A Comparative Study on Silk Dyeing with Acid Dye and Reactive Dye

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Abstract — Silk has always been the symbol of royalty due to its lustrous appearance and peach like softness. The coloration of this royal fiber is also an art form. The process varies largely in the form of hanks and woven pieces. There are numerous ranges of dyestuff available for use of silk dyeing. Almost every class of dyestuff used for cotton or wool can be used for dyeing silk. In general the dyestuffs are applied by techniques similar to those of wool or cotton. This research paper shows a comparative analysis of silk dyeing with acid dye, which is commonly used and reactive dye, which is more commonly applied on cotton. The study focuses on the dye uptake, different types of fastness properties and the strength of the dyed samples. It was found that reactive dyes showed better dye uptake and color fastness on silk than acid dyes but comparatively the strength of the fibre was decreased.

Index Term — Acid dyes, Fastness, Lanasol, Nylosan, Reactive dyes, Silk dyeing.

1.0 INTRODUCTION
Silk is a natural protein, like wool fibre, due to this, mechanism of dyeing silk is dependent not only on free amino and carboxyl groups but also on phenolic with accessible =OH group. Because of slightly cationic character of silk with isoelectric point at above pH 5.0, it can be dyed with anionic dye such as acid, metal complexes, reactive and selected direct dyes. But the main objective of coloration of a textile fibre is that the permanency of the color and should not allow damage of natural abstract of fibre. This implies that it should not destroy its color during processing following coloration and dyeing & subsequent useful life (i.e. washing, light, rubbing, perspiration, and saliva). So whatever dyestuff we use for silk dyeing it is very essential to have permanency of that dyestuff.

In this study there are three major components which are silk fibre, acid dyes and reactive dyes. This paper starts with some information on the silk fibre and about acid dyes and reactive dyes for silk are discussed. Finally, the results and discussions are presented.

2.0 LITERATURE REVIEW
Silk called the “Queen of fibres” is a continuous protein fibre produced by silkworm so as to form its cocoon. The silk fibre is also produced by some spiders belonging to the Arachina family. Unlike the silk worm’s fibre, the spider’s fibre cannot be commercially produced, and therefore the silk fibre referred to in this work is the fibre coming from the silkworm. Most historians agree that silk and sericulture the cultivation of silkworm had their origin in China nearly 2500 BC. After finding this knowledge China kept it as a secret and held a monopoly in the silk industry for nearly 4000 years. After this period, sericulture spread to Korea and Japan and it also spread around the world.

Silk fibre is natural protein fibre. Unlike wool, silk contain very small amount of sulphur. There are two main types of silkworm, mulberry silk also called ‘cultivated silk’ and wild silk of which Tussah silk is the most important representative.

2.1 Chemical Composition of silk
The strands of raw silk as they are unwound from the cocoon consist of the two silk filaments mixed with sericin and other materials. About 75 % of the strand is silk i.e. fibroin and 23 % is sericin; the remaining materials consist of fat and wax (1.5 %) and mineral salts (0.5 %).

The mature silkworm builds its cocoon by extruding viscous fluid from two large glands in the body of silkworm. This solution is extruded in the head of silkworm into a common spinneret. The viscous part (fibroin) is covered by another secretion (sericin) which flows from two other symmetrically placed glands. These two components are cemented together by emerging into the air, coagulating and producing a firm continuous filament. As a consequence of this spinning process, the fibre has two main part sericin and fibroin. Sericin called silk gum a minor component of the fibre (i.e. 25% of the raw silk) and it also has some impurities such as waxes, fats and pigments. Sericin is yellow, brittle, and inelastic substance. It acts a twin fibroin filament and conceals the unique lustre of the fibroin. Sericin is an amorphous structure and it is dissolved in a hot soap solution. The greatest sericin content is present in outer layer of cocoon whereas the least sericin is present in the innermost layer of the cocoon. Fibroin is the principal water insoluble protein (i.e. 75% of the weight of raw silk) .fibroin has highly oriented and crystalline structure.
2.2 Dyeing of silk with acid dye

The acid dyestuff are so called because, in the first place the original members of the class were applied in a bath containing mineral or organic acid and secondly because they were nearly all sodium salts of organic acid and the anion is active colored component. Acid dyes are usually sodium salts of sulphonic acids, of less frequently of carboxylic acids and are therefore anionic in aqueous solution. They will dye fibres with cationic sites. These are usually substituted ammonium ion such as wool, Silk and nylon. These fibres absorb acids. The acid protonates the fibre’s amino groups, so they become cationic. Dyeing involves exchange of the anion associated with an ammonium ion in the fibre with a dye in the bath.

Reaction of silk fibre with acid dye:

\[
\text{Fibre-}\text{NH}_2[\sigma] + \text{H}^+ [aq] + \text{HSO}_4^- [aq] \rightarrow \text{Fibre-}\text{NH}_3^+ \text{HSO}_4^- [\sigma]
\]

\[
\text{Fibre-}\text{NH}_3^+ \text{HSO}_4^- [\sigma] + \text{Dye-}\text{SO}_3^- [aq] \rightarrow \text{Fibre-}\text{NH}_3^+ \text{Dye-SO}_4^- [\sigma] + \text{HSO}_4^- [aq]
\]

Fig. 1. Reaction of silk fibre with acid dyes.

2.2.1 Chemical Structure of acid dyes

Acid dyes are of many different chemical types. Sulphonated azo dyes constitute the major group and are mainly mono and bis-azo compounds ranging in colour from yellow, through red to violet and brown. There are some navy blue bis-azo dyes that can build up to give blacks. The substantivity of azo dyes for polyamide and protein fibres is greater. The higher their molecular weight and the lower the number of sulphonate groups per dye molecule. Anthraquinone acid dyes complement the azo dyes, ranging in colour from violet through blue to green. These dyes often have very good light fastness. Acid dyes with triphenylmethane (blues and greens) and xanthenes (reds and violets) chromophores are less important types noted for their brilliant colours. These often have only poor light fastness. Sulphonated copper phthalocyanine dyes provide bright turquoise dyes of very good light fastness.

Acid dyes are commonly classified according to their dyeing behavior, especially in relation to the dyeing pH, their migration ability during dyeing and their washing fastness. The molecular weight and the degree of sulphonation of the dye molecule determine these dyeing characteristics. The original classification of this type, based on their behavior in silk dyeing, is as follows:

- Level dyeing or equalizing acid dyes;
- Fast acid dyes;
- Milling acid dyes;
- Super-milling acid dyes.

The chemical constitutions of some typical acid dyes are as follows

![Chemical constitutions of some typical acid dyes](image)

In this study NYLASON RED N – 2RBL was used, which is one class of acid dye manufactured by “Clariant” and the recommended properties of this class are given bellow

- The chemicals constitution of these dyes is mono-sulphonated dyes group.
- Good migration property.
- Very good end use fastness properties.
- Good washing fastness and low staining in polyamide.
- Medium light fastness.
- High rate of fixation.
- Good coverage of barre.
- High rate of exhaustion.
- Metal free.
- This is ideal dye for medium to dark shades.

2.3 Dyeing of silk fibre with reactive dye

Fibre reactive dyes are anionic water soluble colored organic compounds that are capable of forming a covalent bond between reactive groups of the dye molecule and nucleophilic groups on the polymer chain within the fibre. Consequently, the dyes become chemically part of the fibre by producing dye-polymer linkages. In this regard, covalent dye-polymer bonds are formed, for instance, with the hydroxyl groups of cellulose, the amino, hydroxyl and mercapto groups of proteins and the amino groups of polyamides (figure 3).
The possibility of forming a covalent bond between dyes and fibres had long been attractive to dye chemists, since attachment by physical adsorption and by mechanical retention had the disadvantage of either low wash fastness or high cost. It was anticipated that the covalent attachment of the dye molecules to the fibre would produce very high wash fastness because covalent bonds were the strongest known binding forces between molecules. The energy required to break this bond would be of the same order as that required breaking covalent bonds in the fibre itself.

Reactive dyes were initially introduced commercially for application to cellulosic fibres, and this is still their most important use. Reactive dyes have also been developed commercially for application on protein and polyamide fibres.

2.3.1 Constitutional characteristics of reactive dyes
The four characteristic features of a typical reactive dye molecule are a reactive group (R) containing leaving group (X), a chromophoric group (C), a bridging group (B) and a solubilising group (S) as shown in following figure.

![Fig. 4. Typical constitutional features of a reactive dye](image)

2.3.2 Reactive dyes for silk
Theoretically, all reactive dyes can be used for silk dyeing; however, to achieve the best quality of dyed silk fibre, reactive dyes have to satisfy the following special requirements:
- Brilliance of shade: This is especially important for silk because many dyes on silk are much duller and the dyed silk shows lower degree of exhaustion.
- pH of the dye bath: Silk is damaged in an alkaline medium at high temperatures, so the reactive dyeing should be carried out in an acidic or neutral dyeing bath.
- Good storage stability: The consumption of dyes in the batch dyeing of silk is small, so the dyes should be highly stable in storage.
- Degree of covalent bonding: A high degree of covalent bonding should be achieved at the end of the dyeing process, minimizing the clearing treatment required to give maximum wet fastness.
- The rate of adsorption should be higher than the rate of reaction; otherwise the dyeing will be uneven.

The reactivity should be moderate. A highly reactive dye will react even at low temperature reducing the possibility of leveling and migration. A dye of low reactivity, on the other hand, requires extended time of dyeing at boil with consequent damage of material.

Three ranges of reactive dye are at present commercially available that can be used on silk (Table II). All these system generally satisfy the requirements that have been discussed earlier.

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Reactive group</th>
<th>Year of introduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZANASOL RED B</td>
<td></td>
<td>1966</td>
</tr>
<tr>
<td>Lanasol Blue 3G</td>
<td></td>
<td>1971</td>
</tr>
</tbody>
</table>

Among the three ranges, Lanasol RED B dye manufactured by Swiss Colours was used to carry out the silk dyeing that has been discussed in the next segment.

![Fig. 5. Chemical constitutions of typical Lanasol range dyes](image)

Lanasol Blue 3G  Lanasol Scarlet 3G

2.3.3 Lanasol dyes
Lanasol dyes (Ciba, 1966) are most successful reactive dyes that can be used on silk. Trichromatic dyeing (i.e. matching of a large number of shades with three dyes) is possible using Lanasol Yellow 3G, Blue 3G, and Red 6G (CI Reactive Yellow 39, Blue 69 and Red 84 respectively) as they have almost identical dyeing properties.

These dyes are noted for their brightness, high reactivity and good all-round fastness to light and wet treatments. These dyes are essentially bi-functional dyes, provided sufficient nucleophilic groups are available for reaction and these reactions are not sterically hindered. The dyes are reported to be α, β-dibromopropionyl amide dyes, which are being converted to α-bromoacrylamide by simple elimination of hydrogen bromide on dissolving in water.

![Fig. 6. elimination of hydrogen bromide](image)
Some Lanasol dyes have two α-bromoacrylamide groups (Scheme ), e.g. Lanasol Red 2G, Lanasol Scarlet 3G, Lanasol orange R (respectively CI Reactive Red 116, Red 178 and Orange 68). The level of fixation of these dye is particularly high, leading to very high wet fastness properties; in fact these dyes maybe looked upon as tetra functional.

2.3.4 Dyeing process and techniques
In similar way to cellulose dyeing, the dyeing of silk can be accordingly divided into three steps:
- Adsorption of the dye to the fibre surface from the dyeing bath
- Diffusion of the dye into the interior of the silk fibre
- Fixation of the dye with reaction centers in fibroin.

The following factors have to be considered when choosing the dyeing conditions:
- The reactivity of the dye
- The ratio of fixation and hydrolysis of the dye
- Protonation of the fibroin
- Damage to silk fibre.

Three modes of dyeing are usually used in silk dyeing:
- Exhaustion in acidic or neutral bath and fixation in alkaline media
- Exhaustion and fixation by a one-step process in an acidic or a neutral bath
- Cold pad-batch in alkaline medium.

3.0 EXPERIMENTAL

3.1 Materials
The fabric used was a scoured and bleached 100% silk (plain weave). The chemicals and reactive dyes (LANASOL) were collected from Swiss color while the acid dyes (NYLASON) were from Clariant.

3.2 Dyeing
Dyeing was done in a bath having material to liquor ratio of 1:60 with different dye concentrations in an automatic laboratory dyeing machine and the dye manufacturers’ recommended processes were followed. The dyed fabrics were then washed, rinsed, and dried. The pH of dyeing solution was maintained with acetic acid and sodium carbonate.

3.3 Color Measurement
Color was evaluated in terms of K/S values, ΔE, and CIE Lab coordinates (Illuminant D65/10° observer) with a Data color 650 spectrophotometer.

3.4 Fastness Testing
Fastness to washing of the dyed samples was evaluated by ISO 105 C03 method in Gyro wash (James H. Heal & co. ltd.; Halifax, England. Model No. : 415). Rubbing fastness was evaluated by ISO 105 X12 method with a crock-meter which has a finger of 1.6 cm diameter and can be moved to and fro in a straight 10 cm track on the specimen and color fastness to perspiration was evaluated by ISO 105 E04 method with artificial perspiration solutions (acidic and alkaline). Two sets of standard grey scales were used to assess the colorfastness:
- Grey Scale for change in color
- Grey Scale for staining.

3.5 Strength Testing
Strength test was carried out by the standard methods of ASTM D5034 with a computerized strength test machine namely “Universal Strength Tester (Titan)”.

4.0 RESULTS AND DISCUSSIONS

4.1 Effect of Dye Concentration on Dye Uptake

![Dye uptake at different dye concentrations](image)

Figure 7 shows the effect of dye concentration on dye uptake. Dye uptake increased progressively as colorant concentration increased. With increasing concentration, more dye transferred to fabric and the depth of color became stronger. From the above bar diagram it is clear that the reactive dyes show higher dye uptake than acid dyes at higher dye concentrations.

4.2 Color fastness to washing
For both acid and reactive dyed silk, the assessment result of changes in color and staining are listed in the table IV & V.
In case of color change, from the grey scale value of table IV it is clear that the color of acid dyed silk is changed more than reactive dyed silk. In case of staining about all fibres of multifibre fabric are stained by acid dyed silk and reactive dyed silk (table V). But it is noticeable in assessment that Di-acetate, polyamide, polyester are more stained than any other fibre of multifibre fabric.

### 4.4 Color fastness to perspiration

The assessment of table VI and VII shows that very little color is transferred to un-dyed cotton cloth from both acid and reactive dyed silk. So it can be said that color fastness to rubbing for both acid and reactive dyes are satisfactory.

### 4.2 Color fastness to rubbing

<table>
<thead>
<tr>
<th>Acid dyed sample</th>
<th>Reactive dyed sample</th>
<th>Multifibre fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid dye 1%</td>
<td>Acid dye 2.5%</td>
<td>Acid dye 5%</td>
</tr>
<tr>
<td>Di-acetate</td>
<td>5</td>
<td>4-5</td>
</tr>
<tr>
<td>Bleached cotton</td>
<td>5</td>
<td>4-5</td>
</tr>
<tr>
<td>Polyamide</td>
<td>5</td>
<td>4-5</td>
</tr>
<tr>
<td>Polyester</td>
<td>5</td>
<td>4-5</td>
</tr>
<tr>
<td>Acrylic</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Wool</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Grey scale value (color change)</th>
<th>1% dye conc. (owf)</th>
<th>2.5% dye conc. (owf)</th>
<th>5% dye conc. (owf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid dyed sample</td>
<td>4-5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Reactive dyed sample</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Grey scale value (color change)</th>
<th>1% dye conc. (owf)</th>
<th>2.5% dye conc. (owf)</th>
<th>5% dye conc. (owf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid dyed sample</td>
<td>Dry</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Wet</td>
<td>5</td>
<td>5</td>
<td>4-5</td>
</tr>
<tr>
<td>Reactive dyed sample</td>
<td>Dry</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Wet</td>
<td>5</td>
<td>5</td>
<td>4-5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Grey scale value (color change)</th>
<th>1% dye conc. (owf)</th>
<th>2.5% dye conc. (owf)</th>
<th>5% dye conc. (owf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid dyed sample</td>
<td>Dry</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Wet</td>
<td>5</td>
<td>5</td>
<td>4-5</td>
</tr>
<tr>
<td>Reactive dyed sample</td>
<td>Dry</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Wet</td>
<td>5</td>
<td>5</td>
<td>4-5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Grey scale value</th>
<th>1% dye conc. (owf)</th>
<th>2.5% dye conc. (owf)</th>
<th>5% dye conc. (owf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid dyed sample</td>
<td>Acidic solution</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Alkaline solution</td>
<td>5</td>
<td>5</td>
<td>4-5</td>
</tr>
<tr>
<td>Reactive dyed sample</td>
<td>Acidic solution</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Alkaline solution</td>
<td>5</td>
<td>5</td>
<td>4-5</td>
</tr>
</tbody>
</table>
From the assessment of table VIII and IX it can be said that the color fastness to perspiration both for the color change and for the staining are satisfactory.

4.5 Strength Test

![Graph showing the effect of dye concentration on the strength of the dyed samples.](image)

Fig. 8. Effect of dye conc. on the strength of the dyed samples.

In case of breaking force acid dyed silk require more force than reactive dyed silk. Reactive dyeing is normally carried out in alkaline medium and an increase of the dye concentration of reactive dyes also increases the pH of the liquor. Silk fibres are sensitive to alkaline media. Figure 8 shows that the strength of acid dyed silk is better than reactive dyed silk.

5.0 CONCLUSION

For the ease of understanding all the results and assessments are summarized in the table 10.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>a). Dye Uptake</td>
<td>Dye uptake percentage of reactive dyes was better than acid dyes.</td>
</tr>
<tr>
<td>b). Wash fastness test (ISO 105 C03)</td>
<td>Reactive dyes showed better results than acid dyes.</td>
</tr>
<tr>
<td>- Color change</td>
<td></td>
</tr>
<tr>
<td>- Color staining</td>
<td></td>
</tr>
<tr>
<td>c). Perspiration test (ISO 105 E04)</td>
<td>Both reactive and acid dyes showed more or less same results.</td>
</tr>
<tr>
<td>- Color change</td>
<td></td>
</tr>
<tr>
<td>- Color staining</td>
<td></td>
</tr>
<tr>
<td>d). Rubbing test (ISO 105 X12)</td>
<td>Both reactive and acid dyes showed more or less same results.</td>
</tr>
<tr>
<td>e). Strength test (ASTM D5034)</td>
<td>Acid dyes showed better results than reactive dyes.</td>
</tr>
</tbody>
</table>

Thus from the table X it can be concluded that in case of better fastness properties and dye uptake reactive dyes may be used but for strength and brightness the conventional acid dyes are better.

REFERENCES

[6] A D Broadbent, Basic principles of textile coloration..