

Dyeing of Indian wool with reactive dyes

V G Kulkarni^a

Department of Textiles, Bapuji Institute of Engineering and Technology, Davangere 577 004, India

Received 17 July 2000; revised received 4 October 2000; accepted 2 January 2001

Wool fibres have been chemically modified by reduction / chlorination under acidic pH /pre-swelling in conc. formic acid prior to their dyeing with indigenous reactive dyes of different molecular configurations to enhance the reactive dye uptake on wool fibre substrate. The pretreatment processes are inexpensive, less harmful and less time consuming as against the use of imported special wool reactive dyes.

Keywords : Dyeing, Reactive dyes, Wool

1 Introduction

India possesses nearly 42 million (4.1%) sheep and ranks 6th in sheep population and 11th in wool production, producing approx. 35 m kg (1.1%) wool per annum. However, no detailed scientific studies have been made on indigenous wool, except the recent published work of Kulkarni *et al.*¹ on indigenous wool, a typical animal fibre which widely varies in gross morphology² and has variable physico-chemical properties due to the genetic and nutritional influences³.

In recent years, the importance has gained for the application of reactive dyes on wool, mainly due to the formation of stable and strong dye-fibre covalent bond⁴, and the partial protection of wool against photo-oxidation under irradiation conditions⁵.

The normal cotton reactive dyes fail to exhaust on indigenous wool unless the fibres are chemically modified undamaged. This is possible by either partial reduction or chlorination or swelling process. Consequently, this may lead to avoid the import of special reactive dyes ideal for wool dyeing. The present work deals with the simple chemical modification of Indian coarse wool by partial reduction/ chlorination under acidic pH / pre-swelling of wool in formic acid at an ambient temperature for a short period to enhance the reactive dye uptake on wool. The results have been compared with those exhibited by the fine wool.

2 Materials and Methods

2.1 Materials

The wool samples from various sources, as

mentioned below, were collected for the study : Australian merino wool (64s) from the Raymond Mills, Mumbai; New Zealand fine Merino wool from the Wool Research Organization of New Zealand (WRONZ), Christchurch; Kashmir Fine Merino wool from the Sheep Husbandry Department, Srinagar; and coarse crossbred Bharat Merino wool from the Central Sheep & Wool Research Institute (CSWRI), Jaipur. The samples were solvent extracted as per the usual method and then conditioned at 65% RH and 27°C prior to further treatments.

2.2 Methods

2.2.1 Reduction of Wool

Disulphide bonds in wool were partially reduced by reacting the wool separately with (i) 0.1 M aqueous sodium bisulphite (AR grade) at 50°C for 4 h, maintaining the pH at 5 and (ii) 0.1 M aqueous thioglycolic acid (TGA) (AR grade) for 4 h, maintaining the pH at 4.5 adjusted by using the 6N – caustic soda solution, followed by blocking of thiol/sulphydryl groups in reduced wool by the treatment with 5% (v/v) ethanolic acrylonitrile (AR grade) for 24 h at pH 9 (ref. 6). The material-to-liquor ratio was maintained at 1: 50 throughout.

2.2.2 Estimation of Total Sulphur Content

Intact and reduced-blocked wool was hydrolysed in 5.7 N hydrochloric acid (AR grade) as reported earlier¹. The total sulphur content of amino acids (cystine and cysteine) of these wool hydrolysates was determined colourimetrically using the original method of Shinohara⁷ later modified by Fletcher and Robson⁸.

^aPresent address: 8 Patel Heritage, Bhusari Colony, Paud Road, Pune 411 038.

Phone: 0091-020-5283250; E-mail: profvgk@indiatimes.com

2.2.3 Chlorination of Wool

Intact wool was treated with a solution of bleaching powder (1.5g/ litre available chlorine) at pH 5.1 for 15 min, maintaining the material-to-liquor ratio at 1:50, followed by antichlor treatment with sodium bisulphite¹.

2.2.4 Formic Acid Treatment

The selected wool was boiled in 98% formic acid (AR grade) for 30 min, maintaining the material-to-liquor ratio at 1:50, followed by vigorous shaking on bench shaker and then centrifugation. Wool was also swollen in formic acid for 30 min and thoroughly washed prior to its dyeing.

2.2.5 Measurement of Dye Uptake

Intact, reduced, formic acid swollen and chlorinated wool samples were dyed separately in aqueous solutions of commercial reactive dyes, namely, Remazol Blue 3 R (C.I. Reactive Blue 28 by Colour-Chem), Procion Yellow MX 3R (C.I. Reactive Orange 86 by Atic), and Cibacron Blue LSG (C.I. Reactive Blue 269 by Ciba), at 1% shade and pH 5.0 using the established procedure⁹. The dyed wool samples were stripped with pyridine-formic acid-water (10:20:100) mixture¹⁰ and then the dye uptake was estimated spectrophotometrically by evaluating the extinction value at maximum wavelength of 570 nm for the Blue 3R dye, 226 nm for the yellow MX 3R dye, and 634 nm for Blue LSG dye using an Elico SL 159 UV-VIS Spectrophotometer.

2.2.6 Microscopic Analysis

Partially descaled wool and released cortical cells from it as a result of boiling formic acid treatment were examined routinely under light/optical microscope at a reasonable magnification. Topography (surface structure) of wool and its cellular components was accessed under JEOL-JSM 848A scanning electron microscope (SEM) using a 40 nm objective aperture at 20kV. The specimens were coated with 24 carat gold (thickness, 300Å – 400Å) in

JFC-1100 E ion sputtering device (JEOL) under vacuum (10^{-4} torr) for 5 min.

3 Results and Discussion

3.1 Sulphur Content of Wool

The reduced wool samples blocked with acrylonitrile to prevent random formation of disulphide bonds by atmospheric oxidation were then used to determine total sulphur content. The sulphur contents of intact and reduced fine and coarse wool samples are given in Table 1. The results indicate that comparatively the fine wool is enriched in sulphur content as observed earlier¹. The reduction in sulphur content for these wool is averaged to 30%, irrespective of the nature of the reducing agent employed. The TGA, employed at an ambient temperature, appears to be slightly more effective than sodium bisulphite used at 50°C in severing the disulphide bonds in wool.

3.2 Dye Uptake of Intact and Modified Wool

The stripping of reactive dye from the dyed wool was affected with pyridine-formic acid-water mixture (pH 2.4) as the pyridine-water mixture alone, being alkaline, promotes dye-fibre covalent bonding¹⁰. The extraction method specified here does not mean that the dye fixation is by adsorption and not by covalent bond formation. It is well established that the reactive dye is held by the wool fibre only and only by the covalent bond formation^{4,5,10} and not by the hydrogen bonding/ionic forces/salt linkages, etc between the reactive dye and the basic groups followed by, to a lesser extent, acidic groups in the unmodified wool keratin, and predominantly by the thiol/sulphydryl groups generated by the fission of cystine linkages in the chemically modified wool fibre. This was indicated by the increase in dye uptake of reduced wool over that of unmodified ones. The dye uptake of intact, reduced, formic acid swollen and chlorinated wool dyed with 1% shade is given in Table 2. It is observed that the dye uptake of intact wool dyed at 100°C is the least. However, when the wool is

Table 1 — Sulphur content of intact and reduced wool

Wool	Intact	Sulphur, %			
		Sulphytolysed		TGA-reduced	
		After reduction	Reduction,%	After reduction	Reduction,%
Australian Fine Merino	3.22	2.31	28.40	2.10	34.80
New Zealand Fine Merino	2.97	2.00	32.60	2.01	32.30
Kashmir Fine Merino	2.76	2.16	22.10	2.06	25.40
Bharat Merino	2.28	1.68	26.30	1.67	26.80

reduced to generate sulphhydryl/thiol groups from the major amino acid cystine present in wool, the dye uptake shows nearly a two-fold increase over that of the blue dyed intact wool for reactive blues, irrespective of the nature of reducing agent used. The dye uptake is nearly one and a half times more when reduced wool is dyed with Procion Yellow MX 3R. This is a clear indication of enhanced reactivity of the thiol groups with the reactive dye as a result of partial wool reduction. This observation is independent of the chemical configuration of the reactive dye and the fineness of wool. The TGA-reduced wool when dyed shows marginal increase in dye uptake over that of the sulphytolysed wool.

Interestingly, it is observed that the reduced wool when dyed at an ambient temperature for a longer duration shows the dye uptake equivalent or slightly less than that of the intact wool dyed at 100°C, indicating that the temperature of the dye bath plays a crucial role in wool dyeing. The absence of thermal energy decreases the mobility of dye molecules and, therefore, reduces the dye uptake on wool.

Wool swollen in formic acid, the best swelling agent for wools at an ambient temperature^{11, 12}, when dyed at an elevated temperature shows nearly a total dye uptake in less than one hour. This is true for both the types of reactive dyes and wool. However, formic acid treated wool loses the tenacity little over 10% when measured on stelometer. The boiling formic acid descales the wool fibre and releases its cellular component (Fig. 1). Diametral swelling may help to increase the dye uptake, but the boiling formic acid is disadvantageous and degradative to wool since the boiling formic acid dissolves some wool protein¹³.

Partially chlorinated wool, like reduced or formic acid swollen wool, exhibits a two-fold increase in dye uptake over that of the dyed intact wool, supporting the observation that the cuticle (the diffusion barrier)

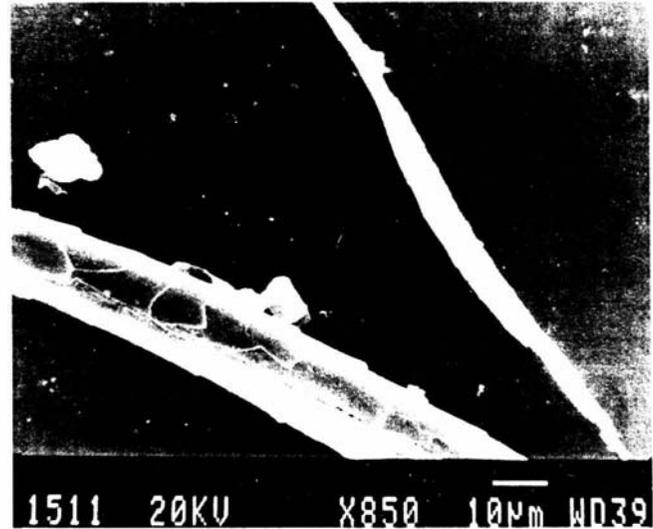


Fig. 1 — Release of cuticle and cortical cells from wool boiled in formic acid

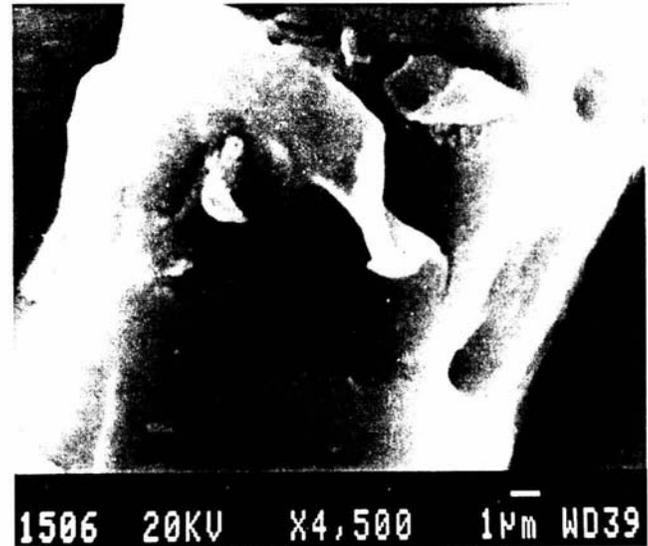


Fig. 2 — Scanning electron photomicrograph of chlorinated Bharat Merino wool

Table 2 — Dye uptake by intact and modified wool

Wool	Remazol Blue 3R					Procion Yellow MX 3R				Cibacron Blue LSG			
	In-tact	Sul-phyto-lysed	TGA-reduced	Chlori-nated	FA swol-len	Intact	Sul-phyto-lysed	TGA-reduced	FA swol-len	Intact	Sul-phyto-lysed	TGA-reduced	FA swol-len
Australian Fine Merino	44.8	87.9	96.3	95.4	99.8	56.2	86.1	94.4	89.6	49.5	86.8	100.0	100.0
New Zealand Fine Merino	47.7	85.8	96.0	95.5	99.8	63.7	85.6	94.4	88.7	49.5	89.2	99.2	94.9
Kashmir Fine Merino	41.9	86.9	98.1	98.2	99.7	63.7	89.6	96.9	93.1	49.5	100.0	95.1	99.4
Bharat Merino	46.7	83.9	98.5	97.6	99.9	66.8	90.0	97.4	89.6	48.5	86.0	100.0	97.6

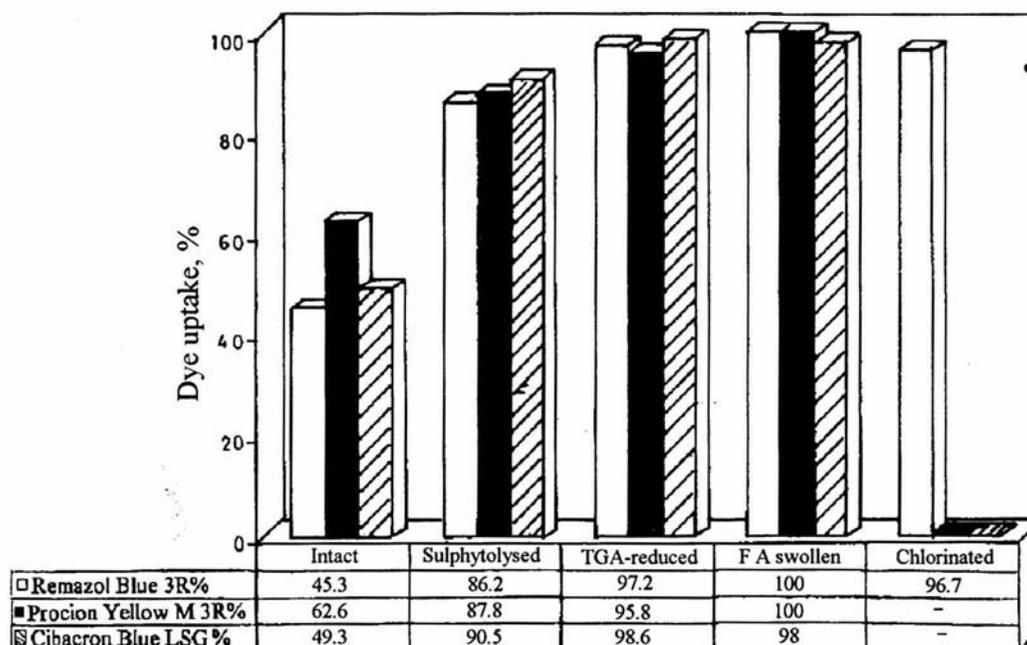


Fig 3 — A comparative dye uptake by dyed intact and modified wool

is a rate determining factor in wool dyeing¹⁴ as the partial opening (Fig. 2) provides more surface area or domains for the free entry of dye molecules. However, the chlorinated wool suffers 20% loss in tensile strength. The strength of hypochlorite and the duration of chlorination appear to be crucial and critical factors.

A comparative dye uptake of the dyed intact and modified wool is shown in Fig. 3. All the three pre-treatment methods are cost effective, less time consuming and fairly less harmful to wool fibre. However, the non-ecofriendly hypochlorite treatment, being critical, needs a careful control. Whereas a short-period formic acid swelling and/or partial reduction of wool can be considered the least objectionable for the substantial increase in the reactive dye uptake on wool. It is expected that the Indian woollen industry, with large export market, would be benefited if it accepts the economical and profitable revised methodology of dyeing wool with indigenous reactive dyes.

4 Conclusions

Partial reduction of wool and/or short-time diametral swelling in formic acid increases the reactive dye uptake on wool fibre substrate. Whereas

partial chlorination increases the dye uptake but the treatment is injurious to wool.

Acknowledgement

The author is thankful to the suppliers of various wool samples and reactive dyes and to the Indian Institute of Science, Bangalore, for providing the electron microscope facilities. He is also thankful to the University Grants Commission, New Delhi, for granting emeritus fellowship.

Reference

- 1 Kulkarni V G, Moses J J & Nagavel A, *Asian Text J*, (5) (1996) 73.
- 2 Kulkarni V G, Robson R & Robson A, *Appl Polym Symp*, 18 (1971) 127.
- 3 Kulkarni V G, *Text Res J*, 53 (1983) 712.
- 4 Zollinger H, *Textilveredlung*, (6) (1971) 57.
- 5 Banumann H, *J Soc Dyers Colour*, 90 (1974) 125.
- 6 Wolfram L S & Underwood D L, *Text Res J*, 36 ((1966) 947.
- 7 Shinohara K, *J Biol Chem*, 112 (1935) 683.
- 8 Fletcher J C & Robson A, *Biochem J*, 84 (1962) 439.
- 9 Praying R S, *Dyeing of Wool, Silk and Man-made Fibres* (Weavers' Service Centre, Mumbai), 1983, 41.
- 10 Lewis D M, *Rev Prog Colour*, (8) (1977) 10.
- 11 Whiteley K J, Balasubramaniam E & Armstrong L D, *Text Res J*, 40 (1970) 1047.
- 12 Whiteley K J & Kaplin I J, *J Text Inst*, 68 (1977) 384.
- 13 Kulkarni V G & Bradbury J H, *Aust J Biol Sci*, 27 (1974) 383.
- 14 Kulkarni V G, *J Soc Dyers Colour*, 90 (1974) 110.