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 large amount of salt, which pollutes fresh watercourses. Due to the hydrolysis of the dye, the dyeing effluent consists of large amount of hydrolyzed dye, and it requires high volume of water to remove the hydrolyzed dye in wash –off process.

Lyocell/Cotton fabrics were dyed with reactive dyes using conventional method and pre-treating the fabric with Polyvinylamine Chloride (at 5 different concentrations). Pretreated samples were dyed without using salt as an electrolyte. 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 the dye uptake and shows good wash fastness and rubbing fastness. There was a slight increase in crease recovery angle and flexural rigidity in pretreated sample. It is considered that Polyvinylamine Chloride is 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.

1. Introduction

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

With growing popularity of reactive dyes for dyeing of cotton, environmental problems associated with their use have also received attention. Since cotton has only moderate affinity for most reactive dyes, large quantities of electrolyte such as NaCl or Na2So4 (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 electrolyte in 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 and recovery of oil 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 level results.

The aim of this work to determine the effectiveness of PVAmHCl as 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 determine the effectiveness of pretreatment of dyed fabrics on 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 see the effect of PVAmHCl. Results obtained were analyzed to arrive at some advantages of the pretreatment.

1.1 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 chromography, treatment of wastewater, recovery of oil, and in polymeric dyes. It has been used in application as diverse as paper making and biomedical research, but its used for modification of cotton for salt free dyeing as not been previously reported.

Interest in PVAmHCl arises from the presence of large number of cationic sites ($NH^+{}_3Cl^-$). Nucleophilic sites involving primary amino group 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 $NH^+{}_3Cl^-$ groups in the molecule decreases and that of NH_2 groups increases.

2. Materials and methods

2.1 Fabric

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

2.2 Dyes and chemicals

Table 1: Geometrical parameters of lyocell/cotton fabric

Fabric	Ends/cm	Picks/cm	Gm/m^2	Warp Count (Tex)	Weft Count (Tex)	Thickness (mm)
lyocell/cotton	34	34	140	24	24	0.18

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

Table 2: Functions of Dye and chemicals used

Sl No.	Dyes and Chemicals	Functions
1	CI RX Red 120A (Generic name) Reactive Red HE-3B (Commercial name)	Dyeing
2	Polyvinylamine Chloride (PVAmHCl)	Pretreatment
3	Potassium di hydrogen Phosphate (KH_2PO_4)	To maintain pH
4	Sodium Carbonate (Na_2CO_3)	Fixing agent
5	Sodium Hydroxide (NaOH)	Swelling agent
6	Sodium Chloride (NaCl) Caustic Lye	Exhaustion agent

2.3 Preparation of Fabric

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

2.4 Pretreatment

Padding method was used for pretreatment of cotton with PVAmHCl the pH of pretreatment liquor was maintained at buffer comprising potassium dihydrogen phosphate (7 gpl) and Sodium Hydroxide (1.45 gpl). Padding was carried out using 2 dips (4 min for each) and 2 nips. Fabric samples were pre dried at room temperature and then baked at 102oC for 12 min in rapid baker. Padding was done at different concentration of PVAmHCl. Pretreatment process conditions are given in Table-3.

Table 3: Process conditions for pretreatment	
PVAmHCl	2.5, 5.0, 10, 15, 20
KH_2PO_4	7 gpl
NaOH	1.45 gpl
pH	7-7.5
Pretreatment time	4 min (2dips) for each
Curing Temperature	102^{o}C
Curing Time	12 min

2.5 Dyeing

The fabric dyed with reactive dye using procedure recommended by dye manufacturer. This fabric sample is considered as control sample. Exhaust dyeing was carried out at liquor ratio 1:30. Dyeing of fabric pretreated with different concentrations of PVAmHCl was carried out at 80^{o}C for 60 min. Fixation was conducted for 20 min. using 6 to 8 gpl of Na_2CO_3 and 0.01 to 0.5 gpl of caustic lye. Process conditions for dyeing are given in Table-4.

Table 4: Process conditions for dyeing	
Percentage Dye (OWF) %	1 to 2
Dyeing Temperature	80^{o}C
Na_2CO_3	6-8 gpl
NaCl	30 gpl (Only for conventional dyeing)
pH	10-11
Time of Dyeing	60 min
Fixation time	20 min

2.6 Testing

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

a. Colour strength (K/S Value)

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

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

Where K- Absorption co-efficient

R- Reflectance of the dyed sample

S – Scattering co-efficient at the wavelength of maximum absorption.

b. 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, aerial density were tested only for control sample and sample treated with 10 gpl concentration of PVAmHCl.

3. Results and Discussion

3.1 Effect of pretreatment on K/S value

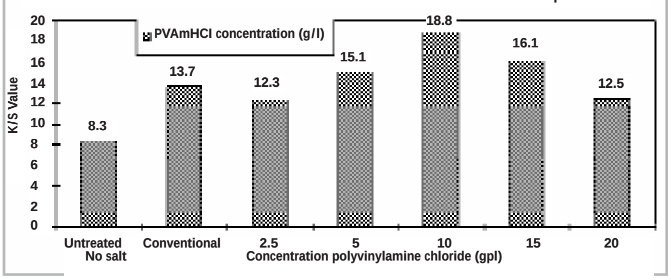
Results of K/S value are presented in Table-6. From the table following observations are made.

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 and no salt	8.3

- ❖ K/S value an untreated sample is comparatively lower than the K/S value of samples treated with 5 & 10 % concentration of Polyvinylamine Chloride.
- ❖ K/S value is found to be less than conventional method when 2.5% Polyvinylamine Chloride was used.
- ❖ Maximum K/S value found at 10% Polyvinylamine Chloride.
- ❖ As the concentration of Polyvinylamine Chloride increases above 10% K/S value found to be decreasing.

Above observations indicate that the pretreatment of lyocell/cotton fabric increases dye uptake. The decrease in K/S value may be due to the following reasons. When excess of Polyvinylamine Chloride is padded on the fabric, the bonding between the fiber and some cationic polymer become weak, and

Bar chart: 1 K/S value of control and treated samples



repulsion force also existed within the cationic Polyvinylamine Chloride. This would lead to 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 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.

3.2 Effect of pretreatment on wash and rubbing fastness properties

Results of wash and rubbing fastness are presented in Table-7.

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 and no salt	2-3	2

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 of the salt-free dyeing, confirming the effectiveness of dye fixing due to the pretreatment with PVAmHCl. Rubbing fastness was also observed to be good when compared with that obtained by conventional dyeing.

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

Sample	Tensile Strength Kgs (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

3.3 Effect of pretreatment on physical properties

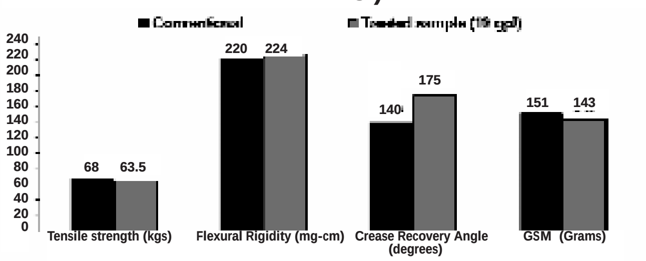
Results of Tensile strength, flexural rigidity, crease recovery angle, aerial density, and thickness are presented in Table-8.

From the table-8 following observations can be made:

- Tensile strength of conventional dyed fabric and pretreated samples is found to be almost same.
- There is increase in crease recovery angle of fabric when treated with PVAmHCl.
- Flexural rigidity of sample increases as a result of pretreatment.

Increase in crease recovery angle, as a result of pretreatment may be explained by a possibility of cross-linking of PVAmHCl between the cellulosic molecules. These cross-links hinder the molecular and fibrillar slippage and stabilize the structure, thereby increasing the crease recovery angle. Increase in Flexural rigidity shows that fabric becomes slightly stiff as a result of treatment of fabric with PVAmHCl.

Bar chart 2: Physical properties of control and treated samples (treatment with 10 gpl concentration of PVAmHCl)



4. Conclusion

When the Lyocell/Cotton fabrics were pretreated with PVAmHCl, the reactivity of reactive dyes on fiber gets increased. Wash fastness and Rubbing fastness of pretreated sample are better than that for conventional dyed sample. Fabric Crease recovery and Flexural rigidity increased as a result of pretreatment. There is no change in the tensile strength of fabric as a result of pretreatment. By using pretreatment method, the following advantages are observed.

- Elimination of salt as an electrolyte.
- Maximum fixation of dye.
- Minimum hydrolysis of dye.
- Low volume of water requirement during wash off process.
- Significant saving in process cost.
- Environmental friendly.

4.1 References

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