

# Finishing of Cotton Fabrics using Monochlorotriazine Reactive Dyes and Citric Acid with Pad-Dry-Cure Methods

Eshetu Solomon

*Department of textile technology federal tvet institute addis ababa, ethiopia*

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**ABSTRACT:** Cotton is one of the most commonly used fibers for textiles, as most apparels are made of cotton. However, cotton fabric normally has shrinkage and wrinkling problems, degrading its aesthetic value. Resin finish is applied to improve the wrinkle problem of cotton fabric. Conventionally, cotton is dyed first, then finished with a cross linking agent (or finished after bleaching to be sold in white) to obtain the desired color and crease recovery properties. If the two steps could be merged, significant savings in energy, water, labor, and machine occupation time would be achieved. Since the 1950s, many researchers have attempted to combine dyeing and resin finishing processes into one step. However, a commercially viable combined dyeing and resin finishing process has not been reported. The main challenge has been producing treated fabrics that have deep shades, good fastness properties, and excellent crease recovery performance simultaneously. In the present research, combined dyeing and resin finishing of cotton fabric was conducted using monochlorotriazine reactive dyes and citric acid as cross-linking agent by pad-dry-cure method. To investigate the dye concentration, citric acid, alkali, catalyst concentration and curing temperature were varied. The method afforded medium shades ( $K/S \approx 6$ ). The strength retention and pilling resistance of the combined treated fabric compared to only dyed fabric does not show significant difference. Fastness to washing and crocking was as good as that from a conventional reactive dyeing method and fabric crease recovery properties show better improvement compared to only dye and bleached (untreated) fabrics.

**KEY WORDS:** Resin finishing, Citric acid, Pad dry cure Methods and Reactive dyes

## I. INTRODUCTION:

Cotton is nearly pure cellulose, which is the most abundant organic polymer with the formula  $(C_6H_{10}O_5)_n$  on earth and it is a polysaccharide consisting of a linear chain of several hundred to

over ten thousand  $\beta(1 \rightarrow 4)$  linked D-glucose units. In textile industry, cotton is still one of the most preferred fibers because of its own natural and distinctive properties while rising sale of synthetic fibers, but have serious disadvantages such as tendency to crease formation and poor crease recovery. Crease resistance is imparted to cellulosic fibers by restricting the slippage of molecular chains through cross linking. Crease resistant finishing resins include: synthetic resins, melamine, epoxy, urea, formaldehyde, vinyl, oxidized starches, thermoplastic resins, linear reactants, and chloral-alkyl compound [6]. The cotton fibers each one of the commercially important species contains many different varieties developed through breeding programs to produce cottons with continually improving properties (e.g., faster maturing, increased yields, and improved insect and disease resistance) and fibers with greater length, strength, and uniformity [13]. Cotton fiber is hydrophilic that easily absorb water, resulting hydrogen bonds breakages and shrinkage. That's why 100% cotton tends to have more wrinkle and shrinkage, especially after laundering [6]. Cotton is a cellulosic fiber which is the most important textile fiber because it has fairly good strength, softness, moisture absorbency, and pliability [1]. The relative amounts of crystalline and amorphous cellulose influence the properties of cellulosic fiber. The crystalline of cotton fiber is between 60 and 70 percent, giving the cotton fiber moderate strength and good abrasion resistance [1]. Fiber strength depends on structural organization of the cellulose chains while fiber's physical properties depend on molecular weight of the polymer. Moreover, molecular weight distribution predicts the polymer performance. The higher the molecular weight and the narrowness of molecular weight distribution, higher is the strength of the polymer [1, 13, and 14].

### 1.1. Chemical Reaction of Cotton Fiber:

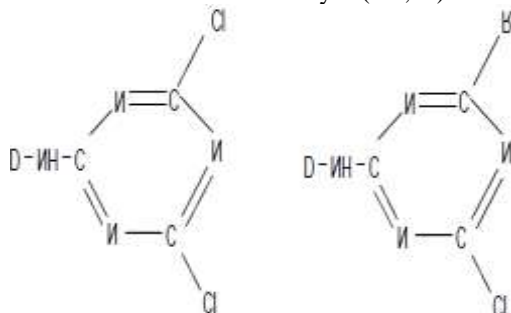
Hydrolysis, oxidation and other chemical reactions showing cellulose degradation is a 1 to 4

linked linear polymer of  $\beta$ -D-glucopyranose. Each and which monomer linked together with another by elimination of one molecule of water between the hydroxyl groups attached to the number 1 carbon atom of one glucose molecule and the number 4 carbon atom of another. 1, 4- $\beta$ -glucosidic linkage or the  $\beta$ -glucosidic oxygen bridge make monomeric units together.

### 1.2. Cotton Dyeing:

The coloration of cotton textiles is a mature and highly efficient industrial technology. Worldwide the consumption of cotton dyes is some 360,000 tons per year comprising a major part of the \$6 billion dollar dye industry. Unlike other textile fibers, there is very little coloration of cotton prior to spinning and the great majority of cotton products are dyed and printed in fabric form. [14]. Reactive dyes are the most popular application class used to dye cellulose fibers. It forms covalent bond with cellulose. Due to the strong primary bonding between dyes and fibers, it possesses high level of fastness [16]. Reactive dyes basically belong to two classes, viz. (i) substitutive and (ii) additive. Substitutive dyes include mono and dichlorotriazines. Additive types include sulphuric acidesters of  $\beta$ -hydroxyethylsulphones [14]. Dichlorotriazines dyes possess two reactive chlorine atoms and are applied at room temperature, called cold brand or M dyes while monochlorotriazine, possessing only one chlorine atom are applied under application of heat and is known as hot brand or H dyes [14].

**Figure 1:** Dichlorotriazines dyes (cold, M)  
Monochlorotriazine dyes (hot, H)



Additive type includes mainly vinyl sulphone dyes (ramazol dyes) possessing a general formula  $DSO_2CH=CH_2$ . These dyes do not give any by-product during reaction with cotton or water, follows a nucleophilic addition mechanism and are applied through application of heat. Chemical attachment takes place in alkaline pH. [3].

## II. MATERIALS AND METHODOLOGY:

### 2.1. Fabrics

A bleached woven 100% cotton fabric was used in this study. The fabric of 150 gram/m<sup>2</sup> weight having plain weave of 68 epi  $\times$  52 ppi (warp  $\times$  weft) construction was used. The weft yarn was cotton count of 32 and the warp yarn cotton count of 32.

### 2.2. Dyes and Chemicals Used

The reactive dye used in this study was monochlorotriazine (MCT). This is because literatures show MCT dyes give better result during combined process (7) and we checked also in our pilot experiment MCT dyes give better result compared to ramazol and direct dyes.

**Table1.** List of Dyes and Chemicals used in the research

Dyes and Chemicals	Reagent grade type
Monochlorotriazine dye (red) reactive-H (BASF)	LR (Laboratory Reagent)
Citric Acid	Commercial
Sodium hydrogen carbonate	LR (Laboratory Reagent)
Sodium di-hydrogen phosphate	LR (Laboratory Reagent)
Non-ionic Softener	LR (Laboratory Reagent)
Urea	LR (Laboratory Reagent)
Standard detergent	LR (Laboratory Reagent)

Tricarboxylic acid (citric acid) was used as a cross linking (crease resistant) agent. sodium hydrogen carbonate ( $NaHCO_3$ ) was used as alkalis for dye fixation and sodium di-hydrogen phosphate ( $NaH_2PO_4$ ) was used to catalyze the esterification of citric acid and hydroxyl groups of adjacent cellulose molecules in cotton fiber for cross-linking process.

### 2.3. Equipments Padder

A horizontal padder from Mathis-Switzerland was used for applying dyes and

finishes to cotton fabric. The air pressure of the padder was set at approximately 5.5 atmospheres for controlling fabric wet pick up at 80%. The padding fabric speed was set for 3.0 m/min.

**Mini-Drier**

A mini-drier was used for drying and curing the fabric after padding. The temperature for drying was 80°C for 3 min; the curing temperature was varied from 150 to 200 °C in order to study the fixation of cross-linking agent and therefore resultant effect on crease recovery and the physical properties of treated fabric.



**Figure .2:** Mini-drier

**Recipes and Formulations**

The formulations used were prepared by systematic and randomly selecting the concentration of dye and chemicals.

**Table 2:** Recipe for Pad dyeing only

Name of Variable	Concentration (g/L)
Reactive dye (Procion H BASF Red)	15
NaHCO <sub>3</sub>	30
Urea	50

Curing temperature was constant at 150°C for 1.5 min

**Table 3.** Recipe for Citric Acid Resin finishing only

Name of Variable	Concentration (g/L)
Citric Acid as cross-linking agent- New method	45

Catalyst-Sodium di-hydrogen phosphate	38
Softener	20
Wetting Agent	2

Cured at 180°C for 1.5 min

**Table 4.** Recipe for Citric Acid Concentration Variation

Name of Variable	Concentration (g/L)	Total experiments
Reactive Dye	15	
Citric Acid	15, 25, 35, 45	4
Sodium di-hydrogen phosphate	20	
Sodium bi-carbonate	40	
Urea	50	

Cured at 180°C for 1.5min

**Methodology Processes:**

Dyeing was carried out under alkaline pH conditions by passing the dry fabric through dye liquor, followed through a padder set at 80% W.P.U(wet pick up)., dried at 80 °C temperature to remove excess moisture. It was then cured at 150-190°C temperature for a period of 1.5 min depending on the formulation above. The cured fabric was rinsed with cold water, washed with hot water and soap at boil (nonionic soap 5 gpl) for 15 minutes and rinsed with cold water.



**III. RESULTS AND DISCUSSIONS**

**3.1. Dyeing By Pad-Dry-Cure Method**

In order to combine the finish application to impart wrinkle resistance property to cotton fabric with coloration, the fabric was treated with a mixture of dye and cross linking chemicals and fixed by using the conventional method of pad-dry-cure using a suitable catalyst. Initial investigations on selection of the class of dyes suggested that MCT dyes are more suitable for combined application than among Di-cholorotriazine, vinyl sulphone based reactive dyes and direct dyes. For comparison, the fabric was only dyed using a conventional pad dyeing process. The table 4.2 shows the properties of fabric dyed only. This sample was used as control for the evaluation of physical and mechanical properties combined dyed

and resin finished fabrics samples obtained by varying different variables

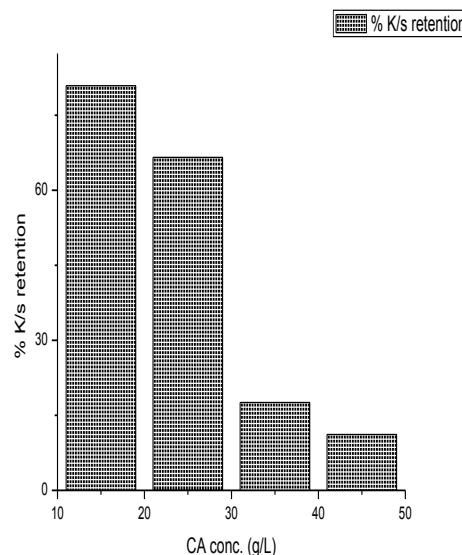
**Table Effect of Varying Curing Temperature on cotton fabric**

Curing Temp (°C)	K/S	TENSILE (N)		Tear (N)		Pilling	DCR A(°)	Fastness Properties(rating scale)					
		Warp	Weft	Warp	Weft			Wash		Crock			
								Change in Color	Stain	Dry		Wet	
										Change in Color	Stain	Change in Color	Stain
160	6.8689	131	79	14.57	13.71	4-5	143	4-5	4-5	4-5	4-5	4	4
170	6.5520	125	77	14.52	13.71	4	158	4-5	4-5	4-5	4-5	4-5	4
180	5.2745	122	77	14.44	13.68	4	184	4-5	4-5	4-5	4-5	4-5	4-5
190	4.3862	98	67	14.00	13.39	3	195	4-5	4-5	4-5	4-5	4-5	4-5

Reactive dye 15 g/L; sodium di-hydrogen phosphate 20 g/L; Citric acid 25 g/L, sodium hydrogen carbonate 40 g/L; curing for 1.5 min.

**Effect of Citric Acid Concentration on Color Yield**

The citric acid concentration was increase from 15 to 45g/L keeping the other variables constant. The result data in table 4.4 show that color yield and its percent retention significantly decreases as the citric acid concentration increases. The possible reason for decreasing the color yield is the drop in the dye bath pH from alkaline to acidic. The shift in pH towards acidic is considered un-favorable for the satisfactory fixation of reactive dyes. The percent K/S retention of the fabrics dyed by combined dyeing and resin finishing by varying the citric acid concentration while the other variables were maintained constant in relative to the only dyed fabric was 80.86%, 66.56%, 17.56%, 11.16% respectively for the citric acid concentration in the dye bath i15, 25, 35 and 45 g/L. These data shows that as citric acid concentration above 25 g/L in the bath K/S value of the fabric badly affected.

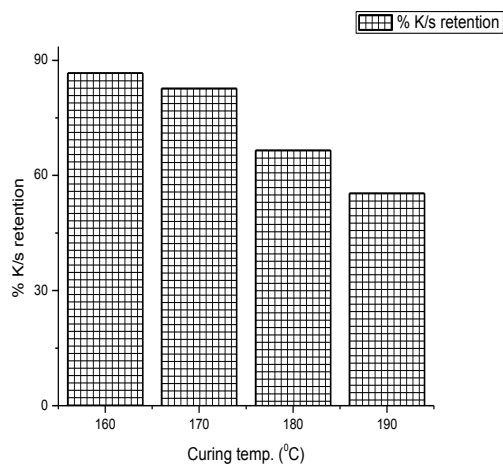


**Figure 4.2:** % K/S retention as function of citric acid concentration

**Effect of Curing Temperature on Color yield**

In pad-dry-cure dyeing method reactive dyes require high temperature for fixation. Similarly cross-linking agents also require high temperature for esterification (cross-linking of cellulose by citric acid). To investigate the effect of curing temperature on color yield (K/S value) of combined dyed and finished fabric curing temperature was varied from 160°C to 190°C by

maintaining other variables constant. The results are presented in table 4.7. The results show that as the curing temperature increases the color yield (K/S) decreases. The reason for drop in color yield with the increase in curing temperature is (1) depolymerization of reactive dyes at high temperature (2) at maximum temperature cross-linking is more effective than the dye fixation i.e. the available attaching sites of cellulose are occupied by the cross-linking agent at high curing temperature and (3) the fabric tends to turn yellow at high curing temperatures and this influences the hue of pale shades. The percentage K/S retention in combined dyed and finished fabric compared to only dyed fabric was 86.67%, 82.56%, 66.56%, 55.34% respectively as the curing temperature was 160, 170, 180 °C and 190 °C. At curing temperature of 190 °C the K/S of the fabric was lower compared to only dyed fabric.



**Figure 4.5:** %K/S retention as a function of curing temperature.

### Wash fastness

The wash fastness properties for the one-step dyed and resin finished fabrics were determined by using ISO Test Method 105(C1S). According to the test change in color of the specimen was compared with the sample from where it was taken to judge rating scale from grey scale. For color staining multi-fiber fabric (cotton and polyester) were used and the result reported from grey scale for every sample.

According to the test results, combined dyed and resin finished fabrics with reactive dye and citric acid possess excellent wash fastness to both, (i) change in color, and, (ii) staining on white. The numerical grey scale rating for staining and change in color was 4 -5 for all. It is inferred, therefore, that the application of a reactive dye from a bath containing cross linking chemicals

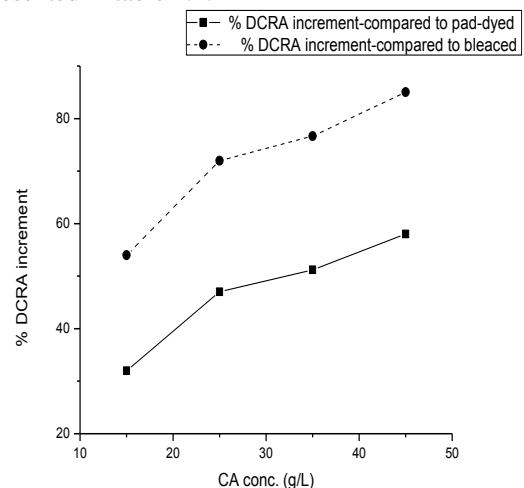
does not have adverse effects on the fastness properties of dyed fabric. .

### Crock fastness

The results from AATCC Test Method 8 on tables 4.3 to 4.7 display colorfastness of combined dyed and resins finished and only pad dyed fabrics. The value of dry crock fastness of combined dyed and finished fabrics was about 4-5 for all fabrics for both change in color and staining according to the gray scale reading, while the rating scale of wet crock fastness of combined dyed and finished fabrics was 4 to 4-5. For the fabrics with higher color yield (K/S value) the wet crock fastness was about 4.

### Effect of Citric Acid Concentration on Crease Recovery

The concentration of cross linking agent in the treatment bath showed significant effect on the DCRA of combined dyed and finished fabrics. As compared to bleached fabric the percentage increase in DCRA of combined dyed and finished fabrics was observed when the citric acid concentration was varied from 15, 25, 35 g/L and 45 g/L whereas other variables were constant. The percent increase was recorded as 54.00, 71.96, 76.64, 85.05 for the citric acid concentrations 15, 25, 35 g/L and 45 g/L respectively. Similarly the percent increase in DCRA of combined dyed and finished fabrics compared to only dyed fabric was 32.00%, 47.00%, 51.20%, 58.00% for citric acid concentrations 15 g/L, 25g/L, 35g/L and 45g/L respectively. These results show that for citric acid concentration 35 g/L and 45g/L, the DCRA was better but the K/S value was affected badly as presented in table 4.4.



**Figure 4.7:** %DCRA increase as a function of citric acid concentration

As shown in the figure above as the concentration of citric acid increases the percent increase in DCRA increased significantly.

#### IV. CONCLUSION:

As the dye concentration in the bath increases the color yield (K/S value) increases and show better strength retention, but the crease recovery angle decreases. Maintaining the other variables constant and increasing cross-linking agent (citric acid) concentration in the dye bath, crease recovery increases, but the color yield and mechanical properties decreases. The findings cited above clearly suggest the possibility of combining dyeing and resin finishing on one stage process. Needless to mention, however, to optimize the condition of a combined process by studying the effect of each parameter on color yield and crease recovery, besides, the mechanical properties of the fabric subject to this process. During combined dyeing and resin finishing of 100% cotton fabric using monochlorotriazine (MCT) type reactive dye and citric acid as cross linking agent it is necessary to ensure that the pH of the bath is alkaline to facilitate the fixation of reactive dye. If the pH moves to neutral or acidic, the fixation of the dye will not be adequate to obtain the desired color yield. In pad-dry-cure process of combined dyeing and finishing the wet pick up of the fabric should be between 75% and 85% in order to avoid migration of dye and cross-linking agent at higher wet pick up.

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