Dyeing of Chamois Leather using Water Soluble Sulphur Dyes

by

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Abstract

Chamois leathers find application in fuel filtration and cleaning. Recently, use of chamois leathers is explored in the development of sports garments, gloves and other personal wear. However, one of the consumer demand *viz.* different colors on the end product is not met by chamois leathers. Hence, dyeing is essential to make it more attractive for end user applications. In the present work an attempt has been made to develop colored chamois leather by employing water soluble sulphur dyes. The offer of sulphur dyes have been optimized based on dyeing characteristics, color fastness and color values. The results indicate that offer of 1 and 2% of the dyes show better colour value and fastness to rubbing. Hence, it could be inferred that coloring of chamois leathers not only improved the aesthetic appeal but also helped in adding value without altering inherent properties of chamois leather.

Introduction

Chamois leathers are made by in-situ oxidation of unsaturated oils, after which the skins turn to golden yellow color. The leathers are then washed using alkali and dried.[1,2] Chamois leathers have gained importance as cleaning material since commercial production of glass have begun and they are widely used for cleaning high-end lenses.[3] Not only as a cleaning material, chamois leather find numerous applications in making garments and sportswear.[4-6] Color of chamois is yellow, which further will not be colored by tanners. However, application of chamois leather as garment and other wearable articles demand pleasing aesthetics, so there is a need for colouring of chamois, which would add value to the leathers.

Sulphur dyes are traditionally used for coloring cotton and cellulose fibers. Solubilized sulphur dyes are thiosulphate derivatives, which are applied to cellulosic fibers in the presence of alkali and reducing agent.[7,8] These dyes produce heavy depth shades of moderate to good light fastness, good wet rub fastness.[9,10]

Several reports are available on the use of sulphur dyes as a coloring agent for cellulosic and textile fabrics. However, very few reports are available on the use sulphur dyes for coloring of leather. The alkaline reducing environment required for the use of these dyes restricts the use in leather processing. Though exact reactive mechanism is unknown, dyeing of leather with insoluble sulphur dyes has been attempted. Reducing agents were used for strengthening of dye in combination with other water soluble colorants.[11] Recently, a report is also available on the use of solubilized sulfur dyes for coloring chrome tanned leathers and tone-in-tone dyeing was shown.[12]

Still, dyeing of chamois leather using soluble sulfur dyes has not been attempted earlier using soluble sulphur dyes from Bunte salts. The main advantage of using this dye in the chamois process is their operational pH (8-11). Another advantage is that the dye can be used directly without addition of alkali or reducing agents and can be fixed using mild acid in order to avoid serious effluent problems.

Objective of the present study is to employ commercially available water soluble sulphur dyes for dyeing of chamois leather. Use of sulphur dyes improves the aesthetic value of chamois leather and makes it attractive to end user. The offer of sulphur dyes has been optimized and the leathers are evaluated in terms of color values, fastness properties and organoleptic properties.

Experimental Section

Materials

Four water soluble sulphur dyes, Tancol Black LSG (C.I. Solubilized Sulphur Black 1), Tancol Prune LBRS (C.I. Solubilized Sulphur Red 6), Tancol Brown LSG and Tancol Chocolate Brown LFP (C.I. Solubilized Sulphur Brown 14) samples were provided by SF Dyes Pvt. Ltd., India. Both brown dyes used in this study have same CI number. Structures of base material used for making sulphur dyes are provided in Figure 1 along with Color Index (CI) numbers. Chamois leathers were procured from Sai chamois Pvt. Ltd., India. All other chemicals used for leather processing are of commercial grade.

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Methods

Dyeing of Chamois Leather

Dye application procedure is given in Table I. Different trials have been carried out by changing the concentration of dye. All chemicals were offered on dry weight of the leather. Entire leather processing was done in a rotating drum at 4-6 revolutions per minute. Initially, chamois leathers were wetted and sulphur dyes were applied in two different concentrations and fixed using acetic acid. Acetic acid was used because of the operational pH of sulphur dyes varies from 8 to 11. The amount of acid required is usually less and need to be mild. After the fixing of the dye, liquor was drained and leathers were rinsed in fresh water.

Color Measurement of Chamois Leathers

Color of the dyed leathers was measured using Spectra Scan 5100A (Premier Colorscan Instruments India Pvt. Ltd) dual beam spectrophotometer equipped with pulse xenon light source having scan wavelength interval of 360 to 740 nm having wavelength accuracy of 0.1 nm and instrument was operated at 25°C with relative humidity <90% (Non- condensing). Prior to the color measurement instrument was calibrated using standard white slab provided by the equipment manufacturer. The perceptive change in color to human eye was analysed by ΔE values (Equation 1), which also denotes Euclidean distance between two color stimuli in CIELUV space.[13]

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (1)$$

Where, difference ΔL is the measure of lightness. Similarly, Δa values indicate difference to red and green; Δb values indicate difference to yellow and blue.

Color Fastness Analysis

Color fastness to rubbing both dry and wet were tested using STD 422 Crock meter instrument from SATRA UK in accordance to IUF 450.[14] This method of testing chamois leathers was intended to determine the degree of surface color transferred from the material during mild dry or wet rubbing. A specimen of dyed leather material was rubbed by a cotton felt, which was linearly moved forward and backwards under the constant force. After a set number of rubs the cotton felt was assessed with the Greyscale for color transfer from the test material.

Wash fastness to washing machine was measured in accordance with IUP 435[15] and final leathers after testing were rated using Greyscale.

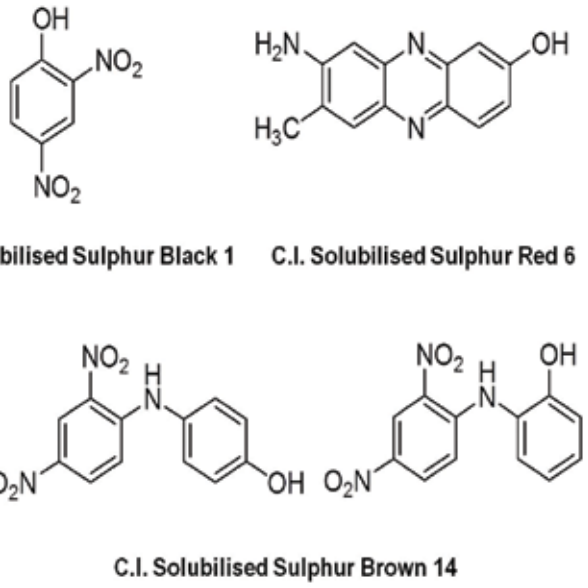

Figure 1. Structure of base compounds of sulphur dyes with respective CI numbers.

Table I

Process for dyeing chamois leathers.

Process	Chemical	Percentage (%)	Duration (min)	Remarks
Washing	Water	600	15	Drain/Wash/Drain
Dyeing	Water	400		
	Sulphur Dye	1,2	60	Check penetration
Fixing	Acetic acid	2	In 3 feeds for 10 each + 30	In 1:10 dilution, set to pH 6-6.5[a]

[a]Check exhaustion, Drain and hook to dry

Water Absorption

Control un-dyed chamois leather and dyed chamois leathers were analysed for static absorption of water in accordance with IUP 7.[16] This method calculates water absorbed by 100g of leather for a duration of 60 minutes (Equation 2). Here Q represents percentage absorption, v is the volume of water absorbed and m is the mass of leather.

$$Q = 100\ v/m \quad (2)$$

Organoleptic Properties

Dyed leathers were evaluated for organoleptic properties; experienced leather technologists rated the leather for softness, visual appearance and dye penetration. Rating was given on scale of 1 to 10, higher value meaning better properties.

Results and Discussion

Dyeing of Leather Matrix

Dyeing of chamois leathers has been found to be uniform and penetration throughout the cross section has been achieved within 30-40 min. This has been confirmed by visual inspection of the cross-section of the leathers. Fixing of dye is achieved by reducing the pH to 6-6.5, where dyes tend to fix to the leather.

Reaction Mechanism and Effect of pH

Sulphur dyes are known to be soluble at alkaline pH and fix with collagen or cellulose fibers permanently after aerial oxidation.[9] Sulphur dyes are believed to have high fastness and resistance to bleaching due to covalent interaction with substrate.[17] Sodium carbonate (Soda ash) is used for washing of chamois after oxidation of oil, hence the alkaline conditions required for dyeing using sulphur dyes is maintained. These conditions also facilitate dye to penetrate throughout the leather matrix. Sulphur dye is applied to leather in the form of soluble leuco compound (containing bunte salt) that subsequently oxidize and gets converted to parent sulphur dye. Plausible interaction of sulphur dye with collagen is represented in Figure 2.[17]

Stability of Dye Solution Towards Acid, Alkali and Hard Water

Stability of dyes solution towards acid,[18] alkali and hard water[19] is an important parameter to understand the behavior of dye in different environments. Though sulphur dyes operate in alkaline region, studying the effect of acids on these dyes gives information about dyes stability to color change and precipitation. From Table II, all the dyes used in the study exhibited good resistance towards acid, alkali and hard water.

Color Measurement of Chamois Leather

Reflectance measurements have been carried out for chamois leathers and *L, *a, *b values are provided in Table III. It is clear from the table that the color intensity increases with an increase in concentration of dye. The decrease in lightness value L was noticed when dye concentration was increased from 1 to 2%, meaning that the color was intensifying. It was observed that ΔE values were higher than 2.9, which give the measure of just noticeable difference (JND)[20] of color, indicating that the color change is perceptive to human eye with increase in dye concentration. This also gives information that darker shades can be produced by increasing the concentration of dyes.

Color Fastness

Color fastness to rubbing was analyzed using Grey scale and rating from 1-5 were awarded based on colour of the felt. Rating close to 5 meaning leathers exhibited superior fastness property. From Table IV, it is observed that, leathers dyed with sulphur dyes showed excellent fastness to dry rubbing and moderate fastness to wet rubbing. Color fastness to washing machine values shows the leather staining towards washing with multi-fabric containing layers of acetate, cotton, nylon, polyester, acrylic and wool fibers (Table V). Staining with cotton is lower for Tanacol Prune LBRS and Tanacol Chocolate Brown LFP, apart from that leather showed good fastness with respect to other fabric materials. Overall it can be concluded that the water soluble sulphur dyes were promising for dyeing chamois leathers.

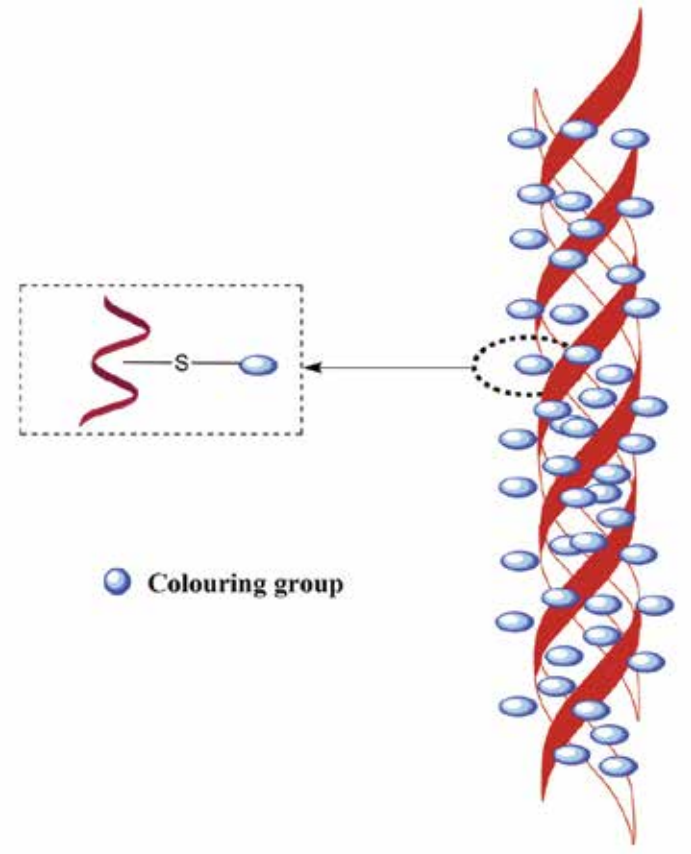

Figure 2. Plausible interaction of sulphur dye with collagen.[17]

Water Absorption

Chamois leathers were tested for static water absorption. Results showed that dyed chamois leather has similar water absorption to that of the control un-dyed chamois leather. Water absorption values for dyed leathers are in the range of 331 to 345%, while control leather sample exhibited 351% with an error of ±5%. This observation indicates that the water absorption capabilities of leathers are not affected due to dyeing.

Evaluation of Organoleptic Properties

Organoleptic properties of dyed chamois leathers were rated by experienced leather technologists and are compared in Figure 3. It is clear that dye penetration is excellent for all the dyes. Softness of leather is unchanged with respect to the un-dyed control chamois leather. There is no change in odor for dyed chamois leathers. Photograph shows some of the dyed chamois leathers in Figure 4.

Table II

Dye resistance to acid, alkali and hard water.

Resistance towards	Acid	Alkali	Hard water
Tancol Black LSG	4-5	4-5	4-5
Tancol Brown LSG	4-5	3-4	4-5
Tancol Prune LBRS	5	4-5	4-5
Tancol Chocolate Brown LFP	4-5	4	4-5

Table III

Color values of chamois leathers dyed with sulphur dyes.

Dye	Concentration (%)	*L	*a	*b	ΔE	Shade card
Tancol Black LSG	1	39.423	-0.811	-3.394	-	
	2	31.716	0.313	-2.601	7.77	
Tancol Brown LSG	1	37.691	23.829	0.488	-	
	2	30.484	21.180	1.703	7.77	
Tancol Prune LBRS	1	40.180	6.772	-12.657	-	
	2	38.238	7.513	-8.003	5.09	
Tancol Chocolate Brown LFP	1	50.664	5.225	17.391	-	
	2	46.146	5.029	13.780	5.78	

L* represents lightness, a* represents redness-greenness and b* represents blueness-yellowness of the color

Conclusion

Chamois leathers were colored using sulphur dyes. The colored chamois leather was assessed for various parameters. It was observed that the application of 1 and 2% sulphur dye showed good colour value and better fastness to rubbing. Also, dyeing of leathers did not have any effect on water absorption capabilities. Hence, it could be concluded that the suphur dyes can be effectively used as coloring agent for chamois leather without affecting the quality of the leather. At the same time, it is believed that this approach may add economic value for chamois leather making.

Table IV
Color fastness due to dry and wet rubbing of chamois leathers.

Dye	Concentration (%)	Dry Rub 10 Rubs	Wet Rub 10 Rubs
Tancol Black LSG	1	4	3-4
	2	4	3
Tancol Brown LSG	1	4	3
	2	4	3
Tancol Prune LBRS	1	4	3
	2	4	2-3
Tancol Chocolate Brown LFP	1	4	3-4
	2	4	3-4

Table V
Color fastness to washing of chamois leathers.[a]

Dye	Concentration (%)	L[b]	A	C	N	P	Ac	W
Tancol Black LSG	1	3-4	4	4	3	4-5	4-5	4
	2	3-4	4-5	4-5	4-5	4-5	4-5	4-5
Tancol Brown LSG	1	3	4-5	4-5	4-5	4-5	4-5	4-5
	2	3-4	4-5	4	4-5	4-5	4-5	4-5
Tancol Prune LBRS	1	1-2	4	2	3-4	4	4	3-4
	2	1-2	3-4	1-2	3-4	3-4	3-4	3-4
Tancol Chocolate Brown LFP	1	1-2	4	2	4	4-5	4-5	4
	2	3	4	1-2	3-4	4	4	3-4

[a]Leather staining towards different fibers, A = Acetate, C = Cotton, N = Nylon, P = Polyester, Ac = Acrylic, W = Wool
[b]Color change on , L= Leather

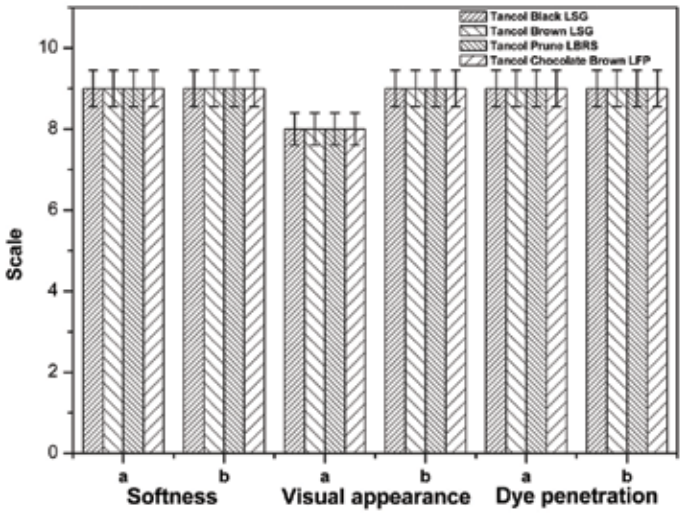

Figure 3. Comparison of organoleptic properties of chamois leathers dyed with different concentration, a=1 and b=2% sulphur dye.

Figure 4. Photograph of a) un-dyed chamois, chamois leather with dye (2%) b) Tancol Black LSG c) Tancol Chocolate Brown LFP d) Tancol Brown LSG and e) Tancol Prune LBRS.

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