

STUDIES IN DYEING OF SILK WITH BIFUNCTIONAL REACTIVE DYES

by

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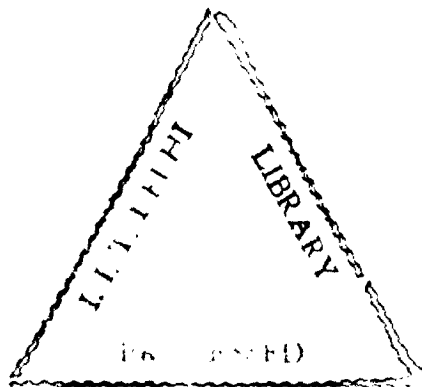


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CERTIFICATE

This is to certify that the thesis entitled, "**STUDIES IN DYEING OF SILK WITH BIFUNCTIONAL REACTIVE DYES**", being submitted by **Ms. Deepali Agarwal** to the **Indian Institute of Technology, Delhi**, for the award of the degree of **Doctor of Philosophy**, in the **Department of Textile Technology**, is a bonafide record of the research work carried out by her. Ms. Deepali Agarwal has worked under our guidance and supervision and the results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.



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(Deepali Agarwal)

ABSTRACT

With the ever increasing use of silk in apparels both formals and casuals, as well as household furnishings, the demand of dyes with superior fastness on silk is but natural. Reactive dyes, in this respect, assume a special significance as these form strong covalent bonds with the fibre. However, the performance of monofunctional reactive dyes, in terms of exhaustion and fixation, is far from satisfactory. Bifunctional reactive dyes, on the other hand, by virtue of two reactive groups, are likely to show higher fixation. The present thesis is a compilation of the detailed investigations carried out on the application of bifunctional reactive dyes on silk in following major areas:

- Efficacy of bifunctional reactive dyes on silk and optimisation of dyeing parameters
- Mechanism of dyeing with reactive dyes and determination of reactive sites in silk
- Formation of crosslinks in silk and their effect on mechanical properties as well as on light fastness and wash fastness.

Studies related to the optimisation of dyeing parameters have been carried out with heterobifunctional reactive dyes, those containing monochlorotriazine and vinyl sulphone groups. Effect of pH, electrolyte concentration, temperature and time, have been reported. The exhaustion and fixation of bifunctional reactive dyes were found to be much higher compared to those of the monofunctional reactive dyes. Maximum exhaustion and fixation have been achieved in the neutral medium.

The effect of electrolyte concentration (glauber's salt, 10-110 g/l) on exhaustion and fixation in acidic, neutral and alkaline medium has also been reported. Under acidic conditions, the action of electrolyte was found to depend on the isoelectric point of silk. Depending on whether the dye bath pH was above or below the isoelectric point, the electrolyte acts either as an exhausting agent or as a retarding agent, respectively. The concentration of electrolyte has been found to have a pronounced effect on the degree of exhaustion in neutral and alkaline media.

The optimum conditions for dyeing of silk with bifunctional reactive dyes have been found to be:

pH	- neutral
temperature	- 90°C
time	- 2 h
glauber's salt	- 40-80 g/l (depending on the depth of shade)

As mentioned above, the fixation as well as the exhaustion was maximum in the neutral medium and the exhaustion values showed very good correlation with the fixation values. Investigations have also been carried out to study the influence of the reactivity of dyes on their exhaustion on silk.

For this, bifunctional reactive dyes of different types - containing two monochlorotriazine or two vinyl sulphone or one monochlorotriazine and one vinyl sulphone groups, have been used. The reactivity of these dyes was altered by inactivating either one or both the reactive groups. Vinyl sulphone group was specifically inactivated by reacting with sodium bisulphite in alkaline medium while complete inactivation of the dye was achieved by hydrolysing with sodium hydroxide. All the dyeings, with modified and unmodified dyes, were carried out in neutral medium using the optimised conditions as mentioned above. The fixation as well as the exhaustion of partially and completely inactivated dyes decreased significantly, suggesting a definite relation between exhaustion and fixation of reactive dyes.

In order to clearly understand the reaction mechanism of reactive dyes on silk, study related to determination of the possible reactive sites in silk was undertaken. The amino acid analysis of silk dyed with a heterobifunctional reactive dye (C.I. Reactive Red 194) has been carried out using Reverse Phase High Performance Liquid Chromatography. The amino groups were found to be the most important reactive sites in silk, especially in the neutral medium. However, in alkaline medium, amino acids containing hydroxyl groups were also found to react with the dye.

Bifunctional reactive dyes, by virtue of the presence of two reactive groups, are capable of forming crosslinks in the fibre. In the present study, the formation of

crosslinks by different types of bifunctional reactive dyes in silk has been investigated by solubility test. Silk yarns were dyed in different depths of shades (1-6% o.w.f.) with different bifunctional reactive dyes and the solubility of dyed and undyed silk was determined in a solution of calcium chloride, ethanol and water mixed in the molar ratio of 1:2:8. The degree of solubility was computed from the residual weight upon filtration. The solubility of silk has been found to be very sensitive to the formation of crosslinks in the fibre. The solubility decreases with the increase in the depth of shade. In the case of bifunctional dyes, a very good correlation has been observed between the percentage solubility and the amount of reacted dye in the fibre.

The effect of crosslinks on the mechanical properties of dyed silk has also been studied. The formation of crosslinks in silk contributed in maintaining the physical integrity of the fibre and prevented any strength loss during dyeing.

The effect of covalent bond formation on the light fastness of reactive dyes on silk has also been studied. For this, silk was dyed with the reactive and the hydrolysed forms of selected mono- and bifunctional reactive dyes. Reactive forms of dyes were applied in the neutral medium, whereas, the hydrolysed dyes were applied in acidic medium so as to achieve approximately the same amount of dye on the fibre. These two sets of samples were exposed to mercury bulb-tungsten filament lamp for different time periods ranging from 3-17 days. The rate of fading was determined in both these cases, by measuring the K/S values of the unexposed and the exposed samples. To study the effect of substrate, similar experiments were conducted on cotton fabric too. The light fastness of the reacted dyes was better compared to that of the hydrolysed dyes. This has been attributed to the formation covalent bonds with the reactive dyes which are considered to result in the better transfer of absorbed energy from the dye molecules to the fibre. The light fastness of the hydrolysed forms of the dyes was found to be influenced by the nature of dye-fibre interaction. In case of silk, where the hydrolysed dye formed ionic bonds, better fastness to light was exhibited compared to cotton where such strong association is missing. The bifunctional dyes have been found to help in containing the degradation of silk, particularly at short exposure to light.

The wash fastness of monofunctional and bifunctional reactive dyes has also been compared. The wash fastness of mono- and bifunctional reactive dyes is comparable, however, the realisation certainly is higher for bifunctional reactive dyes. A Utility Factor has been computed from the percentage realisation and the wash fastness values. Based on the Utility Factor, the bifunctional reactive dyes have been found to rank better than the monofunctional reactive dyes.

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