

# Dyeing of cotton using reactive dyes without Salt

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**Abstract** - In this study 3-chloro-2-hydroxypropyl trimethyl ammonium chloride was used as a cationic agent to cationize cotton fabric by a pad-batch process. The cationized cotton samples were dyed with different reactive dyes containing various reactive groups. The dyeability of the cationized cotton samples with reactive dyes without salt was significantly improved due to an increase in the ionic attraction between the dye and cationized cotton. The results showed that the wash and dry rubbing fastness of the cationized cotton dyed with different reactive dyes are similar to those of the untreated cotton. However, the light fastness of some of the cationized fabric samples was improved.

**Index Terms** - Salt, Reactive dye, Cotton, Cationization, Fastness, Pre-treatment

## INTRODUCTION

Cellulose fibers when they come in contact with water produce slightly negative charge due to the ionization of hydroxyl groups, whereas most of the dye classes suitable for cotton are anionic (such as reactive and direct dyes) in solution. The slightly negative charge on the fibers results in repulsion of anionic dyestuffs and thus the exhaustion of the bath is limited. Therefore, in dyeing of cotton with anionic dyes, a large amount of electrolyte, such as Glauber's salt or sodium chloride is required in order to reduce the charge repulsion between the negatively charged cotton and the anionic dyes. However, normally not all the dye in the dye bath is exhausted, thus causing environmental problems due to the discharge of effluent that is colored as well as having a high salt concentration. Chemical modification of cotton in order to improve its dyeability without the large amount of salt has been considered for a long time. Pre-treating the cellulose fibers with reactive cationic agent could diminish or eliminate the amount of electrolyte required [1]. Chemical modification of cotton is generally performed by reaction with the functional groups (hydroxyl groups) already present in

the fiber. Many studies devoted to improving the dyeability of cotton fibers have used quaternary cationic agents having various reactive groups (e.g. epoxy and chlorotriazine) [2-4]. The most common approach is via reaction of various types of fiber-reactive substituted amino compounds [5-12]. By introducing amino groups, the cellulose fiber will be cationized giving high substantivity for anionic dyes due to columbic attraction between the positive charge on the fiber and the negative charge on the anionic dyes. This cationized cotton could be dye able with reactive dyes under neutral or mild acidic conditions in the absence of electrolyte in the dye bath. It is also known that cotton treated with modified poly carboxylic acid can be dyed with different anionic dyes such as acid, direct and reactive dyes under specific dyeing conditions [13].

Catinization of cotton with UV curable monomers produced a large increase in dye-ability with anionic dyes. This is due to the introduction of dye/fiber ionic interaction [14]. Hebeish et al. [15] and Eleftheriadis et al. [16] reported that quaternization of 2-vinyl pyridine grafted to cotton with epichlorohydrin or an alkyl bromide could enhance the exhaustion values of reactive and/or direct dyes towards the limited value of 95-100 %. Wang and Lewis synthesized a new fiber reactive quaternary compound containing an acrylamide residue. This can be applied to cotton fabrics via pad-dry-cure under alkaline conditions. The treated cotton can be dyed with reactive dyes without additives such as salt or alkali. Reactive dyes can be exhausted almost entirely onto the treated cellulose fiber [17]. In this study various reactive dyes with three different reactive groups including monochloro triazine, dichloro triazine and vinyl sulphone were applied onto the cationized cotton fabrics. The cationic agent used for modification was 2,3- epoxypropyl trimethylammonium chloride (EPTMAC). This compound will react with cotton under alkaline conditions to form a cationized cotton

fiber. The dyeability and fastness properties of the cationized cotton with different reactive dyes were investigated.

## EXPERIMENTAL MATERIALS

Plain weave cotton fabric (desized, scoured and bleached) was used for this work. Cationizing agent, 3-chloro-2-hydroxypropyltrimethylammonium chloride (Fluka) is commercially available as a 65 % solution in water and was used as received. Sodium hydroxide, sodium carbonate, acetic acid and sodium sulphate were all of laboratory reagent grade (Merck). Tinegal W (Ciba) was used as detergent. The reactive dyes used with different reactive groups including monochlorotriazine, dichlorotriazine and vinylsulphone are listed in Table 1. All reactive dyes were from Ciba representative in Iran.

Table 1. Different reactive dyes used

Dye	Commercial name	Reactive groups
1	Cibacron Red HF	Monochlorotriazine
2	Cibacron Blue TGRE	Monochlorotriazine
3	Cibacron Golden Yellow R-E	Monochlorotriazine
4	Cibacron Brilliant Blue BR-P	Monochlorotriazine
5	Cibacron Yellow F3R	Vinylsulphone
6	Cibacron Blue F3G	Vinylsulphone
7	Cibacron Red F-B	Vinylsulphone
8	Cibacron Yellow C-R	Dichlorotriazine
9	Cibacron Red C-R	Dichlorotriazine

### Pre-treatment of Cotton

The solution consisting of 35 g/l of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTMAC) (65 % w/w) and 15 g/l of sodium hydroxide was applied to the well-prepared cotton fabric. The wet pick up was 100 %. To minimize the hydrolysis of reactant, the alkali was added to the bath just before application. The padded fabric was put in plastic bag to prevent chemical migration and water evaporation. The fabric was stored at room temperature for 24 hr, and then rinsed several times with water and finally neutralized with a dilute acetic acid (1 g/l). The final fabric pH was 7.6.

### Dyeing of Treated and Untreated Cotton

Laboratory dyeing with the reactive dyes was carried out in Ahiba Texomat laboratory dyeing machine with liquor to fabric ratio of 40:1. Dyeing of untreated cotton with reactive dyes was performed according to the procedure offered by the manufacturer. For

reactive dyeing with monochlorotriazine reactive groups, 1 % o.w.f. dye was added to a room temperature dye-bath. The fabric sample was then added and the bath was heated to 80°C at a rate of 1.5°C/min. Before approaching to 80°C, sodium sulphate (40 g/l) was added in two portions at 55°C and 65°C. After holding the temperature at 80°C for 10 min, 3 g/l of sodium carbonate was also added. The bath was held at 80°C for 50 min, cooled to 60°C at a rate of 2.5°C/min and then discarded. Dyeing of untreated cotton with vinyl sulphone and dichlorotriazine reactive dyes was performed at 60°C. The fabric sample and 1 % o.w.f. dye were added to a 60°C dye bath and after 20 min 40 g/l of sodium sulphate added, and 10 min later 3 g/l of sodium carbonate was also added. The bath was then held at 60°C for 60 min and discarded. The dyed samples were rinsed with 50°C water and divided into two equal portions. One portion was soaped in a solution containing Tinegal W (1 g/l) and sodium carbonate (1 g/l) at the boil for 15 min at 40:1 liquor to goods ratio. The fabric was rinsed once with 50°C water, and once with cold water. The other portion was left unsoaped. The procedure for dyeing cationized cotton with reactive dyes was the same as that for the untreated cotton (as outlined above), except dyeing cationic cotton was performed in the absence of salt.

### Dye Exhaustion and Fixation

The dye uptake by the cotton was determined using a UV-visible light spectrophotometer and the dye-bath absorbance was measured at the wavelength of maximum dye absorption ( $\lambda_{max}$ ). The percentage of dye-bath exhaustion (E) was calculated using Eq. (1) [17]

$$E\% = (1 - A/A_0) \times 100 \quad (1)$$

where  $A_0$  and  $A$  are the absorbance of the dye solution at the maximum wavelength before and after the process, respectively. The use of reflectance values (R) to determine the concentration of dye in the fabric is well established [18] and the relationship between R and K/S is shown in Eq. (2).

$$K/S = (1 - R)^2 / 2R \quad (2)$$

The color strength of the dyed fabrics was expressed as K/S values obtained for the unsoaped and soaped fabrics. The fixation of adsorbed dye (F) was calculated using Eq. (3) and the total fixation of the

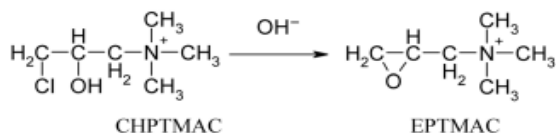
original applied dye (T) was calculated using Eq. (4) [17].

$$F\% = \frac{(K/S)_1}{(K/S)_2} \times 100 \quad (3)$$

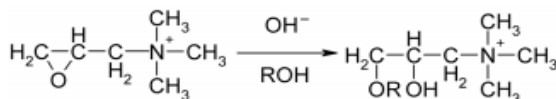
and

$$T = E \times \frac{(K/S)_1}{(K/S)_2} \quad (4)$$

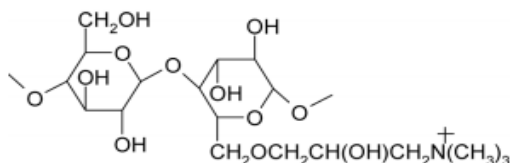
where the subscripts 1 and 2 indicate values obtained before and after soaping respectively. Fastness The dyed samples were tested according to ISO standard methods. The specific tests used were ISO 105 C01:1989, color fastness to washing; ISO 105-X12:1993, color fastness to rubbing. Color change was rated according to the appropriate gray scale. A light fastness test was carried out using the ISO 105 B02:1994, standard method and the degree of fading was assessed by SDC blue wool scales. Nitrogen Content The percentage of nitrogen content of sample was determined by Micro Kjeldahl method [19]. Results and Discussion Reaction of CHPTMAC with Cellulose 2,3-epoxypropyltrimethylammonium chloride (CHPTMAC) was prepared in situ by the reaction of 3-chloro-2-hydroxypropyltrimethylammonium chloride with alkali as shown in



Scheme 1. Reaction of CHPTMAC with alkali.



Scheme 2. Reaction of EPTMAC with alcohol.



Scheme 3. Cationized cotton.

Scheme 1.

EPTMAC will react with alcohols under alkaline conditions to form ethers (Scheme 2) and will thus produce a modified fiber when it reacts with cotton as shown in Scheme 3. As a result, cotton will have cationic dye sites covalently bound to the polymer chains. These dye sites will strongly attract anionic reactive dyes, enabling the use of these dyes without

the large amounts of electrolyte that is normally needed to drive the dyes from the water onto the cotton fiber. In this paper we used the nitrogen content determination for proving cationization. The nitrogen content of the untreated cotton was about zero but the nitrogen content of the cationized cotton was about 0.06 %. This can prove the cationization of the sample by a quaternary ammonium salt

## DYEING RESULTS

Reactive dyes with various reactive groups were examined to assess their suitability for use on the treated cotton. The results showed that all of the dyes employed gave an excellent exhaustion with 1 % o.w.f. and most of them showed a high fixation with good levelness. Also, the reactive dyes were applied to untreated cotton according to the manufacturer recommendations. The results for three different dyeing methods are listed in Table 2. It can be seen that the exhaustion, fixation and color strength values for the most dyes on the treated cotton is higher than those on the untreated cotton. With exception of Cibacron Brilliant Blue BR-P, all the dyes were exhausted very well by the treated cotton. The fixation values varied from dye to dye. In these dyeing systems, the strong attraction between the cationic dye sites on the modified cotton and the anionic dyes existed which led to obtain a very high exhaustion rates without addition of electrolytes to the dye-bath. The color strength of most of the dyeing on the treated cotton was often twice and in some cases up to four times of untreated cotton. However, these high color strength values might be partially attributed to surface dyeing or ring dyeing. The wash fastness of the cationized dyed cotton was similar to that of the untreated dyed fabrics and the cross staining results were good (see Table 3). The excellent light fastness of the reported dyeing on cationic cotton is particularly striking, since cationic pretreatments, as a general rule, are known to impair light fastness. The cationic pretreatment used here is nonpolymeric in nature and can be expected to penetrate the cotton fiber prior to fixation. This uniform modification of the fiber evidently allows for enhanced color yields and wash fastness without adverse effect on the light fastness. The rubbing fastness of both sets of samples was good. The observation of the dyed samples also showed a good level of uniformity.

Table 2. Results of reactive dyes on EPTMAC treated and untreated cotton fabrics

Dye (1 % owf)	EPTMAC-treated cotton <sup>a</sup>				Untreated cotton							
					Conventional dyeing without salt				Conventional dyeing			
	E (%)	F (%)	T (%)	(K/S) <sup>b</sup>	E (%)	F (%)	T (%)	(K/S) <sup>b</sup>	E (%)	F (%)	T (%)	(K/S) <sup>b</sup>
Cibacron Red HF	92.2	97.3	89.7	7.1	9	85.7	7.7	0.6	48.5	88.4	42.9	3.8
Cibacron Blue TGRE	96.5	83.7	80.8	4.1	29.7	62.5	18.5	0.5	79.9	59.3	47.4	1.6
Cibacron Gold. Yellow R-E	96.9	93	90.1	5.3	20	61.5	12.3	0.8	83.5	65.9	55	3.1
Cibacron Brill. Blue BR-P	81.2	96.5	78.3	2.8	9.7	50	4.9	0.1	30.3	77.8	23.6	0.7
Cibacron Yellow F3R	92.9	95.3	88.5	6.1	5.9	80	4.72	0.8	39.31	44	17.3	1.1
Cibacron Blue F3G	96.5	81.6	78.7	4	16.71	63.6	10.6	0.7	66.59	51.4	34.2	1.8
Cibacron Red F-B	91.6	88	80.6	8.1	10.73	72.7	7.8	0.8	58.27	66.7	38.9	4
Cibacron Yellow C-R	91.4	86.7	79.2	6.5	17.54	75	13.1	1.2	44.63	63.9	28.5	2.3
Cibacron Red C-R	89.4	92.9	83	6.5	7.99	83.3	6.6	0.5	28.28	55.5	15.7	1

<sup>a</sup>Conventional dyeing without salt, <sup>b</sup>K/S values after-soaping.

Table 3. Fastness of untreated and cationized cotton fabrics dyed with reactive dyes

Dye (1 % owf)	EPTMAC-treated cotton <sup>b</sup>				Untreated cotton (conventional dyeing)						
	Wash shade change	Cross staining <sup>b</sup>		Light	Dry rubbing	Wash shade change	Cross staining <sup>b</sup>		Light	Dry rubbing	
		C	W				C	W			
Cibacron Red HF	5	5	5	4	5	5	5	5	2	5	
Cibacron Blue TGRE	4	5	5	3	5	4	5	5	2	4.5	
Cibacron Gold. Yellow R-E	5	5	5	5	4.5	4.5	5	5	4	5	
Cibacron Brill. Blue BR-P	4.5	5	5	5	5	4.5	5	5	5	5	
Cibacron Yellow F3R	4	4.5	5	5	5	4.5	5	5	4	5	
Cibacron Blue F3G	4.5	5	5	5	4.5	4.5	5	5	5	5	
Cibacron Red F-B	4.5	5	5	5	4.5	4.5	5	5	3	4.5	
Cibacron Yellow C-R	5	5	5	4	4.5	4.5	5	5	5	5	
Cibacron Red C-R	5	5	5	4	4.5	4.5	5	5	2	5	

<sup>a</sup>Conventional dyeing without salt, <sup>b</sup>C: cotton staining, W: wool staining.

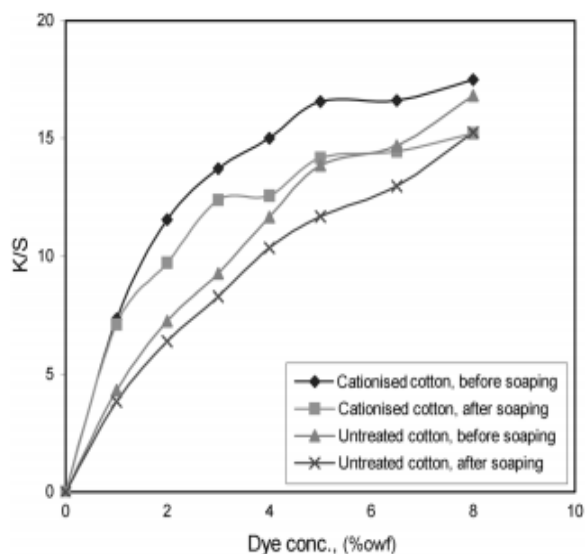


Figure 1. Build-up properties of Cibacron Red HF for treated and untreated cotton fabrics.

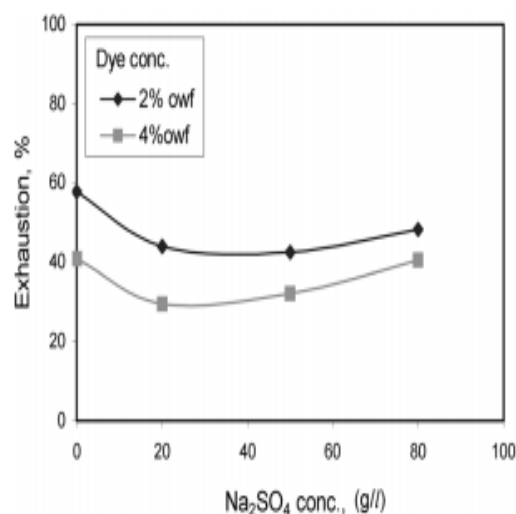


Figure 2. Effect of electrolyte concentration on exhaustion of Cibacron Red HF for treated cotton fabrics.

## INFLUENCE OF ELECTROLYTE IN DYEBATH

The effect of salt on the dyeing of the quarternized cotton is shown in Figure 2. In the dye concentrations applied to the fabrics well below the saturation limit of the treated fibers, the degree of exhaustion decreased with increasing salt concentration. For 2 % o.w.f. Cibacron Red HF, the treated cotton gave 60 % exhaustion of anionic dye in the absence of electrolyte, but the exhaustion dropped to 45 % after adding 20 g/l of sodium sulphate. This unfavorable effect was because of the sulphate anions which have a significant affinity for quarternized cellulose and they were able to compete with dye anions for the quaternary sites in the modified fibers with increase in salt concentration, as nearly all the quaternary sites are occupied and the fiber became neutrally or even negatively charged. In this way dye adsorption was the same as the untreated cotton.

## CONCLUSION

The cotton fabric treated with EPTMAC provides cationic sites which can be dyed with reactive dyes without electrolytes to give excellent results. Reactive dyes can be exhausted almost entirely onto the treated cellulose fibers. Dyeing on the treated cotton gave better color strength than the comparable dyeing on untreated cotton by the conventional method. The color fastness of these dyeing is equal or superior to that of some dyes on untreated cotton. The results on the different reactive groups indicated that the type of reactive groups of reactive dyes had no influences on the dyeing properties of the cationized cotton fabrics.

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