Combination Tanning System Based on Dialdehyde Alginic Acid: An Ecofriendly Organic Approach

by

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ABSTRACT

Dialdehyde alginic acid (DAA) is established as an eco-friendly biodegradable tanning agent. In the present study, combination tanning of DAA using glutaraldehyde, oxazolidine and Tetrakis Hydroxymethyl Phosphonium Sulfate (THPS) was evaluated. The combination tanned leathers resulted in better physiochemical properties. Shrinkage temperature about 97°C was obtained for DAA-glutaraldehyde tanning system. The presence of glutaraldehyde, oxazolidine and THPS in combination tanning with DAA resulted in an increase of hydrothermal stability owing to enhanced degree of crosslinking in all the combination tanning systems. The physical strength characteristics and organoleptic properties of combination tanned leathers were enhanced in comparison with DAA tanned leathers. There was no significant change in intensity of color in the combination tanned leathers. The DAA -THPS combination tanning exhibited good light fastness due to the presence of THPS. The DAA combination tanning process also benefits from reduction in total solids (TS) biological oxygen demand (BOD) and chemical oxygen demand (COD) loads from the identified tanning streams.

RESUMEN

El ácido dialdehídico algínico (DAA) se establece como un agente de curtido ecológico biodegradable. En el presente estudio, un curtido combinado de DAA empleando glutaraldehído, oxazolidina y sulfato de tetrakis-hidroximetil-fosfonio (THPS) fue evaluado. Los cueros curtidos con esta combinación resultaron con mejores propiedades físico-químicas. Temperatura de contracción cercana a los 97°C fue obtenida en el sistema de curtido DAA-glutaraldehído. La presencia de glutaraldehído, oxazolidina y THPS en el curtido combinado con DAA dio lugar a un aumento de la estabilidad hidrotermal, debido a un mayor grado de entrecruzamiento en todas las combinaciones de los sistemas de curtido. Las características físicas y las propiedades organolépticas de los cueros curtidos en combinación se han mejorado en comparación con cueros curtidos con DAA. No hubo cambios significativos en la intensidad de color en los cueros de curtido combinado. El curtido combinado DAA-THPS exhibió buenas solideces a la luz por la presencia de THPS. El proceso de curtido combinado con DAA beneficia también por la reducción en sólidos totales (ST), en la demanda biológica de oxígeno (DBO) y en la demanda química de oxígeno (DQO) de los residuales de los curtidos.

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INTRODUCTION

In the present scenario, there is serious concern for developing ecofriendly tanning systems. The present environment, conscientious world is driving researchers to explore eco-friendly products and processes.[1] The leather industry, similar to most other potential polluting industries, is continuing to implement environment friendly procedures in proportion to the regulatory legislation.[2] Use of chromium in leather industry is being questioned owing to reports emerging on the toxicity and disposal problems associated with it.[3-4] Hence, it is obvious that worldwide research is being focused on chrome free tanning systems. The comprehensive concern on the negative impact of the leather industries on the environment has forced tanners to pay attention to the processes that reduce the problems related to pollution. Alternatives to chromium are being sought actively owing to the stringent regulations on disposal of chromium containing wastewater and solid wastes.[5-6] In order to avoid chromium completely in leather processing; other tanning agents are being investigated. Many alternatives were explored however, no individual tanning agent was able to match the properties of chromium.[7] In this regard, the concept of biodegradable chrome free combination tannage emerge as a suitable option for disposal of solid waste. Any alternative tanning system should not only satisfy environmental criteria, but also be able to match the properties of conventional tanned leathers.[8] There was an ongoing search for modified biopolymers as a biodegradable tanning system to replace chromium.[9] In order to establish such biodegradable tanning system, tanning agents like DAA, Dialdehyde Starch (DAS), Dialdehyde Cellulose (DAC) as modified biopolymers are being used. However, limitations in the form of leather quality exist for these tanning systems. The hydrothermal stability of these leathers is also reported to be in the range of 80-84°C. Hence, to meet these challenging demands, a combination tanning system based on glutaraldehyde, oxazolidine and THPS was explored in this present study.

In this study, "Ecofriendly organic combination tanned leathers" as a potential alternative to "chrome tanned leathers" is being investigated. This was investigated using DAA in combination with glutaraldehyde, oxazolidine and THPS. DAA was established as a biodegradable tanning agent.[9] The tanning potency of glutaraldehyde, oxazolidine and THPS was studied earlier.[10] Glutaraldehyde is the most extensively used reagent for stabilizing collagen. Glutaraldehyde posses difunctionality to exhibit reactivity between two polypeptide chains. Hence, dialdehydes like glutaraldehyde can act as better stabilizing agent for collagen. The oxazolidine structure is unique among waxes, both natural and synthetic, on which one can build a wide variety of compounds having properties that make them significant interest in various fields of applications. Oxazolidine ring has two sites in the 4 position and two in the 5 position where reactive groups may be located. Also, the nitrogen of the oxazolidine is basic and forms salts with acids and quaternary compounds with alkyl halides. Oxazolidine shows affinity to interact with basic amino acids and hydroxyl amino groups. THPS benefits from low toxicity, lower treatment levels, rapid breakdown in the environment, no bioaccumulation and also provides reduced risk to both human health and environment.[11-12] The shrinkage temperature, tanning conditions, physico-chemical characteristics and the versatility of this new combination system in making ecofriendly leathers and the environmental impact of the tanning system are presented in this paper.

EXPERIMENTAL

Raw Material

The raw material used for leather processing was delimed goatskins processed from wet salted goatskins selected in the weight range of 1kg. The process up to deliming was carried out in a conventional way with additional care taken during fleshing operation, to ensure the proper removal of flesh layer. The chemicals used were of commercial grade for leather processing and laboratory grade for analytical techniques.

Selection of Combination System

Three different combination systems were chosen viz. DAA–glutaraldehyde, DAA–oxazolidine and DAA-THPS. All the experiments were carried out on conventionally processed delimed goatskins.[13]

Dialdehyde Alginic Acid– Glutaraldehyde Combination Tanning

Five skins were employed for DAA-Glutaraldehyde combination tanning. Delimed pelts were treated with varying concentrations (0.5-3%) of glutaraldehyde, added to 100% water and the drum was run for 60 mins. 10% DAA was added to the float and the tanning process continued for 90 mins. The pH of the float was adjusted to 4.0 using formic acid. The tanned skins were washed with 200% water. The leathers were piled for 24 hrs. The hydrothermal stability of the DAA-glutaraldehyde tanned leathers was measured using shrinkage tester.

Dialdehyde Alginic Acid– Oxazolidine Combination Tanning

Five skins were used for each trial. To the delimed pelt, 10% DAA was added to 100% water and the tanning process carried out for 90 mins. The pH of the float was adjusted to 4.0 using formic acid. To the float, varying concentrations (0.5-3%) of oxazolidine was added and the drum was run for 60 mins. The tanned skins were washed with 200% water. The leathers were piled for 24 hrs. The hydrothermal stability of the DAA-Oxazolidine tanned leather was measured using shrinkage tester.

TABLE I
Control chrome tanning process

Chemicals	%	Time	Remarks
Pickle Liquor	50		Check pH 2.8-3.0
BCS	8	60 min	Check penetration
Water	50	10 min	
Sodium formate	1	10 min	
Sodium bicarbonate	1		
Water	10	3x10 min + 2 hours	Check pH 3.8-4.0 Drain: aged for 24 hrs

TABLE II
Control DAA tanning process

Chemicals	%	Time	Remarks
Water	50		Check pH 8.0
DAA	10	60 min	Check penetration
Formic acid	1	3x10 min	pH adjusted to 4
Water	10	30 min	Drain: aged for 24 hrs

TABLE III
Post tanning recipe for both control and experimental leathers

Process	Chemical	%	Time (min)	Remarks
Neutralization	Water	100		
	Neutrigan	1	10	
	Sodium bicarbonate	1	3 ×10 +30	Check pH 5.0-5.5
Washing	Water	100	10	
Fatliquoring	Water	50		
	Synthetic oil based fatliquor	4		Fatliquors are emulsified with hot water at 60°C (1:20 dilution)
	Semi-synthetic oil based fatliquor	4		
	Synthetic oil based fatliquor	4	60	
Retanning	Acrylic based syntan	4		
	Light fast syntan with strong tanning action	2		
	Acid Dye	3		
	High fastness syntan for tight grain	2	60	
Fixing	Formic acid	2		
	Water	20	3 ×10 + 30	Check exhaustion and drain
Washing	Water	100		Rinse and pile

Dialdehyde Alginic Acid – THPS Combination Tanning

For DAA-THPS combination tanning, five skins were used for each trial. To the delimed pelt, 10% DAA was added to 100% water and the tanning process continued for 90 min. The pH of the float was adjusted to 4.0 using formic acid. Varying concentrations (0.5-3%) of THPS was added and the tanning process continued for another 60 mins. The tanned skins were washed with 200% water and the leathers were piled for 24 hrs.[14] Subsequently, the hydrothermal stability of the DAA-THPS tanned leather was measured using shrinkage tester after 24 hrs.

Control DAA and Chrome Tanning Process

Five wet salted goat skins were processed to pickled stage by conventional method and were tanned by chrome and DAA for control as given in Table I and II. The post tanning recipe, as given in Table III, was followed to make both control and experimental leathers.

Determination of Shrinkage Temperature

The shrinkage temperature, which is a measure of hydrothermal stability of leather, is determined using a Theis shrinkage tester. A 2 cm^2 sample cut out from the tanned leather was clamped between the jaws of the clamp, which in turn was immersed in a solution of water: glycerol mixture (1:3). The solution was stirred vigorously using mechanical stirrer. The temperature of the solution was gradually increased and the temperature at which the sample shrinks was noted.

Measurement of Degree of Crosslinking

Collagen solution from rat-tail tendon was isolated according to the method described by Chandrakasan et al.[15] The procedure included acetic acid extraction and salting out with NaCl. The purity of collagen preparation was confirmed by SDS-polyacrlyamide gel electrophoresis. The collagen concentration in the solution was determined from the hydroxyproline content according to the method of Woessner.[16] Degree of crosslinking of native collagen (non-crosslinked). and DAA, DAA-glutaraldehyde, DAA-oxazolidine and DAA-THPS treated collagen (crosslinked) was determined by TNBS assay.[17] Collagen solution (1 μM concentration) was crosslinked with varying concentrations (0-1%) of DAA, DAA-glutaraldehyde, DAA-oxazolidine and DAA-THPS at 30°C for 2 hrs. To this solution of crosslinked collagen, 1 ml of 4% (w/v) sodium bicarbonate solution and 1 ml of freshly prepared 0.5% (v/v) TNBS solution in deionized water was treated at 60°C for 4 hrs. The unreacted amino groups in collagen solution react with TNBS to form a soluble complex. The solution (1 ml) was treated with 3 ml of 6M HCl at 40°C for 1.5 hrs and the absorbance was measured at 334 nm after dilution. The native collagen (1μM) (non-crosslinked) was also treated with TNBS in a similar manner. The degree of crosslinking was calculated as follows:

$$\text{Degree of cross linking} = \left\{ 1 - \frac{(\text{absorbance}_{cl}/\text{mass}_{cl})}{(\text{Absorbance}_{ncl}/\text{mass}_{ncl})} \times 100 \right\}$$

where, the subscript 'cl' and 'ncl' stand for the 'crosslinked' and 'non-cross linked' collagen, respectively.

Physical Testing of Leather Samples

The samples for physical testing were obtained as per IULTCS methods. The samples were conditioned at 80°F and 65% R.H. for 48 hrs.[18-20] Physical properties such as tensile strength, % elongation, tear strength and grain crack strength were investigated as per standard procedures. Each value reported is an average of four measurements.

Evaluation of Organoleptic Properties

Crust leathers were assessed for softness, grain smoothness, fullness and general appearance by tactile evaluation. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property.

Determination of Color Difference of Crust Leathers

The control and optimized experimental crust leathers processed in this study were subjected to the reflectance measurements using a Milton Roy color mate HDS instrument.[21] Color measurement (L, a, b, h and C) were recorded and the total color difference (ΔE) and hue difference (ΔH) were calculated using the following equations:

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

$$\Delta H = \sqrt{\Delta E^2 - \Delta L^2 - \Delta C^2} \quad (2)$$

Where ΔE = overall color difference; ΔL = Lightness difference; Δa and Δb = difference of a and b values, where 'a' represents the red and green axis and 'b' represents the yellow and blue axis; ΔH, hue difference, ΔC, chromaticity difference.

Analysis of Spent Tan Liquor

Spent tan liquors from experimental leather processing were collected and analyzed for BOD, COD and TS (dried at 103-105°C for one hour) as per the standard procedures.[22] The values reported are average of three experiments along with their standard deviations.

RESULT AND DISCUSSIONS

DAA- Glutaraldehyde Combination Tanning System

10% DAA tanned leather resulted in 84°C shrinkage temperature was optimized as higher concentration of DAA did not increase the shrinkage temperature significantly. The offer of glutaraldehyde in the DAA-glutaraldehyde combination tanning system was varied between 0.5 to 3.0 % and the shrinkage temperature is seen in Figure 1. From the figure, it is observed that the shrinkage temperature of the combination tanned leathers increased with an increase in the percentage of glutaraldehyde. Crosslinking of DAA and glutaraldehyde can involve Schiff's base formation between the ε-amino groups of lysine or hydroxylysine and arginine side groups of collagen. The shrinkage temperature increased with increase in the concentration of glutaraldehyde. The maximum shrinkage temperature was found to be 97°C at 3% glutaraldehyde in DAA-glutaraldehyde combination tanned leathers.

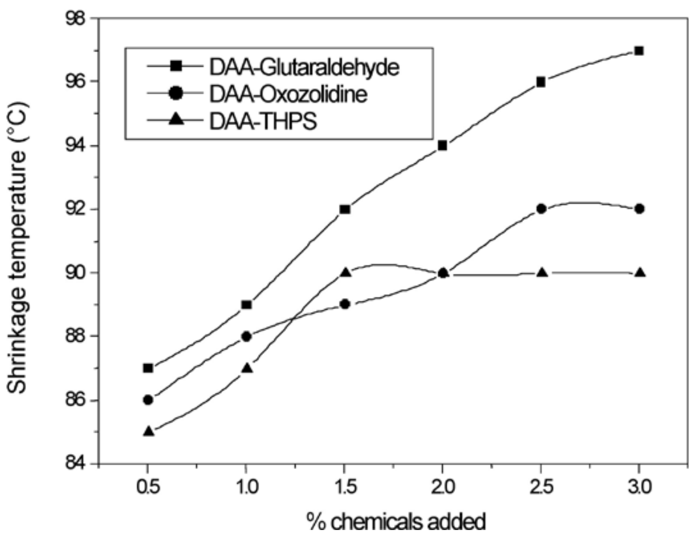

Figure 1: Shrinkage temperature of combination tanned leathers at various concentrations

DAA- Oxazolidine Combination Tanning System

In order to establish the tanning potential of DAA-oxazolidine, the offer of oxazolidine was varied between 0.5 to 3% in the DAA-oxazolidine combination tanning system. The shrinkage temperature of leathers tanned using DAA- oxazolidine combination is given in Figure 1. From the figure, it is observed that there is an increase in the shrinkage temperature with increase in percentage of oxazolidine offered. 2.5% oxazolidine showed a maximum shrinkage temperature of 92°C, beyond which there was no appreciable difference in shrinkage temperature. DAA and oxazolidine exhibit reactive nature towards their interaction with collagen. Moreover, DAA predominantly forms covalent bond with the basic amino acids, whereas oxazolidine crosslinks with hydroxyl aminoacids, primarily to form hydrogen bonds. The presence of oxazolidine enhances the crosslinking due to their complementary nature. Increased concentration of oxazolidine contributes fullness to the leather.

DAA - THPS Combination Tanning System

THPS tannage is known to produce leathers with exceptional strength properties, pastel shades and good shrinkage temperature. THPS were varied between 0.5 to 3% along with 10% DAA in DAA-THPS combination tanning experiments. The shrinkage temperatures of DAA-THPS combination tanned leather are given Figure 1. As seen in Figure 1, the shrinkage temperature of THPS exhibits complementary reactivity to DAA in DAA-THPS combination tanning system. The maximum hydrothermal stability obtained for 1.5% THPS-DAA combination tanned leather was 90°C which was optimized for further experiments. Shrinkage temperature of leathers beyond 1.5% THPS did not bring about any increase. THPS interacts chemically with the hydroxyl sites of collagen possibly by hydrogen bonding and stabilize collagen.

Degree of Crosslinking

Cross-linking of the collagen matrices can be controlled by variation of aldehyde concentration. The degree of cross-linking is inversely proportional to the amount of free amino groups. With increasing concentration of aldehydes, the amount of free amino groups decreases and hence the degree of crosslinking increases. The degree of crosslinking of different aldehydes with collagen can be quantitatively determined by 2, 4, 6-trinitobenzenesulphonicacid (TNBS) assay. The reagent reacts specifically under mild conditions (at pH values near 7 or above) with the availability of free amino groups to give trinitrophenyl derivatives. The unreacted amino groups in collagen react with TNBS to form trinitrophenyl derivatives that have specific absorbance at 334 nm. From the absorbance measurements of varied crosslinked collagen and native collagen (non crosslinked), the extent of crosslinking of aldehydes with the collagen can be determined. Bowes and Cater[23] have shown that the amino groups present in the collagen are involved in interaction with dialdehydes. The most probable reaction of unifunctional aldehydes is the formation of Schiff's base type compounds and the methylene linkages resulting from mannich reaction with the amino functional groups in the collagen. Reaction with formaldehyde may not be able to form a crosslink with the amino functional group in the neighbouring polypeptide chain of the collagen. For effective crosslink formation, the molecule used for crosslinking should posses difunctionality to exhibit reactivity between two polypeptide chains. Hence, dialdehydes can act as excellent crosslinker for collagen. Hence crosslinking in DAA can involve schiff's base formation between the ε-amino groups of lysine or hydroxylysine and arginine side groups of collagen. The amino groups are generally protonated at lower pH and hence aldehyde interaction with proteins is preferable at pH above iso electric point (IEP) of the protein.

The extent of crosslinking after treating the collagen solution with various concentrations of DAA is given in Table IV. It is observed that an increase in concentration of DAA resulted in increased degree of crosslinking by formation of stable crosslink's with amino groups of collagen. The high fixation of DAA with collagen can be attributed to strong binding between the two, as DAA can have both covalent and non-covalent interaction with collagen. The possibility of inter and intra chain crosslinking between collagen and DAA within the collagen matrix brings about stability to collagen. The crosslinking efficiency of DAA was found to be maximum in the presence of glutaraldehyde as observed in Table IV. Similarly, the DAA-oxazolidine combination system also resulted in higher degree of crosslinking as amino groups of oxazolidine can involve in interactions with both DAA and collagen. Moreover interacted intermediate compound can form hydrogen bonding with the collagen, which brings about structural stabilization and increased crosslinking. In DAA-THPS combination system, the influence due to THPS is not significant as compared to as glutaraldehyde and oxazolidine.

Effect of Strength Properties on Combination Tanned Leathers

Tensile, tear strength and grain crack tests were carried out for control and matched experimental crust leathers both along and across the backbone. The mean of average values corresponding to along and across backbone were calculated and are given in Table V. The values of various strength properties of experimental leathers are found to be comparable to that of the control leathers. From Table V, it is apparently clear that DAA-THPS tanned leathers resulted in higher tensile strength values when compared with DAA-oxazolidine and DAA-glutaraldehyde tanned leathers. THPS involves in inter and intra crosslinking with collagen, which result in better tensile strength property in DAA-THPS combination tanned leathers. However, tear strength of DAA-glutaraldehyde tanned leather showed comparatively lesser values when compared to control and other combination tanned leathers. DAA-oxazolidine tanned leather showed comparatively better tensile strength characteristics than DAA-glutaraldehyde tanned leathers. DAA and oxazolidine exhibit reactive nature of interaction with collagen, with DAA predominantly involving covalent bond interaction with the basic amino acids whereas oxazolidine reacts with hydroxyl aminoacids, primarily to form hydrogen bonds.

TABLE IV

Percentage degree of crosslinking of DAA treated collagen of 1% at varying concentration of glutaraldehyde, oxazolidine and THPS (at pH 8 for 24 hrs at 30°C)

Concentration of DAA, glutaraldehyde, oxazolidine and THPS (%)	Degree of crosslinking (%)			
	DAA-Glutaraldehyde	DAA-Oxazolidine	DAA-THPS	DAA
0.2	52.67±0.29	41.25±0.18	36.23±0.38	33.49
0.4	69.45±0.08	57.89±0..05	49.67±0.41	50.18
0.6	76.73±0.25	60.25±0.26	56.56±0.59	58.87
0.8	89.01±0.31	70.15±0.13	63.28±0.43	68.73
1.0	96.33±0.27	81.18±0.29	79.16±1.04	80.24

TABLE V

Physical Strength characteristics of combination tanned leathers

Tanning System	Tensile Strength (kg/cm^2)	% Extension at break	Tear strength (kg/cm)	Grain Crack Resistance	
				Load (Kg)	Distension (mm)
Control-Chrome	255 ± 5	59 ±2	48 ± 2	30±3	9.0±0.2
Control-DAA	235±3	40±2	38±2	31±2	9.3±0.2
DAA-Glutaraldehyde	240 ± 3	49 ±2	40 ±2	29±4	9.1±0.2
DAA-THPS	255 ±3	76 ±2	48±2	38±3	10.8±0.5
DAA-Oxazolidine	250 ±5	66 ±2	46 ±2	36±3	10.5±0.5

TABLE VI
Color measurement data for control and experimental leathers

	ΔL	ΔC	ΔH	Δa	Δb	ΔE
DAA-Glutaraldehyde	d=2.481	S=3.349	D=0.827	MR=0.441	MY=3.089	5.952
DAA-Oxazolidine	d=-4.128	S=-0.302	D=0.259	MR=0.510	MY=0.172	6.502
DAA-THPS	d=-5.114	S=-0.316	D=-0.221	MR=0.441	MY=0.346	7.114

TABLE VII
Fastness to rubbing and light fastness characteristics of control (C), DAA-Glutaraldehyde, DAA-Oxazolidine and DAA-THPS tanned leathers

Sample	Before ageing			After ageing		
	Wet rubbing	Dry rubbing	Light fastness[a]	Wet rubbing	Dry rubbing	Light fastness[a]
Control	4.0 - 4.5	4.5 - 5.0	3.5 - 4.0	4.0 - 4.5	4.5 - 5.0	3.0 - 3.5
DAA- Glu	4.5 - 5.0	4.5 - 5.0	3.5 - 4.0	4.5 - 5.0	4.5 - 5.0	3.0 - 3.5
DAA-Oxa	4.0 – 4.5	4.5 - 5.0	3.5 - 4.0	4.5 - 5.0	4.5 - 5.0	3.0 - 3.5
DAA-THPS	4.5 - 5.0	4.5 - 5.0	4.0 - 4.5	(4.5 - 5.0)	4.5 - 5.0	3.5 – 4.0
			4.5 - 5.0			(4.0-4.5)

[a]Value in parenthesis indicates the corresponding blue wool standard

*All experimental values showed an error of ± 0.1-0.5

Effect of Surface Color on Combination Tanned Leathers

The reflectance measurement vs visible wavelength for control DAA and DAA-glutaraldehyde, DAA-oxazolidine and DAA-THPS combination tanned leathers are shown in Figure 2. The absorbance maximum was 450 nm for both control and experimental leathers. Absorbance maximum is the wavelength at which, the reflectance is minimum as seen in Figure 5. The absorbance maxima for control and all experimental leathers do not bring about significant variation in the color and shade between control and experimental leathers. The ΔL, ΔC, ΔH, Δa and Δb values for combination tanned leathers are given in Table VI. It is observed that DAA-glutaraldehyde, DAA-oxazolidine and DAA-THPS samples show total color difference (ΔE) of 5.952, 6.502 and 7.114 compared to control leather, which means the overall color difference is negligible. The values indicate that the combination tanned leathers did not bring about significant change in color with that of control DAA tanned leather.

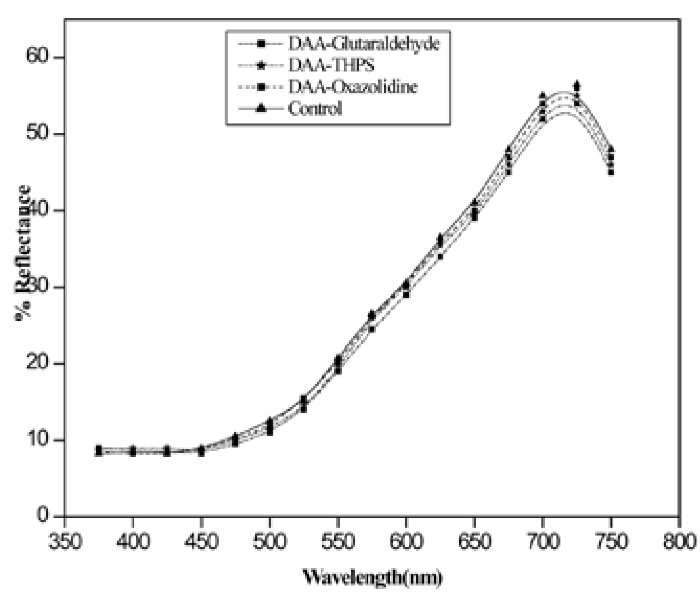

Figure 2: Plot of percentage reflectance vs wavelength for control and experimental garment leathers

Effect of Light Fastness on Combination Tanned Leathers

The fastness characteristics of leathers to light and rubbing of both control and experimental crust leathers under artificial light (Xenon lamp) is given in Table VII. The leathers from both control and matched pair experimental processes exhibit similar values that are equivalent to the Blue wool standards 4.5 (given in parenthesis in Table VII).

Organoleptic Properties Assessed by Tactile Evaluation

The results of hand and visual evaluation method are subjective, which varies from person to person. The values can be taken as reliable on evaluation by experienced persons and statistically averaged. .Visual assessment values data shown in Figure 3, 4 and 5. It is evident from the Figure 3, that the DAA-glutaraldehyde tanned leather showed better bulk properties. Increase in concentration of glutaraldehyde showed reduction in grain smoothness and general appearance. However, softness increased with increase in concentration of glutaraldehyde. Fullness of DAA-glutaraldehyde leathers increased with increase in concentration of glutaraldehyde. Based on these observations, it can be concluded that combination tanned leathers remarkably improve the organoleptic properties of crust leathers due to enhanced crosslinking. DAA-oxazolidine and DAA-THPS combination tanned leathers showed similar characteristics of organoleptic properties as shown in Figure 4 and 5 respectively. As seen from Figure 4, the fullness, grain smoothness, softness and general appearance of DAA-oxazolidine tanned leathers increased with increase in concentration of oxazolidine. As seen from Fig 5, DAA-THPS tanned leathers showed an increase in softness with increase in concentration of THPS. Moreover, fullness, grain smoothness and general appearance followed a similar trend to softness. These observations substantiate the characteristic feature of oxazolidine and THPS in coating of collagen fibers and enhanced crosslinking of glutaraldehyde in DAA-glutaraldehyde tanning.

Environmental Impact

The impact of pickle-less combination tanning system on the environment was assessed by the spent liquor analysis for BOD, COD and TS as the experimental process does not employ pickling, which is known to increase the TDS of the effluent. The environmental impact assessment was made for the experimental spent tanning solution by comparing with spent chrome tanning solution. It can be observed from Table VIII, that there is decrease in TS for all the experimental tanned process liquor of DAA and DAA-combination tanning systems. A reduction in BOD and COD was also observed for the combination tanned leathers.

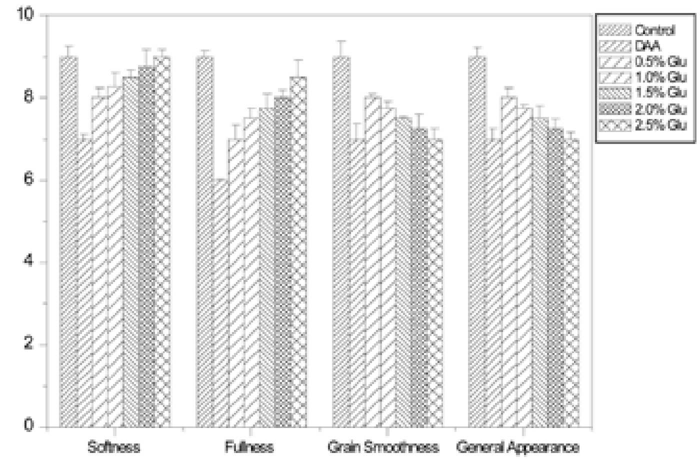

Figure 3: Organoleptic properties of DAA-glutaraldehyde combination tannages

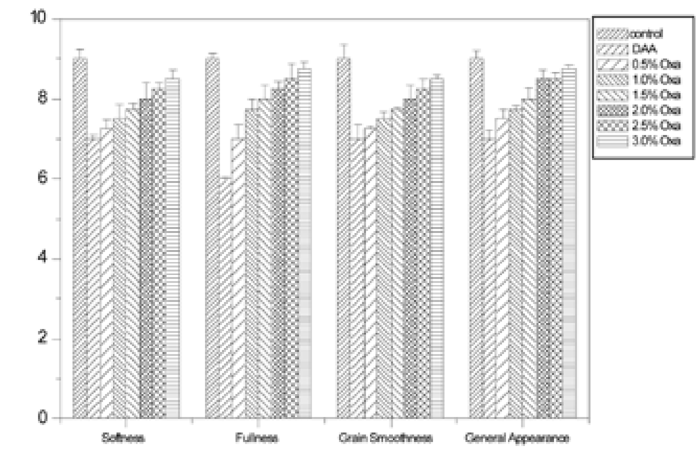

Figure 4: Organoleptic properties of DAA-oxazolidine combination tannages

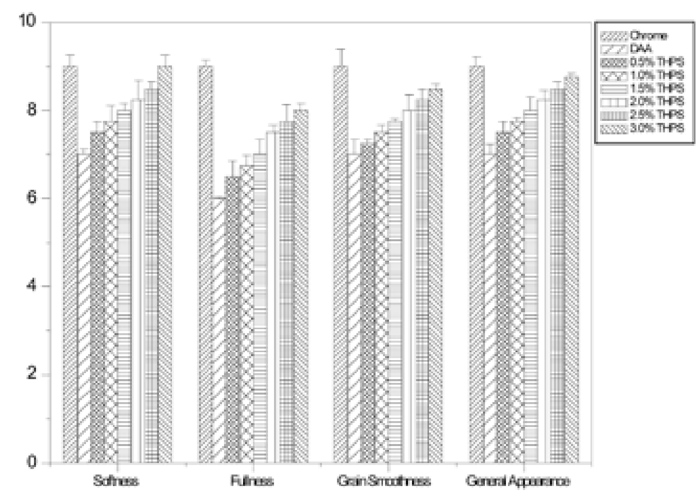

Figure 5: Organoleptic properties of DAA-THPS combination tannages

TABLE VIII
Spent tan liquor analysis of control and experimental leathers

Experiment	BOD (ppm)	COD (ppm)	TS (ppm)
Control-Chrome tanning	625 ± 20	6450 ± 25	9280±10
Control-DAA	395 ± 25	3080 ± 75	7400±10
DAA-Glutaraldehyde	265 ± 25	3865 ± 60	6858±15
DAA-Oxazolidine	325 ± 30	4313 ± 40	7025±13
DAA-THPS	320 ± 20	5429 ± 50	7555±12

CONCLUSIONS

The present study establishes that hydrothermal stability of DAA leather was enhanced by employing combination tannage. DAA-glutaraldehyde resulted in maximum shrinkage temperature of 97°C, where as DAA-oxazolidine and DAA-THPS resulted in 92°C and 90°C. DAA combination tanned leathers exhibits better physical properties to that of DAA tanned leathers. DAA-glutaraldehyde tanned leathers exhibited better bulk properties when compared to DAA-THPS and DAA-oxazolidine tanned leathers. A reduction in the BOD, COD and TS of the effluent liquor was observed for DAA and combination tanned process liquors in comparison with chrome tanned leathers. The main objective of the current approach is a way forward for organic tanning systems; hence, the present investigation provides an abundant scope for the manufacture of eco friendly leathers. The adoption of these organic tannages will bring about a significant change in the tanning industry by making it environmentally sustainable in the context of cleaner production.

REFERENCES

1. Germann, H.P.; The ecology of leather production-present state and development trends. Science and technology for leather in to the next millennium, *Proceedings of the XXV IUCLTS congress, Chennai*, **283**, 1999.
2. Chandrasekaran, B., Rao, J.R., Prasad, V.G.S. and Nair, B.U; *J. of Indian Assoc. for Environ. Manag* **16**, 168-173,1989.
3. Shrivastava, H.Y. and Nair,B.U.; *Biochem.biophys.Res. Commun.* **270**,749-754,2000.
4. Flora, S.D., Bagnasco, M., Serra,d. and Zanachi,P.; *Mut. Res.* **238**,99-172,1990.
5. Madhan, B., Fathima, N.N and Rao, J.R.; *JALCA* **97**,189,2002.
6. Rao, J.R.; *Leather Sci.* **34**, 201,1987.
7. Zauns, R. and Kuhm, P.; *JALC*, **90**,177,1995.
8. Covington, A.D.; *JALCA* **82**, 1,1987.
9. Kanth, S.V., Nirenjana, M., Archana, T.N., Madhan, B., Raghava Rao, J., and B.Unni Nair.; *JALCA* **102**, 353-361,2007.
10. Dasgupta, S.; *J. Soc. Leather Technol. Chem.* **86**, 186, 1998.
11. Fathima, N.N., Chandrabose, M., Aravindhan, R., Rao, J.R. and Nair, BU.; *JALCA* **100**, 273. 2005.
12. Fathima, N.N., Aravindhan, R., Rao, J.R. and Nair, B.U.; *JALCA* **101**, 161, 2006.
13. Fathima, N.N., Prem Kumar, T., Ravi Kumar, D., Rao, J.R. and Nair, BU.; *JALCA* **100**, 58, 2005.
14. Dasgupta, S.; Tanning with Tetrakis hydroxymethyl phosphonium sulfate (THPS)', Forty-ninth Annual Conference for the Tanners and Leather Technologists., New Zealand Leather and Shoe Research Association., 49, 129, 1998.
15. Chandrakasan, G., Torchia, D. A. and Piez, K. A.; *J Biol. Chem.* 251, 6062–6067, 1976.
16. Woessner, J. F.; *Arch. Biochem. Biophys.*, 93, 440-447, 1961.
17. Bubnis, W. A. and Ofner, C. M.; *Anal. Chem.*, 27, 129-33, 1992.
18. IUP 2, Sampling. *J. Soc. Leather Technol. Chem.*, **84**, 303, 2000.
19. IUP 6, Measurement of tensile strength and percentage elongation. *J. Soc. Leather Technol. Chem.*, **84**, 317, 2000.
20. IUP 8, Measurement of tear load-double edge tear. *J. Soc. Leather Technol. Chem.*, **84**, 327, 2000.
21. http://www.gretagmacbeth.com/index/products/products_color measurement products_portablespectros/products_spectrolino/products_spectrolino_details.htm.
22. Clesceri, L.S., Greenberg, A.E. and Trussel, R.R.; *Standard methods for the examination of water and wastewater.* Washington, DC: American Public Health Association, 1989.
23. Bowes, J.H. and Cater, C.W.; *Biochim Biophys Acta* **168**, 341-349, 1968.