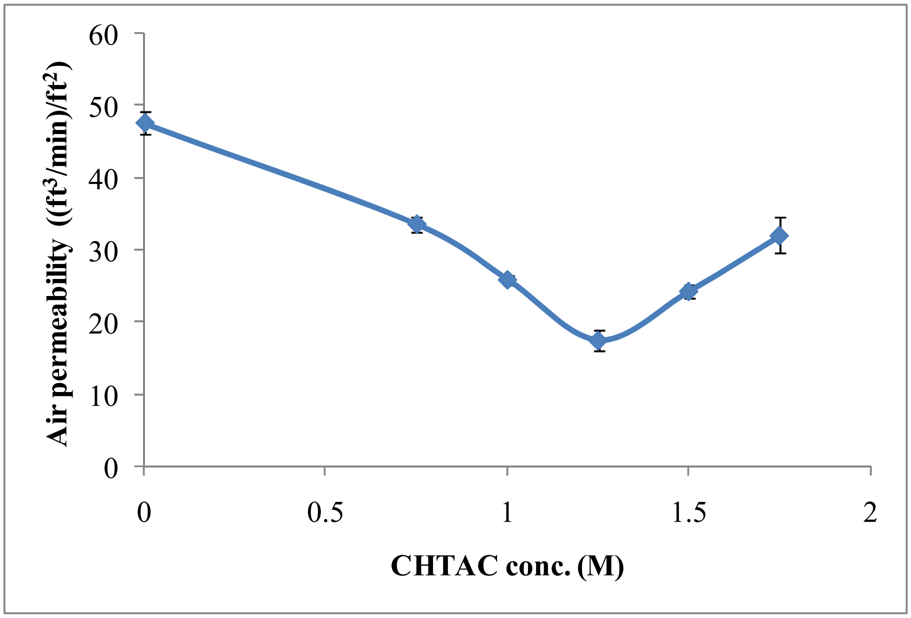


Figure 4.17. Air permeability of untreated cationized samples

Table 4.5. Reduction in air permeability of cationized fabrics in comparison with untreated cotton sample

CHTAC conc.	mmol N/100 g cotton	% Reduction in air permeability
0.75	38.4	29.4 %
1	52.1	45.5 %
1.25	**66.8**	**63.3 %**
1.5	53.4	48.9 %
1.75	43.4	32.8 %

causing more shrinkage. Above 1.25 M CHTAC concentration, the alkali was utilized considerably for the hydrolysis of EPTAC resulting in the presence of lower amounts of NaOH for 1.5 and 1.75 M CHTAC concentrations (as discussed in Section 4.1.1). Hence lower shrinkage was observed for 1.5 and 1.75 M CHTAC cationized samples as compared to 1.25 M CHTAC cationized sample. Similar reduction in air permeability was observed during esterification reaction of the cellulose fabric[4]. Cationization of the cotton fabric also flattened the fiber structure which is evidenced from the confocal image as shown in Figure 4.7. The flattening of the structure also reduces air permeability. Generally, this flattening of fabric substrate is observed during hot calendaring[48]. Table 4.5 shows the reduction of air permeability of cationized fabrics in comparison with untreated fabrics.

The addition of ammonium stearate to cationized samples further reduced the air permeability and the reduction in air permeability is greatest for 1.25 M CHTAC cationized fabric. The air permeability results for Series 5 to 10 are shown in Table 8.6 of the Appendix. Figure 4.18 shows that the curing temperatures 105^0C, 118^0C and 130^0C employed do not affect the air permeability of the resultant fabric, since the percent add-on doesn't vary with different curing temperatures at a given CHTAC and ammonium stearate concentration. The presence of higher amounts of % N or positively charged species in 1.25 M CHTAC facilitated the exhaustion of higher amounts of stearic acid resulting in the reduction of air permeability. The higher the solids add-on, the more interstices will be occupied by solids reducing air permeability.

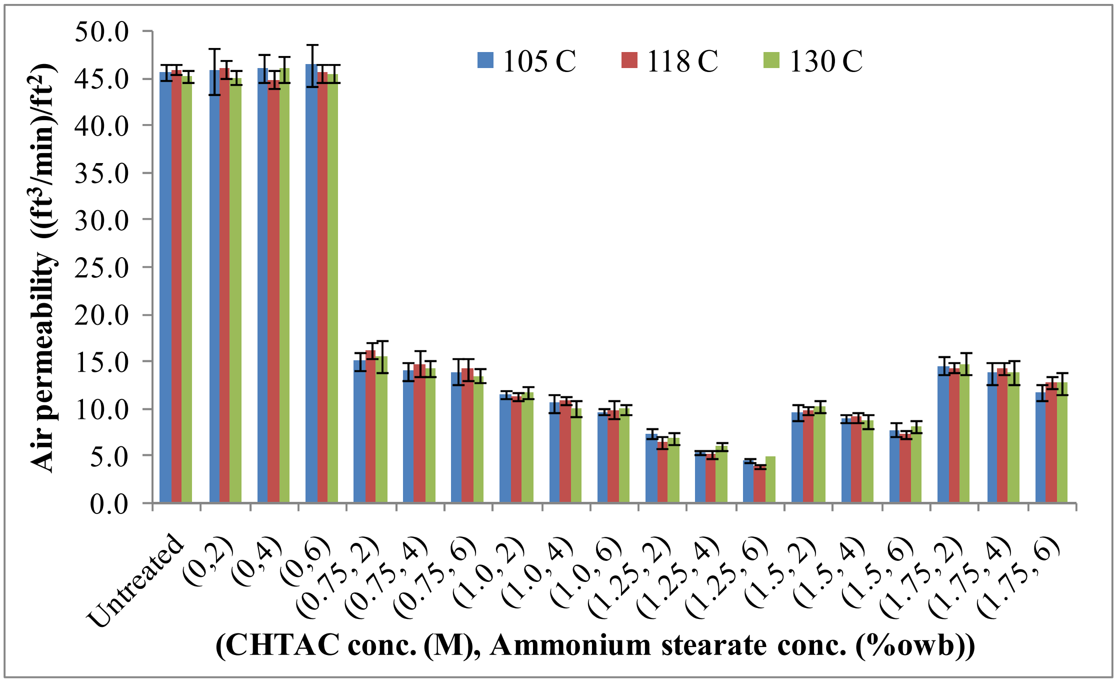


Figure 4.18. Effect of curing temperature on air permeability of cationized fabrics treated with ammonium stearate

Deanin[4] et al. observed the reduction in the air permeability during esterification of cotton with C_{14-18} aliphatic monobasic acid chlorides and the reduction was more significant at longer chain lengths. Air permeability also decreased with the increase in esterificaiton of the cotton with longer fatty chain lengths. In a similar way, the increase of positively charged species increased the amount of ammonium stearate adsorbed onto the fabric decreasing the air permeability. The data from Table 4.4 shows slight shrinkage of the fabric after exhaustion of the ammonium stearate on cationized fabric. Since the fabrics were exhausted with ammonium stearate without tension on the fabric, the fabric shrinkage occurred during the exhaustion process could also have contributed towards the decrease of air permeability.

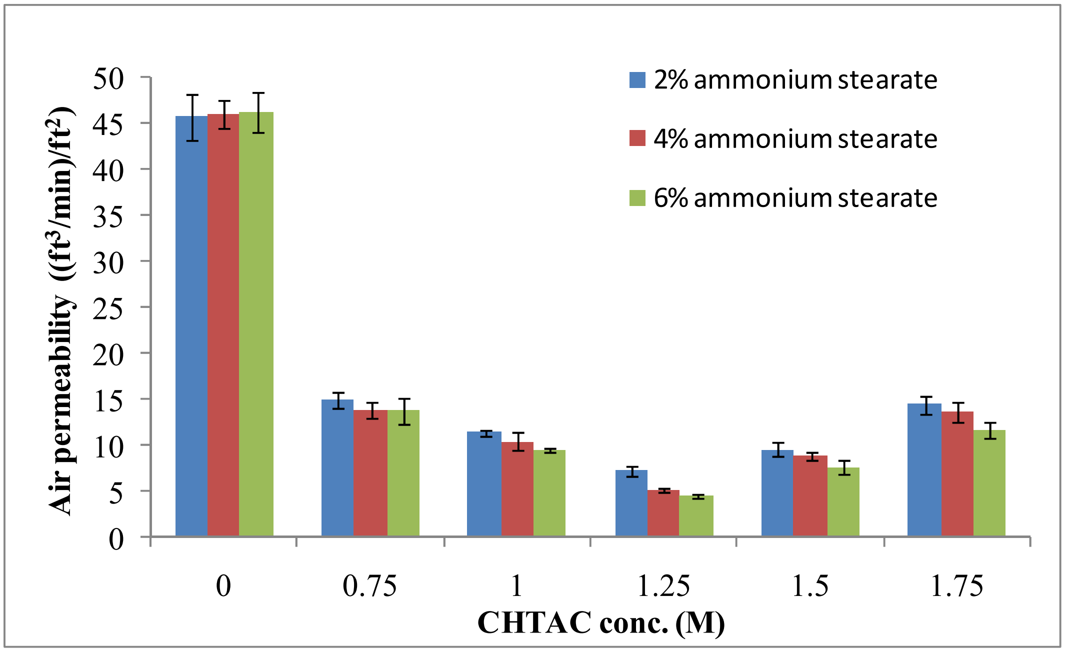


Figure 4.19. Effect of CHTAC and ammonium stearate concentrations on air permeability at 105^0C

Figure 4.19, shows that the air peremability is lower for the fabric with the higher % N content and air permeability is higher for the fabric with negiligible % N content on the fabric at the curing temperature of 105^0C. Increasing order of air permeability is in the order of 1.25 M, 1.5 M, 1.0 M, 1.75 M, 0.75 M, O M. The difference in air permeability values of 1.5 & 1.0 M and 1.75 & 0.75 M cationized fabrics is almost negligible due to the presence of similar % N contents. Fabrics with similar % N contents have almost exhausted the same amount of ammonium stearate. At all the CHTAC concentrations, the increase of ammonium stearate concentraions (% owb) from 2% to 6% showed an indication of the decrease of air permeability. Exhaustion of 2 % ammonium stearate (% owb) may have nearly saturated the fabric due to higher add-on values obtained and the further increase in the concentration had little effect on the increase of the air-permeability values. Since curing temperature has no effect on the air permeability values, similar trends was observed at curing temperature 118^0C and 130^0C and the data is shown in Table 8.6 of the Appendix. Thus, in summary, the 1.25 M CHTAC catioized sample treated with 6 % ammonium stearate (owb) has lower air permeability due to higher solids add–on.

4.6. Analysis of X-ray diffractograms of untreated and ammonium stearate exhausted cationized samples

Wide-angle X-ray diffraction measurements were carried out to observe if any structural changes occurring after the exhaustion of ammonium stearate onto the cationized samples in comparison with untreated control samples as described in Section *3.4.3.* X-ray diffraction was carried out for the cationized samples of 0.75M, 1.0M, 1.25M, 1.5M and 1.75M CHTAC concentrations exhausted with 4 % ammonium stearate and dried and cured at 105^0C.

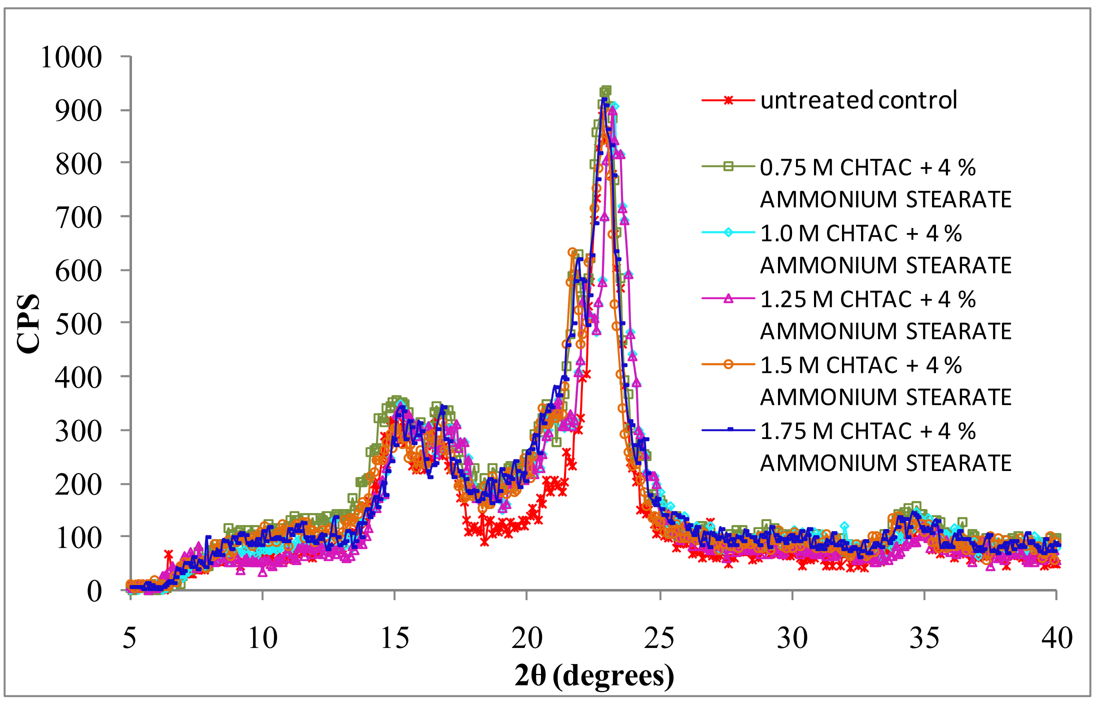


Figure 4.20. X-ray diffractogram of untreated control and cationized fabrics exhausted with ammonium stearate (pad-dry-cure)

X-ray diffractograms for untreated and cationized samples exhausted with ammonium stearate samples are shown in Figure 4.20. A new peak was observed at a diffractometer angle (2θ) of around 21.9 degree after the exhaustion of ammonium stearate onto the cationized samples. This peak was not observed in cationized and untreated control samples. Hence, exhaustion of ammonium stearate on to the cationized samples shows some morphological changes. From Figure 4.21, a similar peak at a diffractometer angle (2θ) of around 20 degree in cellulose – II can be observed. This peak was observed during the conversion of the cellulose-I to cellulose-II. Cellulose-II was produced by treating the native cellulose (cellulose-I) with strong alkali solutions such as NaOH, KOH, LiOH etc. Smaller Na^+ cations penetrate into smaller pores of the fiber to change the lattice distances and the morphology of cellulose to generate cellulose -II.[57]

The cationized samples were exhausted with ammonium stearate, a C_{18} alkyl chain at a temperature of 85^0C. Higher temperatures employed during the exhaustion method softens the polymer structure[60] allowing the movement of the long chain alkyl groups with anionic charges to adsorb on to the positive charges located on and in the interior of the fiber structure. This penetration of the long chain molecules might have disrupted the structure giving rise to a new peak in the X-ray diffractograms along with the shift of the already existing peaks towards right direction. The presence of two peaks around 14.8 and 16.3 degree and 22.6 degreee corresponding to $1\bar{1}0$ and 110 and 020 planes, a signature of cellulose-I polymorph and the peak at around 21 degree is similar to the peak that is observed for cellulose-II at 19.8 degree, a signature of cellulose-II polymorph suggests[55,59] that the ammonium stearate treated samples acquired an intermediate morphological structure of cellulose-I and cellulose-II.

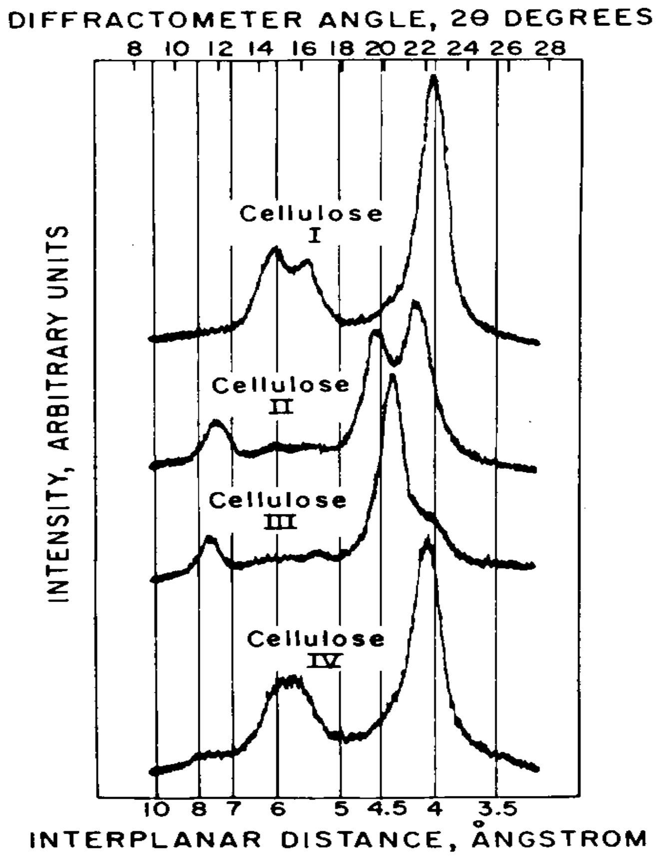


Figure 4.21. Diffractogram of cellulose polymorphs[59]

4.7. Analysis of water repellency ratings – Spray test

The water repellency of textile fabrics was evaluated using the AATCC spray test method as describe in Section *3.4.6.* Untreated control and cationized samples of Series 1 and cationized - ammonium stearate treated samples of Series 5 to 10 were evaluated before washing and after 5, 10 and 20 washings. Washing was carried out as described in Section *3.4.7.* Water repellency evaluation ratings results are shown in Table 8.7-8.11 of the Appendix. Untreated control and cationized samples did not show any water repellency. Figure 4.22 shows that the water repellency of the untreated or uncationized fabric treated with ammonium stearate before washing is zero. Results from Section *4.4* showed a negligible percent add-on of the ammonium stearate on the uncationized fabric. Due to the absence of the ammonium stearate no water repellency is observed. For the cationized fabrics at all the concentrations of CHTAC and ammonium stearate showed a water repellency rating of 100 before washing as shown in Figure 4.22. Since there was a significant percent add-on of the ammonium stearate by the cationized fabrics from 0.75-1.75 M CHTAC concentrations the presence of the stearyl groups imparts water repellency. The curing temperatures 105^0C, 118^0C and 130^0C did not affect the water repellency ratings. After five washings, all the cationized fabrics treated with ammonium stearate at all concentrations showed a water repellency rating of 100 as shown in Figure 4.23. This suggests that the ionic attractions existing between stearyl groups and the positive charges of the cationized fabrics as shown in Figure 2.34 are stable enough to overcome the five washing treatments. Figure 4.24 shows the zero water repellency

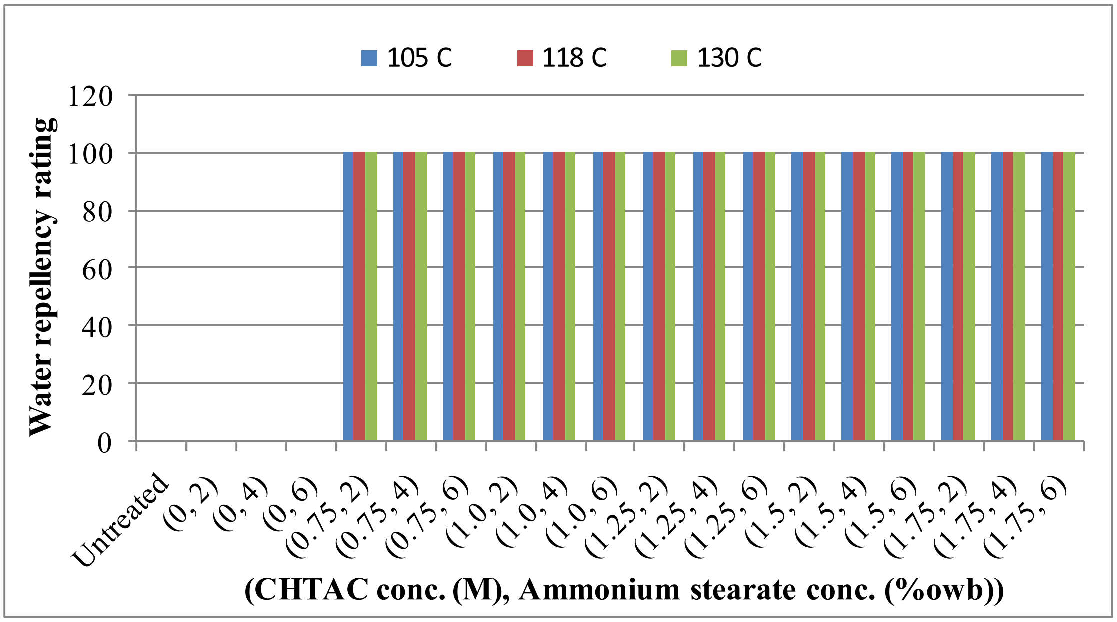


Figure 4.22. Effect of curing temperature on Water repellency rating of cationized fabrics treated with ammonium stearate before washing

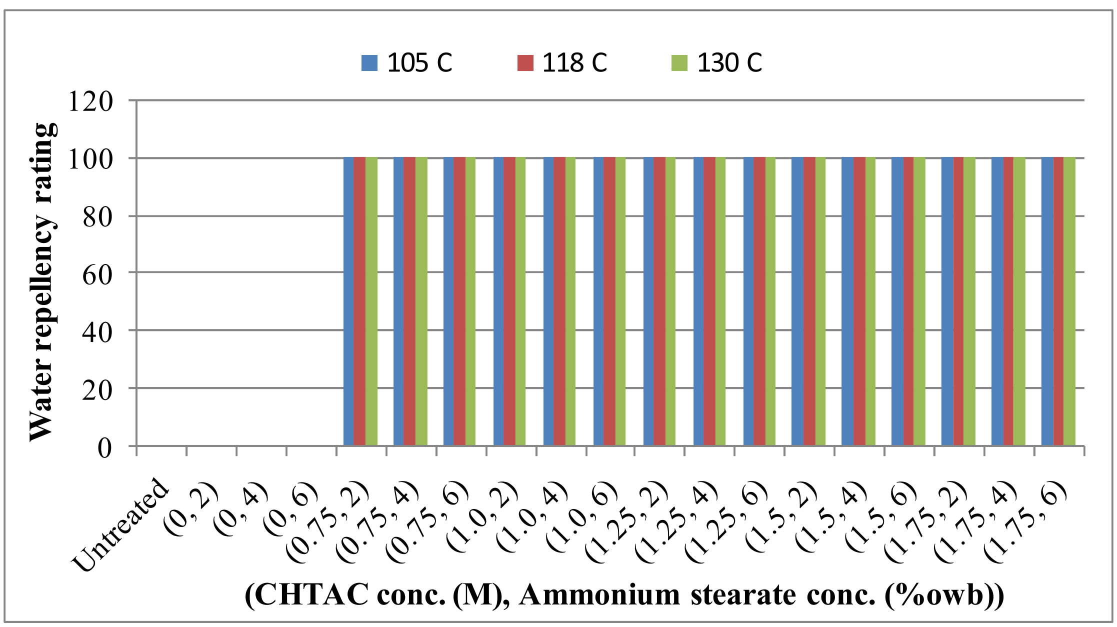


Figure 4.23. Effect of curing temperature on water repellency rating of cationized fabrics treated with ammonium sterate after 5 washing cycles

ratings after twenty laundry wash cycles for 0.75M CHTAC samples and some of the 1.75M CHTAC samples.

As discussed earlier the % N content on 0.75 M CHTAC and 1.75 M CHTAC samples are lower representing fewer positive charges on the cationized fabric, thus the we have fewer ionic interactions between stearyl anion and positive charge of 0.75 M CHTAC.

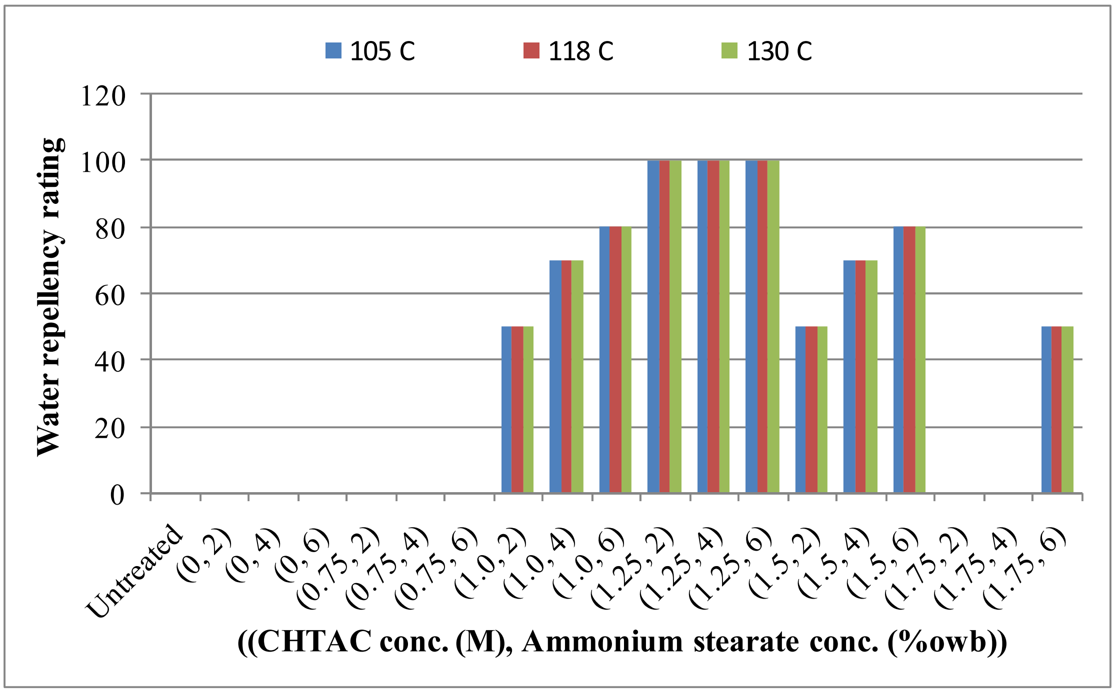


Figure 4.24. Effect of curing temperature on water repellency rating of cationized fabrics treated with ammonium stearate after 20 washing cycles

1.75M CHTAC cationized sample exhausted with 6 % ammonium stearate showed a repellency rating of 50, which suggests the presence of more interactions between stearyl groups and cationized cotton fabric. For 1.0 M and 1.5 M CHTAC samples, water repellency rating decreases with decreasing the ammonium stearate concentrations. With the increase of the ammonium stearate concentration, more than one stearyl group is attached to each positively charged cationized fabric and with increasing the number of washings, this stearyl group comes out of the fabric due to harsh conditions employed during washing. 1.25 M CHTAC cationized fabric gave a water repellency rating of 100 at all the ammonium stearate concentraitons up to twenty washes. 1.25 M CHTAC has the higher number of positive charges forming more ionic interactions with stearyl groups. It is also possbile that during washing, some of the stearyl groups lose ionic interactions with cations of the fabric, and if more cationic charges are present in the fabric, these stearyl groups can easily find other cationic groups and can reform ionic interactions[13]. This might be the reason for imparting a water repellency rating of 100 after 20 washings for highly cationized 1.25 M CHTAC fabrics. As observed in Figure 4.23 and 4.24, curing temperatures of 105^0C, 118^0C and 130^0C did not affect water repellency rating.

As discussed above water repellency ratings remained at 100 up to five washes and the water repellency ratings after ten washings were dependent on the concentration of CHTAC and ammonium stearate. Figure 4.25 shows the reduction in water repellency rating to 50 after ten washes for 0.75 M CHTAC fabric at all the ammonium stearate concnetraions. Due to a lower number of positive charges, the 0.75 M CHTAC cationized fabric gave lower numbers of ionic interactions which were able hold the stearyl groups till five washings and later on some of the stearyl groups are lost with every additional washing. The 1.75 M and 1.0 M CHTAC cationized fabrics exhausted with 2 % ammonium stearate only experience some decrease of water repellency rating while 4 % and 6 % ammonium stearate exhausted fabrics retained 100 % water repellency. 1.25 M CHTAC cationized fabric retained a water repellency rating of 100 at all CHTAC concentrations even after 10 washing cycles due to a greater number of ionic interactions resulting from more postive charges present on the fabric.

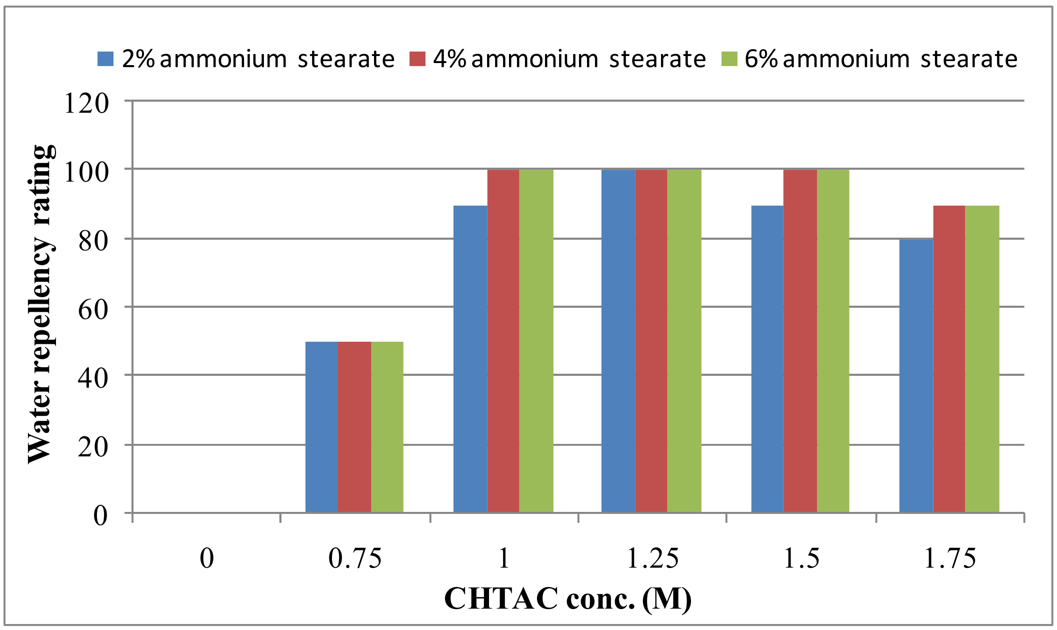


Figure 4.25. Effect of CHTAC and ammonium stearate concentrations on water repellency rating after 10 washing cycles at a curing temperature of 105^0C

As shown in Figure 4.26, after twenty washes the water repellency of 0.75M CHTAC cationized samples reduced to zero due to continuous loss of stearyl groups during washing. 1.0 M, 1.5 and 1.75 M CHTAC cationized fabrics showed a dependence of water repellent rating on ammonium stearate concentrations. As the concentration of ammonium stearate increased, water repellency rating improved, due to the interaction of more than one stearyl group with each positive charge available which results in more ionic interactions. For 1.25 M CHTAC fabrics the water repellency rating remained 100 at all concentrations of ammonium stearate due to the presence of more ionic interactions.

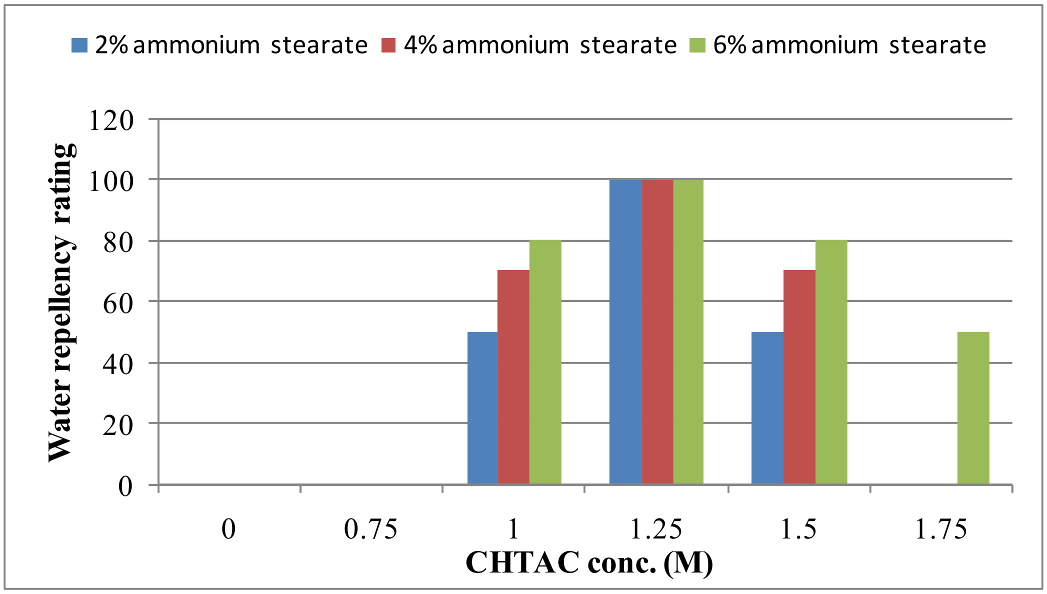


Figure 4.26. Effect of CHTAC and ammonium stearate concentrations on water repellency rating after 20 washing cycles at a curing temperature of 105^0C

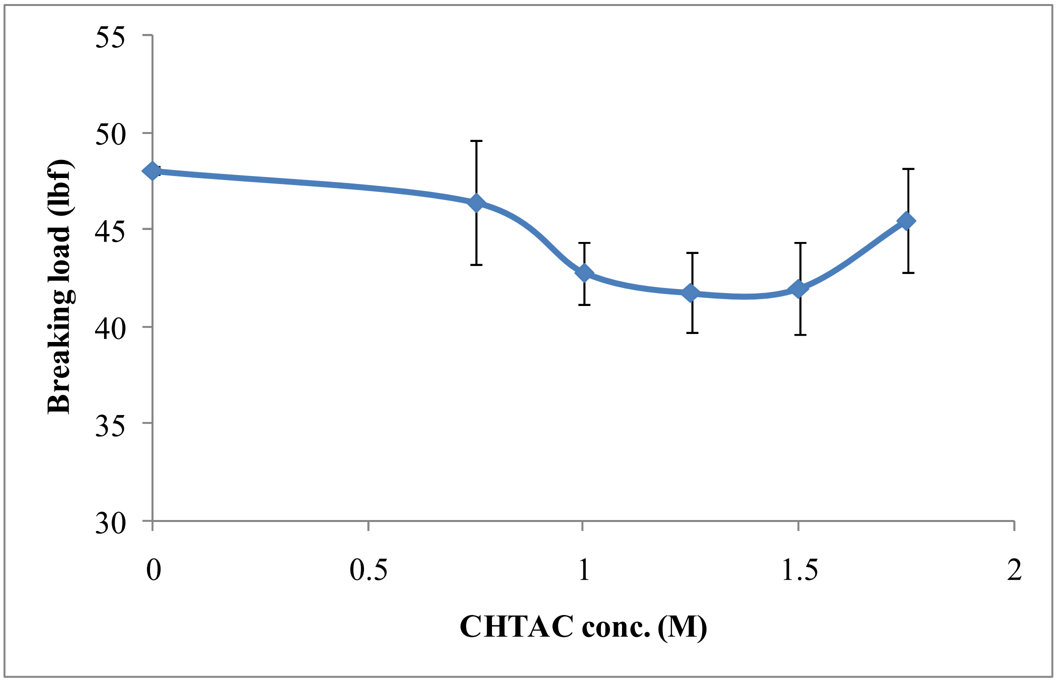
Thus, in summary 1.25 M CHTAC cationized samples exhibited a water repellency rating of 100 at all the ammonium stearate concentrations of 2 %, 4 % and 6 %.

4.8. Analysis of tensile strength and elongation at break values of untreated, cationized and ammonium stearate exhausted cationized samples

Tensile strength and elongation at break were tested for untreated samples, Series 1 and Series 5-10 respectively as described in Section *3.4.8.* The breaking load and elongation at break results are tabulated in Tables 8.12 and 8.13 respectively. Four specimens for each sample in the warp direction were used for the test.

4.8.1. Analysis of strength of fabrics

The cationized samples showed a decrease of strength with the increase of % N content present on the fabric. As discussed in Figure 4.1, Section *4.1.1*, 1.25 M CHTAC cationized fabric has the highest % N content and hence showed a lower tensile strength of about 41.8 lbf as compared to untreated sample tensile strength of about 48.1 lbf and other cationized samples of 0.75 M, 1.0 M, 1.5 M, 1.75 M CHTAC concentrations as shown in Figure 4.27. However, the strength values of 1.0 M, 1.25 M and 1.5 M CHTAC cationized fabrics lie within one standard deviation. The decrease in tensile strength may be due physical changes occurring in the cotton fabric due to sodium hydroxide or CHTAC reagent present in the cationization process[39]. The presence of sodium hydroxide might have introduced increased disorder in the cellulose structure thereby de-crystallizing the structure and decreasing the number of polymer chains parallel to the axis of the fabric to bear the load[12]. The presence of alkali at higher temperatures used for curing might have reduced the degree of polymerization by the scission of cellulosic chains due to the oxidation of hydroxyl groups to carbonyl groups followed by subsequent β-alkoxy elimination[62]. However, these values should not be considered as true strength values of the fabric since the samples were tested only in the warp direction.



4.27. Effect of CHTAC concentration on breaking load

The cationized fabrics further showed an indication of reduction in tensile strength values after the exhaustion of the ammonium stearate. From Figure 4.28, it is understood that curing temperatures of 105^{0}C and 118^{0}C and 130^{0}C have no significant effect on tensile strength of the fabric. The smaller change in the strength values of the fabrics at different curing temperatures lie within one standard deviation. Figure 4.29 shows the dependence of tensile strength on ammonium stearate concentration at different CHTAC concentrations of cationized fabrics cured at 105^{0}C. As can be observed there is no significant change in the tensile strength of the fabric with increase of ammonium stearate concentration for all cationized fabrics.

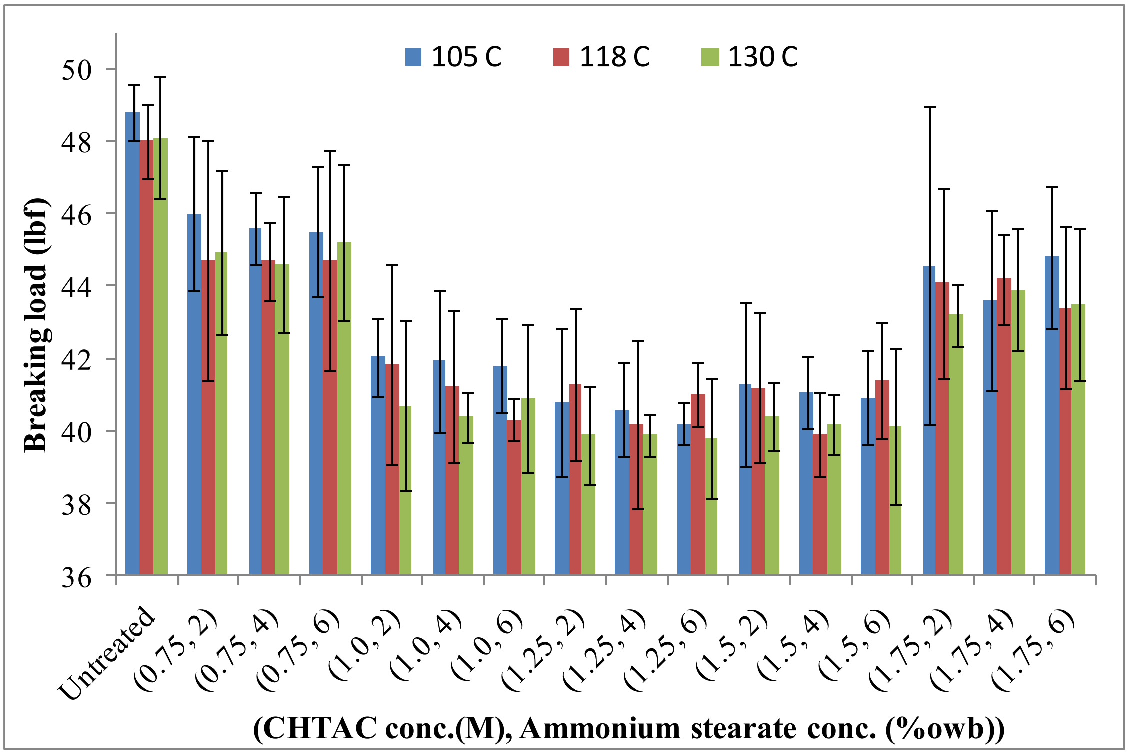


Figure 4.28. Effect of curing temperature on breaking load of untreated and cationized fabrics treated with ammonium stearate

Since all the ammonium stearate concentrations are on weight of the bath and higher % add-on are obtained, fabrics might have been saturated with stearyl groups even at 2 % ammonium stearate concentrations. Thus further increase in the concentration of the ammonium stearate does not show any affect on the tensile strength. Cationized samples at all CHTAC concentrations showed a slight indication of reduction in tensile strength values after treating with 2 % ammonium stearate chemical as compared to only cationized samples. The penetration of the long chain stearyl groups into the cotton fiber structure might have brought about a few changes in physical structure of cotton such as decrease in crystallinity and crystallite size[61]. Since curing temperature has no effect on the breaking load of the samples, the same trend was observed at 118^{0}C and 130^{0}C and the data is shown in Table 8.12 of the Appendix.

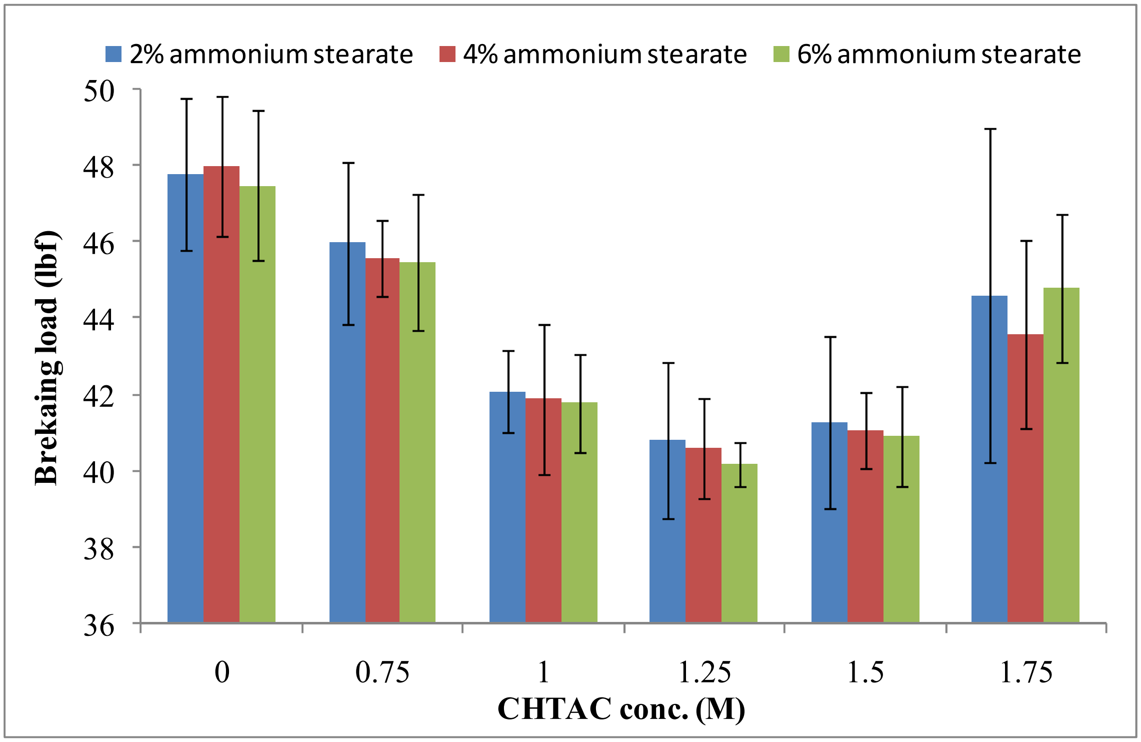


Figure 4.29. Effect of CHTAC and ammonium stearate concentrations on breaking load at a curing temperature of 105^{0}C

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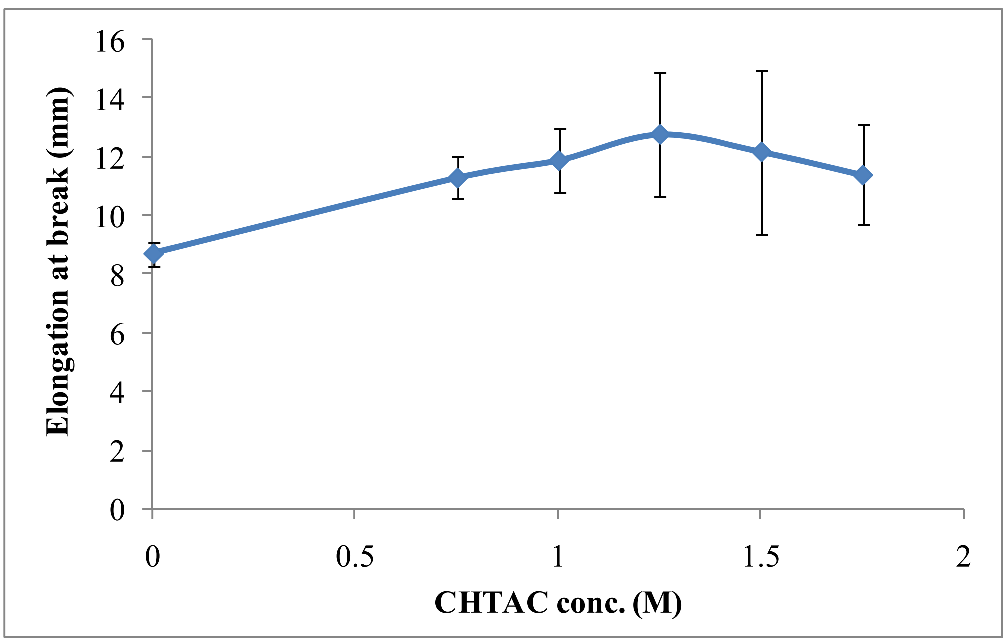
4.8.2. Analysis of elongation at break of fabrics

In contrast to tensile strength results, cationized samples showed an indication of increase in elongation at break with the increase of % N content present on the fabric. As discussed in Figure 4.1, Section *4.1.1*, 1.25 M CHTAC cationized fabric has the highest % N content and hence showed higher elongation at break of about 12.8 mm as compared to untreated sample elongation at break of about 8.7 mm and other cationized samples of 0.75 M, 1.0 M, 1.5 M, 1.75 M CHTAC concentrations as shown in Figure 4.30. El-Aref et al. explains that a decrease in crystallite size and crystallinity without any improvement in molecular orientation during mercerization can result in decrease of tensile strength and an improvement of elongation at break[61].



4.30. Effect of CHTAC concentration on elongation at break

During cationization there was some shrinkage of the fabric in the warp direction evidenced from Table 4.4. The presence of shrinkage may be responsible for the slight increase of elongation at break. However, from the scattering of data in Figure 4.30, there is not a significant difference in the elongation at break values at all the CHTAC concentrations. However, the elongation at break was improved as compared to untreated fabric. All the values lie within one standard deviation. The curing temperature has no effect on elongation at break values on the cationized fabrics treated with ammonium stearate.

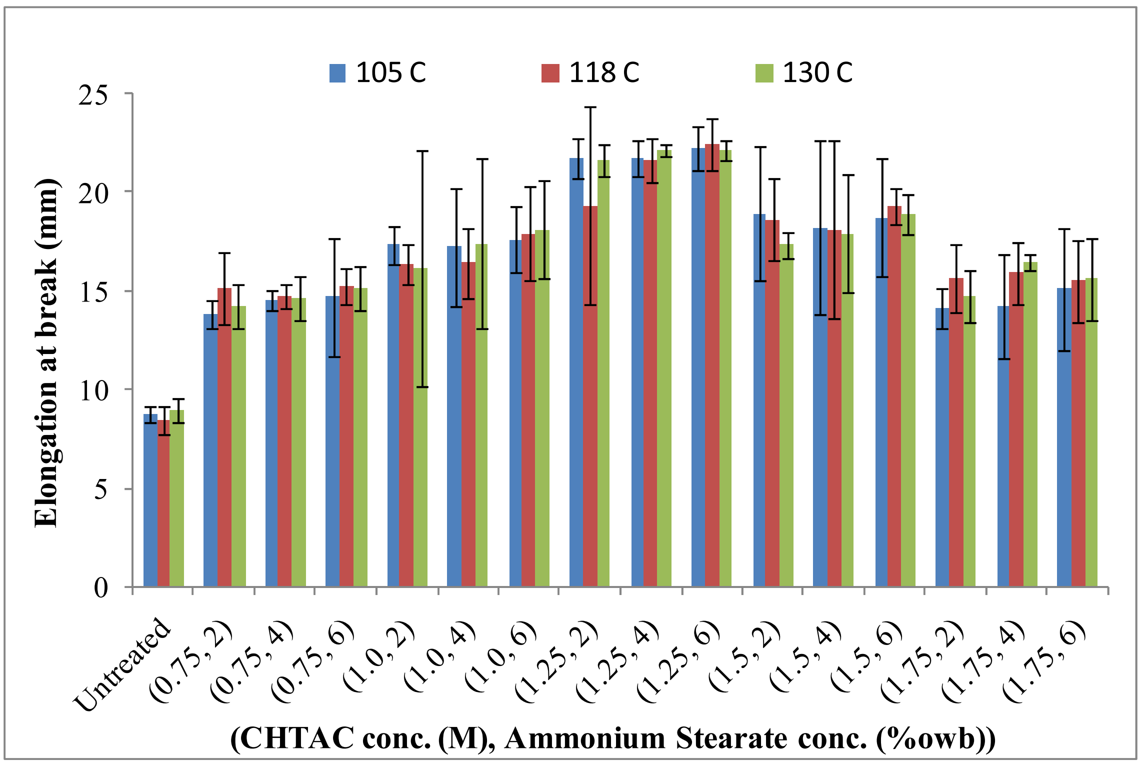


Figure 4.31. Effect of curing temperature on breaking load of untreated and cationized fabrics treated with ammonium stearate

From Figure 4.31 it can be observed that the cationized fabrics with ammonium stearate treated samples exhibited an improvement in elongation at break as compared to untreated fabrics. Some shrinkage in the fabric was observed during exhaustion of ammonium stearate onto the cationized fabrics. Increase in concentration of ammonium stearate does not show any profound effect at all the concentrations of CHTAC cationized fabrics.

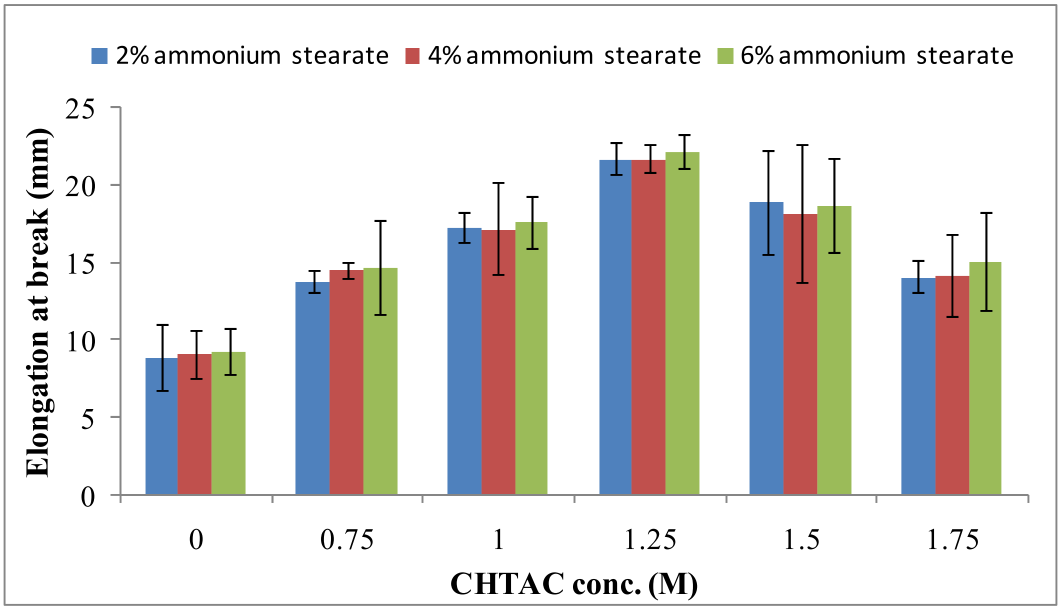


Figure 4.32. Effect of CHTAC and ammonium stearate concentrations on breaking load at a curing temperature of 105^0C

Figure 4.32 shows the effect of ammonium stearate concentration on elongation at break for fabrics cured at 105^0C. 1.25 M CHTAC treated fabric exhausted with 6 % ammonium stearate showed a higher elongation at break value. The elongation at break value may also have increased, due to the lubrication of cellulose polymer chains by stearyl groups or the penetration of the stearyl chains, which might have decreased the crystallinity by allowing the flexible movement of chains which can line up under the application of the tensile forces.[13] Since curing temperature has no effect on elongation at break values, similar behavior was observed for the samples cured at 118^0C and 130^0C and the data is shown in Table 8.13 of the Appendix.

4.9. Analysis of flexural rigidity values for untreated, cationized and ammonium stearate exhausted cationized samples

Flexural rigidity values are calculated for untreated, Series1 and Series 5-10 samples from measured bending length and basis weight values as described in Section *3.4.9.* Flexural rigidity is calculated as $G = W * C^3$, Where W = fabric mass per unit area (mg/cm^2) and C= bending length (cm). C is half of the length of overhang values measured. The basis weight, bending length and flexural rigidity values are summarized in Table 8.14, Table 8.15 and Table 8.16 of the Appendix. Briefly, the basis weight of the samples showed behavior in similar to the percent add-on values obtained, since percent add-on reflects the weight added to the fabric due to chemical pick-up. Bending length also showed a similar trend in similar to percent add-on, since with increase of the stearyl content on the fabric stiffness of the fabric increased, leading to increased bending length. 1.25 M CHTAC fabric exhausted with 6 % ammonium stearate has the highest basis weight and bending length.

The flexural rigidity value of untreated fabric is 111.4 mg.cm. These values vary for cationized fabrics in the range of 137.0 to 269.6 depending on the amount of the % N present on the fabric. Figure 4.33 shows the effect of CHTAC concentration on flexural rigidity values. 1.25 M CHTAC cationized fabric showed highest flexural rigidity as compared to other cationized values. Higher bending length and basis weight values obtained for 1.25 M CHTAC cationized fabric resulted in higher flexural rigidity as compared to other cationized fabrics. The basis weight and bending length of the fabric increased with the increased amount of % N content of the fabric. Hence, 1.25 M CHTAC cationized fabric has higher basis weight and bending length due to the addition of more CHTAC molecules as compared to other cationized fabrics. At lower concentrations of CHTAC, cellulose molecules are extended but with the increase of the ionic groups, the molecules tend to overlap and coil up forming entangled structures. This new configuration makes fabric stiffer[8].

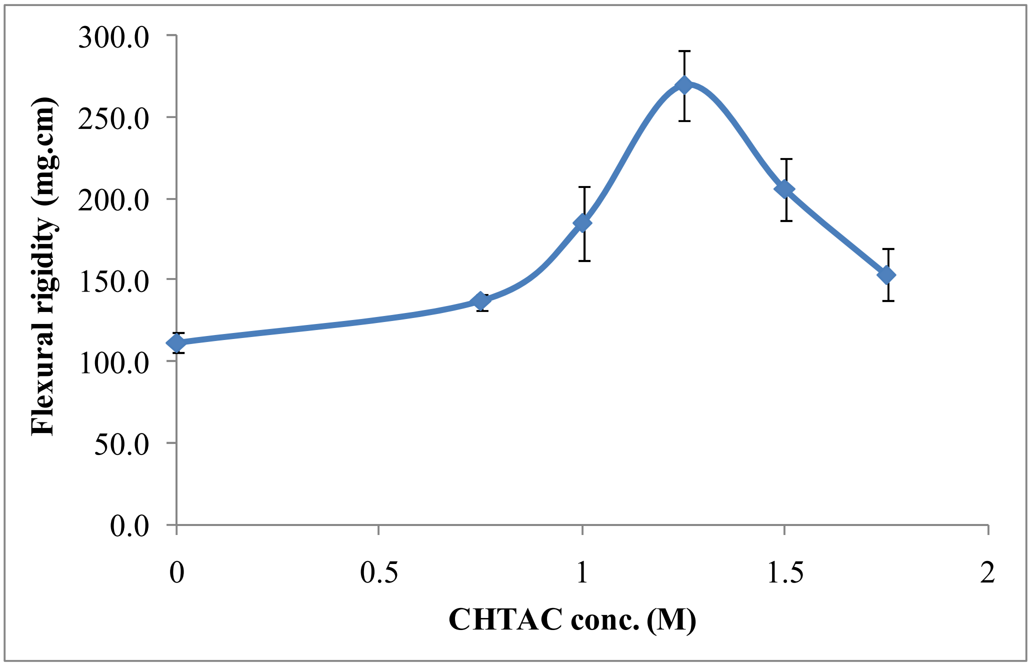


Figure 4.33. Effect of CHTAC concentration on flexural rigidity

An increase of flexural rigidity values was obtained after exhaustion of the ammonium stearate onto the cationized fabric as shown in Figure 4.34. The values varied in the range of 209.6 to 773.9 mg.cm. 0.75 M and 1.25 M CHTAC fabrics after exhaustion with 2 % ammonium stearate and cured at 105^{0}C showed an increase in flexural rigidity values of 57.9 % and 86.0 %. This increase in flexural rigidity values increased with increase in concentration of ammonium stearate. Higher flexural rigidity values are obtained for 1.25 M CHTAC cationized fabric exhausted with 6 % ammonium stearate. Higher percent add-ons obtained at these concentrations of CHTAC and ammonium stearate are responsible for higher flexural rigidity value. The bending length values also increased with % N content on the fabric and ammonium stearate. The increase of stearyl groups on the fabric resulted in a stiffer fabric resulting in higher bending lengths even though basis weight of the fabrics increased simultaneously.

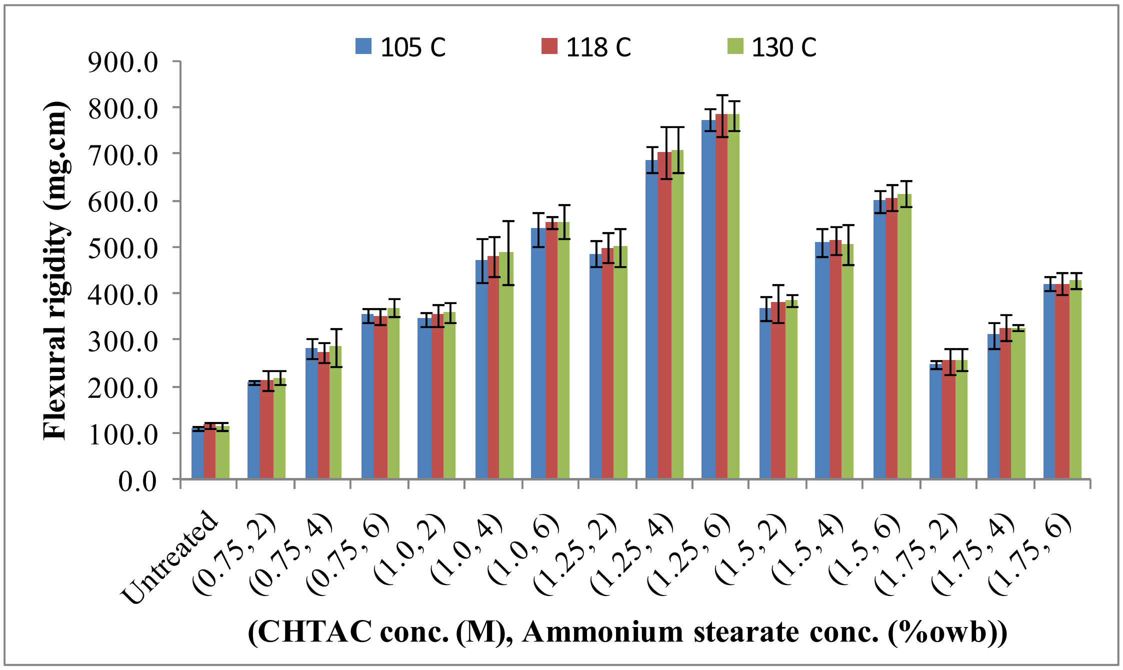


Figure 4.34. Effect of curing temperature on flexural rigidity of untreated and cationized fabrics treated with ammonium stearate

As can be observed from Figure 4.34, the curing temperature has no effect on the flexural rigidity. Since the curing temperature does not affect percent add-on of the fabric, basis weights of the fabric are within one standard deviation.

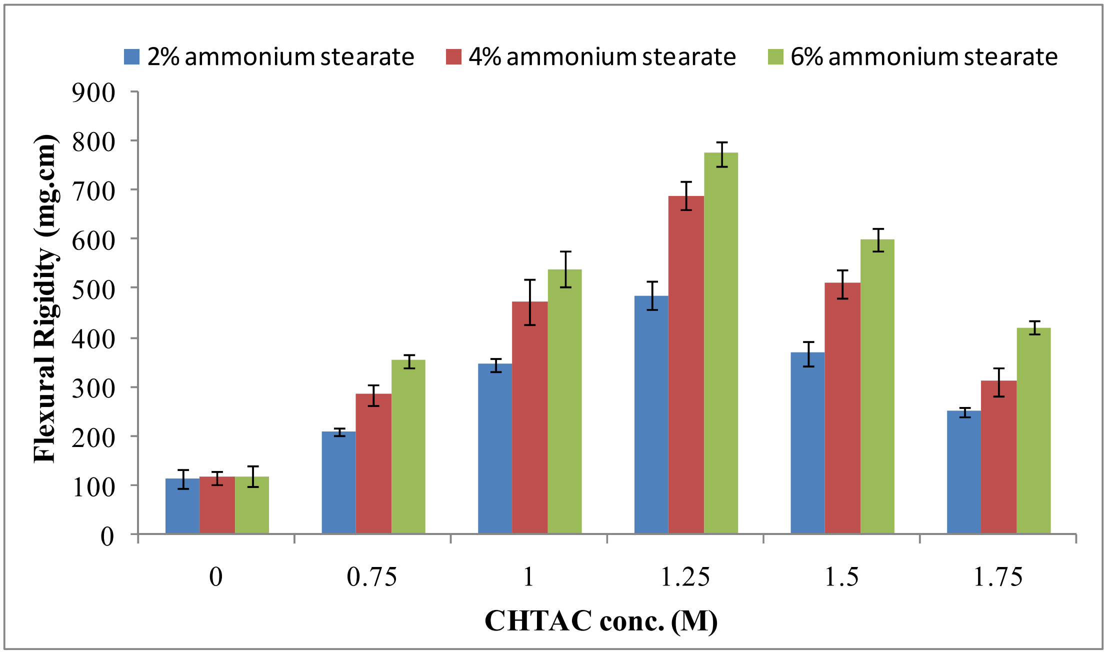


Figure 4.35. Effect of CHTAC and ammonium stearate concentrations on flexural rigidity at a curing temperature of 105^0C

Figure 4.35 shows the effect of ammonium stearate concentration on flexural rigidity for cationized fabrics cured at 105^0C. An increase of ammonium stearate concentration from 2 % to 4 % and 6 % increased the flexural rigidity at all CHTAC concentrations, which is due to the increased basis weight of the fabrics and bending length of the fabric. Since curing temperature has no effect on flexural rigidity, a similar trend in flexural rigidity values was obtained for samples cured at 118^0C and 130^0C and the data is shown in Table 8.16 of the Appendix.

5. CONCLUSIONS

A new process was developed to impart durable water repellency to cellulose fabric by ionic interactions. The process involves two steps. The optimal conditions are the cationization of cellulose fabric with 1.25 M CHTAC by pad-dry-cure method in the first step followed by the exhaustion of ammonium stearate (2% owb) onto the cationized fabric with subsequent drying at 105 ^{0}C for 10 min without curing. The process is economical and not environmentally harmful, since no fluorocarbon, formaldehyde or pyridinium based chemicals are present. The electrostatic bond formation existing between cationic quaternary ammonium groups covalently linked onto the cellulose fabric and the long chain stearyl anion groups are stable enough to overcome multiple laundering cycles and impart excellent water repellency – spray test ratings of 100 up to twenty washing cycles.

Cationization by the pad-dry-cure method gave higher nitrogen fixation values as compared to the pad-batch method. Cationization improved the exhaustion of ammonium stearate onto the fabric which was negligible with untreated cotton fabric. Confocal microscopy images confirmed the uniform distribution and occurrence of the cationization reaction in the interior of the fiber. Higher percent add-on of ammonium stearate onto the fabric resulted in reduced release of chemical waste. Maximum tensile strength loss of 17.2 % was experienced as compared to untreated sample, at higher % N contents (1.25 M CHTAC) and ammonium stearate (6 % owb) employed. Reduction in air permeability was also observed after the cationization process and exhaustion of ammonium stearate. A gain in elongation at break values of about 154 % for higher % N content and ammonium stearate concentrations as compared to untreated fabric was produced. Addition of stearyl groups to the cationized fabric contributed to a large extent to the improvement of elongation at break values. The flexural rigidity values were significantly higher than the untreated fabric.

In summary, this research resulted in optimal treatment conditions that gave durable water repellency – spray rating of 100 up to twenty laundry wash cycles, with some loss of tensile strength and air permeability and an increase of elongation at break and flexural rigidity values.

6. RECOMMENDATIONS FOR FUTURE WORK

This research focused on improving the existing finishing process using ionic interactions. As a part of it, the work resulted in the development of a durable water repellent finish based on electrostatic bond formation between the counter charges of the fabric and the finishing chemical. The ionic interactions do not decrease the tensile strength of the fabric to a significant extent. However, cationization decreased the tensile strength of the fabric to some extent. Future work should focus on developing a new cationic agent which can attach to the cellulose fabric as permanently as CHTAC, but should not decrease the strength and should not cause yellowing of the fabric. Some of the chemicals with cationic charge are Fixogene CXF (copolymer of dimethylamine and epichlorohydrin), epoxy derivatives of diallyl amine and 1,1-dimethyl-3-hydroxy azetidinium chloride[34]. Developing a cationizing agent with multiple cationic charges on a molecule can impart higher amount of cationic charges to the fabric at lower concentrations.

Studying optimum time period required for the complete exhaustion of ammonium stearate. This research investigation showed that curing temperature has no effect on final water repellency rating after the exhaustion of ammonium stearate. The research did not investigate the effect of drying at different temperatures. Such a study may further reduce the temperature conditions required for drying. Percent add-on was taken as a basis to calculate the amount of stearate present on the fabric. However, this process has several experimental errors. A process or analytical technique such as Near Infrared

Spectrometry should be used to evaluate the amount of stearic acid present on the fabric. Studying the minimum concentration of ammonium stearate required to impart durability of up to 20 washing cycles for 1.25 M CHTAC is also very important aspect.

This idea of ionic interaction can also be introduced to improve flame retardant finishing by introducing cationic or anionic groups onto the cellulose fabric followed by treating it with counter charged flame retardant compound.

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APPENDIX

8. APPENDIX

Table 8.1. Effect of CHTAC concentration on mmol N/100 g cotton using pad-dry-cure method

Pad-dry-cure method	**mmol N/100 g cotton**					
Conc. of CHTAC (M)	**Day 1**	**Day 2**	**Day 3**	**Day 4**	**Average**	**Standard deviation**
0.75	39.3 (1A)	37.9 (1F)	34.3 (1K)	42.1 (1P)	38.4	3.3
1	51.4 (1B)	50.7 (1G)	52.1 (1L)	54.3 (1Q)	52.1	1.5
1.25	68.6 (1C)	69.3 (1H)	65.0 (1M)	64.3 (1R)	66.8	2.5
1.5	56.4 (1D)	57.9 (1I)	49.3 (1N)	50.0 (1S)	53.4	4.4
1.75	47.9 (1E)	39.3 (1J)	40.7 (1O)	45.7 (1T)	43.4	4.1

Table 8.2. Effect of soaking time on mmol N/100 g cotton at 1.25 M CHTAC using pad-dry-cure method

Pad-dry-cure method	**mmol N/100 g cotton**					
Soaking time (min)	**Day 1**	**Day 2**	**Day 3**	**Day 4**	**Average**	**Standard Deviation**
0	66.4 (2A)	67.9 (2E)	64.3 (2I)	61.4 (2M)	65.0	2.8
2	65 (2B)	66.4 (2F)	65.7 (2J)	67.9 (2N)	66.2	1.2
4	64.3 (2C)	65.7 (2G)	66.4 (2K)	67.9 (2O)	66.1	1.5
6	65.7 (2D)	64.3 (2H)	61.4 (2L)	67.9 (2P)	64.8	2.7

Table 8.3. Effect of CHTAC concentration on mmol N/100 g cotton using pad-batch method

Pad-batch method	**mmol N/100 g cotton**					
Conc. of CHTAC (M)	**Day 1**	**Day 2**	**Day 3**	**Day 4**	**Average**	**Standard Deviation**
0.75	20 (3A)	20 (3F)	20 (3K)	19.3 (3P)	19.8	0.4
1	22.1 (3B)	22.1 (3G)	22.9 (3L)	22.1 (3Q)	22.3	0.4
1.25	25.7 (3C)	25.7 (3H)	25 (3M)	26.4 (3R)	25.7	0.6
1.5	28.6 (3D)	27.1 (3I)	27.1 (3N)	28.6 (3S)	27.9	0.8
1.75	30.7 (3E)	28.6 (3J)	31.4 (3O)	29.3 (3T)	30.0	1.3

Table 8.4. Effect of multiple cationization treatments on cotton fabric by pad-dry-cure method

Pad-Dry-cure method	**mmol N/100 g cotton**			
Conc. of CHTAC (A*1.25 M)	**Day 1**	**Day 2**	**Average**	**Standard deviation**
1	66.4 (4A)	68.6 (4H)	67.5	1.5
2	101.4 (4B)	121.4 (4I)	111.4	14.1
3	127.9 (4C)	141.4 (4J)	134.6	9.6
4	145.7 (4D)	160.7 (4K)	153.2	10.6
5	161.4 (4E)	172.1 (4L)	166.8	7.6
6	173.6 (4F)	180 (4M)	176.8	4.5
7	177.1 (4G)	185.7 (4N)	181.4	6.1

Table 8.5. Percent add-on values of series 1, 5, 6, 7, 8, 9 and 10

	Conc. of ammonium stearate (% owb)								
	2.0 %			4.0 %			6.0 %		
Curing temperature (^{0}C)	105	118	130	105	118	130	105	118	130
Conc. of CHTAC (M)	**% add-on**								
0 (Series 5)	1.0	1.2	0.9	1.2	1.0	1.1	1.0	1.2	1.1
0.75 (Series 6)	15.1	15.8	15.4	16.0	16.7	16.4	16.7	16.9	17.0
1.0 (Series 7)	17.2	17.8	18.0	18.7	18.2	18.9	19.1	18.9	19.7
1.25 (Series 8)	20.1	20.8	20.5	22.3	22.6	21.8	24.1	24.7	23.9
1.5 (Series 9)	17.9	17.4	18.2	18.8	18.4	18.3	19.8	19.1	19.7
1.75 (Series10)	15.8	15.4	16.1	16.7	16.9	16.2	17.8	17.3	17.9

Table 8.6. Air permeability values of series 1, 5, 6, 7, 8, 9 and 10

Untreated	**47.7**								
Conc. of ammonium stearate (% owb)	2.0			4.0			6.0		
Curing temperature (^{0}C)	105	118	130	105	118	130	105	118	130
Conc. of CHTAC (M)	**Air permeability ((ft^{3}/min)/square feet of fabric)**								
0 (Series 5)	45.7	45.9	45.0	46.0	44.8	45.9	46.3	45.5	45.4
0.75 (Series 6)	15.0	16.1	15.4	13.9	14.7	14.2	13.8	14.1	13.4
1.0 (Series 7)	11.4	11.3	11.7	10.5	10.8	10	9.6	9.8	9.9
1.25 (Series 8)	7.3	6.4	6.8	5.3	5.1	5.9	4.5	3.9	4.9
1.5 (Series 9)	9.6	9.8	10.2	8.9	9.1	8.6	7.7	7.2	8.1
1.75 (Series10)	14.5	14.3	14.7	13.7	14.2	13.8	11.7	12.8	12.6
Untreated (without ammonium stearate and CHTAC)									
Curing temperature (^{0}C)	105			118			130		
Untreated	45.5			45.8			45.1		
Cationized sample (without ammonium stearate)									
0.75 M CHTAC	1.0 M CHTAC	1.25 M CHTAC	1.5 M CHTAC	1.75 M CHTAC					
33.7	26.0	17.5	24.4	32.1					

Table 8.7. Water repellency ratings of series 1, 5, 6, 7, 8, 9 and 10 before wash

Untreated	**0**								
Conc. of ammonium stearate (% owb)	2.0 %			4.0 %			6.0 %		
Curing temperature (^{0}C)	105	118	130	105	118	130	105	118	130
Conc. of CHTAC (M)	**Before wash (Spray test rating)**								
0 (Series 5)	0	0	0	0	0	0	0	0	0
0.75 (Series 6)	100	100	100	100	100	100	100	100	100
1.0 (Series 7)	100	100	100	100	100	100	100	100	100
1.25 (Series 8)	100	100	100	100	100	100	100	100	100
1.5 (Series 9)	100	100	100	100	100	100	100	100	100
1.75 (Series10)	100	100	100	100	100	100	100	100	100
Untreated (without ammonium stearate and CHTAC)									
Curing temperature (^{0}C)	105			118			130		
Untreated	0			0			0		
Cationized sample (without ammonium stearate)									

0.75 M CHTAC	1.0 M CHTAC	1.25 M CHTAC	1.5 M CHTAC	1.75 M CHTAC
0	0	0	0	0

Table 8.8. Water repellency ratings of series 1, 5, 6, 7, 8, 9 and 10 after 5 washes

Untreated	**0**								
Conc. of ammonium stearate (% owb)	2.0 %			4.0 %			6.0 %		
Curing temperature (^{0}C)	105	118	130	105	118	130	105	118	130
Conc. of CHTAC (M)	**After 5 washes (Spray test rating)**								
0 (Series 5)	0	0	0	0	0	0	0	0	0
0.75 (Series 6)	100	100	100	100	100	100	100	100	100
1.0 (Series 7)	100	100	100	100	100	100	100	100	100
1.25 (Series 8)	100	100	100	100	100	100	100	100	100
1.5 (Series 9)	100	100	100	100	100	100	100	100	100
1.75 (Series10)	100	100	100	100	100	100	100	100	100
Untreated (without ammonium stearate and CHTAC)									
Curing temperature (^{0}C)	105			118			130		
Untreated	0			0			0		
Cationized sample (without ammonium stearate)									
0.75 M CHTAC	1.0 M CHTAC	1.25 M CHTAC	1.5 M CHTAC	1.75 M CHTAC					
0	0	0	0	0					

Table 8.9. Water repellency ratings of series 1, 5, 6, 7, 8, 9 and 10 after 10 washes

Untreated	**0**								
Conc. of ammonium stearate (% owb)	2.0 %			4.0 %			6.0 %		
Curing temperature (^{0}C)	105	118	130	105	118	130	105	118	130
Conc. of CHTAC (M)	**After 10 washes (Spray test rating)**								
0 (Series 5)	0	0	0	0	0	0	0	0	0
0.75 (Series 6)	50	50	50	50	50	50	50	50	50
1.0 (Series 7)	90	90	90	100	100	100	100	100	100
1.25 (Series 8)	100	100	100	100	100	100	100	100	100
1.5 (Series 9)	90	90	90	100	100	100	100	100	100
1.75 (Series10)	80	80	80	90	90	90	90	90	90

Untreated (without ammonium stearate and CHTAC)			
Curing temperature (^{0}C)	105	118	130
Untreated	0	0	0

Cationized sample (without ammonium stearate)				
0.75 M CHTAC	1.0 M CHTAC	1.25 M CHTAC	1.5 M CHTAC	1.75 M CHTAC
0	0	0	0	0

Table 8.10. Water repellency ratings of series 1, 5, 6, 7, 8, 9 and 10 after 15 washes

<table>
<tr><td>Untreated</td><td colspan="9">0</td></tr>
<tr><td>Conc. of ammonium stearate (% owb)</td><td colspan="3">2.0 %</td><td colspan="3">4.0 %</td><td colspan="3">6.0 %</td></tr>
<tr><td>Curing temperature (^{0}C)</td><td>105</td><td>118</td><td>130</td><td>105</td><td>118</td><td>130</td><td>105</td><td>118</td><td>130</td></tr>
<tr><td>Conc. of CHTAC (M)</td><td colspan="9">After 15 washes (Spray test rating)</td></tr>
<tr><td>0 (Series 5)</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td></tr>
<tr><td>0.75 (Series 6)</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td></tr>
<tr><td>1.0 (Series 7)</td><td>70</td><td>70</td><td>70</td><td>80</td><td>80</td><td>80</td><td>90</td><td>90</td><td>90</td></tr>
<tr><td>1.25 (Series 8)</td><td>100</td><td>100</td><td>100</td><td>100</td><td>100</td><td>100</td><td>100</td><td>100</td><td>100</td></tr>
<tr><td>1.5 (Series 9)</td><td>70</td><td>70</td><td>70</td><td>80</td><td>80</td><td>80</td><td>90</td><td>90</td><td>90</td></tr>
<tr><td>1.75 (Series10)</td><td>50</td><td>50</td><td>50</td><td>70</td><td>70</td><td>70</td><td>80</td><td>80</td><td>80</td></tr>
<tr><td colspan="10">Untreated (without ammonium stearate and CHTAC)</td></tr>
<tr><td>Curing temperature (^{0}C)</td><td colspan="3">105</td><td colspan="3">118</td><td colspan="3">130</td></tr>
<tr><td>Untreated</td><td colspan="3">0</td><td colspan="3">0</td><td colspan="3">0</td></tr>
<tr><td colspan="10">Cationized sample (without ammonium stearate)</td></tr>
</table>

0.75 M CHTAC	1.0 M CHTAC	1.25 M CHTAC	1.5 M CHTAC	1.75 M CHTAC
0	0	0	0	0

Table 8.11. Water repellency ratings of series 1, 5, 6, 7, 8, 9 and 10 after 20 washes

Untreated	**0**								
Conc. of ammonium stearate (% owb)	2.0 %			4.0 %			6.0 %		
Curing temperature (^{0}C)	105	118	130	105	118	130	105	118	130
Conc. of CHTAC (M)	**After 20 washes (Spray test rating)**								
0 (Series 5)	0	0	0	0	0	0	0	0	0
0.75 (Series 6)	0	0	0	0	0	0	0	0	0
1.0 (Series 7)	50	50	50	70	70	70	80	80	80
1.25 (Series 8)	100	100	100	100	100	100	100	100	100
1.5 (Series 9)	50	50	50	70	70	70	80	80	80
1.75 (Series10)	0	0	0	0	0	0	50	50	50
Untreated (without ammonium stearate and CHTAC)									
Curing temperature (^{0}C)	105			118			130		
Untreated	0			0			0		
Cationized sample (without ammonium stearate)									
0.75 M CHTAC	1.0 M CHTAC			1.25 M CHTAC		1.5 M CHTAC		1.75 M CHTAC	
0	0			0		0		0	

Table 8.12. Breaking load values of series 1, 5, 6, 7, 8, 9 and 10

<table>
<tr><th>Untreated</th><th colspan="9">48.1</th></tr>
<tr><th>Conc. of ammonium stearate (% owb)</th><td colspan="3">2.0</td><td colspan="3">4.0</td><td colspan="3">6.0</td></tr>
<tr><th>Curing temperature (^{0}C)</th><td>105</td><td>118</td><td>130</td><td>105</td><td>118</td><td>130</td><td>105</td><td>118</td><td>130</td></tr>
<tr><th>Conc. of CHTAC (M)</th><th colspan="9">Breaking load (lbf)</th></tr>
<tr><th>0 (Series 5)</th><td>47.8</td><td>47.3</td><td>47.2</td><td>48</td><td>46.8</td><td>46.3</td><td>47.5</td><td>46.1</td><td>45.9</td></tr>
<tr><th>0.75 (Series 6)</th><td>46.0</td><td>44.7</td><td>44.9</td><td>45.6</td><td>44.7</td><td>44.6</td><td>45.5</td><td>44.7</td><td>45.2</td></tr>
<tr><th>1.0 (Series 7)</th><td>42.1</td><td>41.8</td><td>40.7</td><td>41.9</td><td>41.2</td><td>40.4</td><td>41.8</td><td>40.3</td><td>40.9</td></tr>
<tr><th>1.25 (Series 8)</th><td>40.8</td><td>41.3</td><td>39.9</td><td>40.6</td><td>40.2</td><td>39.9</td><td>40.2</td><td>41.0</td><td>39.8</td></tr>
<tr><th>1.5 (Series 9)</th><td>41.3</td><td>41.2</td><td>40.4</td><td>41.1</td><td>39.9</td><td>40.2</td><td>40.9</td><td>41.4</td><td>40.1</td></tr>
<tr><th>1.75 (Series10)</th><td>44.6</td><td>44.1</td><td>43.2</td><td>43.6</td><td>44.2</td><td>43.9</td><td>44.8</td><td>43.4</td><td>43.5</td></tr>
<tr><th colspan="10">Untreated (without ammonium stearate and CHTAC)</th></tr>
<tr><th>Curing temperature (^{0}C)</th><td colspan="3">105</td><td colspan="3">118</td><td colspan="3">130</td></tr>
<tr><th>Untreated</th><td colspan="3">48.8</td><td colspan="3">48.0</td><td colspan="3">47.3</td></tr>
<tr><th colspan="10">Cationized sample (without ammonium stearate)</th></tr>
<tr><td colspan="2">0.75 M CHTAC</td><td colspan="2">1.0 M CHTAC</td><td colspan="2">1.25 M CHTAC</td><td colspan="2">1.5 M CHTAC</td><td colspan="2">1.75 M CHTAC</td></tr>
<tr><td colspan="2">46.4</td><td colspan="2">42.8</td><td colspan="2">41.8</td><td colspan="2">42.0</td><td colspan="2">45.5</td></tr>
</table>

Table 8.13. Elongation at break values of series 1, 5, 6, 7, 8, 9 and 10

Untreated	**8.7**								
Conc. of ammonium stearate (% owb)	2.0			4.0			6.0		
Curing temperature (^{0}C)	105	118	130	105	118	130	105	118	130
Conc. of CHTAC (M)	**Elongation at break (mm)**								
0 (Series 5)	8.9	9.1	8.9	9.1	8.7	8.8	9.3	8.9	9.5
0.75 (Series 6)	13.8	15.1	14.2	14.5	14.7	14.6	14.7	15.2	15.1
1.0 (Series 7)	17.3	16.3	16.1	17.2	16.4	17.4	17.6	17.9	18.1
1.25 (Series 8)	21.7	19.3	21.6	21.7	21.6	22.1	22.2	22.4	22.1
1.5 (Series 9)	18.9	18.6	17.3	18.2	18.1	17.9	18.7	19.3	18.9
1.75 (Series10)	14.1	15.6	14.7	14.2	15.9	16.4	15.1	15.5	15.6
Untreated (without ammonium stearate and CHTAC)									
Curing temperature (^{0}C)	105			118			130		
Untreated	8.7			8.4			8.9		
Cationized sample (without ammonium stearate)									

0.75 M CHTAC	1.0 M CHTAC	1.25 M CHTAC	1.5 M CHTAC	1.75 M CHTAC
11.3	11.9	12.8	12.2	11.6

Table 8.14. Basis weight value of series 1, 5, 6, 7, 8, 9 and 10

Untreated	12.5								
Conc. of ammonium stearate (% owb)	2.0			4.0			6.0		
Curing temperature (^{0}C)	105	118	130	105	118	130	105	118	130
Conc. of CHTAC (M)	**Basis weight (mg/cm^2)**								
0 (Series 5)	12.5	12.3	12.6	12.7	12.8	12.1	13.0	12.1	12.4
0.75 (Series 6)	16.8	16.8	16.9	17.1	17.0	17.0	17.2	17.4	17.5
1.0 (Series 7)	17.6	17.6	17.7	18.0	18.2	18.3	18.6	18.6	18.5
1.25 (Series 8)	19.5	19.5	19.5	19.8	19.8	19.8	20.3	20.6	20.3
1.5 (Series 9)	17.8	18.0	17.9	18.4	18.5	18.5	18.8	18.9	18.9
1.75 (Series10)	17.0	17.0	17.0	17.3	17.2	17.2	17.5	17.6	17.5
Untreated (without ammonium stearate and CHTAC)									
Curing temperature (^{0}C)	105			118			130		
Untreated	12.5			12.5			12.4		

Cationized sample (without ammonium stearate)				
0.75 M CHTAC	1.0 M CHTAC	1.25 M CHTAC	1.5 M CHTAC	1.75 M CHTAC
14.3	14.9	16.1	15.1	14.5

Table 8.15. Bending length values of series 1, 5, 6, 7, 8, 9 and 10

Untreated	**2.1**								
Conc. of ammonium stearate (% owb)	2.0			4.0			6.0		
Curing temperature (^{0}C)	105	118	130	105	118	130	105	118	130
Conc. of CHTAC (M)	**Bending length (cm)**								
0 (Series 5)	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
0.75 (Series 6)	2.3	2.3	2.4	2.6	2.5	2.6	2.7	2.7	2.8
1.0 (Series 7)	2.7	2.7	2.7	3.0	3.0	3.0	3.1	3.1	3.1
1.25 (Series 8)	2.9	2.9	3.0	3.3	3.3	3.3	3.4	3.4	3.4
1.5 (Series 9)	2.7	2.8	2.8	3.0	3.0	3.0	3.2	3.2	3.2
1.75 (Series10)	2.4	2.5	2.5	2.6	2.7	2.7	2.9	2.9	2.9
Untreated (without ammonium stearate and CHTAC)									
Curing temperature (^{0}C)	105			118			130		
Untreated	2.1			2.1			2.1		
Cationized sample (without ammonium stearate)									

0.75 M CHTAC	1.0 M CHTAC	1.25 M CHTAC	1.5 M CHTAC	1.75 M CHTAC
2.1	2.3	2.6	2.4	2.2

Table 8.16. Flexural rigidity values of series 1, 5, 6, 7, 8, 9 and 10

Untreated	**111.4**								
Conc. of ammonium stearate (% owb)	2.0			4.0			6.0		
Curing temperature (^{0}C)	105	118	130	105	118	130	105	118	130
Conc. of CHTAC (M)	**Flexural rigidity (mg.cm)**								
0 (Series 5)	114.5	113.3	112.0	116.2	116.6	115.6	119.6	118.8	117.8
0.75 (Series 6)	209.6	215.6	219.6	284.4	272.5	285.4	353.4	352.4	369.5
1.0 (Series 7)	345.4	353.7	360.8	472.6	481.2	487.8	539.1	552.4	554.3
1.25 (Series 8)	485.5	498.8	500.6	688.0	702.2	709.5	773.9	783.9	784.5
1.5 (Series 9)	368.2	379.8	385.5	510.6	513.0	506.4	599.1	606.1	615.2
1.75 (Series10)	249.8	255.0	257.9	311.2	326.0	326.7	421.1	421.7	428.0
Untreated (without ammonium stearate and CHTAC)									
Curing temperature (^{0}C)	105			118			130		
Untreated	112.0			119.0			115.8		
Cationized sample (without ammonium stearate)									
0.75 M CHTAC	1.0 M CHTAC			1.25 M CHTAC			1.5 M CHTAC		1.75 M CHTAC
137.0	185.1			269.6			205.9		153.6