

A Novel Approach for Enhanced Color Intensity and Uniformity in Leather Dyeing

by

Sujata Mandal,^{1*} J. Durga,^{2,3} G. Jothi,³ Malathy Jawahar³ and C. Muralidharan^{3*}

¹Centre for Analysis, Testing, Evaluation and Reporting Services

²Academy of Scientific and Innovative Research, CLRI Campus

³Leather Processing Department

CSIR-Central Leather Research Institute,

Chennai, India, Pin-600020.

Abstract

Dyeing is a significant process step in leather making that is carried out to enhance the aesthetics of the tanned hides and skins. Due to the heterogeneous nature of the skin matrix, obtaining leathers with consistent color is challenging. The present study describes application of hydrotalcite-like inorganic synthetic material (HTLM) during leather dyeing to bring color uniformity among leathers by maximizing the color intensity within the skin and among the skins processed in a batch. The HTLM has been used in an interim step between two phases of dyeing that enhanced shade intensity as well as color consistency through modification of the leather surface chemically. The efficacy of the HTLM for enhanced color intensity and uniformity in leather has been investigated. Influence of the HTLM on the physical characteristics like, perspiration, color fastness to light and dry/wet rub are also studied.

Introduction

Leathers are dyed to impart color as demanded by the fashion. The process of dyeing is an important step of leather making that is carried out to enhance the aesthetics and valorization of the tanned hides and skins. Since leather has become a fashion element, tanners are required to produce wide and seasonal color ranges as wide as those found in textiles. Therefore, a quick and accurate color matching is a need of the hour for the leather industry. Being natural material, each hide/skin is unique in nature that has variations within the matrix. Due to heterogeneous nature of the raw hide/skin, the process of dyeing is a challenging task for obtaining leathers with consistent color.¹ Nevertheless, color uniformity among leathers processed in a batch or in different batches is a necessity to minimize the productivity and economic loss. Minimizing or eliminating

rejection of leather due to non-uniformity of color within the same skin/hide or among different skins/hides from the same batch of dyeing, has been a topic of research interest for quite some time. Furthermore, maximum uptake of dye should be ensured to minimize environmental pollution. The unutilized dye along with other chemicals used during the dyeing process increases effluent load on common effluent treatment plant.^{2,3}

To overcome the problem of color uniformity and consistency in leather, it is conventional practice to use dye leveling agents.^{4,5} However, till date, no viable and cost effective solution is available to bring color uniformity among all the skins or hides of a batch in leather dyeing.⁶ In a typical study by our research group, an aqueous dispersion of layered double hydroxide (LDH) has been synthesized and used as dye leveling agent to enhance the shade intensity and color uniformity in leather dyeing.⁷ The leather dyed using the LDH dispersion showed excellent color uniformity and consistency with no detrimental effect on color fastness characteristics of the leather. However, due to agglomeration tendency of these materials (LDHs) keeping them in dispersion is a practical problem.⁷

The present communication describes the use of a hydrotalcite-like inorganic synthetic material (HTLM) as an adjunct material for leather dyeing. Dyeing experiments were performed with and without the HTLM and the color intensity/uniformity was assessed. Experiments were performed with three different dyes namely, Yellow 110, Orange GM and Blue N to ascertain the workability of the HTLM with different dyes. Influence of the use of HTLM on the physical characteristics of leathers like, perspiration, color fastness to light and dry/wet rub were studied. The HTLM was characterized for its chemical and morphological properties using X-ray diffraction (XRD), FT-IR spectrometer and Scanning electron microscope.

*Corresponding author's contacts: Tel: +91 44 24437104; e-mail: sujata@clri.res.in Tel: +91 44 24437157; e-mail: cmurali62@yahoo.com
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Materials and Methods

Materials

The dyes, Yellow 110, Blue N and Orange 2GL, used for dyeing experiments are commercial grade dyes and were obtained from M/s Colourtex Pvt. Ltd, Surat, India. The basic chromium sulphate, was procured from Vishnu Chemicals, Chennai, India. The hydrotalcite-like inorganic synthetic material (HTLM) was procured from Shaoyang Tiantang Additives Chemical Co. Ltd, China.

Methods

The process for dyeing of leather involved the following steps chronologically: wetting back, pre fat-liquoring, phase-I dyeing, fat-liquoring, re-tanning, partial fixing, addition of BCS, addition of the HTLM, phase-II dyeing followed by fixing. The name and amount of the chemicals added in each step are presented in Table I. Experiments were performed using different dyes and by following procedure mentioned in Table I. The same process was followed for the control but without the HTLM.

The weight of chemicals to be added were calculated based on the weight of the leather pieces taken for the trials. Two full skin crust leathers from two different sources were taken. Each

leather was cut vertically into two pieces, one piece was used as control and the other piece for the experiment, as shown in Figure 1. In this way, two leather samples for control and two for experiments were taken for trial with three different dyes.

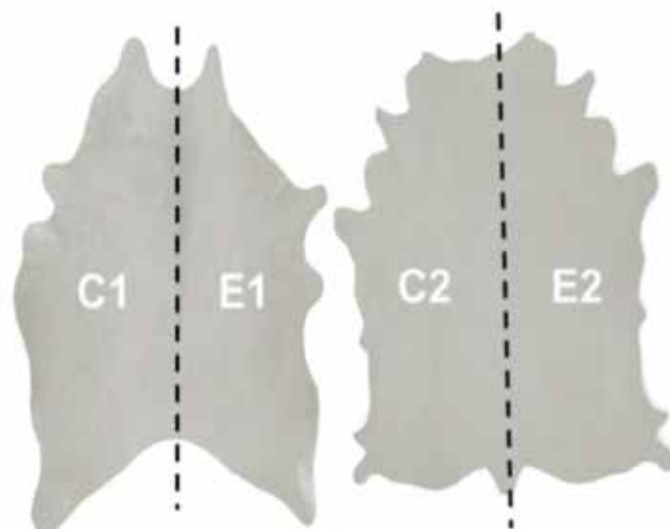


Figure 1. Naming of leather samples for Control (C1 and C2) and Experiment (E1 and E2).

Table I
The process steps followed for the dyeing of leathers.

Process Step	Chemical added	Quantity of chemical used w.r.t. leather (w/w)	Step duration
Wetting back	Water Non-ionic wetting agent	600% 1%	30 min and leave it for overnight
Washing			
Pre fat-liquoring	Water Synthetic fat-liquor	300% 5%	30 min
Phase-I Dyeing	Dye	3%	30 min
Fat-liquoring	Synthetic fat-liquor Semi-synthetic fat-liquor	5% 5%	45 min
Re-tanning	Phenolic syntan	5%	30 min
Partial fixing	Formic acid	1.5%	30 min
Addition of BCS	BCS	0.25%	30 min
Addition of HTLM	HTLM	10%	30 min
Phase-II dyeing	Dye	1%	30 min
Fixing	Formic acid	3%	60 min

The amount and time of addition of the dye and the dye leveling agent (HTLM) during the dyeing process was optimized based on the color consistency performance. The color uniformity among the leather samples processed in the same batch, without (control) and with the HTLM (experiment), was assessed visually as well as by spectrometer in order to ascertain the efficacy of the HTLM.

Color Fastness Testing

Fastness to Dry and Wet Rub

The selected leather samples from control and experiment were tested for color fastness to dry and wet rub using standard procedure such as SLF 450 using rub fastness tester SATRA STM 421, SATRA Technology Centre, UK. The leather was evaluated in grey scale rating that ranged between 1 and 5 in the order of increasing color fastness.

Fastness to Light

The color fastness to light were tested by projecting the leather samples to xenon-arc lamp for 40 h under the conditions mentioned in the standard test method SLF 402 using Xenotest Alpha, Atlas Materials Testing Solutions, USA. The percentage of fading showed by each sample was compared with conventional crust leathers. The samples were assigned a light fastness rating based on the number of the Blue Wool Standard which showed the equivalent degree of color change.

Perspiration

Leather samples from both control and experiment were tested for perspiration using standard procedure (SATRA TM 335). Dyed leathers of both control and experimental crust leathers were monitored in grey scale rating at 3 grades.

Spectroscopic Assessment of Color Intensity and Uniformity

A reflectance spectrometer (Premier Colorscan, model: SS 5100A) was used to study the colorimetric parameters in the visible wavelength range 400–700 nm. The $L^*a^*b^*$ color system based on a uniform color space CIELAB (1976) recommended by CIE (Commission Internationale de l'Éclairage) was used to measure leather surface colors and for calculating the color differences. CIELAB allows the specification of color perceptions in terms of a three-dimensional space. The L^* -axis is known as the lightness and extends from 0 (black) to 100 (white). The other two coordinates a^* and b^* represent redness-greenness and yellowness-blueness respectively. The color strength of the dyed leather samples from the control and the experiments were also measured. The qualitative color difference values are calculated as

$$\Delta L^* = L^*_{\text{batch}} - L^*_{\text{std}}$$

$$\Delta a^* = a^*_{\text{batch}} - a^*_{\text{std}}$$

$$\Delta b^* = b^*_{\text{batch}} - b^*_{\text{std}}$$

$$\Delta C^* = C^*_{\text{batch}} - C^*_{\text{std}}$$

$$\Delta H^* = \{(\Delta a^*)^2 + (\Delta b^*)^2 - (\Delta C^*)^2\}^{1/2}$$

where, the subscripts “std” and “batch” refer to C1 or E1 standard and C2 or E2 batch respectively.

The ΔE values are obtained from CIELAB values using the formula (CIE76)

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

Characterization of the HTLM

X-ray diffraction (XRD) studies of the HTLM was performed on an XRD instrument from GE Inspection Technologies, Germany (model: XRD-3003 TT) using Cu-K α radiation (1.5418 Å). Infrared spectroscopic measurement was performed using a FT-IR spectrometer from JASCO. Scanning electronic microscopic (SEM) images were captured in JEOL FEG-SEM. The elemental composition of the HTLM was analyzed by the energy dispersive X-ray analyzer (EDX) of the FEG-SEM.

Results and Discussion

The images of the leathers processed with and without the HTLM using three different dyes are presented in Figure 2 for visual assessment. Figure 2 shows that the color of the leather



Figure 2. Images of the leathers processed with and without the HTLM.

samples from experiments are significantly more intense than those from the control. The variations in color shades of the two leather samples from the control (C1&C2) are much more than those from the experiments (E1 & E2).

Table II

The colorimetric values for the leather samples from the control and the experiments performed with three different dyes.

Dye	Control (C) / Experiment (E)	L	a	b	ΔE
Yellow 110	C1	52.35	7.79	33.04	3.72
	C2	55.41	6.61	31.28	
	E1	51.60	7.82	35.37	2.72
	E2	53.87	6.75	34.33	
Orange GL	C1	47.69	20.71	34.15	4.39
	C2	48.46	19.14	30.13	
	E1	48.8	19.91	33.35	2.20
	E2	48.7	19.76	31.16	
Blue N	C1	28.13	0.609	-6.20	3.22
	C2	30.73	0.477	-8.08	
	E1	26.45	0.73	-6.38	1.47
	E2	27.90	0.472	-6.29	

The reflectance spectra of the samples from control and experiments for the dyes Yellow 110, Orange GL and Blue N are presented in Figure 3. The reflectance spectra for all the three dyes show that the spectral lines for the E1 and E2 are very close to each other than those for the C1 and C2. This reconfirms that the color uniformity among the experiment leather samples are much higher than those of the control leather samples.

The visual assessment of better color consistency in the leather samples from the experiments are supported by the spectroscopic measurement. The values of L^* , a^* , b^* and ΔE obtained from the CIELAB measurements of the leather samples are presented in Table II.

The overall color difference Delta (Δ) E correlates the human visual judgment of differences between two perceived colors, the lower the ΔE number, the closer the color matching. The values of ΔE obtained for the leather samples from control are higher than those for the samples from experiments. This indicates better uniformity among the two samples from the experiments (E1 & E2) than those from the control (C1 & C2).

From Table II, it can be observed that highest color difference was perceived for the control leathers and the major contribution for the high value was from the difference in the lightness value (ΔL). If ΔL is positive the batch is lighter than the standard. In the case of control leathers, it has become lighter.

The dye/color consistency of the leather primarily depends on the surface characteristics of the leather. In the present process, dyeing was performed in two phases. The first phase ensures penetration of the dye while the second phase brings color consistency. The application of HTLM between the two phases of the leather dyeing is expected to create a uniform layer of the HTLM particles on the leather surface, which on exposure to dye solution adsorbs the dye molecules leading to uniform coloration of the leather surface.

Table III

Physical properties of the leather samples processed without and with the HTLM.

Property	Yellow 110		Orange 2 GL		Blue N	
	Control	Experiment	Control	Experiment	Control	Experiment
Dry Rubs	4	4	4	3/4	4	4
Wet Rubs	4	4	4	4	4	4
Perspiration	4/5	4	4	3/4	4	3

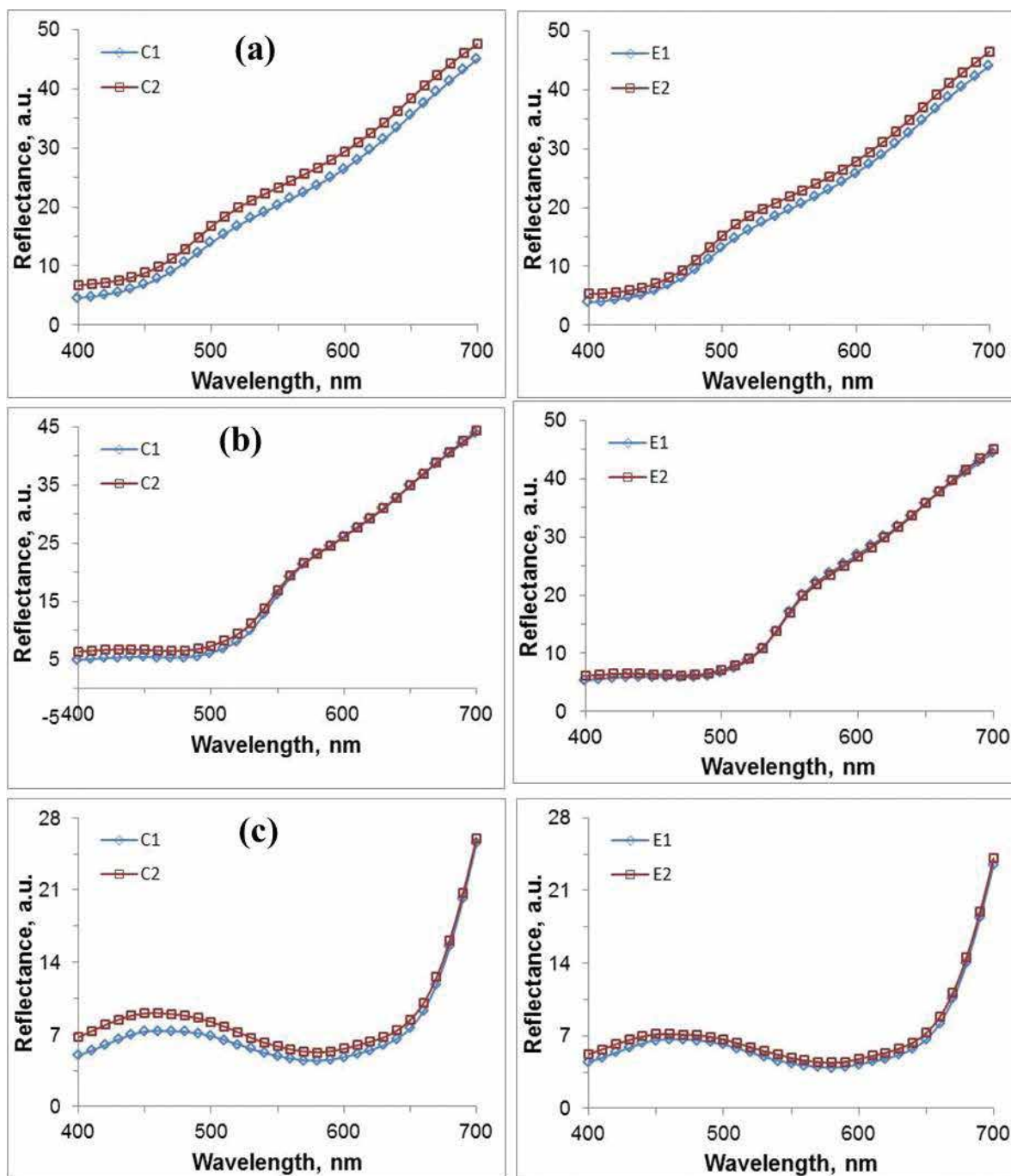


Figure 3. Reflectance spectra of the samples from CONTROL (C1 & C2) and experiments (E1 & E2) for the dyes (a) Yellow 110, (b) Orange GL and (c) Blue N.

The results of color fastness tests of the leather samples processed with and without the HTLM are presented in Table III. The values of color fastness to dry rub, wet rub and perspiration for the leather samples from control and the experiments show no significant difference indicating that the HTLM has no adverse effect on the physical characteristics of the leather.

The HTLM used in the present study is characterized for its mineralogical composition and surface morphology. The X-ray diffraction pattern, FT-IR spectrum, SEM image and EDX analyses of the HTLM are presented in Figure 4a-e. The XRD pattern (Fig. 4a) confirms the hydrotalcite-like layered structure of the HTLM indicated by the diffraction peaks at 2 θ positions

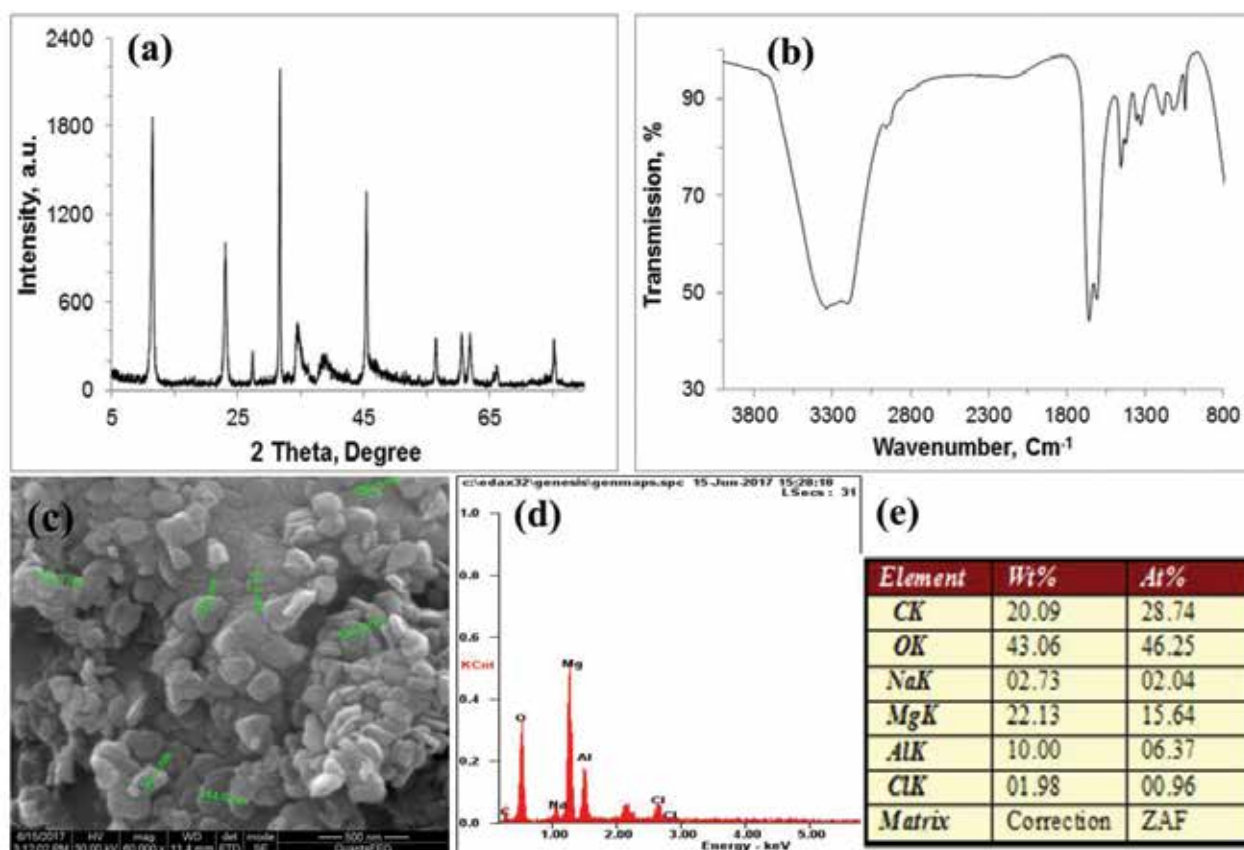


Figure 4. The XRD diffraction pattern (a), FT-IR spectrum (b), SEM image (c) and SEM-EDX analysis (d) of the HTLM.

11.5, 23.0, 34.3, 38.5 and 60.6 degrees.⁶ The sharp and strong diffraction peaks at 2 θ positions 27.4, 31.7, 45.4, 56.5, 66.2 and 75.3 degrees are identified to be due to NaCl⁸.

The FT-IR spectra of the HTLM (Fig. 4b) shows the peaks located around 3200–3500 cm^{-1} (O–H stretching), 2850–3000 cm^{-1} (C–H stretching) and the $-\text{CH}_2$ deformation vibration (1466 cm^{-1}). The peaks between 1060–1162 cm^{-1} due to C–O and C–O–C stretching vibrations can be seen clearly⁹. The band at 1637 cm^{-1} , corresponding to C=C stretching vibration and the band at around 1384 cm^{-1} was assigned to the stretching vibration of the COO^- group.¹⁰ All these peaks indicate the presence of organic functional groups that might have been used during the synthesis process.

The SEM image (Fig. 4c) shows the disc like particle of HTLM stacked one over another having average diameter between 50–150 nm and average thickness between 10–30 nm. The elemental composition obtained by EDX analysis (Figure. 4d) shows that the HTLM is primarily made of Mg and Al with little NaCl and some organic groups, which is also supported by the XRD and FT-IR studies.

Conclusion

The inorganic hydrotalcite-like synthetic material (HTLM) was successfully employed to bring color consistency in leather dyeing using three different dyes. Spectroscopic measurements of the leather samples showed minimum variation of color between the leathers processed using the HTLM. The values of ΔE for the leather samples from experiments (E1 and E2) were much less than those for the samples from control (C1 and C2), for all the three dyes. Leathers processed using the HTLM showed high level of color uniformity with no detrimental effect on perspiration and color fastness characteristics of the leather. Hence, HTLM can be a promising material to bring color uniformity in leather dyeing.

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