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Effective Method Development on Wool Dyeing by Using FI Based Cotton-reactive Dyes

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Abstract— Wool fibre is one of the most important fibres in textile technology. The coloration of wool fibre is usually being done by Acid dyes. Many experiments has been done on different protein fibres like silk fibres and wool fibres dyeing with reactive dyes. In this paper the coloration of wool fabric was conducted through FI based Reactive dyes (Liyuansol® FL & LANASOL®). An efficient dyeing method has been applied for wool dyeing with FI base Cotton - reactive dye. For the assessment of dyeing quality, dyed samples were conducted with several tests like wash fastness, rubbing fastness, effect of pH, Alagal B (Levelling agent) and Na_2SO_4 on dye uptake% and K/S value. Comparison also done among Reactive dyed samples and Acid dyed (Lanacron) samples and all of the results came up with good results and shows an impressive prospect on wool dyeing with cotton-reactive dyes.

Key Words— Wool Dyeing, Acid Dye, Reactive Dye, Liyuansol® FL, LANASOL®

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1. Introduction

Wool is a protein fibre of animal origin, used to manufacture the fabric under assessment. The basic type of wool used was merino wool, sometimes enriched with camel or Kashmir goat hair. Wool fibers of different origins may have varying diameters but still display similar properties. Wool consists of a chain of amino-acids residues joined together by amide linkages in the form of an α-helix. The side-chain methyl (R) groups control the properties of the protein. Wool can absorb almost one-third of its own weight in water. Wool ignites at a higher temperature than cotton and some synthetic fibers. It has a lower rate of flame spread, a lower rate of heat release, a lower heat of combustion and does not melt or drip. It forms a char which is insulating and self-extinguishing. It contributes less to toxic gases and smoke than other flooring products. Wool carpets are specified for high safety environments, such as trains and aircraft although it is specified for garments for firefighters, soldiers and others in occupations. Wool is considered by the medical profession to be hypoallergenic. The carboxylic acid and amino groups in the keratin molecule confer affinity for basic and acid dyes. Acid dyes are extensively used for dyeing wool fabrics. Since the bonds between dye anions and amino groups in the wool fibre are easily broken and re-formed, dyes attached in this way are liable to migrate. This property is advantageous in level dyeing is readily attained but it leads to low wash fastness and any undyed wool present during washing becomes stained.

These characteristics are chiefly apparent in dyes of low molecular weight and fastness to washing is much better in more complex dyes. The larger dye molecules are evidently attached with the fibre by some means other than the ionic bonds. It is believed that they are held by non-polar van der Waals forces exerted between hydrophobic dye anions and hydrophobic regions of the wool fibre [1-4].

TABLE 1: PHYSICAL PROPERTIES OF WOOL [5].

Parameters	Value
Specific Gravity	1.31
Moisture Regain	(13-16)%
strength-> Tenacity--> Dry	1.35 g/d
Elasticity--> Breaking extension	42.5%
Feel	Soft
Resiliency	Excellent
Abrasion resistance	Good
Dimensional Stability	bad

Chemical Composition of Wool:
The wool fibre is composed of several layers of different types of protein keratin, which consists of long polypeptide chains built from eighteen different amino acids. Most of these acids have the general formula $H_2N.CHR.COOH$ in which R is a side chain of varying character. At intervals bridges derived from the amino acid cystine connect the chains. Some of the side chains end in amino groups and others in carboxyl groups. Internal salts are therefore formed and the molecules are bound together by electrovalent linkages. The molecules of keratin are very large and average molecular weight estimated at about 60,000. The wool fibre is readily destroyed by alkali but withstands acid conditions fairly well some hydrolysis of peptide linkages occurs on prolonged boiling with acids [4]. The chemical structure of wool can generally be presented as follows:

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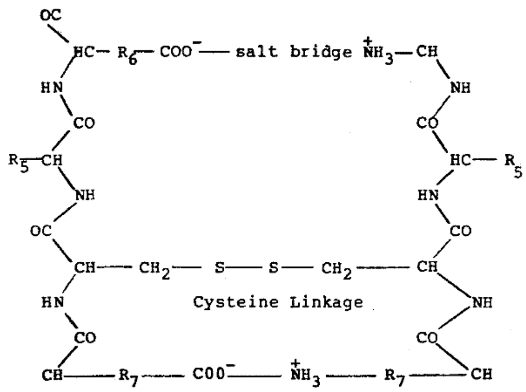


Figure 1: Chemical structure of wool fibre [6]

Where R5 equals groups linking other chains, R6 equals alkyl, amino or side chain groups such as found in proline and tyrosine and R7 equals short chain linkage groups [6]. Concentrated sulphuric acid decomposes wool completely. Wool is resistant to mineral acids of all strength even at high temperature, though nitric acids tend to cause damage by oxidation. Dilute acids are used for removing cotton from mixtures of two fibers. Sulphuric acid is used to remove vegetable matter in the carbonizing process. The chemical nature of wool keratin is such that it is particularly sensitive to alkaline substances. Wool will dissolve in caustic soda solutions that would have little effects on cotton. Strong alkaline effect on wool fiber but weak alkaline does not affect wool. Wool does not affect in organic solvents. Basic dye, direct dye and acid dye are the most common and suitable dye stuffs for dyeing wool [7].

Wool Dyeing With Acid Dye:

Acid Dyes contain acid groups in the dye molecules and the dyeing action takes place in an acidic medium. During the dyeing process the dyestuff can migrate and takes places through three activities. The dyes are absorbed onto the fibre, can diffuse through the dye bath and also be desorbed from the fibre back into the bath. These activities are all occurring at the same time and lead to evenly distributed throughout the fibre before being fixed. The ability of Acid Dyes to dye very evenly is enhanced further by the use of two chemicals – Glauber Salt and a levelling agent. Glauber Salt helps the migration of the dyes. Most dye manufactures develop specific levelling agents for use with their own ranges of acid dyes. An example of this is Lyogen MF developed for use with the Acid dyes. These chemicals promote the penetration of the dye into the fibre and are also particularly good at reducing the variation in color between the root and the tip of the wool fibre. Dyeing processes with Acid dyes commence with warm water (about 50^{o}C) because fixation to the fibre becomes more pronounced as the temperature is raised. If the dye bath is too hot to start with or is heated too quickly, then the dyes would fix rapidly and the resultant dyeing would be uneven. In other words dyestuff would not have the chance to go through the absorption, diffusion, desorption process to become evenly distributed through the fibre [8]. Acid groups presents in acid dyes, such as –COOH and $–SO_3H$ attractions to the slightly basic –NH groups in the amide links of wool, silk and nylon:

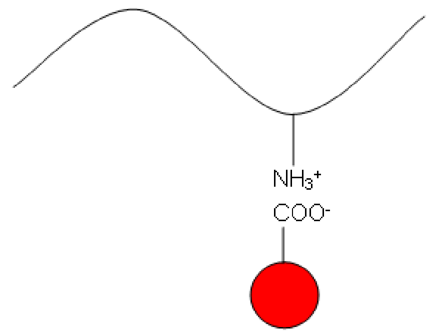
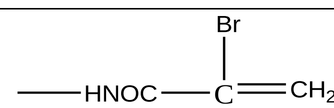
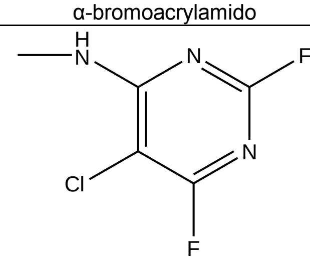
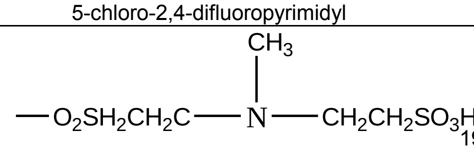
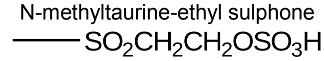


Figure 2: Wool dyeing with acid dye

Wool Dyeing With Reactive Dye:

The groups present in the dyestuff, capable of reacting with sites in the fibre – such as hydroxyl groups in cellulosic fibres, and amino, thiol and hydroxyl groups in wool – is a potential reactive system capable of incorporation in a reactive dye molecule. In practice many restrictions have been found on the type of reactive group employed, such as level of reactivity, stability to hydrolysis, stability of the dye–fibre bond and not least, cost and ease of manufacture. Reactive groups in commercially available reactive dyes used for wool dyeing are of two types: systems that react by nucleophilic substitution reactions and those that react by the Michael addition reaction [9].

TABLE 2: REACTIVE DYES FOR WOOL [9]

Commercial Name	Reactive Group	Year of Introduction
LANASOL® (CGY)	 α-bromoacrylamido	1966
Drimalan F (S)	 5-chloro-2,4-difluoropyrimidyl	1969
Hostalan (HOE), Hostalan E (HOE)	 N-methyltaurine-ethyl sulphone  β-sulphatoethyl sulphone	1971

Specific reactive dyes for wool:

LANASOL® (CGY) dyes was appeared in 1966, have been the most successful class of reactive dyes for wool. Of especial value has been the compatible trichromatic system

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based on LANASOL® Yellow 4G, Blue 3G and Red 6G (respectively CI Reactive Yellow 39, Blue 69 and Red 84). **Drimalan F (S)** dyes are chlorodifluoropyrimidine (FCP) derivatives. They are regarded as bifunctional in their substitution reactions with the nucleophilic sites in wool, since both fluorine atoms are capable of reaction. Hildebrand and Meier [10] observed that the fluorine atom in position 4 reacts first but under dyeing conditions at the boil the fluorine atom in the 2-position, though less strongly activated, is also eliminated by nucleophilic substitution. This bifunctional character, coupled with exceptional resistance to hydrolysis in the pH region 5–7, leads to a very high degree of dye–fibre covalent bonding and hence to very good wet-fastness properties of the dyeings. Again Zollinger et al. [11] found evidence of fibre crosslinking with this type of reactive group, using fibre solubility tests. The high resistance to hydrolysis of the FCP reactive group may be explained by the inability of the pyrimidine ring system to absorb a proton under acid dyeing conditions, unlike the triazine or quinoxaline ring systems. **Hostalan (HOE) and Procilan E (ICI)** dyes are blocked vinyl sulphone derivatives [12, 13] which gradually activate to the reactive vinyl sulphone at elevated temperatures, even under slightly acidic conditions. The main advantage of such a system is an improvement in dye levelness, due to suppression of dye–fibre covalent bonding at temperatures below the boil. It is believed that the Hostalan E brands are the most level-dyeing Nmethyltaurine adducts and the other Hostalans are β-sulphatoethyl sulphones specially selected for their ready formation of the reactive vinyl sulphone form under the weakly acidic boiling conditions required for wool dyeing. Fuchs and Konrad [14] have, however, claimed that the Hostalan E dyes are selected only from aromatic disulphonated chromophores.

Reactive dyes for wool would probably not have been commercially successful without parallel developments in auxiliary products. Without the appropriate auxiliary, dyeings would have been skittery if not grossly unlevel, and the concept of trichromatic mixture shade dyeing unrealised. **Ciba-Geigy** introduced the amphoteric auxiliary product Albegal B at the same time as the launching of the LANASOL® dyes. This unusual group of levelling agents overcome the tippy dyeing properties of wool by forming dye–surfactant complexes which at low temperatures probably exhaust more evenly and extensively on to the surface of the wool fibre than does the dye alone. As the dyebath temperature is raised the dye–surfactant complex breaks down, allowing the dye to penetrate and react with the fibre. The amount of this type of auxiliary normally recommended to be used is 1% o.m.f., but for deep dyeings it is necessary to employ up to 1.5% o.m.f [9].

TABLE 3: AUXILIARY PRODUCTS FOR USE WITH REACTIVE DYES [9]

Range of dyes	Auxiliary product
Drimalan F (S)	Lyogen FN
LANASOL® (CGY)	Albegal B
Hostalan (HOE)	Eganol GES
Verofix (BAY)	Avolan REN

These agents actually promote dye uptake and hence dye fixation on the wool fibre.

2. METHODS AND MATERIALS

2.1 Raw materials

Wool fabric sample was obtained from wool manufacturing company. Reactive dyes LIYUANSOL® Based & LANASOL® were obtained from Color Root (Hubei) Technology Company Ltd. in China & Huntsman Dyes respectively. Sodium Carbonate (Na_2CO_3), Sodium sulphate (Na_2SO_4), Acetic Acid (CH_3COOH) & Detergent have been used as other chemicals and auxiliaries.

LIYUANSOL® (Color Root)

Liyuansol® series is a fluorine based reactive dyes contain a vinyl sulphone and a triazine group, they are economic and often used in the dyeing and printing process. Full range of shades and have some brilliant dyes. Those series are widely used for cotton dyeing.

LANASOL® (Huntsman)

LANASOL® consists of sulfo-group-containing reactive dyes which have been especially developed for wool dyeing. They contain 1 or 2 bromo-acrylamide reactive groups which form a covalent bond with the nucleophilic groups of the wool's amino acids during the dyeing process, resulting in outstanding wet fastness properties.

2.2 Wool dyeing process with reactive dyes

The isoelectric point of wool fibre is pH 3.5 to 4.0. This pH range is comparatively safe for wool dyeing [15]. Dye manufacturers recommended processes have been adapted in this experiment for dyeing of wool with reactive dyes (Figure 3). The wool dyeing recipe was maintained as: Material: Liquor = 1:100, Dye concentration = 2% (owf), Albegal B = 10 ml/l, Na_2SO_4 = 5% (owf), Time = 100-120 min, Temperature = 90°C, pH = variable.

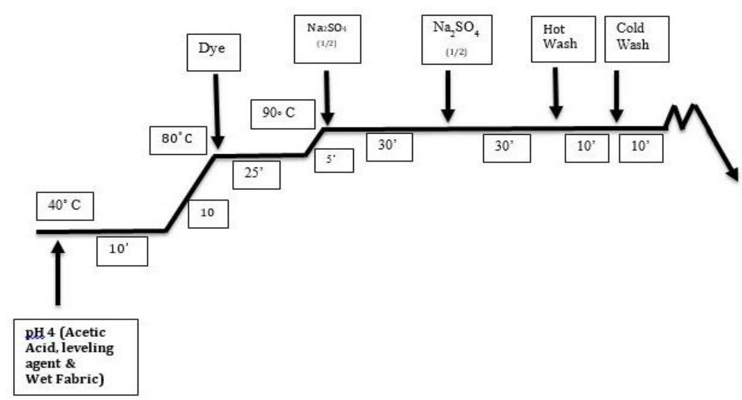

Figure 3: Process curve of wool dyeing with reactive dye

2.3 Measurement of pH

Digital pH meter has been used to measure and maintain the pH in dye bath solution.

2.4 Color Strength (K/S) Measurement

K/S value of the dyed fabric has been measured by using Spectraflash 650 Spectrophotometer (Data Color

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International, USA).

2.5 Dye uptake

Dye concentration was measured by a UV/VIS spectrophotometer and the dye uptake percentage was calculated according to following equation:

$$\text{Up take \%} = (C_o - C)/C \times 100\%$$

C_0 → Concentration of the Dye in solution before dyeing
C → Concentration of the Dye in solution after dyeing

2.6 Fastness Testing

2.6.1 Color Fastness to wash

ISO 105 C03 was followed to carry out the wash fastness test for both acid and reactive dyed samples. Dyed sample was prepared as 10 x 4 cm and placed between two adjacent fabrics and stitched. The sample and the adjacent fabric were washed together. The washing solution was preheated to the required temperature of washing. The liquor ratio 1:50. After soaping treatment, the specimen is removed, rinse twice in cold water and then in cold running tap water. Squeezed and dried in air at a temperature not exceeding 60°C. The value is evaluated with the help of grey scale.

2.6.2 Color fastness to rubbing

ISO 105 X 12 was followed to carry out the rubbing fastness test, for both acid and reactive dyed samples.

3. Result and Discussion

3.1 Effect of pH on dye uptake % & K/S value during wool dyeing with reactive dyes

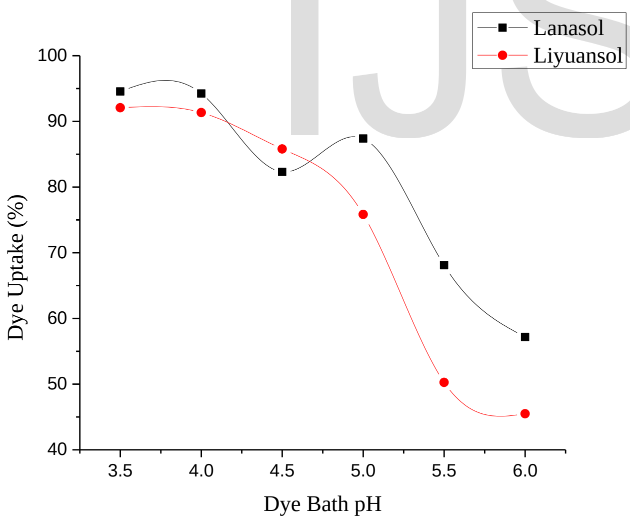

Figure 4: Effect of pH on dye uptake % of wool dyeing with reactive dyes

As wool is also protein fiber it needs to be protonated before dyeing. Acetic acid is used to control the pH. Figure 4 shows that the dye uptake % is maximum at pH 3.5-4.0. For LANASOL® the dye uptake is 94.55% (at pH 3.5) and 94.24% (at pH 4). For Liyuansol® the dye uptake % is 92.08% (at pH 3.5) and 91.34% (at pH 4.0). So, the relation come up as with the increase of pH dye uptake % decreases.

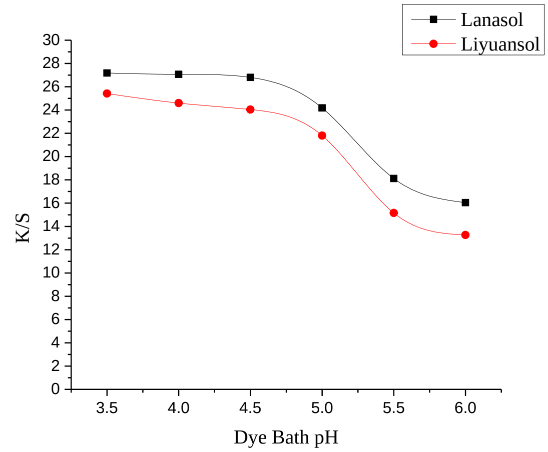

Figure 5: Effect of pH on K/S value of wool dyeing with reactive dyes

The effect of pH on dye strength (K/S) has similar effect like dye uptake %. At 3.5-4.0 the K/S is very high and it decreases with the increase of pH value of dye bath (Figure 5).
So, from Figure 4 & Figure 5 it can be decided that, for optimum level of dye uptake % and K/S value, the pH range should be 3.5-4.0.

3.2 Effect of Albegal B (Leveling Agent) on Dye uptake % & K/S Value of wool dyeing with reactive dyes

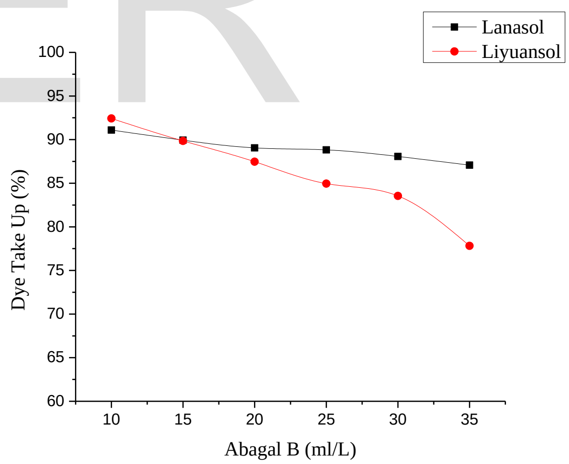

Figure 6: Effect of Albegal B on dye uptake % of wool dyeing with reactive dyes

Leveling agent Albegal B was applied in the process of wool dyeing to get uniform dyeing. From Figure 6Figure 6 & Figure 7 it can be seen that there are little effect of Albegal B on dye uptake % and K/S value and the shade was found uniform by using 10ml/l Albegal B during wool dyeing. The pH was maintained to be around 4.0.

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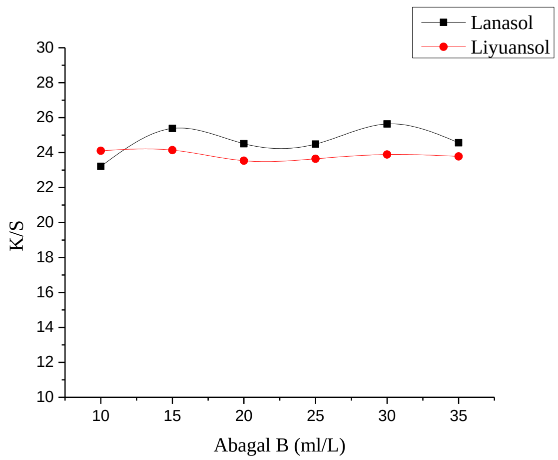

Figure 7 Effect of Albegal B on K/S value of wool dyeing with reactive dyes

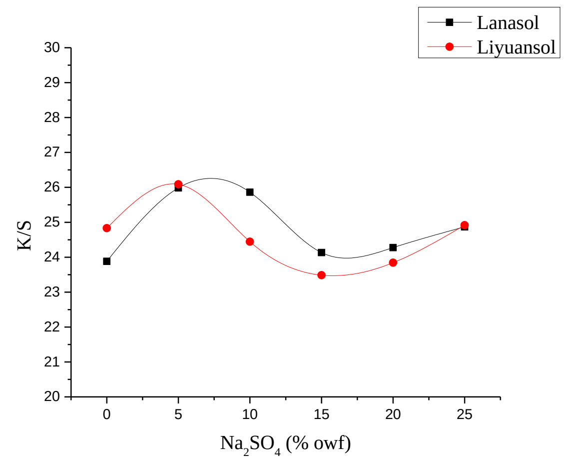

Figure 9 Effect of Na_2SO_4 on K/S value of wool dyeing with reactive dyes

3.3 Effect of Na_2SO_4 on dye uptake % & K/S value of wool dyeing with reactive dyes

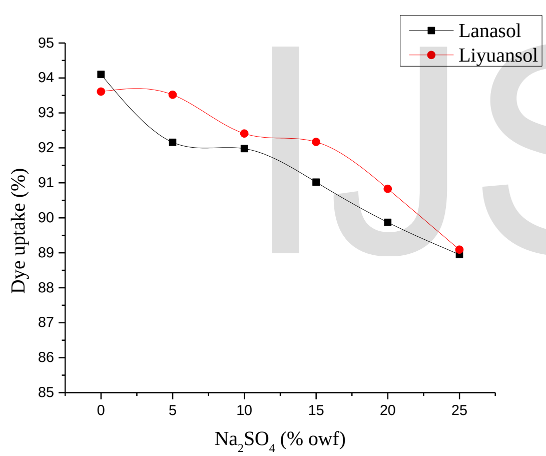

Figure 8 Effect of Na2SO4 on dye uptake % of wool dyeing with reactive dyes

Na_2SO_4 has little effect on dye uptake % (Figure 8) and K/S value (Figure 9). Without any Na_2SO_4 the dye uptake % was approximately 94.0% for both LANASOL® and Liyuansol®. With the increase of amount of Na_2SO_4 the dye uptake % decreased slightly but the change is not significant. Even the dosage of Na_2SO_4 is maximum the dye uptake % was approximately 90%.
According to the experimental result and graph analysis, for getting the optimal level of dye uptake % and K/S value the amount of Na_2SO_4 should be 5% (owf).

3.4 Quality tests for wool

3.4.1 Color Fastness to Wash:

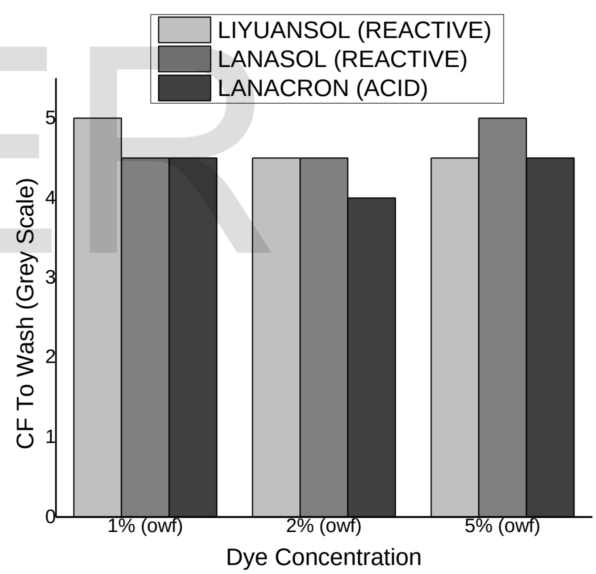

Figure 10: Colum diagram of color fastness to wash

From Figure 10 it can be seen that, reactive dyed samples gave the best wash fastness results comparing to acid dyed samples. For reactive dyed samples the grading belongs to 4.5 to 5 and for acid dyed samples the gray scale grading belongs to 4 to 4.5.

3.4.2 Color Fastness to Rubbing:

Wet Rubbing

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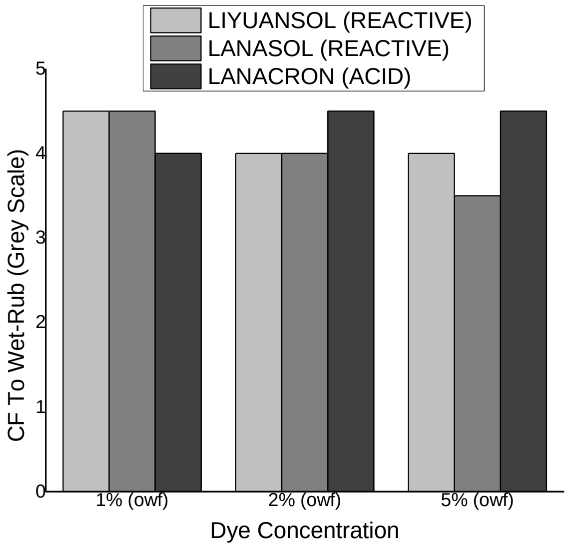

Figure 11: Colum diagram of color fastness to wet rubbing

From Figure 11 it can be seen that, in case of Liyuansol® (Reactive) dyed samples gives good wash fastness result and its grading belongs to 4 to 5. On the other hand LANASOL® (Reactive) dyed samples grading relatively low (3.5 to 4.5). For acid dyed samples the gray scale grading belongs to 4 to 4.5. So, no significant difference was found among reactive and acid dyed samples for wet rubbing fastness.

Dry Rubbing

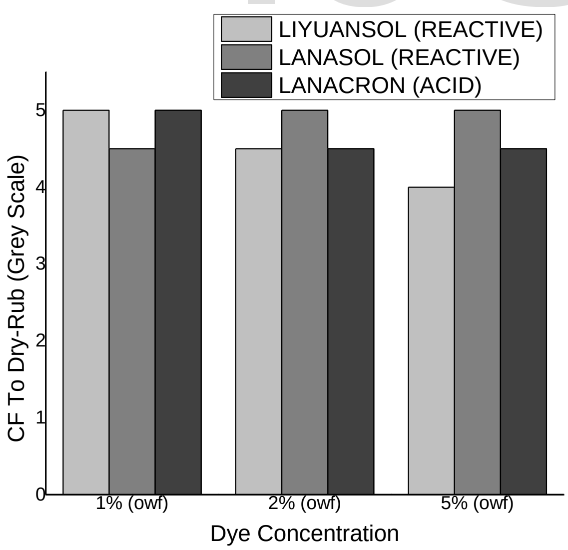

Figure 12: Colum diagram of color fastness to dry rubbing

From Figure 12 it can be seen that, in case of Liyuansol® (Reactive) dyed samples wash fastness result decreased with the increase of shade % but still gives good wash fastness result and its grading belongs to 4 to 5. On the other hand LANASOL® (Reactive) dyed samples gives excellent wash fastness (4.5 to 5). For acid dyed samples the gray scale grading belongs to 4.5 to 5. So, no significant difference was found among reactive and acid dyed samples for wet rubbing fastness.

4. Conclusion

This experiment contains two parts, the first part contains application of a new technique on wool fabric dyeing with two different brands of reactive dyes (Liyuansol® FL, LANASOL®) and in the second part comparison on the fastness properties of reactive dyed samples and acid dyed samples (Lanacron) was made.

In case of reactive dyed samples of wool fabric, the comparative analysis or correlation was made on dye uptake % and K/S value on the basis of pH, Albegal B (levelling agent) and Na2SO4. It has come out that there is no significant difference in those correlations or results due to different dyestuffs of LANASOL® and Liyuansol®. The graphical presentation, about the effect of pH on dye uptake % and K/S value indicated that for the same pH value (3.5) LANASOL® gives more dye uptake % and more K/S value comparing to others., though the difference is not that much significant.

On the other hand, comparing the samples of reactive dyed wool fabrics and acid dyed wool fabrics, it does not show any significant difference but reactive dyed samples (LANASOL® & Liyuansol®) gives comparatively better wash fastness properties than other samples dyed with acid dye.

Over all it can be said that wool fabric dyeing with reactive dyes has a good prospect in the field of textile wet processing.

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