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# Salt Free Reactive Dyeing On Cotton (Cationized) Knit Fabric

Sayed Shokoth Hossain Baten[1] Taoyu yang[2], Minghua Wu[3]
[1]*School of Materials & Textile Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, PR China*
[2] *Engineering Research Center for Eco-Dyeing and Finishing of Textiles, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, PR China*
[3]*Key Laboratory of Advanced Textile Materials & Manufacturing Technology, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, PR China*
*Corresponding Author: Minghua Wu*

***Abstract:*** *Dyeing of cellulose substances with reactive and direct dyes is commercially very famous, but isn't always eco-friendly. Then again, pigment hues cannot be carried out with the aid of conventional exhaust methods. Those troubles may be solved or minimized by means of growing the affinity of cellulose materials. Cat ionization of cellulose fibers improves affinity closer to anionic dyes like reactive dyes, direct dyes, and pigment shades dispersed with anionic dispersal. Cellulose fabrics dyed with reactive dyes require a large amount of salt, which pollutes clean watercourses. Because of the hydrolysis of the dye, the dyeing effluent consists of a large amount of hydrolyzed dye, and it calls for an excessive extent of water to eliminate the hydrolyzed dye in a wash off method. Cotton fabrics had been dyed with reactive dyes the usage of conventional methods and pretreating the fabric with methylamine. Pretreated samples were dyed without using salt as an electrolyte. The influence of pretreatment on wash fastness, rubbing fastness and crease restoration have been determined. It was discovered that pretreatment of cotton fabric with methylamine increases dye uptake and shows properly wash fastness and rubbing fastness. When the fabric is dealt with methylamine, the number one hydroxyl agencies of cellulose is (partially) changed into an amide groups, which intern leads the cellulose to behave like as wool fiber and therefore reactive dyes can be dyed on cotton at moderate acetic pH in the absence of electrolyte and alkali.*
***Keywords:*** *Salt Free Dyeing, Reactive Dye, Methylamine, Cellulose, Amide Groups*

## I. Introduction

In contemporary exercise, cellulose fibers are predominantly dyed with reactive dyes in the presence of a considerable amount of salt and fixed below alkaline conditions. However, dye fixation efficiency on cellulose fibers is typically low (various from 50 - 90%). This, outcomes in an enormously colored dye effluent, that is detrimental on environmental grounds (1). Furthermore, the excessive concentrations (40–100gm/L) of electrolyte and alkali (5–20 gm/L) required in cellulose fiber dyeing may also pose additional effluent troubles.Cotton pretreatment earlier than dyeing can offer a simple and effective technique of enhancing dye fiber affinity, fending off the need for salt within the dye bath (2,4). Cationizing cotton fiber will increase the substantively of anionic dyes due to presence of positive charges imparted to the fiber. Cationizationisthechemical modification of cotton to provide cationic (positive charged) dyeing sites in region of present hydroxyl (-OH) sites. Due to the fact protein fibers like wool and silk have been recognized to have suitable dye capacity (3,6). Dyeing cationic cotton effects in greater use of dye and better color values. Further, the robust dye fiber interactions as a result of cationizing cotton permit dyeing and not using an added electrolytes and minimum rising and after washing. However, a fiber with great dye-attracting properties may additionally maintain to exhibit the ones attributes in later use and end up scavengers for the duration of laundering. It has been found that pretreatment of cotton before dyeing can provide an easy and powerful technique of enhancing dye-fiber affinity, heading off the want for salt as an electrolyte within the dye bath (5). It's been found that could be a physical modifying agent. Its huge variety of properties has discovered use in catalysis, chelating, liquid chromatography, and treatment of wastewater, healing of oil and in polymeric dyes (9). The aim of this work is to determine the effectiveness of methyl amine as a pretreatment agent of cotton fabric in improving its dye capability with reactive dyes and in achieving evenness of dye uptake.

### 1.1Advantages of the Salt-Free Cotton Dyeing over the Conventional Way

Chitosan could be used for change of cotton cloth after which cloth will be dyed with traditional dyeing technique without use of salt (2,3). There are certain advantages in salt unfastened dyeing over the traditional dyeing method, for example

- Elimination of salts an electrolyte
- Maximum fixation of dyes.
- Minimum hydrolysis of dyes.
- Low volume of water requirement during the wash off process.
- To increase the reactivity of reactive dyes.
- To increase the wash fastness and rubbing fastness of pretreated sample.
- To increase the fabric crease recovery and flexural rigidity environmentally friendly.
- Significant savings in process costs.

## II. Literature Review

### 2.1. Dying

Dyeing is the technique of adding color to textile products like fibers, yarns, and fabrics. Dyeing is typically executed in a special solution containing dyes and specific chemical material. After dyeing, dye molecules have uncut chemical bond with fiber molecules. The temperature and time controlling are two key elements in dyeing (9,12).These are 3 application procedures available:

#### 2.1.1. Discontinuous method

Conventional method, Exhaust or constant temperature method, High temperature method, Hot critical method.

#### 2.1.2. Continuous method

Pad-steam method, Pad dry method, Pad thermofix method.

#### 2.1.3. Semi continuous method

Pad roll method, Pad jig method, Pad batch method.

### 2.2. Dyeing of cotton fabric with reactive Dye

Reactive dye is capable of reacting chemically with a substrate to shape a covalent bond among dye and substrate. Here the dye contains a reactive group and this reactive group makes covalent bond with the fiber polymer and act as a crucial part of fiber. This covalent bond is formed between the dye molecules and the terminal –OH (hydroxyl) group of cellulose fibers on among the dye molecules (6,8).

#### 2.2.1. Important factors for Reactive Dyeing

- PH of the substrate prior to dyeing
- PH of the dye bath
- Pretreatment of the substrate.
- Solubility of the dyestuff.
- Dyeing temperature
- Quality of water and salt
- Electrolyte concentration
- Dyeing time
- Washing off sequence
- Type of alkali

#### 2.2.2.Dyeing mechanism of reactive dye

The dyeing mechanism of cotton fabric with reactive dye takes place in 3 stages:
1.Exhaustion of dye in presence of electrolyte i.e. dyes adsorption. 2. Fixation under the influence of alkali. 3. Wash-off the unfixed dye from material surface.

### 2.3. Dye exhaustion

When fiber is immersed in dye liquor, an electrolyte is added to assist the exhaustion of dye. Here NaCl is used as the electrolyte. This electrolyte increases the adsorption of dyes. So when the textile material is immersed into the dye liquor, the dye is exhausted on to the fiber (6,9).

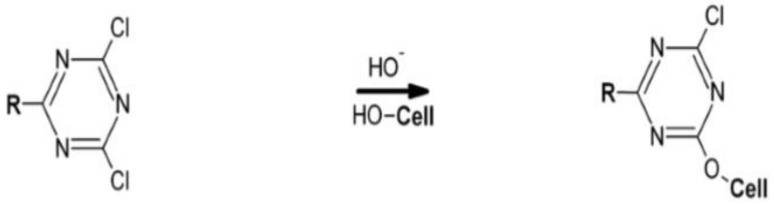
### 2.4. Fixation

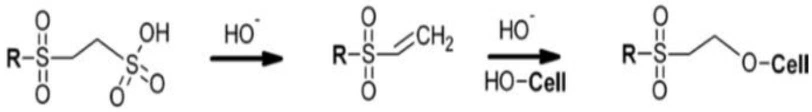
Fixation of dye means the reaction of reactive group of dye with terminal –OH or-NH2- group of fiber and thus forming strong covalent bond with the fiber. This is an important phase, which is controlled by maintaining proper pH by adding alkali. The alkali used for this creates proper pH in dye bath and work as the dye-fixing agent (7). The reaction takes place in this stage is shown below:

$$D - SO_2 - CH_2 - CH_2 - OSO_3Na + OH - Cell$$
$$= D - SO_2 - CH_2 - CH_2 - O - Cell + NaHSO_3$$

$$D - SO_2 - CH_2 - CH_2 - OSO_3Na + OH - Wool$$
$$= D - SO_2 - CH_2 - CH_2 - O - Wool + NaHSO_3$$

**Figure 1:** Covalent bond formed between dye & fiber after dyeing with reactive dye




**2.5. Wash-off**

As the dyeing is completed, a good wash must be applied to the material to remove extra and unfixed dyes from material surface. This is necessary for level dyeing and good fastness properties. It is done by a series of hot wash, cold wash and soap solution wash (3).

**2.6. Techniques Used for Salt-Free Dyeing Process**

he subsequent way are generally used to achieve the salt-free dyeing over cotton cloth using reactive dyes by way of enhancing the cotton surface after introducing a few new functional group with having reactive dye-affinity (13).

## III. Experimental

**3.1. Materials**

100% scoured and bleached cotton fabric, SingleJersey, GSM of the fabric is 160, Stitch length 2.54 mm, Methyl amine($CH_3NH_2$) was used as a cationizing agent.Other Chemicals: Sodium Hydroxide, Green Acid (60% Acetic acid+ 40% Sodium acetate), Sodium Carbonate, nonionic wetting agent, anti-creasing agent, nonionic detergent, water, Dye used: Drimaren Red X- 6BN.All chemicals and fabric were of commercially available analytical grade and used without further purification

**3.2.Methods**

Cationization of cotton fabric

- Methyl amine (40% concentration) - 40% (o.w.f)
- Temperature: 60oc
- Time:  60 min
- M: L= 1:10
- Fabric weight: 5gm

**3.2.1.Dyeing recipe**

- Drimaren Red X- 6BN : 2%, 4% Shade
- Wetting agent : 1 gm/l
- Sequestering agent : 1 gm/l
- Anti-creasing agent : 1 gm/l
- Acetic acid : 1 gm/L (for acid condition)
- Alkali (soda ash) : 2cc//l (for Alkali condition)
- M: L : 1:10
- Temp : 60$^oC$
- Time : 60 min
- Sample weight : 5 gm

**3.2.2.Soaping recipe**:

- Soaping agent: 1gm/L
- Sodium carbonate 1% solution.
- Temp: at 60$^oC$
- Time: 30 min

**3.3. Cationization of cotton fabric procedure description**

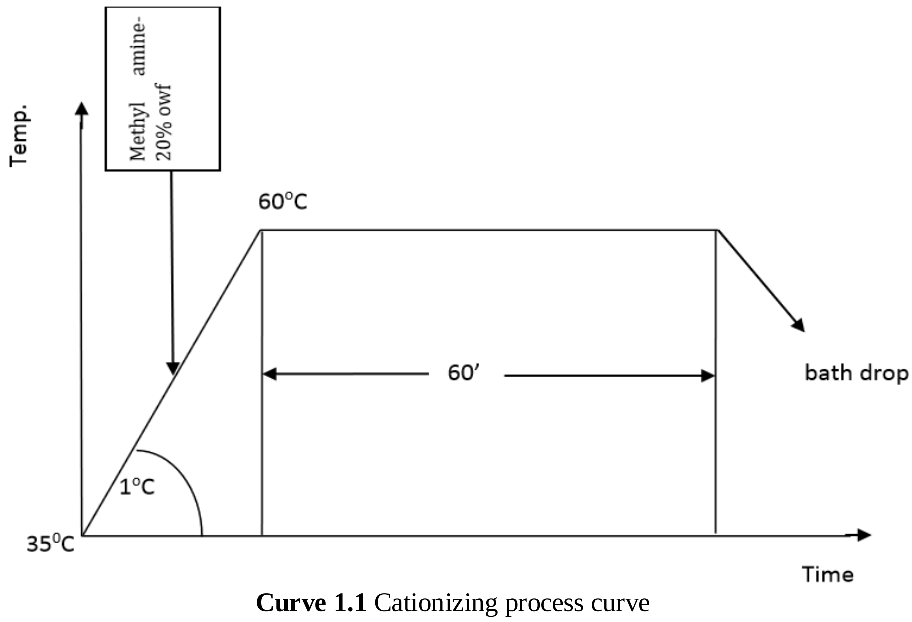
First of all, we took the cotton sample of Wight 5 gm to the pot of the machine. Then we prepared the cationizing bath by adding 40% methylamine of the weight of fabric. Cationizing process was started at 35$^oC$ and was raised at the rate of 1$^oC$ per min until 60$^0C$ for 60 min. After completing the cationization process bath was dropped without any kind of washing. The excess bath contents were fending off by rinsing the fabric. Then it was ready for the dyeing procedure. No salt and soda was needed during this process.

**3.4. Dyeing of cationization of cotton fabric procedure description**

Treated cationizing fabric was taken 5gm as specimen. Then dyeing was bath prepared according to the dyeing recipe. Load on the machine and then temperature was raised at the rate of 1$^oC$ per min from 35$^0C$ to 60$^oC$ and the dyeing was continued for 60 min. Then bath was dropped. Completing dyeing the fabric was treated by hot and soaping agent at 60$^oC$ for 30 min. And the fabric was neutralized by washing it with 1% Sodium carbonate solution. After that the fabric was given cold washed. Then dried the sample and ironing properly.

## IV. Process Curve

**4.1. Cationizing process curve**

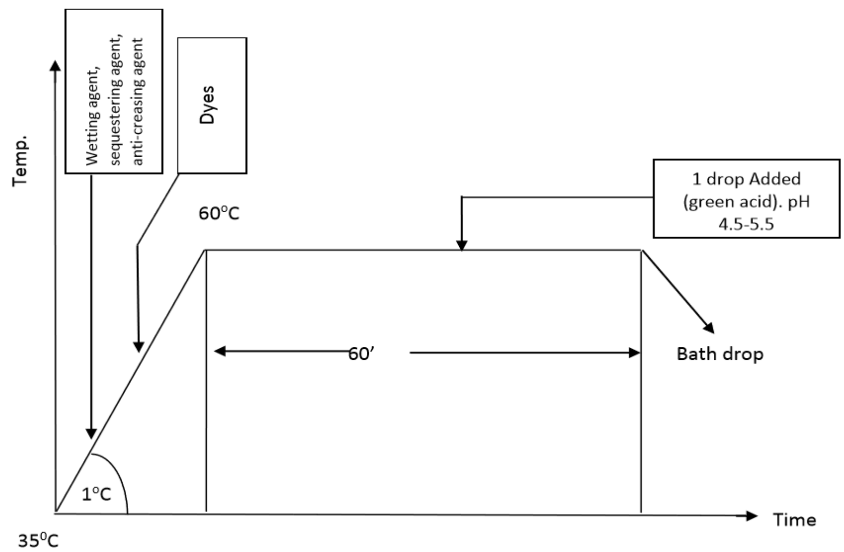



**Curve 1.1** Cationizing process curve

**Description:**

In curve no 1.1 represent X axis depend on time and Y axis depend on temperature. First of all, methyl amine 40% o.w.f is inserted in the cationization bath. In the inclined line means temperature raise at the rate of $1^oC$ per min. to $60^oC$. Its run time is 60 min and then bath drop.

**4.2. Dyeing process curve**

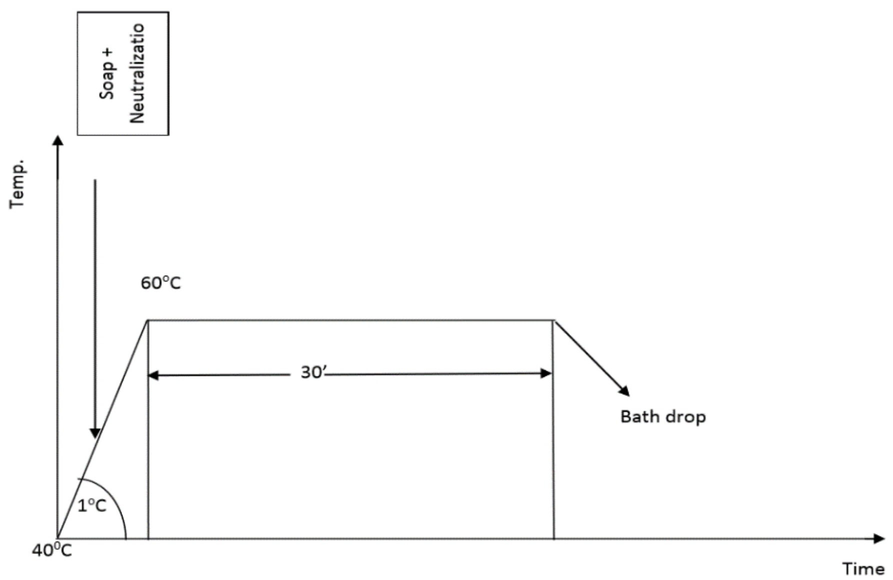



**Curve 1.2:** Dyeing process curve

**Description:**

In curve no 1.2 represent X axis depend on time and Y axis depend on temperature. First of all, wetting agent, anti-creasing agent and dyes are inserted in the dye bath. In the inclined line means temperature raise at the rate of $1^oC$ per min. to $60^oC$. Its run time is 60 min and then bath drop.

**4.3. Hot wash and soaping process curve:**




**Curve 1.3 Hot wash & soaping**

**Description:**

In curve no 1.3 represent X axis depend on time and Y axis depend on temperature. First of all, soap is inserted in the bath. In the inclined line means temperature raise at the rate of 1°C per min. to 60°C. Its run time is 30 min and then bath drop.

## V. TESTING

Testing and analysis of dyed sample

**5.1. For 4% shade:**

Neutral

**Fig: 4% Neutral condition**

Acid

**Fig: 4% Acid Condition**

Spectrophotometer reading difference:

a*= 4.56

b*=1.55

This value taken by D65, 10Deg. From the value a*, b* of spectrophotometer graph and it is seen that in acidic condition the shade is darker than neutral condition.

**5.2. For 4 % Shade**

Neutral

**Fig: 4% Neutral Condition**

Alkali

**Fig: 4% Alkali Condition**

Spectrophotometer reading difference:
a*= 0.17
b*= 0.58
This value taken by D65, 10Deg.
From the value a*, b* of spectrophotometer graph and it is observed that in alkalian condition result is better than neutral condition.

**5.3. For 2% shade**

Neutral
**Fig: 2% Neutral Condition**

Acid
**Fig: 2% Acid Condition**

Spectrophotometer reading difference:
a*= 4.80
b*= 0.14
This value taken by D65, 10Deg.
From the value a*, b* of spectrophotometer graph and visible we can say that in acidic condition result is better than neutral condition.

**5.4. For 2 % shade**

Neutral
**Fig: 2% Neutral Condition**

Alkali
**Fig: 2% Alkali Condition**

Spectrophotometer reading:

a*= 2.40

b*= 0.27

This value taken by D65, 10Deg.

From the value a*, b* of spectrophotometer graph and visible we can say that in alkalian condition result is better than neutral condition.

# VI. Result

### 6.1. Washing Fastness Test Results

**Wash Fastness test result for 4% Shade**

| Color change | | |
|---|---|---|
| 4% Neutral Condition | 4% Alkali Condition | 4% Acid Condition |
| 4 | 4 | 4-5 |

**Wash fastness test result for 2% Shade**

| Color change | | |
|---|---|---|
| 2% Neutral Condition | 2% Alkali Condition | 2% Acid Condition |
| 4 | 4 | 4 |

### 6.2. Color Fastness to Rubbing (Dry & Wet) Test result:

**CF to Rubbing test result for 4% Shade**

| Rubbing Fastness | | | |
|---|---|---|---|
| | 4% Neutral Condition | 4% Alkali Condition | 4% Acid condition |
| Wet | 3 | 4 | 4 |
| Dry | 4 | 4 | 4-5 |

**CF to Rubbing test result for 2% Shade**

| Rubbing Fastness | | | |
|---|---|---|---|
| | 2% Neutral Condition | 2% Alkali Condition | 2% Acid condition |
| Wet | 3 | 4 | 4 |
| Dry | 4 | 4-5 | 4-5 |

### 6.3. Perspiration Fastness Test Results

**CF to Perspiration Test result for 4% shade**

| Perspiration fastness | | |
|---|---|---|
| 4% Neutral Condition | 4% Alkali Condition | 4% Acid Condition |
| Acid- 3 | Acid- 4 | Acid- 4-5 |
| Alkali- 3 | Alkali- 4 | Alkali- 4-5 |

**CF to Perspiration Test result for 2% shade**

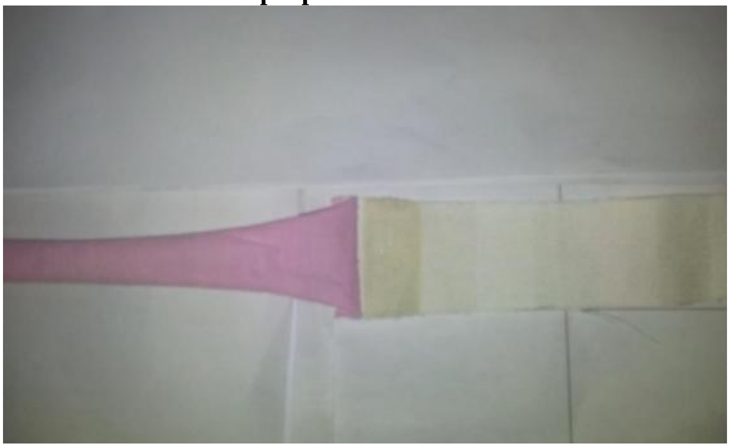
| Perspiration fastness | | |
|---|---|---|
| 2% Neutral Condition | 2% Alkali Condition | 2% Acid Condition |
| Acid- 3 | Acid- 4 | Acid- 4-5 |
| Alkali- 3 | Alkali- 4-5 | Alkali- 4-5 |

# VII. Discussion

### 7.1. Washing Fastness Test discussion:

| 4% Shade | Grade |
|---|---|
| 4% Neutral Condition | 4 Good |
| 4% Alkali Condition | 4 Good |
| 4% Acid Condition | 4-5 Very good |
| **2% Shade** | **Grade** |
| 2% Neutral Condition | 4 Good |
| 2% Alkali Condition | 4 Good |
| 2% Acid Condition | 4 Good |

**Sample picture attachment**



### 7.2. Color Fastness to Rubbing (Dry & Wet) Test discussion

**For 4% Shade**

**Dry Grade**

| | | |
|---|---|---|
| 4% Neutral Condition | 4 | Good |
| 4% Alkali Condition | 4 | Good |
| 4% Acid Condition | 4/5 | Very Good |

**Wet**

| | | |
|---|---|---|
| 4% Neutral Condition | 3 | Poor |
| 4% Alkali Condition | 4 | Good |
| 4% Acid Condition | 4/5 | Good |

**For 2% Shade**

| Dry | Grade | |
|---|---|---|
| 2% Neutral Condition | 4 | Good |
| 2% Alkali Condition | 4-5 | Very Good |
| 2% Acid Condition | 4-5 | Very Good |

**Wet**

| | | |
|---|---|---|
| 2% Neutral | 3 | Poor |
| 2% Alkali Condition | 4 | Good |
| 2% Acid Condition | 4 | Good |

**Sample pictures attachment**

**Fig:** Dry condition

**Fig:** Wet condition

### 7.3. Perspiration Fastness Test

Change in color (acid & alkali)

| For 4% Shade | Grade |
|---|---|
| 4% Neutral Condition | Acid- 3 (poor), Alkali-3 (poor) |
| 4% Alkali condition | Acid-4 (Good), Alkali-4 (good) |
| 4% Acid Condition | Acid- 4/5 (Very good), Alkali- 4/5 (very good) |

| For 2% Shade | Grade |
|---|---|
| 2% Neutral Condition | Acid-3 (poor), Alkali-3 (poor) |
| 2% Alkali Condition | Acid-4 (good), Alkali- 4/5 (very good) |
| 2% Acid Condition | Acid- 4/5 (very good), Alkali-4/5 (very good) |

**Sample pictures attachment**

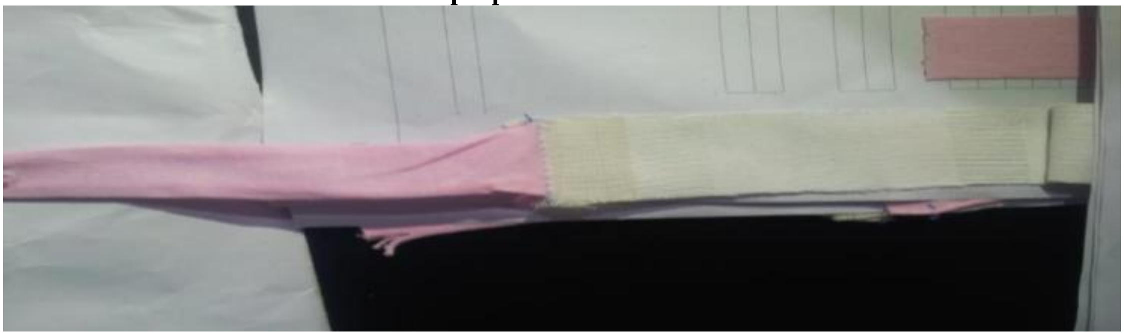


**Fig:** Perspiration Test Sample

**7.4. Effect of cationization on environment**

The effluent clearly depicts that the process with methyl amine produces effluent with an effluent load is more of less equal. Hence the dyeing effluent need not be sent to the effluent treatment plant which reduces the needs of plant capacity and investment. It leads to a substantial reduction in the dyeing cost. But in normal dyeing process produces more effluents. The effluent of cationized cotton dyeing method poses lesser loads than that of conventional dyeing. It is because of no addition of salt and alkali in the dye bath. The most beneficial part of the cationization technique is the reduction of TDS in the effluent as this cannot be removed from the effluent easily which need capital intensive and cost consuming treatments like reverse osmosis, nano filtration ion exchange etc.

## VIII. Conclusion

The purpose of this paper is to give an overall idea about the pre-treatment of cotton with a methylamine could enhance the dye ability of the fiber with reactive dyes. The methylamine contains primary amino groups, with which theoretically, a reactive dye should be able to react under acidic pH conditions. It is also decided to examine whether or not the methylamine could, under appropriate ph. conditions, assume a positive charge and so permit "salt & alkali free" dyeing.Pretreatment of cotton with chitosan enhances the possibility of dyeing cotton at neutral PH with various commercial reactive dyes and such pretreatment also brings about some chemical changes in the treated fabric. Fastness properties are adequate and quite comparable with conventionally dyed samples. The bending resistance of the dyed fabric also improves. The dyeing of cotton with reactive dyes using chitosan with cross-linker in the dye bath improves the dye ability of cellulosic fabrics with reactive dye. when dyeing the modified substrates; reactive dyes can be much more efficiently exhausted and fixed onto cellulosic fabrics under neutral conditions in the absence of salt and alkali

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