

# SALT-FREE DYEING - A NEW METHOD OF DYEING ON LYOCELL/COTTON BLENDED FABRICS WITH REACTIVE DYES

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## Abstract:

Cellulosic/regenerated blended fabrics dyed with reactive dyes require a large amount of salt, which pollutes fresh watercourses. Due to the hydrolysis of the dye, the dyeing effluent consists of a large amount of hydrolysed dye, and it requires a high volume of water to remove the hydrolysed dye in a wash-off process. Lyocell/cotton fabrics were dyed with reactive dyes using conventional methods and pretreating the fabric with polyvinylamine chloride (at five different concentrations). Pretreated samples were dyed without using salt as an electrolyte. The influence of pretreatment on K/S value, wash fastness, rubbing fastness, tensile strength, flexural rigidity and crease recovery were determined. It was found that pretreatment of Lyocell/cotton fabrics with polyvinylamine chloride increases dye uptake and shows good wash fastness and rubbing fastness. There was a slight increase in crease recovery angle and flexural rigidity in the pretreated sample. It was determined that polyvinylamine chloride was found to be effective for pretreatment in salt-free dyeing of Lyocell/cotton fabrics.

## Key words:

Cationic sites, cotton, hydrolysis, Lyocell, polyvinylamine chloride (PVAmHCl), reactive dyes, salt-free dyeing.

## Introduction

Cotton is still the king of fibres, and most of world's apparel is made of cotton. This fibre has good strength and it is known to provide comfort, good moisture absorption and good wicking properties. Lyocell fibre has a high degree of orientation and crystallinity and a higher molecular weight than other cellulosic fibres. As a result, fibre strength and modules of fibre are higher than those for regenerated cellulosic fibres as well as polyester staple fibres. Fabrics produced from Lyocell/cotton are breathable and moisture absorbent and have high dimensional stability.

With growing popularity of reactive dyes for dyeing of cotton, environmental problems associated with their use have received attention. Since cotton has only moderate affinity for most reactive dyes, large quantities of electrolytes such as NaCl or Na<sub>2</sub>SO<sub>4</sub> (40-100 gpl) are normally required for exhaustion. Hence dye bath exhaustion and fixation can still be as low as 50% for some dyes. Wastewater therefore contains a significant quantity of dye and salt, leading to serious environmental problems.

It has been found that pretreatment of cotton before dyeing can offer a simple and effective method of improving dye-fibre affinity, avoiding the need for salt as an electrolyte in the dye bath. It has been found that poly(vinylamine chloride) [PVAmHCl] is a physical modifying agent. Its wide range of properties has found use in catalysis, chelating, liquid chromatography, treatment of wastewater, recovery of oil and in polymeric dyes. Previous studies have shown that a variety of compounds may be effective in this way, all involving chemical modification of Cellulosic. Non-reactive pretreatments including some polymers with affinity for cellulose tend to be desorbed during dyeing and inhibit uptake of dye or cause it to precipitate. Recent work has established the value of polymeric quaternary ammonium compounds, amines or amides, which may be attached to cotton by non-chemical mechanisms. Despite the encouraging results obtained with non-reactive polymers in

the salt-free dyeing of cotton, problems remain in dye selection and obtaining consistent results.

The aim of this work to determine the effectiveness of PVAmHCl as a pretreatment agent of Lyocell/cotton blended fabrics in improving its dyeability with reactive dyes and in achieving evenness of dye uptake. It was also to determined the effectiveness of pretreatment of dyed fabrics on the K/S value and fastness properties like wash fastness and rub fastness. Various physical properties like tensile strength, flexural rigidity, cloth crease recovery angle, aerial density and thickness were also determined to determine the effect of PVAmHCl. The results were analysed to determine some advantages of pretreatment.

## Properties of Polyvinylamine Chloride (PVAmHCl)

PVAmHCl has been used as a physical modifying agent. Due to its wide range of properties, PVAmHCl has found use in catalysis, liquid chromatography, treatment of wastewater, recovery of oil and in polymeric dyes. It has been used in applications as diverse as papermaking and biomedical research, but its use in the modification of cotton for salt-free dyeing as not been previously reported.

Interest in PVAmHCl arises from the presence of a large number of cationic sites (NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>). Nucleophilic sites involving primary amino groups within the PVAmHCl molecule are of particular value for achieving salt-free dyeing of cotton with reactive dyes. As the pH increases, the proportion of NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup> groups in the molecule decreases and that of the NH<sub>2</sub> groups increases.

## Materials and methods

### Fabric

The Lyocell/cotton (40:60) yarns were spun and the fabric was woven. The geometrical properties of the fabric are given in Table 1.

**Table 1.** Geometric parameters of Lyocell/cotton fabric.

Fabric	Ends/cm	Picks/cm	Gm/m <sup>2</sup>	Warp Count (Tex)	Weft Count (Tex)	Thickness (mm)
Lyocell /cotton	34	34	140	24	24	0.18

**Dyes & chemicals**

The details of the dye and the chemicals used are given in Table 2.

**Table 2.** Functions of Dye and chemicals used.

SI No.	Dye and Chemicals	Functions
1	CI RX Red 120A (Generic name) Reactive Red HE-3B (Commercial name)	Dyeing
2	Polyvinylamine Chloride (PVAmHCl)	Pretreatment
3	Potassium dihydrogen Phosphate (KH <sub>2</sub> PO <sub>4</sub> )	To maintain pH
4	Sodium Carbonate (Na <sub>2</sub> CO <sub>3</sub> )	Fixing agent
5	Sodium Hydroxide (NaOH)	Swelling agent
6	Sodium Chloride (NaCl) Caustic Lye	Exhaustion agent

**Preparation of Fabric**

The fabric sample was desized using the acid desizing method. The fabric was scoured by the alkali method using a standard procedure. Then, it was subjected to a bleaching process using hydrogen peroxide as the bleaching agent.

**Pretreatment**

The padding method was used for pretreatment of cotton with PVAmHCl. The pH of the pretreatment solution was maintained by the buffer potassium dihydrogen phosphate (7 gpl) and sodium hydroxide (1.45 gpl). Padding was carried out using two dips (4 min each) and two nips. Fabric samples were pre-dried at room temperature and then baked at 102°C for 12 min in a rapid baker. Padding was done at different concentrations of PVAmHCl. The pretreatment process conditions are given in Table 3.

**Dyeing**

The fabric was dyed with reactive dye using the procedure recommended by the dye manufacturer. One fabric sample was considered as a control sample. Exhaust dyeing was carried out at a liquor ratio of 1:30. Dyeing of the fabric

**Table 3.** Process conditions for pretreatment.

PVAmHCl	2.5, 5.0, 10, 15, 20
KH <sub>2</sub> PO <sub>4</sub>	7 gpl
NaOH	1.45 gpl
pH	7-7.5
Pretreatment time	4 min (two dips) for each
Curing Temperature	102°C
Curing Time	12 min

**Table 4.** Process conditions for dyeing.

Percentage Dye (OWF) %	1 to 2
Dyeing Temperature	80 °C
Na <sub>2</sub> CO <sub>3</sub>	6-8 gpl
NaCl	30 gpl (Only for conventional dyeing)
pH	10-11
Time of Dyeing	60 min
Fixation time	20 min

pretreated with different concentrations of PVAmHCl was carried out at 80°C for 60 min. Fixation was conducted for 20 min using 6 to 8 gpl of Na<sub>2</sub>CO<sub>3</sub> and 0.01 to 0.5 gpl of caustic lye. The process conditions for dyeing are given in Table 4.

**Testing**

The details of various tests conducted on the fabric are as follows.

*Colour strength (K/S Value)*

Colour strength K/S was measured on a Minolta Spectrophotometer. These values are calculated using the following "KUBELKA-MUNK" equation:

$$K / S = \frac{(1 - R)^2}{2R}$$

where *K* is the absorption co-efficient, *R* is the reflectance of the dyed sample and *S* is the scattering co-efficient at the wavelength of maximum absorption.

*Physical properties*

The physical properties of the dyed fabric samples and the instruments used are given in Table 5.

**Table 5.** Physical properties of Lyocell/cotton fabric sample.

No.	Property	Standards	Instrument used
1.	Thickness	ASTM D 1777	Thickness gauge.
2.	Wash fastness	AATCC-107/2002	Wash fastness tester (Lander -o- meter)
3.	Rubbing fastness	AATCC-008/2005	Crockmeter
4.	Tensile strength	ASTM D5034-95	Eureka tensile strength tester
5.	Flexural rigidity	BSI BS 3356-1991	Shirley stiffness tester
6.	Crease recovery angle	AATCC-066/2003	Eureka Crease recovery angle tester
7.	Aerial Density	ASTM D 3776	Quadrant balance

Note: Tensile strength, crease recovery, flexural rigidity and aerial density were tested only for the control sample and the sample treated with a PVAmHCl concentration of 10 gpl.

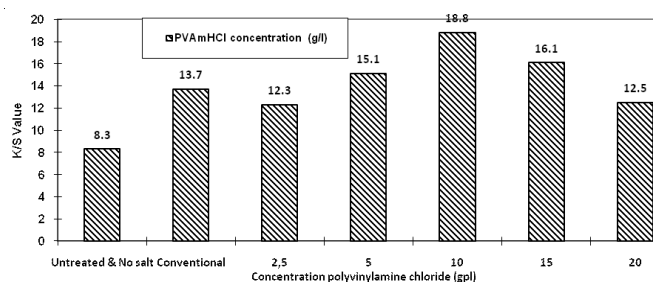
**Results and discussion**

**Effect of pretreatment on K/S value**

The results of K/S value are presented in Table 6.

**Table 6.** K/S value of control and treated samples.

PVAmHCl concentration (g/l)	K/S Value
2.5	12.3
5.0	15.1
10.0	18.8
15.0	16.1
20.0	12.5
Conventional	13.7
Untreated & no salt	8.3



**Figure 1.** K/S value of control and treated samples.

From the table, the following observations were made:

- The K/S value of the untreated sample was comparatively lower than the K/S value of samples treated with 5-10% polyvinylamine chloride.
- The K/S value was found to be less than that of the conventional method when 2.5% polyvinylamine chloride was used.
- The maximum K/S value found with 10% polyvinylamine chloride.
- As the concentration of polyvinylamine chloride increased above 10%, the K/S value decreased.

The above observations indicate that the pretreatment of Lyocell/cotton fabric increases dye uptake. This decrease in K/S value may be for the following reasons. When an excess of polyvinylamine chloride is padded on the fabric, the bonding between the fibre and some cationic polymers becomes weak, and repulsion forces also exist within the cationic polyvinylamine chloride. This would lead to the presence of unbound polymer in the dye bath, thereby hindering the absorption of dye and possibly causing it to flocculate. It can be seen from Table 6 that dye reactivity on pretreated fabric was greater due to the presence of primary amino groups provided by the Polyvinylamine Chloride. This confirms the effectiveness of pretreatment in enabling the fabric to be dyed without salt.

**Effect of pretreatment on wash and rubbing fastness properties**

The results of wash and rubbing fastness are presented in Table 7.

The fastness properties of dyed Lyocell/cotton fabrics pretreated with PVAmHCl were determined. The results were compared with those of conventional dyeing. The wash fastness was excellent for all samples from the salt-free dyeing, confirming the effectiveness of dye fixation due to pretreatment with PVAmHCl. Rubbing fastness was also observed to be good when compared with that obtained by conventional dyeing.

**Table 7.** Fastness properties of control and treated samples.

PVAmHCl concentration (g/l)	Wash fastness	Rubbing fastness
2.5	4	4
5.0	4	4
10.0	4	4
15.0	4	4
20.0	4	4
Conventional	3-4	4
Untreated & No salt	2-3	2

**Effect of pretreatment on physical properties**

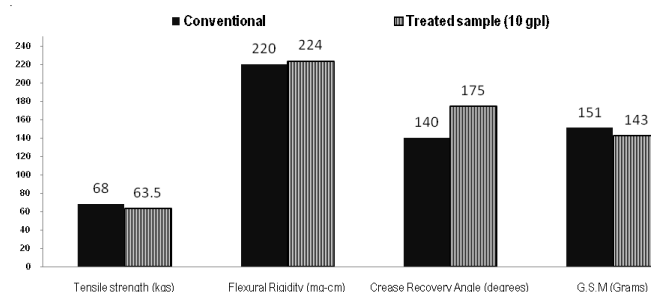
The results of tensile strength, flexural rigidity, crease recovery angle, aerial density and thickness are presented in Table 8.

**Table 8.** Physical properties of control and treated samples (treatment with 10 gpl concentration of PVAmHCl).

Sample	Tensile Strength (kg) (Warp+Weft)	Flexural Rigidity (mg-cm)	Cloth Crease Recovery Angle (degrees)	Aerial Density (GSM)	Thickness (mm)
Sample dyed with conventional process	68	220	140	151	0.56
Treated sample (10 gpl)	63.5	224	175	143	0.48

From Table 8, the following observations can be made:

- The tensile strength of conventionally dyed fabric and the pretreated samples were found to be almost same.
- There was an increase in crease recovery angle of the fabric when treated with PVAmHCl.
- Flexural rigidity of sample increased as a result of pretreatment.



**Figure 2.** Physical properties of control and treated samples (treatment with 10 gpl concentration of PVAmHCl).

The increase in the crease recovery angle as a result of pretreatment may be explained as follows. There might be cross-linking of PVAmHCl between the cellulosic molecules. These cross-links hinder the molecular and fibrillar slippage and stabilise the structure, thereby increasing the crease recovery angle. The increase in flexural rigidity shows that fabric

became slightly stiffer as a result of treatment of the fabric with PVAmHCl.

## Conclusion

When the Lyocell/Cotton fabrics were pretreated with PVAmHCl, the reactivity of reactive dyes on fibre increased. Wash fastness and rubbing fastness of pretreated sample were better than that for the conventionally dyed sample. Fabric crease recovery and flexural rigidity increased as a result of pretreatment. There was no change in the tensile strength of the fabric as a result of pretreatment. By using this pretreatment method, the following advantages were observed:

- Elimination of salt as an electrolyte,
- Maximum fixation of dye,
- Minimum hydrolysis of dye,
- Low volume of water requirement during the wash-off process,
- Significant savings in process costs,
- Environmentally friendly.

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