Studies on Combination Tanning Based on Henna and Oxazolidine

by

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Abstract

Among the innumerable alternative tannages that are currently exploited, the vegetable tannins and oxazolidine combination is one of the most promising options. In this study, an organic combination tanning process based on henna and oxazolidine for the production of upper leather is presented. Extract from the leaves of *Lawsonia inermis* (henna) obtained from Sudan has been utilized for tanning in combination with oxazolidine. It has been observed that this combination tanning, which employs 20% henna extract and 4% oxazolidine results in leathers with shrinkage temperature of 98°C. The differential scanning calorimetry data is in accordance with the observed shrinkage temperature. The change in the order of addition of henna and oxazolidine though showed marginal difference in thermal stability, but significant variations were observed in physical characteristics of leathers. Scanning electron microscopic analysis showed that leathers tanned first with oxazolidine resulted in better fiber splitting. Leather made from oxazolidine followed by henna resulted in relatively softer leathers compared to henna followed by oxazolidine tanning. Leather made from both the tanning combination systems meets the required strength characteristics for upper leathers. The manufacture of upper leathers using combination of henna and oxazolidine appears to be promising.

Resumen

Entre las innumerables alternativas de curtición que son actualmente empleadas, la combinación de taninos vegetales y oxazolidina es una de las opciones más prometedoras. En este estudio, una combinación de procesos de curtido orgánico sobre la base de combinar henna y oxazolidina para la producción de cuero para capellada es presentada. Extracto de las hojas de *Lawsonia inermis* (henna) obtenidos del Sudán se ha utilizado para el curtido en combinación con oxazolidina. Se ha observado que esta combinación de curtido, que emplea 20% de extracto de henna y el 4% oxazolidina, resultan en cueros con temperatura de encogimiento de 98°C. Los datos de escaneo por calorimetría diferencial están en concordancia con las temperaturas de contracción observadas. El cambio en el orden de adición de la henna y la oxazolidina, aunque mostró una diferencia marginal en la estabilidad térmica, se observaron variaciones significativas en las características físicas de los cueros. Análisis microscópico por barrido electrónico mostró que los cueros curtidos en primer lugar con oxazolidina dieron lugar a una mejor separación de las fibras. Cueros curtidos con oxazolidina seguida de la henna, pues resultó en cueros más suaves comparados con cueros curtidos con henna seguido de oxazolidina. Los cueros curtidos con los dos sistemas combinados responden a las características requeridas para los cueros para capellada. La fabricación de cueros de capellada empleando la combinación de la henna y oxazolidina parece ser prometedora.

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INTRODUCTION

The research centers throughout the world have undertaken studies on new tanning processes and have updated old methods in an attempt to find an alternative to conventional chrome tanning.[1] Conventional tanning procedures involving chrome create discharge containing significant amount of chlorides, sulphates, total dissolve solids and chrome making it increasingly difficult to comply with regulations governing the disposal of chrome containing wastes.[2] Till date there is no effective substitution for chrome tanning system. Chrome tanned leathers posses' high stability to wet heat with a shrinkage temperature of 100°C. The characteristics shrinkage temperature (Ts) close to 100°C is a standard especially for upper to which leathers tanned by other tanning process are compared. Considerable research has shown that the tanning effects of minerals other than chromium (Al, Zr, Ti, or Fe) are enhanced when they are used in combination with vegetable tannins, aldehydes, or other organic molecules.[3-5] Leather tanned with these combinations had Ts of near 100°C and physical-mechanical properties adequate for variety of application. The vegetable–oxazolidine combination tanning has been adopted to make different kinds of soft leather.[6,7] Oxazolidine has been found to be bio-degradable.[8] This explicates that oxazolidine is highly potent to be a retanning agent for vegetable tanned leather. The system is also environment friendly.

Oxazolidine is a heterocyclic derivative obtained by the reaction of aminohydroxy compounds with formaldehyde,[9] is an alternative to aldehyde tannage. Under hydrolytic conditions, the rings open to form an N- hydroxymethyl compound, which can react with one or more amino groups to produce effective cross-linking.[9,11] Oxazolidines have been shown to possess high reactivity and good tanning ability. Leather tanned by oxazolidine owns many characteristics: good softness and fullness, good physical/mechanical properties, sweat resistance and washability. These merits recommend oxazolidines to many researchers and series of oxazolidine tanning agents have been synthesized.[10] Oxazolidine will react with the amino groups of collagen to form cross-links improving the shrinkage temperature of leather.[9,11] Leather tanned by Oxazolidine E (Fig.1) has similar shrinkage temperature to that of glutaraldehyde tanned leather,[11] but is less full and less hydrophilic, because the molecular weight of monomeric oxazolidine is smaller than that of polymerized glutaraldehyde.

Recently, henna (*Lawsonia inermis*) has been established as an alternative retanning material for wattle.[12] *Lawsonia inermis* is a member of the family Lythraceae widely spread in tropical regions with relatively few species in temperate region.[13] *Lawsonia inermis* has been well investigated phytochemically by various researchers. *Lawsonia inermis* leaves have been reported to contain a wide variety of molecular species including flavonoids, quinoids, and naphthalene derivatives.[14-19] It is widely available in Sudan, Egypt and India. Since the henna extract contains mixture of several compounds with varied molecular weight including polyphenols, an attempt has been made in this study to utilize them in combination tannage with Oxazolidine.

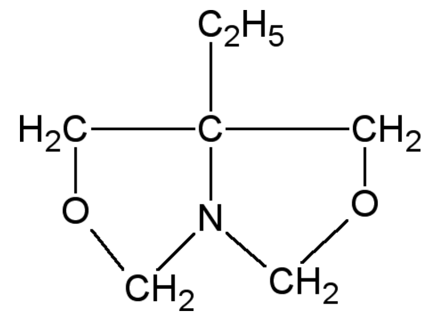

Figure 1. – 1-aza-3, 7-dioxabicyclo-5 methyl (3,3,0) octane (Oxazolidine E or II).

EXPERIMENTAL

Materials

Conventionally processed pickled goat skins were taken for the combination tanning trials. Henna leaves were sourced from Sudan. Chemicals used for post tanning were of commercial grade. Chemicals used for the analysis of spent liquor were of analytical reagent.

Aqueous Extraction of Henna Leaves

Dry henna leaves obtained from Sudan were grounded into powder and known weight of powder was taken in water at the ratio 1:10 w/v of henna to water. The water bath containing henna powder was heated at 80°C for an hour and then filtered through cotton cloth. The henna powder contains a total of 35% water solubles. For example, 1 kg of henna powder 10 liters of water needs to be added, after extraction, 350 grams of water soluble is obtained. The solution was further concentrated to 1 liter. The stock solution thus prepared contains 35% (w/v) solids and the same was used for combination tanning experiments.

Tanning Trials

The tanning experiments were carried out on pickled goatskins. Three pickled pelts in the range of 4–5 sq. ft were taken for each experiment. Experimental combination tanning trial oxazolidine followed by henna (Oxa-Henna) were carried out as per the process mentioned in Table I and combination tanning based on henna followed by oxazolidine (Henna-Oxa) was carried out as per the process mentioned in Table II. Control henna tanning trial was carried out as per process given in Table III. Both experimental and control leathers were processed into upper crusts following the process mentioned in Table IV.

TABLE I

Formulation of Oxa-Henna Combination tanning process for goat pickled skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	50	Water		
	1	sodium bicarbonate	3 x 15	pH 6
Tanning	4	Oxazolidine Granofin TX50(Clariant)	90	
Henna tanning	2	Basyntan P (Phenolic syntan, BASF)	30	
	10	Henna extract	120	
	10	Henna extract	120	
Fixing	0.5	Formic acid	3 x 10 + 30	pH 3.5
Washing	300	Water	10	Check the pH to be 3.5. Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

TABLE II

Formulation of Henna-Oxa Combination tanning process for goat pickled skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	100	Water		
	0.75	Sodium bicarbonate	3 x 15	pH 4.5 -4.7
Tanning	2	Basyntan P (Phenolic syntan)	30	
	10	Henna extract	120	
	10	Henna extract	120	
	4	Oxazolidine Granofin TX50(Clariant)	90	
Fixing	0.25	Formic acid	3 x 15	pH 4
Washing	300	Water	10	Check the pH to be 3.5. Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

Determination of shrinkage temperature:
The shrinkage temperature of both control and experimental leathers were determined using the Theis shrinkage tester.[20] A 2cm sample, cut out from the leather was clamped between the jaws of the clamp, which in turn was immersed in a solution of glycerol: water mixture (3:1). The solution was stirred using mechanical stirrer attached with the shrinkage tester. The temperature of the solution was gradually increased and the temperature at which the sample shrinks was noted. Triplicates were carried out for each sample and the average values are reported.

Visual assessment of the crust leather
Experimental and control crust leathers were assessed for softness, fullness, grain smoothness, grain tightness (break), general appearance and dye uniformity by hand and visual examination. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property, where higher points indicate better property.

TABLE III

Formulation of Henna tanning process (Control) for goat pickled skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	100	Water		
	0.75	Sodium bicarbonate	3 x 15	pH 4.5 -4.7
Tanning	2	Basyntan P	30	
	10	Henna extract	120	
	10	Henna extract	120	
Fixing	0.25	Formic acid	3 x 10 + 30	pH 3.5
Washing	300	Water	10	Check the pH to be 3.5. Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

TABLE IV

Formulation of Post-tanning process for making upper crusts

Process	%	Product	Duration (min)	Remarks
Washing	200	Water	10	
Neutralization	0.75	Sodium bicarbonate	3 x 15	pH 5-5.5
Pre-retannage	100	Water		
	2	Relugan RE (Acrylic syntan)	40	
Pre-fatliquor	2	Lipoderm liquor SAF (Synthetic fatliquor, BASF)	40	
	2	Basyntan DI (Phenol-naphthalene condensation syntan, BASF)	30	
Dyeing	3	Acid dye brown	30	
fatliquoring	3	Lipderm liquor SAF (Synthetic fatliquor, BASF)		
	4	Balmol BL II (Semi synthetic fatliquor, Balmer & Lawrie)	40	
Retanning	3	Basyntan DI		
	4	Basyntan FB6 (Resin syntan based on melamine, BASF)	40	
Fixing	1	Formic Acid	3 x 10 + 30	pH 3.5

Physical testing

Samples for various physical tests from experimental and control crust leathers were obtained as per IULTCS methods.[21] Specimens were conditioned at 20 ± 2°C and 65 ± 2% R.H over a period of 48 hrs. Physical properties such as tensile strength, percentage elongation at break,[22] grain crack strength[23] and tear strength[24] were measured as per standard procedures. Each value reported is an average of four (2 along the backbone, 2 across the back bone) samples.

Measurement of leather Softness

Softness measurement of experimental and control crust leather was carried out as per standard method.[25] Samples were conditioned at 20 ± 2°C and 65 ± 2% R.H over a period of 48 hrs before the measurement. Circular aperture of diameter 35 mm is used for the softness measurement. Each value reported is an average of four measurements.

Scanning Electron Microscopic Analysis of Leather Samples

Samples from experimental and control crust leathers were cut from official sampling position. Samples were directly cut into specimens with uniform thickness without any pretreatment. All specimens were then coated with gold using Edwards E306 sputter coater. A Leica Cambridge Stereoscan 440 Scanning electron microscope was used for the analysis. The micrographs for the cross section were obtained by operating the SEM at an accelerating voltage of 20 KV with different lower and higher magnification levels.

Analysis of Henna Extract Exhaustion

Spent henna extract liquor from control and experimental tanning processing was collected and analyzed for the concentration using a spectrophotometric method by measuring the absorbance value at the λ_{max} of the henna extract used, after suitably diluting the spent extract liquor using *UV–visible spectrophotometer (Hitachi, Japan)*.

$$\% \text{ Henna extract exhaustion} = [(C_o - C_s)/C_o] \times 100$$

Where C_o is the concentration of henna extract offered and C_s is the concentration of henna extract in the spent liquor. Each value reported is an average of four measurements.

Differential Scanning Calorimetry (DSC)

The DSC technique provides a suitable tool for the rapid determination of changes in the collagenous structure of leather. The onset temperature of the DSC curve is defined as shrinkage temperature of the leather or the temperature of phase transformation, the higher onset, the better the hydrothermal stability of collagen.[26] The thermal analysis of the leather samples from experimental and control crust leathers were carried out using Dupont 2910 DSC instrument. The samples weighed (around 3 mg). The heating rate was 10°C per minute in nitrogen atmosphere.

RESULT AND DISCUSSION

Combination tanning trials using henna and oxazolidine were carried out with 4% offer of oxazolidine and 20% offer of henna. The shrinkage temperature and exhaustion data of leathers tanned with Henna-Oxa and Oxa-Henna combination along with henna control is given in Table V. From the table it is seen that both the combination resulted in leathers with good shrinkage temperature. Both the combination tanning resulted in leathers with shrinkage temperature around 98°C, which are better than control leathers from henna of Ts 84°C. From the Table it is seen that the uptake of henna extract by the leather is better for experimental (Oxa-Henna tanning and Henna-Oxa tanning) compared to control (Henna tanning). The exhaustion of both the combination tanning system is greater than 85%, whereas for the control the exhaustion is about 75%. The combination of Henna and Oxazolidine had a synergistic effect resulting in an increase of shrinkage temperature and exhaustion of henna.

Organoleptic properties of crust leathers for experimental and control

The organoleptic properties (visual assessment) of upper crust leathers for experimental and control are shown in Fig. 2. From the figure, it is observed that crust leathers processed by experimental combination tanning system exhibited good softness, fullness, smoothness, general appearance and dye uniformity compared to control leathers from henna tannage. The organoleptic properties of the Henna-Oxa crust leathers exhibited better grain tightness compared to Oxa-Henna crust leathers.

Physical strength characteristics of experimental and control crust leathers

The physical strength measurements of experimental and control leathers are given in Table VI. The physical strength measurements viz., tensile strength, tear strength has been found to be better for experimental leathers. The experimental Henna-Oxa tanning system resulted in leathers with good tensile and tear strength characteristics. The values for load at grain crack for both experimental and control leathers were comparable. All the physical strength parameters for both control and experimental leathers are found to meet the requirement of BIS standards for upper leathers[27]. The softness values for the experimental and control leathers are given in Table VII, higher value indicates better softness. It is seen that the softness of experimental leathers are better than that of the henna control leathers. This is in accordance with the observations made by subjective evaluation on softness (Fig. 2).

TABLE V
Shrinkage temperature and henna exhaustion for experimental and control

Experiment	Shrinkage temperature, Ts (°C)	Exhaustion %
Oxa-Henna	97±1	87±2
Henna-Oxa	98±2	86±3
Henna (Control)	84±0.5	75±2

TABLE VI

Physical strength characteristics of experimental and control crust leathers

Parameter	Oxa-Henna	Henna-Oxa	Henna (control)	BIS standards
Tensile strength (Kg/cm^2)	220±2	250±2	210±3	200
Elongation at break (%)	56±0.7	57±1.6	56±1.6	40-65
Tear strength (Kg/cm)	50±1.5	59±1.5	47±0.7	30
Load at grain crack (kg)	22±0.7	24±0.7	25±0.7	20
Distention at grain crack (mm)	10±1.6	11±0.7	10±07	7

TABLE VII

Softness values for experimental and control crust leathers

Leather	Softness Value
Oxa-Henna	4.50±0.14
Henna-Oxa	4.30±0.14
Henna (control)	3.40±0.47

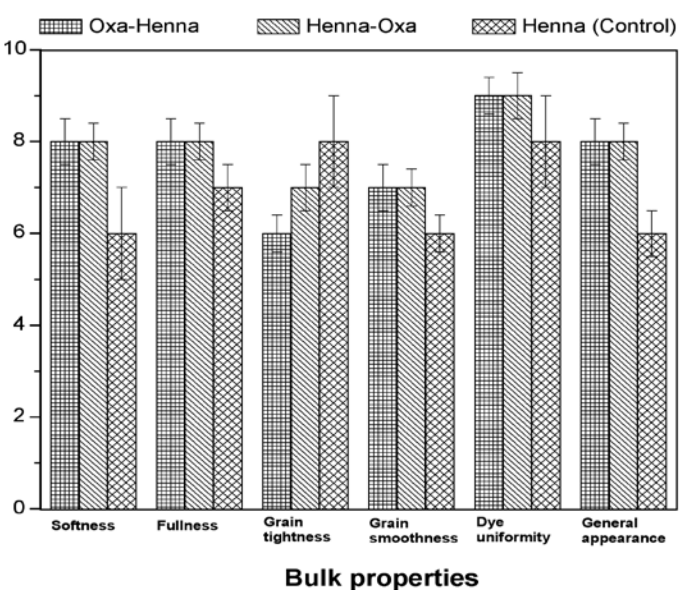

Figure 2. – Graphical representation of organoleptic properties of the Experimental and control leather.

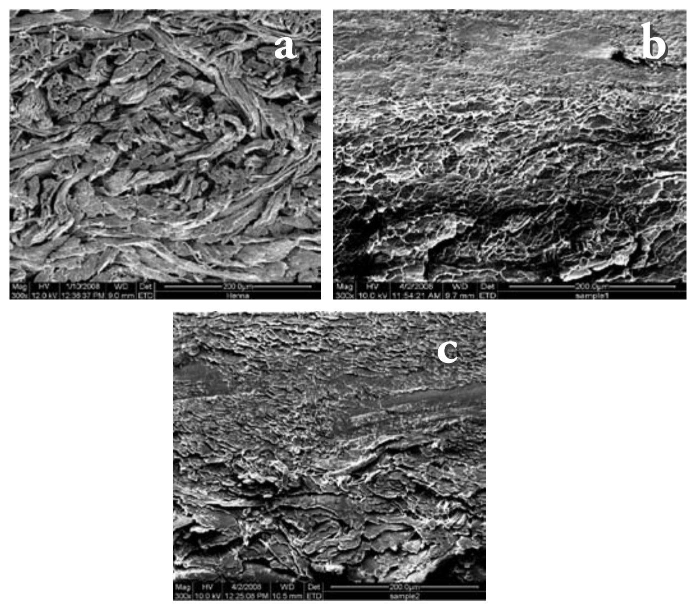

Figure 3. – Scanning electron micrograph of crust leathers (3a) control (henna), (3b) Oxa-Henna and (3c) Henna-Oxa samples showing the cross section at magnification of X300 after tanning.

Scanning Electron Microscopic Analysis of Leather Samples

Scanning electron micrograph of crust samples from control (henna) and experimental tanning process (Oxa-Henna, Henna-Oxa) showing the cross section at magnification of X300 are shown in Figs 3a, 3b and 3c respectively. Well separated and opened up fibres are seen for all the crust leathers. However, cross section of leathers processed from Oxa-Henna(Fig. 3b) combination seem to have more fibre splitting. Generally aldehydic tanning system results in leathers with better fibre splitting, whereas vegetable tannin material are known to coat the fibre bundles. Hence the observation of better fibre splitting for Oxa-Henna seems to be justified. This is in accordance with the softness data (Table VII).

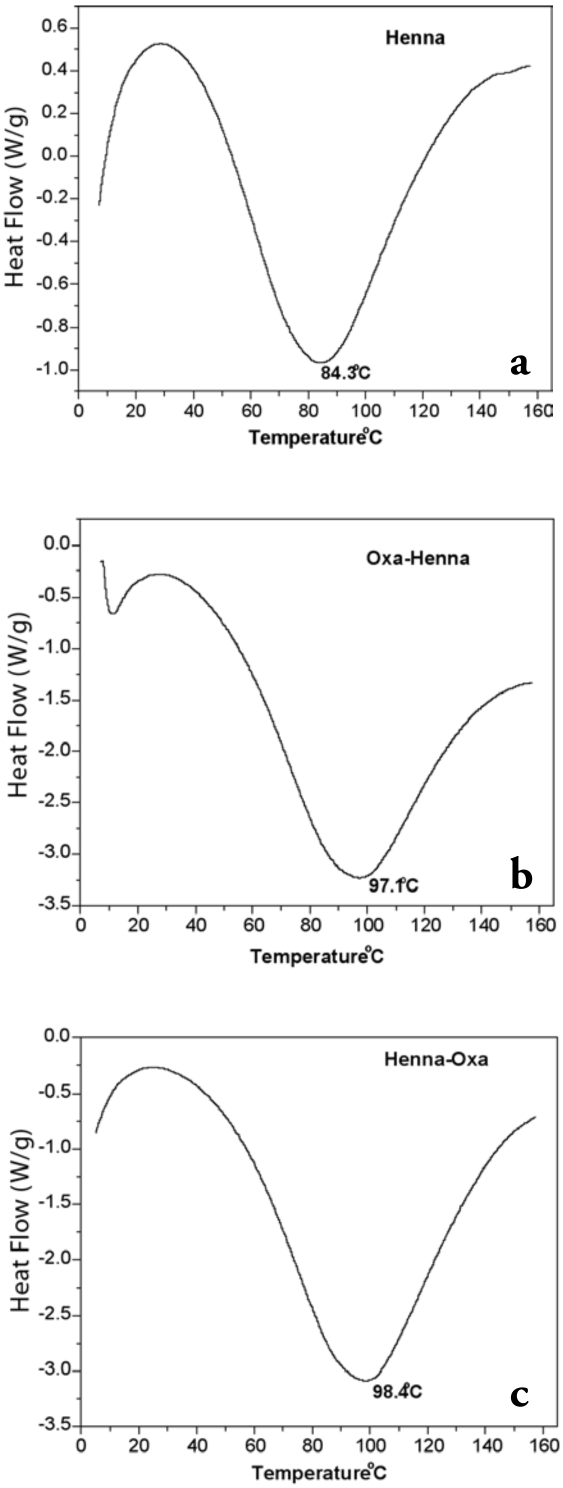

Figure 4. – DSC of crust leathers (4a) Control (henna), (4b) Oxa-Henna and (4c) Henna-Oxa.

DSC Determination

The DSC spectra of control and experimental leathers are shown in Fig. 4a-c. It is seen from the figure that the peaks appear at 97.1°C for Oxa-Henna, 98.4°C for Henna-Oxa tanned crust leathers, respectively. It is seen that the order of addition of henna and oxazolidine has little effect on the thermal stability of the final leathers. The control leathers exhibit a value of 84.3°C. The values observed from DSC are in accordance with the shrinkage temperature values given in Table V. Oxazolidines have the potential to crosslink, as they can undergo ring opening to form a carbocationic intermediate that may interact, depending on the pH value, through covalent bonds with the amino groups of the collagen side-chains. The oxazolidines can also covalently link with the flavonoid ring system.[28, 29] In order to achieve a high hydrothermal stability of the tanned leather, the determining mode, as reported in the literature,[30,31] is to simultaneously promote the formation of covalent bonds between oxazolidine and henna, thereby covalently binding a tannin matrix to collagen in a concerted interaction. The covalent binding of oxazolidine to the amino groups of collagen is favoured by relatively high pH, hence the combination of henna and oxazolidine had resulted in high shrinkage temperature

Henna and Oxazolidine Combination Tanning: An option for upper leather manufacture

Tanners have little choice for making chrome free upper leathers as most of the alternative tanning system do not result in leathers with good thermal stability. The combination tanning based on henna and oxazolidine employed in this work had resulted in leathers with shrinkage temperature around 100°C. Both the combinations, Henna–Oxa and Oxa–Henna resulted in leathers with similar thermal stability. This is a complimentary combination tanning system, where oxazolidine and henna do not compete with each for binding with collagen. Oxazolidine bearing aldehydic group bind with side chain amino groups of lysine and arginine, whereas polyphenolic constituents of henna tend to have non-specific interaction viz., hydrogen bonding, electrostatic and hydrophobic with collagen. Hence the combination of henna and oxazolidine worked synergetically to enhance the hydrothermal stability of collagen. Variation in the order of addition of these two tanning agents resulted in changes in the bulk properties of the leathers. Tanning with oxazolidine followed by henna resulted in leathers with better fibre splitting compared to Henna-Oxa combination. The same is substantiated from the observation made from SEM analysis and softness measurements. Hence the combination Oxa-Henna forms an effective option for making softy upper leathers whereas Henna-Oxa could be better for firm and tighter leathers. Leathers made from both the combination meets the requisite physical strength characteristics of upper leathers. Henna is widely cultivated in tropical regions of the world viz., Sudan, Egypt and India[32]. Hence henna can form a suitable vegetable material for exploitation in developing combinations systems for upper leathers.

CONCLUSIONS

In the present study, an attempt has been made to produce upper leather using combination tanning process based on henna and oxazolidine. It is seen that combination tanning system with 20% henna extract and 4% oxazolidine results in leathers with a maximum shrinkage temperature of 98°C, which is 14°C greater than the control leathers. The exhaustion of henna is 10% more when henna is used in combination with oxazolidine compared to solo henna tanning. The physical strength characteristics of the experimental leathers meet the required norms for upper leather. The combination tanned leathers are softer than control especially Oxa-Henna combination. The bulk properties for the experimental leathers are better than control leathers. Scanning electron microscopic analysis of both control and experimental leather samples show good separation of fiber bundles. The eco friendly organic combination tanning using henna and oxazolidine forms a viable option for the manufacture of upper leathers.

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